Evolution of the surface morphology with temperature, in oxidant atmosphere, of Ba ($Ti_{1-x}Sn_x$)O_3 (x = 0.13) thin films

M. CERNEA*, L. TRUPINA, C. PLAPCIANU, R. TRUSCA[a], C. GALASSI[b]
National Institute of Materials Physics, Str. Atomistilor 105 Bis, RO-77125, P.O. BOX: MG-7, Magurele-Bucharest, Romania
[a]*METAV-R&D S. A., P.O. 22, Bucharest, Romania*
[b]*National Research Council-Research Institute of Science and Technology for Ceramics, Via Granarolo 64, I-48018 Faenza, Italy*

Thin films of $Ba(Ti_{1-x}Sn_x)O_3$ with *x* = 0.13 have been deposited by rf-magnetron sputtering and their growth morphology and structure vs. annealing temperature, in oxygen atmosphere, have been investigated. The films deposited on silicon-platinum substrates, at room temperature, in Ar atmosphere were amorphous. The as-obtained films had a mean surface roughness (RMS) around 6.529 nm and a grain size of about 150 nm. By annealing the film up to 1150 °C in oxygen, the grains size increases up to 1-1.5 µm in diameter. Films containing $BaTi_{0.87}Sn_{0.13}$ as crystalline phase with the cubic structure of $BaTiO_3$ and, bundle-like morphology were obtained by heating the film at 1250 °C for 3h in oxygen. The as-obtained film showed the preferential (110) and (100) orientations.

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1. Introduction

$Ba(Ti_{1-x}Sn_x)O_3$ (x = 0.13), (denoted as BTS_{13}) thin films are used for disk or multilayer capacitors with high dielectric constants around the phase transition temperatures [1-9]. Sn doped $BaTiO_3$ thin films have been prepared using PLD [10, 11], RF sputtering techniques [12] and sol-gel process [13-15]. Epitaxial thin films are advantageous for many applications. In particular, epitaxial thin films with smooth surfaces are necessary for optical waveguide electro-optic devices, due to the requirement of low propagation loss. The processing parameters that influence the quality of $BaTiO_3$ films surface prepared by r.f. planar-magnetron sputtering are: substrate temperature, gas pressure, atmosphere, and annealing temperatures.

The effects of the oxygen annealing atmosphere on the structure and morphology of $Ba(Ti_{0.87}Sn_{0.13})O_3$ thin films surface are presented in this paper. BTS_{13} thin films were deposited by RF sputtering technique at room temperature, using silicon-platinum substrate.

2. Experimental procedure

Ceramic $Ba(Ti_{0.87}Sn_{0.13})O_3$ target was prepared starting from $Ba(Ti_{0.87}Sn_{0.13})O_3$ powder synthesized by the coprecipitation method, as described in a previous paper [16]. The BTS_{13} powder was pressed into pellets with thickness of 5 mm and diameter of 50 mm and then sintered in air at 1350 °C for 4h. BTS_{13} films with thickness of ~ 470 nm were deposited on silicon-platinum substrates, at room temperature, in argon atmosphere, by RF sputtering method. The SBR-1102E (ULVAC) r.f. sputtering system was used.

The BTS_{13} films were annealed at various temperatures until 1250 °C, in oxygen flow.

The thickness of the films was measured using a profilometer. A Quesant® Nomad atomic force microscope (AFM) was used to observe film surface morphology. The phases and crystallographic orientations of the film were investigated by X-ray diffraction technique using a Shimadzu X-Rray Diffractometer XRD-6000. For powder diffraction, CuKα1 radiation, (wavelength 1.5406), a LiF crystal monochromator and Bragg-Brentano diffraction geometry were used. The data were acquired at 25 °C with a step-scan interval of 0.020 ° and a step time of 10 s. The microstructure of the samples was investigated using a Hitachi S-2600N Scanning Electron Microscope. The microanalysis was recorded by EDS using an X-Ray Spectrometry with Rontec Edwin WinTools.

3. Results and discussion

Fig. 1 shows the surface topography of the Sn-doped $BaTiO_3$ film deposited at room temperature, recorded by AFM technique.

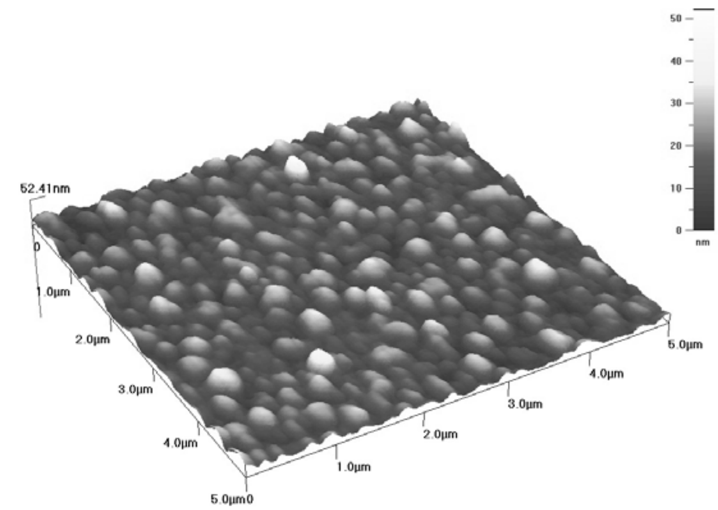

Fig. 1. AFM image of $BaTi_{1-x}Sn_xTiO_3$, x=0.13 thin film deposited at room temperature.

The AFM image of $BaTi_{1-x}Sn_xTiO_3$ film indicated a film surface with average height: 14.84 nm, RMS deviation: 6.529 nm and mean deviation: 5.238 nm. The AFM image shows a good uniformity of the grains size (~150 nm) and the missing of the aggregates on BTS_{13} film surface.

The evolution of the morphology of BTS_{13} surface films vs. temperature was observed using the SEM images (Fig. 2. a-e).

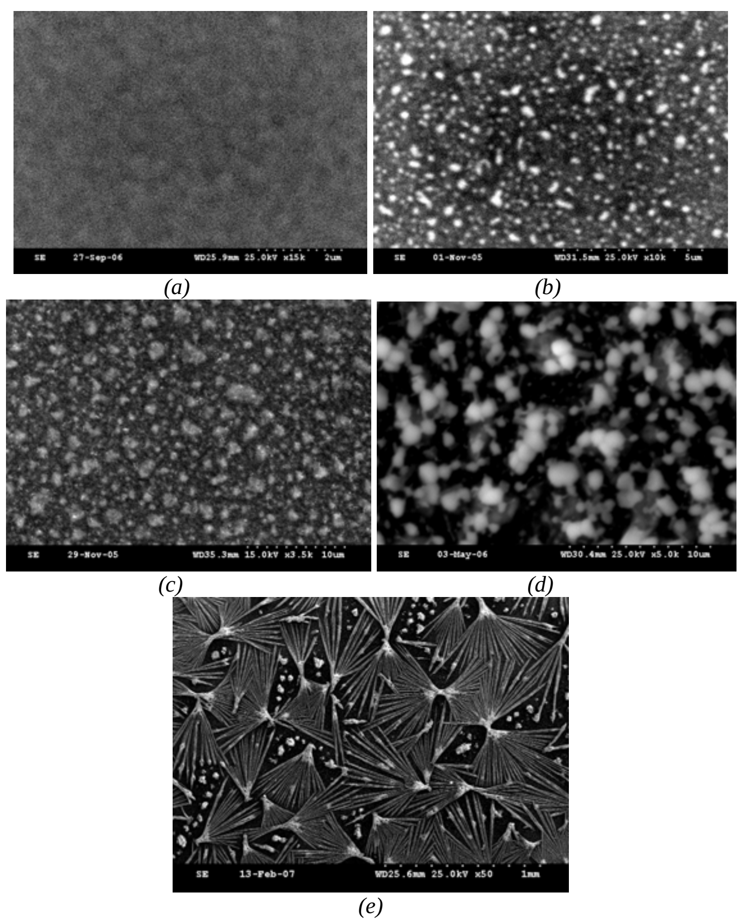

Fig. 2. SEM images of BTS_{13} film deposited at room temperature (a); film annealed in oxygen, 3h at: 750 ºC (b), 1000 ºC (c), 1150 ºC (d) and 1250 ºC (e).

The film deposited at room temperature shows a surface with very fine grains as shown the AFM and SEM pictures (Fig. 1 and Fig. 2a). It was observed that the grains of BTS_{13} film grow to different extent (below 1.5 μm) as the treating temperature increased from the room temperature to 1150 °C. The grain size of BTS_{13} films is more uniform at room temperature than after annealing at higher temperatures. The grains sizes of BTS_{13} film annealed at 1150 °C are between 1 and 1.5 μm (Fig.2d).

Fig. 2e shows the surface morphology of the BTS_{13} film annealed at 1250 °C for 3h in oxygen. The SEM observation shows some BTS_{13} grains (size ~ 5-7 μm) that form aggregates (size in the range 30-50 μm), which coexist with bundles. The SEM observations of BTS_{13} films suggest the steps sequence of the surface morphology changes versus annealing temperature.

The stoichiometric transfer from the target to film was analyzed by EDX analysis. It was considered the entire areas shown in Fig.2e. The EDS results indicated the presence of Ba, Ti, Sn and Pt atoms (Fig. 3).

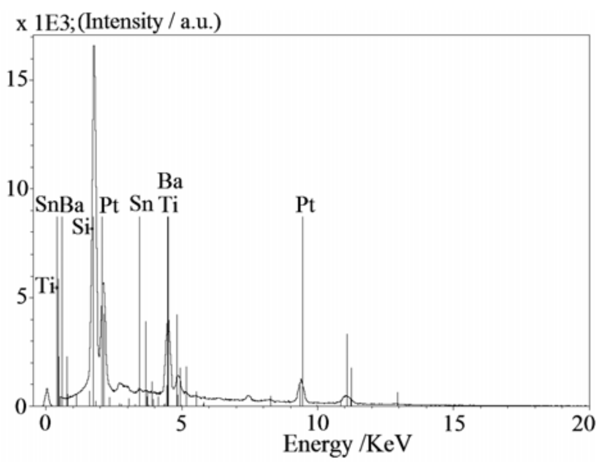

Fig. 3. EDS-spectrum of BTS_{13} film annealed at 1150 °C, in oxygen.

The chemical composition of the Sn-doped $BaTiO_3$ film analyzed by EDX is presented in Table 1.

Table 1. Composition of the BTS_{13} film annealed at 1150 °C.

Element / line	Concentration, (wt)	Concentration, (wt %)	Concentration, (at)	Concentration, (at %)
Ti	9.29	21.22	0.1941	42.74
Sn	7.66	17.49	0.0645	14.21
Ba	26.84	61.29	0.1954	43.05

As can be observed, the value of the dopant concentration in the film (14.21 at % for Sn) is close to that of the target.

XRD investigations revealed that the BTS_{13} film deposited at the room temperature is amorphous, less crystallized, although it was annealed at various temperatures up to 1250 °C, in oxygen flow for different holding time.

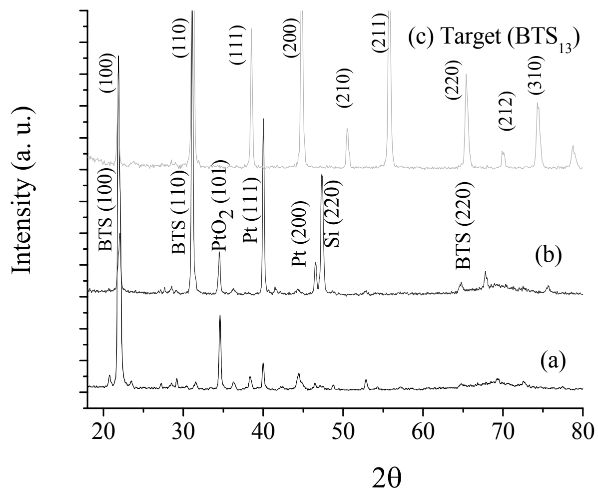

Fig. 4. XRD patterns of BTS_{13} film annealed in oxygen, at 1250 °C, 3h (a); 6h at 1250 °C (b); target (c)

The indexed XRD peaks of BTS_{13} film annealed at 1250 °C, 3h (Fig. 5), correspond to the cubic $BaTiO_3$ structure [17] and, to the substrate phases (cubic silicium [18], cubic platinum [19] and oxidized platinum PtO_2 [20]). The polycrystalline BTS_{13} film exhibits a tendency to have the preferential (110) and (100) orientations.

4. Conclusions

Solid-solution Ba($Ti_{0.87}Sn_{13}$)O_3 films were prepared on Pt/Si substrates by sputtering deposition technique at room temperature.

The as-deposited BTS_{13} films exhibited a smooth surface (RMS deviation of 6.529 nm), a good uniformity of the grains size (~150 nm) and an amorphous structure. The grain size increases gradually up to 1-1.5 μm when the BTS_{13} film was annealed until 1150 °C. The film annealed at 1250 °C for 3h in oxygen exhibits bundle-like morphology. The bundles are present together with agglomerated particles.

Single-crystal Ba($Ti_{0.87}Sn_{13}$)O_3 perovskite phase with the structure of cubic $BaTiO_3$ was obtained after annealing the film in oxygen at 1250 °C for 3h. These BTS_{13} films show grain crystallized with preferential (110) and (100) orientations. The annealing temperature and oxygen atmosphere were the main factors in determining the structure evolution, morphology and preferred orientations of the films.

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*Corresponding author: mcernea@infim.ro