Ferroelectric properties of barium titanate thin films grown on nichrome substrates by RF sputtering

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Ferroelectric thin films have attracted attention because of their possible applications in new microelectronic devices. In particular, the $BaTiO_3$ thin films, a material with a high dielectric constant, low leakage current and the quality of the change of its ferroelectric properties by adding and modifying the concentration of a doppand [1], can be used for a wide range of functional purposes, from simple capacitors to complicated microwave devices [2–6].

$BaTiO_3$ films have been grown by many deposition techniques [1, 4,7, 8] but RF sputtering is known to be one of the best because it preserves the stoichiometry under the right deposition conditions.

A major disadvantage of $BaTiO_3$ is that it possesses a mechanical fragility, therefore, one of the main technological challenges for this material is to find an electrode-substrate that could offer mechanical stability. Also, this electrode-substrate must have a good thermal stability, low electrical resistance, high resistance to oxidation and good adherence for the film. $Pt/TiO_2/SiO_2/Si$ is commonly used because it posseses the mentioned characteristics [2]. Nevertheless, it has many problems because titanium can migrate to the platinum surface during the annealing process, adding electrical resistively to electrode [9–12]. It also generates cracking in by thermal stress in the $BaTiO_3$ thin films. The nichrome is suggested for a suitable electrode because it fulfills the requirements mentioned above [13–17] and, in contrast to $Pt/TiO_2/SiO_2/Si$, its commercial availability and its low price. Therefore, in this work, $BaTiO_3$ films were grown on nichrome substrates by RF-sputtering, and their structural and ferroelectric properties were measured and improved in comparison with those deposited on $Pt/TiO_2/SiO_2/Si$ substrates using the same method and under same deposition conditions.

$BaTiO_3$ thin films on nichrome substrates were prepared by RF magnetron sputtering in an off-axis geometry at room temperature. A 50.8 mm diameter. $BaTiO_3$ target, 99.9% pure, from SCI Engineered Materials, Inc., was used. The nichrome was obtained from a commercial strip, nichrome 80, with 0.127 mm thickness from H. Cross Company, Inc. The films were also grown over $Pt/TiO_2/SiO_2/Si$ substrates in order to compare the associated properties, the details of the fabrication of these substrates can be found in a previous work [9].

Prior to film deposition, the substrates were thoroughly cleaned in a series of organic solvents by ultrasonic waves using acetone, methanol and isopropanol, and then they were rinsed with deionized water and then dried with N_2 gas.

The sputtering chamber was evacuated at 9×10^{-6} Torr, after that, it was flushed with Ar at 3 mTorr for 10 min. A mixture of Ar and O_2 gases with Ar/O_2 ratio of 90/10 was admitted in a controlled way to keep a pressure of 50 mTorr to turn, on the plasma, and then this pressure was reduced to 10 mTorr using a 75 W power. Then, a pre-sputtering was done for 15 min. Finally, the shutter was opened, to deposit the films, for 2.5 hr. Also, the substrate was rotated at 100 rpm to promote a surface uniformity.

After their deposition, the films were annealed at 700 °C for 2 hr in O_2 atmosphere. To avoid cracks, the heat-up and cool-down processes were controlled, during full-heat treatment, to reduce thermal shocks. The temperature was increased, or reduced, by steps of 100 °C/min, keeping the temperature for 20 min in each step.

The thickness of the deposited films was measured using a Dektak^{3}ST profilometer by Veeco Instruments. The microstructure of the surface and the chemical composition of the samples were measured with a JSM-5300 Scanning Electron Microscope (SEM) from Jeol, equipped with an Electron Dispersive Spectroscopy (EDS) detector. The X-ray diffraction (XRD) measurement was performed with a Phillips X'pert diffractometer using the CuK_α line ($\lambda_{k\alpha 1} = 1.54056$ Å and $\lambda_{k\alpha 2} = 1.54439$ Å).

For ferroelectric measurement, Pt top electrodes of 200-nm thickness and 6.5×10^{-4} cm^2 of area, were deposited on the $BaTiO_3$ films by DC magnetron sputtering through a mask. The room temperature hysteresis loops were measured by a ferroelectric RT-66A tester system from Radiant Technologies, Inc.

After annealing, profile measurements show that the $BaTiO_3$ films were obtained with 360 nm thickness without holes and in spite of the presence of off-axis

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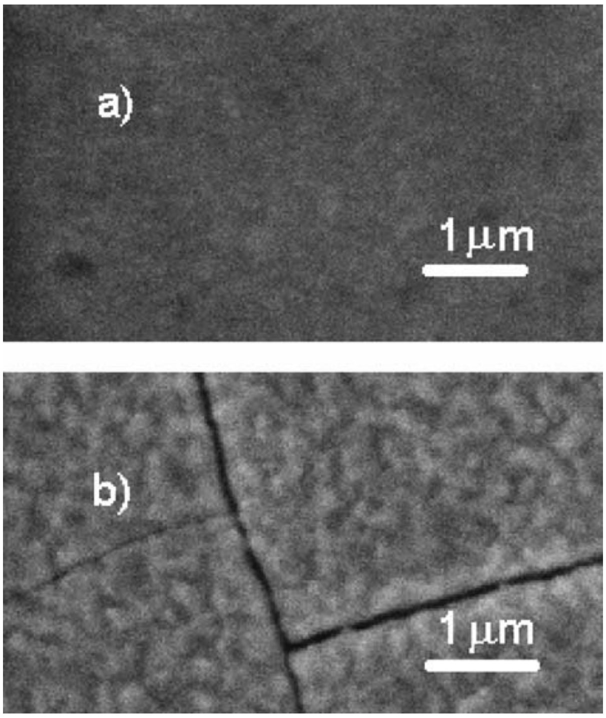

Figure 1 SEM micrographs of the surface morphology of $\mathrm{BaTiO_3}$ thin films grown on a) nichrome and b) $\mathrm{Pt/TiO_2/SiO_2/Si}$ substrates.

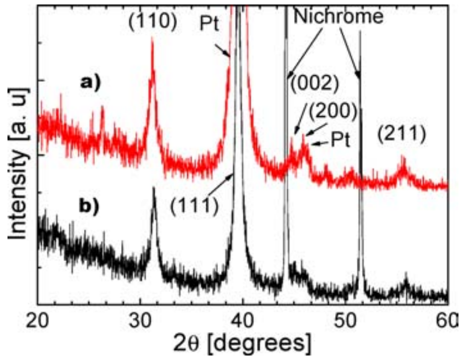

Figure 2 XRD diffractograms of the $\mathrm{BaTiO_3}$ thin films grown over a) $\mathrm{Pt/TiO_2/SiO_2/Si}$ and b) nichrome substrates.

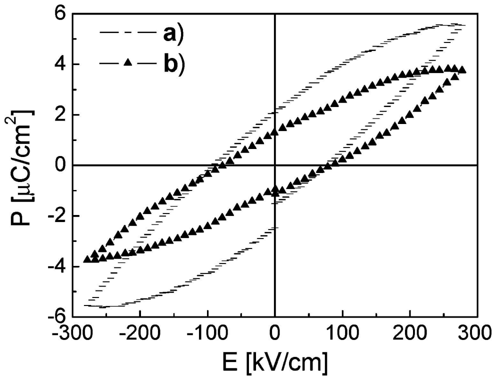

Figure 3 P-E loops of the $\mathrm{BaTiO_3}$ films deposited on a) nichrome and b) $\mathrm{Pt/TiO_2/SiO_2/Si}$ substrates with the same electric field applied.

geometry, it suggests that the rotation of the substrate could provide uniformity to the surface. On other hand, the composition of the films are the correct in accord to EDS measurements.

Even though the films deposited over nichrome and $\mathrm{Pt/TiO_2/SiO_2/Si}$ substrates were grown and annealed at the same conditions, the morphologies are very different. The films on nichrome are homogeneous and more uniform than those deposited on traditional $\mathrm{Pt/TiO_2/SiO_2/Si}$ substrates, SEM micrographs on Fig. 1. More remarkable fact is that, although the thermal expansion mismatch between $\mathrm{BaTiO_3}$ film on nichrome is greater than on Pt-coated substrate [18], the film on nichrome did not develop cracks, as the film over $\mathrm{Pt/TiO_2/SiO_2/Si}$. This could be due to the excellent elasticity of the nichrome material [19], that may allow the relaxation of the thermal stress that causes the cracking phenomenon.

The XRD diffractograms of the annealed $\mathrm{BaTiO_3}$ films deposited on nichrome and $\mathrm{Pt/TiO_2/SiO_2/Si}$ substrates show a pure crystalline $\mathrm{BaTiO_3}$, with no secondary phases (Fig. 2). From the peak related to (0 0 2) plane, if is inferred that the films grow in a tetragonal structure over both substrates. Also, it is known that the $\mathrm{BaTiO_3}$ has a tetragonal structure at room temperature.

The films on nichrome are preferentially oriented in the direction of the (1 1 1) plane, as is shown in the bottom X-ray spectra on Fig. 2. It is difficult to affirm the same for the films over $\mathrm{Pt/TiO_2/SiO_2/Si}$ because the Pt (1 1 1) peak overlaps with the $\mathrm{BaTiO_3}$ (1 1 1) peak, as is shown in the top spectra (Fig. 2a). The peaks in the diffractograms of the films show a shift from the Bragg angles associated to the bulk material (ICSD, Inorganically Crystal Structure Database and PDF, Power Diffraction File, card 050626). These displacements are larger for the film deposited on $\mathrm{Pt/TiO_2/SiO_2/Si}$ than those on nichrome, suggesting that this film is submitted to a higher stress during the annealing procedure.

The hysteresis loops of the $\mathrm{BaTiO_3}$ films deposited on nichrome and $\mathrm{Pt/TiO_2/SiO_2/Si}$ substrates, taken at the same voltage, are shown on Fig. 3. Although both films show similar coercive fields, 82 kV/cm, the film grown on nichrome has a higher remnant polarization, $P_r = 2.5\ \mu\mathrm{C/cm^2}$, than that grown on $\mathrm{Pt/TiO_2/SiO_2/Si}$, $P_r = 1.3\ \mu\mathrm{C/cm^2}$. Besides, possibly due to presence of cracks, [9–12, 20–22], the loop of the film grown on $\mathrm{Pt/TiO_2/SiO_2/Si}$ is less sloped than the one on nichrome.

The room temperature P–E measurements, at the maximum electric field that each film can hold without leakage (Fig. 4), show that the film on nichrome tolerates a higher electric field than that grown on $\mathrm{Pt/TiO_2/SiO_2/Si}$. This may be due to the electric leakages by the presence of cracks in the film on $\mathrm{Pt/TiO_2/SiO_2/Si}$. The maximum remnant polarization obtained in this film is of $1.87\ \mu\mathrm{C/cm^2}$, with a coercive field of 150 kV/cm, while, in contrast, on nichrome, the remnant polarization is larger, $5.4\ \mu\mathrm{C/cm^2}$, and the coercive field, 200 kV/cm, is still not so high. This remnant polarization for the $\mathrm{BaTiO_3}$ on nichrome is higher in comparison with that reported in the literature for films of the same material grown over other substrates and deposited by the same or other techniques [23–28].

The results obtained above suggest that nichrome, is not only a suitable electrode-substrate to be used for the growth of ferroelectric films of $\mathrm{BaTiO_3}$, but it also improves the ferroelectric properties of the films. Thus, larger remnant polarizations, $5.4\ \mu\mathrm{C/cm^2}$, with coercive fields of about the same magnitude, 200 kV/cm,

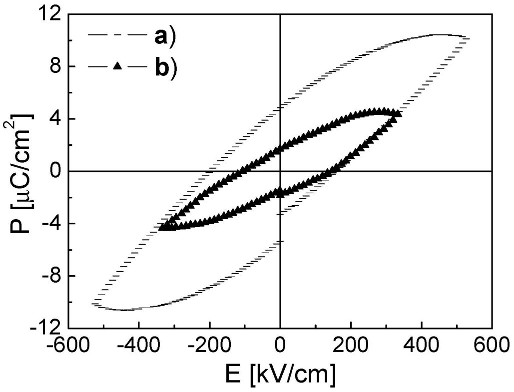

Figure 4 P-E loops of the $BaTiO_3$ films deposited on a) nichrome and b) Pt/TiO_2/SiO_2/Si substrates at maximum electric field applied.

can be obtained in these films. It is so, mainly because this substrate avoids the presence of cracks in the $BaTiO_3$ films.

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