Ferroelectric Thin Films for Microsystems

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Abstract

Deposition, integration and application issues of ferroelectric thin films are briefly reviewed. Applications in ultrasonic micromotors and infra-red sensors are treated in more detail. Current results on stress measurements across the ferroelectric phase transition and on pyroelectric devices are presented.

1 Introduction

For many years, ferroelectric materials with excellent piezoelectric and pyroelectric properties have been known. Bulk ceramics or single crystals are routinely applied in, e.g., vibration sensors, ultrasonic motors, surface acoustic wave devices, acoustic generators and receivers for medical applications, and pyroelectric detectors for security and temperature sensing systems. The application of thin films in microsystems is not yet as advanced. However, in recent years, a number of research groups have concentrated their efforts on the preparation of such materials as thin films and their integration into micro-actuators, sensors, and microwave and electro-optical devices. An even greater research activity exists in the area of ferroelectric static memories and dynamic RAM devices based on such films due to their switching properties and high permittivities.

Various obstacles were and are encountered on the way to achieving a perfect film for a given device. High quality films require deposition or annealing temperatures of around 600 °C in oxygen or air. For this reason the deposition process often is not compatible with other materials in the device: Interdiffusion and/or delamination may occur. Film growth conditions and integration technology influence each other and both affect the device performance.

Due to its outstanding properties, i.e. high piezoelectric coefficients and its high ferroelectric polarization, the perovskite structured compound $PbZr_xTi_{1-x}O_3$ (PZT) is one of the most studied materials for ferroelectric thin films. At high Ti concentrations a suitable pyroelectric material with a fairly high pyroelectric coefficient and a rather low dielectric constant is obtained. Compositions near the morphotropic phase boundary (x=0.5) are chosen for high piezoelectric coefficients. The latter are about ten times higher than in ZnO. which is a non—ferroelectric piezoelectric material that is often used in micro devices due to its better compatibility with semiconductor processes.

In this paper different aspects of deposition, integration, device fabrication and applications of PZT films are reviewed. Emphasis is given to piezoelectric thin films for micromotors and pyroelectric thin films for infra-red detectors.

2 Thin film deposition

A historical review of ferroelectric thin film deposition is given in ref. 1. Whereas before 1990 mostly physical deposition techniques (evaporation, RF sputtering) were applied, chemical methods dominate at present. Metal-organic-chemical vapor deposition (MOCVD) is the preferred technique for IC applications, because of its superior step coverage. Metal-organic deposition (MOD), with or without sol-gel reactions, is likely to emerge as the leading method for actuator and sensor applications because of the low investment needed.

PZT thin films are grown between 500°C and 700°C with in-situ deposition techniques like sputtering [2,3] or MOCVD [4,5]. A post-anneal for sol-gel deposition has to be carried out at temperatures between 600 and 650°C [6]. All processes usually work with an excess of lead. Lead or PbO desorb quickly from the surface at these temperatures, as long as they are not incorporated in the perovskite lattice. With in-situ deposition techniques one observes a self stabilization of the lead content at stoichiometry above a critical temperature, even for large quantities of excess lead flux. The critical temperature depends on the deposition method and is 700°C for $PbTiO_3$ grown by MOCVD [7], and was found to be lower for sputter deposition (550°C) due to plasma effects [3].

3 Integration

The choice of substrate is usually dictated by the application or by the need to lower production costs. Hence, the substrate is often not the most ideal one for growing the ferroelectric thin film. The integration technology has to solve adhesion and interdiffusion problems and should provide means to arrive at the required film microstructure. Finally, also the patterning, i.e. the etching of the involved films, has to be mastered.

The most important substrate for micro systems is silicon. High quality PZT films cannot be grown directly on it. Buffer layers are needed to prevent interdiffusion and oxidation reactions. For most applications, the PZT film has to be grown on an electrode, which obviously should not oxidize and not become insulating. The most often reported materials include platinum, and the metal oxides RuO_2 (rutile structure) [8] and $(La,Sr)CoO_3$ (LSC, perovskite structure) [9]. Normally, a thin adhesion layer is needed between the buffer layer and the electrode.

A very popular sequence is $PZT/Pt/Ti/SiO_2/Si$. Platinum does not inhibit the diffusion of Ti to the PZT side, where it reacts with oxygen and serves as nucleation centers for PZT. There is also evidence that oxygen migrates along the grain boundaries through the platinum film and reacts with the Ti layer [10]. For stable electrodes the latter has to be preoxidized [10].

The requirements with respect to film microstructure depend on the application. For pyroelectric applications it is advantageous to have a textured film with the ferroelectric polarization perpendicular to the substrate plane. Also for piezoelectric applications textured films are sufficient. Electrooptic and probably also high density memory applications need epitaxial films. The PZT film orientation is governed by process conditions and electrode texture. The intrinsic preference is the (100) orientation, and is best obtained at high lead fluxes (in-situ sputtering)[3]. Since $PbTiO_3$ is easier to orient than PZT, the latter is also grown on $PbTiO_3$ templates (see figure 1). Certain nucleation conditions allow to grow (111) oriented films on the typically (111)-textured Pt, because of a near lattice match between Pt and PZT [11]. For epitaxial growth the buffer layer has to be grown epitaxially on silicon. A complete epitaxial sequence was obtained with yttria stabilized zirconia as buffer layer, $Bi_4Ti_3O_{12}$ (a layered perovskite) as a link to perovskites, and LSC electrodes [9].

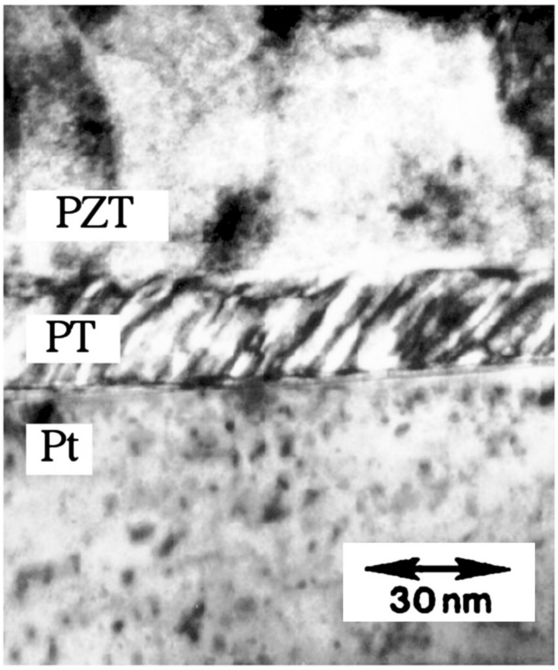


Figure 1. Transmission electron microscope image of a 30 nm thick $PbTiO_3$ template film between the platinum electrode (bottom) and the PZT film. The oblique stripes are caused by the domain structure of alternating (100) and (001) orientations (from ref. 12).

In $PbTiO_3$ an additional complication arises due to the cubic-to-tetragonal ferroelectric phase transition below the deposition temperature. The tetragonal c-axis, which is the polarization axis, becomes larger with decreasing temperature, whereas the a-axis shrinks. Statistically, a perfectly textured (100) film of the high temperature phase would have only 1/3 of its polarization perpendicular to the substrate plane (c-axis orientation). In reality this ratio is influenced by the thermal expansion mismatch between substrate and film [13,14]. Well c-axis oriented films are obtained on $SrTiO_3$ [15] and MgO [16] substrates, because their high thermal expansion compresses the film upon cooling down from the growth temperature and the smaller a-axis is switched into the plane.

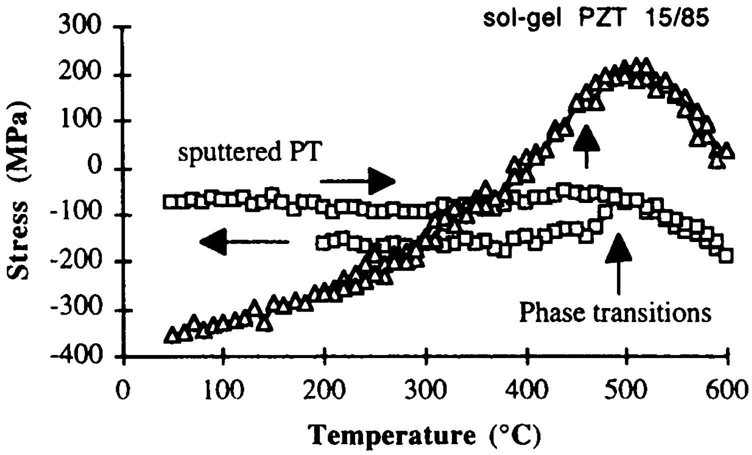


Figure 2: Film stress vs. temperature. The measurements have been performed with a commercial system (FLX 2900). The curves result from the difference between the substrate curvatures with and without (etched off) PZT film. Positive values indicate tensile stress, while negative indicate compressive stress. The phase transitions are marked as known from bulk ceramics.

Due to its smaller thermal expansion, the opposite takes place on silicon substrates. Tensile stress is compensated by switching the c-axis into the plane and thus useful polarization is lost. The splitting between the a and c-axis is so large that stress anomalies can be observed (see fig. 2) as a function of temperature. Pure c-axis orientation would give a peak towards compressive stress, pure a-axis orientation towards tensile stress. The sol-gel film in fig. 2 obviously has much more a than c-axis orientation and most of the polarization is in the plane. The sputter deposited film has more c-axis orientation, due to a compressive stress built up by bombardment of high energy particles and a lower deposition temperature. A part of this c-axis orientation is lost during thermal cycling. Stress measurements also show that stress relaxation by 90° domain flipping does not occur below 300°C.

4 Applications

4.1 Memory applications

The further down scaling of the charge storage capacitors of dynamic memories requires materials with high dielectric constants, such as $(Ba,Sr)TiO_3$ [17], which exhibits values of 200 to 800. This material is operated above the ferroelectric phase transition, which is below room temperature, and possible problems due to poling and depoling phenomena are thus avoided. In order to judge the film quality of $(Ba,Sr)TiO_3$ with respect to the currently applied SiO_2/Si_3N_4 films one has to compare the charge density at a given leakage current density. The best reported results correspond to an equivalent SiO_2 thickness of 0.4 nm [18,19].

The switching polarization of ferroelectric films allows fabrication of static memories, which could replace EPROM's for instance. The best studied materials in this case are PZT [20] and $SrBi_2Ta_2O_9$ [21,22]. Intrinsic switching times of less than 2 us have been observed in PZT [23]. Although a number of thin film processing problems have been solved, there are still some open questions concerning integration, performance and reliability. The most important reliability issue is the fatigue of polarization after a number of switching cycles observed in PZT with platinum electrodes. Piezoelectric measurements show that the polarization just stays in one state and no longer switches [24]. PZT films showing no fatigue up to 10^{12} cycles have been demonstrated by using oxide electrodes [9]. The same life time was demonstrated with $SrBi_2Ta_2O_9$, applying platinum electrodes [22]. However, 10^{15} cycles (one year test time!) are demanded by the IC industry. The main problem in mastering fatigue is that the underlying physics are not yet understood, and thus no accelerated tests can be designed. One of the major differences between films and bulk ceramics lies in their semiconductor properties, since the depletion layer is of similar thickness as the film. It is also thought that oxygen vacancies play an important role.

However, in spite of some lack of understanding at the present time, ferroelectric films might become a part of the standard repertoire of modern semiconductor fabrication lines in the future, as the current rate of advancement is rather fast.

4.2 Ultrasonic micromotor

Piezoelectricity is a competitive actuation principle for micro-actuators. The heat dissipation is much smaller than with thermal bi-metal actuation and there is practically no upper frequency limit imposed by the material. With regard to electrostatic actuation, a higher energy density per volume can be achieved (PZT has a dielectric constant of around 1000) and the required structures are usually simpler. The saturated piezoelectric constant d33, as determined by means of optical interferometry, approaches the bulk ceramics values of undoped PZT [25].

An especially fruitful field of application is ultrasonic micromotors. These are considered to be superior to other types of micromotors for down scaling [26]. Such micromotors could allow further miniaturization accompanied by an increase in the functionality of micro robots, autofocusing lens systems, watches and precision positioning devices. The fabrication technology has to be adapted to the small dimensions, though. One possible approach is a so-called hybrid micromotor, where the stator consists of a piezoelectric thin film on a micro-machined silicon diaphragm. The rotor is fabricated by rather classical means and added in an assembly step.

The first well working PZT ($PbZr_xTi_{1-x}O_3$) thin film micro motor has recently been demonstrated [27,28] by the authors, applying a hybrid type motor with an elastic fin rotor [29]. The motor was operated with voltages as low as 1.0 Vrms, which is sufficiently low for standard battery and IC supply voltages. In fact, for the same speed, 3 to 6 times less voltage was needed as compared to the previously published ZnO version [30] (see fig. 3).

The stator can be run without switching the polarization. It is possible to make one polarization direction more stable than the other one, as revealed by deflection measurements at the stator diaphragm (see fig. 4). This built-in asymmetry is process related and helps also to raise the polarization at zero field. Without switching of polarization, fatigue is no issue. However, depoling with time might occur. First degradation tests under operating conditions revealed a decrease in amplitude of 5 % in 100 hours [31].

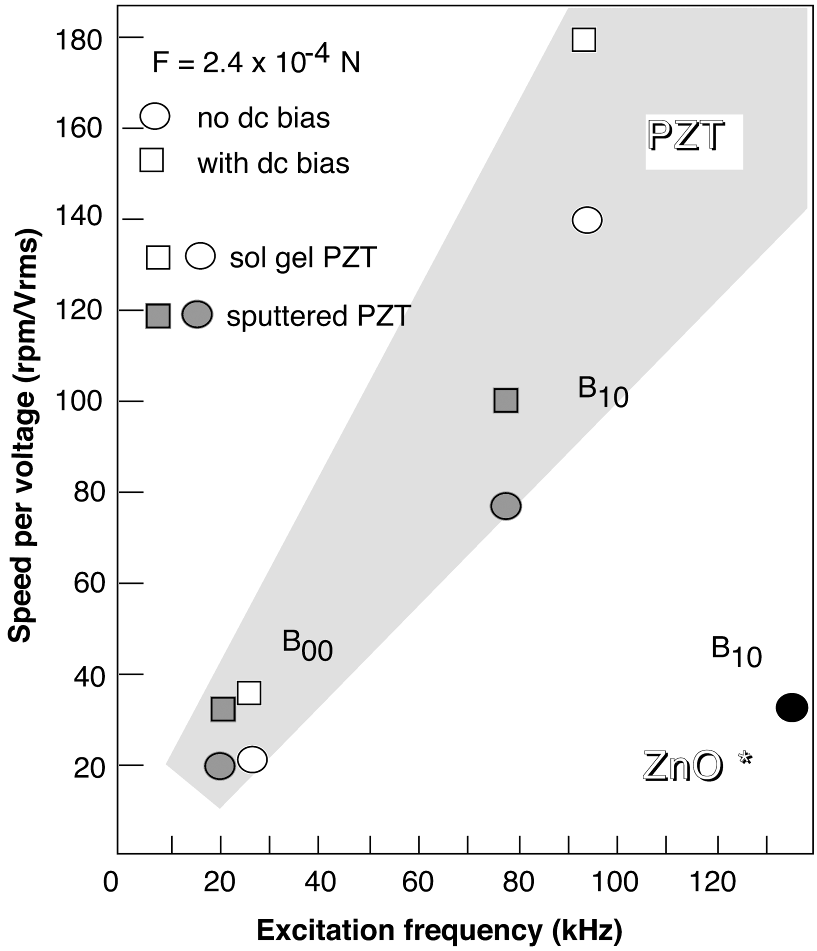
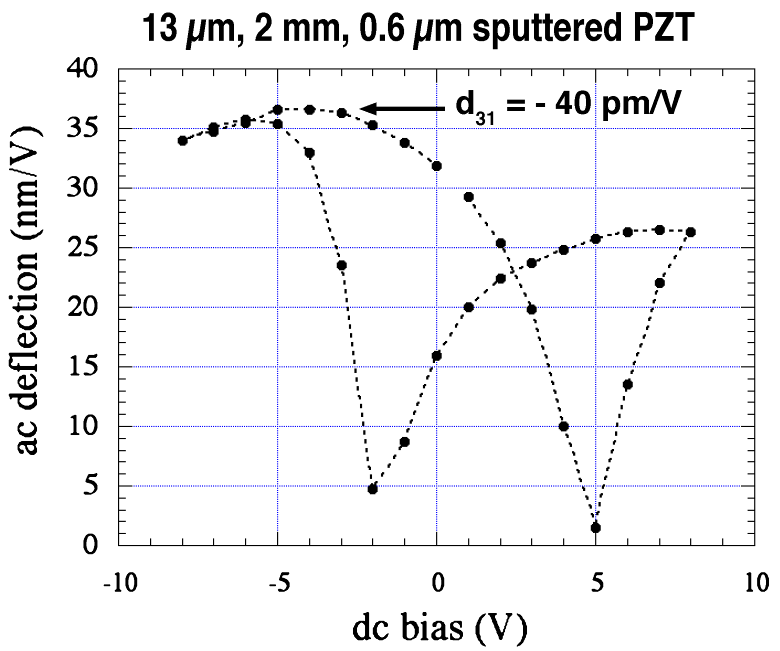


Figure 3. The speed per voltage for different operating conditions and membrane modes (from ref. 28). The data for ZnO are from ref. 30.

Figure 4. Interferometric deflection measurements at circular diaphragm at quasi static operation (from ref. 30). The ac frequency was much below the first resonance.



4.3 Infra-red detectors

Pyroelectric infra-red detection could be a very fruitful application for ferroelectric thin films. Preliminary calculations show that the potential sensitivity of micro machined thin film devices is the same as that of single crystal devices. This is achieved by an extremely good thermal isolation of the element. In addition, the estimated production costs are low and interesting for sensor arrays. Several industrial laboratories have programs for the development of 2-dimensional arrays for thermal imaging [33]. The work presented in the following is part of a project for the development of a security sensor [34,35] with 2 or more elements.

The schematic cross section through two elements of an array is shown in fig. 5. The devices were fabricated on standard 300 µm thick, 3 inch diameter silicon wafers with 0.65 µm of thermal oxide and 0.2 mm of Si_3N_4. The two layers serve as thermally insulating membrane material and as a mask for backside etching in KOH. First the back-side Si_3N_4 was patterned by plasma ion etching. A continuous bottom electrode of 0.1 µm Pt on a 10 nm Ta adhesion layer was deposited by sputter deposition on the front of the wafer. A 1.5 µm PZT film was then deposited by the sol-gel technique and then patterned by standard photolithography. For good thermal insulation and low cross talk between neighboring elements, the platinum and PZT layers were removed where it was possible. The structured top electrodes of Au/Cr served as seed layers for the electrolytic black platinum deposition. Anisotropic etching of the backside was carried out in aqueous KOH solution, while protecting the front side, to leave SiO_2/Si_3N_4 membranes 0.7 to 0.8 µm thick, 2.4 by 11 mm in dimension and carrying 12 to 50 elements.

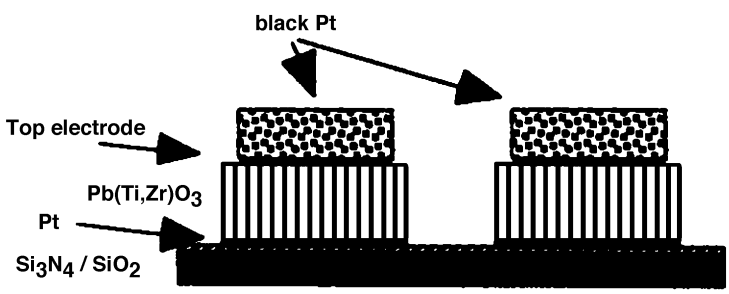


Figure 5: Schematic cross section through two elements of an infra-red detector array.

The PZT films had a low Zr content of 15%. Zr allows growth of thicker films and a lowering of the dielectric loss as compared to $PbTiO_3$. The disadvantage lies in the fact that the dielectric constant increases. The (111) growth direction was chosen, since a high c-axis orientation is not possible with the sol-gel method on silicon substrates. After poling at 125 °C a pyroelectric coefficient of 170 $\mu C/m^2/K$, a dielectric constant of 250 and a loss of 1.1% were measured. Current and voltage responses of the device were tested with a 1 mW Ar laser as the radiation source and a mechanical chopper to provide modulation in the range 0.1 to 100 Hz. The resulting responsivities are shown in fig. 6. Their values are quite satisfying, since they are much higher than in thermopile structures. On the other hand, the responsivity of monocrystal devices is still a factor of 4 higher.

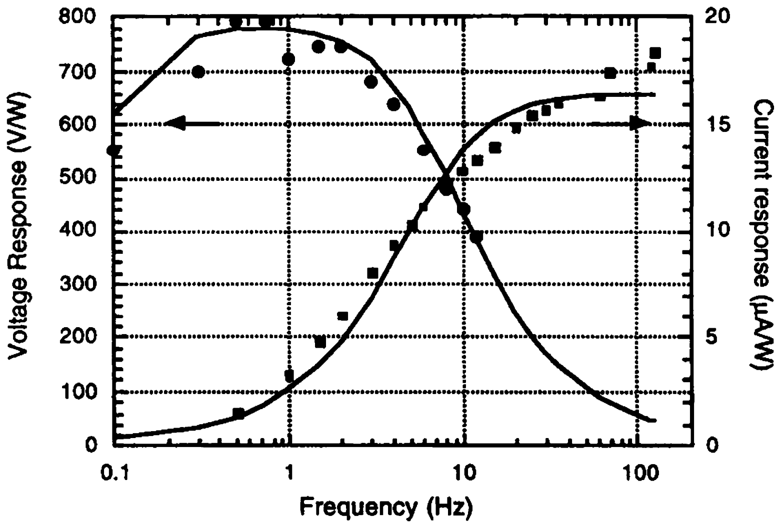


Figure 6: Measured voltage and current responsivities as a function of modulation frequency for PZT pyroelectric array element.

5 Conclusions

Ferroelectric thin films offer alternative and new solutions for microsystems. The deposition and integration technology have advanced to such a level that the first ferroelectric thin film products will see the daylight in the near future. There are still open questions regarding stability, degradation and reliability. Research has to concentrate efforts on these questions and has to improve the performance of the basic materials.

Acknowledgements

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