Microstructural properties of $BaTiO_3$ ceramics and thin films

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A microstructural study of $BaTiO_3$ ceramics obtained by the conventional ceramic method is presented. Targets were produced to grow $BaTiO_3$ thin films by pulsed laser deposition on Pt/Ti/Si(100) substrates. X-ray diffraction, Auger Electron Spectroscopy, X-ray Photon Spectroscopy and Scanning Electron Microscopy were used to study the properties of the $BaTiO_3$ ceramic samples and thin films, as deposited and after an annealing process.

Keywords: Ferroelectric thin films; laser ablation; microstructure

Se presenta un estudio de la microestructura de cerámicas de $BaTiO_3$ preparadas por la técnica convencional. Estas cerámicas son posteriormente utilizadas para producir blancos a partir de los cuales se obtienen películas delgadas por ablación por láser pulsado sobre substratos de Pt/Ti/Si(100). Las propiedades de la cerámica de $BaTiO_3$ y de las películas delgadas son estudiadas por difracción de rayos X, espectroscopía de electrones Auger, espectroscopía de fotones de rayos X y microscopía electrónica de barrido, antes y después de someterlas a un tratamiento térmico.

Descriptores: Películas delgadas ferroeléctricas; ablación láser; microestructura

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1. Introduction

Ferroelectric $BaTiO_3$ thin films are a promising system for pyroelectric detectors [1, 2], non-volatile memory [3], thin film capacitors [4], electro-optic switches [5], and frequency doublers [6, 7]. Also, $BaTiO_3$ optical thin films and waveguide structures are important for the fabrication of optical devices in the near future. Recently, $BaTiO_3$ thin films grown by metallorganic chemical vapor deposition (MOCVD) [8] have been reported as optical gain media. Among the many different techniques, pulsed laser deposition (PLD) has shown to be a promising thin film fabrication method because, under the proper conditions, there is a good replication of the target stoichiometry in the deposited film [9].

The most remarkable property of $BaTiO_3$ is its high dielectric permittivity [10–12] and a significant research effort has been devoted to the preparation of $BaTiO_3$ thin films that maintain such high permittivity [13–16]. Most of these efforts, however, have failed and while the values for the ceramic are of the order of 2000 [11, 12], thin films usually have relative permittivities in the range of a few hundred.

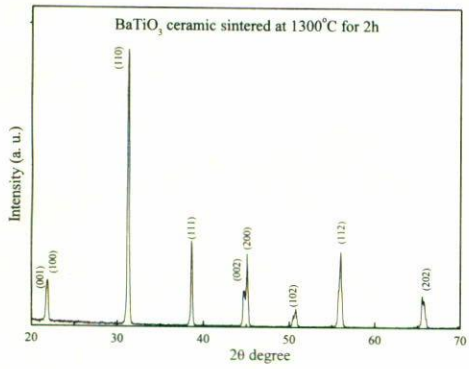
A typical problem in understanding $BaTiO_3$ thin films is the large variation in the reported values of the temperatures at which the maximum permittivities occur. Although the effects of the processing parameters, such as deposition conditions, deposition rate, *in situ* or post-annealing temperature, on the dielectric properties of $BaTiO_3$ thin films have been investigated, the origin of the large variation in the values of the room temperature permittivity has not been clearly identified.

The objective of our present study is to produce and characterize high quality, well-adhered thin films starting from $BaTiO_3$ ceramic targets using PLD for the deposit and X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), X-ray Photon Spectroscopy (XPS) and Auger Electron Spectroscopy (AES) for the characterization. For this purpose, polycrystalline $BaTiO_3$ was deposited on Pt/Ti/Si, substrates. Since the growth of epitaxial $BaTiO_3$ single crystal films is practically impossible, the so-called "grain size effect" [11, 12] becomes an important factor to improve the dielectric properties of the films.

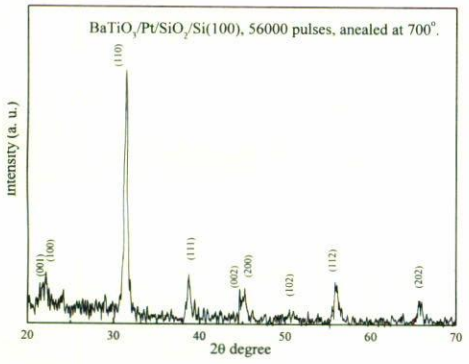
2. Experimental procedure

The $BaTiO_3$ ceramics were prepared by the conventional ceramic method from high purity reactants (E. Merk, Darmstadt, Germany): BaO (>99%), TiO_2 (>99%). These powders were finely ground and properly mixed, calcined at 800°C for 2h and finally sintered at 1300°C for 2h with a heating rate of 1°C/min and an identical cooling rate.

Slabs of the ceramics obtained were used as targets to grow $BaTiO_3$ thin films by PLD on Pt/Ti/Si substrates, using



(a)



(b)

FIGURE 1. XDR for the $BaTiO_3$ (a) in the bulk and (b) in thin films.

a KrF excimer laser with 284 nm wavelength, 30 ns pulse width and 10 Hz repetition rate. The laser energy density on the target was 2J cm^{-2} approximately. The films were deposited at an oxygen partial pressure of 30 mTorr with the substrate heated to 300°C. The crystal orientations, lattice constants and epitaxial nature of the films were determined by XRD using the Cu Kα_1 ($\lambda_1 = 1.54056$Å) and Kα_2 ($\lambda_2 = 1.54439$Å) lines with a scanning rate of 2°/min of a XRD Phillips X'Pert-MPD diffractometer. The surface and cross-sectional morphology of the films were analyzed by SEM in a JSM-5300 scanning electron microscope by JEOL. Heat treatment was performed on the samples after measuring them as deposited.

3. Results and discussion

Figure 1a shows the XRD $\theta/2\theta$ scans of the $BaTiO_3$ ceramic sintered at 1300°C for 2h, indicating a pure perovskite phase. Figure 1b shows the XRD pattern of a $BaTiO_3$ film deposited on a Pt/Ti/Si substrate annealed at 700°C for 10 minutes with heating and cooling rates of 10°C/min. A very good match between the ceramic and the film patterns can be observed, showing first, a good replication of the target stoichiometry on the film and second, a good crystallization of the film after the thermal treatment. This result clearly indicates that 700°C is a sufficiently high temperature to promote the crystallization of perovskite $BaTiO_3$ thin films.

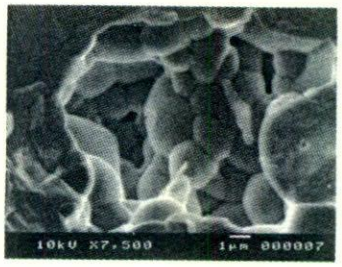


FIGURE 2. SEM micrograph of the $BaTiO_3$ ceramic.

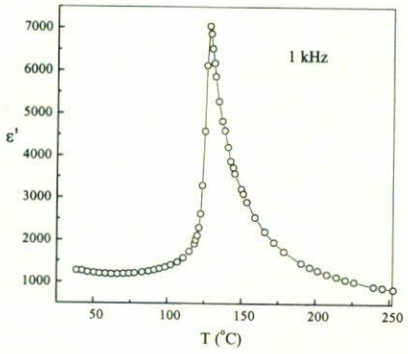


FIGURE 3. Temperature dependence of the dielectric permittivity, ε for the $BaTiO_3$ ceramic measured at 1kHz.

SEM micrographs of the polished surface of a $BaTiO_3$ ceramic sample sintered at 1300°C for 2h are shown in Fig. 2. The particle size is 2–4 μm approximately. The density of the ceramic was higher than 95% of the theoretical value [17]. The sample was clearly ferroelectric as shown in the dielectric constant *vs.* temperature curve presented in Fig. 3 for a $BaTiO_3$ ceramic. The Curie Temperature of the tetragonal-cubic phase transition is around 128°C, similar to the value previously reported in the literature for $BaTiO_3$ [18].

Figure 4 shows SEM micrographs of the $BaTiO_3$ films grown with 10 000 and 20 000 laser pulses before and after thermal treatment. The as-deposited films were amorphous and non-uniform whereas the annealed films were crystalline, more uniform and stressed as cracking started to appear. For the thicker films (36 000 and 56 000 pulses) shown also in Figure 4, a more uniform distribution of the material was observed but cracking appeared even in the as-deposited films. Annealing produced good crystallinity and very well defined cracks. A different scale (5 μm) was intentionally used in Figs. 4(c2) and 4(d2) to show a larger area map of the surface defects since no substantial information is lost from the 1 μm scale micrographs.

The resulting films were polycrystalline and since there is no epitaxial growth of the $BaTiO_3$ films, the cracking cannot be attributed to lattice mismatch but to the different thermal expansion coefficients of the film and the substrate. The thermal coefficient for tetragonal $BaTiO_3$ [10] is $6.5 \times 10^6/°C$ whereas for Pt it is $9 \times 10^6/°C$. The lattice parameter for Pt is 3.9231 Å and 4.03 Å for the $BaTiO_3$ perovskite layer, which

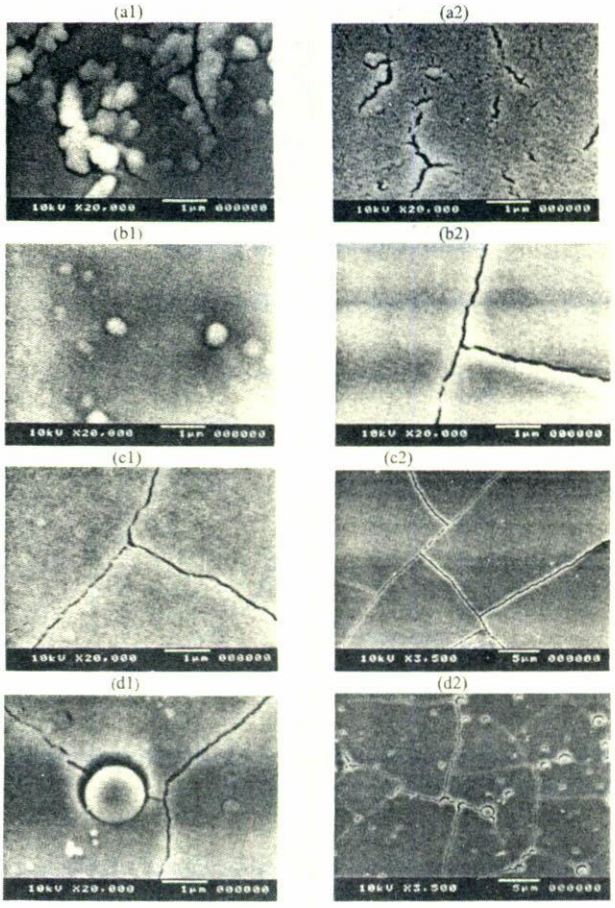


FIGURE 4. SEM micrographs of the $BaTiO_3$ thin films, before (1) and after annealing (2) at 700°C for 10 minute, (a1,2)= 10 000 pulses, (b1,2)= 20 000 pulses, (c1,2)= 36 000 pulses, (d1,2)= 56 000.

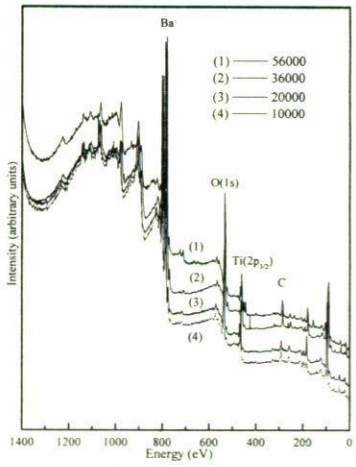


FIGURE 5. XPS spectra for samples of different thickness after annealing.

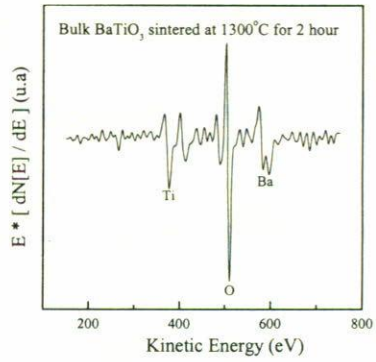


FIGURE 6. Auger spectrum of the $BaTiO_3$ ceramic sintered at 700°C for 2 hours.

would produce a 2.6% lattice mismatch, in the case of epitaxial growth. Particulate, characteristic of the PLD technique, was present in most of the films as no special effort was made to avoid it. Figure 5 shows the XPS spectra of the PLD grown films. The Ti($2p_{3/2}$) peak is centered at an energy of 458.9 eV in all cases evidencing the presence of Ti in the $BaTiO_3$ perovskite structure according to the XPS reference tables [18].

Figure 6 shows the Auger spectrum of the $BaTiO_3$ samples in the bulk. Similar spectra were obtained for the films as deposited and after heat treatment. Auger Electron Spectroscopy is a surface analysis technique and the results presented here correspond to the first few atomic layers of the bulk ceramic and the films. Such results evidently differ from the $BaTiO_3$ stoichiometry, but it is a known fact that compounds containing barium are slightly barium rich on the surface. Therefore, it is expected that the relative concentrations so determined are not representative of the composition of the bulk material. However, the Auger spectra are useful in showing the incorporation of oxygen to the material through the annealing process. A better evaluation of the element relative concentrations can be performed by digging a small crater into the sample using argon ions and making the Auger analysis far from the surface. However, technical difficulties prevented us from performing this kind of analysis. The relative concentrations of the different elements in the ceramics and films at the surface, calculated from the Auger spectra are presented in Table I.

From the results shown in Table I, we can observe that the oxygen content is different in every case. It is clear that oxygen is lost in the deposition process, a phenomenon typically observed in PLD grown ceramic films. The loss of oxygen also explains the difficulty in obtaining the perovskite structure. However, the post annealing process solves the oxygen loss problem. As a matter of fact, the oxygen relative concentration is higher in the annealed films than in the bulk material. A variation in the Ti and Ba concentration is also observed and is essentially due to the evaluation technique used in AES, that is, as the concentration of one of the elements goes up, the concentration of the others will go down and the relative concentrations of the component elements will be the relevant figure for stoichiometric considerations. In our case,

TABLE I. Comparison of the relative concentrations of the component elements of the target and the films, as deposited (AD) and heat treated (HT), as determined from Auger Electron Spectroscopy analysis.

Pulse number	AD Ti(%)	HT Ti(%)	AD Ba(%)	HT Ba(%)	AD O_2(%)	HT O_2(%)
Bulk	15		39		45	
10 000	13	19	37	30	49	50
20 000	23	18	34	33	41	48
36 000	21	16	45	36	32	47
56 000	22	19	40	31	37	49

the relative concentration of oxygen will increase at the expense of Ti and Ba, but the relative concentration of Ti and Ba will not change significantly.

4. Conclusions

A $BaTiO_3$ ceramic with good ferroelectric and structural properties was obtained. Thin films deposited by PLD from the $BaTiO_3$ ceramic targets on Pt/Ti/Si substrates resulted in polycrystalline films, as shown by XRD, well adhered to the substrate. Cracking evidenced the presence of stresses, particularly in the thicker films. Heat treatment increased the stress producing cracking even on the thinner films. Auger electron spectroscopy showed a good replication of the stoichiometry from the target to the films. The quality of the films will, in general, depend on the deposit conditions (substrate temperature and ambient pressure and composition) and on the characteristics of the substrate (lattice parameters matching and thermal expansion coefficient). Elimination of cracking of the films will require further studies along these lines. Nevertheless, PLD showed to be a promising technique for the production of ferroelectric $BaTiO_3$ films.

Acknowledgments

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