

Pyroelectric and electrocaloric effects in hafnium oxide thin films

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Abstract

The material class of hafnium dioxide (HfO_2) -based ferroelectrics adds an unexpected and huge momentum to the long-known phenomenon of pyroelectricity. In this thesis, a comprehensive study of pyroelectric and electrocaloric properties of this novel ferroelectric material class is conducted. HfO_2 is a lead-free, non-toxic transition metal oxide, and abundant in the manufacturing of semiconductor devices. The compatibility to existing fabrication processes spawns the possibility of on-chip infrared sensing, energy harvesting, and refrigeration solutions, for which this dissertation aims to lay a foundation.

A screening of the material system with respect to several dopants reveals an enhanced pyroelectric response at the morphotropic phase boundary between the polar orthorhombic and the non-polar tetragonal phase. Further, a strong pyroelectric effect is observed when applying an electric field to antiferroelectric-like films, which is attributed to a field-induced transition between the tetragonal and orthorhombic phases. Primary and secondary pyroelectric effects are separated using high-frequency temperature cycles, where the effect of frequency-dependent substrate clamping is exploited. The piezoelectric response is determined by comparing primary and secondary pyroelectric coefficients, which reproduces the expected wake-up behavior in HfO_2 films.

Further, the potential of HfO_2 for thermal-electric energy conversion is explored. The electrocaloric temperature change of only 20 nm thick films is observed directly by using a specialized test structure. By comparing the magnitude of the effect to the pyroelectric response, it is concluded that defect charges have an important impact on the electrocaloric effect in HfO_2 -based ferroelectrics.

Energy harvesting with a conformal HfO_2 film on a porous, nano-patterned substrate is performed, which enhances the power output. Further, the integration of a pyroelectric energy harvesting device in a microchip for waste heat recovery and more energy-efficient electronic devices is demonstrated. High dielectric breakdown fields of up to $4 \,\mathrm{MV}\,\mathrm{cm}^{-1}$ in combination with a sizable pyroelectric response and a comparably low dielectric permittivity illustrate the prospect of HfO_2 -based devices for future energy conversion applications.

Kurzfassung

Die Klasse HfO_2 -basierter Ferroelektrika hat das Potential, neue Impulse für die Erforschung des pyroelektrischen Effektes sowie dessen Anwendungen zu geben. Im Rahmen der vorliegenden Arbeit wird eine umfassende Analyse der pyroelektrischen und elektrokalorischen Eigenschaften dieser neuartigen Ferroelektrika vorgestellt. HfO_2 ist ein ungiftiges Übergangsmetalloxid, welches in der Halbleiterfertigung breite Anwendung als Dielektrikum findet. Die Kompatibilität zu bestehenden Herstellungsprozessen in der Halbleitertechnologie ermöglicht neuartige, integrierte Bauelemente. Beispiele sind Infrarotsensor-Chips, Applikationen zur Rückgewinnung von Verlustwärme (sog. *Energy Harvesting*), sowie die elektrokalorische Kühlung.

Der Vergleich verschiedener Stöchiometrien und Dotanden zeigt, dass der pyroelektrische Effekt an der morphotropen Phasengrenze zwischen der zentrosymmetrischen tetragonalen sowie der polaren orthorhombischen Phase am ausgeprägtesten ist. Weiterhin wird eine deutliche Erhöhung der pyroelektrischen Koeffizienten durch einen feldinduzierten Phasenübergang zwischen den tetragonalen und orthorhombischen Kristallstrukturen beobachtet. Mit Hilfe von hochfrequenten Temperaturzyklen werden primäre und sekundäre Beiträge zum pyroelektrischen Effekt getrennt. Dazu wird ausgenutzt, dass die mechanische Ausdehnung des Substrates bei hohen thermischen Frequenzen beschränkt ist. Der Vergleich primärer und sekundärer Anteile erlaubt weiterhin die Bestimmung piezoelektrischer Koeffizienten, welche eine Abhängigkeit von der elektrischen Zyklierung zeigen (sog. *wake-up*).

Ein weiterer Schwerpunkt der vorliegenden Arbeit ist die Erforschung des Potentials HfO_2 -basierter Dünnfilme für die Umwandlung zwischen elektrischer und thermischer Energie. Eine spezialisierte Teststruktur erlaubt die direkte Beobachtung elektrokalorischer Temperaturänderungen in den nur 20 nm dünnen Filmen. Die im Vergleich zum pyroelektrischen Effekt höheren elektrokalorischen Koeffizienten werden durch den Einfluss von elektrisch geladenen Defekten erklärt.

Um die Rückgewinnung von thermischer Energie zu demonstrieren, werden pyroelektrische HfO_2 -Filme auf oberflächenvergrößerten, porösen Substraten hergestellt. Dadurch wird die Leistung des *Energy Harvesters* gegenüber einer planaren Geometrie deutlich erhöht. Weiterhin wird in der vorliegenden Arbeit die Integration eines *Energy Harvesters* in einem Mikrochip gezeigt. Die Rückgewinnung von Verlustwärme wird als möglicher Weg zu einer höheren Energieeffizienz zukünftiger elektronischer Schaltungen diskutiert. Insbesondere die vergleichsweise hohen Durchbruchfeldstärken im Bereich von 4 MV cm⁻¹ sowie die niedrige dielektrische Permittivität machen die Klasse HfO₂-basierter Materialien vielversprechend für die Umwandlung zwischen elektrischer und thermischer Energie.

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Acronyms

- ${\bf AFE}$ antiferroelectric.
- **ALD** atomic layer deposition.
- $\mathbf{AWG}\xspace$ arbitrary waveform generator.
- ${\bf BEoL}\,$ back-end of line.
- **CMOS** complementary metal-oxide-semiconductor.
- **CSD** chemical solution deposition.
- $\mathbf{CVD}\,$ chemical vapor deposition.
- **DART-PFM** dual-frequency resonance-tracking piezoresponse force microscopy.
- **DBLI** double-beam laser interferometry.
- \mathbf{DFT} density functional theory.
- \mathbf{DRAM} dynamic random access memory.
- **EBSD** electron back-scatter diffraction.
- EFTEM energy-filtered transmission electron microscopy.
- ${\bf EXAFS}\,$ extended X-ray absorption fine structure.
- **FeFET** ferroelectric field-effect transistors.
- ${\bf FEM}$ finite element method.
- ${\bf FEoL}\,$ front-end of line.
- ${\bf FOM}\,$ figures of merit.
- FORC first-order reversal curves.
- **FRAM** ferroelectric random access memory.

FWHM full width at half maximum.

GI-XRD grazing incidence X-ray diffractometry.

GOF goodnes-of-fit.

GPIB general purpose interface bus.

HRTEM high resolution transmission electron microscopy.

KAI Kolmogorov-Avrami-Ishibashi.

 $La(iPrCp)_3$ tris(isopropylcyclopentadienyl)lanthanum.

 $\mathbf{MFM} \hspace{0.1in} \mathrm{metal-ferroelectric-metal.}$

 $\mathbf{MPB}\xspace$ morphotropic phase boundary.

NEMS nanoelectromechanical systems.

 ${\bf NLS}\,$ nucleation-limited switching.

 ${\bf NVM}\,$ non-volatile memory.

PF Poole-Frenkel.

PFM piezoresponse force microscopy.

PUND positive-up negative-down.

 $\mathbf{PVD}\xspace$ physical vapor deposition.

RAM random access memory.

RBS Rutherford backscattering spectrometry.

 \mathbf{RC} resistor-capacitor.

RRAM resistive random access memory.

RTA rapid thermal annealing.

 ${\bf SAED}$ selected area electron diffraction.

SC single crystal.

 ${\bf SE}\,$ spectroscopic ellipsometry.

SECE synchronized electric charge extraction.

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SEM scanning electron microscopy.

SMU source measure unit.

 \mathbf{SNR} signal-to-noise ratio.

STEM scanning transmission electron microscopy.

TCR temperature coefficient of resistance.

TDMAS tris(dimethylamino)silane.

 \mathbf{TDPAC} time differential pertubed angular correlation.

 ${\bf TDTR}\,$ time-domain thermore flectance.

 ${\bf TEG}\,$ thermoelectric generators.

TEMAHf tetrakis(ethylmethylamino)hafnium.

 ${\bf TEMAZr} \ tetrak is (ethylmethylamino) zirconium.$

 ${\bf TF}\,$ thin film.

THD total harmonic distortion.

 ${\bf TKD}\,$ transmission Kikuchi diffraction.

TMA trimethylaluminium.

ToF-SIMS time of flight secondary ion mass spectrometry.

XAS X-ray absorption spectroscopy.

XPS X-ray photoelectron spectroscopy.

XRD X-ray diffractometry.

Symbols

Σ_i	electrocaloric coefficient
Σ_i''	secondary electrocaloric coefficient
α	temperature coefficient of resistivity
α_{ij}	thermal expansion coefficient
ϵ_i	strain
η	energy conversion efficiency
$\gamma_{\rm FWHM}$	diffraction peak half-width
λ	thermal wave length
λ_{X}	X-ray wave length
ν	Photon frequency
$\omega_{ m e}$	electrocaloric excitation frequency
$\omega_{ m h}$	temperature variation frequency
$\omega_{ m s}$	sensor frequency
ϕ	work function
σ_i	stress
θ	temperature variation amplitude
$\theta_{\rm s}$	sensor temperature amplitude
θ	thermal insulance
ε_{ij}	dielectric permittivity
ρ	density
ξ	Wheatstone bridge ratio
A	area
C	electrical capacity, heat capacity
$C_{\rm c}$	Curie constant
$C_{\rm s}$	specific heat capacity
$C_{\rm v}$	volumetric heat capacity
$d_{\rm film}$	film thickness
D_i	displacement field

 d_{ij} piezoelectric coefficient

$d_{ m p}$	particle size
e	elementary charge
E_i	electric field
e_{ij}	constant-strain piezoelectric coefficient
$E_{\rm B}$	binding energy
$E_{\rm c}$	coercive field
$E_{\rm K}$	kinetic energy
h	heat transfer coefficient, Planck constant
Ι	electric current
i	imaginary unit
$I_{ m h}$	heating current amplitude
$i_{\rm p}$	pyroelectric current
j	current density
K	Scherrer parameter
k	thermal conductivity
L	heating strip length
$F'_{\rm E}$	alternative energy harvesting FOM
$F_{\rm E}$	energy harvesting FOM
F_{I}	current-mode pyroelectric sensor FOM
$F_{\rm V}$	voltage-mode pyroelectric sensor FOM
${\mathcal F}$	Gibbs free energy
P_i	polarization
p_i''	secondary pyroelectric coefficient
p_i^ϵ	primary pyroelectric coefficient
p_i^σ, p	total pyroelectric coefficient
$P_{\rm E}$	electrocaloric power
$P_{\rm r}$	remanent polarization
$P_{\rm s}$	spontaneous polarization
Q	heat, charge
$Q_{ m s}$	surface charge
R	electrical resistance, thermal resistivity
r_{10}	aging rate per decade
$R_{ m h}$	heater electrical resistance
$R_{\rm s}$	sensor electrical resistance
S	entropy
s_{ij}	mechanical compliance
T^{T}	temperature
t	time

- $T_{\rm C}$ Curie temperature
- $T_{\rm c}$ cold side temperature
- $T_{\rm h}$ hot side temperature
- U internal energy, voltage
- $U_{3\omega}$ third-harmonic voltage
- $U_{\rm e}$ electrocaloric excitation voltage
- $U_{\rm s}$ \$ sensor voltage amplitude
- $U_{
 m surf}$ surface potential
- W work
- Z thermal impedance
- $Z_{\rm T}$ total thermal impedance

Chapter 1

Introduction

The recently discovered material class of HfO_2 -based ferroelectrics [1–3] provides an unexpected and huge momentum to the long-known phenomenon of pyroelectricity. HfO_2 is a non-toxic material that combines unique properties such as advanced complementary metal-oxide-semiconductor (CMOS)-compatible processing with a sizable spontaneous polarization and a high coercive field. Ultimately, this results in a broad range of novel applications, specifically in the fields of pyroelectric sensors, solid-state cooling, and energy harvesting. Since HfO_2 -based materials are readily available in both front-end of line (FEoL) and back-end of line (BEoL) manufacturing processes, they are an ideal candidate for applications which are integrated on-chip.

The ferroelectric behavior of doped HfO_2 is exceptional in the sense that it is most pronounced in nanometer-thin films, whereas other materials lose their spontaneous polarization when approaching this thickness range [4]. In HfO_2 , ferroelectricity has been shown recently in 1 nm films [5], and nanoscopic, scale-free domains have been proposed by computational methods [6]. It has been established that a variety of dopants can be used to induce ferroelectricity [7], making the HfO_2 material class promising for probing the physics of ultra-thin ferroelectrics. Recent advances such as the demonstration of ferroelectricity in epitaxial yttrium-doped HfO_2 [8] and evidence for a previously unknown polar rhombohedral phase [9] illustrate that the analysis of the HfO_2 system is by no means complete today.

Pyroelectric minerals have been known since ancient times, when the ability of tourmaline to attract dust upon heating was observed [10]. The pyroelectric effect leads to a change of the spontaneous electric polarization in certain materials when they are subjected to a temperature variation. Ferroelectrics are a sub-group of these pyroelectric (i.e., polar) materials, in which the polarization state can be switched. Historically, pyroelectrics were discovered much earlier than ferroelectrics, since the latter form randomly polarized domains and therefore lack a macroscopic polarization in the pristine state [11].

Some 100 years ago, the first report of a reconfigurable polarization by applying an electric field was published by Valasek [12, 13]. In that work, parallels to the longknown phenomenon of ferromagnetism were noted. Further, the hysteretic behaviors of the polarization with respect to the electric field and temperature were described. However, polar crystals were then believed to be a niche phenomenon.

One breakthrough in the history of polar materials came with the discovery of ferroelectricity in potassium dihydrogenphosphate (KH₂PO₄) in 1935 [14]. Compared to the previously known potassium sodium tartrate tetrahydrate (KNaC₄H₄O₆ · 4 H₂O), it represents a rather simple model system with 16 atoms per unit cell, which subsequently spawned the first microscopic model of ferroelectricity by Slater in 1941 [15]. In 1945, the discovery of barium titanate (BaTiO₃) [16] introduced the class of oxygen octahedral ferroelectrics. Reports on polarization switching in potassium niobate (KNbO₃) [17], lithium niobate (LiNbO₃), lithium tantalate (LiTaO₃) [17], and lead titanate (PbTiO₃) [18] followed. While the efforts on describing the microscopic reasons for polar behavior continued [19], macroscopic thermodynamic concepts proved to be useful by providing an analytical model considering dielectric, piezoelectric and elastic properties [11, 20]. Most importantly, the Landau theory of phase transitions [21, 22] has been applied to describe a wide range of ferroelectric materials [11, 23, 24].

Many of the oxygen octahedral ferroelectrics find wide use today, with LiTaO₃ being employed in pyroelectric infrared detectors and LiNbO₃ for non-linear optical devices. Since the discovery of the lead zirconate titanate (PbZr_xTi_{1-x}O₃) solid-solution, it has become arguably the most intensively studied ferroelectric material with countless applications, especially in piezoelectric devices. In the last years, lead magnesium niobate-lead titanate (Pb(Mg_{1/3}Nb_{2/3})O₃-PbTiO₃) has challenged PbZr_xTi_{1-x}O₃ as a high-performance piezoceramic.

Today, the novel HfO_2 material class receives extensive research interest due to their application potential in non-volatile memory [25–27], neuromorphic computing [28], and more, but the pyroelectric and piezoelectric properties remain relatively understudied. However, understanding these phenomena is essential: First, the HfO_2 material system has the potential to evolve pyroelectric applications from their niche existence towards scalable, mass-market solutions for infrared sensors, energy harvesters, and electrocaloric refrigeration. Secondly, since polar behavior forms the basis of ferroelectricity, the investigation of pyroelectric properties is a step towards a deeper physical understanding of the material system.

In this dissertation, a comprehensive investigation of the pyroelectric and electrocaloric responses in the HfO_2 material class is conducted. First, an overview of the relevant physical properties of pyroelectric, HfO_2 -based thin films are given. Since the coupling of thermal, elastic, and electronic properties has important consequences in thin films, secondary contributions to pyroelectric and electrocaloric effects need to be considered. The most significant methods for determining pyroelectric and electrocaloric coefficients in such thin films are described concisely. This is of particular importance since the methods for determining such responses in nanometer-thin films are often different as compared to bulk materials. Effects like substrate clamping, mechanical interaction with electrode layers, and defect-induced physics, are prominent in such films and need special attention.

Pyroelectric coefficients are determined by using a dedicated, phase-sensitive measurement method. The impact of doping, film thickness, and electric field cycling the pyroelectric effect as well as aging phenomena are investigated. Four film types are assessed: Al-doped, Si-doped, and La-doped HfO₂ as well as the hafnium zirconium oxide (Hf_{1-x}Zr_xO₂) solid solution. Further, an external electric field is used to significantly enhance the pyroelectric response in antiferroelectric (AFE)-like HfO₂ layers.

To further explore the physics of the pyroelectric effect in nm-thin films, samples are subjected to rapid temperature cycles in a specialized, micro-fabricated test structure. Thereby, primary and secondary pyroelectric coefficients are separated. By relating these contributions to the mechanical properties of the multi-layer film stacks, piezoelectric coefficients are estimated, and the wake-up effect of the piezoelectric response in HfO_2 -based films is observed.

The electrocaloric temperature change of nm-thin HfO_2 films is observed directly, which is challenging due to the very low heat capacity of the active material. The different contributions to the electrocaloric effect are discussed, and results are compared to indirect measurements. Finally, the opportunity of energy harvesting is discussed, where thermodynamic cycles in analogy to the Ericsson process are utilized. The harvested power is optimized by means of depositing the HfO_2 -based material on an substrate with a high specific area, resulting in a substantial increase of apparent pyroelectric coefficients. The integration of pyroelectric energy harvesting in the BEoL of integrated circuits is discussed as a pathway towards more energy-efficient electronic devices.

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Chapter 2

Fundamentals

In this chapter, the fundamental properties of polar crystals are described. First, the coupling of elastic, electronic, and caloric quantities is discussed phenomenologically. Then, definitions for pyroelectric and electrocaloric coefficients are introduced. It is discussed how the interplay of mechanical, electric, and thermal effects spawns secondary and tertiary contributions to pyroelectric and electrocaloric effects. For thin films, mechanical interactions with the substrate or other layers in a laminate structure have significant implications. Then, the phenomenon of ferroelectricity is discussed, which exists in a sub-group of polar materials. The Landau theory of phase transitions is used to discuss polarization switching and temperature-dependent behavior of ferroelectric thin films. Finally, general material parameters of HfO_2 and requirements for the stabilization of the polar phase at ambient conditions are reviewed.

2.1 Phenomenology of polar materials

Of the 32 crystal classes, 11 possess a centrosymmetric structure, which exhibits solely electrostrictive behavior. Of the remaining 21 crystal classes, 20 exhibit piezoelectricity. This means, that an electric polarization is observed when mechanical stress is applied. Of the piezoelectric crystal classes, 10 are polar, which means that they possess a spontaneous polarization even in equilibrium conditions without an external electric field or stress. When subjected to a temperature change, the spontaneous polarization changes, which is referred to as pyroelectricity. Finally, ferroelectricity is the existence of multiple stable polar crystal states, which can be changed by application of an electric field, while conserving the crystal class [11]. Conversely, this definition implies that any ferroelectric crystal also exhibits pyroelectric and piezoelectric properties.

A Venn diagram of the crystal classes is shown in Figure 2.1. Some non-ferroelectric polar materials like tourmaline [29] were already discovered in ancient times, because they cannot reduce their surface charge density via the formation of domains. Further examples are aluminum nitride (AlN) and gallium nitride (GaN), which both have the wurzite crystal structure with the space group $P6_3mc$ [30]. For most ferroelectrics, a



Figure 2.1: Venn diagram of crystal classes in dielectric materials. Of the total 32 crystal classes, 20 exhibit piezoelectricity, and 10 show the pyroelectric effect.

phase transition to a paraelectric phase of higher symmetry exists at rising temperatures, with the transition points ranging from few K to >1000 K [4]. This is referred to as the Curie temperature.

2.1.1 Polar crystals

In the macroscopic thermodynamic model of polar materials, any atomic structure is ignored, and the crystal is described as infinite and homogeneous. With these simplifications in mind, the relations of the independent variables temperature T, electric field E_i , and stress σ_i to the dependent variables strain ϵ_i , displacement field D_i , and entropy S is discussed.

In an insulating, linear material, the displacement field is given as

$$D_i = \varepsilon_0 E_i + P_i, \tag{2.1}$$

where ε_0 is the dielectric permittivity of the vacuum, and P_i denotes the polarization. When transferring an infinitesimal amount of heat dQ to an unit volume of the material, the internal energy U changes by

$$\mathrm{d}U = \mathrm{d}Q + \mathrm{d}W,\tag{2.2}$$

where dW is the work done during the process. Applying the second law of thermodynamics and writing dW as the combination of mechanical and electric effects [11] yields

$$dU = TdS + \sigma_i d\epsilon_i + E_i dD_i.$$
(2.3)

In most experimental situations, it is not possible to clamp the material at a defined strain value. Hence, the Legendre transformation of Equation 2.3 yields the Gibbs free energy \mathcal{F} , with a more convenient set of independent variables T, σ_i , and E_i . The differential form of \mathcal{F} is

$$d\mathcal{F} = -SdT - \epsilon_i d\sigma_i - D_i dE_i.$$
(2.4)

Fixing pairs of two independent variables at a constant value yields the three equations of state

$$S = \left(\frac{\partial \mathcal{F}}{\partial T}\right)_{\sigma,E} \qquad \epsilon_i = \left(\frac{\partial \mathcal{F}}{\partial \sigma_i}\right)_{E,T} \qquad D_i = \left(\frac{\partial \mathcal{F}}{\partial E_i}\right)_{T,\sigma}.$$
(2.5)

The linear differential form of the quantities in Equation 2.5 are

$$dS = \left(\frac{\partial S}{\partial \sigma_i}\right)_{T,E} d\sigma_i + \left(\frac{\partial S}{\partial E_i}\right)_{T,\sigma} dE_i + \left(\frac{\partial S}{\partial T}\right)_{\sigma,E} dT, \qquad (2.6)$$

$$\mathrm{d}\epsilon_i = \left(\frac{\partial\epsilon_i}{\partial\sigma_j}\right)_{T,E} \mathrm{d}\sigma_j + \left(\frac{\partial\epsilon_i}{\partial E_j}\right)_{T,\sigma} \mathrm{d}E_j + \left(\frac{\partial\epsilon_i}{\partial T}\right)_{\sigma,E} \mathrm{d}T, \text{ and}$$
(2.7)

$$\mathrm{d}D_i = \left(\frac{\partial D_i}{\partial \sigma_j}\right)_{T,E} \mathrm{d}\sigma_j + \left(\frac{\partial D_i}{\partial E_j}\right)_{T,\sigma} \mathrm{d}E_j + \left(\frac{\partial D_i}{\partial T}\right)_{\sigma,E} \mathrm{d}T.$$
(2.8)

Equations 2.6 to 2.8 introduce nine couplings, each of which corresponds to a physical phenomenon. They are classified as caloric, elastic, and dielectric responses: The partial differentials of the temperature corresponding to heat capacity $\partial S/\partial T$, thermal expansion $\partial \epsilon_i/\partial T$, and the pyroelectric effect $\partial D_i/\partial T$. Elastic effects are the piezocaloric effect $\partial S/\partial \sigma_i$, mechanical compliance $\partial \epsilon_i/\partial \sigma_j$, and direct piezoelectricity $\partial D_i/\partial \sigma_j$. Field-induced responses are the electrocaloric effect $\partial S/\partial E_i$, the inverse piezoelectric effect $\partial \epsilon_i/\partial E_j$, as well as the dielectric permittivity $\partial D_i/\partial E_j$.

By introducing parameters for mechanical compliance s_{ij} , piezoelectric response d_{ij} , thermal expansion α_{ij} , dielectric permittivity ε_{ij} , pyroelectric response p_i , electrocaloric response Σ_i , and heat capacity C, Equations 2.6 to 2.8 are rewritten as

$$dS = \alpha_i^{T,E} d\sigma_i + \Sigma_i^{T,\sigma} dE_i + (C^{\sigma,E}/T_a) dT, \qquad (2.9)$$

$$d\epsilon_i = s_{ij}^{T,E} d\sigma_j + d_{ij}^{T,\sigma} dE_j + \alpha_i^{\sigma,E} dT, \text{ and}$$
(2.10)

$$\mathrm{d}D_i = d_{ij}^{T,E} \,\mathrm{d}\sigma_j + \varepsilon_{ij}^{T,\sigma} \,\mathrm{d}E_j + p_i^{\sigma,E} \,\mathrm{d}T.$$
(2.11)

where superscripts indicate constant quantities. For simplicity, the thermodynamic equivalence of direct and inverse piezoelectric effects is used, with only one variable d_{ij} . Similarly, α_i is assigned to both thermal expansion and piezocaloric response.

The relations from Equations 2.9 to 2.11 are depicted schematically in Figure 2.2. The independent variables are located in the outer circles, while dependent variables are shown in the inner part. Interactions are represented by lines, with pyroelectric and electrocaloric effects indicated in red. Further, the diagram helps to understand secondary contributions. As an example, a pyroelectric response can also be created by an indirect path via thermal expansion (green) and the pyroelectric effect (red). In most materials, primary (intrinsic) and secondary contributions to the pyroelectric effect appear simultaneously, and the secondary contribution can be of positive or negative sign [30]. The magnitude of secondary responses depends on the crystal geometry (i.e., bulk or thin-film), which is discussed in the following section. For better readability,



Figure 2.2: In a Heckmann diagram, the relations of thermodynamic variables in a polar material are visualized. For instance, the pyroelectric effect results from the dependence of the displacement field D on the temperature T.

the indication of constant quantities are dropped with the exception of pyroelectric coefficients.

When considering a bulk crystal with constant field and stress, the pyroelectric response is calculated from Equations 2.1 and 2.11 as

$$p_i' = E_j \frac{\partial \varepsilon_{ij}}{\partial T} + p_i^{\sigma}.$$
(2.12)

In addition to the intrinsic response p_i^{σ} , a field-induced contribution to the pyroelectric coefficient occurs due to the temperature dependence of the dielectric permittivity. This means that even a non-polar material has a pyroelectric-like current response with an applied electric field. From the crystallographic standpoint, this is explained by the symmetry-breaking displacement of ions from their lattice positions. On the other hand, in the field-free case, the change of spontaneous polarization with temperature is simply

$$\mathrm{d}P_i = p_i^\sigma \,\mathrm{d}T.\tag{2.13}$$

2.1.2 The pyroelectric effect in thin films

In most experimental conditions, the sample is free to expand when heated. In bulk crystals, this is equivalent to the condition of constant stress. However, for a thin-film on a substrate, the case of constant strain should be considered, since the underlying substrate influences the elastic properties. With strain as an independent variable, the total differential of D_i is [31]

$$\mathrm{d}D_i = \left(\frac{\partial D_i}{\partial \epsilon_j}\right)_T \mathrm{d}\epsilon_j + \left(\frac{\partial D_i}{\partial E_j}\right)_{\sigma,T} \mathrm{d}E_j + \left(\frac{\partial D_i}{\partial T}\right)_{\sigma} \mathrm{d}T.$$
(2.14)

Using Equations 2.1 and 2.8 in the field-free case, this simplifies to

$$\mathrm{d}P_i = \left(\frac{\partial P_i}{\partial \epsilon_j}\right)_T \mathrm{d}\epsilon_j + \left(\frac{\partial P_i}{\partial T}\right)_\epsilon \mathrm{d}T,\tag{2.15}$$

where e_{ij} is the piezoelectric response with respect to strain. At zero field, Equation 2.7 simplifies to

$$d\epsilon_i = \left(\frac{\partial \epsilon_i}{\partial \sigma_j}\right)_T d\sigma_j + \left(\frac{\partial \epsilon_i}{\partial T}\right)_\sigma dT.$$
(2.16)

Combining Equations 2.15 and 2.16 then yields

$$\mathrm{d}P_i = \left(\frac{\partial P_i}{\partial \epsilon_j}\right)_T \left(\frac{\partial \epsilon_j}{\partial \sigma_k}\right)_T \mathrm{d}\sigma_k + \left[\left(\frac{\partial P_i}{\partial \epsilon_j}\right)_T \left(\frac{\partial \epsilon_j}{\partial T}\right)_\sigma + \left(\frac{\partial P_i}{\partial T}\right)_\epsilon\right] \mathrm{d}T.$$
(2.17)

Using the previously defined coupling parameters, Equation 2.17 is rewritten as

$$dP_i = \left(e_{ij}s_{jk}\right)d\sigma_k + \left(p_i^{\epsilon} + e_{ij}\alpha_j\right)dT.$$
(2.18)

Comparing Equations 2.18 and 2.11 at zero electric field yields

$$d_{ik} = e_{ij}s_{jk},\tag{2.19}$$

where piezoelectric coefficients at constant strain and stress are denoted by d_{ij} and e_{ij} , respectively. Both piezoelectric coefficients are directly proportional, and related by the mechanical compliance. For the pyroelectric coefficients, the constant-stress condition corresponds to

$$p_i^{\sigma} = p_i^{\epsilon} + \underbrace{e_{ij}\alpha_j}_{p_i''}.$$
(2.20)

Hence, the pyroelectric response of an un-clamped (constant-stress) case is the sum of a primary (intrinsic) part p_i^{ϵ} and a secondary contribution p_i'' via thermal expansion and the piezoelectric effect. While p_i^{ϵ} is negative in all known materials, p_i'' can have either sign. In most materials, the primary response exceeds the secondary contribution, with triglycine sulfate ((NH₂CH₂COOH)₃ · H₂SO₄) being a notable exception [30]. Equation 2.20 further indicates that it is possible to determine piezoelectric coefficients when both p_i^{σ} and p_i^{ϵ} are known. This approach is demonstrated in Section 4.3.3.

When considering a pyroelectric thin-film with planar symmetry, the secondary effect in Equation 2.20 is rewritten as a sum of out-of-plane and in-plane thermal expansion

$$p_3^{\sigma} = p_3^{\epsilon} + 2e_{31}\alpha_1 + e_{33}\alpha_3. \tag{2.21}$$

When the film is rigidly attached to a substrate with a thermal expansion coefficient $\alpha_{i,s}$, Equation 2.21 is not valid anymore. If the expansion coefficients α_i and $\alpha_{i,s}$ are different, the magnitude of the secondary effect changes. For a thin-film on an infinite substrate, the pyroelectric response is then

$$\frac{\mathrm{d}P_3}{\mathrm{d}T} = p_3^{\sigma} - \frac{2d_{31}(\alpha_1 - \alpha_{1,\mathrm{s}})}{s_{11} + s_{12}}.$$
(2.22)

In applications, more complicated layer stacks are often used, which comprise additional electrode layers or light absorbers. The elastic interactions in such multi-layer systems can significantly alter pyroelectric behavior [32]. Additionally, residual strains may be present since the individual deposition processes happen at different temperatures.

Additional contributions to the pyroelectric effect can arise from lateral strain gradients. Causes are non-uniform heating, or partial clamping of the crystal, which was observed with LiNbO_3 [33]. This is referred to as tertiary pyroelectricity and usually has a small magnitude. Precautions are taken throughout this work to suppress tertiary effects as much as possible, e.g., by uniform heating throughout the pyroelectric device. Further, it has been shown that interface effects can have a significant impact on the pyroelectric properties of thin ferroelectric films [34].

2.1.3 The electrocaloric effect

When discussing the total differential of the Entropy in Equation 2.6, three terms occur: The dependence on strain $\partial S/\partial \sigma$, corresponding to the piezocaloric effect, the temperature dependence $\partial S/\partial T$ associated with heat capacity, and the electrocaloric response $\Sigma = \partial S/\partial E$, arising from the coupling to the electric field.

The last term is rewritten with Equation 2.5, and by using Schwarz's theorem, the equivalence of electrocaloric and pyroelectric coefficients is shown readily as

$$\Sigma_i = \left(\frac{\partial S}{\partial E_i}\right)_T = \left(\frac{\partial^2 \mathcal{F}}{\partial T \partial E_i}\right) = \left(\frac{\partial^2 \mathcal{F}}{\partial E_i \partial T}\right) = \left(\frac{\partial D_i}{\partial T}\right)_{\sigma} = p_i^{\sigma}.$$
(2.23)

Relations of this type are called Maxwell equations. By changing the differentiation order of the thermodynamic potential, such formula can be deduced. Equation 2.23 may be the reason why the electrocaloric effect is often pictured as an inversion of the pyroelectric effect. Thus, in many reports of electrocaloric coefficients, values are calculated from temperature-dependent polarization measurements as described in Section 3.2.1. While this is easier to realize experimentally, such an indirect approach is limited. In particular, it is noted that using the Maxwell relations in Equation 2.23 relies on reversible thermodynamic processes, which may not be present near phase transitions [35]. Further, the mechanical clamping to a substrate breaks the equivalence of pyroelectric and electrocaloric effects in thin films [36].

Varying the electric field under constant stress yields an isothermal entropy change

$$\Delta S = \int_{E_{i,1}}^{E_{i,2}} \Sigma_i \, \mathrm{d}E_i, \tag{2.24}$$

which in an adiabatic process corresponds to a temperature change

$$\Delta T = -T \int_{E_{i,1}}^{E_{i,2}} \frac{1}{c_E} \Sigma_i \, \mathrm{d}E_i, \tag{2.25}$$

where c_E is the specific heat capacity. In a real measurement, adiabatic conditions cannot be met. First, the current flow onto the electrodes is finite due to the series resistance of electrical connections. This limits the rate of electric field change, which should occur on a time scale shorter than the characteristic time of heat transfer [37]. Secondly, the electrocaloric temperature change decays exponentially due to heat transfer. This is especially the case in thin films, which have a strong thermal coupling to electrode layers or the substrate. As a result, direct electrocaloric measurements with thin films are challenging, and only sparsely reported [36, 38, 39].

Similarly to the pyroelectric effect, a secondary contribution to the electrocaloric coefficient exists. It arises from the piezoelectric effect, which creates strain and thereby modulates the vibrational entropy [36, 40]. This is described by a secondary coefficient [41, 42]

$$\Sigma_i'' = e_{ij}\alpha_j,\tag{2.26}$$

and the corresponding isothermal entropy change is

$$\Delta S'' = \int_{E_{i,1}}^{E_{i,2}} \Sigma_i'' \, \mathrm{d}E_i.$$
(2.27)

Hence, Σ'' is expected to have the same magnitude as the secondary pyroelectric coefficient p''. Secondary contributions to the electrocaloric effect have been analyzed for barium strontium titanate $(BaSn_xTi_{1-x}O_3)$ and $Pb(Mg_{1/3}Nb_{2/3})O_3$ -PbTiO₃, where the magnitude was found to be less than 20% of the total response, respectively [42, 43]. In $PbZr_xTi_{1-x}O_3$, the secondary electrocaloric effect has been found to reduce the overall magnitude, becoming comparable to the primary coefficient at elevated temperatures [41].

2.2 Ferroelectricity

The phenomenological treatment of pyroelectric and electrocaloric effects in Chapter 2.1 does not consider any non-linear or divergent physical processes such as polarization switching or phase change. However, since this work focuses on the ferroelectric HfO_2 material system, these phenomena have important implications for the pyroelectric and electrocaloric responses. For instance, the sign of the pyroelectric current depends on the ferroelectric polarization state, and phenomena related to domain formation and de-polarization are prominent.

In the following section, the Landau-Devonshire theory of phase change is used to examine polarization switching and temperature dependent properties of ferroelectric materials. In Section 2.2.2, the Ginzburg-Landau theory is used to describe the boundary conditions found in thin ferroelectric films with electrodes.

2.2.1 Phenomenology of ferroelectrics

The Landau theory of phase transitions has proven to be an invaluable tool in describing many physical systems; it has been applied to ferromagnets, superconductors, and ferroelectrics. To apply the Landau theory to bulk ferroelectrics, several assumptions are made [23, 24]. First, the electric field and the displacement field are directed perpendicular to the film surface. Further, a stress-free film with an uniform polarization P is assumed. The ansatz for the free energy density is a series expansion

$$\mathcal{F} = \frac{a}{2}P^2 + \frac{b}{4}P^4 + \frac{c}{6}P^6 - EP, \qquad (2.28)$$

with a temperature-dependent coefficient

$$a = a_0(T - T_0). (2.29)$$

The parameters b and c are assumed to be constant. In all known ferroelectric materials, a_0 and c are positive [4]. The critical temperature of the phase transition is denoted by T_0 . It is noted that T_0 is distinguished from the Curie temperature $T_{\rm C}$, above which the spontaneous polarization vanishes. The equilibrium configuration is defined by $\partial \mathcal{F} / \partial P = 0$, which yields

$$E = aP + bP^3 + cP^5. (2.30)$$

Differentiating Equation 2.30 with respect to the temperature at E = 0 yields

$$\frac{\mathrm{d}}{\mathrm{d}T} \left(\frac{\partial \mathcal{F}}{\partial P} \right) \bigg|_{P=P_{\mathrm{s}}} = \frac{\partial^2 \mathcal{F}}{\partial P^2} \bigg|_{P=P_{\mathrm{s}}} \frac{\partial P_{\mathrm{s}}}{\partial T} + \frac{\partial^2 \mathcal{F}}{\partial T \partial P} \bigg|_{P=P_{\mathrm{s}}} = 0.$$
(2.31)

By using the definitions of the pyroelectric coefficient

$$p = \frac{\partial P_{\rm s}}{\partial T} \tag{2.32}$$

and the dielectric permittivity

$$\varepsilon^{-1}|_{P=P_{\rm s}} = \frac{\partial^2 \mathcal{F}}{\partial P^2},\tag{2.33}$$

we obtain

$$\frac{p}{\varepsilon} = a_0 P_{\rm s} = \frac{P_{\rm s}}{C_{\rm c}},\tag{2.34}$$

where C_c denotes the Curie constant [44]. Equation 2.34 provides an useful link between the dielectric permittivity, the spontaneous polarization, and the pyroelectric response when approaching the transition temperature.

The free energy landscape $\mathcal{F}(P)$ is depicted in Figure 2.3 a). At a temperature below T_0 , two distinct minima are visible (green line). They correspond to stable spontaneous polarization states $P_{\rm s}$. It is noted that the spontaneous polarization is a zero-field



Figure 2.3: a) Free energy vs. polarization for temperatures above, equal to and below T_0 in the field-free case. Since b = 0, the system exhibits a second-order continuous transition at T_0 . b) Polarization as function of temperature for a first order (b < 0) and a second-order $(b \ge 0)$ phase transition. c) Pyroelectric response vs. temperature for a first order (b < 0) and a second-order $(b \ge 0)$ phase transition.

property. When the temperature rises, the graph $\mathcal{F}(E)$ changes continuously. Assuming $b \geq 0$, the minima merge at T_0 , and for $T > T_0$ only one stable state at P = 0 remains (blue line). Neglecting the fifth-order term in Equation 2.30, the temperature dependence of the spontaneous polarization is

$$P_{\rm s} \approx \left[\frac{a_0}{b}(T_0 - T)\right]^{\frac{1}{2}}.$$
 (2.35)

Equation 2.35 is visualized in Figure 2.3 b) (blue line). As mentioned, $P_{\rm s}$ vanishes at T_0 and the spontaneous polarization undergoes a continuous, second-order phase transition. The pyroelectric response

$$\frac{\partial P_{\rm s}}{\partial T} = -\frac{a_0}{2b} \left[\frac{a_0}{b} (T_0 - T) \right]^{-\frac{1}{2}} \tag{2.36}$$

is graphed in Figure 2.3 c) (blue line). Below T_0 , the pyroelectric coefficient exhibits a negative sign and the magnitude increases towards the transition point, finally diverging at T_0 . Above T_0 , no spontaneous polarization and no pyroelectric response are present.

In the case of a negative coefficient b, the transition temperature is increased to a value $T_{\rm C} > T_0$. As shown in Figure 2.3 b), the spontaneous polarization exhibits a finite jump at $T_{\rm C}$ (red line). Thus, the case of b < 0 corresponds to a first-order (discontinuous) transition. In the intermediate range $T_0 < T < T_{\rm C}$, an additional local minimum of \mathcal{F} exists at P = 0 (not shown here). Above $T_{\rm C}$, only the global minimum at P = 0 remains. Thus, a ferroelectric material which is described by a Landau model with b < 0 exhibits different transition temperatures for cooling and heating, respectively. This effect is referred to as thermal hysteresis.

When an electric field is applied, the free energy landscape $\mathcal{F}(P)$ is skewed by the linear term -EP. This is depicted in Figure 2.4 a) and b) for negative and positive values of E, respectively. At low electric fields, the transition between local minima at $P = \pm P_{\rm s}$ is prohibited by the maximum at P = 0 (gray dashed line). When reaching the coercive field $\pm E_{\rm c}$, the transition to the global minimum becomes energetically favorable (red and blue lines).

The resulting polarization-field hysteresis is shown in Figure 2.4 c) (green line). In contrast to the free energy landscape, the *P*-*E* characteristic is straightforward to obtain experimentally. Above T_0 , the hysteretic behavior vanishes, and a paraelectric *P*-*E* graph is predicted by the Landau theory (purple line). The *P*-*E* characteristic directly yields the coercive field and spontaneous polarization values. However, effects such as leakage currents and imprint can lead to artifacts in the hysteresis graphs (see Figure 3.11).



Figure 2.4: a) With an external electric field $E < -E_c$, the system switches towards the negative polarization state. b) When exceeding E_c , the system switches to the positive polarization state. c) Hysteretic behavior of the polarization-field characteristic occurs for $T < T_c$. The positive and negative coercive fields are marked. For $T > T_c$, paraelectric behavior is predicted by the Landau theory.

2.2.2 Ferroelectricity in thin films

In thin films, surface effects are of particular importance. Since the electrostatic interactions of ions in the crystal lattice have a long-range character, electromechanical boundaries have a significant impact on the ferroelectric properties [45]. The Landau-Ginzburg theory incorporates small spatial variations of the order parameter $\vec{P}(\vec{r})$ [46] to describe finite crystals and the formation of domains. The free energy is now expressed as a volume integral [4]

$$\mathcal{F}^{\mathrm{LG}} = \int \mathrm{d}V \left(\gamma \left|\nabla \vec{P}\right|^2 - \frac{a}{2} \left|\vec{P}\right|^2 + \frac{b}{4} \left|\vec{P}\right|^4\right),\tag{2.37}$$

where the term proportional to γ describes the interaction of non-parallel polarization vectors.

A detailed discussion of the Landau-Ginzburg ansatz in Equation 2.37 can be found in Reference [4]. In the scope of this work, only the most relevant results are summarized. One result are depolarization effects due to charge buildup at the film interfaces. When separating volume and surface contributions of Equation 2.37, the latter cannot be neglected in thin-film systems. In practical implementations of ferroelectric layers, electrodes are used for electrical contact. Such a capacitor structure with short-circuited electrically conductive electrodes is shown in Figure 2.5 a). The electrodes reduce charge buildup to a small vicinity of the ferroelectric-metal interface, which is shown in Figure 2.5 b). The length scale of the charge distribution decreases for larger electrical conductivity of the electrode layers, and Q is represented by a δ function in the ideal case. The presence of charges at the interfaces leads to a potential drop throughout the film, which is depicted in Figure 2.5 c). The corresponding electric field is shown in Figure 2.5 d). As it is directed in the opposite direction of the polarization vector, it is referred to as the depolarization field E_{dep} . The magnitude of E_{dep} scales inversely with the film thickness, until ferroelectric behavior is completely suppressed at a certain minimal film thickness d_{\min} [47, 48]. The value of d_{\min} depends on the electrode properties [49] and the domain structure [50]. It is noted that the introduction of paraelectric interlayers, which are used for crystallization control in ferroelectric thin films [51], can also lead to depolarization effects.

For a metal-ferroelectric-metal (MFM) thin-film structure, the measurement of *ab-solute* polarization values is impractical. As discussed before, the polarization of the ferroelectric material is screened by a charge layer at the electrode interface. Further,



Figure 2.5: a) Schematic view of a pyroelectric capacitor with metal electrodes connected in short circuit. The film polarization is indicated by an arrow. Lateral dimensions of the film are large compared to the thickness (not shown here). b) Spatial distribution of charge, c) potential, and d) depolarization field. Adapted from Reference [4].

in the case of pyroelectric applications, absolute polarization values are not relevant in the first place (in contrast to charge-controlled devices such as FeFETs). Instead, the macroscopic polarization is defined via an adiabatic current flow [4]

$$\frac{\mathrm{d}P(t)}{\mathrm{d}t} = j(t). \tag{2.38}$$

Integration of Equation 2.38 with respect to the time t yields a polarization change

$$\Delta P = \int_0^{\Delta t} \mathrm{d}t \, j(t). \tag{2.39}$$

The pyroelectric response is then measured through a current flow instead of an "absolute" polarization change. The pyroelectric response of a ferroelectric thin-film with electrodes is shown in Figure 2.6 a-c). Cases for decreasing, constant, and rising temperatures are shown, respectively. It is noted that the resulting electric current does not originate from the pyroelectric material itself since charge carriers in the crystal lattice are immobile. Instead, the current flow is caused by the redistribution of the charge equilibrium at the electrode interface.



Figure 2.6: Electric current flow between the electrodes of a pyroelectric thin-film when the temperature is a) decreasing, b) constant, and c) rising.

Until now, the ferroelectric material has been treated as uniformly poled. However, in most real samples, this is not the case. Many important physical properties of these crystals stem from the existence of ferroelectric domains. The formation of domains arises from electrostatic reasons even in ideal crystals [4]. The mono-domain state is energetically unfavorable due to the large, uncompensated surface charge density. Domain walls have been found to contribute significantly to the pyroelectric effect in some materials. For instance, in lead zirconate titanate (PbZr_{0.2}Ti_{0.8}O₃), an extrinsic pyroelectric contribution due to domain wall motion has been found [52, 53]. Further, domains can be introduced by strain, an electric field [54], laser light [55], and many other mechanisms. The domain structure of HfO₂ films is analyzed by means of dual-frequency resonance-tracking piezoresponse force microscopy (DART-PFM) in Appendix A.
2.3 The HfO₂ material system

Hafnium dioxide (HfO₂) is a colorless, solid transition metal oxide with a high density of $9.68 \,\mathrm{g\,cm^{-3}}$. It has found use as a ceramic material, especially in a solid solution with zirconium dioxide (ZrO₂). In this combination, it forms a compound with high hardness and fracture toughness, which is referred to as "ceramic steel" [56, 57]. In electronics, the material is used as a capacitor dielectric [58], and as a replacement for the ubiquitous silicon dioxide (SiO₂) as a gate dielectric in field-effect transistors [59]. Further, HfO₂ thin films have been researched intensively for applications in dynamic random access memory (DRAM) cells [60–62]. As a standard material of field effect transistor technology, in the so-called high-k metal gate process, HfO₂ is ubiquitous in semiconductor manufacturing today.

In the pursuit of stabilizing polymorphs with higher dielectric permittivity, researchers at Qimonda and Infineon ultimately obtained the polar orthorhombic phase of HfO₂. This led to the unexpected discovery of the new class of HfO₂-based ferroelectrics in 2007 [63], with first publications in 2011 [1, 2]. Due to the high scalability, semiconductor-compatible manufacturing, and a sizable spontaneous polarization, the HfO₂ material class adds an unprecedented potential to the phenomenon of ferroelectricity. Some general properties of bulk HfO₂ are summarized in Table 2.1. Notably, HfO₂ exhibits a comparably large density, a high melting point, and a sizable hardness similar to that of aluminum oxide (Al₂O₃) [64].

In the following section, the structural properties of polar and non-polar HfO_2 polymorphs are discussed. The prerequisites for obtaining the polar orthorhombic phase are reviewed in Section 2.3.2.

Property		References
Melting point	$3070\mathrm{K}$	[57, 65]
Density	$9.68{ m gcm^{-3}}$	[66]
Heat capacity	$2.63{\rm MJm^{-3}K^{-1}}$	[67, 68]
Hardness	$(14.4\pm1.2)\mathrm{GPa}$	[69]
Poisson ratio	0.25 to 0.31	[57]
Elastic modulus	$283\mathrm{GPa}$	[70]
Dielectric permittivity	16	[71, 72]
Band gap	$5.8\mathrm{eV}$	[73]

Table 2.1: Some properties of monoclinic HfO₂.

2.3.1 Structural properties of HfO₂

At ambient conditions, bulk HfO_2 occurs in the monoclinic phase with the space group $P2_1/c$. With rising temperatures, a transition to the tetragonal phase (space group $P4_2/nmc$) is reported at 2050 K. The transition has been determined to be martensitic, meaning that the ions retain their respective neighbors. A further transition to the cubic fluorite parent phase (space group $Fm\bar{3}m$) occurs in the range of 2760 K to 2970 K [74]. The melting point of HfO₂ is reported at 3070 K [65, 75, 76]. At high pressures, two orthorhombic polymorphs with room-temperature transition points of 5 GPa (oI) and above 10 GPa (oII) have been observed [77, 78]. Using X-ray diffractometry (XRD) and diamond anvil cells, several space groups have been proposed for oI, including *Pbcm*, *Pcba*, and *Pca2*₁ [78–81]. A pressure-temperature diagram is shown in Figure 2.7 a), indicating monoclinic, tetragonal, and orthorhombic oI and oII phases [78].

The fluorite structure is the parent phase of further binary oxides such as cerium dioxide (CeO₂) and ZrO₂. The latter is structurally similar to HfO₂, and also exhibits the described transformation from the monoclinic to cubic and tetragonal phases with lower transition temperatures [63, 75]. In Figure 2.7 b), the phase diagram of the $Hf_{1-x}Zr_xO_2$ solid solution is shown [77]. The results indicate solubility throughout the whole composition range and an almost linear lowering of transition temperatures with an increasing Zr content. The tetragonal phase of ZrO₂ is of interest since it is reported to exhibit a large dielectric permittivity of up to 39 [62, 71].

Fortunately, high temperatures and pressures are not the only pathways to obtain the polymorphs of HfO_2 . It has been shown that the tetragonal and cubic phases can be stabilized in HfO_2 and ZrO_2 powders with particle sizes in the nanometer range [82, 83]. This is explained by the increased surface energy, which promotes the formation of the phases with a higher symmetry [84].



Figure 2.7: a) Pressure-temperature diagram of bulk HfO_2 determined with grazing incidence X-ray diffractometry in combination with a diamond pressure cell [78]. Circles, squares, triangles and diamonds correspond to m, t, oI and oII phases, respectively. b) Phase transitions in the $Hf_{1-x}Zr_xO_2$ solid solution, as suggested by [65]. An almost linear lowering of the transition temperature is obtained with rising Zr content. Adapted from [57] with the permission of Springer Nature.

More recent investigations have been performed with HfO_2 nanotubes [85] and nanorods [86]. In these studies, it has been shown that an increased specific surface lowers transition temperatures towards the tetragonal polymorph. However, unlike in ZrO_2 , the stabilization of non-ambient phases remains challenging with HfO_2 even in nanometerthin films [87].

A more controllable and very successful strategy to control the phase of HfO_2 is the admixture of other atomic species. A lowering of the monoclinic to tetragonal transition point has been shown in the $Hf_{1-x}Zr_xO_2$ solid solution [57]. Doping with rare earth elements and Si have been employed for permittivity enhancement in HfO_2 -based random access memory (RAM) devices [61, 88, 89]. It is noted that the addition of dopants is often not sufficient to stabilize non-ambient phases. Ultimately, the combination of a thin-film geometry and doping led to the stabilization of the polar orthorhombic phase in HfO_2 [1–3, 90].

The crystal structures of cubic, tetragonal, polar orthorhombic, and monoclinic polymorphs of HfO_2 are depicted in Figure 2.8 a-d). In polycrystalline HfO_2 films, a mixture of these phases is found in most cases. The corresponding lattice constants are summarized in Table 2.2. The monoclinic and orthorhombic phases exhibit a seven-fold coordination of oxygen around the Hf^{4+} ion [91]. On the other hand, the tetragonal and cubic structures have an increased coordination number of 8, meaning that bond



Figure 2.8: Crystal structure of the a) cubic, b) tetragonal, c) orthorhombic, and d) monoclinic polymorphs of HfO_2 .

breaking occurs during the corresponding phase transitions. The transformation from the monoclinic phase towards the polar orthorhombic, tetragonal and cubic phases of higher symmetry is accompanied by a shrinking unit cell volume. The stabilization of the polar orthorhombic phase, which is shown in Figure 2.8 d), is discussed in the following section.

	a (nm)	b (nm)	c (nm)	β (deg.)	Space group	Vol. (nm^3)
Cubic	0.504				$225~(Fm\bar{3}m)$	0.1284
Tetragonal	0.505		0.514		137 $\left(P4_{2}/nmc\right)$	0.1311
Orthorhombic	0.504	0.523	0.506		$29~(Pca2_1)$	0.1335
Monoclinic	0.512	0.518	0.529	99.7	$14 \ (P2_1/c)$	0.1384

Table 2.2: Lattice parameters of HfO_2 polymorphs determined by ab-initio calculations [92].

2.3.2 Stabilizing the polar orthorhombic phase in HfO_2

The search for prerequisites of ferroelectric behavior in HfO_2 -based films has spawned a large number of publications over the last years. In one of the first reports on ferroelectricity in Si-doped HfO_2 by Böscke in 2011, it has been stated that the film thickness, doping, and the electrode layer play important roles for the phase composition after cooling [90]. In the following years, the material has been studied with a wide range of methods, including

- Electrical measurements, such as P-E hysteresis [1–3, 90], harmonic analysis [93–95], first-order reversal curves (FORC) [96–98], positive-up negative-down (PUND) [9, 25, 99, 100], double-beam laser interferometry (DBLI) [101, 102] and pyroelectric [103, 104] measurements. Further, many specialized measurement techniques have been applied for specific applications such as HfO₂-based non-volatile memory [105–107].
- Physical methods, such as XRD [1, 81, 108, 109], X-ray photoelectron spectroscopy (XPS) [110–112], extended X-ray absorption fine structure (EXAFS) [113–115], X-ray absorption spectroscopy (XAS) [116], Rutherford backscattering spectrometry (RBS) [111], and time of flight secondary ion mass spectrometry (ToF-SIMS) [109, 117, 118].
- *Microscopy*, such as scanning transmission electron microscopy (STEM) [109, 119–122], energy-filtered transmission electron microscopy (EFTEM) [123], transmission Kikuchi diffraction (TKD) [124, 125], electron backscatter diffraction (EBSD) [126], piezoresponse force microscopy (PFM) [121], selected area electron diffraction (SAED) [121], and DART-PFM [127, 128].
- Computational methods, such as density functional theory (DFT) [92, 129–132], modeling of defect migration [133–135], surface energy considerations [92, 136],

molecular dynamics [137], time differential pertubed angular correlation [138], and phase field modeling [139].

As a result, certain factors which are promoting polar behavior in HfO_2 -based films have been identified. As mentioned in Section 2.3.1, one key aspect for stabilizing the polar orthorhombic phase is surface energy. Ferroelectric behavior in HfO_2 is a distinct thin-film phenomenon [140], and the film grain size can be used to tune ferroelectric properties [141–143]. In most reports, film thicknesses of 5 nm to 30 nm are used, and the largest spontaneous polarization is commonly obtained around 10 nm [144]. The thickness limit has recently been extended down to 1 nm [5], which is favorable for highdensity ferroelectric non-volatile memory (NVM), and thicker films of up to 1 µm have been reported for piezoelectric applications [145].

Dopants such as Al [146], Si [1], Zr [3], Y [2, 147], Gd [117, 148], La [97, 149], Sr [150], N [151, 152], Sc [152], or Ge [152] are used to stabilize the polar orthorhombic phase. Although ferroelectric behavior has been obtained in undoped HfO₂ [153–155], such films often contain impurities or are oxygen-deficient. The stoichiometry of HfO₂ thin films is affected by the deposition method. Throughout this work, metal-organic atomic layer deposition (ALD) is employed, where C and N are among the most critical contaminants. Careful tuning of deposition processes (e.g., oxidant dosing and process temperature) is crucial to minimize the amount of impurities that are present in the film. Details of the film deposition process are discussed in Section 3.4.1. Other manufacturing methods such as halogenide-based ALD lead to a different defect chemistry, which has to be considered when comparing literature results. Computational analysis from first principles indicates that certain dopant arrangements in the HfO₂ matrix can stabilize the orthorhombic phase, making the monoclinic phase a higher-energy metastable state [156].

Oxygen vacancies are an important defect type in HfO_2 -based films. They are prominent especially in films with aliovalent doping (e.g., La^{3+} , Al^{3+}), where oxygen vacancies neutralize local excess charges by creating cation-vacancy pairs [63, 157]. Oxygen defects have been related to several properties of HfO_2 -based films, such as the "wake-up" effect of the spontaneous polarization upon electric field cycling [158, 159], dielectric breakdown [160, 161], and resistive switching [162, 163]. It has also been argued that oxygen vacancies can change the phase composition of polycrystalline HfO_2 films by promoting the transition to tetragonal and orthorhombic structures [117]. Practically, the dosing of the oxidizer (i.e., O_3) during the growth of HfO_2 thin films by ALD has a strong influence on the phase formation (see Section 3.4.1).

Further, an effect of the electrode material and the induced film stress has been reported [90, 164]. It has been shown that the electrode choice is critical for the stabilization of the polar orthorhombic phase [142, 165]. Electrode deposition processes can have an significant impact on the chemical composition of HfO_2 -based films. In particular, the electrode interface region exhibits a complex defect chemistry, which is linked to phenomena such as the wake-up effect, imprint, and fatigue [110, 166]. Asymmetric characteristics of the leakage current density, coercive field or pyroelectric coefficients for opposite polarization states are often linked to different characteristics of the top and bottom electrode interfaces. A commonly used material is titanium nitride (TiN), which is also employed throughout this work, although a range of materials such as metals, oxides, nitrides, and semiconductors have been demonstrated as electrodes [63]. Epitaxial growth has been demonstrated on lanthanum strontium manganite ($La_{0.7}Sr_{0.3}MnO_3$) substrates [9], on Y-doped ZrO₂ [167], and directly on Si [168, 169].

Lastly, ferroelectric behavior in HfO_2 -based films can be field-induced. This results in AFE-like hysteresis characteristics, which has been observed with many dopant species [170–172]. However, there is an ongoing debate on the origin of AFE-like hysteresis in doped HfO_2 films. Computational methods indicate that the AFE-like behavior is caused by a field-induced transformation from the tetragonal to the polar orthorhombic phase [92, 130, 173]. Another possible explanation for AFE-like behavior is an depolarization field which is induced by the existence of a non-polar interface dead layer [174].

It is important to note that no comprehensive model of the ferroelectric phase stabilization in HfO_2 -based films is available yet. While the aforementioned factors have been identified, there is still an ongoing debate on the exact mechanism which is responsible for the orthorhombic phase formation.

2.3.3 Properties of HfO₂-based ferroelectric thin films

Thin films often exhibit properties that are significantly different from these found in bulk crystals. This is especially true for the HfO_2 material class, where polar behavior is a distinct thin-film phenomenon. For many previously known ferroelectric materials, the opposite is the case: ferroelectricity vanishes at the nano-scale. The initial skepticism regarding the intrinsic ferroelectricity in the HfO_2 material class have since been dispelled by hundreds of publications. The observation of the pyroelectric effect and the analysis of its reversibility in this dissertation will contribute to proofing the intrinsic nature of ferroelectricity in HfO_2 -based films.

Si-doped HfO_2 was one of the first HfO_2 -based materials in which ferroelectricity was observed [1]. It is well suited to illustrate the formation of ferroelectric behavior since a continuous evolution of the phase composition occurs throughout the stoichiometry range. In Figure 2.9, the phase evolution in the HfO_2 material class is illustrated. Structural and electrical properties are shown for Si-doped HfO_2 , however, comparable results are obtained for other materials, such as Al-, La- and Zr-doped films.

From the top towards the bottom row in Figure 2.9, the phases are ordered with an decreasing crystal symmetry. In thin films, the structural evolution from the monoclinic towards the orthorhombic and tetragonal phases is induced by an increasing Si content. This is illustrated by the XRD patterns, which are obtained for films with a thickness of 10 nm and TiN electrodes.

The diffractogram of pure HfO_2 (bottom of Figure 2.9) matches the monoclinic phase, with characteristic diffraction peaks at 28.3° and 31.7°. On the other hand, the reflexes for the highly Si-doped HfO_2 match the tetragonal $P4_2/nmc$ pattern. The



Figure 2.9: Illustration of the phase evolution in HfO_2 -based thin films, where Si-doped HfO_2 is used as an example. The cubic structure is the parent phase, from which the tetragonal phase originates. Further symmetry breaking leads to the orthorhombic and monoclinic phases. The phase change is accompanied by an evolution of the electric behavior from an AFE-like to ferroelectric and finally paraelectric response.

polar orthorhombic $Pca2_1$ phase exists in the intermediate range [175]. However, exact determination of the phase composition by Rietveld refinement [176, 177] is challenging due to the low film thickness and polycrystallinity of films manufactured by ALD. It is further complicated by the structural similarity of the tetragonal and orthorhombic polymorphs. The de-convolution of diffractograms is discussed in Section 4.1.1.

The change from the monoclinic to the polar orthorhombic and finally to the tetragonal phases is accompanied by an evolution of the electrical behavior. Exemplary polarization hysteresis characteristics of three stoichiometries are shown on the right side of Figure 2.9. Pure monoclinic HfO_2 is a dielectric without hysteretic behavior. In the intermediate range, ferroelectric switching is observed. Besides doping, the ferroelectric properties are sensitive to many fabrication parameters such as deposition conditions, film thickness and annealing temperature. Finally, the highly Si-doped films exhibit a low spontaneous polarization and an AFE-like, pinched hysteresis loop.

Comparison to other ferroelectric materials

The HfO_2 material class exhibits properties which differ significantly from previously known polar materials. In contrast to perovskites, polarization switching in HfO_2 -based ferroelectrics is not induced by a displacement of the metal cations, but by the oxygen anions. Most notably, ferroelectricity persists in doped HfO_2 down to a thickness of 1 nm [5], and vanishes in films thicker than 30 nm. However, this lamination has been overcome by nano-lamination or artificial grain boundaries [51] and in yttriumsubstituted hafnium oxide ($\text{YO}_{1.5}$: HfO_2) [178]. In comparison to perovskites, HfO_2 based films exhibit large breakdown fields around 4 MV cm^{-1} . Additionally, coercive fields are comparably high at approximately 1 MV cm^{-1} . Both values exceed these of perovskite ferroelectrics significantly, in some cases by one order of magnitude.

HfO₂-based ferroelectrics exhibit a comparably low dielectric permittivity compared to materials such as $PbZr_xTi_{1-x}O_3$ or $Pb(Mg_{1/3}Nb_{2/3})O_3$ -PbTiO₃. Further, HfO₂ possesses a large band gap of approximately 5.6 eV [179], which effectively suppresses leakage currents even at small film thickness values. In comparison, a band gap of 3.4 eV has been reported for $PbZr_xTi_{1-x}O_3$ [180]. Some properties of doped HfO₂, $PbZr_xTi_{1-x}O_3$, and LiTaO₃ are summarized in Table 2.3. A thorough comparison of HfO₂-based films to other ferroelectric material systems is outside the scope of this dissertation. However, it is clear that the HfO₂ material class adds a unique combination of properties to the available ferroelectric materials. Many of these properties have an interesting application potential. For example, the rather low dielectric permittivity would reduce de-polarization fields which arise from interface dead layers [181], which would be beneficial for the stability in pyroelectric sensor applications.

Very recently, further unique properties have been described for the HfO_2 material system. Lee et al. have found scale-free nanoscopic domains as small as single unit cells by computational methods. Another group proposed an unusual negative piezo-

electric effect in HfO_2 . These examples make clear that the HfO_2 material class exhibits properties which are fundamentally different from previously known ferroelectrics.

Property	Doped ${\rm HfO}_2$	BaTiO_3	${\rm LiTaO_3}$
Coercive field	$1 {\rm MV cm^{-1}}$ [1]	$0.02\mathrm{MVcm^{-1}}$	$0.02{\rm MVcm^{-1}}$ [182]
Displaced species	Anion	Cation	Cation
Remanent polarization	$23\mu Ccm^{-2}$ [97]	$35\mu Ccm^{-2}$ [4]	$50\mu Ccm^{-2}$ [4]
Band gap	$5.6{ m eV}$ [179]	$3.2{\rm eV}$ [183]	$4.7{\rm eV}$ [184]
Curie temperature	290 to $450 ^{\circ}$ C [63, 185]	$135 ^{\circ}\mathrm{C} [11]$	$665 ^{\circ}\mathrm{C} [11]$

Table 2.3: Comparison of properties for doped HfO_2 , $BaTiO_3$, and $LiTaO_3$ from the literature.

Chapter 3

Methods

This chapter describes methods for determining pyroelectric and electrocaloric responses in polycrystalline, HfO_2 -based thin films. A wide range of measurement principles have been proposed in the literature [186]. However, previous reports were often focused on bulk crystals or thick films. Nanometer-thin films spawn some challenges for pyroelectric measurements. The comparably high defect density prohibits methods susceptible to leakage currents, thermal fatigue effects, or metastable contributions. Further, the mechanical clamping by the substrate and interactions with other films in the multi-layer stack have to be considered.

In Section 3.1, two approaches for the quantification of pyroelectric coefficients are discussed: The low-frequency Sharp-Garn method and a high-frequency measurement technique, which utilizes a specialized test structure. Both methods complement each other. The first method offers the possibility of a comprehensive pyroelectric screening of the HfO_2 material class at a feasible characterization effort. The latter method is utilized to obtain a more in-depth understanding of the effect, e.g., by separating primary and secondary contributions.

The characterization of the electrocaloric effect with direct and indirect methods is discussed in Section 3.2. Since the heat capacity of the thin HfO_2 films is very small, a specialized test structure is used to directly observe electrocaloric temperature changes. Further, the implementation of energy conversion experiments is discussed in Section 3.3.

Finally, in Section 3.4.1, the deposition of HfO_2 -based ferroelectric films by ALD is discussed. A specialized ALD regime is proposed to enhance the intermixing between dopant species and the HfO_2 matrix.

3.1 Quantification of pyroelectric coefficients

The quantification of pyroelectric coefficients is generally based on observing a polarization change upon a temperature variation. Particular measurement principles differ in the heating concept, the thermal equilibrium conditions, the temperature slope or waveform, and the mechanism of measuring the polarization change. Methods have been reviewed by Lang et al. [187], Lubomirsky et al. [188], and Jachalke et al. [186], and are divided into static and dynamic approaches. Static methods probe the polarization state of a material for a range of temperatures, which are held constant during individual measurements. The polarization state is determined by a hysteresis measurement [189] or XPS [190] (see Section 4.2). In dynamic methods, a temperature waveform (e.g., sinusoidal) is applied. The resulting polarization change induces an alternating current flow between electrodes, which is quantified. Heating methods include Peltier elements [191, 192], dielectric heating [193], local Joule heating [39], and the use of modulated light sources such as lasers [194], each offering different frequency and temperature amplitude ranges.

3.1.1 Sharp-Garn method

A quasi-static method was proposed by Sharp and Garn [191, 192] to distinguish the pyroelectric response from non-pyroelectric contributions. In this approach, the temperature is varied sinusoidally, and the resulting current is registered. Therefore, the pyroelectric material is contacted with electrodes. In this work, metal-pyroelectric-metal structures on a Si substrate are used, which are manufactured according to Section 3.4.1. Typical values of the temperature variation are below 1 Hz with an amplitude θ of few Kelvin to ensure thermal equilibrium throughout the sample. Being a phase-sensitive, small-signal method, it reliably eliminates spurious contributions. The polarization change due to the pyroelectric effect results in a compensation current

$$I_{\rm p}(t) = p A \frac{\mathrm{d}T}{\mathrm{d}t} \tag{3.1}$$

between short-circuit electrodes, where A is the area, and p denotes the out-of-plane pyroelectric coefficient. The harmonic temperature change is described as

$$T(t) = \theta \sin(\omega_{\rm h} t) + T_{\rm offs}, \tag{3.2}$$

where $\omega_{\rm h}$ is the angular frequency of the temperature oscillation, and $T_{\rm offs}$ denotes a constant temperature offset. Then, the short-circuit pyroelectric current

$$I_{\rm p}(t) = p A \theta \,\omega_{\rm h} \,\cos(\omega_{\rm h} t). \tag{3.3}$$

exhibits a characteristic phase-shift by $\varphi = \frac{\pi}{2}$ with respect to the temperature waveform. In Figure 3.1 a), the waveforms of temperature and pyroelectric current are shown schematically. Non-pyroelectric contributions occur mostly in-phase with the temperature variation, and thus lead to a phase $\varphi \neq \frac{\pi}{2}$. Such in-phase contributions may be caused by the thermally stimulated release of trapped charges, which are injected during poling or electric field cycling [186]. Further contributions to the current response upon temperature variation are discussed in Section 4.1. In the calculation of the pyroelectric coefficient

$$p = \frac{I_{\rm p} \sin \varphi}{A \,\omega_{\rm h} \,\theta} \tag{3.4}$$



Figure 3.1: a) Temperature waveform (red line) and corresponding electric current (blue line) obtained with the Sharp-Garn measurement method. For an ideal pyroelectric material, current and thermal excitation are phase-shifted by $\frac{\pi}{2}$. b) Schematic view of the Sharp-Garn method measurement setup. The sample is mounted on a Peltier element, which allows precise temperature manipulation.

only the out-of-phase response is considered.

The method is implemented by placing the sample on a Peltier element (Quick-Ohm GmbH, model QC-241-1.4-8.5M), as shown in Figure 3.1 b). A copper heat spreader and thermal paste are used to achieve a homogeneous temperature profile. Simultaneously, the sample temperature is monitored using a precision sensor (IST AG, model P.232.4SW) and a multimeter with four-wire connections (Keithley, model 2000). A control loop is implemented by means of a Python program, which adjusts the source measure unit (SMU) (Agilent, model B2900) output voltage. The Peltier element is driven by the SMU in order to achieve a stable sinusoidal temperature variation. The pyroelectric sample is contacted by a micro-manipulator with a tungsten needle, and via the electrically conductive substrate. The generated current is then measured with a high-sensitivity amperemeter (Agilent, model B2981A). All measurement devices are controlled via a general purpose interface bus (GPIB), and results for measurement settings, time, temperature and current are recorded by the Python program. Samples are polarized and field-cycled prior to pyroelectric measurement using an ferroelectric analyzer (Aixacct, model TF3000).

Accurate temperature profiles are achieved with a control loop, which applies a voltage output proportional to the temperature error. Additionally, the time integral of the temperature mismatch is considered as well. This combination is referred to as proportional-integral control [195]. Careful tuning of parameters is crucial to achieve an optimal temperature response and suppress higher harmonics. In Figure 3.2 a) the step response of the controller is shown. The performance is optimized by tuning the proportional and integral coefficients until reaching the desired behavior (red line) [196].

The used amperemeter permits a minimum measurement range of 20 pA with a settling time to 0.1% of 1.4 s [197]. For reduced phase lag, the 2 nA range with a settling



Figure 3.2: a) Step response of the Peltier element control loop with three different values of the proportional coefficient. b) Frequency spectrum of a sinusoidal temperature oscillation with an amplitude of 1 K at 50 mHz. c) Frequency spectrum of the corresponding current measurement of a 20 nm thick Si-doped HfO_2 film.

time of 13 ms can be used. A frequency spectrum of the observed temperature oscillation is depicted in Figure 3.2 b). It is visible that the temperature amplitude and frequency match the desired values, and that the second harmonic amplitude is below 2 mK. A total harmonic distortion (THD) of 1.5×10^{-3} is calculated. In Figure 3.2 c), the frequency spectrum of the corresponding current measurement is shown, indicating a distinct response at 50 mHz. A low noise floor is achieved even in an unshielded probe station by using triaxial cables and integration times which are multiple of 20 ms, eliminating power line noise. Some higher harmonics are visible, indicating slight nonlinearity in the pyroelectric response. The raw data of the pyroelectric current is then evaluated by modeling with a sine function superimposed with an exponential decay, which accounts for relaxation currents which may occur after poling.

In the Sharp-Garn method, the sample is assumed to be in thermal equilibrium. Since the Peltier element, temperature sensor, and sample possess a considerable heat capacity, sufficiently low frequencies have to be used. In Figure 3.3 a), extracted pyroelectric coefficients are shown exemplary with $\omega_{\rm h}$ varied in a range of 10 mHz to 100 mHz. A decrease of p by 5% is detected from the lowest to the highest frequency, which is explained by the increasing difference between the sensed and actual temperatures. From an exponential model (red line), a time constant of 0.6 s is estimated. The corresponding phase shift in Figure 3.3 b) matches the ideal value of $\frac{\pi}{2}$ or 90° closely at the lowest frequency. With rising $\omega_{\rm h}$, the condition of thermal equilibrium is violated, and a deviation from the ideal phase is observed. A default value $\omega_{\rm h} = 50 \,\mathrm{mHz}$ is chosen as a compromise with decent measurement speed and minor phase lag. Unless noted otherwise, measurements are performed at $\theta = 1 \,\mathrm{K}$, with a constant temperature offset of 30 °C.



Figure 3.3: Exemplary pyroelectric measurement result for a 20 nm thick Si-doped HfO_2 film. a) Pyroelectric coefficients calculated according to Equation 3.4 for a range of excitation frequencies of 10 mHz to 100 mHz. b) Phase of the current, which deviates from the ideal value of 90° with increasing frequencies.

The measurement setup is verified with a commercial LiTaO₃ reference sample with a thickness of 50 µm and metallic electrodes. The calculated pyroelectric coefficient of $(-183 \pm 3) \,\mu\text{C}\,\text{m}^{-2}\,\text{K}^{-1}$ has a relative deviation of 4% from the reported literature value of $-176 \,\mu\text{C}\,\text{m}^{-2}\,\text{K}^{-1}$ [30, 198]. The measurement uncertainty is calculated from five successive measurements. The registered phase of 95° indicates a clear pyroelectric response.

3.1.2 Contact-less pyroelectric measurement by XPS

Most pyroelectric measurement methods use electrical connections to measure the charge flow between electrodes which is caused by the pyroelectric effect (see Equation 2.38). X-ray photoelectron spectroscopy (XPS) offers a method to access the temperature dependent polarization directly.

Ehre et al. have proposed a measurement approach where XPS is used for contactfree pyroelectric measurements [190]. The method has been demonstrated with bulk LiTaO₃ samples. It is based on the fact that a polar material with electrodes develops a surface charge density Q_s , as described in Section 2.2.2. The pyroelectric effect then modulates Q_s , which results in a shift of the photoelectron spectra. Here, the technique is extended to ferroelectric thin films.

A sketch of the measurement setup is shown in Figure 3.4 a). As a XPS instrument, a Physical Electronics Quantes system with Al K_{α} radiation at 1486 eV is used. The analyzer pass energy is set to 69 eV. The sample holder comprises a computer-controlled heating circuit with a feedback loop. The measurement is conducted on a MFM capacitor structure. The analysis region is located so that both the Pt top electrode as well as the un-poled HfO₂ are illuminated by X-rays. Initially, the polarized capacitor structure



Figure 3.4: a) Sketch of the pyroelectric measurement via XPS (not to scale). In this experiment, the analyzer is oriented at an 45° angle with respect to the sample surface. The region of interest includes the pyroelectric capacitor with a Pt top electrode and the exposed HfO₂. The latter does not possess a macroscopic net polarization. b) Cross-sectional sketch of the pyroelectric capacitor (not to scale). Upon heating, the surface charge density Q_s is reduced, and the energy spectrum of the Pt 4f peak is shifted.

exhibits a large surface charge density, as indicated in the cross-sectional sketch in Figure 4.22 b). When the sample is heated, the polarization of the film is reduced due to the pyroelectric effect. In a vacuum, and without using charge neutralization, this results in a reduction of the charge density in the top electrode, as indicated in Figure 4.22 b) on the right side.

When an electron is emitted by means of the photoelectric effect, the binding energy

$$E_{\rm B} = h\nu - E_{\rm K} - \phi + eU_{\rm surf} \tag{3.5}$$

depends the X-ray photon energy $h\nu$, the measured kinetic energy $E_{\rm K}$, the spectrometer work function ϕ and the surface potential of the sample $U_{\rm surf}$. Thus, any change of the surface charge density directly alters the obtained binding energies. The pyroelectric coefficient is then calculated as

$$p = \frac{\varepsilon_0 \varepsilon_r}{d_{\text{HfO}_2}} \frac{\mathrm{d}E_{\text{B}}}{\mathrm{d}T},\tag{3.6}$$

where d_{HfO_2} is the thickness of the pyroelectric film. Equation 3.6 indicates that the sensitivity of the method is higher for thicker films with a low permittivity.

Nonetheless, accurate results are possible even for nm-thin films when the effects of sample charge-up are eliminated. This is achieved by a differential approach, where the binding energy difference between the Pt top electrode and the randomly polarized HfO_2 without a top electrode

$$\Delta E_{\rm B} = E_{\rm B,Pt} - E_{\rm B,Hf} \tag{3.7}$$

is considered.

3.1.3 Local thermal excitation method

To overcome the limited frequency range of the Sharp-Garn method, the requirement of thermal equilibrium throughout the sample is dropped. Instead, temperature change is achieved by means of local Joule heating with a miniaturized metal thin film heater. Since there is a strong thermal coupling between the pyroelectric material and the heat source in such a multi-layer film stack, a greatly increased frequency range is accessible. The test structure has been proposed by Bathia et al. [199] in order to characterize the pyroelectric response of epitaxial PbZr_{0.2}Ti_{0.8}O₃ films. A refined design has been used by Pandya et al. [39, 200].

Here, a similar test structure is used, which is shown schematically in Figure 3.5 a). It comprises a capacitor structure with the pyroelectric thin film (green) and TiN electrodes (yellow). A SiO₂ layer (blue) and an electrically conducting Ni film (purple) are located on top of the capacitor structure. The SiO₂ film serves as an electrical insulation layer, which protects the pyroelectric film from the applied heating voltage.

In this dissertation, the test structure is also used for electrocaloric measurements, which are discussed in Chapter 3.2. Further, a high current sensitivity below 2 pA and a frequency range of up to 1 kHz are demonstrated. The method is an advancement of the 3ω -technique [201, 202], which has found wide use for determining the thermal properties of thin films.

A heat transport model is required to relate the temperature amplitude in the heater, which is measured by the 3ω -method (see Section 3.1.4), to the actual variation in the HfO₂ layer. There are several possible approaches, including an one-dimensional transport model [39, 203], finite element method (FEM) simulation, and analytical descrip-



Figure 3.5: a) Cross-sectional illustration of the test structure for pyroelectric measurements. The thermal wave originates at the Ni heater (top) and propagates through the multi-layer film stack towards the bulk substrate. b) Representation of the thermal impedance of the multi-layer, where each thin film is modeled as the combination of a heat capacity and a thermal resistivity. From the schematic it is evident that the overall thermal impedance depends on the frequency of the heat dissipation.

tions [204]. One particular challenge arises from the wide variety of length scales in the pyroelectric device: While the HfO_2 film exhibits a thickness of only 20 nm, heat propagation in the substrate may extend into the mm scale. Thus, a hybrid approach is employed, which combines an one-dimensional transport model for the multi-layer film stack with an analytical or experimental thermal impedance of the substrate.

The heat propagation in the multi-layer film stack can be understood in analogy to an electrical current flow. In this simplified picture, a thermal resistivity and a heat capacity are assigned to each thin film of the multi-layer. The corresponding equivalent circuit is shown in Figure 3.5 b). Each layer is assigned a thermal resistivity R_i and a heat capacitance C_i . It is evident that the thermal impedance of each individual layer

$$Z_i = \left(\frac{1}{R_i} + i\omega C_i\right)^{-1} \tag{3.8}$$

depends on the frequency of the source, where $i = \sqrt{-1}$. Each term Z_i results in an attenuation and a phase shift of the thermal wave which is generated at the heating element. Additional terms in the model may be added to consider the thermal properties of interfaces. In the substrate, the one-dimensional approximation is not applicable anymore. Temperature oscillations of a line heater have been analyzed by Carslaw and Jaeger [205], where heat flow has a cylindrical symmetry. Experimentally, the complex thermal impedance of the substrate is assessed by using the 3ω -Method, which is discussed in Section 3.1.4. Further, FEM modeling is employed to examine the heat transport in the particular test structure layout, with results discussed in Section 4.3.1.

The multi-layer is characterized by an overall thermal impedance $Z_{\rm T}$

$$Z_{\rm T} = Z_{\rm Ni} + Z_{\rm SiO_2} + \dots + Z_{\rm TiN} + Z_{\rm sub}.$$
(3.9)

The temperature change of the heater line $\tilde{\theta}$ with respect to ambient conditions is

$$\tilde{\theta}(\omega,\omega_{\rm h}) = \tilde{Q}(\omega,\omega_{\rm h})\,\tilde{Z}_{\rm T}(\omega),\tag{3.10}$$

where the tilde sign indicates quantities in the frequency domain, and \tilde{Q} denotes the thermal energy dissipated by Joule heating [204]. In the time domain, this corresponds to a convolution

$$\theta(t,\omega_{\rm h}) = Q(t,\omega_{\rm h}) * Z_{\rm T}(t). \tag{3.11}$$

In the case of a sinusoidal current flow $I_{\rm h}\sin(\omega_{\rm h}t)$ through the heater, the dissipated power

$$Q(t) = \frac{I_{\rm h}^2 R}{2} \left(1 - \cos(2\omega_{\rm h} t)\right)$$
(3.12)

oscillates at the second harmonic frequency, superimposed with a constant contribution. The latter leads to an initial temperature increase in the test structure. After sufficient time, the contribution from the static term $I_{\rm h}^2 R/2$ is in equilibrium. Then, the temperature of the heater oscillates as

$$T(t) \approx \theta \cos(2\omega_{\rm h} t + \varphi) + T_{\rm offs}, \qquad (3.13)$$

ź

where $T_{\rm offs}$ corresponds to the temperature offset due to ambient conditions and constant-current heating. A phase shift φ accounts for thermal lag. This may be caused by heat transfer through the multi-layer film stack, as well as the lateral propagation in interaction with the bulk substrate. The characteristic length of temperature propagation is given as

$$\lambda = \sqrt{\frac{k}{2\omega_{\rm h}C_{\rm s}\varrho}},\tag{3.14}$$

where k denotes the thermal conductivity, ρ is the density, and $C_{\rm s}$ is the specific heat capacity of the material. Equation 3.14 can be used to estimate the range of the temperature oscillation in the monocrystalline Si substrate. For instance, at a frequency of 10 Hz this corresponds to a value of $\lambda = 840 \,\mu\text{m}$, which is larger than the substrate thickness of 750 µm. Thus, at low frequencies, the whole substrate is considered to experience nearly homogeneous temperature increase. At 10 kHz, a value of $\lambda = 26 \,\mu\text{m}$ is calculated, meaning that only the uppermost part of the substrate experiences temperature oscillations, while the rest of the silicon remains close to thermal equilibrium.

According to Equation 3.1, a pyroelectric short-circuit current flow

$$I_{\rm p}(t) = -2\omega_{\rm h}Ap\,\theta\sin\left(2\omega_{\rm h}t + \varphi\right) \tag{3.15}$$

is generated. Thus, for a solely pyroelectric response and no thermal lag ($\varphi = 0$), an ideal phase shift of π is expected with respect to the heating current. It is noted that this difference to the optimal value in the Sharp-Garn method is caused by the heating mechanism. While the Peltier effect is capable of both sinking and sourcing heat, Joule heating is leading to the aforementioned frequency doubling. The pyroelectric coefficient is calculated as

$$p = \frac{I_{\rm p}}{2\omega_{\rm h}\,\theta\,A}\cos(\varphi).\tag{3.16}$$

Current measurements are performed with a digital lock-in amplifier (Zurich Instruments MFLI), which is shown schematically in Figure 3.6. Since the pyroelectric current is generated at the second harmonic frequency $2\omega_{\rm h}$, capacitive coupling between the heater and the top electrode at $\omega_{\rm h}$ is strongly suppressed in the lock-in measurement.

For all measurements, AC coupling and an amplifier transimpedance gain setting of 10^6 V A^{-1} with a specified bandwidth of 450 kHz [206] are used. The reference oscillator of the lock-in amplifier is used to generate the micro-heater current. Since the output impedance of 50 Ω is too high for the test structure, a self-made voltage-to-current converter is used. To ensure a linear response, an operational amplifier (LMH6672, Texas Instruments) with a high bandwidth of 90 MHz, a high output current of 200 mA and low THD is used. The gain is set by the electric resistance R_1 , where a 5 Ω value with low temperature coefficient is used. The function principle of the operational amplifier ensures that currents through the integrated micro-heater and the resistor R_1 are always equal, adjusting the amplifier output voltage accordingly. Measurements are



Figure 3.6: Schematic top view of the test structure with an amplifier circuit generating the sinusoidal heater current (red). Pyroelectric current measurement is performed with a lock-in technique (blue).

performed for both polarization states of the ferroelectric material, and only the current difference is considered in the calculation of pyroelectric coefficients. Thereby, spurious contributions arising from capacitive coupling are further reduced.

3.1.4 Thermal impedance analysis with the 3ω -method

To calculate pyroelectric coefficients, knowledge of the amplitude and phase of the temperature oscillation in the test structure are essential. As discussed before, these quantities are dictated by the thermal impedance of the multi-layer film stack and the underlying substrate. The 3ω -method allows accurate analysis of the heat flow by exploiting the temperature-dependent electrical resistance in the micro-fabricated heater. The method was proposed by Cahill et al. in 1987 [201, 202], and since then found extensive use for investigation of thermal properties in thin films and nanostructures.

The electrical resistance $R_{\rm h}$ of the heater (see Equation 3.12) exhibits a temperature dependence, which is characterized by a coefficient

$$\alpha(T) = \frac{1}{R_{\rm h}(T)} \frac{\mathrm{d}R_{\rm h}}{\mathrm{d}T}.$$
(3.17)

In the case of small temperature variations θ , $R_{\rm h}(T)$ is approximated by a linear function

$$R_{\rm h} \approx R_{\rm h,0} \left(1 + \alpha \theta\right),\tag{3.18}$$

where $R_{\rm h,0}$ is the resistance at the reference temperature. The current flow through a thin metal strip leads to Joule heating, which in turn changes $R_{\rm h}$. A harmonic temperature change, as in Equation 3.13, thereby effectively modulates the heater current. Thus, the voltage drop over the heater line comprises harmonics at $\omega_{\rm h}$, $2\omega_{\rm h}$, and $3\omega_{\rm h}$, and a constant offset. The third harmonic voltage

$$U_{3\omega} = -\frac{1}{2} \alpha R_{\rm h,0}^2 I_{\rm h}^3 \ Z(2\omega_{\rm h}) \tag{3.19}$$

is then directly proportional to the thermal impedance Z [207]. Combining Equations 3.10 and 3.19 yields the temperature amplitude

$$\theta(2\omega_{\rm h}) = \frac{2U_{3\omega}}{\alpha R_{\rm h,0}I_{\rm h}},\tag{3.20}$$

which is directly proportional to the third harmonic voltage, hence the name of the method. It is worth mentioning that this expression does not require a particular heating line geometry [204]. For a line heater with length L, and a width which is much smaller than the thermal wavelength $W \ll \lambda$, Cahill [202] calculated the thermal impedance as

$$Z_{\rm sub}(\omega_{\rm h}) = \frac{-1}{2\pi k_{\rm sub}L} \left(\ln \omega_{\rm h} + \text{const.}\right), \qquad (3.21)$$

where $k_{\rm sub}$ is the thermal conductivity of the substrate. In case of a finite substrate, Equation 3.21 is still valid if the thickness is much larger than λ . On a 750 µm thick silicon substrate, the frequency should be larger than 10 Hz.

The measurement setup is depicted in Figure 3.7. A precision alternating current source (Keithley 6221) is used to force a sinusoidal current through the metal strip (red circuit). The voltage drop is then measured by the lock-in amplifier (blue circuit). To achieve accurate readings, a low-pass time constant of 0.5 s and a settling delay of 10 s between measurements are used. The current amplitude is set to 20 mA, and the waveform is synchronized to the reference signal of the lock-in amplifier.

In Figure 3.8 a), an exemplary frequency spectrum of the voltage drop over the thin film heater is shown. The dimensions of the Ni strip are 150 µm by 900 µm, with a thickness of 100 nm. The largest peak is visible at $\omega_{\rm h} = 117.75$ Hz, and second, third, and fourth harmonic frequencies are registered as well. No significant static voltage drop is registered, which indicates that the constant contribution is in a thermal equilibrium. The first harmonic voltage $U_{1\omega}$ scales linearly with $I_{\rm h}$, as expected by Ohm's law. In



Figure 3.7: Circuit diagram of the measurement setup for the differential 3ω method. A sinusoidal current is applied to the heater by the precision alternating current source. The voltage drop is then measured by the lock-in amplifier.

Figure 3.8 b), a magnified view of the contribution at $3\omega_{\rm h}$ is shown, indicating a strong increase in amplitude for rising values of $I_{\rm h}$. According to Equation 3.19, the third harmonic voltage is proportional to $I_{\rm h}^3$, which is confirmed in Figure 3.8 c).



Figure 3.8: a) Frequency spectrum of the voltage drop over a 150 µm by 900 µm Ni strip with a thickness of 100 nm at heater current amplitudes of 20 mA, 40 mA and 80 mA. The alternating current frequency is set at 117.75 Hz, and voltage peaks at $\omega_{\rm h}$ and the higher harmonics are visible. b) Magnified view of the $3\omega_{\rm h}$ contribution. c) Amplitude of the third harmonic voltage with respect to the heater current (blue circles).

Differential 3ω -method

When probing thermal properties of nanometer-thin films on an infinite substrate, very high frequencies would be needed in order to confine the thermal wave to the thin layer. For instance, a 20 nm HfO_2 film would require a temperature oscillation in excess of 500 MHz (see Equation 3.14), which is difficult to realize without specialized test structures and equipment.

The differential 3ω method solves this problem by considering a set of samples, where only the layer of interest is varied in thickness, and all other properties are kept constant [207]. The layer stack is considered as a series connection of thermal impedances. Then, the thermal properties of the film is extracted from the difference of the values in two samples with different film thicknesses as

$$Z_{\rm film} = Z - Z_0.$$
 (3.22)

The thermal resistivity is then calculated as

$$R_{\rm film} = \frac{\mathrm{d}}{\mathrm{d}d_{\rm film}} \frac{\theta}{I_{\rm h} U_{1\omega}},\tag{3.23}$$

where d_{film} denotes the film thickness.



Figure 3.9: a) Circuit for ferroelectric hysteresis measurement with the virtual ground method. b) Triangular electric field waveform with a frequency of 1 kHz and c) corresponding current response during measurement, where peaks indicate ferroelectric switching.

3.2 Quantification of electrocaloric coefficients

Methods for the quantification of electrocaloric coefficients are divided in indirect and direct techniques. Indirect methods utilize the temperature dependence of the remanent polarization, which is commonly extracted from ferroelectric hysteresis characteristics. These measurements exploit the thermodynamic equivalence of pyroelectric and electrocaloric effects, which is only valid under certain conditions (see Equation 2.23). On the other hand, direct methods observe the actual electrocaloric temperature change, which is induced by the application of an electric field under adiabatic conditions.

In the literature, approximately two thirds of the reports on electrocaloric properties employ indirect methods [208]. Indirect measurements can be implemented with commonly available measurement equipment [209, 210], while analysis of thin films with direct (calorimetric) methods is challenging due to their minute volume and total heat capacity.

3.2.1 Polarization-field hysteresis method

The observation of ferroelectric hysteresis characteristics at different temperatures was one of the first methods used to analyze the pyroelectric and electrocaloric effects systematically [12, 189]. The ferroelectric response of potassium sodium tartrate tetrahydrate (KNaC₄H₄O₆ · 4 H₂O), which is also known as Rochelle salt, is reduced with rising temperatures and eventually vanishes. Sawyer et al. performed the measurement by using a capacitor voltage divider, which displays the ferroelectric hysteresis loop on a cathoderay tube [11, 189].

In modern test systems, the charge flow onto the ferroelectric capacitor is measured with an operational amplifier circuit. In this "virtual ground" method, parasitic effects (e.g., by cable capacitance) are dramatically reduced [95, 211]. A schematic view of the electric circuit is shown in Figure 3.9 a). To obtain the hysteresis characteristic, a triangular electric field waveform is applied to the sample. The voltage drop which is registered at the shunt circuit is then directly proportional to the transient current flow between the electrodes. The applied field and the corresponding current flow are shown in Figure 3.9 b) and c), respectively, where ferroelectric switching events are visible as peaks. Integration of the current with respect to time then yields the polarization density

$$P(t) = \int_0^t \frac{I}{A} dt + \text{const.}, \qquad (3.24)$$

where A is the area of the ferroelectric capacitor and I is the total electric current. Plotting the polarization P(t) with respect to the voltage U(t) then yields ferroelectric hysteresis graphs. Such a measurement result is shown exemplary in Figure 3.10. The current response exhibits clear polarization switching peaks, which are superimposed on a baseline current corresponding to charging of the dielectric capacitance. Integration of the current over time yields the macroscopic polarization (blue line). Measurements of the polarization hysteresis are performed at a range of temperatures, which are held constant during each individual measurement. The electrocaloric coefficient is then calculated as

$$\Sigma = \frac{\mathrm{d}P_{\mathrm{r}}}{\mathrm{d}T},\tag{3.25}$$

where the remanent polarization $P_{\rm r}$ is defined as the mean value $(P_{\rm r,+}-P_{\rm r,-})/2$. Since this measurement relies on polarization switching, it is not applicable to non-ferroelectric polar materials. The field amplitude has to be sufficiently high to ensure saturation of the *P-U* graph. The method is susceptible to non-electrocaloric contributions. First, thermal fatigue effects due to defect migration become prominent especially at raised temperatures. In thin films, de-polarization fields reach a significant magnitude, which leads to an accumulation of defect charges at the electrode interfaces, inhibiting ferroelectric switching [185, 212, 213]. Further, at high fields, degradation of the ferroelectric by defect generation and, eventually, electric breakdown occur [214].

Additionally, the remanent polarization may be affected by other effects such as imprint, where both coercive fields are shifted in the same direction, as shown in Figure 3.11 a) [215]. Another influence are leakage currents, which are of special importance in thin films at raised temperatures. The impact of leakage is shown in Figure 3.11 b). It is evident that increased leakage currents at higher temperatures can lead to apparent *positive* electrocaloric coefficients. Thus, care has to be taken to reduce the electric field to a magnitude where such currents are minor. Lastly, in the HfO₂ material system, the magnitude of the remanent polarization is dependent on previous electric cycling [216]. This is visualized in Figure 3.11 c). It is important that sufficient electric field cycling



Figure 3.10: a) Current-field response (red line) of a 20 nm thick, Si-doped HfO_2 ferroelectric film and the corresponding polarization hysteresis graph (blue line). b) Evolution of the hysteresis characteristic for rising temperatures.



Figure 3.11: The effect of a) imprint, b) leakage currents, and c) wake-up or fatigue on polarization hysteresis characteristics.

is applied beforehand any electrocaloric measurements, to ensure that a stable state is reached.

With these limitations in mind, the method offers a straightforward way of characterizing electrocaloric and ferroelectric properties in a wide temperature range with standardized measurement equipment. It is useful to perform wafer-level measurements in an application-related environment, and to explore degradation mechanisms. Measurement results which are obtained with the P-E hysteresis method are discussed in Section 5.1. *P-E* measurements are performed with an Aixacct TF3000 ferroelectric analyzer. Unless noted otherwise, a frequency of 10 kHz is used for dynamic hysteresis measurement. Field cycling of samples is performed with a rectangular voltage waveform, also at a frequency of 10 kHz. A shielded probe station (PA300, FormFactor) with a temperature-controlled chuck and nitrogen purging is employed. Samples are wire-bonded on a custom printed circuit board with high thermal conductivity, to reduce artifacts from repeated needle placement with varying contact resistance. After reaching the intended measurement temperature, an additional soak time of 300 s is introduced to ensure thermal equilibrium. Triaxial wiring and connectors are used to reduce leakage currents. Electrical connections between probe station and ferroelectric analyzer are controlled by a low-leakage switch matrix (Model B2200A, Agilent Technologies).

3.2.2 Direct quantification of electrocaloric coefficients

Pandya et al. have demonstrated a pathway for direct (i.e., calorimetric) electrocaloric measurement with an integrated, micro-fabricated resistive thermometer [39]. Therefore, the same test structure which has been described for pyroelectric measurements in Section 3.1.3 is used. Instead of serving as a heater, the metal thin film is now used as a temperature sensor. A lock-in measurement technique is employed to separate the electrocaloric response from spurious contributions by capacitive coupling and heating due to leakage currents.

In Section 2.1.3, it has been described that an electric field variation leads to a temperature change. The corresponding electrocaloric power is

$$P_{\rm E}(t) = C_{\rm s} \, \varrho \, A \, d_{\rm film} \, \frac{\mathrm{d}T}{\mathrm{d}t}. \tag{3.26}$$

Now, a sinusoidal excitation waveform with an amplitude $U_{\rm e}$ and a frequency $\omega_{\rm e}$ is considered. Combining equations 2.25 and 3.26 yields

$$P_{\rm E}(t) = TA \Sigma \,\omega_{\rm e} \,U_{\rm e} \,\cos(\omega_{\rm e} t), \tag{3.27}$$

where Σ denotes the electrocaloric coefficient. It is apparent that the electrocaloric temperature change occurs at the excitation frequency $\omega_{\rm e}$. As a result, the electrocaloric material is sourcing and sinking heat alternately. The flow of thermal energy towards the temperature sensor is characterized by a thermal impedance $Z_{\rm t}$, and the corresponding impedance towards the substrate is denoted as $Z_{\rm b}$. In the schematic view of the test structure cross-section in Figure 3.12 a), this is indicated. In contrast, Joule heating occurs at a frequency of $2\omega_{\rm e}$, and is rejected in the measurement.

The thermal coupling towards the substrate via $Z_{\rm b}$ is strong, since the thermal conductivity of monocrystalline Si is comparably large at a value of 122 W K⁻¹ m⁻¹ [217]. Additionally, the 20 nm thick HfO₂ film exhibits a total heat capacity which is small compared to the other layers in the film stack. Hence, the induced temperature change in the sensor is expected to be in the order of a few mK, and the corresponding relative electrical resistance change in the thin film sensor is estimated to be in the order of 1×10^{-5} . To measure such a small variation, a Wheatstone bridge circuit is used, which is shown in Figure 3.12 b). The variable resistance R_2 is set equal to the sensor resistance R_s , so that the bridge circuit is balanced. This means that 0 V are registered by the lock-in amplifier, regardless which voltage U_s is applied by arbitrary waveform generator (AWG) number 1. Thereby, U_s is effectively canceled out, allowing for a lower voltage range setting at the amplifier, thus increasing the measurement sensitivity. Any small change of the sensor resistance leads to a mismatched (unbalanced) Wheatstone bridge, creating a voltage at the lock-in amplifier input.

The electrical resistance in the sensor upon a small temperature variation $\theta_{\rm s}$ is approximated as

$$R_{\rm s} = R_{\rm s,0}(1 + \alpha \theta_{\rm s}),\tag{3.28}$$

where $R_{\rm s,0}$ denotes the resistance value under ambient conditions, and α is the temperature coefficient of resistance (TCR) of the Ni temperature sensor. The voltage drop over the sensor is then

$$U_{\rm r} = U_{\rm s} \, \frac{R_{\rm s,0}(1+\alpha\theta_{\rm s})}{R_{\rm s,0}(1+\alpha\theta_{\rm s}) + R_{\rm 1}} \tag{3.29}$$



Figure 3.12: a) Cross-sectional schematic of the test structure for electrocaloric characterization (not to scale). The directions of heat flow are hinted by arrows corresponding to thermal impedances Z_t and Z_b . b) Schematic diagram of the electrical connections for direct electrocaloric measurements. The lock-in amplifier connected to the Wheatstone circuit (red) is capable of sensing small alternating resistance variations in the metal thin film sensor (purple). The electrocaloric temperature change is excited by a sinusoidal waveform at frequency ω_e (blue circuit).

The sensitivity of the Wheatstone circuit is determined by the bridge ratio $\xi = R_s/R_1$. In case of $\xi \ll 1$, Equation 3.29 simplifies to

$$U_{\rm r} = U_{\rm s} \, \frac{R_{\rm s,0}(1+\alpha\theta_{\rm s})}{R_1}.\tag{3.30}$$

The voltage detected by the lock-in amplifier upon a small, temperature-induced change of $R_{\rm s}$ is then calculated as

$$U_{\rm LI} = U_{\rm s} \,\alpha \,\theta_{\rm s} \frac{\xi}{(1+\xi)^2} \tag{3.31}$$

via Kirchhoff's circuit laws [218].

The electrocaloric effect is excited by applying a sinusoidal voltage waveform with frequency $\omega_{\rm e}$ to the buried ferroelectric capacitor (blue circuit in Figure 3.12). However, the excitation waveform is also capacitively coupled to the temperature sensor. Pandya et al. therefore proposed a measurement scheme where the Wheatstone bridge is not driven by a constant voltage, but another AWG. Thereby, the electrocaloric signal is shifted to a side-band frequency, thus enhancing the signal-to-noise ratio (SNR) significantly and eliminating capacitive coupling. Hence, a sinusoidal waveform with frequency $\omega_{\rm s}$ is supplied at the metal thin-film sensor (red circuit in Figure 3.12). Modifying Equation 3.31 accordingly yields

$$U_{\rm LI} = U_{\rm s} \sin(\omega_{\rm s} t) \,\alpha \,\theta_{\rm s} \,\sin(\omega_{\rm e} t) \frac{\xi}{(1+\xi)^2}. \tag{3.32}$$

Thus, the electrocaloric temperature change at $\omega_{\rm e}$ effectively modulates the sensor current at $\omega_{\rm s}$, creating side-band contributions at $\omega_{\rm e} \pm \omega_{\rm s}$. In frequency space, the signal created by electrocaloric temperature change is separated from the capacitively coupled signals. Fourier transformation of Equation 3.32 yields the side-band amplitudes

$$\tilde{U}_{\rm LI}(\omega_{\rm s} \pm \omega_{\rm e}) = \frac{1}{2} \alpha \,\theta_{\rm s} U_{\rm s} \,\frac{\xi}{(1+\xi)^2},\tag{3.33}$$

which is similar to the result of the 3ω -approach in Equation 3.20. The sensor temperature amplitude is directly proportional to the side-band voltages $\tilde{U}_{\rm LI}(\omega_{\rm s} \pm \omega_{\rm e})$. As a further measure to reduce capacitive coupling effects, the excitation waveform is applied to the substrate, and the top electrode is kept at a constant 0 V potential.

Heat transfer between the sensor and the electrocaloric film

In order to relate the thermal amplitude in the sensor to an actual electrocaloric temperature change θ_{ECE} in the film, the heat transport model from Section 3.1.3 is adapted. In contrast to the pyroelectric measurement with the same device in Section 3.1.3, heat flow is now possible in two directions: Towards the metal thin-film temperature sensor via

$$Z_{\rm t} = Z_{\rm Ni} + Z_{\rm SiO_2} + Z_{\rm Si} + Z_{\rm TiN} + Z_{\rm HfO_2}, \tag{3.34}$$

and in the direction of the substrate via

$$Z_{\rm b} = Z_{\rm HfO_2} + Z_{\rm TiN} + Z_{\rm sub}.$$
 (3.35)

The substrate term $Z_{\rm sub}$ is modeled by the thermal impedance of a thin line heater on an infinite half-volume, as given in Equation 3.21. Since the frequency of electrocaloric temperature change is in the kHz range, the characteristic length of temperature diffusion (compare Equation 3.14) is much smaller than the wafer thickness, and the substrate is treated as infinite. Thus, heat flows at the surface and substrate vanish, which ultimately yields a sensor temperature amplitude [39]

$$\theta_{\rm s} = P_{\rm E} Z_{\rm T} \tag{3.36}$$

Combining Equations 3.36 and 3.27 finally allows calculation of the electrocaloric response

$$\Sigma = \frac{\theta_{\rm s}}{T\omega_{\rm e}U_{\rm e}} \frac{1}{Z_{\rm T}}.$$
(3.37)

The thermal properties of the materials in the multi-layer film stack are summarized in Table 3.1. Modeling results are confirmed by measurements of the thermal impedance with the 3ω -method (see Section 3.1.4).

 Table 3.1: Thermal properties used for modeling of the heat transfer in the electrocaloric test structure.

	k	$C_{\rm s}$	Q	d	Ref.
	$({ m Wm^{-1}K^{-1}})$	$({ m Jkg^{-1}K^{-1}})$	$(\mathrm{gcm^{-3}})$	(nm)	
Ni	27	445	8.9	100	[219]
${\rm SiO}_2$	1.3	730	2.2	30	[220]
poly. Si	47.0	678	2.3	350	[221]
TiN	11.0	601	5.2	10	[222]
HfO_2	1.2	274	9.6	20	[67, 223]
mono. Si	122	700	2.3	775000	[217]
Interface	1.0	100	1.0	1	[39]

Experimental setup

Two AWG units (Agilent, model 33250A) are used for the excitation of the electrocaloric effect and for generating the sensor waveform, respectively. The sinusoidal excitation waveform has an amplitude of $U_{\rm e} = 500 \,\mathrm{mV}$ and a frequency of $f_{\rm e} = 54.345 \,\mathrm{kHz}$. For the Wheatstone measurement bridge, a ballast resistor value of $R_1 = 150 \,\Omega$ is used. For measurement of the resistivity change, a sinusoidal waveform with an amplitude of $U_{\rm s} = 3 \,\mathrm{V}$ and a frequency of $f_{\rm s} = 2.222 \,\mathrm{kHz}$ is supplied. The voltage drop over

the sensor is then measured by using a digital lock-in amplifier (Zurich Instruments MFLI). The electrocaloric response is obtained at the side-band frequencies $\omega_e \pm \omega_s$ of 56.567 kHz and 52.123 kHz. The lock-in amplifier is set to a voltage range of 3 mV at a time constant of 10 s. Differential, floating input terminals are used. Beforehand each measurement, a settling time of 100 s is inserted. The AWG as well as the lock-in amplifier are synchronized to ensure a consistent phase measurement of the electrocaloric signal. To ensure low and repeatable connection resistances and an optimal SNR, the test devices are diced and bonded to a custom printed circuit board, which is mounted in a shielded enclosure.

3.3 Thermal-electric energy conversion cycles

In the previous sections, methods for the accurate determination of pyroelectric and electrocaloric responses were discussed. Both effects lay the foundation for the conversion between thermal and electrical energy, which is investigated in Chapter 5. In the following, it is discussed how thermodynamic processes for energy harvesting can be implemented with a focus on *efficiency*, and what parameters should be addressed to optimize their performance. In contrast to thermoelectricity, which relies on a spatial temperature gradient, pyroelectric energy harvesting utilizes temperature variations in time. Sometimes, such fluctuations are random (e.g., the ambient temperature). However, many heat sources distribute thermal energy in an oscillatory manner, such as combustion engines or integrated circuits. In the latter case, pyroelectric energy harvesting can be synchronized to the heat source, and reach considerable efficiencies close to the theoretical limit [224].

As a reference, the efficiency of the Carnot cycle

$$\eta_{\rm Carnot} = 1 - \frac{T_{\rm c}}{T_{\rm h}} \tag{3.38}$$

is used, which represents the maximal achievable efficiency for given cold and hot reservoir temperatures $T_{\rm c}$ and $T_{\rm h}$, respectively.

Resistive harvesting is certainly the most simple implementation of a thermal-electric energy conversion cycle, where a resistive load is connected directly to a pyroelectric capacitor [225, 226]. When the material experiences a temperature change, the corresponding polarization change produces a current flow through the resistive load. The corresponding thermodynamic cycle is depicted schematically in Figure 3.13 a). The energy density, which is converted in one cycle, is given by the integral of the polarization-field characteristic

$$W = \oint P \mathrm{d}E. \tag{3.39}$$

To express the thermodynamic efficiency, a dimension-less electrothermal coupling factor

$$h^{2} = \frac{p^{2} T_{\rm h}}{C_{\rm s} \, \varrho \, \varepsilon_{33}^{\sigma}} \tag{3.40}$$

is defined [226], where $\varepsilon_{33}^{\sigma}$ is the out-of-plane dielectric permittivity. This coupling factor is similar to the electromechanical coupling factor, which is commonly used to characterize piezoelectric materials [227]. The efficiency of resistive harvesting is then given as

$$\eta_{\text{resistive}} = \frac{\pi}{4} h^2 \eta_{\text{carnot}}.$$
(3.41)

Lefeurvre et al. discuss the resistive load approach in detail [228], stating an optimal impedance of $(\omega \varepsilon_r \varepsilon_0)^{-1}$ in the case of a sinusoidal temperature variation with a frequency ω . However, the resistive approach comes with certain shortcomings: First, the optimal load resistance is dependent on the frequency of the temperature change, which is not known or variable in most applications. Impedance matching of the resistive load, which is also known as maximum power point tracking, has been demonstrated [229, 230], but complicates the energy conversion setup and may introduce losses. Another drawback is that without an external electric field, depolarization of the material is possible when large temperature variations are applied. This is especially relevant since ferroelectrics exhibit the largest pyroelectric response near the Curie point $T_{\rm C}$.

Pyroelectric energy conversion became feasible with the work of Olsen et al., who describes a "pyroelectric Ericsson" cycle [231–233]. As the name implies, the sequence of such an Olsen cycle is analogous to an Ericsson thermodynamic heat engine. In this analogy, the polarization corresponds to the volume, and the electric field substitutes the pressure of the working fluid. The corresponding *P*-*E* diagram is shown in Figure 3.13 b). It consists of four steps: An isothermal polarization $(1 \rightarrow 2)$, where the temperature is kept at the lower value T_c , isoelectric heating to $T_h (2 \rightarrow 3)$, an isothermal depolarization step $(3 \rightarrow 4)$, and finally isoelectric cooling to the initial state $(4 \rightarrow 1)$. The process has been investigated with a range of materials [234–238], and some of the largest conversion



Figure 3.13: a) Thermodynamic cycle for energy harvesting with a simple resistive load. b) Thermodynamic cycle for pyroelectric energy harvesting under active electric field variation.



Figure 3.14: Schematic view of the measurement setup for pyroelectric energy conversion cycles. The sample temperature is set by the Peltier element, and the electric field is supplied by an AWG.

efficiencies

$$\eta_{\text{olsen}} = \frac{\oint P dE}{\int_{T_1}^{T_h} C_s(T) \,\varrho \, dT + W_{\text{ECE}}} \tag{3.42}$$

have been reported with the Olsen cycle [30], where $W_{\rm ECE}$ denotes the electrocaloric work.

Neglecting the voltage- and temperature dependence of pyroelectric coefficients and heat capacity, as well as electrocaloric contributions, the energy density is approximated as

$$\oint P dE \approx p \,\Delta E \,\Delta T. \tag{3.43}$$

Combining with Equation 3.42 yields

$$\eta_{\text{olsen}} \approx \frac{\Delta E p}{C_{\text{s}} \, \varrho}.$$
(3.44)

When compared to resistive harvesting, the Olsen cycle is reported to generate over an order of magnitude more electric power [232]. It is worth noting that a range of other possible thermal-electric energy conversion cycles exist. For instance, the synchronized electric charge extraction (SECE) cycle realizes larger efficiencies than resistive harvesting, but does not rely on active control of the electric field [226, 239].

Experimental setup

The experimental implementation of pyroelectric energy harvesting is shown in Figure 3.14. The measurement method is similar to that for the determination of pyroelectric coefficients. A Peltier element and a Pt-100 temperature sensor are used in a control loop to apply accurate temperature variations to the sample. Part numbers are identical to these specified in Section 3.1.1. However, in this case, an arbitrary waveform generator (Agilent, model 33250A) is connected in series with the amperemeter (Keysight, model B2981A) to supply the electric field waveform used in the Olsen cycle. Since the method relies on a thermal equilibrium throughout the sample, the frequency of energy conversion cycles is limited below 1 Hz. Trapezoidal waveforms with an adjustable steepness, phase shift, and amplitudes are used for both temperature and electric field. The steepness parameter allows continuous tuning from triangular towards rectangular shapes. The temperature control loop, arbitrary waveform upload to the AWG, phase synchronization of temperature and field waveforms, and data acquisition are implemented by means of a Python script.

3.4 Sample manufacturing

Throughout this dissertation, three types of test structures are used:

- 1. Metal-pyroelectric-metal capacitor structures on Si substrates, which are used for low-frequency pyroelectric characterization with the Sharp-Garn method, pyroelectric evaluation by XPS, and for indirect electrocaloric measurements.
- 2. A specialized test structure with a miniaturized heater, which is used for pyroelectric measurements with rapid temperature cycles and direct electrocaloric measurements, as well as some energy harvesting experiments.
- 3. For energy harvesting experiments, metal-pyroelectric-metal capacitor structures on nano-patterned, area-enhanced substrates are used.

In the following sections, the deposition of ${\rm HfO}_2$ films by ALD and manufacturing of the test structures are discussed.

3.4.1 Atomic layer deposition of doped HfO_2

When the ferroelectricity of doped HfO_2 was first observed at Qimonda and Infineon in 2007, researchers were focusing on novel dielectrics with high dielectric permittivity for DRAM memory cells. Since DRAM technology was based on deep-trench capacitors, highly conformal deposition techniques were needed. Consequently, the first publications on ferroelectric HfO_2 employed ALD [1, 90]. Until today, ALD remains the predominant manufacturing technique, but other methods attract increasing attention. Both physical vapor deposition (PVD) and chemical vapor deposition (CVD) have been employed to deposit HfO_2 as dielectric in transistor gate stacks [240, 241]. Ferroelectric behavior in sputtered yttrium-doped HfO_2 was first reported by Olsen et al. [147] and has been demonstrated for other dopants as well [152]. With pulsed laser deposition, a wide range of thickness scaling up to 1 µm has been achieved [178], which is interesting especially for piezoelectric and electrocaloric applications. Another method for manufacturing thicker

films is chemical solution deposition (CSD) [101, 242], where films are formed using precursors in a liquid solvent.

In this work, all films are manufactured by ALD, since the method provides a mature and stable process with a consistent film quality. Films manufactured with this method have a high repeatability of thickness and stoichiometry, which is essential for a systematic study of pyroelectric properties in doped HfO_2 films. Some important elastic and thermal properties of HfO_2 layers manufactured by ALD are summarized in Table 3.2.

Property		References
Density	$(9.5\pm0.6){ m gcm^{-3}}$	[243]
Thermal expansion coefficient	$5.8 \times 10^{-6} \mathrm{K}^{-1}$	[66]
Thermal conductivity	$1.26{\rm Wm^{-1}K^{-1}}$	[223]
Specific heat capacity	$(2.6\pm0.5){ m MJm^{-3}K^{-1}}$	[223]
Elastic modulus	$(261\pm20)\rm GPa$	[70, 244, 245]

Table 3.2: Some properties of HfO_2 thin films manufactured by ALD.

ALD is a method for thin film manufacturing, where a substrate is sequentially exposed to two or more precursors in the gas phase, which undergo a self-terminating surface reaction [246]. Key capabilities of ALD include thickness control down to the sub-monolayer range and conformal coating of complex geometries [247]. A typical ALD process is shown in Figure 3.15, where the initial state of the substrate is indicated in the top left, presenting surface hydroxyl groups. One ALD cycle then typically consists of four steps:

- 1. Introduction of a first precursor (A) in the process chamber, which adsorbs and reacts at the surface sites. In this work, metal-organic precursors are used for this step.
- 2. Purging of remaining precursor molecules and reaction byproducts in the gas phase with an inert gas.
- 3. Introduction of a second precursor (B), which reacts with the surface species.
- 4. Another purging step with an inert gas.

The ALD cycle is then repeated multiple times to achieve the desired film thickness. The following precursors are used throughout this work:

- Tetrakis(ethylmethylamino)hafnium (TEMAHf),
- tetrakis(ethylmethylamino)zirconium (TEMAZr),
- trimethylaluminium (TMA),
- tris(dimethylamino)silane (TDMAS), and



Figure 3.15: Schematic view of an ALD process. Steps 1 to 4 are repeated to achieve the desired film thickness.

• tris(isopropylcyclopentadienyl)lanthanum (La(iPrCp)₃).

The corresponding ALD process parameters are summarized in Table 3.3, and more details have been reported in Reference [248]. In order to manufacture doped HfO_2 layers, deposition cycles with TEMAHf/O₃ and the dopant precursors are then alternated in a nano-lamination process scheme.

Many dopants such as Si and Al require low concentrations of less than 4 cat % to achieve a large spontaneous polarization, and often only few dopant ALD cycles are sufficient [152]. This is contradictory to a good intermixing between the HfO₂ matrix and the dopant species. Little is known about the impact of dopant distribution throughout the depth of HfO₂ thin films. Lomenzo et al. found that an inhomogeneous dopant concentration effectively lowers the remanent polarization [119]. Further, doping has an influence on the defect chemistry [249], thus creating internal bias fields in the ferroelectric thin films, which directly influence switchable polarization, fatigue, and wake-up effects in the material [96]. Charged defect sites can lead to pinned domains, which require extensive electric field cycling to switch [128]. Therefore, in this work, some films are manufactured by intermixing of precursors in the process chamber. The process has been suggested for Lithium-based films first [250], and a more detailed description for HfO₂-based films has been published in Reference [248].

In the precursor mixing process scheme, TEMAHf and the dopant precursor molecules both adsorb at the wafer surface, and then both species are oxidized simultaneously. Since the dopant precursor molecules experience steric hindrance effects from the presence of TEMAHf adsorbants, less dopant cations are incorporated in the HfO_2 matrix. Thereby, the doping ratio is controlled more precisely, and the dopant dis-

Material	HfO_2	$\rm ZrO_2$	$\rm Al_2O_3$	${\rm SiO}_2$	$\rm La_2O_3$
Precursor	TEMAHf	TEMAZr	TMA	TDMAS	$La(iPrCp)_3$
Pulse/purge time (s)	3/20	3/20	0.5/10	2/20	20/30
Oxidizer	O_3	O_3	O_3	O_3	O_3
Pulse/purge time (s)	4/20	4/20	2/10	4/20	4/30
Purge gas	Ar	Ar	Ar	Ar	Ar
Chamber pressure (mbar)	0.73	0.63	0.72	0.73	0.66
Temperature (°C)	280	280	280	280	280
Growth per cycle (nm)	0.10	0.11	0.10	0.13	0.21

Table 3.3: Process conditions for ALD processes used in this work.

 Table 3.4: Process conditions for ALD processes with in-situ precursor mixing used in this work.

Material	$\rm Si:HfO_2$	$\mathrm{Al:HfO}_2$	${\rm La:}{\rm HfO}_2$
Precursor	TEMAHf	TEMAHf	TEMAHf
Pulse/purge time (s)	3/20	3/20	3/10
Dopant precursor	TDMAS	TMA	$La(iPrCp)_3$
Pulse/purge time (s)	2/20	0.5/10	20/30
Oxidizer	O_3	O_3	O_3
Pulse/purge time (s)	4/20	2/10	4/30
Purge gas	Ar	Ar	Ar
Chamber pressure (mbar)	0.73	0.72	0.75
Temperature (°C)	280	280	280
Growth per cycle (nm)	0.10	0.13	0.12

tribution throughout the film is improved. Process conditions for these processes are summarized in Table 3.4.

Deposition processes are carried out using a Jusung Eureka 3000 single-wafer warmwall reaction chamber. The gas inlet is dome-shaped with a central inlet, which results in typically centrosymmetric uniformity of thickness and stoichiometry throughout the wafer. Bottom and top TiN electrodes are formed by ALD and CVD in an ASM A412 batch furnace, respectively. Therefore, titanium tetrachloride (TiCl₄) and ammonia (NH₃) are used.

After deposition of the MFM multi-layer, several analysis methods are available.
- To analyze the film thickness, spectroscopic ellipsometry (SE) is conducted with a KLA Tencor FX100 Accufilm device. Modeling of the multi-layer stack, which is composed of substrate, bottom TiN and HfO₂, is done by the internal software. Film thickness values change slightly after rapid thermal annealing (RTA) and top electrode deposition, however, a more accurate result is achieved without the opaque top electrode.
- For chemical analysis results in Section 4.1.1, XPS with a ReVera Veraflex apparatus is employed. X-ray radiation with an energy of 1486 eV is used, corresponding to the Al K_{α} emission band. Data analysis is conducted with the CasaXPS software package. No indication of sputter damage effects or major sample charge-up are found.
- Grazing incidence X-ray diffractometry (GI-XRD) patterns are obtained with a Bruker Discover D8 tool, which employs a Cu K_{α} source and a Göbel collimator. A grazing angle of 0.5° is used for all measurements. Crystallographic reference patterns are obtained with the EVA software package, which accesses the International Centre for Diffraction Data powder diffraction file database.
- Depth profiling of the chemical composition is conduced with ToF-SIMS. An ION-TOF TOF.SIMS 300R apparatus is used, which comprises two sputter sources. The formation of the sputter crater is achieved with Cs ions, while element analysis is performed with Bi ion pulse of few ps. By alternating sputtering and analysis pulses, qualitative composition depth spectra of the multi-layers are obtained.

For pyroelectric and electrocaloric measurements with static or low-frequency methods, as discussed in Sections 5.1 and 4.1, simple MFM structures are used. Therefore, Ni is deposited through a shadow mask by electron beam evaporation. In a subsequent etch step with a mixture of water (H₂O), hydrogen peroxide (H₂O₂), and ammonium hydroxide (NH₄OH) with a ratio of 20:2:1, the exposed TiN is removed, thereby forming capacitor structures. The area uncertainty of the test devices is typically less than 5%. Pyroelectric capacitor structures manufactured with both methods are shown schematically in Figure 3.16. For electrical measurements, samples are contacted via the Ni top electrode and the highly doped, electrically conductive substrate.

Pyroelectric films on area-enhanced substrates

Since deposition processes used throughout this work (ALD and CVD) are capable of coating complex geometries, pyroelectric capacitor structures are formed on areaenhanced substrates. Therefore, holes are formed by reactive ion etching, where an opening diameter of 500 nm and a depth of 8.2 μ m are measured by scanning electron microscopy (SEM). Then, the doped HfO₂ and TiN electrodes are deposited, as described before. The holes are then filled with electrically conductive, boron-doped silicon, forming the top contact.



Figure 3.16: a) Schematic view of metal—ferroelectric—metal structures with etched top electrode (not to scale) showing the dopant distribution in a classic ALD process. b) Enhanced dopant distribution achieved by in-situ precursor mixing. Reprinted with permission from Ref. [248]. Copyright 2019 American Chemical Society. c) Shadow mask for preparation of pyroelectric capacitor structures.

3.4.2 Test structure for high-frequency temperature cycles

The manufacturing process of the test structure for pyroelectric and direct electrocaloric measurements is shown in Figure 3.17. Highly doped (100)-cut silicon substrates with a resistivity of less than $0.02 \,\Omega \,\mathrm{cm}$ are used. First, the MFM film stack is deposited, as depicted in step 2. The TiN bottom electrode with a thickness of 10 nm is manufactured by ALD in an ASM A412 batch furnace. Then, the 20 nm thick doped HfO₂ layer is fabricated by metal-organic ALD in a Jusung Eureka single wafer reactor. Details of this process are discussed in Section 3.4.1.

Afterwards, a 10 nm thick TiN top electrode is deposited by CVD at a temperature of 400 °C followed by an etching mask of 350 nm electrically conductive B-doped Si (CVD, 520 °C). The top electrode is structured using electron beam lithography, where a two-



Figure 3.17: Schematic cross-sectional view of successive manufacturing steps of the test structure (not to scale). The position of needles for electrical connections is indicated.

step process approach is used: First, the doped silicon layer is dry-etched using resist as a mask. Then, the resist is ashed by means of plasma treatment. The TiN top electrode is subsequently removed in the exposed area by wet etching with hydrogen peroxide and ammonia solution. Thereby, the active pyroelectric device area of $0.1125 \,\mu\text{m}^2$ is defined, which is shown in step 3. In order to isolate the Ni thin film heater and the underlying electrode, a conformal SiO₂ coating is used (step 4). At the contact pads, the SiO₂ is then removed by a further lithography step and dry etching (step 5). Finally, the 100 nm thick Ni film is deposited by electron beam evaporation with a shadow mask.

The photolithography layout is prepared using the KLayout software package. In Figure 3.18, the reticle with a size of 10 mm by 10 mm is shown. The first lithography mask (red) defines the top electrode area of the pyroelectric structures. The second mask (blue) defines the contact area, where the SiO_2 is removed. Further, the shadow mask layout for the deposition of Ni is shown (gray). In total, 16 dies are arranged in the center area of the wafer, with sufficient spacing for dicing. The design comprises several structures, which are indicated by numbers in Figure 3.18.

- 1. Alignment markers for electron beam photolithography processes and shadow mask adjustment
- 2. Test structures for electrode sheet resistance and lateral insulation resistance



Figure 3.18: Electron beam lithography layout for patterning of the top electrode (red) and the SiO₂ insulation layer (blue). The shadow mask layout for Ni deposition (gray) is shown as well. The reticle outline dimensions are 10 mm by 10 mm.

- 3. Capacitor structures for electrical characterization of the HfO_2 material and reliability analysis
- 4. The previously described structures for pyroelectric experiments, with a range of geometry variants. In this work, pyroelectric capacitors with an area of 0.1125 mm^2 are used.

A STEM micrograph of the pyroelectric test structure is shown in Figure 3.19, confirming the thickness target of 20 nm for the Si-doped HfO_2 layer. An EFTEM analysis (right side) clearly indicates electrodes (Ti, red, 456 eV), the HfO_2 layer (Hf, green, 1662 eV), and the Si substrate and etch mask (Si, blue, 99 eV).



Figure 3.19: STEM and EFTEM micrographs of the test structure for pyroelectric and electrocaloric experiments.

Chapter 4

The pyroelectric response of doped hafnium oxide

In this chapter, a comprehensive screening of the pyroelectric response in the HfO_2 material class is conducted. First, low-frequency (mHz) measurements are performed with the Sharp-Garn method, which has been described in Section 3.1.1. Several dopants are investigated, namely Al, Zr, Si and La. The impact of conditions such as layer thickness and the electric history (poling and field cycling) are discussed. Then, a dedicated test structure with an integrated micro-heater (see Section 3.1.3) is used to analyze the pyroelectric effect in the frequency domain. Here, high-frequency (kHz) temperature variations enable further investigation of thin film effects such as substrate clamping, which ultimately allow to separate primary and secondary pyroelectric coefficients.

In one of the first publications on ferroelectric behavior in doped HfO₂, temperature dependent hysteresis measurements were presented by Böscke et al. [90]. Soon, the potential for pyroelectric applications was suggested [146, 170], and first measurements were performed by Hoffmann et al. [172] by assessing the temperature dependence of the remanent polarization. Dedicated pyroelectric measurements using the Sharp-Garn method have been performed by Smith et al. [103]. The latter yielded somewhat lower pyroelectric coefficients, and demonstrated that small-signal methods are needed to accurately assess the pyroelectric response of HfO₂ thin films. The disagreement between early literature reports on the pyroelectric response of HfO₂ has been related to thermal fatigue effects (see Section 5.1) [104, 185].

Part of the results in Section 4.1 have been published previously in References [104], [97], and [248]. Experimental findings presented in Section 4.3 have been published previously in References [251] and [244].

4.1 Pyroelectric coefficients

The Sharp-Garn method [191, 192] provides an accurate approach to determine pyroelectric responses, and it is well suited for bulk and thin-film materials alike. As described in Section 3.1.1, the sample is subjected to a small, low-frequency temperature variation, and the pyroelectric current response is registered simultaneously. As a small-signal method, the Sharp-Garn approach allows the determination of the amplitude and phase of the pyroelectric current. Thereby, the influence of spurious or non-reversible contributions such as phase change or the thermally stimulated release of trapped charges is quantified.

In Figure 4.1 a) and b), temperature and current density waveforms of such a measurement are shown for 20 nm thick, Si-doped HfO₂, respectively. Three Si concentrations are evaluated: $3.5 \operatorname{cat} \%$, $4.1 \operatorname{cat} \%$, and $5.3 \operatorname{cat} \%$. Samples are field-cycled 10^5 times at a field amplitude of $3 \operatorname{MV} \operatorname{cm}^{-1}$ beforehand measurement. A temperature waveform with a sinusoidal shape at an amplitude of $\theta = 2 \operatorname{K}$ and a frequency of 50 mHz is applied.

The resulting current density waveforms exhibit phase shifts of 96°, 99°, and 97° with respect to the temperature waveform, respectively. This is close to the expected value for an ideal pyroelectric response of 90°. It is evident that the amplitude of the pyroelectric current response is dependent on the Si dopant concentration in the thin film. The largest signal is obtained for the 3.5 cat % Si-doped sample, with a value of 6.0 nA cm^{-2} . For samples with an increasing dopant concentration, amplitudes reduce to 3.3 nA cm^{-2} and 0.2 nA cm^{-2} , respectively.

The Lissajous graphs in Figure 4.1 c) provide a graphical representation of the pyroelectric response, for a total measurement time span of 400 s. The non-ideal phase shift



Figure 4.1: a) The sample is subjected to a sinusoidal temperature waveform, which is maintained by a control loop. b) Total measured short-circuit current density between the sample electrodes for three different Si-doped HfO_2 films. Note the phase shift of approximately 90° with respect to the temperature profile. c) Corresponding total current density vs. temperature Lissajous figures. A slight skew is visible due to non-pyroelectric contributions and thermal lag.

is visible as a skew of the ellipse. Reasons for the observed shift result from imperfections of the measurement setup and the sample characteristics:

- While the temperature sensor is in a distance of less than 3 mm to the pyroelectric capacitor, a certain thermal propagation delay may be present. Further, the thermal resistance at the interface between sensor and sample and the heat capacity of the sensor lead to a deviation from the ideal 90° phase shift. [252]. As discussed in Section 3.1.1, a lower measurement frequency reduces the thermal lag. However, this generally comes at the cost of lower SNR and an increased total measurement time. The careful placement of the temperature sensor, clean sample faces, and repeatable application of thermal grease are important concerns for measurement repeatability. Repeated positioning of the sample and sensor yields a statistic variation $\Delta p/p$ of less than 3%.
- In-phase contributions to the measured current waveform arise from thermally stimulated de-trapping of defect charges [192]. Such trap states are prominent in thin films, which often exhibit higher defect densities than bulk crystals [199]. For hafnium zirconium oxide ($Hf_{0.5}Zr_{0.5}O_2$) films, experimental reports suggest singly-and doubly-charged oxygen vacancies as the main cause of such currents [253].
- A part of the film polarization can be caused by quasi-static dipoles or a heterogeneous charge distribution [254] in the film, which is referred to as electret effect [255, 256]. In poly(vinylidene fluoride) (PVDF), even amorphous films are found to exhibit a pyroelectric response via this mechanism [257]. The effect manifests as a out-of-phase contribution, and is difficult to separate from the pyroelectric response. Depending on the lifetime of the dipoles or charges, long-term pyroelectric measurements can be applied to quantify electret effects.
- Thermal fatigue effects [185] and phase change are expected to be strongly reduced in this approach due to the low temperature amplitude. The total measurement duration must be long enough to allow for a decay of such transient effects.
- Since pyroelectric measurements are commonly performed in the field-free state, leakage currents are not present. However, when applying an external electric field, as in Section 4.1.4, a in-phase contribution occurs. In $Hf_{1-x}Zr_xO_2$, Poole-Frenkel (PF) emission [258] with a characteristic behavior

$$\log\left(\frac{I}{E}\right) \propto E^{1/2} \tag{4.1}$$

has been identified as the predominant conduction mechanism at raised fields [259]. The PF emission is based on the thermionic transport via bulk defects, where significant field-induced Schottky barrier lowering occurs. Since the effect is temperature-activated, leakage currents become significant especially at raised temperatures.

Using Equation 3.4, pyroelectric coefficients are calculated from the obtained temperature and current amplitudes, where only the out-of-phase (pyroelectric) contribution is considered. For the 3.5 cat % Si-doped material, a coefficient of $-95.4 \,\mu C \,m^{-2} \,K^{-1}$ is determined. For higher Si concentrations of 4.1 cat % and 5.3 cat %, diminishing values of $-40.2 \,\mu C \,m^{-2} \,K^{-1}$ and $-3.5 \,\mu C \,m^{-2} \,K^{-1}$ are obtained, respectively.

Mechanical interactions and clamping

Since the HfO₂ layers are part of a multi-layer film stack, their lateral expansion is not free. The mechanical interaction with the electrode layers, metalization and Si substrate lead to altered in-plane thermal expansion coefficient $\alpha_1 = \alpha_2$. Using Equation 2.21, the pyroelectric response is then represented with an effective $\alpha_{1,\text{eff}}$ as

$$p_3^{\sigma} = p_3^{\epsilon} + 2e_{31}\alpha_{1,\text{eff}} + e_{33}\alpha_3. \tag{4.2}$$

By using FEM simulations with the COMSOL software package, values of $\alpha_{1,\text{eff}}$ are determined for various film stacks. The results are summarized in Table 4.1. It is evident that the choice of the electrode material can have a significant impact on the secondary pyroelectric coefficient. Since the in-plane contribution $2e_{31}\alpha_{1,\text{eff}}$ is responsible for approximately one third of the total response, [244] the overall electrode material influence is estimated as $\pm 10\%$.

Table 4.1: Effective in-plane thermal expansion coefficients of 20 nm thick HfO₂ for different top electrode metalization variants.

Top electrode layers	$\alpha_{1,\rm eff}$	$\alpha_{1,\rm eff}/\alpha_1$
Bulk m-HfO ₂ [66]	$5.8 \times 10^{-6} \mathrm{K}^{-1}$	1.0
$10\mathrm{nm}$ TiN, $100\mathrm{nm}$ Ni	$7.5 imes 10^{-6} { m K}^{-1}$	1.30
$10\mathrm{nm}$ TiN, $100\mathrm{nm}$ Pt	$5.7 imes 10^{-6} { m K}^{-1}$	0.98
$10\mathrm{nm}$ TiN, $350\mathrm{nm}$ Si	$3.9\times 10^{-6}{\rm K}^{-1}$	0.67

4.1.1 Stoichiometry dependence

The observed dependence of the pyroelectric response on the film stoichiometry is expected, since the ferroelectric properties of doped HfO_2 are usually tuned by the dopant content, ranging from ferroelectric to AFE-like and finally paraelectric behavior [7, 175, 248]. In this section, the Sharp-Garn method is utilized to perform a comprehensive study of pyroelectric properties Al-, Si-, and La-doped HfO_2 as well as the $\text{Hf}_{1-x}\text{Zr}_x\text{O}_2$ solid-solution. The film stoichiometry is adjusted by varying the ALD deposition cycles of HfO_2 and the dopant species (e.g., SiO₂).

Deposition processes for Al-, Si-, and La-doped films are carried out by the precursor mixing process which is described in Section 3.4.1. Thereby, the dopant incorporation in the HfO_2 matrix is controlled more precisely in the mixing process, which allows for

an accurate investigation of pyroelectric characteristics with respect to stoichiometry. This is of importance especially for the cases of Al and Si doping, where the largest orthorhombic phase fraction occurs at concentrations below 4 cat %. In a classic ALD process, such concentrations correspond to only few dopant ALD cycles, which results in an uneven distribution throughout the depth of the film. Further details of the manufacturing method are available in Reference [248]. For manufacturing of the $Hf_{1-x}Zr_xO_2$ mixed oxide, only the classic ALD deposition is employed, since the largest ferroelectric response is reported for an Zr content around 50 cat % [3].

The film stoichiometry is determined by means of XPS, beforehand deposition of the TiN top electrode, as described in Section 3.4.1. Exemplary results for three HfO₂ films with a successively increasing Si content are displayed in Figure 4.2. The O 1s, Si 2p, and Hf 4f regions of the binding energy $E_{\rm B}$ are depicted, respectively. The O 1s peak is composed of two contributions with an energy difference of 1.61 eV, which originate from Hf-O and -OH bonds [260]. Interstitial oxygen atoms have been proposed as an alternative explanation for the secondary peak [111, 262].

The area of the Si 2p peak scales linearly with an increasing amount of SiO₂ ALD pulses incorporated in the film. A distinct splitting is visible for the Hf 4f orbital due to the spin-orbit interaction, with an energy difference of 1.67 eV, which is very close to the literature value of 1.68 eV [263]. No evidence for other charging states than tetravalent Hf⁴⁺ is detected. Further, no indications of surface damage or charging effects are found in the XPS analysis.

In Figure 4.3, dopant concentrations determined from XPS spectra are shown for 10 nm thick HfO_2 with all four evaluated dopants. The dopant concentrations are determined from peak areas of the respective Hf 4f, Al 2p, Si 2p, La 3d and Zr 4f orbitals, and scale linearly with the ratio of dopant ALD pulses. In the case of Si and La doping,



Figure 4.2: XPS spectra of the a) O 1s, b) Si 2p (scaled $\times 100$), and c) Hf 4f binding energy regions for increasing Si content in 20 nm thick HfO₂ films. The Shirley background model [261] is subtracted from the data.

the proportionality factor in Figure 4.3 is lowered significantly by the deposition with the precursor intermixing approach in comparison to doping by nano-lamination.



Figure 4.3: Dopant content measured via XPS vs. ALD doping ratio for 10 nm thick ${\rm HfO}_2$ films.

X-ray diffractometry

In order to analyze the crystal phase compositions of the manufactured samples, GI-XRD is applied. In Figure 4.4 a-d), results are depicted for Al-, Si-, and La- doped HfO₂, and Hf_{1-x}Zr_xO₂, respectively. Accurate dissemination of the crystal phase composition is difficult due to the small grain size, which broadens the reflexes in the diffractograms. It is further complicated by the structurally similar polymorphs of HfO₂, namely, monoclinic (m), tetragonal (t), orthorhombic (o), and cubic (c) phases (see Section 2.3.1). As established in the literature, monoclinic peaks are observed in the lowest doped films. This is expected, as undoped HfO₂ thin films with a thickness around 10 nm are monoclinic [90, 264]. The distinct monoclinic (-111) and (111) peaks at 28.3° and 31.7° are visible. It is noted that even in undoped HfO₂, the polar orthorhombic phase can be achieved by controlling the oxygen content [153, 265].

With rising dopant content, the monoclinic peaks vanish and a singular peak forms at a 2θ value around 30°, which is attributed to the orthorhombic (111) or tetragonal (101) reflex, with nearly identical reported values of 29.9° and 30.3°, respectively [267, 268]. The vicinity of the aforementioned reflexes has been identified as helpful for understanding the phase evolution upon film doping [7]. For Al-, Si-, and La-doped films, increasing dopant concentrations lead to a shift of the orthorhombic (111) or tetragonal (101) peak. For example, in the case of La-doped HfO₂, the 2θ value increases from 30.58° at the lowest La content of 1.1 cat % to 30.70° at the highest doping of 8.9 cat %. Simultaneously, the angle of the orthorhombic (002) or tetragonal (110) peak decreases from 35.71° to





35.55°. These observations are associated with a lattice parameter change and formation of the polar orthorhombic phase [269]. For $\text{Hf}_{1-x}\text{Zr}_x\text{O}_2$, the phase evolution is obtained for the whole stoichiometry range $0 \le x \le 1$. The material exhibits a purely monoclinic diffraction pattern for x = 0, which transforms into a purely tetragonal diffractogram for x = 1. The polar orthorhombic phase occurs as an intermittent phase present in the mixed oxide.

Rietveld refinement

By using Rietveld refinement [177, 270], the GI-XRD diffractograms are deconvoluted, where diffraction data of monoclinic, tetragonal, and orthorhombic phase fractions, as well as TiN electrodes [271] are included. The cubic (flourite) parent structure (space group $Fm\bar{3}m$) is structurally very similar to the tetragonal phase, and the diffraction peaks are significantly widened due to the film thickness of 10 nm. According to the Scherrer equation [272], the full width at half maximum (FWHM) angle is equal to

$$\gamma_{\rm FWHM} = \frac{K\lambda_{\rm X}}{d_{\rm p}\cos(\theta)},\tag{4.3}$$

where K = 0.9 denotes the shape factor [273], $\lambda_{\rm X}$ is the X-ray wavelength at 0.154 nm, $d_{\rm p}$ is the particle size, and $\cos(\theta) \approx 1$ in the grazing incidence geometry. For the prominent peak in the 30° vicinity, FWHM values of 1.00° to 0.95° are extracted in the case of Si-doped HfO₂. This corresponds to a dimension of 8.8 nm to 9.3 nm, which is close to the film thickness.

Weighted-profile R-factors are used to quantify agreement between refinement results and experimental data. Values of 14 to 17 (Al:HfO₂), 10 to 14 (Si:HfO₂), and 15 to 19 (La:HfO₂) are obtained, which is comparable to other reports on phase analysis of doped HfO₂ with similar instrumentation [149, 269].

An exemplary deconvolution result is shown in Figure 4.5 a) for undoped HfO₂, as well as 1.4 cat % and 2.8 cat % Si-doped HfO₂. The undoped film found to be mainly in the monoclinic phase (blue line). The monoclinic pattern fails to model the strong reflex at 36°, which is attributed to the monoclinic (002) planes. A similar behavior has been observed in other publications before [153], and is ascribed to a (001) texture of the monoclinic grains. This is consistent with prior GI-XRD experiments with monoclinic HfO₂ films deposited by ALD, in which a significant (001) texture is observed in the deposition temperature range from 300 °C to 500 °C [274]. For an increasing Si content, the orthorhombic $Pca2_1$ phase fraction increases, and the 2.8 cat % Si-doped sample exhibits a negligible monoclinic fraction. The extracted lattice parameters of a = 0.503 nm, b = 0.514 nm and c = 0.507 nm are close to the literature values (see Table 2.2). At even higher Si concentrations, a significant tetragonal phase fraction emerges (not shown here).

Calculated unit cell volumes for the orthorhombic $Pca2_1$ phase are shown in Figure 4.5 b) with respect to the dopant content. As expected, the unit cell volume depends on the dopant species: Al-doped HfO₂ exhibits the smallest unit cell with 0.123 nm³ to



Figure 4.5: a) Exemplary Rietveld refinement results of GI-XRD measurements for HfO_2 and Si-doped HfO_2 . The background is fitted with a 4th-order Chebyshev function and is subtracted for better visibility. b) Unit cell volume of the orthorhombic phase fraction calculated by deconvolution of the GI-XRD diffractograms for Al-, Si-, and La-doped HfO_2 . Lines are guides to the eye. Adapted with permission from Ref. [248]. Copyright 2019 American Chemical Society.

 0.128 nm^3 , followed by Si:HfO₂ with a volume of 0.125 nm^3 to 0.130 nm^3 . Even though Si has a smaller ionic radius of 54 pm compared to Al at 68 pm [275], the tetravalence of Si may cause the observation of a larger unit cell. Such a trend has been reported for the structurally similar ZrO₂ [276]. For Hf_{1-x}Zr_xO₂, a similar trend is obtained, where the unit cell volume reduces from 0.129 nm^3 for x = 0.3 to 0.127 nm^3 at an increased Zr content of x = 0.8. The La-doped HfO₂ films reach the largest unit cell volumes at 0.128 nm^3 to 0.132 nm^3 , at an ionic radius of 117 pm for La³⁺. The unit cell volume reduces for increasing La doping, while the ionic radius of Hf⁴⁺ at 85 pm is smaller than that of La³⁺. This illustrates that the variation of the unit cell volume is caused by the the formation of other crystal phases rather than simple geometry.

Doped HfO_2 thin films are composed of a phase mixture of the several polymorphs. The reduction of unit cell volume for all three dopant species indicates a common cause of this trend, namely the transformation of monoclinic grains to polar orthorhombic and then ultimately tetragonal or cubic phases with increasing dopant content, which has also been observed in other studies [269]. This explanation is supported by theoretical investigations [92], where monoclinic, polar orthorhombic, tetragonal, and cubic phases show decreasing unit cell volumes of 0.138 nm^3 , 0.134 nm^3 , 0.131 nm^3 and 0.128 nm^3 , respectively. While there is a slight deviation in the absolute values, the trend suggests a common phase evolution of all three examined material systems. The increasing unit cell volume for the highly Al- and Si-doped HfO₂ layers is explained by an increased crystallization temperature, which leads to partially amorphous films.

Macroscopic polarization measurements

In Figure 4.6 a), the remanent polarization $P_{\rm r}$ extracted from polarization—field graphs is depicted for Al- (red), Si- (blue), and La-doping (green), as well as ${\rm Hf}_{1-x}{\rm Zr}_x{\rm O}_2$ (orange). All samples are field cycled 10⁴ times beforehand.

A maximum $P_{\rm r}$ value of $16.5\,\mu{\rm C\,cm^{-2}}$ is determined for an Al concentration of 2.2 cat %. This is considerably larger than previously published values by Müller et al., where a remanent polarization of $6\,\mu{\rm C\,cm^{-2}}$ is obtained with an Al concentration of $11\,{\rm cat}\,\%$ in 16 nm thick films [146]. Other groups published values of $14\,\mu{\rm C\,cm^{-2}}$ and $16\,\mu{\rm C\,cm^{-2}}$ for material with an Al dopant content around $7\,{\rm cat}\,\%$ [277, 278].

For Si doping, an optimized remanent polarization of $18.8 \,\mu C \,\mathrm{cm}^{-2}$ is obtained at a concentration of $2.8 \,\mathrm{cat} \,\%$. In the literature, a $P_{\rm r}$ of $15 \,\mu C \,\mathrm{cm}^{-2}$ is reported at a



Figure 4.6: a) Remanent polarization with respect to dopant concentration for Al-, Si-, and Ladoped HfO₂ as well as $Hf_{1-x}Zr_xO_2$ after field cycling 10^4 times. b) Corresponding pyroelectric coefficients, where the stoichiometry with the largest value p is systematically increased compared to that with the optimal P_r for all material systems. Lines are guides to the eye for better readability.

slightly higher concentration around $3.5 \operatorname{cat} \%$ [7, 25]. In the case of La doping, a value of $23.6 \,\mu\mathrm{C}\,\mathrm{cm}^{-2}$ is observed at approximately $5 \operatorname{cat} \%$. In a previous report, Schröder et al. [149] obtained $27.7 \,\mu\mathrm{C}\,\mathrm{cm}^{-2}$ at $10 \operatorname{cat} \%$ La doping. $\mathrm{Hf}_{1-x}\mathrm{Zr}_x\mathrm{O}_2$ exhibits the largest remanent polarization of the examined samples with $24.9 \,\mu\mathrm{C}\,\mathrm{cm}^{-2}$ at a Zr content of x = 0.75. Thus, the stoichiometry with an optimized P_{r} is more Zr-rich than previously reported, with published values of x = 0.5 [175] and x = 0.65 [103], where metal-organic precursors and thermal ALD are used as well. It is noted that deposition conditions such as the O_3 pulse time can have a strong influence on the optimal stoichiometry for the formation of the ferroelectric orthorhombic phase.

The recorded $P_{\rm r}$ values illustrate that the proposed in-situ precursor mixing ALD approach is especially useful for challenging [279] processes which exhibit a comparably narrow process window, such as doping with lanthanum oxide (La₂O₃). In comparison to experiments with doping by nano-lamination [248], the precursor mixing process achieves sizable and repeatable $P_{\rm r}$ values and enables finer tuning of the film stoichiometry.

Pyroelectric measurements

Pyroelectric properties are assessed by the Sharp-Garn method, where a sinusoidally varying temperature is applied to the sample, as described in Section 3.1.1. In Figure 4.6 b), pyroelectric coefficients are shown for all samples. For Al-doped HfO₂, almost identical coefficients of $-71 \,\mu\text{C}\,\text{m}^{-2}\,\text{K}^{-1}$ are determined at 1.0 cat % and 1.4 cat %. With Si doping, the largest value of $-95 \,\mu\text{C}\,\text{m}^{-2}\,\text{K}^{-1}$ is obtained for a Si content of 3.5 cat %. In the case of La doping, pyroelectric coefficients benefit significantly from the enhanced dopant distribution with the precursor-mixing process scheme. At a La concentration of 7.2 cat %, a coefficient of $-78 \,\mu\text{C}\,\text{m}^{-2}\,\text{K}^{-1}$ is obtained (see Reference [97]). In contrast, a classic nano-lamination doping approach yields coefficients of no more than $-51 \,\mu\text{C}\,\text{m}^{-2}\,\text{K}^{-1}$. Hf_{1-x}Zr_xO₂ exhibits the largest pyroelectric response at a Zr content of x = 0.75, with a value of $p = -79 \,\mu\text{C}\,\text{m}^{-2}\,\text{K}^{-1}$.

Interestingly, the results of the material screening indicate that pyroelectric coefficients of approximately $-80 \,\mu \text{C} \,\text{m}^{-2} \,\text{K}^{-1}$ can be achieved with all four dopants. The pyroelectric response occurs only in a specific stoichiometry range, and vanishes at a certain admixture of Al, Si, La or Zr. Similarly, no evidence for pyroelectricity in undoped HfO₂ is found with the previously described deposition conditions.

Over the course of the dissertation project, several groups used the Sharp-Garn method to determine pyroelectric coefficients in the HfO_2 material class. One report on 5.0 cat % Al-doped HfO_2 states a pyroelectric coefficient of $-38 \,\mu C \,m^{-2} \,K^{-1}$ [280]. Jachalke et al. obtained a value of $-46 \,\mu C \,m^{-2} \,K^{-1}$ for 12 nm thick 6.0 cat % Si-doped HfO_2 [67]. For $Hf_{0.42} Zr_{0.58} O_2$, Smith et al. determined an pyroelectric coefficient of $-58 \,\mu C \,m^{-2} \,K^{-1}$ [103, 281]. Other reports employ a high-frequency pyroelectric measurement method, which is discussed in Section 4.3. These results are somewhat lower than the values obtained here, with reported values of $-27 \,\mu C \,m^{-2} \,K^{-1}$ to $-60 \,\mu C \,m^{-2} \,K^{-1}$ [251, 282]. It is noted that different clamping conditions are real-

ized when high-frequency temperature variations are imposed on a pyroelectric film by means of a laser or an integrated heater. Therefore, these methods observe reduced pyroelectric coefficients in the kHz range [244]

When comparing pyroelectric coefficients to other material systems, values are similar to that of LiNbO₃ at $-83\,\mu\text{C}\,\text{m}^{-2}\,\text{K}^{-1}$ [283], and considerably higher than these of non-ferroelectric polar materials such as AlN ($6\,\mu\text{C}\,\text{m}^{-2}\,\text{K}^{-1}$) or GaN ($-5\,\mu\text{C}\,\text{m}^{-2}\,\text{K}^{-1}$) [284] and the pyroelectric polymer polyvinylidene fluoride ($-27\,\mu\text{C}\,\text{m}^{-2}\,\text{K}^{-1}$) [198, 247]. Materials with higher pyroelectric coefficients include the widely used $\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$ at $-380\,\mu\text{C}\,\text{m}^{-2}\,\text{K}^{-1}$ and $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ with a large coefficient of $-1790\,\mu\text{C}\,\text{m}^{-2}\,\text{K}^{-1}$ [285]. A comprehensive comparison of our experimental results to literature values is provided in Section 4.5.

It is evident that the values of remanent polarization and pyroelectric coefficient are correlated. This is expected, since all ferroelectrics exhibit the pyroelectric effect, as discussed in Section 2.2. Literature reports indicate that ferroelectrics have the tendency to exhibit larger pyroelectric coefficients than non-ferroelectric polar materials like AlN or GaN [30]. The dopant content corresponding to the largest coefficient p is systematically higher than that corresponding to an optimal $P_{\rm r}$, for all four examined material systems.

The zero-field polarization $P_{\rm r}$ is not proportional to the pyroelectric coefficients p. In Figure 4.7, this is shown exemplary for the case of Si-doped HfO₂. While the 2.1 cat % Si-doped (red line) sample exhibits the most pronounced ferroelectric behavior, the pyroelectric current amplitude of the 3.5 cat % Si-doped samples is larger, as shown in Figure 4.7 b) (blue circles).

This phenomenon is also observed with the other evaluated dopants. Pyroelectric coefficients are depicted vs. $P_{\rm r}$ in Figure 4.8 a), where colored arrows indicate an increas-



Figure 4.7: a) Polarization-field hysteresis graphs of HfO_2 thin films with two different Si doping ratios. b) Pyroelectric current induced by sinusoidal heating. Notably, the pyroelectric current is higher for the sample with the lower remanent polarization (red lines).



Figure 4.8: a) Pyroelectric coefficients vs. remanent polarization of Si:HfO₂, La:HfO₂ and Al:HfO₂ films. Arrows indicate an increasing dopant content. The similar trajectory indicates a common phase evolution of the materials with changing stoichiometry. Lines are guides to the eye. b) Pyroelectric coefficients vs. phase composition of Si-doped HfO₂ films, which is extracted by deconvolution of GI-XRD data with the Rietveld method. An increasing Si content from 1.4 cat.% to 5.3 cat% is indicated by an arrow, and tetragonal and cubic phases are combined due to their structural similarity. Lines are guides to the eye.

ing dopant content. It is evident that a common trajectory exists, which is suspected to arise from the phase evolution from monoclinic, pure HfO_2 towards the polar orthorhombic phase with maximal P_r , and finally to the non-polar tetragonal or cubic phase.

To correlate the observed pyroelectric coefficients with structural properties, the phase composition of Si-doped HfO_2 is analyzed. The grain fraction of the respective monoclinic, orthorhombic, and tetragonal/cubic polymorphs are extracted by means of Rietveld refinement [177] with the respective diffraction data [266–268, 286]. Phase fractions of the tetragonal and cubic polymorphs are difficult to distinguish, and are therefore combined. Weighted-profile R-factors between 11.5 and 12.1 indicate a good agreement between experimental and modeled diffractograms. In Figure 4.8 b), the pyroelectric coefficients are visualized with respect to the film composition. It is evident that the pyroelectric effect is most pronounced in the transition region between the polar orthorhombic and the centrosymmetric tetragonal phase. The largest response is found for a composition ratio of approximately 2:1 for the orthorhombic vs. tetragonal and cubic phase fractions. It is noted that the very small film thickness could lead to uncertainties in the quantitative phase composition; however, the qualitative trend of an enhanced pyroelectric response in the transitional region is clearly confirmed by the deconvolution results. Further, it is concluded that the presence of monoclinic grains leads to a strong inhibition of the pyroelectric response.

For applications, an important conclusion is the fact that pyroelectric devices will generally require higher doping of the HfO_2 film than ferroelectric devices (e.g., ferroelectric field effect transistors). The monoclinic and tetragonal polymorphs are not pyroelectric, as expected from their centrosymmetric crystal structure. The largest pyroelectric response is registered in the transitional region between the polar orthorhombic and the tetragonal phase. We speculate that a similar mechanism may be valid for the optimization of the piezoelectric response in HfO_2 -based films. The observed effect could be more pronounced in epitaxial films [9], where the transition temperature between the orthorhombic and the tetragonal phase is not broadened by grain size effects [8].

According to Equation 2.34, the pyroelectric coefficients and the remanent polarization are linked by the dielectric permittivity and the Curie constant

$$C_{\rm c} = \frac{-\varepsilon_{\rm r} P_{\rm r}}{p}.\tag{4.4}$$

Calculated values of C_c vs. Si dopant content are displayed in Figure 4.9. Two regimes are observed: At a low Si content <2 cat.%, a Curie constant of 1.4×10^5 K is observed, and at an increased Si content >4 cat.% the value decreases to 0.7×10^5 K. The two ranges are attributed to the monoclinic/orthorhombic and orthorhombic/tetragonal and cubic phase mixtures. Physically, the observed behavior of C_c could be explained by the fact that the low-doped films are below the orthorhombic to tetragonal transition point, while the highly-doped HfO₂ already satisfies the condition $T > T_C$ at room temperature. In a recent report, a Curie constant of 0.62×10^5 K is reported at a Si content of 4.0 cat.%, which is compatible with our results [287]. However, we find that the recently reported universal value of C_c in the HfO₂ material system [287] is only valid when films with a similar phase composition are compared.

The extracted Curie constants are similar to these of LiTaO₃, where values of 1.6×10^5 K and 0.7×10^5 K are extracted below and above the transition temperature,



Figure 4.9: Curie constants calculated for Si-doped HfO₂ vs. dopant cation ratio.

respectively [288, 289]. Landau coefficients in the order of magnitude of 1×10^5 K are typical for many displacive ferroelectrics, while order-disorder ferroelectrics tend to have much lower values of $C_{\rm c}$ [11, 290].

In the Landau-Devonshire theory of ferroelectrics, the Curie temperature inversely proportional to the coefficient a_0 in the free energy ansatz [287], so that $a_0 = (C_c \varepsilon_0)^{-1}$. Coefficients in the range of $0.8 \times 10^6 \,\mathrm{m \, F^{-1} \, K^{-1}}$ to $1.64 \times 10^6 \,\mathrm{m \, F^{-1} \, K^{-1}}$ are calculated for Si concentrations below and above the phase transition, respectively. Hoffmann et al. extracted an absolute Landau parameter $a = a_0(T_0 - T)$ recently at with a value of $-4.6 \times 10^8 \,\mathrm{m \, F^{-1}}$ for $\mathrm{Hf}_{0.5}\mathrm{Zr}_{0.5}\mathrm{O}_2$.

Liu et al. observe a similar behavior with molecular dynamics simulations in Si-doped HfO_2 , which predict a large pyroelectric response associated with the orthorhombic to tetragonal phase transition [280]. By introducing Si cations, the authors report an enhancement of this response as well as a lowering of the phase transition temperature. By precisely tuning the dopant content, it is possible to adjust a large grain fraction of the ferroelectric thin film to the morphotropic phase boundary (MPB) between orthorhombic and tetragonal polymorphs [291].

In conclusion, the pyroelectric response of doped HfO_2 is optimized with regard to film stoichiometry for La-, Si-, and Al-doping, as well as the $\text{Hf}_{1-x}\text{Zr}_x\text{O}_2$ mixed oxide. Similar optimized pyroelectric coefficients are obtained for all dopants, with the highest response of $-95\,\mu\text{C}\,\text{m}^{-2}\,\text{K}^{-1}$ in the case of 3.5 cat.% Si doping. Tuning of the film phase towards the morphotropic orthorhombic to tetragonal phase boundary is associated with large pyroelectric coefficients. Using the determined film compositions, further influences on the pyroelectric effect in nanometer-thin films are analyzed in the next sections. A more detailed comparison of the experimental results to published values of HfO₂-based films and other material systems is provided in Section 4.5.

4.1.2 Wake-up effect of pyroelectric response

In the pristine state, doped HfO_2 thin films commonly exhibit pinched hysteresis loops with an AFE-like shape [292]. Only after field cycling, the full ferroelectric response is realized. This so-called "wake-up effect" is a prominent feature in the HfO_2 material system and has important practical implications for applications, e.g., pyroelectric sensors. The initially pinched ferroelectric hysteresis has been attributed to several effects, namely the inhibition of domain formation by charged defects, field-induced phase change, and de-polarization effects [134, 174, 293]. The increasing spontaneous polarization upon electric field cycling is linked to the migration of charged defects, and their accumulation at the electrode interfaces [294, 295]. However, a decisive quantitative description is not available, yet.

Oxygen vacancies are among the most common defects in doped HfO_2 thin films, which is used in HfO_2 -based resistive random access memory (RRAM) technology [296, 297]. Further, they have an major impact on the leakage current density [298] and electric breakdown [161, 299]. The generation of oxygen vacancies upon application of an electric field bias has been observed directly using transmission electron microscopy techniques [300], and is discussed as the main fatigue mechanism in HfO₂-based ferroelectrics [63]. Schenk et al. suggested that the wake-up effect is linked to the migration of charged defects [94]. With temperature dependent measurements of the wake-up process, the group extracted activation energies of approximately 100 meV for Sr-doped HfO₂, which is lower than values reported for $PbZr_xTi_{1-x}O_3$ [301]. Starschich et al. performed combined ferroelectric hysteresis and resistive switching measurements, where results indicate a redistribution of oxygen vacancies during wake-up [158]. Pešić et al. proposed a model for wake-up and fatigue mechanisms in doped HfO₂ [134]. According to their analysis, internal bias fields cause local variations of the switching field, and the re-distribution of oxygen defects is discussed as the cause of the hysteresis de-pinching upon field cycling.

As discussed before, the ferroelectricity of doped HfO_2 is associated with the polar orthorhombic phase, and AFE-like behavior has been reported to arise from an increasing tetragonal grain fraction [90, 302]. Pešić et al. also include a transformation of pristine monoclinic or tetragonal phase fractions towards the orthorhombic structure in their model [134], which increases the switchable polarization. Recently, Fields et al. found evidence for such a phase exchange during wake-up with the help of synchrotron XRD [303]. The phenomenon of field-assisted transformation from an AFE towards a ferroelectric state has also been observed in lead-based ferroelectric thin films [304–307].

In Figure 4.10 a), ferroelectric hysteresis loops of two 10 nm thick, 3.5 cat % Si-doped HfO₂ layers nano-laminated with a single, approximately 0.5 nm thick Al₂O₃ separator are shown. The graphs are obtained in the pristine state, and after an cumulative electric



Figure 4.10: a) Polarization-field hysteresis of 20 nm thick, 3.5 cat.% Si-doped HfO₂, nano-laminated with an approximately 0.5 nm thick Al₂O₃ interlayer. Successive electric field cycling with an amplitude of 3 MV cm^{-1} is applied. b) Corresponding current-field characteristics, indicating pronounced ferroelectric switching peaks after wake-up. c) Dielectric permittivity vs. electric field.

field cycle count of 10^3 , 10^4 , and 10^5 . While the initial *P*-*E* characteristic resembles a pinched, AFE-like graph, distinct ferroelectric switching is observed after 10^5 cycles. The corresponding *j*-*E* graphs in Figure 4.10 b) show a merging of the initially split current peaks. The depicted results are characteristic for all examined dopants, where initially asymmetric, split switching current peaks are observed, and field cycling leads to a merging and amplitude increase. For high doping levels, the AFE-like (pinched) polarization response is stabilized in the case of Si-doped HfO₂, Al-doped HfO₂, and Hf_{1-x}Zr_xO₂, and the wake-up effect diminishes.

In Figure 4.10 c), the dielectric permittivity is shown with respect to an electric field bias in the range from $-2.5 \,\mathrm{MV}\,\mathrm{cm}^{-1}$ to $2.5 \,\mathrm{MV}\,\mathrm{cm}^{-1}$. While the zero-field permittivity changes only slightly for the pristine vs. field-cycled state from 43.0 to 45.2, the shape of the characteristic transforms from a double-butterfly figure towards a typical ferro-electric butterfly graph. The dielectric permittivity is suppressed at increased fields in the woken-up state, which could be beneficial for sensor applications. Maxima of the dielectric permittivity after field cycling (blue curve) coincide with the coercive field at $-0.8 \,\mathrm{MV}\,\mathrm{cm}^{-1}$ and $0.9 \,\mathrm{MV}\,\mathrm{cm}^{-1}$.

In Figure 4.11 a), the coercive field distributions extracted from first-order reversal curve measurements (FORC) [95, 308, 309] are shown for an as-deposited 2.8 cat % Si-doped HfO₂ thin film. The depicted Preisach density can be understood as a distribution of coercive fields $E_{\rm C,+}$ and $E_{\rm C,-}$ for individual domains in the film. In comparison to the *j*-*E* graphs in Figure 4.10 b), it provides a more detailed assessment of internal bias fields and their evolution during wake-up. Additionally, the causality of switching, i.e., which current peak pairs correspond to one physical effect, is determined.



Figure 4.11: Coercive field distributions of 20 nm thick Si-doped HfO_2 obtained a) as-deposited, b) after 10 electric field cycles and c) after 10^5 cycles. Switching densities are calculated from FORC measurements. For successive field cycling with an amplitude of 3 MV cm^{-1} , the formation of a distinct ferroelectric switching peak is visible, which is marked (white cross). Films are nano-laminated with a thin Al_2O_3 inter-layer to control crystallinity (see Section 3.4.1).

In the initial state, the contributions (1) and (2) marked in the graph correspond to AFE-like contributions. Contributions (3) and (4) exhibit more symmetric coercive fields, with a wide distribution roughly corresponding to the (ferroelectric) diagonal $E_{\rm C,+} = -E_{\rm C,-}$. This is explained by local field variations due to charged defects, leading to domain pinning. Schenk et al. also note that such a distribution may be caused by texture, where the polarization axis deviates from the direction of the applied electric field, altering the effective coercive field value [95]. The slight deviation of contributions (3) and (4) from the $E_{\rm C,+} = -E_{\rm C,-}$ line is referred to as imprint, an uniform shift of both coercive fields due to electrode work function differences or an asymmetric dopant or defect distribution throughout the film. Upon application of electric field cycles in Figure 4.11 b), the asymmetric (AFE-like) distributions (1) and (2) begin to vanish, and the symmetric (ferroelectric) peaks (3) and (4) merge towards a single switching peak. After 10^5 cycles at $3 \,\mathrm{MV \, cm^{-1}}$, a single, confined switching peak remains, which is shown in Figure 4.11 c). The corresponding coercive fields of $0.8 \,\mathrm{MV \, cm^{-1}}$ for $E_{\mathrm{C},+}$ and $-1.2\,\mathrm{MV\,cm^{-1}}$ for $E_{\mathrm{C},-}$ are comparable to the value extracted from *P-E* hysteresis loops in Figure 4.10 (white cross).

Since electric field cycling changes the ferroelectric response of doped HfO₂ due to the impact on defect distribution and phase composition, an effect on the pyroelectric response is expected. Sharp-Garn measurements are performed for films with different electric field cycling states. Results for 20 nm thick Si-doped HfO₂ are depicted in Figure 4.12 a) (see Reference [104]). After a single poling cycle, a pyroelectric coefficient of $-8.4\,\mu\mathrm{C\,m^{-2}\,K^{-1}}$ and a $P_{\rm r}$ value of $2.4\,\mu\mathrm{C\,m^{-2}\,K^{-1}}$ are registered. With successive cycling, these values increase to a final value of $-80\,\mu\mathrm{C\,m^{-2}\,K^{-1}}$ and $12.8\,\mu\mathrm{C\,cm^{-2}}$ for p



Figure 4.12: a) Pyroelectric coefficient vs. remanent Polarization for 20 nm thick Si-doped HfO_2 with increasing field cycling counts. b) Curie constant vs. electric field cycles. The susceptibility of the spontaneous polarization to the temperature rises during wake-up. The logistic model serves as a guide to the eye. Note the similarity to Fig. 4.9.

and $P_{\rm r}$, respectively. The increase of p during wake-up has been confirmed by other groups [281, 282].

While the relationship between P_r and -p is monotonically rising, there are different regimes visible throughout the wake-up process. The slope of the data points steepens beginning at 2×10^3 field cycles, and after 1×10^5 switching events, the wake-up process slows down, with P_r and -p remaining almost constant. In Figure 4.12 b), calculated Curie constants are shown with respect to the electric field cycle count. The reduction of C_c during wake-up can be interpreted as an increasing susceptibility of the spontaneous polarization to the temperature. A phase change induced by electric field cycling would not explain the large initial C_c . Hence, experimental results are in favor of a wake-up model based on the defect-induced inhibition of ferroelectric switching [96, 174]. This is further supported by the complex coercive field distribution in pristine films (see Figure 4.11). The exact mechanism of the inhibition of pyroelectricity by the defect structure warrants further investigation, and could be connected to internal bias fields or the inhibition of domain formation.

4.1.3 Film thickness scaling and lamination

In sensor applications, the electrical capacitance of the pyroelectric layer is an important criterion, since it determines the frequency response [310]. A high sensor capacitance further leads to limitations regarding the amplifier design with regard to stable and low-noise operation. Hence, it is important to optimize the layer thickness of the HfO₂ material to find a balance between sensor performance and film deposition time. The comparably low dielectric permittivity of doped HfO₂ in comparison to lead-based ferroelectrics such as $PbZr_xTi_{1-x}O_3$ is beneficial for many pyroelectric applications. The HfO₂ material class is exceptional in the sense that ferroelectric behavior has been reported in HfO₂-based films as thin as 1 nm [5], but is challenging to stabilize in thick films above 30 nm. Optimal ferroelectric and pyroelectric properties are reported around 10 nm [144]. Additionally, the deposition time becomes an significant criterion at increased film thicknesses, since this work focuses on the ALD manufacturing process. An interesting direction for future work would be the investigation of pyroelectric properties in films manufactured by CVD and PVD.

The impact of film thickness on the ferroelectric and pyroelectric properties of $Hf_{1-x}Zr_xO_2$ has been studied by Smith et al. [281]. With increasing layer thickness, the group observed a growing remanent polarization, but diminishing pyroelectric coefficients with an maximal value of $-58 \,\mu C \,m^{-2} \,K^{-1}$ registered for a 10 nm film. The strong impact of thickness effects is somewhat expected, since ferroelectricity in doped HfO_2 is a distinct thin-film phenomenon. Proposed reasons for this include surface energy effects [311] and strain from grain size and electrode interfaces [312].

To obtain ferroelectric films in a wide thickness range, a nano-lamination technique has been proposed [51, 141]. Nano-laminates have been used in other material systems before, e.g. for enhancing the electrical characteristics of ZrO_2 in DRAM capaci-



Figure 4.13: a) Film thickness determined by SE vs. laminate layer count. b) HRTEM micrograph of two 10 nm thick Si-doped HfO₂ layers laminated with a thin, approximately 0.5 nm thick, amorphous Al₂O₃ interlayer. In the EFTEM micrograph, the signals of Si (blue), Ti (red) and Hf (green) are corresponding to the substrate, electrodes and the pyroelectric layer, respectively. c) In the magnified micrograph, the disruption of the grain orientation by the Al₂O₃ interlayer is visible.

tors [313]. Following the approach, 10 nm thick Si-doped HfO₂ and Hf_{0.5}Zr_{0.5}O₂ layers, which are laminated up to five times with thin, amorphous Al₂O₃ separators are investigated. The Al₂O₃ inter-layers are manufactured with five ALD cycles of TMA/O₃ precursors, yielding a thickness of approximately 0.5 nm. In Figure 4.13 a), film thicknesses determined by SE are displayed for one, two, three and five laminated Si-doped HfO₂ layers. It is evident that the film thickness increases linearly, as expected, and that the Al₂O₃ interlayer has only a minor influence on the overall value.

The goodnes-of-fit (GOF) values give qualitative indication whether thicknesses determined by SE are reliable, with values of 0.99 for the 10 nm layer with a minute decrease to 0.98 at 50 nm. A high resolution transmission electron microscopy (HRTEM) image of a laminate with two Si-doped HfO₂ layers in Figure 4.13 b) confirms the target thickness. In the EFTEM micrograph, the monocrystalline Si substrate (blue), 10 nm thick titanium nitride electrodes (red), and the laminated Si-doped HfO₂ (green) are clearly visible. Filter energies of 99 eV, 456 eV, and 1662 eV are used for Si, Ti, and Hf, respectively. Between the bottom electrode and the Si substrate, a thin SiO₂ interface layer is visible.

In the magnified HRTEM micrograph in Figure 4.13 c), the disruption of grain growth at the amorphous Al_2O_3 interlayer (IL) is clearly visible. As indicated by white lines, the orientation of the crystallites is clearly different in the top and bottom HfO₂ layers. These artificial grain boundaries lead to an increase of the surface energy, and thereby stabilize the polar orthorhombic phase in films with a thickness of up to 50 nm.



Figure 4.14: ToF-SIMS results with respect to sputter time for a) $10 \text{ nm Si-doped HfO}_2$ as well as laminates with an overall thickness of b) 20 nm, c) 30 nm, and d) 50 nm. The Al₂O₃ separator layers are clearly visible in the laminated films.

In Figure 4.14 a), ToF-SIMS measurement results are depicted for a single Si-doped HfO_2 layer. By sputtering of the sample, alternating with element analysis via mass spectrometry, the method provides a high depth resolution and element sensitivity. However, it is noted that ToF-SIMS yields only qualitative composition information. Signals of ²⁷Al (red), the dopant ²⁸Si (green), ⁶²(TiN) (orange), and ¹⁹⁶(HfO) (purple) are shown. The different film regions are clearly distinguished, namely the TiN top electrode, the Si-doped HfO₂, the TiN bottom electrode, and the Si substrate.

The Si-doping of the HfO_2 film is clearly observed, and decreases slightly towards the bottom electrode. A reduction of the 62 (TiN) signal at the bottom electrode interface is observed. This is explained by an oxidation of the bottom electrode by the ALD process, which leads to the formation of titanium oxide. Slight variations in the observed signals may also arise from charge buildup at the metal—ferroelectric interface by ion bombardment [314]. Additionally, variations of the sputter rate in regions of high defect density (e.g., at interfaces) can lead to artifacts.

Results for the 20 nm thick, nano-laminated film are shown in Figure 4.14 b). The individual HfO_2 layers and the Al_2O_3 separator are visible. The ¹⁹⁶(HfO) layer seems continuous, since the Al_2O_3 has a thickness of approximately 0.5 nm, which is concealed

by the non-uniformity of the ToF-SIMS sputter crater and roughness effects. In the 30 nm and 50 nm laminates, two and four Al_2O_3 peaks are observed, respectively, as shown in Figure 4.14 c) and d). The concentration of ^{12}C is found to be independent on the lamination count (not shown here).

In Figure 4.15 a), the results of ferroelectric hysteresis measurements are shown for both Si-doped HfO₂ (blue circles) and $Hf_{1-x}Zr_xO_2$ (orange squares). Identical electric field amplitudes of $3.0 \,\mathrm{MV}\,\mathrm{cm}^{-1}$ are used for all measurements, and values are extracted after 10^5 electric field cycles. It is evident that both materials exhibit increasing remanent polarization values with the lamination technique. This is somewhat surprising since the potential drop over the Al_2O_3 with a low dielectric permittivity of ≈ 9 leads to a slight reduction of the electric field in the doped HfO₂ layers [51]. For the Si-doped HfO₂ layers, P_r values range from $8.7 \,\mu\mathrm{C}\,\mathrm{cm}^{-2}$ for the single layer to $13.3 \,\mu\mathrm{C}\,\mathrm{cm}^{-2}$ at a total thickness of $50 \,\mathrm{nm}$. As expected, $Hf_{1-x}Zr_xO_2$ generally exhibits larger P_r values [175], with a value of $19.9 \,\mu\mathrm{C}\,\mathrm{cm}^{-2}$ for the 10 nm layer. Towards higher total thicknesses, P_r values increase, reaching $24.1 \,\mu\mathrm{C}\,\mathrm{cm}^{-2}$ at $50 \,\mathrm{nm}$. Breakdown fields in the range of $3.5 \,\mathrm{MV}\,\mathrm{cm}^{-1}$ to $4.0 \,\mathrm{MV}\,\mathrm{cm}^{-1}$ are registered for all samples.

Pyroelectric measurements are performed with the Sharp-Garn method, as described in Section 3.1.1. The determined pyroelectric coefficients with respect to the laminate thickness are plotted in Figure 4.15 b). For Si-doped HfO₂, a value of $-55 \,\mu \text{C} \,\text{m}^{-2} \,\text{K}^{-1}$ is obtained with the non-laminated film. For a double laminate structure, p increases considerably to $-84 \,\mu \text{C} \,\text{m}^{-2} \,\text{K}^{-1}$. For even higher thicknesses, pyroelectric coefficients reduce again, reaching $-64 \,\mu \text{C} \,\text{m}^{-2} \,\text{K}^{-1}$ for the 50 nm film. The phase of the pyroelectric current with respect to the temperature waveform remains stable at a value of



Figure 4.15: a) Remanent polarization of $Hf_{0.5}Zr_{0.5}O_2$ and 3.8 cat% Si-doped HfO_2 layers in a thickness range of 10 nm to 50 nm. To optimize the pyroelectric response, electric field cycle counts of 10^5 and 10^2 were applied to the HSO and HZO samples, respectively. b) Corresponding pyroelectric coefficients.

 $95^{\circ}\pm2^{\circ}$ for all examined lamination counts. The decreased pyroelectric coefficient for the non-laminated film is comparable to the results of Jachalke et al., where a value of $-46 \,\mu C \,m^{-2} \,K^{-1}$ is reported. However, the reason for such a large benefit of nano-lamination for the pyroelectric response with Si-doped HfO₂ warrants further study.

One possible explanation is related to the different interface configurations in the films. The 10 nm film has two, partially oxidized titanium oxynitride $(\text{TiO}_x N_y)$ interfaces, whereas the double laminate layers have one amorphous Al_2O_3 and one TiO_xN_y boundary. The interface configuration can have a prominent influence on the ferroelectric and pyroelectric properties due to defect accumulation, and the resulting de-polarization fields. Alternatively, Al species at the interlayer could act as a dopant, or could enhance the pyroelectric effect by providing meta-stable defect sites, which lead to an electret effect.

For the $Hf_{1-x}Zr_xO_2$ mixed oxide, monotonically decreasing P_r values of $-66 \,\mu C m^{-2} K^{-1}$ to $-49 \,\mu C m^{-2} K^{-1}$ are registered in the thickness range of 10 nm to 50 nm. The $Hf_{1-x}Zr_xO_2$ material does not seem to be strongly impacted by the described interface effects.

The coercive field distribution of a 10 nm thick, Si-doped HfO₂ layer is displayed in Figure 4.16 a). It is visible that the ferroelectric switching peak exhibits fringes and an asymmetric shape. In comparison, the 20 nm thick, nano-laminated layer in Figure 4.16 b) exhibits a more confined switching peak. The observed Preisach densities provide further evidence for an improved interface configuration in the nano-laminated layers.

In conclusion, nano-lamination of doped HfO_2 thin films with thin, amorphous Al_2O_3 separator layers is identified as a viable approach for film thickness scaling while maintaining the ferroelectric and pyroelectric properties of the material. Overall, the



Figure 4.16: Coercive field distributions obtained by means of FORC after 10^4 electric field cycles. a) A single, 10 nm thick, $3.8 \operatorname{cat}\%$ Si-doped HfO₂ film. b) Two nano-laminated Si-doped HfO₂ layers with an approximately 0.5 nm thick Al₂O₃ inter-layer.

largest pyroelectric coefficient of $-84 \,\mu\text{C}\,\text{m}^{-2}\,\text{K}^{-1}$ was determined for a laminate of two, 3.8 cat % Si-doped HfO₂ layers with a total thickness of 20 nm. TEM micrographs indicate that the separator layer introduces an artificial grain boundary in the nanolaminates, whereby the crystallization temperature of the films is increased. Further, the nano-lamination technique is fit to improve the pyroelectric performance by means of an increased coefficient p and a reduced capacitance density.

4.1.4 Field-induced enhancement of the pyroelectric effect

The AFE-like behavior in HfO_2 films with a tetragonal phase fraction provides an opportunity to further enhance the pyroelectric response. Several explanations for the effect are discussed in the literature, with the most prominent being a field-induced phase transition from the centrosymmetric tetragonal towards the polar orthorhombic phase [90, 171]. Several groups have reproduced the effect in HfO_2 with computational methods [6, 120, 129, 173]. These studies have shown that the energy barrier between the tetragonal and orthorhombic phase is lowered by doping, allowing a field-induced transformation.

Field-, temperature-, and stress-induced phase transitions have been observed in relaxor ferroelectrics [315], which lead to a field-enhancement of the pyroelectric coefficient in such materials [200, 316–318]. However, other explanations such as depolarization fields [174] or Kittel-type AFE behavior due to the scale-free nature of domains in HfO_2 [6] are discussed for the HfO_2 material class as well.

In lead- and barium-based materials, pyroelectricity has been found to be modulated in the transitional region from the ferroelectric to an anti-ferroelectric phase [319, 320]. AFE films exhibit a strong enhancement of the pyroelectric coefficient with an applied electric field. Pandya et al. have recently shown a more than five-fold increase of the pyroelectric response in $Pb(Mg_{1/3}Nb_{2/3})O_3$ -PbTiO₃ relaxor ferroelectric films with an applied electric field, while suppressing the dielectric response at the same time [200]. This is explained by the combined effect of field- and temperature-induced changes of the polarization magnitude and direction.

Further, an electric field contributes to the pyroelectric effect via the temperature dependence of the dielectric permittivity. From a crystallographic standpoint, such fieldinduced pyroelectricity is plausible since an electric field breaks the centrosymmetry of any crystal lattice.

Thirdly, the Landau-Devonshire theory predicts another contribution to the pyroelectric effect with an applied electric field in the vicinity of the Curie temperature $T_{\rm C}$. In this simplified picture, the spontaneous polarization of a ferroelectric decreases monotonically with T, as depicted in Figure 4.17 a). An external electric field leads to an increased polarization, even in the range $T > T_0$. Without a field bias, the transition to the non-polar state occurs at $T_{\rm C}$. With an external electric field, the free energy landscape is skewed, resulting in a broadened transition temperature range.



Figure 4.17: a) Temperature dependence of the spontaneous polarization calculated from Landau theory (Equation 2.28) for a second-order (continuous) phase transition without and with a constant electric field. b) Corresponding temperature differential of the spontaneous polarization.

When calculating pyroelectric coefficients, the field-free case corresponds to a divergent behavior $p \to \infty$ when approaching $T \to T_0$, as shown in Figure 4.17 b). With an applied field, the temperature with the highest pyroelectric response rises, and the transition range is extended [11]. Depending on the temperature, the pyroelectric coefficients may decrease or increase with an applied external field. The described effects have been observed in bulk ferroelectrics BaTiO₃ and KH₂PO₄ [321, 322]. For the HfO₂ layers discussed herein, no clear transition temperature is found, since the grains in the thin films may possess different $T_{\rm C}$ values, depending on their size, local stress, and defect structure. Additionally, complex bias fields [96] which may reach hundreds of kV cm⁻¹ broaden the transition temperature range. In turn, this implies that large pyroelectric, dielectric and piezoelectric constants may be obtained in the vicinity of T_0 in epitaxial HfO₂-based films [9, 323].

While the Landau theory of phase transitions is helpful to understand some fundamental aspects of pyroelectricity in the HfO_2 material class, it does not capture the influence of field-induced phase transitions. To study the effect of an electric field on the pyroelectric response, the Sharp-Garn method used in previous sections is modified by introducing a voltage source in series with the amperemeter and pyroelectric capacitor.

Results of ferroelectric and pyroelectric measurements are shown in Figure 4.18 for HfO_2 thin films with three different Si concentrations.

In the first row, P-E characteristics are shown for pristine samples and after the application of 10^5 electric field cycles. All graphs exhibit pinched, AFE-like hysteresis loops in the as-deposited state (red lines). Upon electric field cycling, the P-E characteristic of 3.8 cat % Si-doped material in Figure 4.18 a) exhibits the previously discussed wake-up effect (see Section 4.1.2). A ferroelectric hysteresis loop with a remanent po-



Figure 4.18: a-c) Polarization-field characteristics of 20 nm thick Si-doped HfO_2 thin films with a dopant content of 3.8 cat %, 4.8 cat %, and 5.6 cat % for as-deposited and field-cycled states. d-f) Corresponding pyroelectric coefficients for as-deposited and field-cycled films with offset fields ranging from $-1.3 \,\mathrm{MV \, cm^{-1}}$ to $1.3 \,\mathrm{MV \, cm^{-1}}$.

larization of $12.4 \,\mu\text{C}\,\text{cm}^{-2}$ and almost symmetric coercive fields of $\pm 0.9 \,\text{MV}\,\text{cm}^{-1}$ are obtained (blue line). In contrast, the $4.8 \,\text{cat}\%$ Si-doped layer in Figure 4.18 b) exhibits nearly no wake-up effect. The stabilization of an AFE-like behavior with higher Si concentrations has been described in the literature [302], and has been proposed for energy storage applications [324, 325]. For the 5.6 cat % Si-doped HfO₂ in Figure 4.18 c), hysteresis loops show minute wake-up, and an increasing paraelectric film fraction leads to a reduced maximal polarization and less pronounced AFE-like features.

For pyroelectric measurements, the applied electric field is limited to $1.3 \,\mathrm{MV \, cm^{-1}}$ to prevent degradation of the doped HfO₂ and reduce contributions from leakage currents. In Figure 4.18 d), the pyroelectric coefficients of $3.8 \,\mathrm{cat} \,\%$ Si-doped HfO₂ are depicted for the as-deposited (red squares) and the field-cycled state (blue circles). It is noted that the electric field amplitude is reduced with respect to *P-E* measurements to prevent degradation. Qualitatively, pyroelectric coefficients behave similar to the hysteresis graphs in Figure 4.18 a). In the pristine state, the values at $0 \,\mathrm{MV \, cm^{-1}}$ are

 $11 \,\mu C \,m^{-2} \,K^{-1}$ and $-39 \,\mu C \,m^{-2} \,K^{-1}$ for negative and positive film polarizations, respectively. Pyroelectric coefficients increase significantly with an applied field in the pristine state, reaching $47 \,\mu C \,m^{-2} \,K^{-1}$ and $-89 \,\mu C \,m^{-2} \,K^{-1}$ at $\pm 1.3 \,MV \,cm^{-1}$.

Upon electric field cycling, the p-E graphs evolve towards a more symmetric behavior. After 10⁵ cycles, values of 77 µC m⁻² K⁻¹ and $-90 µC m^{-2} K^{-1}$ are registered at 0 MV cm^{-1} . Coercive fields determined from pyroelectric measurements are 0.65 MV cm^{-1} and -0.85 MV cm^{-1} , which is slightly lower than the values determined in ferroelectric hysteresis measurements. This is expected, since the acquisition time for a full voltage sweep is orders of magnitude longer in Sharp-Garn measurements in comparison to the ferroelectric hysteresis characterization at 1 kHz. Towards the electric field maximum, pyroelectric coefficients decrease slightly for the woken-up films. Electric field cycling leads to a transformation from field-induced pyroelectricity in the pristine state towards an intrinsic pyroelectric effect in the woken-up state for the 3.8 cat.% Sidoped films. While no quantitative model is available yet, the *p*-*E* characteristic of this film is interpreted as an superposition of two effects: At low fields, a contribution arises from the dielectric term $\partial \varepsilon_r / \partial T$. At higher fields, the pyroelectric effect is suppressed as predicted by the Landau-Devonshire model.

Interestingly, the field-induced pyroelectric behavior of 4.8 cat % Si-doped HfO₂ in Figure 4.18 e) exhibits a pronounced evolution upon application of electric field cycling as well. After 10^5 cycles, a large field-induced pyroelectric response is observed, with $-142 \,\mu\text{C}\,\text{m}^{-2}\,\text{K}^{-1}$ at $0.8\,\text{MV}\,\text{cm}^{-1}$. The maximal field-induced pyroelectric response coincides with the largest opening of the AFE hysteresis graph in Figure 4.18 b). In Figure 4.18 f), pyroelectric coefficients of the 5.6 cat.% Si-doped material are shown. While the pyroelectric response is mainly field-induced, the magnitude is significantly reduced. The operation at a bias voltage may also reduce de-polarization effects (aging), which are relevant for infrared sensor applications.

The field-induced pyroelectric effect observed in the AFE-like 4.8 cat % Si-doped film is deemed too large to be explained by a dielectric contribution or the Landau model. It is concluded that only a field-induced phase change from the centrosymmetric tetragonal to the polar orthorhombic phase can lead to the strong enhancement. The wake-up effect has been associated with the re-distribution of charged defects. In the case of AFE-like HfO₂, it is speculated that the re-distribution of charged defects enhances the susceptibility of a field-induced phase change to the temperature. This is supported by the fact that the electric field for which the largest opening of the AFE-like hysteresis is observed reduces upon field cycling. A field-induced phase transition would also explain the large displacement which is observed in piezoelectric DBLI measurements of AFElike HfO₂ films [326].

The sizable field-induced pyroelectricity of Si-doped HfO_2 leads to a increase of the related figures of merit (FOM), which are summarized in Section 4.5, and further increases the application potential of the material class. A similar enhancement of the piezoelectric response of HfO_2 remains to be confirmed experimentally, opening up a direction for further research.

4.1.5 Pyroelectric aging

The phenomenon of aging is a well-known effect in polycrystalline ferroelectrics, and has been analyzed for many material systems such as $PbZr_xTi_{1-x}O_3$ [301], BaTiO₃ [327, 328], and BaSn_xTi_{1-x}O₃ [329]. In contrast to fatigue, aging describes the gradual decay of material properties under near-equilibrium conditions. Aging occurs without an applied electric field, and is therefore relevant for the operation of pyroelectric infrared detection devices. Aging can be caused by effects associated with the bulk ferroelectric, interfaces, and domains [301]. In many material classes, the largest contribution arises from the redistribution of charged defects, such as oxygen vacancies, which lead to the formation of defect dipoles [330]. It has been established that aging effects may be reversed by repeated field cycling or heating above the transition temperature [331].

To describe the aging process theoretically, the nucleation-limited switching (NLS) model is applied, which proposes a polarization back-switching due to the electric field in an interface dead layer [332]. In comparison to the Kolmogorov-Avrami-Ishibashi (KAI) model, [333, 334] which is commonly used to describe switching kinetics in ferroelectrics, the NLS approach is also applicable to thin films. The time dependence of the switching process is described by three equations

$$P(t) = \Gamma h \left(\frac{\pi}{2} - \arctan \frac{z_1 - z_0}{\Gamma}\right) \text{ for } z_0 < z_1,$$

$$(4.5)$$

$$P(t) = \Gamma h\left(\frac{\pi}{2} + \frac{z_0 - z_1}{\Gamma}\right) \text{ for } z_1 < z_0 < z_2, \text{ and}$$
(4.6)

$$P(t) = \Gamma h \left(\frac{\pi}{2} + \frac{z_2 - z_1}{\Gamma} + \arctan \frac{z_0 - z_2}{\Gamma} \right) \text{ for } z_2 < z_0,$$
(4.7)

with a parameter

$$h = (z_2 - z_1 + \Gamma \pi)^{-1}. \tag{4.8}$$

Here, Γ is the decay rate, $z_1 = \log(\tau_{\min})$ and $z_2 = \log(\tau_{\max})$ are parameters corresponding to the minimal and maximal switching time constants τ_{\min} and τ_{\max} , respectively, and $z_0 = \log(t)$.

A retention model based on the NLS approach has been proposed by Stolichnov et al. [335]. It is proposed that a non-polar interface dead layer induces a de-polarization field

$$E_{\rm dep} = \frac{d_{\rm IF}}{d_{\rm film}} \frac{P}{\varepsilon_0 \varepsilon} \tag{4.9}$$

in the pyroelectric film. Here, $d_{\rm IF}$ is the thickness of the interface layer. The effect is illustrated in Figure 4.19 a). Dead layers can occur at one or both electrode interfaces, but also in the film, e.g., in nano-laminates.



Figure 4.19: a) De-polarization fields emerge in polar films due the existence of non-polar dead layers. b) Pyroelectric coefficients of $2.8 \operatorname{cat} \%$ Si-doped HfO₂ extracted from measurements over the course of 16.7 h and relaxation behavior obtained with the NLS model.

While E_{dep} is much smaller than the coercive field in most situations, it leads to domain nucleation or growth according to the NLS model. The field dependence of the time constants of the switching process are calculated as

$$\tau_{\min} = \tau_0 \text{ and} \tag{4.10}$$

$$\tau_{\max} = \tau_0 \exp\left(\frac{E_0}{E}\right)^n. \tag{4.11}$$

Gong et al. applied the retention model to ferroelectric HfO₂, and obtained parameters $\tau_0 = 1 \times 10^{13}$ s, n = 1.87, $\Gamma = 0.5$, and an activation energy of $E_0 = 12.7$ MV cm⁻¹. Further, a dielectric permittivity of 30, an interface dead layer of 0.7 nm, and a HfO₂ film thickness of 20 nm are set. The model is adapted to pyroelectric aging by assuming $p \propto P_{\rm r}$.

To assess the aging behavior of doped HfO_2 , repeated pyroelectric measurements are conducted after electric field cycling. Here, a 2.8 cat % Si-doped HfO_2 layer with a positive polarization state is used. Each measurement has a duration of 400 s, and 150 data points over the course of 16.7 h are obtained. The extracted pyroelectric coefficients are shown in Figure 4.19 b). Measurements at offset temperatures of 20 °C and 50 °C are conducted, and values are normalized for better comparability. It is visible that the aging process is slightly faster for higher temperatures. The phase of the current increases slightly towards the ideal value of 90° with time, which indicates a reduction of the in-phase current due to successive de-trapping of charges in the ferroelectric film.

It is evident that the model (red lines in Figure 4.19) matches the experimental results reasonably well. For temperatures of 20 °C and 50 °C, switching activation energies of $12 \,\mathrm{MV}\,\mathrm{cm}^{-1}$ and $11 \,\mathrm{MV}\,\mathrm{cm}^{-1}$ are extracted, respectively, which is close to the

previously reported value and DFT calculations for HfO₂ [336, 337]. The lowering of E_0 for a rising temperature is expected [336], and corresponds to lowered characteristic switching times τ . After 10 years, the remaining pyroelectric responses are predicted as 76 % and 73 % at 20 °C and 50 °C, respectively.

For infrared sensor applications, the aging rate per decade is of practical importance. From the simple logarithmic model

$$p = -r_{10} \cdot \log_{10}(t) + \text{const.}, \tag{4.12}$$

mean aging coefficients r_{10} are extracted, which increase slightly from (6.13 ± 0.03) % at 20 °C to (6.44 ± 0.07) % at 50 °C. The temperature dependence of the aging coefficient r_{10} is shown in Figure 4.20 a). The aging process results in a considerable internal bias field in the order of 200 kV cm⁻¹, which results in a shift of the positive coercive field $E_{c,+}$. The bias field is induced by the diffusion of charged defects due to the depolarization field E_{dep} . The effect is reversed by the subsequent application of electric field cycling, which is shown in Figure 4.20 b). Interestingly, aging occurs asymmetrically, which is explained by the diffusion of positively charged defects (oxygen vacancies) to the bottom electrode.

The NLS model provides some strategies to reduce the magnitude of the pyroelectric aging process. Most importantly, the thickness of the interface layer should be minimized, while a larger thickness of the HfO_2 material is beneficial. Moreover, the operation at an offset voltage would inhibit the de-polarization process, and enable large field-induced pyroelectric coefficients in combination with AFE-like doped HfO_2 (see Section 4.1.4).



Figure 4.20: a) Temperature dependence of the aging rate per decade. b) Evolution of ferroelectric switching current peaks during field cycling after the aging process ("de-aging").

4.2 Pyroelectric coefficients obtained by XPS

Instead of probing the current flow which is caused by the pyroelectric effect (see Equation 2.38), XPS can be used to directly measure the temperature-dependent macroscopic polarization of the pyroelectric HfO_2 films. As described in Section 3.1.2, a specialized sample holder is used to perform XPS measurements of a polarized film at different temperatures. In an ultra-high vacuum environment, the polarization change of the films is not equalized by charge carriers. Thus, the top electrode of the pyroelectric capacitor exhibits a shift of the peak in the corresponding photoelectron spectrum.

The contact-less pyroelectric measurement is demonstrated with a 50 nm thick, 3.5 cat.% Si-doped HfO₂ film. TiN top and bottom electrodes with a thickness of 10 nm are used. The top electrode is further covered with a 100 nm thick Pt layer, which screens the photoelectron emission from the HfO₂ film in the capacitor area. A XPS spectrum over the full binding energy range is shown in Figure 4.21. The peaks corresponding to the top electrode (Pt) and the surrounding area (Hf and O) are identified, as shown by the corresponding labels. The fine structure splitting of the 4p and 4d peaks of Pt and Hf is visible in the spectrum.



Figure 4.21: XPS spectrum over the full binding energy range. The analysis region includes the Pt top electrode and the surrounding exposed HfO_2 .

In Figure 4.22 a) and b), XPS binding energy spectra of the Hf 4f and Pt 4f vicinity are shown. For Pt 4f, the line shape is described well by an asymmetric Lorentzian model (LA(1,2.4,0) in CasaXPS). Asymmetric line shapes are common in metals due to the interaction with conduction band states [338]. For the Hf 4f peaks, a symmetric Gaussian-Lorentzian model GL(30) is employed.

The initial measurement is conducted at 30 °C, and maxima for Hf $4f_{7/2}$ and Pt $4f_{7/2}$ are obtained at 18.4 eV and 72.6 eV, respectively. Fine structure splitting energies of 1.7 eV and 3.3 eV are obtained for Hf and Pt. For the Hf $4f_{7/2}$ orbital, a somewhat lower binding energy of 16.7 eV is reported in the literature for pure HfO₂, and the peak splitting is equal at 1.7 eV [263]. For the Pt $4f_{7/2}$ peak, a literature value of 71.2 eV and a splitting of 3.33 eV are available [263]. The area ratio of the respective 7/2 and 5/2 peaks is 0.75, as expected from theory.



Figure 4.22: a) XPS spectrum of the Hf 4f vicinity at 30 °C (top) and 100 °C (bottom). Since the HfO₂ layer without a top electrode lacks a macroscopic net polarization, the shift of $E_{\rm B}$ is small. b) The Pt 4f peak energy is reduced noticeably upon heating. This is caused by the pyroelectric effect, which reduces the surface charge $Q_{\rm s}$.

When heating to 100 °C, the binding energies of Hf $4f_{7/2}$ and Pt $4f_{7/2}$ decrease to 18.2 eV and 71.7 eV, respectively, while the fine structure splitting is unchanged. The binding energy shift is indicated by dashed lines in Figure 4.22 a) and b). Over the temperature difference of 70 K, the corresponding surface potential change is -0.76 eV. By using Equation 3.6 with a value $\varepsilon = 40$, a pyroelectric coefficient of $-73 \,\mu\text{C}\,\text{m}^{-2}\,\text{K}^{-1}$ is calculated. This is similar to the value of $-64 \,\mu\text{C}\,\text{m}^{-2}\,\text{K}^{-1}$, which has been extracted by the Sharp-Garn method in Section 4.1.3 for this sample.

When repeating the experiment with an oppositely polarized sample, no surface potential change is measured (not shown here). At 30 °C, binding energies are 70.9 eV and 18.3 eV for Hf $4f_{7/2}$ and Pt $4f_{7/2}$, respectively. At 100 °C, the values remain nearly unchanged. This is expected, since negatively charged species in the XPS chamber readily neutralize the corresponding positive charges which are present at the Pt electrode [190].

4.3 High-frequency temperature cycles

The previously described pyroelectric measurement methods rely on a thermal equilibrium throughout the sample, which limits the accessible frequency range to less than 0.1 Hz. For many applications, such as infrared sensors, characterization of the pyroelectric effect up to the kHz range is desired. Accessing such raised frequencies also lays the foundation for characterizing the electrocaloric effect, which is discussed in Section 5.2.
In this Chapter, an on-chip pyroelectric test device with an integrated micro-heater is used. The test structure as well as the associated implementation in the characterization setup have been introduced in Chapter 3.1.3.

Integrated test structures for probing pyroelectric properties of thin films have been proposed by Bathia et al. [199] for probing $PbZr_{0.2}Ti_{0.8}O_3$ thin films. Foundations for the method were developed by Cahill and Pohl [201, 202], who investigated temperature propagation with deposited metal heating strips and their use for characterization of thermal properties in thin films. Subsequently, similar structures were used to study pyroelectric properties and energy harvesting in $0.68Pb(Mg_{1/3}Nb_{2/3})O_3-0.32PbTiO_3$. Recently, publications from this group [251] and UC Berkeley [282] reported high-frequency pyroelectric measurement results using Si-doped HfO₂, demonstrating the feasibility of the approach for nanometer-thin pyroelectric films.

The test structure which is used in this work is shown in Figure 4.23 a), where the pyroelectric/electrocaloric test structures are marked by a white arrow. A micrograph of bonded samples is depicted in Figure 4.23 b), where outlines of the thin film temperature sensor (red) and the buried, pyroelectric capacitor (blue) are indicated. Bond wires are visible as black lines. Only three bond wires are needed since the bottom electrode of the pyroelectric material is contacted via the substrate.

In the following sections, the thermodynamic properties of the micro-heater structures are discussed. To determine the amplitude and phase of rapid temperature oscillations in the test structure, the 3ω -method is used. Results are then compared to a finite element model of temperature propagation. Next, a frequency domain analysis of the pyroelectric effect in doped HfO₂ is performed. The wide measurement range is employed to investigate thin-film effects which impact the pyroelectric response, whereby primary (intrinsic) and secondary (thermal expansion induced) pyroelectric coefficients



Figure 4.23: a) Photograph of a diced pyroelectric test chip. The die outline size is 1 cm by 1 cm. The pyroelectric test structures used in this chapter are indicated by a white arrow. b) Micrograph of bonded pyroelectric test structures, where the thin-film heater (red) and the buried pyroelectric material (blue) is indicated.

are separated. Knowledge of both contributions further allows the estimation of the out-of-plane piezoelectric coefficient. Finally, the dependence of pyroelectric coefficients on ambient temperature is investigated.

4.3.1 Determination of micro-heater temperature oscillation

The amplitude of the temperature oscillation is determined experimentally using the 3ω method [201, 202], where the temperature dependent electrical resistance of the nickel film is exploited. The method is introduced in Section 3.1.4, where a simple expression for the temperature oscillation amplitude θ in the thin-film heater is derived in Equation 3.20. Besides the heating current amplitude and the electrical resistance, which are known, precise measurement of the TCR α in the thin film heater is necessary. This is accomplished by four-wire resistivity measurement on a temperature-controlled chuck utilizing a Keithley 2000 digital multimeter. Throughout the assessed temperature range of -10 °C to 130 °C, the electrical resistance increases from 15.0 Ω to 23.0 Ω . Temperature coefficients are calculated according to Equation 3.17, and are depicted in Figure 4.24 a). At 20 °C, a value of $(3.32 \pm 0.08) \times 10^{-3} \text{ K}^{-1}$ is determined. While bulk values are somewhat larger at $6 \times 10^{-3} \text{ K}^{-1}$ [339], literature reports confirm a lower α in thin films [340, 341]. For increasing temperature, coefficients rise slightly, which is indicated by a linear model (red line).

To validate the 3ω measurement approach, the third harmonic voltage $U_{3\omega}$ is assessed for a range of heating current amplitudes. Results for a current frequency of 117.75 Hz are depicted in Figure 4.24 b). As mentioned in Section 3.1.4, the alternating current generates a temperature oscillation at the double frequency of 235.5 Hz, and consequently the reference frequency of the lock-in amplifier is set to the third harmonic



Figure 4.24: a) Temperature coefficient of the electrical resistance in the thin film heating strip in a temperature range of -10 °C to 130 °C. A linear model is used to approximate the temperature dependence of α . b) Amplitude of the third harmonic voltage U_3 with respect to the applied alternating heating current amplitude $I_{\rm h}$ at a frequency of 117.75 Hz.

at 353.25 Hz. According to Equation 3.19, the signal scales with the third power of the heater current amplitude. This is confirmed by the cubic model (red line), which matches the experimental results. A slight deviation is observed for the lowest current amplitudes, which may be caused by the low signal to noise ratio. In all further investigations, a current amplitude of 40 mA is used, yielding sufficient signal strength while maintaining a low constant temperature offset due to direct current heating.

The 3ω method allows probing the thermal impedance of the film stack. Therefore, the heating current frequency $f_{\rm h} = \omega_{\rm h}/2\pi$ is varied in the range of 1 Hz to 100 kHz, corresponding to temperature oscillation frequencies $2f_{\rm h}$ of 2 Hz to 200 kHz. The measured third harmonic voltage drop $U_{3\omega}$ decreases from 392 µV to 12.0 µV throughout the frequency range. Using Equation 3.20, and using the previously determined values of α , temperature amplitudes in the thin film heater are calculated.

Results are depicted in Figure 4.25 a) (blue line) with respect to the frequency of temperature oscillation. For the lowest frequency of 2 Hz, an amplitude of (113 ± 10) mK is obtained. Towards higher frequencies, a nearly logarithmic decrease of the temperature amplitude is observed. For a line heater, this behavior is expected, as derived in Equation 3.21 [201]. Ultimately, the slope decreases and a value of (3.5 ± 1.7) mK is obtained at 200 kHz. The characteristic length of heat diffusion λ is given by Equation 3.14 [39]. The low thickness of the layer stack leads to a very fast thermal coupling between heater and pyroelectric film, with an estimated time constant below 0.5 µs [221, 342]. Therefore, phase and amplitude of the pyroelectric temperature oscillation are dominated by the substrate influence. For the whole frequency span, λ ranges from 1.9 mm to 1.9 µm, where a thermal diffusivity of 8.8×10^{-5} m² K⁻¹ is used for the Si substrate [343]. Thereby, thermal propagation in the substrate should not be influenced by the boundaries of the sample. Although the substrate thickness is 775 µm, no significant deviation



Figure 4.25: a) Temperature amplitude in the pyroelectric test structure obtained experimentally via the 3ω -method as well as FEM modeling. b) Corresponding phase lag of the temperature oscillation with respect to the current waveform.

from the linear relationship due to propagation of the thermal wave into the steel chuck of the probe station is registered below 10 Hz in Figure 4.25 a). Further, the phase of the temperature oscillation is analyzed with respect to the heating current waveform, which is shown in Figure 4.25 b). For the lowest frequency, a small value of -6° is measured, which is expected as the vicinity of the heating strip is close to thermal equilibrium. With rising frequency, the interaction of the thermal wave originating at the thin film heater with the surrounding substrate increases, consequently increasing the phase shift.

To verify the experimental results, FEM modeling of the test structure is used. Therefore, the COMSOL software package is employed. The heater is modeled as a twodimensional film on a three-dimensional, cuboid substrate. Care has been taken to verify that results are independent of model parameters such as mesh size and time resolution. Like before, the current frequency is varied between 1 Hz and 100 kHz. The temperature propagation is then evaluated for ten periods in the time-dependent model. Resulting temperature and strain values are exported and mean values throughout the test structure area are calculated by means of a Python script, and evaluated by fitting of sinusoidal waveforms. The resulting amplitudes and phases are shown as red squares in Figures 4.25 a) and b). The experimental results are closely matched, which is attributed to the well known material properties of Nickel and Si, which dominate the thermal behavior of the test structure.

The spatial distribution of the temperature amplitude is shown in Figure 4.26 b) for a current frequency of 1 kHz and an amplitude of 40 mA. It is evident from the graphic that the thermal wave is confined to the direct vicinity of the heater at raised frequencies. From the finite element model, the strain amplitude caused by alternating thermal expansion and shrinking is extracted. At the previously described conditions, strain amplitudes of up to 3×10^{-7} are realized, as shown in Figure 4.26 c). Outside of the device outline, the positive strain amplitude is compensated by a region with inverse sign. Knowledge of the strain oscillation upon cyclic heating and cooling is exploited in Section 4.3.3 to determine in-plane piezoelectric coefficients of doped HfO₂.



Figure 4.26: a) Discretization for FEM modeling of a diced test structure. b) Top view of the temperature amplitude distribution in the three-dimensional FEM simulation of the pyroelectric test structure (black outline). c) Thermal strain amplitude distribution resulting from the alternating temperature change in the test structure.

4.3.2 Frequency domain analysis of the pyroelectric effect

The knowledge of the temperature propagation in the pyroelectric test device lays the foundation for the interpretation of pyroelectric measurements in this Section. The pyroelectric material is now connected to the current input of the lock-in amplifier (see Section 3.1.3). Here, 20 nm thick, 3.8 cat % Si-doped HfO₂ is used. By combining pyroelectric current measurements and the temperature amplitudes extracted with the 3ω method, pyroelectric coefficients are characterized in the frequency domain.

In Figure 4.27 a), the current generated in the MFM structure by the thermal cycles is plotted with respect to the temperature oscillation frequency in the positive (\downarrow) and negative (\uparrow) ferroelectric polarization states. Agreement of the current measurement for both polarization states is observed in the frequency range of 10 Hz to 1 kHz. However, deviations are visible in the low- and high-frequency limit, especially for the as-deposited sample. Measurement artifacts include thermally stimulated current contributions [186], asymmetric electrode work functions due to titanium dioxide (TiO₂) formation [344], and cross-talk of the heating voltage. The impact of the wake-up effect is clearly visible, causing an increase in the current response after successive electric field cycling.

While this is a strong indication for the pyroelectric nature of the measured current, the signal phase is another important criterion, with the measurement results depicted in Figure 4.27 b). For low frequencies, the as-deposited material in the positive polarization state (blue line) exhibits a phase shift of approximately 10°. After 10^4 cycles, a phase shift of -5° is observed for the positive polarization (red line), which is in accordance with the results obtained by the 3ω method. The pyroelectric current is expected to



Figure 4.27: a) Pyroelectric current amplitude generated by 20 nm thick, $3.8 \cot \%$ Si-doped HfO₂ with respect to temperature oscillation frequency $2f_{\rm h}$ for positive (\downarrow) and negative (\uparrow) sample polarizations and different electric field cycle counts. b) Corresponding phase of the registered current with respect to the heating current waveform.

match the phase of the heater current, because Joule heating and pyroelectric effect contribute canceling phase shifts of -90° and 90° , as discussed in Chapter 3.1.3. At frequencies above 100 Hz, the non-ideal phase shift increases. While the as-deposited sample suffers from cross-talk of the heater voltage due to the weak pyroelectric current level below 1 nA, the phase after wake-up is more stable. At a frequency of 10 kHz, a shift of -62° is observed for the positively polarized sample. This is close to the value determined with the 3ω method (black circles), and the small offset is attributed to phase lag originating from the transimpedance amplifier.

The phase difference for opposite polarization states is varying in a wide range for the as-deposited sample, with a value of 149° at 2 Hz, which indicates out-of-phase contributions to the measured overall current, such as the thermally stimulated release of trapped charges. After wake-up, only a small deviation $<15^{\circ}$ from the ideal 180° phase difference is registered over the full frequency range, which is further evidence for the pyroelectric origin of the observed current.

Using Equation 3.16, pyroelectric coefficients are calculated from the measured current densities. In Figure 4.28 a), values are depicted for the frequency range of 2 Hz to 20 kHz. In accordance with the findings in Section 4.1.2, the pyroelectric coefficients increase strongly with successive electric field cycling. After 10^4 cycles at 3 MV cm^{-1} , a coefficient of $(-71.7 \pm 1.4) \,\mu\text{C}\,\text{m}^{-2}\,\text{K}^{-1}$ is determined at 10 Hz. This value is slightly lower than the result of $-84 \,\mu\text{C}\,\text{m}^{-2}\,\text{K}^{-1}$ obtained with the Sharp-Garn method in Chapter 4.1.1. The mismatch is associated with different process conditions, as manufacturing of the test structure occurs at a higher thermal budget of 530 °C compared to 450 °C for the capacitor structures. This may lead to partial premature crystallization of the pyroelectric material prior to rapid thermal processing or diffusion of dopant species.



Figure 4.28: a) Calculated pyroelectric coefficients of as-deposited samples and after application of electric field cycling vs. frequency of temperature oscillation. b) Illustration of heat propagation in the case of low-frequency and high-frequency temperature cycles (not to scale).

Pandya et al. published a value of $p = -27 \,\mu C \,m^{-2} \,K^{-1}$ with a similar test structure and 10 nm thick Si-doped HfO₂.

While the pyroelectric coefficient after wake-up (triangles) is consistently close to $-70 \,\mu \mathrm{C} \,\mathrm{m}^{-2} \,\mathrm{K}^{-1}$ for frequencies below 100 Hz, it decreases at higher frequencies and eventually reaches a plateau in the range of 10 kHz to 20 kHz at a value of $-53 \,\mu \mathrm{C} \,\mathrm{m}^{-2} \,\mathrm{K}^{-1}$. In the literature [36, 39], this has been explained by a secondary contribution to the pyroelectric coefficient, as the lateral thermal expansion of the substrate during heating results in the generation of a current via the piezoelectric effect [345]. At high frequencies, the penetration depth of the thermal wave is low, and most of the substrate remains at a constant temperature, as illustrated in Figure 4.28 b). Thereby, the thermal expansion is confined, and the secondary contribution vanishes, causing p to decrease. Thus, primary and secondary pyroelectric coefficients of $-53 \,\mu \mathrm{C} \,\mathrm{m}^{-2} \,\mathrm{K}^{-1}$ and $-19 \,\mu \mathrm{C} \,\mathrm{m}^{-2} \,\mathrm{K}^{-1}$ are determined by comparing values of p in low- and high-frequency limits. The influence of substrate clamping is discussed further in the next section, and piezoelectric coefficients are estimated from the secondary pyroelectric coefficient.

4.3.3 Secondary contribution via the piezoelectric effect

In the previous section, an estimate for the secondary pyroelectric coefficient has been calculated. In the following, primary and secondary effects are separated by sweeping the heating frequency of a pyroelectric thin film. Further, the relation between secondary pyroelectric and direct piezoelectric coefficients is known (Equation 2.21), which allows us to give an estimate for the in-plane piezoelectric response.

In Section 4.3.1, the characteristic length of the thermal wave propagation decreases from $1.9 \,\mathrm{mm}$ to $1.9 \,\mathrm{\mu m}$ for the frequency span of of $2 \,\mathrm{Hz}$ to $200 \,\mathrm{kHz}$. To verify this behavior experimentally, lock-in thermography is applied, where the infrared camera



Figure 4.29: a) Lock-in thermography results of the manufactured test structure with a heater current amplitude of 76 mA for a temperature oscillation frequency of 3 Hz and b) 30 Hz. When increasing the frequency, the thermal oscillation is localized to a smaller substrate volume. The thin-film heater is depicted as a dark stripe due to its high reflectivity. The device under test is marked (white arrow).

system is synchronized to the alternating heating current. Employing this technique, any static temperature offset is excluded, and an excellent sensitivity of few mK is reached. In Figure 4.29 a) and b), results are shown for a temperature oscillation frequency of 3 Hz and 30 Hz, respectively. The metal thin film heater appears dark in the image, which is attributed to its high reflectivity. Indeed, the aforementioned localization of the temperature oscillation with increasing frequencies is observed. Simultaneously, the amplitude of the temperature change due to Joule heating decreases.

The thermal strain distribution in a multi-layer is shown in Figure 4.30 a). It comprises layers of Ni, Si, and HfO₂ with thicknesses of 100 nm, 350 nm, and 20 nm, respectively. The underlying Si substrate is clamped ($\epsilon = 0$) at a depth of 100 nm. Experimentally, the clamping boundary condition corresponds to rapid heating, where the thermal wave is confined to the surface of the test structure. It is visible that substrate clamping leads to a thermal strain gradient throughout the multi-layer. Additionally, Ni exhibits a comparably large thermal expansion coefficient (red area). This means that the *secondary* pyroelectric effect is suppressed at high frequencies when the effective lateral strain is low.

In Figure 4.30 b), the substrate clamping condition is increased to 1 µm. As a result, the HfO₂ layer is able to expand more freely upon heating, leading to an increased secondary pyroelectric effect. Thus, reduced substrate clamping results in an increased pyroelectric response (compare Equation 2.21). In Figure 4.30 c) the thermal expansion coefficient of the HfO₂ film is calculated for a range of substrate thicknesses ranging from 10 nm to 100 µm. It is evident that the thermal expansion coefficient α_{eff} is inversely proportional to the clamping depth initially. For substrate thicknesses of more



Figure 4.30: a) Thermal strain distribution in a multi-layer calculated with a finite element model using the COMSOL software package. The substrate is clamped at a depth of 100 nm. b) With the substrate clamped at a depth of $1 \,\mu\text{m}$, the HfO₂ film experiences a larger strain upon heating. c) Effective thermal expansion coefficient in the HfO₂ film in dependence of the clamping depth.

than 300 nm, the interaction with the adjacent layers becomes dominant. The thermal expansion coefficient of the film ultimately exceeds the bulk value (red line) [346] due to the high expansion coefficient of Ni. The example illustrates that the effective pyroelectric response can be enhanced by mechanical coupling with materials that exhibit high thermal expansion coefficients.

In the next step, the thermal and elastic properties of the test structure are combined, and the strain and temperature amplitudes in the HfO_2 film are determined with respect to the heating frequency. Results are shown in Figure 4.31 (red squares), and are compared to the thermal oscillation amplitude θ (blue circles). While both parameters reduce monotonically with frequency, the thermal strain exhibits a steeper reduction in magnitude. Above a temperature oscillation frequency of 1 kHz, the behavior of ϵ can be modeled as $\propto f_{\rm h}^{-1/2}$, while strain is fitted by the relationship $\propto f_{\rm h}^{-1}$. This is attributed to the substrate clamping effect [347], which leads to a reduction of the effective expansion coefficient $\alpha_{\rm eff}(f) = \epsilon/\theta$.

As derived in Equation 2.21, the total pyroelectric response is then composed of three components:

- A primary (intrinsic) component, which stems from the temperature dependence of the spontaneous polarization.
- The secondary pyroelectric coefficient caused by in-plane thermal expansion of the substrate and via the piezoelectric effect $e_{31} \cdot \alpha_{\text{eff}}$.



Figure 4.31: a) Modeled frequency dependence of the strain amplitude caused by thermal oscillation (red squares) and modeled amplitude of the temperature oscillation (blue circles). b) Remanent polarization $P_{\rm r}$ and c) in-plane piezoelectric coefficient d_{31} vs. number of applied electric field cycles of 20 nm thick, 3.8 cat % Si-doped HfO₂.

• The in-plane secondary coefficient caused by thermal expansion of the pyroelectric material in the out-of-plane direction $e_{33} \cdot \alpha_3$ [31].

It is evident that the pyroelectric coefficient is reduced when $\alpha_{\rm eff}$ becomes small. The parameter $\alpha_{\rm eff}$ vanishes proportional to $f_{\rm h}^{-1/2}$ above 1 kHz, as displayed in Figure 4.31 a). The transition frequency to the observed power function behavior is dependent on the geometry of the area subjected to temperature variation [36], which is confirmed by the COMSOL model (not shown here). It is worth mentioning that the method is only sensitive to the in-plane response e_{31} , as the secondary contribution $e_{33}\alpha_3$ does not show a frequency dependence, and therefore is not detected in this approach. Contributions from thermal misfit strain are neglected, as temperature amplitudes are small, expansion coefficients of TiN electrodes and HfO₂ are similar, and no frequency dependence is expected.

Extracted values of e_{31} range from $-0.9 \,\mathrm{C}\,\mathrm{m}^{-2}$ for the sample cycled once to $-3.3 \,\mathrm{C}\,\mathrm{m}^{-2}$ after 10^5 field cycles. Experimental reports of the elastic modulus in HfO₂ range from 246 GPa to 284 GPa [70, 348], and ab-initio calculations yielded 254 GPa [245]. Elastic properties of HfO₂ are reported to vary strongly with thickness, and Si incorporation has been associated with a reduced modulus [349]. Using an averaged value of $(261 \pm 10) \,\mathrm{GPa}$, mean coefficients d_{31} of $(-3.2 \pm 0.2) \,\mathrm{pm}\,\mathrm{V}^{-1}$ for the pristine sample and $(-11.5 \pm 0.9) \,\mathrm{pm}\,\mathrm{V}^{-1}$ after 10^5 cycles are obtained. This is lower than reported values for most classic ferroelectrics like PVDF ($21 \,\mathrm{pm}\,\mathrm{V}^{-1}$) or PZT ($-273 \,\mathrm{pm}\,\mathrm{V}^{-1}$), but exceeds values of non-ferroelectric GaN ($-1.9 \,\mathrm{pm}\,\mathrm{V}^{-1}$) and AlN ($-2 \,\mathrm{pm}\,\mathrm{V}^{-1}$) [284].

The wake-up effect upon electric field cycling is found to impact both remanent polarization, which is shown in Figure 4.31 b), and calculated piezoelectric coefficients in Figure 4.31 c). The increase of piezoelectric coefficients is associated with the *P*-*E* characteristic progressing from a pinched, AFE-like shape towards ferroelectric switching during field cycling, which has been discussed in Section 4.1.2. Observation of wake-up in both pyroelectric and piezoelectric properties is further evidence for the intrinsic nature of ferroelectricity in doped HfO₂ films. This is significant since other piezoelectric characterization methods for thin films such as DBLI [350] and DART-PFM [351] have not been able to reproduce the wake-up behavior in the piezoelectric effect. Similarly, in the PbZr_xTi_{1-x}O₃ material system, the largest pyroelectric current response in the polarized state is associated with maxima of the remanent polarization and the piezoelectric response [352, 353]. The proposed voltage-free measurement method by rapid thermal cycles could be applied to other material systems in future work. The approach offers a highly sensitive measurement pathway which may be suitable to analyze the piezoelectric properties of polar thin films and even mono-layer materials.

Out-of-plane piezoelectric coefficients obtained by interferometry

The previously described measurement method is only sensitive for the piezoelectric response in the in-plane direction, since the thermal expansion of the substrate is exploited. To complete the analysis of the piezoelectric response, out-of-plane coefficients are obtained by means of double-beam laser interferometry (DBLI). The method employs a sensitive interferometer, which eliminates the influence of substrate bending by a differential measurement technique, as described in References [350, 354]. It is noted that this method can only access the indirect piezoelectric effect, since it quantifies the mechanical expansion of the film upon application of an electric field. The piezoelectric response of a thin film in the out-of-plane direction in the case of substrate clamping is

$$d_{33,\rm f} = d_{33} - \frac{2d_{31}s_{13}}{s_{11} + s_{12}}, \tag{4.13}$$

where s_{ij} denotes the elements of the mechanical compliance tensor [355]. It is noted that Equation 4.13 is similar to the pyroelectric coefficient for a clamped thin film in Equation 2.22.

In Figure 4.32, results of DBLI measurements of 3.8 cat % Si-doped HfO₂ are shown. The vanishing displacement in Figure 4.32 b) around 0.80 MV cm^{-1} is similar to the coercive field extracted from the *P*-*E* measurements in Figure 4.32 a) at 0.84 MV cm^{-1} .

A linear model in the range of $\pm 0.2 \,\mathrm{MV}\,\mathrm{cm}^{-1}$ is applied to extract piezoelectric coefficients. For the positive polarization, a coefficient $d_{33,\mathrm{f}}$ of $(11.5 \pm 1.8) \,\mathrm{pm}\,\mathrm{V}^{-1}$ is determined. By using elastic properties from ab-initio calculations [356], the mechanical compliance tensor is calculated, with $s_{11} = 3.78 \times 10^{-12} \,\mathrm{m}^2 \,\mathrm{N}^{-1}$, $s_{12} = -1.30 \times 10^{-12} \,\mathrm{m}^2 \,\mathrm{N}^{-1}$, and $s_{13} = -0.68 \times 10^{-12} \,\mathrm{m}^2 \,\mathrm{N}^{-1}$. With Equation 4.13, a corrected, mean piezoelectric coefficient d_{33} of 17.9 pm V⁻¹ is determined. It is noted that the elastic properties of orthorhombic HfO₂ may deviate from these of the monoclinic phase, leading to a slight correction of Equation 4.13. The result presented here is comparable to the values published by Starschich, who obtained 10 pm V⁻¹ for ZrO₂



Figure 4.32: a) Ferroelectric current-field and polarization-field graphs after 2×10^5 electric field cycles for 20 nm thick, $3.8 \cot \%$ Si-doped HfO₂. b) Piezoelectric displacement in the out-of-plane direction measured by DBLI.

films fabricated by CSD [102]. Further, our values are similar to recent theoretical estimations obtained with DFT calculations, where a value of 20 pm V^{-1} is stated [357].

Piezoelectric coefficients of some commonly used materials as well as 3.8 cat % Sidoped HfO₂ are summarized in Table 4.2. While PbZr_xTi_{1-x}O₃ achieves much higher coefficients, doped HfO₂ is among the best-performing CMOS compatible materials. The results presented herein should be confirmed by other methods, since ultra-thin films are challenging subjects for piezoelectric measurements. Further, field induced phase transitions or re-orientation effects in HfO₂ are not fully understood, yet. Nonetheless, doped HfO₂ films add exciting new opportunities for integrated nano-electromechanical (NEMS) devices which are compatible with semiconductor manufacturing processes.

	_	_	_	
Material	d_{33}	d_{31}	Ferro-	CMOS
	$\rm pmV^{-1}$	$\rm pmV^{-1}$	electric	$\operatorname{compatible}$
PZT [284]	289	-123	1	
AlN [284]	5	-2		1
$Al_{1-x}Sc_xN$ [358]	13	-6	1	
Si-doped ${\rm HfO}_2$ (this work)	18	-12	✓	✓

Table 4.2: Piezoelectric coefficients of some commonly used materials, and of $3.8 \operatorname{cat} \%$ Si-doped HfO_2 .

4.4 Determination of the thermal conductivity of HfO_2 thin films

The thermal conductivity of the pyroelectric material is an important factor for determining the application potential of HfO_2 , e.g., for infrared sensors. The differential 3ω method provides an extremely sensitive way of determining thermal properties in thin films. For instance, it has proven useful in the thermal analysis of Si-Ge super-lattices and the graphene-SiO₂ interface [359, 360]. Here, the method is applied to determine the thermal resistivity of Si-doped HfO₂ as thin as 10 nm.

As described in Section 3.1.4, a set of samples with three different thicknesses of the HfO_2 layer is fabricated, while the electrode layer thickness is held constant. Omitting the top electrode is no alternative, since the interface and the induced strain are important for the formation of the ferroelectric orthorhombic $Pca2_1$ phase [110, 117]. In Figure 4.33, the prepared samples are depicted schematically. By using SE, layer thicknesses of 10.0 nm, 30.7 nm, and 52.5 nm are determined.

The heating frequency dependence of the thermal insulance

$$\vartheta = \frac{\theta}{I_{\rm h} U_{1\omega}} \tag{4.14}$$

100



Figure 4.33: Schematic cross-section of the test structure with three different HfO_2 layer thicknesses. d) Temperature oscillation amplitudes normalized to the dissipated power. The experimental results are modeled with a logarithmic function. e) Thickness dependence of the normalized thermal amplitude. The thermal resistivity is extracted from the slope of the linear model.

is shown in Figure 4.33 d) for all three HfO_2 thickness values. It is noted that the thermal insulance with the unit $\text{m}^2 \text{KW}^{-1}$ is not a material parameter and depends on the device geometry. However, it is directly accessible with the 3ω method. It is evident that the graphs follow a logarithmic trend

$$\vartheta = a\log f + \vartheta_0,\tag{4.15}$$

as indicated by solid lines. The thicker HfO_2 layer leads to a systematic offset of the thermal insulance. Towards a heating frequency of 100 Hz, the effects of the non-ideal connection resistance become prominent and the measured values deviate from the model. The thickness-dependent thermal resistivity is extracted from the offset ϑ_0 .

The thickness dependence of the thermal insulance is displayed in Figure 4.33 e). The experimental results increase linearly with the HfO_2 thickness. From the slope of the linear model (red line), a thermal conductivity of $k = (1.18 \pm 0.10) \,\mathrm{m\,K\,W^{-1}}$ is extracted. The value is similar to previously reported results obtained with time-domain thermoreflectance (TDTR) at $1.27 \,\mathrm{m\,K\,W^{-1}}$ for $\text{Hf}_{1-x}\text{Zr}_x\text{O}_2$ [223]. For 3 nm thin HfO_2 films, thermal resistivities between $1.1 \,\mathrm{m\,K\,W^{-1}}$ and $2.0 \,\mathrm{m\,K\,W^{-1}}$ have been measured by another group [361].

4.5 Summary of pyroelectric properties

In the previous sections, pyroelectric coefficients of the HfO₂ material class were determined for a range of dopants and stoichiometries. Further, primary and secondary coefficients were extracted from rapid thermal oscillations. The measurements were subject of several publications [97, 104, 244, 251, 362]. Over the course of the dissertation project, pyroelectric and piezoelectric properties of HfO₂ have received increasing research interest. Reports on dedicated pyroelectric measurements with the Sharp-Garn method (see Section 3.1.1) are summarized in Figure 4.34. The magnitude of the pyroelectric coefficients reported herein (open symbols) is rather large, which is explained by the use of state of the art, industry-grade ALD equipment, which is designed for 300 mm substrate sizes. A correlation between $P_{\rm r}$ and p is evident in the diagram (gray line). In Section 4.1.1, it was demonstrated that the largest pyroelectric coefficients are obtained with Si-doped HfO₂, but that La- and Al-doping and Hf_{1-x}Zr_xO₂ are achieving values larger that $-70 \,\mu {\rm C} \,{\rm m}^{-2} \,{\rm K}^{-1}$ as well after sufficient stoichiometry and ALD process tuning.



Figure 4.34: Literature values of the pyroelectric coefficient and the remanent polarization for HfO_2 -based thin films with various dopants. A proportional relationship $p \propto P_r$ is depicted as a guide to the eye (gray line).

Pyroelectric coefficients obtained with HfO_2 -based films are compared to other material systems in Figure 4.35. In the diagram, the main groups of pyroelectric materials are represented: non-ferroelectrics (open blue symbols), polymers (green symbols), lead-free perovskites (open orange symbols) and lead-based perovskites (closed blue symbols). It is evident that a correlation exists between p and ε . The HfO₂ material class is represented by Si-doped HfO₂ here (red symbols), with properties similar to LiNbO₃. By using the field-induced pyroelectric effect in AFE-like Si-doped HfO₂, a value of p similar to that of LiTaO₃ is obtained, which is a standard material in pyroelectric sensor applications. By using area-enhanced substrates, which are discussed in Section 5.3.1, it is



Figure 4.35: Comparison of the pyroelectric coefficient and dielectric permittivity of common bulk ceramics, thin films (TF), and single crystals (SC) to the results obtained in this work for doped HfO₂.

possible reach very high pyroelectric coefficients similar to these of $Pb(Mg_{1/3}Nb_{2/3})O_3$ -PbTiO₃, while maintaining a comparatively low dielectric permittivity.

Interestingly, the coercive field of HfO_2 -based ferroelectrics is orders of magnitude higher than that of $LiTaO_3$ or $LiNbO_3$, but they exhibit similar pyroelectric and dielectric properties. In a recent work, the fundamental difference to previously studied ferroelectric pyroelectrics has been attributed to the existence of scale-free domain switching in HfO_2 -based films [6].

To evaluate the potential of HfO_2 for applications such as sensors and pyroelectric energy harvesting, several FOMs exist. Depending on the scope of the applications, they consider the pyroelectric, dielectric and thermodynamic properties. Bowen et al. have provided an overview of FOMs and provide values for many pyroelectric materials [30, 366]. Pyroelectric sensors may be operated in voltage- or current-mode, where the two schemes correspond to a high or a low input impedance of the sensor amplifier circuit, respectively [310]. The corresponding FOMs are

$$F_{\rm V} = \frac{p}{C_{\rm v}\varepsilon_{\rm r}}$$
 and (4.16)

$$F_{\rm I} = \frac{p}{C_{\rm v}},\tag{4.17}$$

where $C_{\rm v}$ is the volumetric heat capacity.

The potential for energy harvesting applications is estimated as [367]

$$F_{\rm E} = \frac{p^2}{\varepsilon_{\rm r}}.\tag{4.18}$$

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 $F_{\rm E}$ has found wide use as a guide for material selection [30]. An alternative energy harvesting FOM has been proposed by Bowen et al. [366] as

$$F'_{\rm E} = \frac{p^2}{\varepsilon_{\rm r} C_{\rm v}^2},\tag{4.19}$$

which also takes into account the heat capacity of the pyroelectric material. It is noted that none of the FOMs take dielectric losses, electrode resistivity or heat transfer into account. In Table 4.3, pyroelectric, dielectric and thermal properties of common materials and HfO_2 -based films are listed. HfO_2 -based films show promising values of F_V and F_I , which are similar to these of LiTaO₃. Especially the field-induced pyroelectricity of AFE-like films in combination with their relatively low permittivity leads to promising FOMs.

Further, the HfO₂ material class displays favorable parameters for energy harvesting. Especially area-enhanced HfO₂-based capacitor structures exhibit some of the largest recorded values of $F_{\rm E}$ and $F'_{\rm E}$ [123]. However, it is noted that such area-enhanced or porous substrates provide "virtual" coefficients, and that their scalability is limited. The energy harvesting potential of AFE-like HfO₂ films is comparable to that of PbZr_xTi_{1-x}O₃. Since HfO₂-based materials can be integrated in semiconductor manufacturing, this opens up the possibility of on-chip energy harvesting solutions.

igures	
es of commonly used materials and results for HfO_2 -based films obtained in this work. Figures	ors [310] as well as energy harvesting are calculated according to Reference [30, 366].
ic properties	-mode senso
of pyroelectr	e and voltage
Comparison	$current-mod\epsilon$
Table 4.3:	of merit for

Material	d	ω	$C_{\rm s}$	k	F_{I}	$F_{\rm V}$	$F_{ m E}$	$F_{ m E}^{\prime}$
	$\mu Cm^{-2}K^{-1}$	Ļ	$\mathrm{MJ}\mathrm{m}^{-3}\mathrm{K}^{-1}$	$\rm W~m^{-1}~K^{-1}$	${\rm m}V^{-1}$	${ m m^2~C^{-1}}$	$\rm J~m^{-3}~K^{-2}$	$\mathrm{m}^3\mathrm{J}^{-1}$
$PbZr_xTi_{1-x}O_3$ [247, 363]	-380	290	2.5	0.8	1.52	0.059	56.3	06.0
$Pb(Mg_{1/3}Nb_{2/3})O_3$ - $PbTiO_3$ [285]	-1790	2100	2.5	2.5	7.16	0.039	172	2.8
P(VDF-TrFE) [247]	-40	18	2.3	0.14	0.17	0.109	10.0	0.19
$LiTaO_3$ [198, 365]	-176	47	3.2	3.9	0.55	0.132	74.5	0.73
AlN [284]	7	10	2.4	140	0.03	0.038	0.55	0.010
$3.5 \text{ cat.}\% \text{ Si:HfO}_2$	-95	45	2.6	1.2	0.37	0.081	20.0	0.30
${ m Hf}_{0.23}{ m Zr}_{0.77}{ m O}_2$	-79	39	2.6	1.2	0.31	0.078	16.1	0.24
7.2 cat.% La:HfO ₂	-78	39	2.6	1.2	0.30	0.077	15.8	0.23
1.1 cat.% Al:HfO ₂	-81	37	2.6	1.2	0.31	0.084	17.7	0.26
4.8 cat.% Si:HfO ₂ (AFE)	-142	33	2.6	1.2	0.55	0.166	61.1	0.90
$3.8 \text{ cat.}\% \text{ Si:HfO}_2 (3D)$	-1442^{a}	512	2.6	1.2	5.6	0.108	406	6.0

^aProjected to the device footprint.

Chapter 5

Thermal-electric energy conversion: refrigeration and harvesting

Equipped with the knowledge about pyroelectricity in the HfO_2 material class, this chapter explores the conversion between thermal energy and electricity. The first part is focused on the characteristics of doped HfO_2 for solid-state refrigeration. Electrocaloric materials receive renewed interest due to emerging material classes such as ferroelectric thin films, multi-layers, and relaxors [368]. Other refrigeration devices based on the Peltier effect are limited by the need for a combination of low thermal and high electrical conductivities, which is difficult to achieve. Practically, this reduces the efficiency of thermoelectric devices well below the Carnot limit. On the other hand, electrocaloric devices could theoretically approach the Carnot limit.

However, more research is needed to explore implementations that utilize the potential for high efficiencies which are achievable with electrocaloric materials. Beneficial properties such as high breakdown strength and sizable electrocaloric coefficients for solid-state cooling have been reported for the HfO_2 material system before [170, 282]. The possibility of CMOS compatible manufacturing enables the integration of such refrigeration concepts in the FEoL and BEoL for integrated thermal management solutions.

In the second part of this chapter, the recovery of low-grade waste is be demonstrated. Therefore, a thermodynamic process analog to the Ericsson cycle is implemented. First, an energy harvester with HfO_2 deposited on a porous, nano-patterned substrate is demonstrated, which achieves strongly enhanced virtual pyroelectric coefficients. Then, the integration of a pyroelectric energy harvester into an active, integrated circuit is explored, demonstrating high operating frequencies and energy conversion efficiencies.

Results in Section 5.1 have been published previously in Reference [185], and results from Section 5.3 have been published in References [362], [123], and [224].

5.1 The electrocaloric effect: indirect measurements

The electrocaloric effect leads to a temperature change when an electric field is applied to (or removed from) a polar material in an adiabatic process. A simplified schematic is shown in Figure 5.1. The prompt increase of the configurational entropy in Figure 5.1 b) upon electric field removal leads to a temperature reduction. It is noted that contributions from the vibrational entropy and defect dipoles have been reported as well [282, 369]. Indirect methods are commonly used to analyze the electrocaloric response, since the measurement is relatively simple to implement with commonly available instruments. As described in Section 3.2.1, ferroelectric hysteresis loops are obtained at several temperatures. Electrocaloric coefficients are then calculated by analyzing the temperature dependence of the remanent polarization [170, 370].



Figure 5.1: Simplified schematic of a capacitor structure with a polar material a) with and b) without an applied electric field. The change of the configurational entropy leads to a temperature reduction when the electric field is removed in an adiabatic process.

However, indirect methods can be inaccurate especially in thin film geometries. The thermodynamic equivalence of pyroelectric and electrocaloric effects relies on a reversible processes, which is not necessarily present near phase transitions [35]. Furthermore, the thin film geometry introduces boundary conditions and partial substrate clamping, questioning the validity of Eq. 2.23.

In Figure 5.2 a), P-E hysteresis loops are shown in the temperature range of -10 °C to 80 °C. At -10 °C, hysteresis graphs indicate ferroelectric switching with nearly symmetric coercive fields of $-0.9 \,\mathrm{MV \, cm^{-1}}$ and $0.8 \,\mathrm{MV \, cm^{-1}}$. With rising temperature, the positive coercive field decreases, and at 80 °C a value of $-0.6 \,\mathrm{MV \, cm^{-1}}$ is obtained while the negative coercive field remains nearly unchanged. This is of special importance for non-volatile memory concepts such as the ferroelectric field effect transistor (FeFET) [26, 107], where a reduced or shifted coercive field results in less reliable data storage. The remanent polarization $P_{\rm r}$ decreases from $11.4 \,\mu{\rm C \, cm^{-2}}$ to $7.6 \,\mu{\rm C \, cm^{-2}}$ over the temperature range used above. The described behavior is reflected in the corresponding current measurement in Figure 5.2 b), where the switching current peaks shift towards lower electric fields, while their area decreases simultaneously.

At elevated temperatures, antiferroelectric-like split current peaks emerge, which have been explained with a partial transition to the tetragonal phase in earlier re-



Figure 5.2: a) Polarization-field characteristics of a 3.8 cation% Si-doped HfO₂ thin film measured at an increasing temperature of -10 °C to 80 °C with 10 K steps. b) Corresponding current-field data, indicating an amplitude reduction and coercive field shift at increased temperatures. c) After the temperature ramp, electric field cycling is necessary to restore the remanent polarization. d) The corresponding current graphs indicate a shift of the switching current peaks after heating (imprint), which is reduced by field cycling. Adapted with permission from Ref. [185]. Copyright 2020 AIP Publishing.

ports [90]. For all temperature values, the baseline displacement current is nearly constant, and no leakage contributions are detected. When returning to -10 °C, the hysteresis graph remains pinched. The stabilization of the antiferroelectric-like tetragonal phase is attributed to the migration of charged defects, which is discussed later. However, it is possible to restore the original P_r by electric field cycling at -10 °C, which is shown in Figure 5.2 c). The current-field graphs in Figure 5.2 d) indicate that the imprint is removed and that the original coercive fields are restored. It is noted that the observed behavior is similar to aging and de-aging phenomena in lead zirconate titanate (PZT) ceramics [331].

Extracted values of the remanent polarization with respect to temperature are shown in Figure 5.3 (solid blue squares), and are fitted reasonably well by the Landau theory of a second-order phase transition $P_{\rm r} \propto (T_{\rm C} - T)^{1/2}$. The model yields a critical temperature of (160 ± 3) °C. Using Equation 2.23, electrocaloric coefficients are calculated (red solid squares), where a mean value of $\Sigma = (-423 \pm 14) \,\mu {\rm C} \,{\rm m}^{-2} \,{\rm K}^{-1}$ is obtained.



Figure 5.3: Indirect evaluation of the electrocaloric coefficient. The remanent polarization is extracted from ferroelectric hysteresis loops in a temperature range of -10 °C to 80 °C in 10 K steps. Electrocaloric coefficients are then calculated according to Equation 2.23. Reproduced with permission from Ref. [185]. Copyright 2020 AIP Publishing.

When subjecting the sample to a second increasing temperature cycle, a reduced slope is observed (open blue squares), which corresponds to lower Σ (open red squares). In a third cycle, the trend progresses (blue and red dots), and a mean coefficient of $(-131 \pm 10) \,\mu\text{C}\,\text{m}^{-2}\,\text{K}^{-1}$ is calculated. The extracted $T_{\rm C}$ raises to (291 ± 6) °C.

The large variation in successive indirect electrocaloric measurements spawns the question of the origin of the observed fatigue effect. In Figure 5.4, repeated ferroelectric hysteresis measurements at a temperature of 80 °C are shown, where the interval between individual measurements is 10 min. The ferroelectric hysteresis in Figure 5.4 a) evolves towards a more pinched, antiferroelectric-like shape during the total time of 70 min. From the *j*-*E* measurement in Figure 5.4 b) it is evident that the amplitude of the ferroelectric switching peaks is reduced, and that the corresponding positive coercive field value decreases. If the sample is kept at the temperature of 80 °C continuously, $P_{\rm r}$ is reduced with a logarithmic time dependence. This is similar to results obtained for strontium barium tantalate (SrBi₂Ta₂O₉) films [371], and has been suggested to be caused by the Poole-Frenkel conduction mechanism [372]. The latter is a defect-mediated effect, which is characterized by a reduction of the Coulomb barrier with an electric field. However, more recent work suggests that non-linear or competing imprint mechanisms can occur [373].

The temperature-induced fatigue observed in Figure 5.4 c) is too large to be explained by a self-depolarization mechanism according to the NLS model [332]. When using model parameters proposed earlier for the ferroelectric HfO₂ material system [336], much larger



Figure 5.4: a) Repeated ferroelectric hysteresis measurement at a constant temperature of 80 °C in intervals of 10 min. b) Corresponding current-field measurements, where the shifting of switching current peaks (imprint) is visible. c) Reduction of the remanent polarization at a temperature of 80 °C up to a total measurement time of 70 min.

time constants are obtained than these observed experimentally. Further, no agreement was found with the KAI model with physically reasonable parameters.

When extracting the coercive field values, a linear decrease of $P_{\rm r}$ for an increasing imprint is observed, which is shown in Figure 5.5. It has been shown that passive layers at the electrode interface cause significant de-polarization fields in ferroelectric films [212]. In the case of HfO₂, this leads to a migration of charged oxygen defects to the electrode interfaces, causing an increasing defect density. For PZT, such an inhibition of the switching process has been found with an increasing defect concentration at the electrode interface [213]. Repeated electric field cycling then redistributes defect charges in the film, and domain nucleation is enhanced again [374]. The initial data point at -10 °C exceeds the linear extrapolation (red line in Figure 5.5).

It is concluded that the reduction of $P_{\rm r}$ cannot be used straightforward to calculate electrocaloric coefficients since it is amplified by a partial transition towards the antiferroelectric-like tetragonal phase, and the inhibition of ferroelectric switching by the accumulation of charged defects at the electrode interfaces.

5.2 Direct observation of the electrocaloric temperature change

To directly observe electrocaloric temperature changes, the test structure which has been used for the high-frequency pyroelectric characterization in Section 4.3 is employed again. However, in the following experiments, the thin metal film is used as a miniaturized temperature sensor instead of a heater. When the electrocaloric effect is excited by



Figure 5.5: Remanent polarization vs. electric field shift of the ferroelectric switching current peaks (imprint) for successive hysteresis measurements at 80° repeated in 10 min intervals. The inhibition of ferroelectric switching is explained by an increasing density of charged defects at the electrode interface. Reproduced with permission from Ref. [185]. Copyright 2020 AIP Publishing.

an electric field change, the induced thermal wave propagates through the test structure, and eventually reaches the sensor. The temperature change of the sensor is expected to be very small, since the heat capacity of the 20 nm thick, $3.8 \cot \%$ Si-doped HfO₂ is minute compared to the bulk of the test structure. Nevertheless, a small variation in the electrical resistance of the sensor is induced. As elucidated in Section 3.2, the signal is then quantified by a lock-in technique, which eliminates the effects of capacitive coupling.

5.2.1 Verification of the direct measurement method

To excite the electrocaloric temperature change, a sinusoidal electric field waveform with a frequency $\omega_{\rm e}$ is applied to the ferroelectric material. The voltage drop over the temperature sensor is then shifted to a side-band in frequency space by a second waveform at $\omega_{\rm s}$. As discussed in Section 3.2, measurements at the side-band frequency $\omega_{\rm e} \pm \omega_{\rm s}$ ensure a strong suppression of the capacitive coupling between the heater and the electrocaloric capacitor.

The direct measurement of electrocaloric temperature change in nanometer-thin films is challenging since the low thickness of the HfO_2 film results in a small heat capacity. Thus, the temperature variation of the metal sensor occurs in the mK scale, and resulting voltage amplitudes at the Wheatstone measurement circuit are estimated to be in the nV range. Care has to be taken to make sure that the measured voltage at the side-band frequency $\omega_e \pm \omega_s$ is of electrocaloric origin.

Therefore, it is verified that calculated electrocaloric coefficients are not dependent on the following measurement settings:

- The amplitude and frequency of the electric field applied to the ferroelectric material $E_{\rm e}$ and $f_{\rm e}.$
- The amplitude and frequency of the sinusoidal voltage applied at the Wheatstone measurement bridge $U_{\rm s}$ and $f_{\rm s}.$

First, an excitation frequency of $\omega_{\rm e} = 54.345 \,\rm kHz$ and a sensor frequency of $\omega_{\rm s} = 2.222 \,\rm kHz$ are applied. The electric field amplitude is varied in a range of $0.05 \,\rm MV \, cm^{-1}$ to $0.25 \,\rm MV \, cm^{-1}$. It is noted that no electric field offset is used in the measurement. The resulting electrocaloric signal is shown in Figure 5.6 a). Indeed, a linear relationship $U_{\omega_{\rm e}\pm\omega_{\rm s}}\propto E_{\rm e}$ is obtained, which is in accordance to Equations 3.33 and 3.37. The heat transfer from the electrocaloric material towards the sensor is calculated according to Equation 3.36. Therefore, a Python script with the numpy library is used, and a thermal impedance $Z_{\rm T}$ of $1.19 \times 10^{-7} \,\rm m^2 \, K \, W^{-1}$ is determined.

Finally, electrocaloric coefficients Σ are calculated. Results are shown in Figure 5.6 b). It is evident that the coefficients are not dependent on the excitation amplitude within reasonable deviation. The mean value of $\Sigma = (85.4 \pm 3.5) \,\mu\text{C}\,\text{m}^{-2}\,\text{K}^{-1}$ is indicated in the graphic (red line). Towards larger field amplitudes, the measurement deviation reduces noticeably, which is explained by an increasing SNR. For all further measurements, the highest amplitude of $0.25 \,\text{MV}\,\text{cm}^{-1}$ is used. Even higher amplitudes could be chosen, but would limit the measurement resolution when characterizing electrocaloric coefficients with an electric field bias. Further, small-signal behavior is favored to suppress field-induced phase change and other non-linear effects.

Next, the impact of the electrocaloric excitation frequency f_e is assessed, where values in a range of 6.31 kHz to 59.345 kHz are used. Throughout the frequency range, the measured voltage drop at the side-band frequencies $\omega_e \pm \omega_s$ rises from (1.2 ± 0.9) nV to (5.5 ± 0.6) nV, as shown in Figure 5.6 c). While a linear scaling $U_{\omega_e \pm \omega_s} \propto \omega_e$ is expected from theory, the electrocaloric signal is attenuated by the connection resistance. This is mainly caused by the sheet resistance of the electrode layers and the substrate, and could be improved in future implementations by using metal (e.g., Cu) electrodes instead of TiN and doped polycrystalline Si. The capacitance of the ferroelectric material in combination with the series resistance then acts as a low-pass filter. From the RC model (red line), a cut-off frequency of 27.6 kHz is determined.

Calculated electrocaloric coefficients are shown in Figure 5.6 d). Again, the SNR enhances towards increasing frequencies, and Σ decreases when approaching the cut-off frequency. Only after correction of the RC attenuation, constant values are obtained (green circles). A mean value of $(94.4 \pm 1.2) \,\mu\text{C}\,\text{m}^{-2}\,\text{K}^{-1}$ is determined, which matches the value discussed before for the amplitude variation (compare Figure 5.6).

As discussed earlier, the Wheatstone measurement bridge is operated with an alternating voltage, whereby the electrocaloric signal is shifted to the side-band frequencies. Thereby, the influence of capacitively coupled disturbances is greatly reduced. It is



Figure 5.6: a) Electrocaloric voltage at an excitation frequency of 54.345 kHz and a sensor frequency of 2.222 kHz for different excitation amplitudes applied to the MFM structure. A linear model is applied, indicating proportionality between excitation amplitude and electrocaloric response. b) Corresponding electrocaloric coefficients, where the mean value is indicated (red line). c) Electrocaloric signal for a range of excitation frequencies at an amplitude of 0.5 V and a sensor frequency of 2.222 kHz. The experimental data is fitted with a low-pass resistor-capacitor (RC) model. d) Corresponding electrocaloric coefficients with and without correction of low-pass attenuation.

important to verify that extracted electrocaloric coefficients are not dependent on the amplitude and frequency of the sinusoidal voltage which is supplied at the Wheatstone bridge. Therefore, the side-band voltage amplitude $U_{\omega_e \pm \omega_s}$ is measured at three different amplitudes U_s in a range of 1 V to 3 V. As expected from Equation 3.33, a linear increase from (1.8 ± 0.8) nV to (4.9 ± 1.6) nV is observed, which is shown in Figure 5.7 a). This indeed corresponds to almost constant values of Σ (not shown here). While even higher amplitudes would further improve SNR, the insulating SiO₂ layer could be degraded and the possibility of noticeable self-heating of the sensor arises.

Further, the electrocaloric signal is expected to be independent of the sensor frequency $f_{\rm s}$. Indeed, constant values of $U_{\omega_e \pm \omega_s}$ are observed in a range of 222 Hz to



Figure 5.7: a) Electrocaloric signal for sensor amplitudes ranging from 1 V to 3 V at a fixed sensor frequency of 2.222 kHz. b) Dependence of the electrocaloric signal on the sensor frequency.

 $10 \,\mathrm{kHz}$, as shown in Figure 5.7 b). Some deviation from the constant behavior is observed for the highest frequency. While a lower measurement uncertainty is indicated by the lock-in amplifier, frequencies above $10 \,\mathrm{kHz}$ may again result in losses due to connection resistance or the parasitic inductance of the heater element. Thus, a sensor frequency of $2.22 \,\mathrm{kHz}$ is used in further measurements.

In summary, the electrocaloric measurement technique is successfully verified by assessing the influence of several measurement parameters. It is confirmed that the observed signal $U_{\omega_e \pm \omega_s}$ is directly related to an electrocaloric temperature change in the Si-doped HfO₂.

5.2.2 Electrocaloric coefficients

In this section, the verified method is employed to directly assess the electrocaloric effect in Si-doped HfO₂, and its dependence on the ferroelectric polarization state. Electrocaloric measurements are performed with an electric field bias in the range of $-1.5 \,\mathrm{MV}\,\mathrm{cm}^{-1}$ to $1.5 \,\mathrm{MV}\,\mathrm{cm}^{-1}$, which is superimposed onto the sinusoidal variation. Indeed, at the smallest and largest bias fields, electrocaloric signals of $(-5.5 \pm 0.2) \,\mathrm{nV}$ and $(4.4 \pm 0.2) \,\mathrm{nV}$ are registered, respectively.

The temperature amplitude which is caused in the sensor by the electrocaloric effect is calculated according to Equation 3.33. Values of θ are depicted in Figure 5.8 a), and a hysteretic behavior is clearly visible, which coincides with ferroelectric polarization switching of the film. Symmetric coercive field values of $\pm 0.7 \,\mathrm{MV \, cm^{-1}}$ are observed. The graph is qualitatively similar to ferroelectric hysteresis loops obtained for the same material (see Figure 4.10). The observed hysteretic behavior provides further evidence for an electrocaloric origin of the temperature change.

Calculated electrocaloric coefficients are shown in Figure 5.8 b) (blue squares). As discussed in the last section, a thermal impedance $Z_{\rm T}$ of $1.19 \times 10^{-7} \,\mathrm{m^2 \, K \, W^{-1}}$ is used



Figure 5.8: a) Temperature amplitude measured with the thin-film nickel sensor at different bias voltages at an excitation frequency of 54.345 kHz and a sensor readout frequency of 2.222 kHz. b) Calculated electrocaloric coefficients vs. electric field offset of 20 nm thick, 3.8 cat % Si-doped HfO₂. Adapted with permission from Ref. [185]. Copyright 2020 AIP Publishing.

to relate the electrocaloric power to the sensor temperature change. At zero volt, values of $(-82 \pm 4) \,\mu\text{C}\,\text{m}^{-2}\,\text{K}^{-1}$ and $(-107 \pm 3) \,\mu\text{C}\,\text{m}^{-2}\,\text{K}^{-1}$ are observed for negative and positive polarization states, respectively. Towards higher voltages, coefficients increase, until they reach $(-97 \pm 3) \,\mu\text{C}\,\text{m}^{-2}\,\text{K}^{-1}$ and $(-128 \pm 4) \,\mu\text{C}\,\text{m}^{-2}\,\text{K}^{-1}$ at $1.5\,\text{MV}\,\text{cm}^{-1}$ and $-1.5\,\text{MV}\,\text{cm}^{-1}$, respectively. The observed asymmetry is likely linked to the deposition process, in which the bottom TiN electrode is partially oxidized, which leads to an asymmetric electronic band structure and an internal bias field [166]. Our results are similar to those found by Pandya et al., where a slightly larger value $\Sigma = -135\,\mu\text{C}\,\text{m}^{-2}\,\text{K}^{-1}$ is reported for Si-doped HfO₂.

Our results are similar to those found by Pandya et al., where a slightly larger value $\Sigma = -135 \,\mu \text{C} \,\text{m}^{-2} \,\text{K}^{-1}$ is reported for Si-doped HfO₂, as summarized in Table 5.1 [282]. A certain increase of Σ in as-deposited vs. field-cycled samples is observed, but similar to

with small-signal methods.

Table 5.1: Electrocaloric and pyroelectric coefficients for Si-doped HfO₂ determined at 0 V

	$p~(\mu{\rm C}{\rm m}^{-2}{\rm K}^{-1})$	$\Sigma~(\mu Cm^{-2}K^{-1})$
Ref. [282]	-13 (as dep., $1 \mathrm{kHz}$)	-135 (as dep.)
	-25 (10 ⁵ cy., 1 kHz)	-136 (10^5 cy.)
This work, Ref. [251]	-12 (as dep., $1 \mathrm{kHz}$)	-80 (as dep.)
	-60 (10 ⁵ cy., 1 kHz)	$-107 (10^5 \text{ cy.})$

Reference [282], it is not proportional to the wake-up effect of the pyroelectric coefficient. The large coefficient of as-deposited samples could be explained by defect dipoles, which are present at the electrode interfaces. When the material is field-cycled, two competing effects would occur: The defect re-distribution would increase the intrinsic electrocaloric effect, but reduce the contribution related to defect dipoles.

It is important to note that the film is clamped laterally by the substrate, but is in a constant-stress condition in the out-of-plane direction. Tong et al. discuss the electrocaloric effect in such a partially-clamped case [41]. The total observed Σ is a sum of a primary contribution $\Sigma' = p'$, the piezocaloric effect $\Sigma'' = e_{33}\alpha_3$, and the entropy change related to defect dipoles. Here, p' is the constant-strain pyroelectric coefficient, e_{ij} are the piezoelectric coefficients, and α_i is the thermal expansion coefficient in the film stack.

The adiabatic electrocaloric temperature change is calculated according to Equation 2.25. Using values of $274 \,\mathrm{J\,kg^{-1}\,K^{-1}}$ for the specific heat capacity [68], $9.6 \,\mathrm{g\,cm^{-3}}$ for the density, and a maximal electric field change of $3 \,\mathrm{MV\,cm^{-1}}$, a value of $\Delta T = 4.4 \,\mathrm{K}$ is obtained.

By using piezoelectric [244] and high-frequency pyroelectric [251] coefficients for Si-doped HfO_2 , primary, piezocaloric and defect-dipole-induced contributions can be estimated. It is important to note that the film is clamped laterally by the substrate, but is in a constant-stress condition in the out-of-plane direction. Tong et al. discuss the electrocaloric effect in such a partially-clamped case [41]. The pyroelectric coefficient in the high-frequency limit is reported as

$$p' + e_{33}\alpha_3 = -53\,\mu\text{C}\,\text{m}^{-2}\,\text{K}^{-1},\tag{5.1}$$

where p' is the constant-strain pyroelectric coefficient, e_{33} is the out-of-plane piezoelectric coefficient, and $\alpha_3 = 5.76 \times 10^{-6} \,\mathrm{K}^{-1}$ is the thermal expansion coefficient in the film stack. With e_{33} from Section 4.3.3, the primary electrocaloric coefficient is calculated as

$$\Sigma' = p' = -81 \,\mu\text{C}\,\text{m}^{-2}\,\text{K}^{-1}.$$
(5.2)

The piezocaloric effect is estimated as

$$\Sigma'' = e_{33}\alpha_3 = 28\,\mu\text{C}\,\text{m}^{-2}\,\text{K}^{-1}.$$
(5.3)

Then, the contribution from defect dipoles is calculated as the difference to the experimental value $\Sigma_{Exp} = -107 \,\mu C \,m^{-2} \,K^{-1}$ at

$$\Sigma_{DD} = \Sigma_{\rm Exp} - \Sigma' - \Sigma'' = -54 \,\mu {\rm C} \,{\rm m}^{-2} \,{\rm K}^{-1}.$$
(5.4)

The electrocaloric temperature change obtained with various thin-film materials is summarized in Table 5.2. Mischenko et al. [210] have obtained very large values of ΔT , and their work has renewed the interest in electrocaloric materials. Vats et al. obtained an even higher electrocaloric response by using multi-layered nanostructures. Most

	T	ΔE	ΔT	Direct	Ref.
	(K)	$(\rm kVcm^{-1})$	(K)		
$PbZr_{x}Ti_{1-x}O_{3}$	495	776	12.0		[210]
$\mathrm{Pb}(\mathrm{Mg}_{1/3}\mathrm{Nb}_{2/3})\mathrm{O_3}\text{-}\mathrm{PbTiO_3}$	298	720	9.0		[375]
$\mathrm{Pb}_{0.8}\mathrm{Ba}_{0.2}\mathrm{ZrO}_3$	290	598	45.3		[376]
$\mathrm{La:PbZr}_{x}\mathrm{Ti}_{1-x}\mathrm{O}_{3}$	303	308	-5.0		[377]
BaTiO_3	490	150	0.4	1	[378, 379]
P(VDF-TrFE)	278	774	6.5		[380]
P(VDF-TrFE)	343	3000	21.0		[209]
$\mathrm{Hf}_{0.5}\mathrm{Zr}_{0.5}\mathrm{O}_{2}$	448	3260	-10.8		[370]
$\mathrm{Hf}_{0.2}\mathrm{Zr}_{0.8}\mathrm{O}_{2}$	298	3260	13.4		[170]
Si-doped HfO_2	298	3000	4.4	1	this work

Table 5.2: Electrocaloric temperature change obtained for various thin film materials. Values obtained by means of direct electrocaloric measurements are indicated by a check mark.

reports are obtained by means of indirect measurements, which rely on the Maxwell Equation 2.23.

In the first reports on electrocaloric responses of doped HfO₂, large positive and negative coefficients with ΔT of up to 13.4 K have been stated [170, 370]. However, direct measurements reported herein do not confirm such large coefficients or negative electrocaloric responses. While higher values of ΔT have been reported in the literature for doped HfO₂, the direct measurement approach gives confidence that the temperature change is realistic and available for applications. Recently, it has been shown that indirect electrocaloric measurements of HfO₂ thin films are suffering from thermal fatigue effects [185], which explain the large difference in reported values for direct and indirect measurements.

In Figure 5.9, the electrocaloric temperature change is visualized with respect to the applied electric field differential. Promising material groups include lead-based crystals (filled, blue symbols), polymers (open, blue symbols) and the HfO₂ material class. While poly(vinylidene fluoride-co-trifluoroethylene) (P(VDF-TrFE)) and HfO₂-based films exhibit lower electrocaloric coefficients than lead-based materials, their high breakdown strength allows for competitive values of ΔT .

Further research may be directed at confirming the negative electrocaloric responses obtained for some HfO_2 -based films with direct methods. The CMOS compatible manufacturing process makes HfO_2 a promising material for future solid-state refrigeration solutions. For instance, the high scalability of the material may enable refrigeration in nanoelectromechanical systems (NEMS) or integrated circuits (see Section 5.3.3).



Figure 5.9: Literature reports of positive and negative electrocaloric coefficients in various thin-film materials.

5.3 Pyroelectric energy conversion cycles

Computers and integrated circuits take up an ever-growing part of the global electric energy consumption, and contribute significantly to greenhouse emissions [383]. Since electronic devices convert virtually all of the supplied electrical power to waste heat, the recovery of low-grade thermal energy has attracted significant research interest. Pyroelectric materials can be used to reclaim a portion of the dissipated power in a process called energy harvesting.

Ferroelectric materials have been considered for energy harvesting applications in the 1960's and 1970's [30], however, thermoelectric generators (TEG) are mostly in use today. The thermoelectric effect relies on a spatial temperature gradient, which may be achieved by connecting a heat sink to the device. In contrast, pyroelectric devices rely on a temperature change in time.

However, the efficiency of TEGs is intrinsically limited by the balance of electrical and thermal conductivity, which is expressed by the FOM ZT. For pyroelectric energy harvesting, the efficiency is only limited by the laws of thermodynamics, where the optimum is defined by the Carnot limit as given in Equation 3.38.

Strategies for using the pyroelectric effect to harvest thermal energy have been discussed in Section 3.3. It has been shown that thermodynamic cycles based on the Ericsson process offer superior power density compared to passing the pyroelectric current through a simple resistive load [232, 233]. These Olsen cycles rely on cyclic polarization, heating, de-polarization and cooling of the ferroelectric material (see Figure 3.13). Pyroelectric energy conversion based on Olsen cycles has been performed with a range of different materials, which have been reviewed by Bowen et al. in Reference [30].

Ferroelectric thin films open up new opportunities for pyroelectric energy conversion, since they favorably change the balance of heat input (scaling with volume) and electric work (scaling with area) [200]. Since ferroelectricity in doped HfO_2 is a distinct thin-film phenomenon, and has been achieved in layers as thin as 1 nm [5], the material might enable large energy density and efficient operation. Further, a comparably low dielectric permittivity and heat capacity in combination with the sizable pyroelectric response lead to favorable FOMs for energy harvesting, as discussed in Section 4.5.

5.3.1 Doped hafnium oxide on area-enhanced substrates

To assess thermal-electric energy conversion cycles quantitatively, an increased pyroelectric current response in the nA or μ A range is beneficial. Since the deposition techniques used throughout this dissertation are compatible with challenging geometries (i.e., porous or nano-patterned substrates), three-dimensional pyroelectric capacitor structures are manufactured. The fabrication process is discussed in Section 3.4.1.

The resulting capacitor structure is depicted in Figure 5.10 a), where 20 nm thick, Si-doped HfO₂ is used as ferroelectric material. By using a truncated cone model, an area enhancement factor of 19.5 is calculated. Using EFTEM, the element distribution in a cross-section of a single deep-trench structure is visualized [123]. Filter energies of 99 eV, 456 eV, and 1662 eV are set for O, Ti, and Hf, respectively. The results in Figure 5.10 b) indicate the conformal Si-doped HfO₂ layer (Hf, green) sandwiched between the electrodes (Ti, red), proving conformal material deposition in the trenches. The silicon substrate and the polycrystalline filling of the holes are depicted as well (Si, blue). The STEM micrographs in Figure 5.10 c) confirm the 20 nm film thickness target. Further, the thin Al_2O_3 layer in the middle of the Si-doped HfO₂ is visible. Grain forma-



Figure 5.10: a) Schematic view of the manufactured test structure for energy conversion experiments. The MFM stack is deposited on an area-enhanced substrate. b) EFTEM element analysis of a single hole structure cross-section, visualizing TiN electrodes, the HfO₂ pyroelectric layer, and Si filling. c) STEM micrograph of the deposited MFM stack, where the Si-doped HfO₂ with a thin Al_2O_3 interlayer is visible. Reprinted with permission from Ref. [123]. Copyright 2019 John Wiley & Sons.

tion during the RTA process is separated by this interlayer, thus successfully controlling the crystallization behavior of the pyroelectric material. A very low film roughness is obtained with the ALD processes, which is of critical importance for the reliability of large-scale devices. Here, a top contact area of 15.2 mm^2 and a trench count of more than 2.4×10^7 are used.

Results of small-signal capacitance–field (C-E) measurements are shown in Figure 5.11 a) for both fresh and field-cycled devices. While the (C-E) characteristic resembles a double-butterfly curve initially, the graph after cycling exhibits two pronounced maxima which are associated with ferroelectric switching. The capacitance density varies between 227 nF mm⁻² and 293 nF mm⁻², which corresponds to permittivity values of 26.3 and 33.9, with the area enhancement factor of 19.5 taken into account. The corresponding loss tangent measurements are shown in Figure 5.11 b). The as-deposited samples show a high loss, which is attributed to redistributions of defects associated with the wake-up effect [216]. After 10×10^4 field cycles, the loss tangent reduces to 0.04 to 0.05, with peaking at the coercive voltages. Current–field measurements confirm low leakage, in the manufactured devices, below 5 nA cm⁻² in the range up to $2.5 \,\mathrm{MV \, cm^{-1}}$ and an electric breakdown field of $4.2 \,\mathrm{MV \, cm^{-1}}$.



Figure 5.11: a) Capacitance density of 20 nm thick, Si-doped HfO_2 deposited on an areaenhanced substrate obtained at a frequency of 10 kHz. Results for an increasing electric field cycle count from 1 to 10^4 are displayed. b) Corresponding measurement of the loss tangent.

To confirm the ferroelectric behavior of the 3D-integrated, Si-doped HfO₂ thin films, polarization–voltage measurements are performed. In Figure 5.12, the results are depicted for as-deposited samples and after successive application of electric field cycling. Fresh samples exhibit a pinched, AFE-like hysteresis loop, which is a common observation in HfO₂-based ferroelectrics. The wake-up effect is visible in the *P*–*U* characteristic, and the remanent polarization $P_{\rm r}$ increases to a value of 124 µC cm⁻² after 10 × 10⁴ field cycles.



Figure 5.12: a) Polarization-field hysteresis characteristic of 20 nm thick, Si-doped HfO_2 deposited on an area-enhanced substrate measured at a frequency of 100 Hz for successive electric field cycling. b) Pyroelectric coefficients vs. electric field offset measured by using the low-frequency Sharp-Garn method (see Section 3.1.1).

Characterization of the pyroelectric response is performed using the Sharp–Garn method (see Section 3.1.1). Measurement results with respect to bias voltage are displayed in Figure 5.12 b), for as-deposited samples (green circles) and after field cycling (blue squares). For the field-cycled sample, a large virtual pyroelectric coefficient of $(-1442 \pm 10) \,\mu\text{C}\,\text{m}^{-2}\,\text{K}^{-1}$ is obtained at 0V with respect to device footprint, which corresponds to a planar value of $-74\,\mu\text{C}\,\text{m}^{-2}\,\text{K}^{-1}$ with an area enhancement factor of 19.5. This is similar to measurement results obtained for planar Si-doped HfO₂ in Section 4.1.1, indicating a successful vertical integration. At increasing voltages, the pyroelectric response decreases slightly, reaching $(-1042 \pm 23)\,\mu\text{C}\,\text{m}^{-2}\,\text{K}^{-1}$ at 3V. Thus, by increasing the substrate surface with nano-patterning, the pyroelectric response of doped HfO₂ is enhanced significantly, exceeding the values for PbZr_xTi_{1-x}O₃ ($-380\,\mu\text{C}\,\text{m}^{-2}\,\text{K}^{-1}$) [247]. The increased virtual pyroelectric coefficients lay the foundation for energy conversion cycles, which are discussed in the next section.

5.3.2 Pyroelectric energy conversion cycles

For the following experiments with pyroelectric energy conversion cycles, 20 nm thick, Si-doped HfO_2 on an area-enhanced substrate is identified as suitable material for several reasons. First, a large pyroelectric response has been observed in planar measurements (see Section 4.1.1), and is maintained when moving to three-dimensional substrates. Additionally, the material realizes low leakage currents, which is beneficial especially in low-frequency harvesting cycles.

As described in Section 3.3, the Olsen process relies on a synchronized variation of electric field and temperature in the pyroelectric material. For this purpose, the pyroelectric material is placed on a Peltier element. An exemplary trapezoidal temperature waveform is shown in Figure 5.13 a), for an amplitude of 5 K and a frequency of 40 mHz. The electric field at the electrodes of the pyroelectric capacitor is then phase shifted by an angle φ , as depicted in Figure 5.13 b). While applying temperature and field variations, the pyroelectric current is sampled. Results are shown in Figure 5.13 c). Distinct regions are visible, which correspond to the individual steps of the Olsen cycle, and are designated with numbers in the graph.

- 1. Isoelectric heating, where the linearly rising temperature leads to a depolarization of the material and therefore induces a constant, negative pyroelectric current. The amplitude of temperature change is denoted by θ . Integration of the current with respect to time yields the corresponding polarization change in this step. A value of $(-1.10 \pm 0.02) \,\mu\text{C}\,\text{cm}^{-2}$ is calculated, which is consistent with pyroelectric coefficients determined before (see Figure 5.12).
- 2. Isothermal depolarization, where the electric field is removed from the pyroelectric capacitor. The integral of the corresponding displacement current depends on the



Figure 5.13: a) Temperature waveform applied during the energy conversion experiment with an amplitude of 5 K and a frequency of 50 mHz b) Electric field waveform for a range of amplitudes, with a phase shift of approximately 90° with respect to the temperature waveform c) Corresponding current between the electrodes of the test structure showing the response upon temperature change (1 and 3) as well as electric field change (2 and 4).

electric field amplitude, with three values ranging from $0.1 \,\mathrm{MV \, cm^{-1}}$ (green line) to $0.3 \,\mathrm{MV \, cm^{-1}}$ (blue line) shown in the graphic.

- 3. Isoelectric cooling, where the pyroelectric material is cooled down to the initial temperature. If no losses or non-pyroelectric current contributions occur, the integrated charge is equal to that of the isoelectric heating step (1). Indeed, a value of $(1.11 \pm 0.01) \,\mu\text{C}\,\text{cm}^{-2}$ is determined.
- 4. Isothermal polarization, where an electric field is applied to the pyroelectric capacitor.

The cycle is then repeated periodically. Integration of the current density *i* then yields a periodic polarization change $\Delta P(t)$. For the case of a field amplitude of 50 kV cm⁻¹, results are displayed in Figure 5.14. In the examined temperature amplitude range of 3 K to 7 K, the polarization change during isoelectric steps (1) and (3) increases linearly. By integrating the inscribed area, energy densities *w* of 0.15 µJ cm⁻² to 0.38 µJ cm⁻² are calculated with increasing temperature amplitudes of 3 K to 7 K, where the mean temperature was held constant at 30 °C. The results are depicted in Figure 5.14 b) (blue squares), and a linear relationship $W \propto \theta$ is obtained (blue line), which is in accordance to Equation 3.43. Further, the normalized efficiency η/η_{Carnot} is depicted (red circles). At the lowest temperature amplitude of 3 K, a remarkable value of 63 % of Carnot efficiency is reached, which corresponds to an absolute efficiency of 0.63 % (not shown here). With rising values of θ , the scaled efficiency reduces to 28 %, while the absolute value η rises slightly to 0.67 %. The observed results



Figure 5.14: a) Polarization change of the ferroelectric material vs. electric field for a range of temperature differentials. The inscribed area corresponds to the harvested energy per cycle. b) Calculated energy density and normalized energy conversion efficiency with respect to the temperature amplitudes.
are in agreement with Equations 3.44 and 3.38 (red line), where a heat capacity of $2.1 \,\mathrm{MJ}\,\mathrm{m}^{-3}\,\mathrm{K}^{-1}$ [223, 346] is used. The pyroelectric coefficient is used as a fitting parameter, where a value of $-1061\,\mu\mathrm{C}\,\mathrm{m}^{-2}\,\mathrm{K}^{-1}$ is extracted, which is slightly lower than values shown in Figure 5.12 b). The most probable causes for the slightly reduced energy density are aging (see Section 4.1.5), dielectric losses, and the series resistance of the electrodes.

Further, the Olsen cycle is optimized with respect to the phase shift φ between field and temperature waveforms, where fixed amplitudes of 100 kV cm⁻¹ and 5 K are used, respectively. Thereby, the timing of the isoelectric steps with respect to the isothermal steps is altered. Energy conversion cycles are performed with phase shifts in a range of 0° to 180°, and the energy density is calculated after each run. Results are depicted in Figure 5.15 a). It is visible that the highest energy density is achieved in a broad operating range between 75° and 135°. The maximal value of 0.48 µJ cm⁻² is achieved for $\varphi = 120^{\circ}$, which is slightly larger than the theoretical optimum of 90°. One reason for the slight shift of the optimal operation point are minor inaccuracies in the temperature control loop. This results in an asymmetric pyroelectric signal, as shown in steps 1 and 3 of Figure 5.13 c), and might be improved by using a different control loop type, e.g. by implementing a differential term [195]. The broad region with an almost constant energy density is achieved since the slew rate of the trapezoidal waveforms is sufficient at the low cycle frequency of 40 mHz.

One of the main benefits in using ferroelectric thin films for energy harvesting is the large breakdown field, which allows increased electric field differentials, thus increasing the energy density and conversion efficiency (see Equations 3.43 and 3.44). Thus, electric field amplitudes of up to $0.5 \,\mathrm{MV}\,\mathrm{cm}^{-1}$ are probed. Calculated energy densities are shown in Figure 5.15 b). For rising temperature differentials, the electric field amplitude



Figure 5.15: a) Work per cycle vs. phase shift between temperature and electric field waveforms, indicating an optimal energy harvesting performance 90° to 135°. b) Work per cycle for a range of temperature amplitudes and electric field ampltudes.

with the largest work density shifts towards higher values. At $\theta = 7 \text{ K}$, the highest energy density of $1.92 \,\mu\text{J}\,\text{cm}^{-2}$ is obtained at $0.45 \,\text{MV}\,\text{cm}^{-1}$. The electric field amplitude is larger than values in most other reports on pyroelectric energy conversion with ferroelectric films [200, 235, 384–386], and matches with the P(VDF-TrFE) co-polymer [387]. However, the thickness of only 20 nm enables a voltage amplitude of just 0.9 V, whereas polymer-based pyroelectric harvesting often requires voltages in the kV range.

It is concluded that a major limitation of the presented experimental setup arises from the low cycle frequency. By implementing sample heating with a quasi-continuouswave infrared laser, faster cycles have been run on the samples by another group, with results reported in a joint publication [123]. At a frequency of 5 Hz, an energy density of $0.15 \,\mu J \,\mathrm{cm}^{-2}$ has been achieved with an electric field and temperature amplitudes of $250 \,\mathrm{kV} \,\mathrm{cm}^{-1}$ and 1 K, respectively. This corresponds to a power density of $0.75 \,\mu \mathrm{W} \,\mathrm{cm}^{-2}$. Ultimately, the operation frequency is limited by the electrode resistance and associated loss.

5.3.3 High-frequency, on-chip energy harvesting

Microelectronic devices are an interesting application area for the recovery of waste heat, since thermal energy is dissipated at high frequencies and at a reasonably high power density due to the small form factor. Since HfO_2 is ubiquitous in CMOS device manufacturing, the integration of an HfO_2 -based energy harvesting device in the BEoL of an integrated circuit is proposed. Such an approach is illustrated in Figure 5.16 a). When power is dissipated by the active devices (i.e., transistors) in the FEoL, heat ins transmitted towards the HfO_2 -based capacitors, which experience a minute temperature change. Via the previously described Olsen cycle, the pyroelectric effect is used to convert a part of this heat into electrical energy. FEM simulations indicate that a strong thermal coupling between the FEoL and the BEoL by means of vias is beneficial



Figure 5.16: a) Illustration (cross-section) of an integrated circuit with BEoL capacitor structures. b) STEM micrograph of a BEoL capacitor. The TiN electrodes, a Cu contact via and the HfO₂ dielectric are visible. c) STEM micrograph of the bottom electrode contact with a Cu via.

for the energy harvesting process, and that operation frequencies in excess of 1 MHz are possible (not shown here). STEM cross-sections of a HfO_2 -based capacitor in the BEoL are shown in Figure 5.16 b) and c). Ferroelectric devices in the BEoL have the potential for further novel applications such as ferroelectric random access memory (FRAM) [388], energy storage, and electrocaloric refrigeration [185].

To investigate the potential of such an integrated energy harvester, the previously described pyroelectric test structure is adapted (see Section 3.1.3). In comparison to the energy harvesting experiments in the previous section, considerably faster thermal cycles are accessible. An oscillating power dissipation in the range from $36 \,\mathrm{W \, cm^{-2}}$ to $144 \,\mathrm{W \, cm^{-2}}$ is simulated by the integrated heater. These power densities are typical values which are found in integrated circuits, which would be one possible application field of an integrated pyroelectric harvesting device. However, the solution could also be adapted to other high-frequency heat sources such as combustion engines or pulsed lasers.

Similarly to the previously discussed harvesting approach, the Olsen cycle is implemented by applying a synchronized electric field waveform to the pyroelectric material (compare Figure 5.13). This is accomplished by connecting an AWG (Agilent, model 33250A) in series with the pyroelectric capacitor. The current measurement is carried out with a lock-in amplifier (Zurich Instruments MFLI) in the oscilloscope mode. An important difference to the low-frequency energy harvesting experiments in Section 5.3.2



Figure 5.17: a) Current waveform of the pyroelectric energy harvester. Distinct peaks are visible when the electric field is applied to or removed from the pyroelectric capacitor. The pyroelectric current response is visible as well at a smaller magnitude. b) Calculated polarization of the pyroelectric material. c) Experimental energy harvesting cycles for an increasing thermal power dissipation.

is the use of a planar HfO_2 layer, with a lower apparent ferroelectric polarization. In Figure 5.17 a), the resulting current waveform is displayed for a frequency of 36.8 Hz. Distinct peaks are visible, which correspond to the displacement current. At a lower magnitude, the pyroelectric effect (PEE) manifests as a superimposed oscillation.

By integration of the current density with respect to time, the polarization change is calculated, as displayed in Figure 5.17 b). Further, the polarization change is displayed with respect to the electric field change at an amplitude of 12.5 kV cm^{-1} in Figure 5.17 c). As discussed before, the energy density corresponds to the enclosed area of the *P-E* diagram. It is evident that the energy density increases for a rising thermal power dissipation.

In order to optimize the power density of the Olsen cycle, a careful synchronization of the electric field waveform with respect to the thermal oscillation is necessary. The measurement results in Figure 5.18 a) indicate an optimal value of 180°. A deviation from the optimal phase value leads to a rapidly reducing power density. For a deviation of more than $\pm 45^{\circ}$ from the ideal value, the harvester enters the loss regime.

Measurements with respect to an electric field bias in the range of $\pm 1.75 \,\mathrm{MV \, cm^{-1}}$ clearly illustrate the dependence of the Olsen cycle on the polarization of the HfO₂ film. More importantly, the experimental results in Figure 5.18 b) indicate that the obtained power density is indeed of pyroelectric origin, since the hysteretical behavior of the effect is reproduced. With the selected phase $\varphi = 180^{\circ}$, energy harvesting is only possible in the downward polarization state.

Next, the impact of the energy harvesting frequency is analyzed. In Figure 5.18 c), the energy density is calculated for a range of thermal power dissipation values and in a frequency range from $13.9 \,\mathrm{Hz}$ to $4156 \,\mathrm{Hz}$. In the low-frequency regime, the energy density is large, but the harvested power in Figure 5.18 d) is low due to the rate of the Olsen cycles. For a rising frequency, the energy density is reduced, but an optimal power density is reached. In the case of the highest thermal power dissipation, the largest power output of $93.4 \,\mathrm{mW} \,\mathrm{cm}^{-3}$ is found at $549 \,\mathrm{Hz}$. Above $1 \,\mathrm{kHz}$, the power density decreases sharply, which is attributed to losses from the electrode series resistance. The temperature amplitude in the on-chip harvesting approach is just $0.18 \,\mathrm{K}$, since no thermal switch is employed [386], and the power dissipation is tuned in a realistic, application-related range.

In Figure 5.18 e), the energy harvesting efficiency normalized to η_{Carnot} is shown (see Equation 3.42). In the low-frequency limit, a high scaled efficiency of 52% is obtained. For the case of an optimal power output, an efficiency of 15% of the Carnot limit is measured. This is similar to the theoretical estimation from Equation 3.44, which yields a scaled efficiency of 13%.

In analogy to thermoelectric materials, an effective pyroelectric ZT can be defined via

$$\frac{\eta_{\text{Olsen}}}{\eta_{\text{Carnot}}} = \frac{\sqrt{1+ZT}-1}{\sqrt{1+ZT}+T_{\text{c}}/T_{\text{h}}}.$$
(5.5)



Figure 5.18: a) Optimization of the phase between the thermal power dissipation of the energy source and the electric field waveform which is applied to the pyroelectric capacitor. b) Operation of the energy harvester with an electric field offset. It is visible that harvesting is only achieved in for a downward polarization of the HfO₂ film. c) Generated energy density and d) power density of the pyroelectric energy harvester vs. the frequency for a equidistant range of thermal power dissipation densities from $36 \,\mathrm{W \, cm^{-2}}$ to $144 \,\mathrm{W \, cm^{-2}}$. e) Harvesting efficiency normalized to the Carnot limit.

At the maximum output power, an effective value of ZT = 1.35 is calculated, which is larger than that of the commonly used bismuth telluride (Bi₂Te₃) at less than 1.0 at room temperature [389, 390].

5.3.4 Summary of properties for energy conversion

In the previous section, the pyroelectric properties of doped HfO_2 have been analyzed with an emphasis on energy harvesting. The previously discussed experiments illustrated that there are some technical limitations. Most importantly, the operation frequency is limited due to the resistive losses in the electrodes. In an application-related context, multiple energy harvesters may be arranged in series to increase the absolute power

output, which could be subject of future research. Further, it has been demonstrated that the efficiency of HfO_2 -based energy harvesting may surpass that of thermoelectric generators.

In comparison to other materials, the HfO_2 material class has some important benefits, e.g., the potential for an integration of harvesting devices in the BEoL of integrated circuits. As discussed before, lead-based materials exhibit higher FOMs for pyroelectric energy harvesting (see Table 4.3). Accordingly, the highest reported energy harvesting power density has been achieved with the lead-based $Pb(Mg_{1/3}Nb_{2/3})O_3$ -PbTiO₃ [200], as shown in Figure 5.19. When normalized to the temperature differential, HfO₂-based materials reach sizable power densities.



Figure 5.19: Energy harvesting power densities demonstrated with various materials, normalized to the applied temperature variation. While many reported approaches operate at frequencies below 1 Hz, recent publications achieve harvesting from rapid temperature oscillations in the kHz range.

In Table 5.3, energy and power densities of several materials are summarized. Research on pyroelectric materials for energy harvesting has been focused on lead-based materials due to their high pyroelectric coefficients and on polymers as for their high breakdown fields. HfO₂ has the potential to combine both properties. Further optimization of HfO₂-based pyroelectric energy harvesting could address the following challenges:

- The implementation of highly conducting electrical connections, which would enable harvesting in the MHz range, which is relevant for power-beaming and on-chip thermal energy recovery. Ideally, the highly conducting electrodes would be maintained in a 3D integration, either by stacking of multiple harvesting devices, or by deposition on an area-enhanced substrate as demonstrated in Section 5.3.1.
- Increasing the applied electric field differential. In the current implementation, the electric field change is limited at hundreds of $kV \, cm^{-1}$. However, due to its high breakdown strength, HfO₂-based thin films have the potential of working at

much higher fields, while still maintaining low-voltage operation due to their low thickness.

• The utilization of large, field-induced pyroelectric coefficients in AFE-like $\rm HfO_2$ for energy harvesting. As proposed by Pandya et al., the use of field-induced effects is a viable option in thin films, and may enable the use of further materials, such as $\rm ZrO_2$ [200].

Material	d	θ	f	W	P	P/ heta	Ref.
	μm	К	$_{\rm Hz}$	${ m J}{ m cm}^{-3}$	${ m Wcm^{-3}}$	$\mathrm{Wcm^{-3}K^{-1}}$	
$\text{La:PbZr}_x \text{Ti}_{1-x} \text{O}_3$	190	170	0.03	1.014	0.026	$1.6 imes 10^{-4}$	[235]
$\text{La:PbZr}_x \text{Ti}_{1-x} \text{O}_3$	200	170	0.06	0.800	0.048	$2.8 imes10^{-4}$	[235]
$PbZr_xTi_{1-x}O_3$ - $PbNi_xNb_{1-x}O_3$	200	220	0.03	1.420	0.047	$2.1 imes 10^{-4}$	[384]
$\mathrm{Pb}(\mathrm{Mg}_{1/3}\mathrm{Nb}_{2/3})\mathrm{O}_3 ext{-}\mathrm{PbTiO}_3$	0.15	56	1000	0.526	526	9.4	[200]
$Pb(Mg_{1/3}Nb_{2/3})O_3$ -PbTiO $_3$	0.15	90	40.00	1.060	42	0.47	[200]
P(VDF-TrFE) 60/40	10	$\frac{5}{8}$	0.07	0.155	0.010	$1.2 imes 10^{-4}$	[391]
P(VDF-TrFE) 56/44	υ	80	0.40	0.350	0.140	$1.8 imes 10^{-3}$	[386]
P(VDF-TrFE)	25	57	0.71	0.279	0.199	$3.5 imes 10^{-3}$	[392]
$BaTiO_3$	0.2	100	3000	0.010	30	0.30	[385]
Si-doped HfO_2 (3D)	0.02	1	5.00	0.004	0.019	$1.9 imes 10^{-2}$	[123]
Si-doped HfO_2 (3D)	0.02	14	0.04	0.038	0.002	$1.1 imes 10^{-4}$	this wor
doped HfO_2	0.02	0.18	549	0.0002	0.092	0.51	this wor

Table
5.3 3
Literature
reports of
on
pyroelectric
energy
harvesting
with
ferroelectric
$_{\mathrm{thin}}$
films.

Chapter 6

Conclusion and outlook

In this dissertation, the pyroelectric and electrocaloric properties of the HfO_2 material class have been investigated comprehensively. Based on previous work on the stabilization of the ferroelectric phase in doped HfO_2 thin films, many aspects of the coupling of caloric, elastic and electronic properties have been examined throughout this work.

The results presented herein establish the HfO_2 material system as an alternative to existing pyroelectric materials, with many unique properties such as CMOS compatibility, being non-toxic, high scalability, a large breakdown field, and many more. While the systematic analysis of pyroelectric and electrocaloric properties of HfO_2 -based films began only recently, applications are emerging already.

Over the course of the dissertation project, HfO_2 -based pyroelectric infrared detectors have been developed in cooperation with Infratec GmbH, Fraunhofer ENAS, ASIC- und Mikrosensoranwendung Chemnitz GmbH (AMAC) and Technical University Chemnitz. A functional prototype of a HfO_2 -based infrared sensor is shown in Figure 6.1. Further applications such as pyroelectric on-chip energy harvesting and integrated solid-state cooling become feasible with the HfO_2 material class due to its availability in FEoL and BEoL manufacturing processes.

A screening of the pyroelectric response in HfO_2 -based films has been conducted with regard to stoichiometry for several dopants. A reversible and stable pyroelectric response has been found for all evaluated materials (Al-, Si-, Zr- and La-doped HfO_2). The pyroelectric coefficients are highly sensitive to the film composition. Further, they are dependent on the electrical history and are increased by electric field cycling (wakeup).

It has been found that the pyroelectric response is enhanced significantly in the vicinity of the MPB between the polar orthorhombic and centrosymmetric tetragonal polymorphs. This means that HfO_2 -based films for pyroelectric applications require higher dopant concentrations than films for ferroelectric applications such as the ferroelectric field-effect transistors (FeFET). The Curie constant, which describes the susceptibility of the spontaneous polarization to the temperature in the Landau-Devonshire theory,



Figure 6.1: Functional pyroelectric infrared sensor based on Si-doped HfO_2 . Prototypes are manufactured in cooperation with Infratec GmbH, Technical University Chemnitz, and Fraunhofer ENAS.

has been found to be reduced significantly throughout the stoichiometry range. The obtained values are typical for a displacive phase transition.

The nature of the polarization hysteresis in the HfO_2 -based films has been disputed initially since the material class exhibits significantly different properties than previously known ferroelectrics (see Table 2.3). The results of the pyroelectric screening of several HfO_2 -based materials provide strong evidence for intrinsic ferroelectricity.

For pyroelectric sensor applications, the layer thickness scalability and the aging of the pyroelectric response are analyzed. It is found that the manufacturing of 50 nm thick films by ALD is feasible. Even thicker films may be manufactured with methods such as PVD or CSD to reduce the electrical capacitance, which is beneficial since it improves sensor noise and the frequency response. The aging of the pyroelectric effect is described well by a fatigue mechanism based on the NLS model. According to the simulation, a depolarization field induced by an interfacial dead layer is responsible for reducing the coefficients with time. It is deducted that thicker films should possess a reduced aging rate, which is yet to be proven experimentally.

Further, a significant enhancement of the pyroelectric response is observed in AFE-like films with an external electric field. While the exact origin of the AFE-like behavior in HfO_2 and ZrO_2 films is not entirely understood yet, a field-induced phase change or a field-induced unit cell orientation change seem to be the most probable causes. Both effects would lead to a strong susceptibility of the field-induced polarization to the temperature.

In many experiments throughout this work, the Sharp-Garn method has been proven to be an accurate and reliable tool to analyze the pyroelectric response in nm-thin films. These results are complemented by measurements with temperature changes in the kHz range obtained with a dedicated pyroelectric test structure. While both methods yield similar pyroelectric coefficients in the low-frequency limit, mechanical clamping effects become prominent for rapid temperature cycles. The results illustrate that mechanical interactions in pyroelectric thin film devices significantly influence the current response.

By exploiting the frequency-dependent clamping effect, primary and secondary pyroelectric coefficients are separated, and piezoelectric coefficients are extracted. Piezoelectric properties of HfO_2 films are scarcely reported since the measurement is challenging in nanometer-thin films. The piezoelectric response is found to be subject to the wake-up effect, which has not been reported by previous publications which employ DART-PFM or DBLI.

Further, the electrocaloric effect in HfO_2 has been analyzed through indirect and direct measurements. In the latter approach, it was possible to determine electrocaloric coefficients and give estimations for primary, secondary (piezocaloric), and defect-induced contributions. In contrast, the indirect determination of electrocaloric coefficients via the ferroelectric hysteresis is impacted by thermal fatigue and is not recommended for nm-thin films.

Two approaches have been implemented to use the pyroelectric effect in HfO_2 for the recovery of low-grade waste heat. The deposition of doped HfO_2 on area-enhanced substrates is used successfully to enhance the power output of a pyroelectric harvester in the low-frequency regime. The same approach has been applied to increase the energy storage capabilities in AFE-like films [325]. In the second approach, the possibility of on-chip, high-frequency energy harvesting in the BEoL of an integrated circuit is demonstrated. The harvester reaches a high scaled efficiency, which exceeds that of common thermoelectric materials, without using a thermal switch to modulate the heat flow. The conductivity of the electrical connections in the harvester is identified as critical for increasing the operating frequency further into the MHz range.

All of the previously mentioned effects are quantified throughout the dissertation. Some of the essential characteristics and coefficients determined in this work are summarized in Table 6.1. While a wide range of chemical compositions and phase configurations have been assessed, 20 nm thick, 3.8 cat.% Si-doped HfO₂ serves as a typical example of the material class here. For more detailed results, the individual experimental sections are indicated in the table.

Undoubtedly, the study of the HfO_2 material system is by no means complete today. Throughout this work, it has become clear that the coupling of caloric and electronic properties is an essential puzzle piece in advancing the understanding of the HfO_2 material system as a whole. Exciting experimental and theoretical reports continue to stimulate new debate about prominent topics such as AFE-like behavior, scalability, and wake-up effects [5, 6, 173]. Epitaxial HfO_2 -based ferroelectrics [9] offer the possibility of analyzing pyroelectric and electrocaloric effects unaltered by polycrystallinity, which could be a direction for future investigations.

With a view on applications, one direction of further research regards the possibility of films which exceed the typical thickness limit of ALD at approximately 50 nm. HfO₂ manufactured by CVD or PVD processes promise less pronounced aging effects and a lower electric capacitance, which is beneficial for pyroelectric sensor applications. CMOS

Property		Value	Section
ε	Permittivity	45	4.1.2
$E_{\rm BD}$	Breakdown field	$4.0\mathrm{MVcm^{-1}}$	4.1.3
p	Pyroelectric coefficient	$-72\mu Cm^{-2}K^{-1}$	4.3.2
p'	Primary pyroelectric coeff.	$-53\mu Cm^{-2}K^{-1}$	4.3.2
p''	Secondary pyroelectric coeff.	$-19\mu Cm^{-2}K^{-1}$	4.3.2
r_{10}	Pyroelectric aging rate	6% per decade	4.1.5
d_{33}	Piezoelectric coefficient	$18\mathrm{pm}\mathrm{V}^{-1}$	4.3.3
d_{31}	Piezoelectric coefficient	$-12\mathrm{pm}\mathrm{V}^{-1}$	4.3.3
R	Thermal resistivity	$0.85\mathrm{mKW^{-1}}$	4.4
Σ	Electrocaloric coefficient	$-107\mu Cm^{-2}K^{-1}$	5.2.2
ΔT	Electrocal. temperature change	$4.4\mathrm{K}$	5.2.2

Table 6.1: Summary of properties determined for $3.8\,\mathrm{cat.\%}$ Si-doped HfO_2 in this dissertation.

compatible electrocaloric refrigeration solutions would be nefit from an advanced three-dimensional integration of $\rm HfO_2$ -based films with optimized electrodes and low dielectric losses. As evident by the different FOMs in Equations 4.16 to 4.19, specific applications require individual optimizations and specializations of the $\rm HfO_2$ material.

Appendix A

Piezoresponse microscopy

To illustrate the ferroelectric behavior of HfO_2 -based films, piezoresponse force microscopy (PFM) is conducted. In this method, an AC voltage is applied to the sample by an electrically conductive cantilever. Classic PFM [393] reaches its limitations with the nanometer-thin films due to the low absolute displacement, yielding low signal strength. Additionally, changing tip apex during the scan can lead to resonance frequency instability.

Dual-frequency resonance-tracking piezoresponse force microscopy (DART-PFM) [351] compensates for such drift effects by tracking the tip contact resonance frequency $f_{\rm C}$. Additionally, working in contact resonance significantly enhances signal-to-noise ratios while allowing lower driving amplitudes. Thus, the method offers a way to directly visualize ferroelectric domains in HfO₂-based films. The implementation of the DART-PFM method is depicted schematically in Figure A.1. Here, a diamond-coated cantilever (DCP11, K-TEK Nanotechnology) with a resonance frequency of approximately 250 kHz is used. The generated deflection is measured by a laser diode and a four-quadrant photo diode detector. Two lock-in amplifiers compare



Figure A.1: Schematic of DART-PFM, where the excitation of the piezoresponse is achieved with two function generators, and the contact resonance frequency $f_{\rm C}$ is tracked by two lock-in amplifiers.

the cantilever deflection signal to the reference oscillators (red and blue circuits), and quantify the piezoresponse amplitude and the corresponding phase. The mean frequency of both oscillators is tracked so that the amplitudes A_1 and A_2 remain equal; the frequency difference is held constant.

In Figure A.2, DART-PFM measurement results of a 20 nm thick, $2.8 \cot \%$ Si-doped HfO₂ film with 10 nm TiN top and bottom electrodes are shown. No poling of field-cycling has been applied beforehand the measurement.

The piezoresponse amplitude is shown in Figure A.2 a), where adjacent ferroelectric domains of opposite polarization states are circumscribed by characteristic fringes with vanishing amplitude. Some domains exhibit a size as low as 40 nm, which is in the range of the grain size. Larger domains of up to 350 nm seem to span multiple grains. The results are comparable to other reports, in which a similar method is employed [127, 128]. The PFM phase map is shown in Figure A.2 b). It is visible that domains indeed



Figure A.2: DART-PFM measurement results of 20 nm thick, 2.8 cat % Si-doped HfO₂. a) PFM amplitude, where ferroelectric domains are circumscribed by fringes with vanishing amplitude. b) PFM phase, where regions of opposite phase correspond to the fringed domains in the amplitude plot. c) DART-PFM frequency. d) Film topography. Measurements are conducted with a Cypher AFM apparatus (Asylum research) at a resonance frequency of 780 kHz and an excitation amplitude of 700 mV.

correspond to opposite phases of the piezoelectric response. A phase contrast of nearly $\pm 90^{\circ}$ is detected. The contact resonance frequency in Figure A.2 c) exhibits a faint contrast between oppositely polarized domains. No pronounced correlation between the sample topography, which is shown in Figure A.2 d), and the ferroelectric domain structure is observed.

To illustrate the formation of ferroelectric domains, the piezoresponse amplitude and phase are extracted along the red line in Figure A.2. The results are shown in Figure A.3 a) and b), respectively. The DART-PFM amplitude nearly vanishes at the supposed domain walls. The amplitude minima coincide with phase jumps of approximately 180°, which is expected for neighboring, oppositely polarized domains.

In future experiments, the opportunity of vector DART-PFM could be explored to obtain further insights into the domain structure of doped HfO_2 thin films. Further related methods, such as switching spectroscopy, allow for a microscopic electrical characterization of the ferroelectric domains.



Figure A.3: a) Piezoresponse amplitude extracted along the red line in Figure A.2. The minima correspond to a ferroelectric domain wall. b) Corresponding extracted phase. The coincident $\pm 180^{\circ}$ steps provide further evidence for the observation of ferroelectric domains.

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6. C. Mart, A. Viegas, W. Weinreich, D. Mutschall, A. Kaiser, N. Neumann, T. Großmann, K. Hiller, L. M. Eng. "Pyroelectric CMOS Compatible Sensor Element Based on Hafnium Oxide Thin Films". *IEEE International Symposium* on Applications of Ferroelectrics (ISAF), Keystone, Colorado, DOI: 10.1109/IFCS-ISAF41089.2020.9234892

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- A. Viegas, C. Mart, M. Czernohorsky "Antiferroelectric Si:HfO₂ for High Energy Storage using 3D MIM Capacitors". *IEEE International Symposium on Appli*cations of Ferroelectrics (ISAF), Keystone, Colorado, 19.7.–23.7.2020. Virtual conference due to the COVID-19 pandemic.
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Supervised theses

1. N. Kohlenbach. "Pyroelectric HfO_2 nano-laminates for infrared sensor applications". *Master thesis*, Westfälische Wilhelms-Universität Münster, January 2020.

Peer-review contributions

The author has contributed to the peer-review process of the following journals:

- ACS Applied Materials & Interfaces
- Acta Materialia
- ACS Applied Nano Materials
- ACS Applied Electronic Materials
- Applied Physics Letters
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