

PREPARATION AND PROPERTIES OF Ce-DOPED BaTiO₃ THIN FILMS BY R. F. SPUTTERING

M. Cernea, Monica Iliescu, I. Matei^a, A. Iuga^a, C. Logofatu^b

S.C.MATPUR S.A. Bucharest

^aNational Institute for Physics and Technology of Materials, Bucharest.

^bNational Institute for Lasers, Plasma and Radiation Physics, Bucharest.

Ce-doped BaTiO₃ thin films prepared on silicon-platinum by r.f. sputtering has been investigated. BaTiO₃ doped with 5.5 mol.%CeO₂ thin film was deposited at 550 °C substrate temperature in Ar atmosphere. The crystal structure and shape were examined by X-ray diffraction and scanning electron microscopy with EDAX. Analysis by X-ray diffraction patterns show that the crystalline film with a cubic structure of BaTiO₃, was obtained. The surface morphology (roughness, the grain size and the droplet size) of the thin film surface was examined by atomic force microscopy (AFM). The grain size is about 160 nm, the droplet size is about 0.675 μm and the roughness is 36.88 nm. EDAX analyse established a composition of the film identically with that of target (BaTiO₃ doped with 5.5 mol.%CeO₂). The broad peak in the capacitance versus temperature curve at Curie point indicate that the r.f. sputtered Ce-doped BaTiO₃ film is ferroelectric. The values of the capacitance of the thin film at 1 KHz were found to be 86 pF and the loss dielectric was tanδ=0.0875. The film have presented dielectric anomaly peak at 23 °C showing ferroelectric to paraelectric phase transition.

Keywords: Barium titanate, Sputtering, Thin film

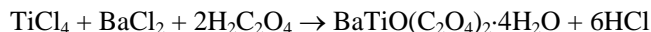
1. Introduction

Barium titanate (BaTiO₃) is a ferroelectric material widely studied because of its many potential useful properties. There are numerous proposals part its application in electronic [1] and electro-optic devices [2] apart from its high permittivity phenomena, associated with the basic ferroelectric behaviour. Obtaining thin films of BaTiO₃ and doped BaTiO₃ with properties approaching those of bulk BaTiO₃ (and doped- BaTiO₃) would both contribute general insight into thin-physics and also have application in the microelectronic industries. Extensive work has been done using the r.f. sputtering and other thin-film fabrication technics [3-6]. Preparation of BaTiO₃ thin films by sputtering was intensely studied for find the influences of procesing parameters on the thin films quality [4,7,8]. Nagatomo et al. [4] reported the relationship between the substrate temperature and total gas pressure for the fabrication of BaTiO₃ films on platinumium and fused quartz substrate by r.f. planar-magnetron sputtering. They obtained various structural films with no phase transition occuring. Another paper on the preparation of BaTiO₃ films by sputtering [8], described the dependence of amorphous, cubic and tetragonal phase transitions on the substrate and annealing temperatures. In this paper, the preparation and characterization of thin films of CeO₂-doped BaTiO₃ are reported.

2. Experimental procedure

A SBR-1102E (ULVAC) r.f. sputtering system was used to make the Ce-doped BaTiO₃ thin film on silicon-platinum substrate. A chromel-alumel thermocouple was attached to control the

temperature of the substrate. The powder for the target was prepared from BaTiO₃, CeO₂ and TiO₂. From barium chloride, titanium chloride and oxalic acid we precipitated BaTiO(C₂O₄)₂·4H₂O following the reaction [9]:



This process leads to a high-purity titanate with a Ba/Ti ratio near to 1.00 and very small grains of about 0.6 μm, by calcination up to 900 °C [10]. We added CeO₂ and TiO₂ in molar ratio 1:1 to BaTiO₃. The concentration of the donor dopant CeO₂ was 5.5 mol.%. The sputtering chamber was initially evacuated to a base pressure of 3x10⁻³ Pa, then argon gas, controlled with separate flowmeter, was introduced into the sputtering chamber until a pressure of 1 Pa. The substrate was clamped on a steel substrate holder at 550 °C. The sputtering conditions are summarized in Table I.

Table I. Summary of sputtering conditions

Target to substrate distance	30 mm
Sputtering gas	100 vol.% Ar
Gas pressure	1 Pa
Substrate	Si-Pt
Substrate temperature	550 °C
Deposition rate	2.5 nm/min
Thickness sputtered film	900 nm.

Single-crystal silicon wafers doped with phosphorous (n-type) and cleaved parallel to the (100) plane were used as substrate material for a platinum thin film deposited by sputtering at 550 °C. Before the Pt film deposition, the wafers were thoroughly cleaned and etched in an HF buffer solution to strip off the SiO₂ layer. To test the ferroelectric properties of Ce-modified BaTiO₃ film, a structure was formed from Ti film as the lower electrode and a layer of silver. We used a DRON 3 for X-ray diffraction and a SEM515 with EDAX, Philips for the surface morphology analyse. Capacitance and dielectric loss were measured at 1 KHz characteristic frequency of a Hewlett-Packard Model 4194A Impedance meter.

3. Results and discussion

The structure of Ce-doped BaTiO₃ film deposited on Si-Pt was studied by X-ray diffraction technique using CuK_α radiation at room temperature. The film deposited at a substrate temperature of 550 °C was found to be crystallized. The Ce-doped film sputtered at 550 °C has the cubic polycrystalline structure (randomly oriented) of BaTiO₃ (Fig.1). Absence of the characteristic peaks of Ce-species in the diffraction pattern suggests the complete solubilization of Ce in BaTiO₃. Absence of the characteristic peaks of Ce-species in the diffraction pattern suggests the complete solubilization of Ce in BaTiO₃.

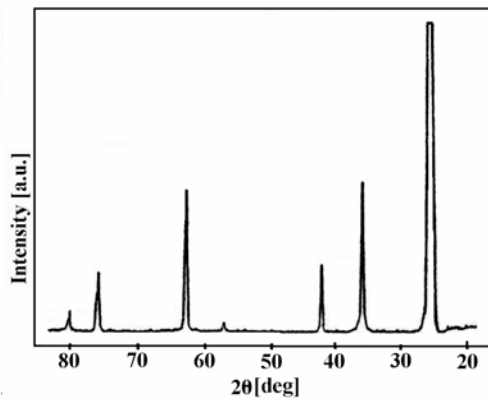


Fig. 1. XRD patterns of BaTiO₃ doped with 5.5 mol.% CeO₂ film.

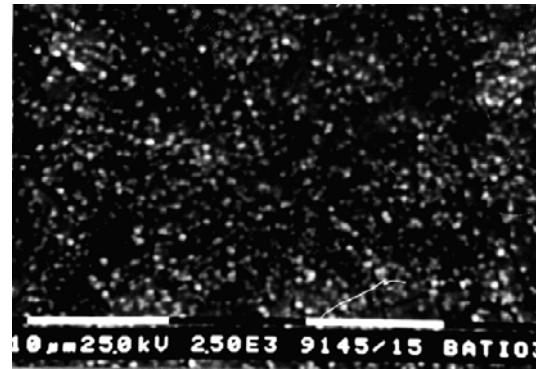


Fig. 2. Scanning electron micrographs of BaTiO₃ doped with 5.5 mol.% CeO₂ film.

The surface morphology of film was observed by SEM. The scanning electron micrograph in Fig.2 show that the grains grown were homogeneous. Also, they can seen the droplets on the surface of film.

The stoichiometric transfer from the target to film was analysed by EDAX. The chemical composition of the Ce-doped BaTiO₃ film was analysed in three different zones:

- on an aggregate;
- in an area between the aggregates;
- on the entire area showed in micrograph of Fig.2 (Table 2).

The aggregate presents a CeO₂ concentration in the droplet analysed (7.41 %) bigger than of the target (5.5 %). This rise on the CeO₂ concentration in the droplet is determined by segregation of the dopant at grain boundary and by the local inhomogeneity of the target composition. The composition on an aggregate and the composition between two droplets are approximately identicals, in the analysed points. Though, the closest value of the dopant concentration (5.61 %) comparative whit that of the target, was obtained for entire area presented in micrograph SEM (Fig.2). That prove the same composition for film and for target.

Table 2. Composition on the entire area showed in Fig.2

Element	Composition	
	Element [wt.%]	Oxide [mol.%]
Ba	38.10	42.54
Ti	31.08	51.85
Ce	4.57	5.61
Total:	100.00	

The particulars of the film surface topography and the growth mechanism can be carried out using the AFM. The average surface roughness over a scan area of the surface of the Ce-doped BaTiO₃ film deposited at 550 °C, is 36.88 nm. The top view of this film looks like a network with a grain size of 160 nm. On the other hand, we can see some grains in around 0.675 μm, that rise the roughness. The grain size are in good agreement with previous results for the particle-size dependence. For particle sizes less than 120 nm, the symmetry at room temperature is cubic, while for larger particle sizes, the tetragonal, ferroelectric phase is found [8,11]. The capacitance was measured as a function of temperature at 1 KHz to verify the existence of the ferroelectric-paraelectric phase transition. Fig.3, shows the temperature characteristics of capacitance and dielectric loss for the Ce-doped BaTiO₃ film. A broad transition in the region of 23 °C is seen. The maximum values of capacitance and dielectric loss at 23 °C (Curie point) were 86 pF respectively, tanδ=0.0875 (Fig.4). The small grains size of the film contributes to peaks broadening.

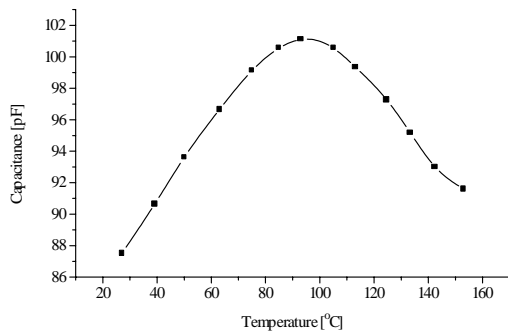


Fig. 3. Capacitance vs temperature of BaTiO₃ doped with 5.5 mol.% CeO₂ film sputtered on Si-Pt.

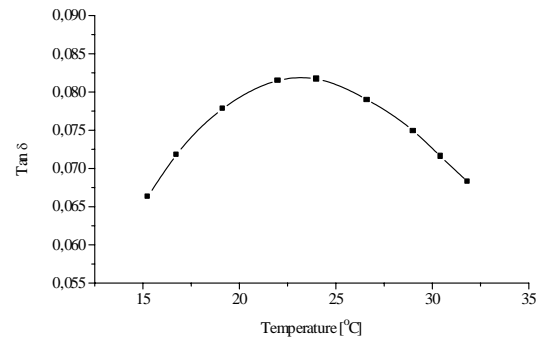


Fig. 4. Dielectric loss ($\tan\delta$) vs temperature of BaTiO₃ doped with 5.5 mol.% CeO₂ film sputtered on Si-Pt.

In general, the decrease and broadening of the dielectric peak, and the increase of the loss tangent in film may be attributed to the smaller grain size and lower packing density of the films compared to that of the bulk ceramics. Also, the lower value of the capacitance may be due to the existence of non-ferroelectric surface layer at the film-electrode interface [12,13].

4. Conclusions

Ferroelectric thin films of Ce-doped BaTiO₃ have been deposited by rf sputtering in a 100 %Ar, at substrate temperature 550 °C. The X-ray diffraction and EDAX studies indicate that the cubic films with perovskite-type structures are obtained on Si-Pt substrate. The broad peaks in the C-T and $\tan\delta$ -T curves at Curie temperature confirm the ferroelectricity of the rf sputtered BaTiO₃ doped with 5.5 mol.% CeO₂ films. The decrease of the Curie temperature from 125 °C (T_c of BaTiO₃ undoped) to 23 °C (T_c of BaTiO₃-5.5 mol.% CeO₂ film) and SEM-EDAX analysis confirm the deposition of the BaTiO₃-5.5 at.% Ce film with the target composition.

Acknowledgements

We would like to express our thanks to Mr. P. Budau from NANOTECH.-Company for AFM analysis.

References

- [1] P. J. Harrop, D. S. Campbell, *Thin Solid Films*, **2**, 273 (1968).
- [2] A. B. Kaufman, *IEEE Trans. Electron. Devices* ED-16, 562 (1969).
- [3] K. Fujimoto, Y. Kobayashi, K. Kubota, *Thin Solid Films* **169**, 249 (1989).
- [4] T. Nagamoto, T. Kosaka, S. Omari, O. Omoto, *Ferroelectrics* **9**, 91 (1971).
- [5] C. A. T. Salama and E. Siciunas, *J. Vac. Sci. Technol.* **9**, 91 (1971).
- [6] O. X. Jia, Z. Q. Shi, W. A. Anderson, *Thin Solid Films* **209**, 2230 (1992).
- [7] J. H. Kim, S. Hishita, *Journal of Materials Science*, **30**, 4645-4650 (1995).
- [8] K. Uchino, N. Lee, T. Toba, N. Usuki, H. Aburatani, Y. Yto, *J. Ceram. Soc. Jpn.*, **100**, 1091 (1992).
- [9] W. S. Clabaugh, E. M. Swiggard, R. Gilchrist, *J. Res. Natl. Bur. Std.*, **56** (5)289, RP 2677 (1956).
- [10] T.-T. Fang, H. B. Lin, *J. Am. Ceram. Soc.*, **72** (10) 1899 (1989).
- [11] K. Uchino, E. Sadanaga, T. Hirose, *J. Am. Ceram. Soc.* **72**, 1555 (1989).
- [12] Y. Ijima, *Japan J. Appl. Phys.* **24**, 401 (1985).
- [13] T. Kawano, T. Sei, T. Tsuchia, *J. Mater. Sci.*, **31**, 2178 (1991).