Thickness and erbium doping effects on the electrical properties of lead zirconate titanate thin films


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Abstract

Thin films of erbium doped lead zirconate titanate (PZT) of different thickness were deposited by sol–gel technique on Pt/TiO₂/SiO₂/Si substrates. Capacitance–voltage measurements show that the dielectric constant continuously increases with the thickness. This is interpreted in terms of effects due to a low permittivity interfacial layer in series with the ferroelectric bulk. The linear fit of the reciprocal of capacitance vs. thickness leads to a true dielectric constant of the ferroelectric of 774 and interfacial capacitance of 14.6 nF. The leakage current properties also depend on thickness and temperature. The calculated interfacial potential barrier height amounts to 0.81 and 0.74 eV, respectively for erbium doped and pure PZT thin films.

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1. Introduction

Thickness effects on dielectric and leakage current properties of ferroelectric thin films have been investigated for years for both barium–strontium–titanate (BST) [1–4] and lead-based titanates [5–9]. It is reported that an interfacial layer between electrode and ferroelectric bulk could cause the deterioration of the dielectric properties due to its low dielectric constant and high trap density. Whether this interfacial layer consists of different chemistry to that of the bulk is still the subject of controversy. Paek et al. [4], Chung et al. [10] and Algueró et al. [9] report on the observation of an intermediate layer in Pt/BST/Pt [4], Pt/lead zirconate titanate (PZT)/Pt [10] and Pt/lanthanum doped lead titanate (PLT)/Pt [9] capacitors using high resolution transmission electron microscopy and Auger electron spectroscopy, whereas Sakashita et al. [8] deny the formation of such a layer between PZT and Pt electrodes on the basis of X-ray photoelectron spectroscopy (XPS) investigations. Sakashita et al. [8] suggest that the stress due to thermal expansion mismatch between ferroelectric and substrate could play a role in the dielectric properties of the metal–ferroelectric–metal (MFM) structure systems. In this case, the dielectric constant would not increase linearly with the thickness, but would show a peak before it decreases with thickness.

For the leakage current behaviour in MFM structures, a popular view is that the leakage current mechanism is mainly due to the Schottky emission which reflects itself as a typical quadratic dependence of the leakage current curves on applied voltage [11–13]. Thickness effects on leakage current have been investigated mostly on BST [4,11] and PZT [7] systems. The Schottky-type conduction mechanism has been reported both for BST [11,12] and PZT [7,12]. However, depending on thickness and voltage range the space charge limited current (SCLC) has also been advanced as a conduction mechanism [7]. It appears that conduction in PZT films is quite complex and may involve different mechanisms depending on processing, temperature, voltage range and thickness [12–14]. As stated by Scott [12], it is difficult to isolate the operating mechanisms since voltage dependence of the leakage current density may give rise to similar behaviour (voltage exponents) for different mechanisms.

Doping of ferroelectric perovskite with donor or acceptor elements on A or B sites is a common strategy to improve or tailor specific properties. Donor doping is known to compensate for oxygen vacancies and so to
lead to higher resistivity and lower leakage currents [15]. Due to the fact that donor doping is compensated by A site vacancies, a higher domain mobility is expected which in turn results in higher dielectric constant and higher losses [15]. In contrast, acceptor doping is compensated by oxygen vacancies, and would rather lead to higher leakage currents and stronger domain pinning. Reports about thickness effects on doped perovskite ceramics are rare [5,9], and a systematic investigation is still lacking. In this article, we investigate the microstructure, dielectric and ferroelectric properties as well as leakage current behaviour of erbium doped PZT (PEZT) thin films as a function of thickness. The results are to some extent compared to those obtained on non-doped PZT.

2. Experimental

Lead acetate, erbium acetate, titanium and zirconium propoxides were used as starting materials. The ratio between zirconium and titanium was 35:65 in mole ratio, and 5 mol% of erbium was designated to replace lead. Acetylacetone was used to stabilize the solution, and 2-methoxyethanol was added to dilute the solution to the desired concentration of 0.5 mol/l. The preparation details were described before [16]. For the deposition of PEZT thin films on (1 1 1)Pt/TiO$_2$/SiO$_2$/Si substrates, two stages of deposition steps were applied: first 800 rpm for 6 s to cover the substrates and the following 5000 rpm for 20 s to get a dense uniform layer. Pyrolysis of the layers was conducted on a plate at 350 °C for 5 min. After each two-layer coating, the specimen was treated in preheated furnaces at 500 °C for 15 min followed by 700 °C for 10 min for crystalization of the films. We have prepared four specimens with two, three, six and eight layers. The thickness was determined by scanning electron microscopy on cross-section specimens.

The crystalline structure was investigated via X-ray diffraction (Seifert 3000 PTS powder diffractometer, Cu Kα radiation, λ = 1.5418 Å), and microstructure was observed in the SEM (Philips XL 30). Electrical measurements were conducted on capacitors obtained by sputtering of Pt electrodes with the area of 2.8×10$^{-3}$ cm$^2$ through a shadow mask. A post top electrode annealing at 400 °C for 15 min was performed before measurements. The small signal dielectric properties were characterized using a computer controlled Agilent 4192A impedance analyser at 50 mV drive signal. Capacitance vs. DC bias voltage curves were obtained in the voltage range from −20 to +20 V using a voltage step of 0.1 V. Ferroelectric properties were investigated using a commercial system RT6000S (Radiant Technology Inc., USA). The leakage currents vs. DC voltage and vs. time at constant voltage were measured by a programmable electrometer (Keithley 6517A) using a staircase increment of 0.1 V and 5 s dwell time.

3. Experimental results

3.1. Microstructure

A typical X-ray diffraction pattern of a six-layer specimen is shown in Fig. 1, where the diffraction peaks were mainly (1 1 0) and (1 1 1) of the tetragonal perovskite phase, with a weak (1 1 1) peak. No second phase could be detected. This suggests that the crystallized thin film have preferred (1 1 0) and (1 1 1) orientation on the (1 1 1)Pt/TiO$_2$/SiO$_2$/Si substrate.

Regardless of film thickness fine, columnar microstructures were obtained with a grain size in the range from 50 to 100 nm. This is exemplified in Fig. 2. The SEM micrograph of Fig. 2a shows an almost featureless surface topography. The cross-section micrograph of Fig. 2b illustrates the fine columnar structure obtained. The processing conditions and processing parameters adopted seem therefore to be appropriate for the processing of high quality thin films.

3.2. Thickness effects on the dielectric properties

The capacity of PEZT thin films as a function of thickness was investigated systematically at ambient temperature. Fig. 3a shows a frequency sweep from 100 Hz to 100 kHz, where some frequency dispersion of the capacity can be seen. According to the widely accepted model for metal–ferroelectric–metal structure where the whole structure is treated as a ferroelectric bulk capacitor with the capacity $C_b$ in series with an interfacial capacitor between the electrode and ferroelectric bulk with the capacity $C_i$, the measured capacity $C_m$ of the MFM structure can be expressed as follows [3,9,17]:

![Fig. 1. X-ray diffraction pattern of a 600-nm thin PEZT film.](image-url)
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Fig. 2. Back-scattered electron micrographs of a 600-nm thin film: (a) surface topography; (b) cross-section.

\[
\frac{1}{C_m} = \frac{1}{C_b} + \frac{1}{C_i} = \frac{d_b}{\varepsilon_o \varepsilon'_b A} + \frac{1}{C_i}
\]  \hspace{1cm} (1)

where, \(d_b\) represents the thickness of the ferroelectric bulk in the MFM structure, and is usually treated as the thickness of the specimen since the interfacial layer is assumed to be very thin compared to the whole thickness of the capacitor; \(\varepsilon_o\) and \(\varepsilon'_b\) are the vacuum dielectric constant and relative dielectric constant of the ferroelectric bulk, respectively; \(A\) is the area of the capacitor.

From Fig. 3a, the value of capacity at 10 kHz is selected for different thickness. The plot of the reciprocal of \(C_m\) vs. film thickness \(d\), Fig. 3b, can be well fitted to a straight line in agreement with Eq. (1). The intercept with the ordinate axis yields an interfacial capacity \(C_i\) of 14.6 nF, and the slope allows an effective, thickness independent dielectric constant, \(\varepsilon'_b\), of 774 for the ferroelectric to be calculated. This value is higher than that found for PEZT bulk ceramics of similar composition [18], and may be attributed to effects related to thin film formation, microstructure and stress states.

3.3. Capacity vs. voltage (C–V) behaviour

The C–V curves were measured via changing the DC bias voltage from negative maximum value to positive maximum ‘sweep up’ followed by the opposite process ‘sweep down’. For each specimen, the C–V curves were measured at different temperatures.

In Fig. 4a the DC bias voltage dependence of the dielectric constant at different temperatures for the 600 nm specimen is shown. At all temperatures, the dielectric constant vs. applied voltage displays the characteristic butterfly shape, which is specific to ferroelectrics and denote the contribution of domain wall oscillations to the dielectric constant. With increasing temperature, the dielectric constant increases steadily indicating enhanced mobility of ferroelectric domains at elevated temperatures. It can also be noticed that the coercive field and the coercive field asymmetry (internal bias field) decrease with increasing temperature. The C–V curve
of a non-doped 455 nm thin PZT Film processed under the same conditions is also shown in Fig. 4b. In comparison to PEZT thin film of similar thickness, the dielectric constant is lower (550 in comparison to 620 for PEZT, both measured at 1 kHz and 50 mV drive signal amplitude) whereas the coercive fields are very similar.

In Fig. 4c, the $C$–$V$ curves of PEZT are compared for different film thickness. It can be seen that the dielectric constant increases with thickness, which can be attributed to the contribution of the interfacial layer being more and more attenuated with increasing thickness. Further the curves clearly show that the coercive field and coercive field asymmetry decrease with increasing thickness. These results may be due to the effects of the disturbed interfacial layer on the pinning of domain boundaries, and the existence of an internal bias field. Furthermore, it is well known that the $C$–$V$ curves, which are measured in a nearly statistic way, can deliver more information on the ferroelectric domain reversal under electric field than normal hysteresis loops. In all specimens, the apparent coercive field derived from voltage difference between voltages corresponding to the dielectric constant peaks in the $C$–$V$ curves which were smaller than those derived from the P–E loops (not shown here), which indicates that the reorientation of ferroelectric polarization under applied electric field is time dependent.

It is believed that there exists a coercive field, which is thickness independent in MFM structures, and can be expressed as [19]:

$$V_C = V_{C1} + E_C d$$  \hspace{1cm} (2)

where, $V_C$ represents the apparent voltage difference, $E_C$ the thickness independent coercive field for the ferroelectric bulk in the MFM structure, $V_{C1}$ is the voltage drop due to the interfacial layer, $d$ the apparent thickness of MFM structure.

Fig. 4d shows that $2V_C = +V_C + | -V_C |$ vs. thickness $d$ can be fitted to a straight line with the slope of 60
kV/cm being the thickness independent coercive field $E_C$ and the intercept of 1.60 V being the interfacial voltage drop.

A further characteristic of the $C$–$V$ curves obtained is their asymmetric behaviour with respect both to the dielectric constant peak and the coercive field/voltage. This behaviour can be attributed to different thermal and stress histories of the top and bottom interfaces during the preparation of specimen [17,20,21].

With regard to the voltage asymmetry which might be related to the built-in field in the MFM structure, Fig. 5a compares the thickness dependence of voltage corresponding to the dielectric constant peaks during sweeping up and sweeping down cases at 1 kHz and room temperature. The mean value of the coercive field given by $(E_x^+ + E_x^-)/2$ can represent the built-in field to some degree, and appears, together with the coercive field shift, to decrease with thickness. This might be also explained in terms of the built in field being due to some kind of disturbed interfacial layer with high trap density or to a space charge layer. That the asymmetry is more pronounced for the films with lower thickness that delineates the higher contribution of this layer to the overall ferroelectric properties.

To investigate the asymmetry of the dielectric constant, the relative difference between the dielectric constant peaks on the $C$–$V$ curves, defined as:

$$\Delta \varepsilon = \frac{\varepsilon_{\text{max}}^+ - \varepsilon_{\text{max}}^-}{\varepsilon_{\text{max}}^+ + \varepsilon_{\text{max}}^-}$$

(3)

where, $\varepsilon_{\text{max}}^+$ and $\varepsilon_{\text{max}}^-$ represent the dielectric constant value corresponding to the sweeping up and sweeping down cases, respectively, is plotted vs. temperature in Fig. 5b for the thickness range investigated. It can be seen that $\Delta \varepsilon$ decreases for all films with increasing temperature which suggests that screening effects of the switching field by entrapped charges at the electrode–ferroelectric interface are relieved with increasing temperature. This may be achieved either by the thermally activated recombination of defect pairs or the migration of defects (also thermally activated). The results might also be explained in terms of the stress state of the films and its relaxation at higher temperatures. Spierings et al. [21] measured the residual stress in Pt/PZT/Pt stacks and showed that compressive residual stresses are generated in the PZT films after top electrode deposition and annealing (similar to the processing procedure of the present work). They also showed that during thermal cycling the stress decreases before it changes sign at certain temperature. Because residual stresses are known to affect domain switching, their relief either with increasing temperature [21] or thickness [22] would lead to symmetrical $C$–$V$ curves of the ferroelectric film.

3.4. Leakage current properties

The leakage current density as a function of the applied voltage and temperature is exemplified in Fig. 6a for the 330 nm PEZT thin film. For comparison the leakage current curves of a non-doped PZT film with a thickness of 455 nm are also displayed (Fig. 6b). In both cases, the shape of the curves is similar to that reported by [13] for PZT thin films. It can be noticed that the leakage current increases with increasing voltage, first steeply then slowly suggesting a parabolic law. Furthermore, at fixed voltage the leakage current density increases with increasing temperature. Comparison of PEZT and PZT shows also that at similar temperatures PZT is characterized by higher leakage currents (at 5 V and 80 °C, the leakage current density of PZT is higher by approximately 3 orders of magnitudes). The double logarithmic plots shown in Fig. 6c yield straight lines at all temperatures with decreasing slopes at increasing temperatures. Such a behaviour has also been reported by Shin et al. [7] for sol–gel derived PZT thin films. The thickness effect on the leakage current is shown in Fig. 7a at a fixed temperature. It can be noticed that the leakage current density decreases with increasing thickness. The double logarithmic plots can be fitted to straight lines with slopes depending on thickness and temperature. With increasing temperature and/or thickness, the slopes decrease. The double logarithmic plot of the leakage current density, $J$, vs. thickness, $d$, at

![Fig. 5. Asymmetric behaviour of $C$–$V$ curves as function of thickness: (a) coercive fields; (b) relative difference of peak dielectric constants.](image)
constant voltages yields also straight lines with slopes depending on voltage, Fig. 7b. At high voltage a slope of 5 is obtained whereas, the slope decreases to 3.8 at lower voltage. These results, in the voltage and temperature ranges investigated, suggest that the SCLC may be the predominant conduction mechanism in the present PEZT thin films. In the SCLC mechanism the current density depends on voltage and thickness through [12,7]:

\[ J = C \frac{V^n}{d^m} \]  \hspace{1cm} (4)

where \( C, n \) and \( m \) are constants. This mechanism has been shown to operate for non-doped PZT, where values of \( n \) higher than 3 have been reported to arise from the continuous distribution of the trap energy in the energy band gap [7,12].

The time dependence of the leakage current density at constant voltage and different temperatures is shown in Fig. 8a for the 330 nm thin PEZT film. It can be seen that at the conditions indicated the current relaxes and relatively reaches a quasi-state value rapidly, depending on temperature. The values of the activation energy determined from semi-logarithmic plots of the current density dependence on the reciprocal of temperature were found to be 0.87 and 0.80 for PEZT and PZT, respectively. Plotting the current density dependence on temperature in the Schottky coordinates \( J/T^2 \) vs. the reciprocal of temperature \( (1/T) \) shown in Fig. 8b yields barrier heights \( \phi_b \) of 0.81 and 0.74 eV for
PEZT and PZT, respectively. The values found for PZT are lower than those reported in [13] for sol–gel derived PZT with a composition near the morphotropic phase boundary (Zr/Ti ratio of 45/55). The higher barrier height found for PEZT may arise from the effects of Er in compensating oxygen vacancies, known to be the origin of p-type conductivity of PZT.

3.5. Ferroelectric properties

The hysteresis loops of PZT and PEZT thin films of close thickness are shown in Fig. 9. It can be seen that similar properties are obtained, though the PZT film is characterized by somewhat higher remnant polarization. As to the thickness effects on the ferroelectric properties, all specimens exhibit well defined hysteresis loops with high remnant polarization in the range of 20 μC/cm². A slight increase of saturated and remnant polarization with thickness was observed, although the highest saturated polarization of 40.5 μC/cm² and remnant polarization of 27.6 μC/cm² were achieved in the 250 nm specimen.

4. Discussion

The present work shows that it is possible to prepare high quality thin films of erbium doped PZT by solution deposition with fine single phase columnar microstructure. In a recent work, Boyle et al. [23] investigated lanthanide series doping effects on PZT thin films. Based on X-ray diffraction results and unit cell volume they concluded that erbium rather occupy B sites (Ti, Zr) and would act as acceptor dopant. Their electrical results show a very close dielectric constant of PZT and PEZT but lower remnant polarization of PEZT. The results reported in the present work do not agree with those of Boyle et al. The processed thin films are characterized by higher dielectric constant than non-doped PZT. The leakage current is also lower than in PZT. These results agree with investigations conducted recently on Er doped lead titanate thin films [24], and would point to erbium being substituted on to Pb sites or at least being amphoteric. Because acceptor doping is compensated by highly mobile oxygen vacancies, a pure acceptor doping character of erbium would have resulted in higher leakage currents, lower dielectric constant and lower remnant polarization.

The electrical properties of erbium doped PZT thin films are affected by thickness as in the case of non-doped PZT. Similar results on effects of thickness on dielectric properties have been reported for lead–lanthanum–titanate (PLT) [9] and lanthanum doped PZT thin films [5], and the existence of a low permittivity interfacial layer in series with the ferroelectric film has been made responsible for these effects. Alguero et al. [9] claim an interfacial layer of 50–100 nm based on Rutherford back-scattering data. According to them this interfacial layer would form as a result of Ti diffusion from the perovskite to the substrate or to the formation of La deficient area of the film near the bottom electrode. Chung et al. [10] report on the formation of an Pb...
deficient interfacial layer of 25 nm using Auger electron spectroscopy and high resolution transmission electron microscopy. Park et al. [17] also reports on the formation of a ‘broad’ interfacial region of ‘incorrect stoichiometry’ in epitaxial Bi,Ti,O thin films deposited on Pt. In this region Ti has been shown by XPS to take different oxidation states near the bottom electrode, and so to give rise to a space charge layer which in turns has been made responsible for imprint failures (asymmetries in $C-V$ and hysteresis curves). It seems that the formation of an interfacial layer, its chemistry and thickness depend on such conditions as processing route and processing conditions. Taking into account the capacity of the interfacial layer obtained from Fig. 3b and assuming a thickness of 50 nm, the dielectric constant of the interfacial layer in the PEZT thin films can be estimated to be in the range of 258 which would imply that the interfacial layer is composed of a ferroelectric with different stoichiometry. However, until the chemistry and structure of the interfacial layer has been elucidated we can only speculate about its thickness and properties.

Finally, the leakage current properties were found to strongly depend on thickness and temperature. This suggests a conduction mechanism based on SCLC. However, the results shown above illustrate the complexity of the phenomenon. In the voltage and temperature ranges investigated we notice variations of the voltage exponent with temperature for a given thickness and with thickness for a given temperature. In both cases the exponent decreases with increasing temperature and/or thickness. The decrease of the voltage exponent with increasing temperature has been also reported for PZT thin films and has been attributed to the narrowing of the traps energy distribution [7]. It seems that increasing the thickness of the films leads to similar effects as temperature in terms of traps energy distribution. In his discussion of the exponents appearing in the equation of the SCLC mechanism (Eq. (4)), Scott [12] points to the different corrections that can be made to the basic equation ($J = \text{constant } V^2/d^3$) which leads to the generalized Eq. (4). Based on results from literature he distinguishes two regimes: (i) a low voltage regime with $J$ varying as $V^2/d^3$, and (ii) a high voltage regime with $J\sim V^3/d^3$. Fig. 7b shows that at high voltage the $1/d^3$ dependency is satisfied whereas at lower voltage the results rather show a $1/d^4$ dependency, although omitting the results of the 330 nm (5.9 V belongs probably to the high voltage regime of the 330 nm film) would yield a lower exponent (dashed line in Fig. 7b). However, despite the fact that the experimental results point to an SCLC mechanism, they probably cannot be interpreted solely on the basis of this mechanism. As discussed by Scott [12] and Stolichnov and Tagantsev [13], more than one mechanism can be operating depending on voltage, temperature and microstructure, and more work is needed in order to elucidate the operating mechanisms and their ranges.

5. Conclusions

The effects of thickness and erbium doping on the microstructure and electrical properties of solution-deposited PZT thin films have been investigated in the present work. The following conclusions may be inferred:

In the thickness range investigated, the microstructure and crystalline structure do not change with thickness. Furthermore, the superior electrical properties of PEZT in comparison to those of PZT suggest that Er substitutes Pb sites, or at least is amphoteric.

The thickness dependence of the dielectric constant is interpreted in terms of the interfacial layer model for MFM structure. The linear fittings of reciprocal apparent capacitance and coercive voltage with thickness lead to thickness independent materials properties, i.e. dielectric constant of 774 and a coercive field of 60 kV/cm.

The leakage current is found to depend strongly on thickness and temperature. The results suggest that a conduction mechanism based on SCLC may be operating. The potential energy barriers have been found to be 0.81 and 0.74 eV, respectively for PEZT and PZT.

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