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Comparison between PZT thin films deposited on stainless steel and on platinum/silicon substrate

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Abstract. Pb(Zr₁₋ₓTiₓ)O₃ (PZT) thin films were prepared by sol-gel method on stainless steel (SS) and on platinum-coated silicon substrate (Pt/Si). The structure revealed by X-ray diffraction shows strong crystallographic orientation: (110) and (100), respectively. The crystallite size shows significant differences: \( d_{(SS)}^{(001)} = 27.1 \, \text{nm} \), \( d_{(Pt)}^{(100)} = 88 \, \text{nm} \). The tetragonal splitting is \( (\Delta c/c)_{SS} = 3.55 \% \) and \( (\Delta c/c)_{Pt} = 3.32 \% \). The ferroelectric hysteresis loop in the static mode is characterized by remanent polarization of 25 \( \mu \text{C/cm}^2 \) and coercive field of 45 kV/cm for SS substrate, while for Pt/Si substrate the values are 10 \( \mu \text{C/cm}^2 \) and 39 kV/cm, respectively. The leakage current is about 3 orders of magnitude lower in the PZT film deposited on SS. The better properties of the PZT deposited on SS are explained by the presence of large single crystal-like crystallites, which make the film closer to epitaxial ones. The results show the potential of growing epitaxial films on low-price substrates such as stainless-steel.

1. Introduction

Because of their ferroelectric, piezoelectric, pyroelectric and non-linear dielectric properties PbZr₁₋ₓTiₓO₃ (shortly PZT) thin films are good candidates for a large variety of applications such as non-volatile memories, microelectromechanical systems (MEMS), ultrasonic transducers, pyroelectric detectors, membranes, micro-accelerometers, micromotors, etc. [1-7]. Various deposition methods, including the sol-gel one [8] have been used to produce ferroelectric PZT films.

It is well known that the properties of the PZT thin films are strongly dependent on the crystallographic orientation, film thickness and microstructure, Zr/Ti ratio [9-10]. However, the interest was focused mainly on Zr/Ti ratios around the morphotropic phase boundary because of the large piezoelectric and electromechanical coefficients. An important factor influencing the PZT film microstructure is the substrate on which the film is deposited. Most of the studies are performed on PZT films deposited on Pt used also as bottom electrode for the ferroelectric capacitor. This metal is
not the best choice in case of applications because is inducing fatigue effects [11] and it is expensive. Another tested metal is the stainless-steel (SS) [12-14].

We report here on the ferroelectric properties of the tetragonal PZT thin films (Zr/Ti ratio of 20/80) deposited on stainless steel and on platinum-coated silicon substrates.

2. Experimental procedures

2.1. Preparation of sol-gel PZT films
The sol-gel method has been extensively used for the deposition of PZT films because it allows to get stoichiometric compositions at relatively low crystallization temperatures (500°-700°C). For deposition on metal substrates the crystallization temperature should be low enough to avoid inter-diffusion and reaction between the substrate and film. A seed layer is used (PbTiO₃ in our case) to promote crystallization. The precursor solutions were prepared using reagent-grade chemicals: lead acetate Pb(CH₂COO)₂*3H₂O (Reactivul Bucuresti), titanium isopropoxid Ti[OCH(CH)₂]₄(Alfa) and zirconium n-propoxide Zr[OCH₂CH₂CH₃]₄ (Alpha). The solvent was 2-methoxyethanol CH₃OCH₂CH₂OH (2ME) (Fluka) and the drying agent was dimethyl-formamide [15,16]. The preparation was carried out in inert atmosphere (N₂). Two types of substrate were used: optically polished stainless steel (SS) and platinum deposited on silicon wafer (Pt/TiO₂/SiO₂/Si).

The precursor solutions were deposited on both SS and platinum-coated silicon substrates by spin-coating at 2500 rpm for 60 s. This deposition sequence was as follows: first, two layers of PbTiO₃ (PT) solution (with an excess of 10 wt% lead acetate trihydrate) as the "seed" layer and then, 10 layers of PZT solution. After each spin-coating process the film was heated (pirolysed) for 2 min. at 200°C and 4 min. at 400°C in order to eliminate the organic components. Thermal annealing was performed in air, at 650°C for 30 min, with a heating rate of 20°C/ min. The thickness of the films was in the 0.8-1 µm range.

2.2. Structural measurements
The films were investigated by X-ray diffraction (XRD), atomic force microscopy (AFM) and Scanning electron microscopy (SEM). A TUR M-62 diffractometer provided with a copper target (λ = 1.54178 Å) was used in the measurements. The X-ray diffraction patterns were recorded by collecting the scattered X-ray quanta at equally spaced angular position (0.02°θ) in the range 8-24°. AFM analysis was performed with a standard ThermoMicroscopes apparatus. SEM investigation was performed within a JEOL6300M microscope.

2.3. Measurements of ferroelectric properties
Hysteresis loops were recorded both in the dynamic and static regime using a TF2000 Analyser. The capacitance-voltage (C-V) characteristic was measured with a HP 4194A Impedance-Gain Analyzer and the current voltage (I-V) one with a Keithley 6517 electrometer.

3. Results and discussions

3.1. Structural investigations
The structure of the films corresponds to tetragonal perovskite and this feature is revealed by the splitting of the diffraction lines (see Fig. 1): (001)/(100), (101)/(110), (002)/(200). The tetragonal splitting (∆c/c) was calculated from the position of the twin peaks (where ∆c = c-a). For the films deposited on SS substrate (∆c/c)_{SS} = 3.55 % (average from (001)/(100) and (002)/(200) lines) while for the film deposited on Pt/Si substrate (∆c/c)_{Pt} = 3.32 % (average from (001)/(100) and (002)/(200) lines).

A remarkable feature of the diagrams is related to the intensities of the diffraction lines. In the case of the PZT film deposited on SS substrate the (101) line is very high while (001)/(100) pair
and (002)/(200) pair exhibit low intensity. This speaks in favour of a good preferential orientation of the film crystallites with the plane (101) parallel to the substrate.

The microstrains and the mean size of the crystallites [26] can be determined simultaneously if one uses the diffraction lines corresponding to two or more orders of diffraction. In the limiting case of pure particle size broadening the line breadth $\beta_D$ is related to the effective (or mean) particle size, $D$, the X-ray wavelength, $\lambda$, and the Bragg angle, $\theta$, according to the equation:

$$ \beta_D = \frac{\lambda}{D \cos \theta} \quad (1) $$

For pure stress broadening the breadth $\beta_\eta$ is related to the effective strain $\eta$ and the Bragg angle, $\theta$, by the equation:

$$ \beta_\eta = \eta \tan \theta \quad (2) $$

If both types of broadening are present, the resultant breadth $\beta$ should be the convolution of the widths. Wood and Rachinger [27] have shown that for a commonly occurring line shape the widths are additive. This means that $\beta = \beta_D + \beta_\eta$. In this case one can write:

$$ \beta \cos \theta / \lambda = 1/D + \eta \sin \theta \lambda \quad (3) $$

The mean size of the crystallites, $D$, and the mean square strain or the width of the microstrain distribution, $\eta$, can be calculated from the eq. 3 if two diffraction peaks of the same type are considered: in our case the X-ray diffraction peaks (001) and (002) or (100) and (200).

For PZT films deposited on Pt/Si substrate the diffraction lines exhibit low intensities, except the (001)/(100) and (002)/(200) pairs which show high intensities. The average crystallite size and the internal stress for the direction perpendicular to the (00l)SS and (h00)Pt planes, that are orientated along the substrate are $D_{(00l)}=27.1$ nm, $\eta_{(00l)}= 0.98$ % and $D_{(h00)}=88.0$ nm, $\eta_{(h00)}= 1.05$ % for the films deposited on SS and Pt/Si substrates, respectively.

![X-ray diffraction patterns](image)

**Figure 1**: The X-ray diffraction of PZT films deposited a) on SS: b) on Pt/Si. The peak at $20^\circ (\theta)$ is given by well oriented (111) Pt crystallites of the substrate.

The stainless steel substrate was analysed by X-ray diffraction. Two phases were revealed: a main ferrite phase ($\alpha$-Fe) and a minor phase of austenite ($\gamma$-Fe)[28]. The calculated percent of austenite is 17.4 mol%. The Pt/Si substrate consists of (111) oriented platinum crystallites on silicon wafer as evidenced on X-ray diffraction diagram in Figure 1b.

A careful analysis of the diffraction pattern of PZT deposited on stainless steel substrate revealed several small peaks, probably due to a very small amount of a second crystalline phase. The peak
situated at ~14.5° could be ascribed to the pyrochlore phase which sometimes occurs during PZT preparation at low firing temperatures. The pyrochlore Pb₂(Zr,Ti)₂O₆, a paraelectric phase [17] is formed at temperature below the crystallization temperature of the perovskite phase. The pyrochlore phase, even in small amount, can be detrimental for the ferroelectric properties [18].

However, the present PZT films were crystallized at 650 °C, a temperature high enough to prevent the presence of the pyrochlore phase. The results presented in the section 3 show that the amount of the secondary phase in the PZT film deposited on SS, either pyrochlore or not, is too small to significantly affect the ferroelectric properties.

SEM analysis revealed that, on SS substrate, there are large single-crystals of PZT (see Fig. 2), which can reach several micrometers in size. This result is normal, considering that it is possible to grow epitaxial films on SS [13]. These large crystals are overlapping a thin layer of small crystalline grains. The size of the grains is different from the size of the crystallites determined from the X-ray diffraction, as a single crystalline grain might contain several crystallites.

![Figure 2: SEM image of PZT films deposited on SS (a) and Pt/Si (b) substrates.](image)

On Pt/Si the PZT films shows large rosettes, which are typical for sole-gel deposited films on Pt. The large single-crystals are absent in this case. This fact could lead to diminished ferroelectric properties in the case of PZT films deposited on Pt/Si. On the other hand, it is known that one unavoidable defect in PZT is the oxygen vacancy (V₀). The Pt electrodes in the case of PZT on Pt/Si are not permeable to the V₀ and the vacancies accumulate near the electrodes forming stable networks that can change the properties of the PZT/Pt interfaces [19]. In the case of the film deposited on SS, the vacancies can be filled with oxygen coming from the SS substrate. It is known that any SS has some oxygen dissolved in it [20], the substrate acting as a reservoir of oxygen or as sink for oxygen vacancies. In fact, the unique property of SS to resist corrosion is due to a thin oxide layer formed on the surface. The formation of this layer is promoted by the added elements such as Cr, Ni, V, Ti, Mo and passivates the surface, preventing the iron oxidation.

The roughness evaluated from the AFM analysis is higher for the PZT film deposited on SS substrate (60-100 nm) than for the film deposited on Pt/Si (3-5 nm). This fact could be explained by excessive growth of large single-crystal particles in PZT film deposited on SS, as observed from the SEM analysis.

3.2. Ferroelectric properties

Both dynamic and static hysteresis loops were measured. The loops in the static mode were recorded at a frequency of 100 Hz with a relaxation time of 1s. For measuring the relaxed polarization the film is brought first into the negative polarization state, where it is kept for 1s and then into positive saturation by a short voltage pulse (1 ms). The charge released by polarization switching during this short pulse is integrated and gives the relaxed polarization value. The next point is obtained by bringing again the film into the negative saturation of polarization, setting the voltage to the next value, keeping the film at this voltage for another second, and forcing again the film into positive saturation. The integrated charge gives the next point on the loop. The cycle is repeated until the entire
loop is obtained. The voltage steps are obtained by dividing the voltage amplitude to the number of points (40 in this case) and the raising time of the voltage pulses is in accordance with the chosen frequency. In the static mode of measurement the contribution of parasitic polarization sources is strongly reduced. The static mode is characterized by pulse integration as opposite to the dynamic mode where a continuous integration of charge is performed during the measurement with a triangular voltage of fix frequency. The recorded hysteresis loops, in the static mode, are shown in Figure 3a. The film deposited on SS substrate shows symmetric, almost rectangular, hysteresis loop with a remanent polarization of 25 µC/cm² and a coercive field of 40kV/cm. The saturation is well defined for both polarization orientations. The PZT film deposited on Pt/Si shows a slim loop, slightly shifted toward negative fields. This indicates the presence of an internal bias in the film deposited on Pt/Si substrate. The polarization in this case is 10 µC/cm² and the average coercive field is 39 kV/cm. The dynamic hysteresis loops are shown in Figure 3b, for a frequency of 1 kHz. The remanent polarization values, obtained after extracting the leakage contribution to the integrated charge, are around 15 µC/cm² in both cases. The saturation value seems to be larger in the case of PZT deposited on Pt/Si. The coercive field is around 210 kV/cm for PZT film deposited on SS and 85 kV/cm for the film deposited on Pt/Si. Compared with the static measurement, the remanent polarization from the dynamic loop decreases in PZT/SS and increases in PZT/Pt/Si. The coercive field increases in both structures, more accentuated for PZT deposited on SS. The negative shift of the loop in the case of the PZT on Pt/Si is less obvious in the dynamic measurement. These differences will be discussed in more detail later on.

The C-V characteristics recorded for a frequency of 1 kHz are shown in Figure 4. It is remarkable that the C-V characteristic is symmetrical for PZT film deposited on SS. The “up” and “down” branches cross at zero field and the peak values are equal in spite of the different electrodes (bottom electrode is stainless steel, top electrode is platinum). In the case of PZT film deposited on Pt/Si the electrodes are identical, but the C-V characteristic is asymmetrical in the sense that the peak values are not equal.

![Figure 3: The static (a) and dynamic (b) hysteresis loops for PZT film deposited on SS and Pt/Si substrates](image-url)
Figure 4: Capacitance-voltage (C-V) characteristics of the PZT films deposited on a) SS substrate b) Pt/Si substrate.

The I-V hysteresis characteristic was measured at room temperature with a waiting time of 1s between the voltage steps and current reading. One second was found to be a good compromise between reaching a quasi-static value and the avoidance of capacitor breakdown under prolonged voltage stress. Figure 5 shows that the current density is much smaller in the case of PZT film deposited on SS substrate. The I-V characteristic is symmetrical and even the current peaks due to polarization switching are seen for both polarities of the voltage. The I-V characteristics of the PZT film deposited on Pt/Si substrate is strongly asymmetric. The current density is three orders of magnitude higher than that in the PZT films deposited on SS substrate.

It seems that the overall ferroelectric-electric properties of the PZT films deposited on SS are better than those of the similar films deposited on Pt/Si. The relaxed remanent polarization is higher, the C-V characteristic is symmetric and the leakage current is orders of magnitude lower than for PZT deposited on Pt/Si. One intriguing feature appears, however, in PZT/SS, where, contrary to the normal case, as observed for PZT/Pt/Si, the relaxed polarization, measured in static conditions is higher than the polarization measured in dynamic conditions. To explain this behaviour we have to consider that both static and dynamic hysteresis measurements are based on charge integration. In the static method what is integrated is a current flowing through the structure in a time of 1 ms, under a voltage which brings the film into positive polarization saturation. This signal includes the current due to the polarization switching from the current state of polarization to the positive saturation, the normal leakage current at the voltage corresponding to positive saturation and the emission current from the deep traps. It was shown recently that the metal-ferroelectric-metal (MFM) structure can be assimilated with two back-to-back Schottky diodes, in which the built-in potentials and depletion depths are directly affected by the magnitude and orientation of the polarization [21,22]. It was also shown that the occupation state of the deep traps located in the depletion region can change when the polarization changes its orientation [23]. Traps which are located below the Fermi level for one orientation of polarization, and are filled with carriers, might be brought above the Fermi level for the opposite direction of polarization. The traps will release carriers, during the 1 second relaxation time, and will contribute thus to the total current [24]. The charges released from the deep traps will also contribute to the screening of the depolarization field in real time, immediately after polarization switching. If the measurement time is long enough to allow emission from the deep traps and effective compensation of the depolarization field, then the coercive field will be considerably reduced and the polarization will be close to its normal value. The back-switching effects due to the incomplete screening of the depolarization field immediately after switching will be negligible.
In the dynamic mode the entire hysteresis measurement takes 1 ms (the frequency is 1 kHz). Deep traps do not respond at this frequency and they will no longer contribute to the screening of the depolarization field leading thus to a considerable increase of the coercive field. The compensation charge will be supplied by the electrodes, through the leakage current. The full compensation of the depolarization field will require a longer time if the leakage is small. Some of the polarization switches back during this process of screening, finally leading to a smaller polarization in the dynamic mode. The observation that the C-V and I-V characteristics are very different in case of PZT films deposited on SS and Pt/Si substrates can be explained by the net differences in the microstructure. The fact that microstrains in the films deposited on Pt/Si substrates \( \eta =1.05 \% \) are larger than in the films deposited on SS \( \eta =0.85 \% \) could be an explanation. The different strain values, different orientations and microstructure can influence the formation of the potential barriers with the metal electrodes. In the case of the symmetric Pt/PZT/Pt structure both the C-V and I-V characteristic are asymmetric. This behaviour might be unexpected. However, the two interfaces were not processed in the same way. The bottom interface was formed at elevated temperatures, during the crystallization annealing, while the top interface was formed by RF-sputtering at room temperature. We presume that the density of the interface states is different, with impact on the height of the potential barriers. I-V measurements performed at different temperatures will help to evaluate the height of the potential barriers for PZT films deposited on SS and Pt substrates.

The presence of oxygen in SS substrate can be responsible for the difference between the PZT film deposited on it and the film deposited on Pt/Si. The oxygen vacancies act as donors and their absence results in a lower leakage current (see Fig. 5). The absence of the \( V_0 \) coupled with the presence of a large amount of small single crystal-like crystallites in the PZT film on SS leads to properties closer to those of the high quality epitaxial films [25]. That means a larger polarization, a lower leakage current and a symmetric C-V characteristic.

4. Conclusions

The structure and ferroelectrics properties of PZT films deposited on SS and Pt/Si substrates have been investigated. The orientation of PZT crystallites is (101) for SS and (100) for Pt/Si substrates deposition. The roughness of the films is larger for PZT deposited on the SS than of those deposited on Pt/Si substrate.

The films deposited on SS show enhanced ferroelectric hysteresis loop in the static mode, lower leakage current and symmetric C-V characteristic. This is explained by the large amount of single crystal-like crystallites of micrometers size in the PZT film deposited on the SS. It can be assumed that
SS promotes local epitaxial growth of the PZT, leading to properties much closer to those of high quality epitaxial films or single crystals. Possible absence of $V_o$ in the films deposited on SS, due to their filling with oxygen coming from the substrate, can also lead to enhanced properties compared with PZT on Pt/Si.

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