Temperature dependence of dielectric properties for Ba(Zr_{0.25}Ti_{0.75})O_3 thin films obtained from the soft chemical method

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Received 19 August 2006; received in revised form 25 April 2007; accepted 26 April 2007

Abstract

Ba(Zr_{x}Ti_{1-x})O_3 (BZT) thin films prepared by the polymeric precursor method (PPM) were annealed at 500, 600, and 700 °C for 4 h. All films crystallized in the perovskite structure present a crack-free microstructure. Dielectric properties of the BZT thin films were investigated as a function of frequency and applied voltage. The dielectric constant of the films were 36, 152 and 145 at 1 kHz, while the dielectric loss were 0.08, 0.08, and 0.12 at 1 MHz.

Keywords: Dielectric properties; BZT; Thin films; Temperature dependence

1. Introduction

The interest of dielectric properties in thin films has increased a lot in the last years due to its high potential for technological applications. BaTiO_3 obtained in the ceramic form present various interesting applications as multilayer capacitors, pulse signal generation, transducers and infrared detectors [1–4] or as thin films [5–7]. BaZrO_3 in doped or pure forms is much promising material to be applied in refractory in the electroceramic industry [8,9]. Also, can be used against corrosion problems during the single growth of superconductors [10]. Barium zirconate titanate Ba(Zr_{x}Ti_{1-x})O_3 (BZT) is usually obtained by substituting the B site of the BaTiO_3 by Zr. This is possible because of the Zr^{4+} ion has larger ionic size (0.087 nm) than Ti^{4+} (0.068 nm) [11,12]. Pontes el al. [13] reported that this substitution promote an expansion in the unit cell and that the Zr addition around 25 at.%, making the BZT thin films to crystallize in the cubic structure. These materials could be valuable because they are environment-friendly and lead free. Beyond that, presents excellent dielectric properties, dynamic random access memory applications, tunable microwave devices and optical properties [14–17].

In this paper, we report the effect of temperature on the dielectric properties of Ba(Zr_{0.25}Ti_{0.75})O_3 (BZT) thin films prepared through the soft chemical method.

2. Experimental details

Ba(Zr_{x}Ti_{1-x})O_3, with x = 0.25, thin films were synthesized through the polymeric precursor method (PPM). Barium carbonate 99.9% purity (Aldrich), titanium(IV) isopropoxide 99.9% purity (Aldrich), zirconium(IV) tetra-n-butoxide 99.9% purity (Aldrich), ethylene glycol 99% purity (J.T. Baker) and citric acid 99.5% purity (Mallinckrodt) were used as starting materials. Titanium citrate and zirconium citrate were formed by the dissolution of, respectively, titanium(IV) isopropoxide and zirconium(IV) n-propoxide in water solutions of citric acid, under constant stirring. These solutions were homogenized and were mixed in a molar proportion of 25:75 of zirconium and titanium, respectively. The citrate solution was stirred for some hours at 60 °C to yield a clear and homogenous solution. Barium carbonate was dissolved in water, after then it was added in a stoichiometric quantity, to the titanium–zirconium citrate solution.

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To measure electrical properties, Au dot electrodes of 3 factor were measured as a function of frequency in the range of 100 Hz–1 MHz. A small AC signal of 10 mV at 100 kHz. The dielectric constant and dissipation impedance/gain phase analyzer, in which the capacitance value was taken using in a metal–thin film–metal configuration, using a Hewlett-Packard (4194A) microscopy (SEM).

Digital Instruments Multimode Nanoscope IIIa. The films thickness were evaluated observing the cross-section using a Zeiss DSM940A scanning electron microscopy. Which images were taken using a diffractometer, model DMax-2000PC. The morphology and grain size were studied by atomic force microscopy (AFM). The films thickness were evaluated observing the cross-section using a Zeiss DSM940A scanning electron microscopy (SEM).

The capacitance–voltage (C–V) properties were measured in the films in a metal–film–metal configuration, using a Hewlett-Packard (4194A) impedance/gain phase analyzer, in which the capacitance value was taken using a small AC signal of 10 mV at 100 kHz. The dielectric constant and dissipation factor were measured as a function of frequency in the range of 100 Hz–1 MHz. To measure electrical properties, Au dot electrodes of 3 factor were measured as a function of frequency in the range of 100 Hz–1 MHz. A small AC signal of 10 mV at 100 kHz. The dielectric constant and dissipation impedance/gain phase analyzer, in which the capacitance value was taken using in a metal–thin film–metal configuration, using a Hewlett-Packard (4194A) microscopy (SEM).

Digital Instruments Multimode Nanoscope IIIa. The films thickness were evaluated observing the cross-section using a Zeiss DSM940A scanning electron microscopy (SEM).

The polycrystalline BZT thin films were annealed at different temperatures. The roughness is a very important factor because the interface between the electrode and dielectric material will greatly influence the leakage current and dielectric constant that the BZT thin films present a homogeneous, smooth and crack-free surface. This indicates that the chemical soft method allows the preparation of films with controlled morphology. The values of the average grain size and surface roughness were shown in Table 1. This increase of surface roughness at higher temperature is due to the crystallization of the BZT film, which results from the increase of atomic mobility as a consequence of the temperature.

3. Results and discussion

Fig. 2 shows the XRD patterns for the BZT thin films, annealed from 500 to 700 °C for 4 h. We can observe the presence of a single perovskite Ba(Zr0.25Ti0.75)O3 phase. XRD results show polycrystalline BZT films with (1 0 0), (1 1 0), (1 1 1) and (2 0 0) crystallographic planes. BZT crystallize in cubic structure, as confirmed by the “JCPDS” (Joint Committee on Powder Diffraction Standards) card (No. 36-0019) [20]. The unit cell parameters of BZT annealed at 500, 600, and 700 °C are a = b = c = 4.041, 4.046, and 4.049 Å, respectively, with a cubic perovskite-type structure and space group Pm3m. The lattice parameters were calculated using the least square refinement from the REDE93 program.

In Fig. 2 it is clear evident that the increase of thermal treatment improves the crystallinity of the BZT films. The film annealed at 500 °C for 4 h shows less intense peaks at (1 1 0) and (1 1 1) planes. However, the improved crystallinity and the perovskite phase of BZT films were achieved at higher temperatures. The intensity of Pt peak increases as the substrate temperature is raised. This result is assumed to be due to the grain growth or recrystallization of the Pt bottom electrode[21]. Pontes el al. [13] showed that the increase of the Zr content the peaks shift to lower diffraction angles. This indicates an increase in the lattice parameter caused by the fact that the electronic density of Zr ions is higher than the electronic density of Ti ions and, therefore, the substitution of Ti by Zr ions leads to an expansion in the unit cell.

Fig. 3 shows the surface morphology of BZT thin films annealed at different temperatures. The roughness is a very important factor because the interface between the electrode and dielectric material will greatly influence the leakage current and a breakdown electric field of the BZT thin film. The average grain size and the surface roughness of the BZT thin films were estimated using an atomic force microscope.

The surface morphology was obtained using an area of 1 μm × 1 μm, as shown in Fig. 3. Analysis of AFM data indicated that the BZT thin films present a homogeneous, smooth and crack-free surface. This indicates that the chemical soft method allows the preparation of films with controlled morphology. The values of the average grain size and surface roughness were shown in Table 1. This increase of surface roughness at higher temperature is due to the crystallization of the BZT film, which results from the increase of atomic mobility as a consequence of the temperature.
Fig. 3. AFM surface micrographies of the BZT thin films on Pt/Ti/SiO₂/Si substrate, annealed at (a) 500 °C, (b) 600 °C and (c) 700 °C for 4 h.

Fig. 4. Cross-sectional view of BZT thin film on Pt/Ti/SiO₂/Si substrate, annealed at (a) 500 °C, (b) 600 °C and (c) 700 °C for 4 h.
The thickness of the BZT thin films was obtained for scanning electron microscopy in Fig. 4. In the micrographs is possible to observe clearly the interface between the film and the substrate, the different thickness is resulted of the thermal treatment and of the speeds of deposition. The thickness of the BZT thin films through this process are shown in Table 1.

Table 1 shows the average grain size, thickness, surface roughness, dielectric constant and dielectric loss of BZT thin films.

Pantou et al. [22] showed the effect of Ti substitution for Zr in the dielectric properties of BaTiO3 thin films prepared by MOCVD. A secondary ZrO2 phase when the Zr concentration is 30%. The dielectric constant is significantly lower when the Zr concentration increase.

The obtention of the dielectric constants ($\varepsilon_r$), by the study of the dielectric properties was extracted using Eq. (1):

$$\varepsilon_r = \frac{C d}{\varepsilon_o A},$$

where $\varepsilon_o$ is the permittivity of free space, $C$ the capacitance, $d$ the film thickness, and $A$ is the capacitor area.

Fig. 5 shows the frequency dependence of the dielectric constant ($\varepsilon_r$) and dielectric loss (tan $\delta$) as a function of applied frequency of the BZT thin films annealed at different temperatures on Pt/Ti/SiO2/Si substrates. The dielectric constant shows a slight decrease and the dielectric loss slowly increases with increasing frequency.

This dielectric loss behavior is non-linear, can be explained by the fact that the thin films present fatigue high frequencies. Zhai et al. [23] showed that different thickness has great influence in

<table>
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<th>Method</th>
<th>Temperature (°C)</th>
<th>Time</th>
<th>$x$</th>
<th>$\varepsilon_r$</th>
<th>Reference</th>
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<td>130</td>
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</tr>
<tr>
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<td>30 min</td>
<td>0.35</td>
<td>280</td>
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<td>0.20</td>
<td>95</td>
<td>[24]</td>
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<tr>
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<td>700</td>
<td>30 min</td>
<td>0.35</td>
<td>150</td>
<td>[25]</td>
</tr>
<tr>
<td>CSD</td>
<td>700</td>
<td>15 min</td>
<td>0.45</td>
<td>175</td>
<td>[26]</td>
</tr>
<tr>
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<td>0.35</td>
<td>236</td>
<td>[27]</td>
</tr>
<tr>
<td>PPM</td>
<td>600</td>
<td>4 h</td>
<td>0.25</td>
<td>152</td>
<td>This work</td>
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Fig. 5. The variation of dielectric constant ($\varepsilon_r$) and dielectric loss (tan $\delta$) for the BZT thin films deposited on Pt/Ti/SiO2/Si substrates annealed at 500, 600, and 700 °C.

Fig. 6. C–V characteristics of the MIM capacitor with BZT thin films annealed at (a) 500 °C, (b) 600 °C and (c) 700 °C for 4 h, which were measured at the frequency of 1 MHz.
dielectric constant in this material. The high dielectric constant in BZT films annealed at 600 °C for 4 h is due to low roughness, small thickness and homogeneous surface. The switching in films with fine grains is relatively difficult. The domain walls in larger grains were easiness to switch under external field.

Table 2 shows the dielectric constants of thin films herein measured at room temperature compared with other BZT thin films reported in literature.

We can observe in Table 2, that depending on the preparation method, temperature, time of annealing and Zr/Ti ratio, BZT thin films present significant variation in their dielectric properties.

Capacitance–voltage (C–V) characteristics (at a frequency of 1 MHz) of MIM structure (Au/BZT/Pt) are shown in Fig. 6.

The C–V curves have been used for the measure of ferroelectric behavior of the BZT thin film at room temperature. The dielectric constant and dielectric loss for the film heat treated at 600 °C for 4 h, with 3.1 × 10⁻⁴ cm² electrode area obtained from C–V curves at zero bias, are about 152 at 1 kHz and 0.08 at 1 MHz, respectively. It can be seen that the center of C–V curves is located at zero bias field, that suggests the absence of internal electric fields [28]. Their cause is due to space charge, asymmetric distribution of trapped charges, more specifically, trapped electrons, or charge accumulation at the interface between the thin film and the electrodes [29]. The films annealed at 500 and 700 °C also show less asymmetric curve about 0 V and the capacitance decreases when the applied voltage is increased beyond 0 V. BZT film annealed at 600 °C shows asymmetric C–V characteristics about 0 V and also the capacitance decreases when the applied voltage is increased beyond 0 V. The C–V curve has two peaks, which is a result of the ferroelectric properties and has a switching voltage of about 1.5 V. These results suggest the strong ferroelectric properties of BZT thin films.

4. Conclusions

Polycrystalline and single-phase perovskite Ba(Zr₀.₂₅ Ti₀.₇₅)O₃ thin films were grown onto Pt/Ti/SiO₂/Si substrates by the polymeric precursor method at several temperatures. AFM analysis revealed that the surface roughness and average grain size are temperature dependent. The dielectric constant at the frequency of 1 kHz was measured as 36, 152, and 145 for the films annealed at 500, 600, and at 700 °C, respectively. The increase in temperature leads to better crystalline films with superior dielectric constants. C–V characteristic was observed for the BZT films evidencing non-paraelectric character.

Acknowledgements

The authors gratefully acknowledge the financial support of the Brazilian financing agencies CAPES, CNPq, FAPESP and to Prof. João Mariz Gumêrê Neto of the Department of Physics of the Universidade Federal of the Piauí-UFPI.

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