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Aerosol Deposition of $Ba_{0.8}Sr_{0.2}TiO_3$ Thin Films

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Abstract:

In this work we optimized conditions for aerosol deposition of homogeneous, nano-grained, smooth $Ba_{0.8}Sr_{0.2}TiO_3$ thin films. Investigation involved optimization of deposition parameters, namely deposition time and temperature for different substrates. Solutions were prepared from titanium isopropoxide, strontium acetate and barium acetate. Films were deposited on Si (1 0 0) or Si covered by platinum (Pt (1 1 1) /Ti/SiO_2/Si). Investigation showed that the best films were obtained at substrate temperature of 85ºC. After deposition films were slowly heated up to 650ºC, annealed for 30 min, and slowly cooled. Grain size of BST films deposited on Si substrate were in the range 40-70 nm, depending on deposition conditions, while the same films deposited on Pt substrates showed mean grain size in the range 35-50 nm. Films deposited under optimal conditions were very homogeneous, crack-free, and smooth with rms roughness lower than 4 nm for both substrates.

Keywords: *Thin films; Aerosol deposition, Barium Strontium Titanate, Roughness*

1. Introduction

Aerosol deposition is a versatile technique for producing various thin films in a wide range of compositions, thicknesses and morphologies. Thin film is formed by spraying, drying and pyrolytical decomposing onto a heated substrate a solution of precursor salts containing desired constituent ions [1, 2]. This method connects many features of the gas-phase and liquid-phase techniques having the following advantages: (a) one-step, simple, cheap equipment, (b) universal precursors (inorganic, organic or metal-organic compounds), (c) easy and precise composition control, (d) various film morphologies possible, and (e) accurate control of the deposition kinetics [3]. The aerosols may be generated by pneumatic or ultrasonic atomizers. Among numerous ferroelectric materials, solid solutions of $BaTiO_3$ and $SrTiO_3$, i.e. $Ba_{1-x}Sr_xTiO_3$ (BST) has merits of high dielectric constant of $BaTiO_3$ and the structural stability of $SrTiO_3$ [4-6]. BST solid solution is a ferroelectric material with tetragonal structure for $x<0.3$ at room temperature. Curie temperature can be easily adjusted by changing the value of x. Thin films with $x<0.3$ were intensively investigated for various applications such as for example high-density capacitors or phase shifters [6].

In this work we optimized conditions for aerosol deposition of homogeneous, nano-grained, smooth $Ba_{0.8}Sr_{0.2}TiO_3$ thin films. Investigation involved optimization of deposition parameters, namely deposition time and temperature for different substrates.

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Experimental

Equipment for thin film deposition was constructed on such a way to enable homogeneous distribution of aerosol on a substrate surface, and was already described in our previous paper [7]. The precursor solutions were prepared from a titanium citrate, strontium acetate and barium acetate. Titanium citrate was formed by dissolution of titanium (IV) isopropoxide in an ethylene glycol solution of citric acid according to the following molar ratio: Ti-ion : citric acid : ethylene glycol = 1 : 4 : 16. The stoichiometric amounts of strontium and barium acetates were dissolved in water. Further, the two solutions were mixed. Water content was changed to obtain the molar concentrations of the metal ions equal to 0.05 mol/dm^3. Prepared solution was deposited on Si (1 0 0) or Si covered by platinum (Pt (1 1 1) /Ti/SiO2/Si). Deposition was performed at substrate temperatures of 70-95ºC. Flow rates of the carrier gas, i.e. oxygen and other parameters were chosen from our previous investigation [7]. Deposition time was varied (1 and 2 h) to obtain films with different thickness. After deposition, the films were heat treated at 650 ºC on the following heating regime: the films were slowly heated (2 ºC/min) up to 400 ºC, then annealed at 400 ºC for 2 h and finally heated (5 ºC/min) up to the temperature 650 ºC at which films remained for 30 min. Films were slowly cooled to prevent crack formation. Crystal structure of the films was determined by X-ray diffraction analysis, and microstructure was examined by AFM.

Results and discussion

Several different deposition temperatures were examined. It was found that deposition at temperatures lower than 70ºC leads to spray condensation on the substrate's surface resulting in inhomogeneous microstructure. On the other hand, higher temperatures led to very fast evaporation of the precursor from a substrate surface. Evaporation occurred before the particles were deposited. As a result, films were not formed at temperatures higher than 100 ºC. Investigated films were deposited at different times of deposition, to obtain films of different thickness.

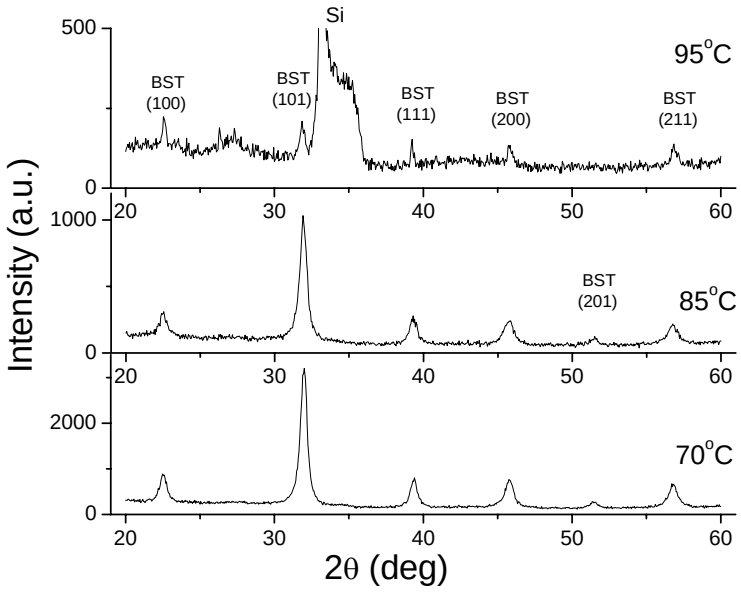

Fig. 1. X-ray diffractogram of BST film deposited on Si substrate at temperatures: 70°C, 85°C and 95°C.

All the films deposited showed a presence of single phase BST (Figs. 1 and 2). Unit cell parameters of the BST phase are given in Tab. I.

Tab. I. Unit cell parameters of the BST films.

Substrate-temperature and deposition time	a (Å)	c (Å)	V(Å^3)
Pt-70°C-2h	3.969(5)	3.967(8)	62.5(1)
Pt-85°C-2h	3.971(1)	3.984(2)	62.83(4)
Si-70°C-2h	3.964(4)	3.973(8)	62.4(1)
Si-85°C-2h	3.963(4)	3.973(4)	62.38(9)

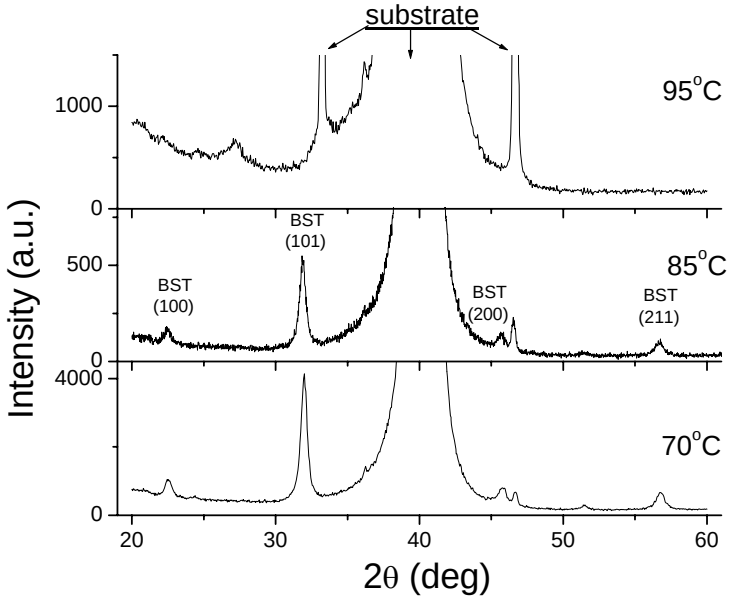

Fig. 2. X-ray diffractogram of BST film deposited on Pt substrate at the temperatures: 70°C, 85°C and 95°C.

Tab. II. Grain size and roughness of the BST films.

Substrate-temperature-deposition time	Grain size (nm)	Roughness(nm)
Pt-70ºC-1h	35.26	5.23
Pt-70ºC-2h	43.47	3.77
Pt-85ºC-1h	47.12	4.98
Pt-85ºC-2h	50.13	3.95
Si-70ºC-1h	42.55	5.75
Si-70ºC-2h	61.14	4.70
Si-85ºC-1h	49.81	5.12
Si-85ºC-2h	62.12	3.32
Si-95ºC-2h	70.79	3.62

After microstructural investigation it was obvious that temperature of 85°C was the optimal one for film deposition. Films deposited on Si substrates at 85°C for 2 h were generally very homogeneous, well-crystallized and without cracks and fractures (Fig. 3b).

Also, they showed spherical grains, with similar grain size and random orientation. However, films deposited for 2 h at 70° and 95°C showed significantly lower quality. Although films deposited at 70°C are well crystalline and show low roughness and narrow grain size distribution, in some parts of the film pores and small cracks were clearly visible (Fig. 4). According to XRD and AFM results films deposited at 95°C are of lower crystallinity and with coarse distribution of grain size (Figs. 1 and 3d). Grain size of BST films deposited on Si substrate was in the range 40-70 nm, depending on deposition conditions. As can be seen from the Fig. 3c the films deposited for 1 h at 85ºC were not of sufficient homogeneity, had higher roughness and lower grain size in comparison to the films deposited at the same temperature but for 2 h (Fig. 3b and Tab. II). Quality of the film deposited at 70ºC for 1 h was even worse. The substrate was not uniformly covered and grains were very small.

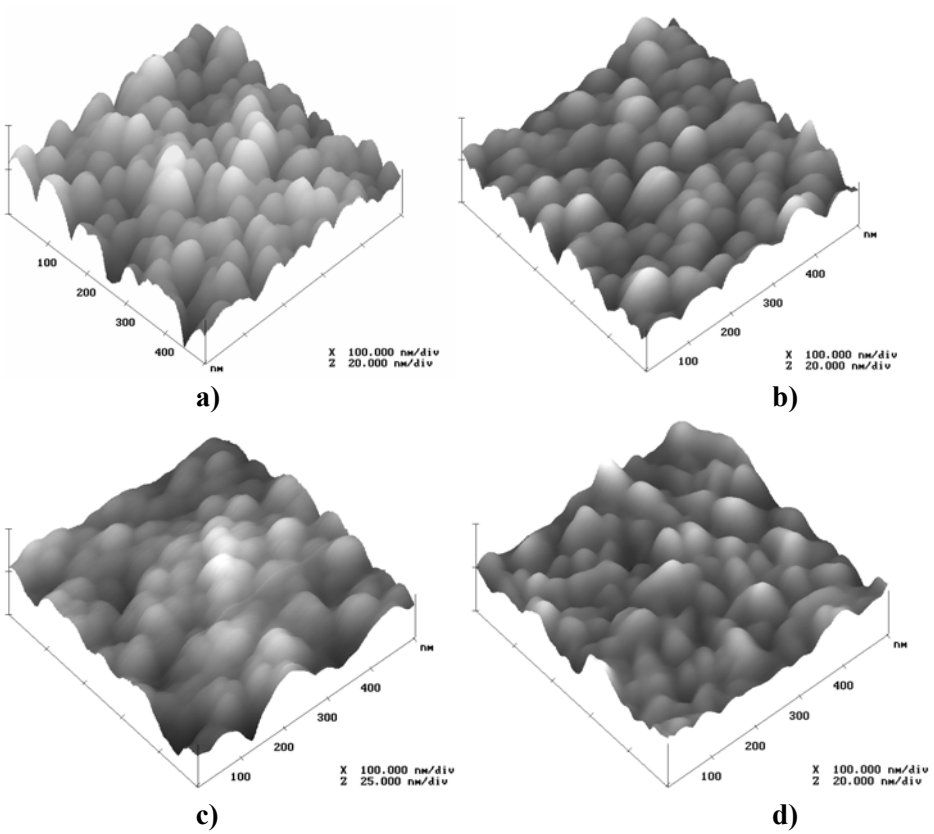

Fig. 3. AFM micrographs of the $Ba_{0.8}Sr_{0.2}TiO_3$ films deposited on Si substrates under the following conditions a) 70°C and 1 h, b) 85°C and 2 h, c) 85°C and 1 h and d) 95°C and 2 h.

Films deposited on Pt-covered substrates showed larger volume of unit cells in comparison to films deposited on Si substrates at 85°C (Tab. I). XRD results showed that deposition temperature of 95°C was not appropriate for Pt substrate; peaks were very small confirming that evaporation of solvent disabled film's growth. Also, these films showed small differences in grain morphology in comparison to films deposited at lower temperatures. Although films deposited at 70° and 85°C for 2 h seem to be of the same quality, after detailed microstructural investigation it was found that films deposited at 70°C exhibited wider grains size distribution. Because of that thermal treatment at 85°C for 2 h was proposed as the optimal one for both substrates.

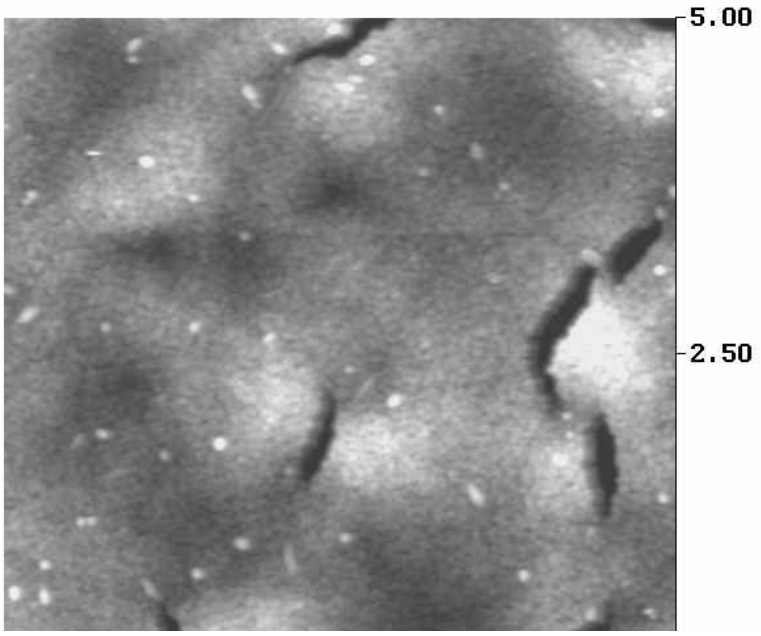

Fig. 4. AFM micrograph of the BST film deposited on Si substrate at 70°C for 2 h.

Films deposited on Pt substrates showed mean grain size in the range 35-50 nm. Also, these films revealed significantly higher quality than the strontium titanate (ST) films deposited under the same conditions [7]. Contrary to the ST films they were continuous and not in the form of separated islands (Fig. 5). Besides comparison with ST films obtained by the same method it is interesting to compare our results with results of other authors who used different methods of BST film deposition. For example, F.M. Pontes et al [8, 9], used similar precursors (titanium citrate + ethylene glycol + barium and strontium carbonates), but they used dip-coating and spin-coating techniques for deposition of the ST and BST films on Pt substrates [8, 9].

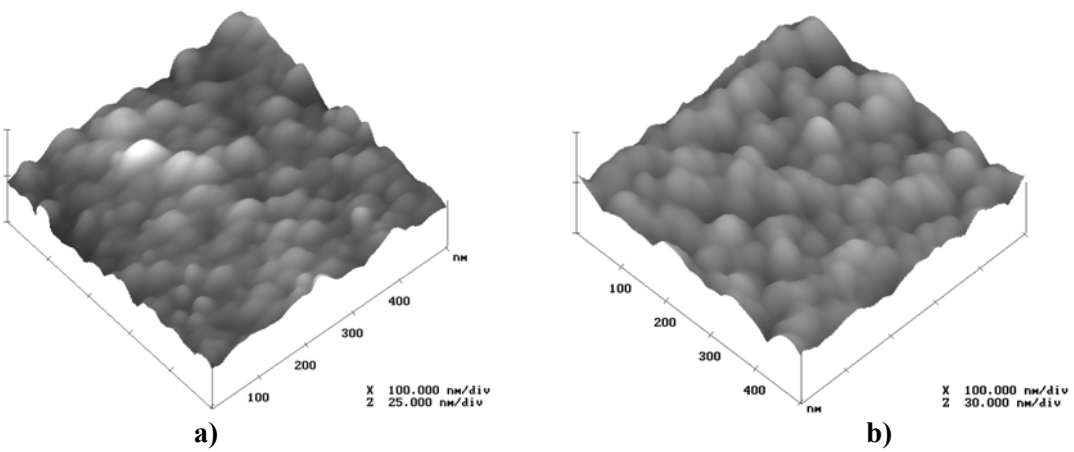

Fig. 5. AFM micrographs of $Ba_{0.8}Sr_{0.2}TiO_3$ films deposited on Pt subtrates under the following conditions: a) 70°C and 2 h and b) 85°C and 2 h.

They obtained films with larger grains and higher roughness. Low roughness of our films deserves to be highlighted since the roughness is one of the crucial parameters for good

electrical properties and application potential.

Conclusions

Single phase BST was successfully obtained on Si and Pt substrates by the method of aerosol deposition. BST films deposited under optimal thermal conditions (85°C for 2h) on both substrates were continual, very homogeneous, well-crystallized, without pores and cracks. Grain size of BST films deposited on Si substrate were in the range 40-70 nm, depending on deposition conditions, while the same films deposited on Pt substrates showed mean grain size in the range 35-50 nm. Films deposited on Si substrates at 85°C for 2h showed lower roughness (3.32 nm).

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Садржај: *У овом раду оптимизирани су услови за добијање хомогеног, глатког и наноструктурног танког филма $Ba_{0.8}Sr_{0.2}TiO_3$ методом депозиције из аеросола. Истраживања су обухватила оптимизацију параметара депозиције, као што су време и температура депозиције, за различите субстрате. Филмови су депоновани на Si (1 0 0) или силицијумским супстратима прекривеним платином (Pt (1 1 1) /Ti/SiO_2/Si). Показано је да се најбољи филмови добијају ако се депозиција врши на супстрате чија је температура 85ºC. Након депозиције филмови су споро грејани до 650ºC, а затим термички третирани на тој температури током 30 мин и споро охлађени до собне температуре. Средња величина зрна BST филмова депонованих на Si супстрате износила је 40-70 nm, у зависности од параметара депоновања, док су филмови депоновани на Pt супстратима показивали средњу величину зрна у опсегу 35-50 nm. Под оптималним условима депоновања добијају се хомогени филмови, без пукотина, веома глатки, са рмс храпавошћу испод 4 nm за оба типа супстрата.*

Кључне речи: *Танки филмови, депозиција аеросолом, баријум стронцијум титанат, храпавост*