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Rhombohedral Hf0.5Zr0.5O2 thin films

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Summary

In the context of the information age, ideal memories with high-speed, low-power, high-endurance and non-volatility are desired in order to achieve both fast processing and high-density storage. Various types of emerging memories have been proposed to reach this goal. A promising one is the ferroelectric memories, based on the effect of two different remanent polarization states in ferroelectrics, which can be switched by the external electrical field (providing “0” and “1” for binary logic, that are non-volatile when the electrical field is removed). Although some products of ferroelectric memories have been commercialized, they still face various challenges to compete with the mainstream memories and massively making it to the market. For example, poor CMOS-compatibility due to the perovskite structure of conventional ferroelectrics, makes them hard to integrate with the current silicon-based electronic technology; too large critical thickness to keep ferroelectricity due to large depolarization fields and interface quality, hamper their miniaturization in devices.

The ferroelectricity found in the simple oxide doped-HfO_2 thin films recently, brings a big surprise to the ferroelectrics community. Compared to the conventional ferroelectrics (perovskite-type), this new type of ferroelectrics overcome many issues, especially the above mentioned Si-compatibility, as its amorphous form has been widely used in the transistor industry as the gate insulator. In addition, very unexpectedly, the ferroelectricity in this material exists only at the nanoscale, disappearing at larger sizes, which is a totally opposite trend compared to conventional ferroelectrics, enabling the miniaturization of ferroelectric devices in the future. Thus this material promises to be a definite advance in driving the field towards applications, and many groups have been excited to work on it.

From the fundamental view point, it also appeals to many researchers in this field. To understand the unventional origin of ferroelectricity in these materials could greatly help the improvements in the properties of devices for future appli-

cations. Ferroelectricity is strongly related to the crystal structure, so the structural characterization of the material is very important. However, it is very challenging to extract enough information to undoubtfully assign a polar phase to polycrystalline (multiphase) ultrathin ferroelectric films, especially with many other phases having very subtle structural differences. Thus high quality "clean" (single-phase) films are needed and they are obtained in this work by pulsed-laser-deposition method using advantage of its high kinetic energy with respect to other thin film deposition techniques. The availability of better materials should enable better understanding of the origin of ferroelectricity in this type of ferroelectrics.

In this thesis, Chapter 3 reports a polar rhombohedral (r-) ferroelectric phase in $Hf_{0.5}Zr_{0.5}O_2$ (HZO) with a large remanent polarization up to 34 $\mu C/cm^2$, epitaxially grown on the (001)-$SrTiO_3$ substrate buffered with $La_{0.7}Sr_{0.3}MnO_3$ (LSMO) as back electrode. This phase is very different from the reported polar orthorhombic phase, which is widely believed to be the origin of ferroelectricity. This new r-phase can be obtained by the strategy of strain engineering of nano-sized domains. Cubic high-temperature, high-pressure phases can be stabilized in nanoparticles by the large internal pressure induced by the surface nergy, and when combined with the compressive strain from the substrate, a polar r-phase can form. When the film thickness increases, the strain from the substrate relaxes and domain size grows, thus gradually destabilizing the ferroelectric phase. The insights gained in this work provide the missing clues in the understanding of robust nanoscale ferroelectricity in HfO_2 – based films. Since the as-grown films of this work are a well-oriented single phase, it also helps to overcome one of main issues for their device utilization: electrical cycling usually needed in polycrystalline films for waking up ferroelectricity, called wake-up effect. In addition, this work suggests a pathway to generate large ferroelectricity not only in HfO_2 – based films, but also in other simple oxides.

For further studying the strain-effect on the stabilization of this newly reported ferroelectric r-phase, structures of HZO films on various (001)-oriented perovskite substrates with different lattice parameters but with same back electrode LSMO, are compared in Chapter 4. We reveal that the strain imposed by the substrate on the back electrode plays a big role in the stabilization of ferroelectric phase of HZO film. When the back electrode is under the tensile strain, the HZO films grow (111)-oriented, which favors the single polar r-phase. Once LSMO starts to be under the compressive strain, (001)-oriented crystal grains starts to appear, favoring the non-polar phases (with monoclinic and tetragonal symmetry). With increasing compressive strain of LSMO, the films are single (001)-oriented and non-polar. In addition, we find an oxygen-deficient interface layer between LSMO and HZO, only when LSMO is under tensile strain but not in films with LSMO under compressive strain. This interface induced by the tensile LSMO layer is considered to be crucial to stabilize the (111)-oriented r-phase. The oxygen-deficiency in the layer could help the screening of the polarization charges and reduction of the depolarization field in this ultrathin ferroelectric layer. More systematic studies are needed to perform in the future to evidence this hypothesis. Encouraged by the results on the perovskite substrates showing that (111)-oriented films favor the polar r-phase, HZO thin films grown directly on top of hexagonal substrates (GaN and sapphire) are also studied. In agreement with the expectations, experiments show these films are also (111)-oriented and with the polar r-phase. This work provides guidelines to grow ferroelectric single-phase rhombohedral HfO_2 – based films.

Next, we integrate this new phase into ferroelectric memories in Chapters 5 and 6. Taking advantage of its nanoscale ferroelectricity and large bandgap, this material is perfect for ferroelectric tunnel junction devices, in which two polarization states of ferroelectric tunnel barriers give two different resistance states. In addition, by growing ultrathin ferroelectric HZO layers on a ferromagnetic (FM) back electrode LSMO, a multiferroic system is created.

In Chapter 5, by covering the previously developed heterostructures with a layer of FM cobalt as top electrode, a multiferroic tunnel junction (MFTJ, LSMO (FM)/ HZO (FE)/ Co (FM)) is reported for the first time using an ultrathin ferroelectric HZO barrier of only 2 nm in thickness. Besides two resistance states from the ferroelectric polarization switching (known as tunneling electroresistance effect, TER), the different relative magnetic configurations of the two electrodes (parallel or antiparallel), will also give two different resistance states (known as tunneling magnetoresistance effect, TMR). Thus four non-volatile resistance states have been obtained in this MFTJ with HZO film as a tunnel barrier, by both electric and magnetic field switching. This phenomenon can be the concept of multifunctional devices. Besides this, the junctions also display several other appealing characteristics, such as bias-dependent inverse TMR and memristive behavior. In addition, all of the devices with such thin barriers show excellent homogeneity, and allows working with fixed electrodes. Compared to similarly thin barriers of other conventional ferroelectric materials, which can only be investigated using scanning probes, HZO films bring clear advantages, pushing MFTJs closer to applications.

By combining two ferroic orders (ferromagnetic and ferroelectric), the coupling between the magnetic and electric degrees of freedom (magnetoelectric (ME) coupling) could realize electric field controlled spintronics, promising for the development of low-power and fast devices. However, in Chapter 5, the TMR effect at the two ferroelectric polarization states are similar, which indicates negligible ME coupling. Electrical cycling test of the same junctions are shown in Chapter 6. With increasing numbers of electrical pulses, a huge increase in TER is developed (up to 10^6% compared to the of 440% of beginning stages). In addition, a strong ME coupling shows up, with sign reversal of the TMR effect upon electric pulse stimulus. The experiments presented in Chapter 6, point to the magneto-ionic effect as the origin of the large TER and strong ME coupling, showing that ferroelectric polarization switching of the tunnel barrier is not the main contribution.

To summarize, this thesis reports a new polar r-phase, with large polarization and robustness. According to the crystal studies on different substrates, specific guidelines are given on how to achieve this new ferroelectric r-phase in HZO thin films. Taking advantage of the great properties of HZO thin films with this new phase, the films were integrated as tunnel barriers into multiferroic tunnel junction. The properties of this device are studied, which give some insights for the future possible application. An intermediate stage has been achieved which unites 4-resistance states, 10^6% TER and TMR reversal upon electric field switching. Success in stabilizing such a stage for a large enough number of cycles will offer a new type of multifunctional device with important advantages with respect to current solutions.