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SOL-GEL DERIVED (Ba,Sr)TiO_3 THIN FILMS FOR TUNABLE DEVICES

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The present study is devoted to synthesis and investigation of basic properties of ferroelectric thin films. The sol-gel-type chemical solution deposition method was used for preparation of $(Ba_{0.6}Sr_{0.4})TiO_3$ (BST) thin films. The thin films were characterized in terms of their microstructure, crystalline structure, chemical composition and dielectric properties. It was found that the BST thin films adopted cubic crystallographic symmetry of the space group *Pm3m*, whereas the chemical composition of the thin films corresponded well with the chemical composition of the solution. Complex impedance spectroscopy was used to measure frequency-dependent dielectric properties of the thin films. Due to the high tunability and low dielectric loss, great application potential of these ferroelectric thin films was considered especially as tunable dielectric devices.

Key words: ferroelectrics, thin films, tunability.

1. Introduction

Materials which show a spontaneous electric polarization and in which the direction of the polarization can be reoriented between crystallografically defined states by an external electric field are called ferroelectrics [1]. Ferroelectric materials have a lot of useful properties. High dielectric coefficients over a wide temperature and frequency range are used as dielectrics in integrated or surface mounted device capacitors. The large piezoelectric coefficient is applied in variety of electromechanical sensors, actuators and transducers [2, 3].

The high dielectric constant of perovskite-type alkaline earth titanates make them attractive for use in the integrated thin-film capacitors for microwave circuits. Due to its outstanding pyroelectric coefficient, high dielectric constant, low loss tangent and high dielectric breakdown strength barium strontium titanate $(Ba_{1-x}Sr_x)TiO_3$ is usually applied for high frequency capacitor and ferroelectric dynamic random access memories (FEDRAMs), as replacement for SiO_2/Si_3N_4 dielectrics as the storage medium in conventional DRAMs. It is also considered as high permittivity dielectric for tunable filters, waveguide phase shifters, infrared detectors and electroacoustic transducers [4].

Goal of the present work was to grow $Ba_{0.6}Sr_{0.4}TiO_3$ (BST) thin films by means of sol-gel method on stainless steel substrates and study their structure, microstructure, chemical composition and dielectric properties.

2. Experimental

Barium acetate ($Ba(C_2H_3O_2)_2$), strontium acetate ($Sr(C_2H_3O_2)_2$), and tetrabutyl titanate ($Ti(OC_4H_9)_4$) were used as starting materials for the sol-gel-type chemical solution deposition of $(Ba_{0.6}Sr_{0.4})TiO_3$ (BST) thin films. Glacial acetic acid (CH_3COOH) was used as a catalyst, whereas n-butanol ($CH_3(CH_2)_3OH$) was used as a solvent. All above reagents were analytic purity. After stoichiometrically dissolved, mixed and stirred the precursor solution was deposited by spin coating on stainless steel substrates.

Amorphous films were kept in a preheated furnace at 620 K for 5 min to remove the volatile organic components. The coating process (i.e., spinning – drying – pyrolysis) was repeated up to 15 times yielding thin films of 300 nm in thickness. The as-deposited BST thin films were then heat-treated at 920 K for 2 hours (the heating rate was 1 K/min) by conventional furnace annealing to form a good crystal structure.

Microstructure and chemical composition of the BST thin films was studied by scanning electron microscopy (Hitachi S-4700-type equipped with EDS – the chemical composition analysis system of Vantage Noran).

Crystalline structure of the BST thin films was examined by X-ray diffraction (XRD) analysis, using the Philips PW 3710 X-ray diffractometer ($\Theta - 2\Theta$ method, $CoK_{\alpha 1 \alpha 2}$ radiation, counting time 8 s, step $\Delta 2\Theta = 0.01°$) at room temperature.

Pt top electrodes were formed onto the BST thin film by vacuum evaporation through a shadow mask so as to define capacitors for electrical testing. The sandwich-type capacitor design is shown in Fig. 1.

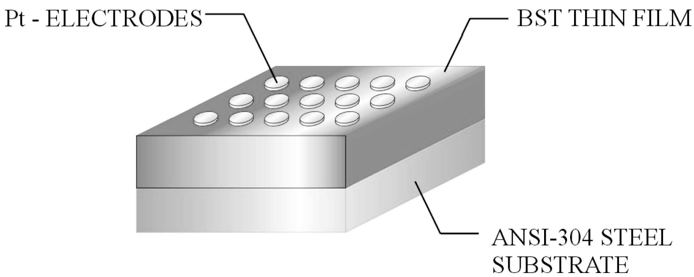

Fig. 1. Sandwich-type capacitor design.

The low-frequency ($\nu = 10$ Hz-1 MHz) dielectric properties of BST thin films were measured using QuadTech 1920 impedance analyzer at room temperature.

3. Results and discussion

Phase identification of the experimental XRD spectrum have shown the presence of two cubic phases, namely $Ba_{0.6}Sr_{0.4}TiO_3$ of the space group *Pm3m* (No. 221), and austenitic steel Ni-Fe of the space group *Fm3m* (No. 225). Contribution of austenitic steel was due to the substrate as far as AISI 304-type stainless steel was used.

On the basis of the phase identification fitting of the X-ray pattern was performed with the computer program PowderCell [5] equipped with the possibility of the Rietveld refinement. It has been found that the BST thin film adopts the regular structure with the unit cell parameter $a = 3.9581$ Å and results are given in Fig. 2.

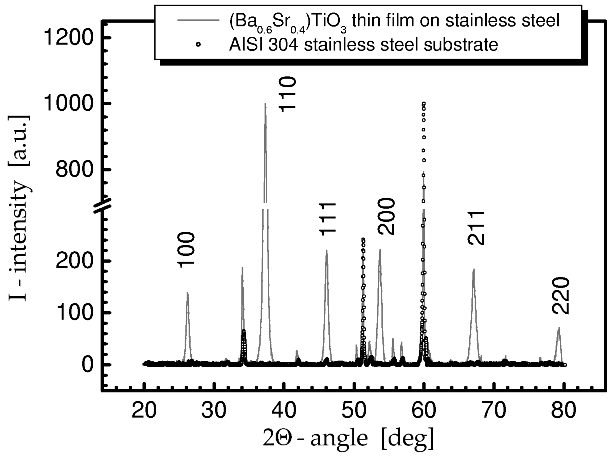

Fig. 2. Results of the X-ray pattern fitting for BST thin film on stainless steel substrate.

Surface morphology of the BST thin films grown on stainless steel substrate as well as results of the point analysis of the chemical composition in the microarea for BTO on stainless steel substrate was studied by EDS ()chemical composition analysis are given in Fig. 3. We can conclude that sol-gel technique yields homogeneous dense microstructure, similar with those arising from films prepared by sol-gel technique elsewhere [6].

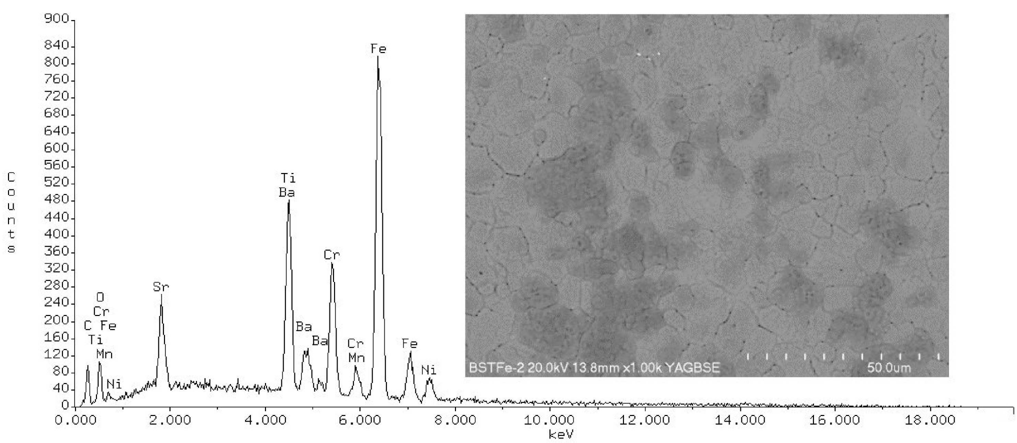

Fig. 3. Results of EDS analysis and microstructure of $Ba_{0.6}Sr_{0.4}TiO_3$ thin film.

The calculations performed on the basis of the EDS measurements have proved a stoichiometric chemical composition of the sol-gel derived $Ba_{0.6}Sr_{0.4}TO_3$ thin films.

The capacitance-voltage (C–V) measurements were conducted on sandwich – type capacitor (Fig. 1) to analyze the tunability of $Ba_{0.6}Sr_{0.4}TiO_3$ thin films. The C–V measurements were conducted by applying a small ac signal of 10 mV amplitude and 1 kHz frequency across the sample while the dc field was swept from a negative to positive bias. The tunability of the capacitance obtained for BST thin film is given in Fig. 4. It was found to increase with increase in the applied electric field.

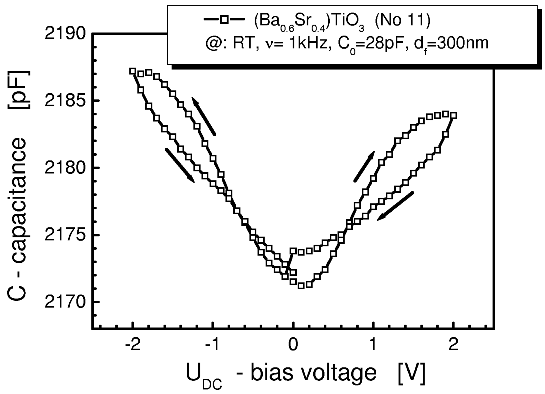

Fig. 4. C–V characteristics of BST thin film.

Low-frequency measurements $(\nu = 10\ \mathrm{Hz}{-}1\ \mathrm{MHz})$ are very useful to evaluate the dielectric properties such as dielectric constant, the dissipation factor, the intergranular resistance, and the time dependence of the oxidation, as well as the contribution of external factors as humidity or of electrode/thin film interfaces [7]. This is an important technique in describing the electrical processes occurring in a system on applying an ac signal as input perturbation. The output response, when plotted in a complex plane plot, represents electrical phenomena due to bulk material, grain boundary effect and interfacial phenomena if any. In view of this specialty, complex impedance spectroscopy (CIS) makes it possible to separate the contribution due to different components in a polycrystalline sample, that of course have different time constants, in the frequency domain.

It is commonly known [8] that for the perovskite type materials one may expect great differences between the electrode, grain boundary and bulk relaxation frequencies, i.e. $\nu_{\mathrm{el}} \ll \nu_{\mathrm{gb}} \ll \nu_{\mathrm{B}}$. In this type of conditions one should expect impedance spectra to show well-resolved bulk, grain boundary, and electrode terms (i.e., nearly separate semicircles in the imaginary part of impedance Z'' vs. real part of impedance Z' plot). However, unusual microstructures with broad size distributions, odd particle shapes, etc., might yield impedance spectra with unexpected features [9].

As an example, the impedance spectra for the $Ba_{0.6}Sr_{0.4}TiO_3$ thin film measured at room temperature is presented in Fig. 5. The residuals plot obtained after the Kramers–Kronig transformation [10] (Fig. 6) shows a deviation of about 1% for the frequencies $\nu > 100$ Hz indicating good quality data.

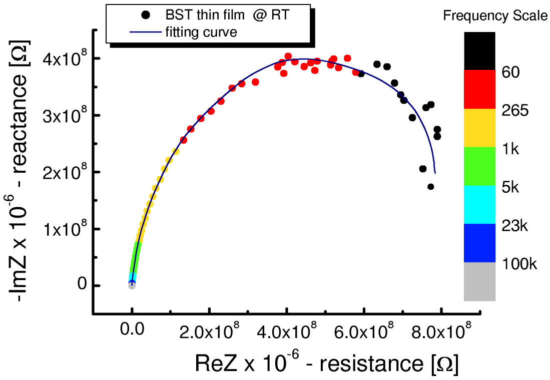

Fig. 5. Complex impedance plot obtained at room temperature. Simulated curve is also shown.

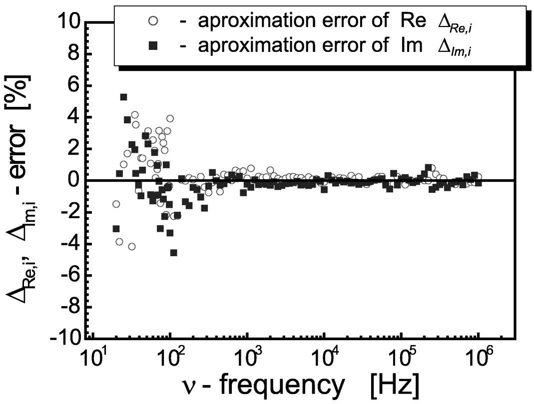

Fig. 6. The residuals plot: relative differences, $\Delta_{\mathrm{Re},\,i}$ and $\Delta_{\mathrm{Im},\,i}$, between the impedance data and its Kramers Kronig-compliant fit plotted versus log(frequency).

Simultaneous presenation of the imaginary part of the complex modulus M'', (sensitive to determining small capacitances [11]), and impedance Z'' (useful for determining dominant resistance [11]) is given in Fig. 7.

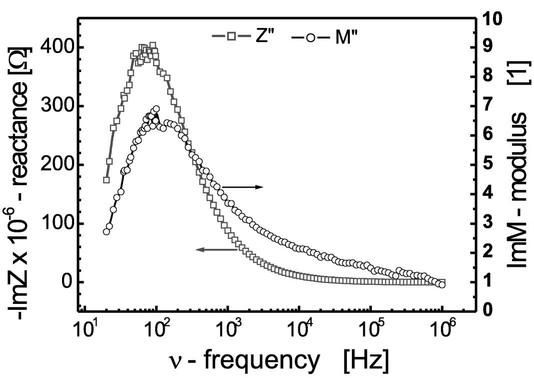

Fig. 7. Simultaneous representation of the moduli Z'' and M''.

4. Conclusions

Research on synthesis, characterization and determination of processing-structure-property relationships of commercially important ferroelectric thin films has been performed. Sol-gel-type deposition technique was applied to produce good quality thin films of $Ba_{0.6}Sr_{0.4}TiO_3$ chemical composition on stainless steel substrates. Results of investigation of their functional properties have shown that they posses a great application potential especially as voltage-tunable transducers.

Acknowledgments

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References

[1] WASER R. [Ed.], *Nanoelectronics and information technology*, Wiley-VCH, Weinheim 2005.

[2] CZEKAJ D., *Technology, properties and applications of PZT thin films*, Wyd. UŚ, Katowice 2002.

[3] KOZIELSKI L., LISIŃSKA–CZEKAJ A., CZEKAJ D., *Materiał gradientowy na bazie ceramiki PZT do zastosowań w przetwornikach piezoelektrycznych*, Ceramika Polski Biuletyn Ceramiczny, **89**, 72–77 (2005).

[4] DOBRUCKI A., *Postępy technologii a przetworniki elektroakustyczne*, XLIV Owarte Seminarium z Akustyki, OSA' 97, pp. 59–68, Gdańsk – Jastrzębia Góra 1997.

[5] KRAUS W., NOLZE G., *Powder Cell – a program for the representation and manipulation of crystal structures and calculation of the resulting X-ray powder patterns*, J. Appl. Cryst., **29**, 301–303 (1996).

[6] LEE S.-J., MOON S. E., KWAK M.-H., RYU H.-C., KIM Y.-T., KANG K.-Y., *Enhanced dielectricproperties of (Ba,Sr)TiO_3 thin films for high-performance microwave phase shifters*, Integrated Ferroelectrics, **72**, 39–46 (2005).

[7] IVANOV D., CARON M., OUELLET L., BLAIN S., HENDRICKS N., CURRIE J., *Structural and dielectric properties of spin-on barium-strontium titanate thin films*, J. Appl. Phys., **77**, 6, 2666–2671 (1995).

[8] ABRANTES J. C. C., LABRINCHA J. A., FRADE J. R., *Representations of impedance spectra of ceramics. Part I. Simulated study cases*, Mat. Res. Bull., **35**, 955–964 (2000).

[9] FLEIG J., MAIER J., *A finite element study on the grain boundary impedance of different microstructures*, J. Electrochem. Soc., **145**, 2081–2084 (1998).

[10] BOUKAMP B. A., *Electrochemical impedance spectroscopy in solid state ionics: recent advances*, Solid State Ionics, **169**, 65–73 (2004).

[11] SINCLAIR D. C., WEST A. R., *Effect of atmosphere on PTCR properties of $BaTiO_3$ ceramics*, J. Mater. Sci., **29**, 6061 (1994).