Thin piezoelectric films for micro-electro-mechanical components

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Abstract

$PbZr_xTi_{1-x}O_3$ (PZT) films on silicon substrates can be used for various micro mechanical devices. An in-situ reactive sputter deposition process at 600 °C has been developed for this application. Three magnetron sources with metal targets have been applied simultaneously. Within a certain process window, the [Pb]/([Zr]+[Ti]) ratio in the film is self stabilized at stoichiometry by desorption of the excess Pb. Films of up to 1 micron thickness have been fabricated. For the composition x = 0.4 the films exhibit a remanent polarization of 20 to 25 µC/Cm^2 . a dielectric constant of 1100 and a piezoelectric coefficient of 40 pic/N. The classical Pt/Ti bottom electrode needed to be improved by an additional layer of TiO_2 between Ti and Pt. As a second choice the metallic oxide RuO_2 has been investigated, too. PZT films on prototype membrane structures are currently processed. They will be applied in prototype micromotors for the watch industry.

1. State of the knowledge

In the past few years, the feasibility of piezoelectric micro mechanical devices, such as micromotors, has been demonstrated using ZnO films [1,2]. However, the performance of these devices could be substantially improved by applying ferroelectric materials for the actuation. The well known $Pb(Zr,Ti)O_3$ (PZT) exhibits a 5 to 10 times higher electro-mechanical conversion efficiency than ZnO. The application of PZT will therefore allow to increase the amplitudes and/or decrease the necessary voltages. A PZT micromotor has been demonstrated recently [3, 4]. The duration of its operation was, however, very short due to the fast degradation of the material. In fact little is known on life time aspects with regard to mechanical applications. The recently published piezoelectric constants of thin films are lower than the ones of the bulk ceramic . In most of the films the constants in zero field (d_{33} = 70 pm/V [5]) are only about half of the constants at a saturated polarization in an external field (d_{33} = l50 pm/V [5]). This behaviour reflects the fact that the remanent polarization of the film is also much lower than the saturated one.

The main part of this project is the development and the investigation of sputter processes for PZT. It is expected that the film quality of in-situ sputter deposited films is higher than the one of recently developed Sol Gel films. There are several methods for the sputter deposition of ferroelectric oxide films such as PZT. Single sources. with a two-metal segmented target [7], or with a composite oxide target [8], as well as cosputtering with metal or oxide targets, have been applied. Three different geometries exist in the latter case: static cosputtering with focused sources, facing target sputtering [9]. and simultaneous sputtering onto a rotating substrate holder , where the substrate passes the two sources alternately [10,1 1,12]. In addition one has the choice of in-situ deposition at elevated temperatures or a deposition at moderate temperatures followed by an anneal. In the latter case the as deposited film needs to have excess lead (10 % or more) to compensate for the reevaporation of lead during the post-deposition anneal. This lead loss causes pits and holes along grain boundaries [13].

For this reason we decided to apply an in-situ technique. Since the relative fluxes of the three oxides needed is expected to depend on temperature and sputter conditions the multi-source target approach with single metal targets is much more practical.

2. Experimental description

The PZT and the electrode films were grown in a NORDIKO 2000 sputter-system with three 100 mm magnetron sources on the bottom of the chamber. The oxides were grown by reactive sputtering from metallic targets. The oxidation of the Pb target was achieved with less oxygen in case of rf excitation. A careful anode design turned out to be necessary to obtain reproducible results and to avoid flaking and particles. Above about 8 mtorr sputter gas pressure, Ar could no longer be used because the Pb target started to eject particles, leaving holes in the target surface. The process conditions for PZT finally chosen are given in table 1.

	Pb	Zr	Ti	$PbZr_{0.5}Ti_{0.5}O_3$
power (W)	200 rf	170 dc	250 dc	
dc voltage (V)	410	340	500	
substrate temp.	600 °C			
sputter gas	16 mtorr O_2			
rate (nm/min)	5.2	1.2	0.7	3.0

Table 1. Growth conditions of the sputter process. The rates for the individual sources are for oxide depositions at room temperature.

The wafers were mounted on the disk-like substrate carrier, face down. The dynamic rate obtained with the rotating substrate carrier was 10 times lower than the static rate. The rotation speed was usually 6 rpm, which roughly corresponds to a monolayer of PZT per cycle. The substrate was heated indirectly by radiation from the 4" steel substrate holder.

3. Results

3.1. PZT thin film growth

We investigated the growth of the films with varying PbO fluxes at constant ZrO_2 and TiO_2 fluxes. and for several Zr/Ti ratios. In a broad temperature range the‘ Pb content of the film is stabilized at stoichiometry when more PbO is offered than needed. This means that excess Pb(O) is desorbed from the surface of the growing film. This desorption is not only of thermal nature, it is to a larger extent caused by the high energy of atoms, ions and electrons of the sputter process and the plasma. While this behaviour has already been reported for $PbTiO_3$ (PT) [11,14]. it is a new result for PZT. With high PbO fluxes of 2 times the TiO_2 flux or more, we were able to grow <100> oriented PT films at 560°C [iii]. The behaviour of the $PbZrO_3$ system is much different from that of the PT system. It was not possible to grow PZ films with the same method at 560°C. PbO and ZrO_2 did not form a perovskite compound. However, the method worked in the range between 0 and 53 % Zr content at 600°C. Once the perovskite was formed, it was possible to decrease the Ti flux. In this way we could extend the limit to 70 % Zr. We succeeded in growing <100> oriented PZT films on a thin layer of <100> oriented PT (Fig.1). TEM investigation revealed a fairly good quality of our films with no second phases. The TEM photograph on Fig. 2 shows the large difference in domain structure between Ti rich and Zr rich compositions.

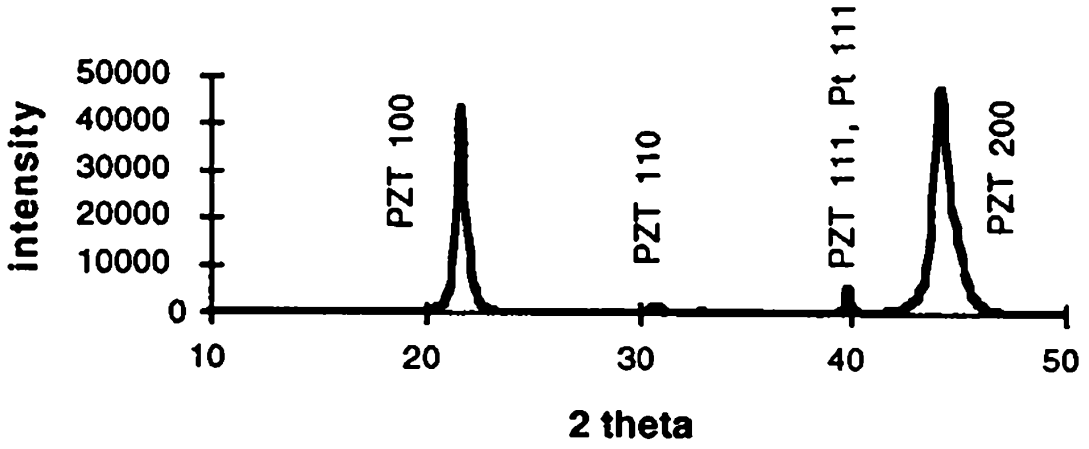

Fig. 1. Spectrum of x-ray Bragg peaks for a 1.2 pm thick PZT film grown on a 30 nm thick PT seed layer.

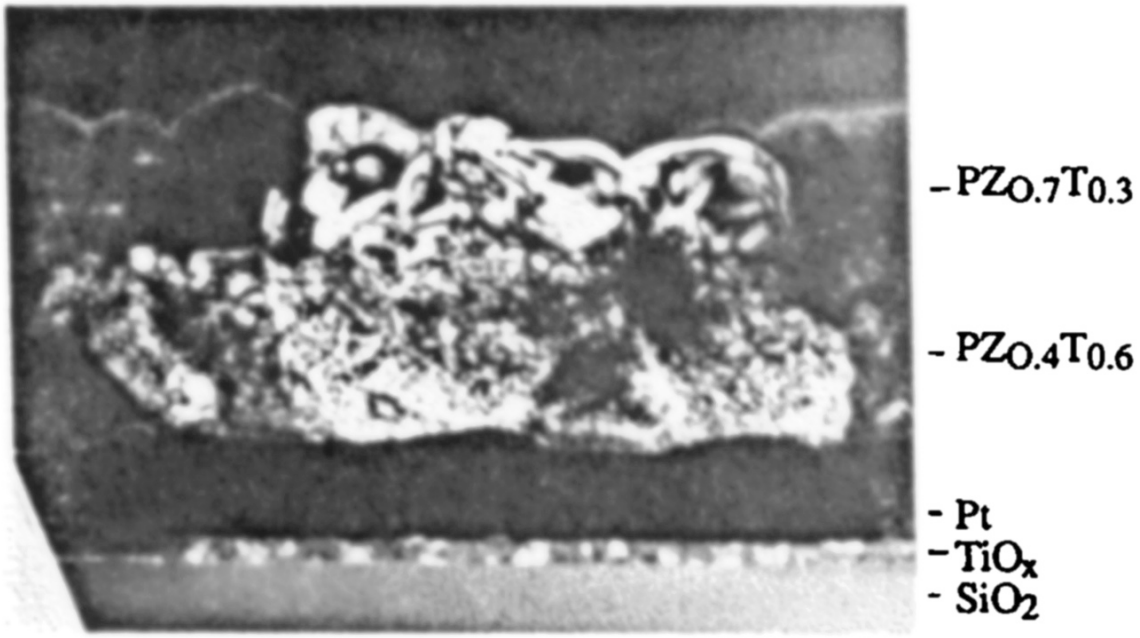

Fig 2. TEM image showing the cross section of a PZT/Pt film in the dark field view. The upper half of the PZT film has a Zr content of 70 %, the lower of half 40 %.

3.2. PZT thin film properties

We have no data yet of the optimal composition for the highest piezoelectric constants. The film with the highest dielectric constant so far was a <100> oriented, 1.2 µm thick film with 40 % Zr, grown on 30 nm of PT. The measured value of 1100 for the dielectric constant is higher than expected for this composition. The loss tan δ of 4% at 10 kHz is usual for PZT films. The hysteresis curves for the polarization and the piezoelectric constant d_{33} of this film are shown in fig. 3. The remanent polarization amounts to 20 µC/cm^2 and the piezoelectric constant d_{33} is 45 pC/N at 100 kV/cm and 20 pC/N at zero electric field. The low d_{33} values correspond to the 40 % Zr content. The asymmetry of the curves must be assigned to the asymmetrical layer sequence introduced by the PT sub-layer, to non uniform stresses or to unequal interfaces to top and bottom electrode.

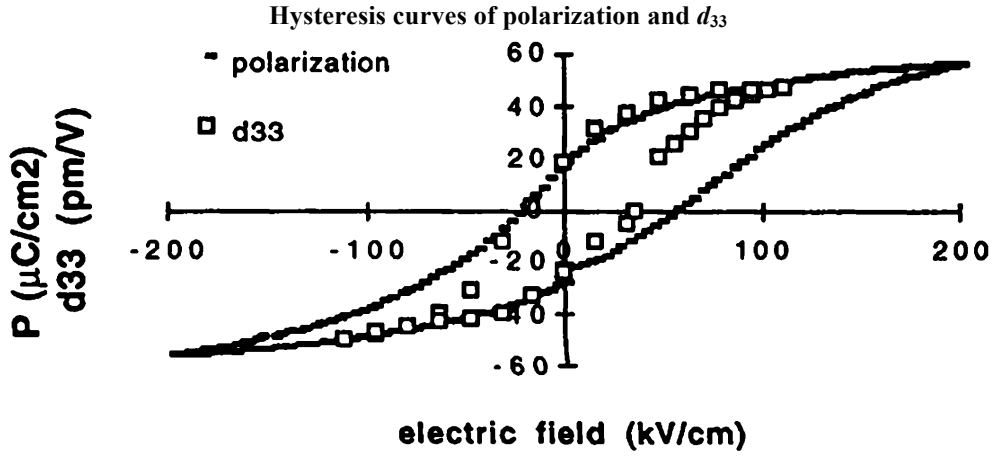

Fig. 3. Hysteresis loops of polarization and piezoelectric coefficient d_{33} for a 1.2 µm thick $PZ_{0.4}T_{0.6}$ film grown on 30 nm PT (platinum electrodes on both sides). In order to illustrate the similarities of the two loops, the sign of d_{33} is inverted for a negative polarization. d_{33} has been measured by means of interferometry.

3.3. Electrodes

The efforts made in the period 92/93 of the project enabled us to stop the deterioration of the Pt/Ti electrode by introducing a TiO_2 layer between Ti and Pt [i]. The new electrode allows to grow in-situ PZT films by sputtering and to fabricate 1 micron thick Sol Gel films, which require several heat treatments [iv]. In addition to platinum based electrodes we studied also deposition processes for the metallic compound RuO_2, which proved to be an excellent barrier material against oxygen diffusion.

Films with resistivities of less than 50 µΩ·cm were obtained. Thermal oxidation tests of RuO_2 directly on silicon showed that the interface remains intact up to 650 ‘C, above which the contact resistivity increases due to oxidation of Si or alloying.

3.4. Thin film integration onto membranes

The processing for the integration of the sputter deposited PZT films on membrane structures is currently investigated in the "laboratoire de céramique". The membranes are composed of SiO_2 and Si_3N_4 layers and are identical to the ones used in the LESIT project on pyroelectric detectors [15].

Membranes with PZT on top and dimensions of 4×4 mm have been fabricated. As an alternative to the insulating membranes we also fabricated a metallic membrane with low thermal expansion metals (Mo,W). Its strength needs to be improved, though.

The design of piezoelectric prototype micromotors has been accomplished by ASULAB/IMT (NB). First structures have been fabricated.

4. Outlook

Once the fabrication of membranes with PZT is mastered, a systematic study of the membrane behaviour is planned. The variables will be film thickness, film composition and membrane size and geometry. PZT films will be investigated with regard to composition, doping (e.g. Nb), stress and orientation. Possible new electrodes as RuO_2 or $(SrBa)CoO_3$ will be checked in the membrane structure. With their good oxygen barrier properties, such new oxide electrodes facilitate the growth of PZT on metallic membranes.

In parallel PZT films integrated in motor test structures will be evaluated by ASULAB in collaboration with the "institut de microtechnique" of the university of Neuchatel. The goal of the project is to arrive at a well reproducible fabrication process, a high piezoelectric efficiency of structure and materials together with a low degradation with time, in order to enable the fabrication of piezoelectric micromotors for watches.

5. Literature of the project

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