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Structural and electrical characterization of barium strontium titanate films prepared by sol-gel technique on brass (CuZn) substrate

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The crystal structure, surface morphology and electrical properties of polycrystalline (Ba,Sr)TiO_3 films were investigated. The barium strontium titanate (BST) films were prepared by sol–gel processing using barium acetate ($Ba(CH_3COO)_2$), strontium acetate ($Sr(CH_3COO)_2$) and titanium isopropoxide ($Ti(OC_3H_7)_4$) as starting materials. Acetic acid and acetylacetone were selected as solvents. Six different types of gels were prepared, increasing the Sr^{2+} content from 0% to 50%. The films were deposited on brass (CuZn) substrate and then sintered at 750 °C for 2 h and annealed at 500 °C for 1h. The single layer thickness of the films was about 10 μm. The surface morphology of the film was observed using a scanning electron microscope (SEM). X-ray diffraction (XRD) results show that the film exhibits a pure perovskite phase. The temperature dependence of resistance of films has been investigated and the results showed that the room-temperature resistivity decreases by increasing the Sr^{2+} content. In all cases the films showed a large negative temperature coefficient of resistivity, apart from the ferroelectric transition temperature where a PTCR peak response also appears. Such large temperature coefficient is attributed to the zinc and copper oxides, formed on the CuZn substrate due to its oxidation at elevated temperature, thus offering a significant temperature dependence effect for possible use in sensing applications.

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1. Introduction

From the moment that the positive temperature coefficient of resistance (PTCR) characteristics of semiconducting $BaTiO_3$ materials was firstly observed in 1955 [1,2], a lot of research has been conducted to improve their thermal sensitivity and to understand the conduction mechanism [2,3]. Furthermore, some composite systems, such as (Ba, Sr)TiO_3 and (Ba, Pb)TiO_3 solid solutions, have been investigated in order to broaden the applications of $BaTiO_3$-based thermistors into a wider temperature range at present [4,5].

Recently, strontium titanate-based ceramics have been widely used to fabricate electronic components, such as grain boundary layer capacitors (GBLC) [6], varistors [4, 7], sensors [8], and so on. The Curie temperature (Tc) of pure $SrTiO_3$ is about 110 K, which can shift to higher temperatures by substituting Sr^{2+} with Ba^{2+}. In this way, composite perovskite structure materials, such as (Sr,Ba)TiO_3 and (Sr,Pb)TiO_3 have been developed to fabricate some devices [9-10]. (Ba,Sr)TiO_3 ferroelectric ceramics have paid much attention due to its thermal sensitivity. This kind of semiconducting materials exhibits the negative temperature coefficient of resistance (NTCR) effect below the Curie temperature (Tc) and the positive temperature coefficient of resistance (PTCR) effect above Tc [11]. These materials can be utilized as precise temperature controllers, self-regulating heaters and overflow protect devices etc.

Donors and acceptors can influence the PTCR effect significantly, for example, some 3d acceptors such as Mn, Fe, Cu can enhance PTCR greatly, whereas this is not the case for the other acceptors such as K, Na, Ni, Mg [12]. Heywang proposed early that the PTCR effect can be greatly enhanced by the existence of high concentration of acceptor levels at grain boundary layers, which can be formed by piling up of excess donors at grain boundaries or by the addition of some acceptors [13]. However, that was not true in pure donor doped $BaTiO_3$ ceramics. It has been found [14] that the PTCR effect decreases with the increase of the donor content. If the donor content is high enough, the material tends to insulator and becomes negative temperature coefficient resistor (NTCR).

The methods by which BST films are deposited include sputtering [15], metal–organic chemical vapor deposition [16] and sol–gel synthesis [17]. Among these, sol–gel method is one of the most important approaches which is being used for the preparation of complex oxide films. The sol–gel processing has the advantage of delivering films with extremely uniform composition over large area, ease of dopant incorporation, and non-vacuum processing.

The sol–gel method implies a stable colloidal (“sol”) solution, which gels into a film when dried. The solution preparation is traditionally based on dissolved organometallic molecular precursors. Hydrolysis and polycondensation occur and thus macromolecular oxide network is formed. The rates that these two processes proceed are generally responsible for obtaining either: precipitate, gel or stable colloidal solution. In this way, homogeneous barium strontium titanate gels can be made by controlling the hydrolysis kinetics and avoiding the precipitation.

In the present approach BST films has been deposited on CuZn (brass) substrates by using the sol-gel synthesis method. X-ray diffraction (XRD) and scanning electron microscopy (SEM) were used to gather the detailed structural characteristics of the film. The electric resistivity - temperature (R–T) characteristics were also studied and analyzed with respect to the combined PTCR and metal oxide semiconducting characteristics.

2. Experimental

Barium acetate ($Ba(CH_3COO)_2$) and strontium acetate ($Sr(CH_3COO)_2$) were dissolved in hot glacial acetic acid (60 ^oC). Ti-isopropoxide ($Ti(OC_3H_7)_4$) was mixed with isopropanol (chelating agent) at room temperature and then mixed with the acetate solutions drop by drop under constant stirring. Hydrolysis was performed by adding water. Then, the gelation occurs within two hours. Acetylacetone is a bidentate ligand, which produces relatively strong chelate type complexes with metals. Introduction of acetylacetone molar ratio Ti/acetylacetone = 2:1 into the acetate gel resulted in progressive peptization of the gel. By this way the gel is transformed into a yellowish sol after 25 h at room temperature. The viscosity of the sols increased with the prolonging of the aging time along with the solvent evaporation. Six different gels were prepared, increasing the Sr content from 0% to 50% (Table 1).

Table 1. Gel Composition.

Sr %	$(Ba(CH_3COO)_2)$ (gr)	$(Sr(CH_3COO)_2)$ (gr)	$Ti(OC_3H_7)_4$ (ml)	$CH_3COCH_2COCH_3$ (ml)
0	17	0	17,40	13,73
10	17	1,52	19,34	15,26
20	17	3,42	21,76	17,15
30	17	5,86	24,87	19,61
40	17	9,11	29,00	22,87
50	17	13,68	34,81	27,46

Uniform coatings of BST on CuZn (brass) substrates were obtained by dipping in the colloidal solution and then withdrawing. The as-deposited amorphous films were heated to 150°C for 30 minutes to evaporate solvents and other condensation byproducts such as isopropanol and water. Further heat treatment, in oxygen atmosphere, of the dry gels at 750°C for 2 h afforded crystalline $BaSrTiO_3$ fine particles. All samples were subsequently annealed in air at 500°C for 1 h in order to get the desired perovskite phase.

The mineralogical phases of the produced films were determined by X-ray diffraction (XRD) using a Siemens D5000 diffractometer with nickel-filtered $CuK\alpha_1$ radiation (=1.5405 A), 40 kV and 30 mA. The thickness of films, as well as their surface and cross-sectional morphology were studied with the aid of a Jeol 6100 Scanning Electron Microscope (SEM). The chemical composition of the produced films was examined by a Noran TS 5500 Electron Dispersive Spectrometer (EDS) connected to the SEM. Film resistivity values were obtained by measuring the electrical resistance (R) at room temperature and at elevating temperatures.

3. Results and discussion

3.1 Mineralogical Analysis of the Deposited Films by X-Ray Diffraction

Fig. 1 shows the XRD patterns of BST films deposited on brass (CuZn) substrate, by annealing at 500 ^oC. The diffraction data was collected with 0.03 step width, over a 2θ range from 10^o to 80^o.The XRD patterns showed only perovskite peaks with a strong CuZn peaks. The presence of copper and zinc oxides were attributed to the partial oxidation of the substrate at 750 ^oC.

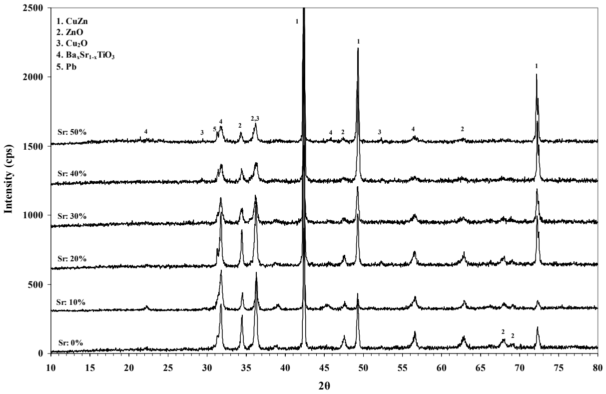


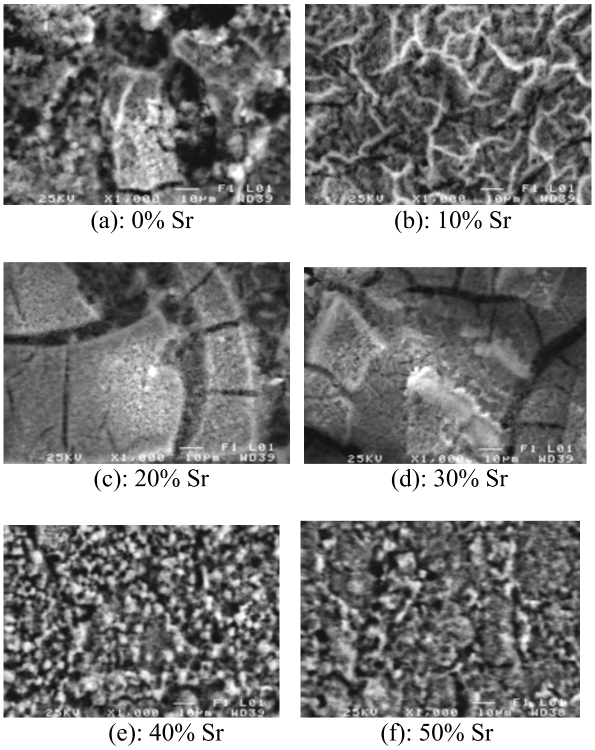
Fig. 1. XRD patterns of sol–gel derived BST films on brass (CuZn) substrate.

The films were found to be polycrystalline with (110), (111) and (200) peaks arising at 2θ values of 32.2°, 39.5°and 45.9°, respectively and contain the perovskite phase only. The intensity of (110) peak was higher than (111) and (200) peaks. The diffraction peaks, during annealing became stronger and sharper, indicating the growth of grain and the improvement of crystalline structure, a fact that indicates that organic phases were well evaporated and there was no observable effect on the crystalline structures of BST films.

All the six films showed high peak intensities indicating good crystallinity. By the comparison of intensity and the full width at half maximum of the (110) peak, it can be deduced that the crystallinity increases with the increase of Ba content. As the Sr content increased, the diffraction lines shift towards larger angles indicating lower values of lattice spacing. This lattice shrinkage is due to the substitution in the lattice of the larger in size Ba^{2+} ions (r=0.135 nm) by the smaller in size Sr^{2+} ions (r=0.113 nm) [18,19].

3.2 Examination of the deposited films' microstructure by SEM

Fig. 2 shows the Scanning Electron Microscopy images of the surface morphology of BST films, synthesized by sol–gel method, sintered at 750 °C and annealed at 500 °C. In all cases microcracks were observed. The creation of the films cracking was attributed to the large volume change when the wet solution is thermally treated to inorganic oxides during sintering.



(a): 0% Sr (b): 10% Sr

(c): 20% Sr (d): 30% Sr

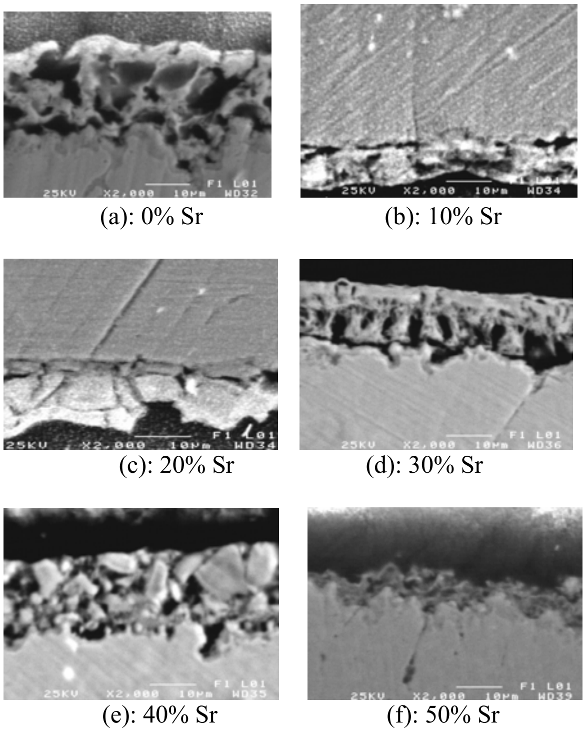
(e): 40% Sr (f): 50% Sr

Fig. 2. SEM images of the surface of the BST films on brass (CuZn) substrate.

When films are subjected to heat treatment, i.e., solvent vaporization, organic decomposition, and crystallization, pores collapse and film densification caused by condensation reaction result in rather high stress in the films, and crack formation occurs when the films strength cannot withstand the stress. These crack gaps open up on the films randomly and intersect one another.

The grain size of the films increases with increasing strontium concentrations, a fact that could be attributed to higher grain growth rates from the more rapid diffusion of the Sr ion, which has a smaller ionic radius than Ba.

The SEM cross-sectional morphologies of the BST films, derived from barium replacement content with strontium from 0% to 50%, are shown in Fig. 3. Although the cleavage plane shows a random orientation, an apparent boundary can be found between the BST film and the CuZn substrate. This result shows that the interface between the BST film and the brass is clear.



(a): 0% Sr (b): 10% Sr

(c): 20% Sr (d): 30% Sr

(e): 40% Sr (f): 50% Sr

Fig. 3. SEM cross-sectional morphology of the BST films on brass (CuZn) substrate

Moreover, as can be seen in Fig. 3, the BST films have a columnar structure, and the columnar grains are extended over the whole thickness of the films or, at least, a large part of them. There is no apparent distinction in the shape or size of the grains on the films that would allow distinguishing between BST and zinc (Zn: 5-15%) or copper (Cu: 3-5%) oxide grains in the SEM images. The maximum thickness was less than 10 μm.

From the cross-sectional micrograph of the films, one can find that the films have microcracks and they are porous, whereas their surface is rough and therefore, could adsorb water vapor when exposed to humid environment. These cracks should have been generated from the stress formed by interdiffusion toward relatively weak gel structure of organic compounds. The pores were produced during sintering, where organic evaporation is taken place and left pores, which are exist before annealing.

3.3. Electrical characterization

Fig. 4 gives the resistivity (R) temperature (T) plots of the produced BST films, on CuZn substrate, synthesized by sol–gel, sintered at 750 °C and annealed at 500 °C. The semiconducting polycrystalline $BaTiO_3$ is characterized by its positive temperature coefficient of resistivity (PTCR) around the Curie temperature. The effect of isovalent substituent of Sr^{2+} in $BaTiO_3$ is known to shift the Tc to lower temperature regions. The typical curve for

$Ba_{1-x}Sr_xTiO_3$ shows sharp PTCR characteristics around Tc. However, in all cases, the resistivity dropped down with elevating temperature and, as a result, the temperature dependence of resistivity of the films shows the a large negative temperature coefficient of resistivity, apart from the ferroelectric transition temperatures where a PTCR response also appears.

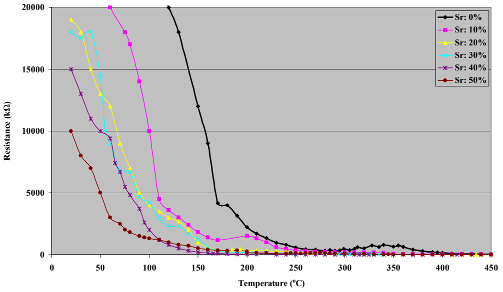


Fig. 4. Temperature dependence of resistivity of BST films on brass (CuZn) substrate.

The above observation can be explained by the presence of zinc and copper oxides, in the examined films, which were formed during sintering from the CuZn substrate oxidation. The residual ZnO and Cu_2O segregated on the grain boundaries to form an isolation layer, which decrease the resistance of $Ba_xSr_{1-x}TiO_3$ semiconducting films. These oxides form a concentration gradient between the grain boundary and the grain interior during sintering, which decreases the transfer of Sr^{2+} ions and prevents the formation of the Sr-deficient grain boundary layers. Certainly, the residual ZnO/Cu_2O at the grain boundaries also decrease the films resistivity with temperature because formed the isolation layers [20]. Such a monotonic and large temperature response can serve for temperature sensing applications.

The Curie temperature of BST is decreased with decreasing of the mole ratio of Ba:Sr, and the resistivities are markedly dependent on the strontium substitution. The room-temperature resistivity decreases with the increasing of the Sr^{2+} content in the low doping level, and reaches the minimum value at a 50 % substitution, most probably due to the lower degree of crystallinity observed in the XRD analysis and the higher mobility of Sr^{2+} ions, due to their smaller ionic radius.

4. Conclusions

Under the experimental conditions of the present research work, polycrystalline BST ceramic films were deposited on brass (CuZn) substrates by sol–gel processing.

XRD patterns studies, showed only perovskite peaks and it was confirmed that the crystallinity decreases with the increase of Sr content, a fact that was attributed to the difference in size between the Ba^{2+} and Sr^{2+}. Zinc and copper oxides, were formed during thermal treatment, from the oxidation of CuZn substrate.

The cross sectional SEM observations indicated that the BST films had a columnar structure, whereas there was not apparent distinction in the shape or size of the grains that would allow distinguishing between BST and ZnO/Cu_2O grains.

The investigation of the films' temperature dependence of resistance showed that they had semiconductive properties. Although, the semiconducting polycrystalline BST is characterized by its positive temperature coefficient of resistivity (PTCR), in all cases, the resistivity dropped down with elevating temperature, showing characteristics of negative temperature coefficient of resistivity, a fact that was attributed to the presence of zinc and copper oxides, in the examined films. Finally, the room-temperature resistivity decreased with the increasing of the Sr^{2+} content.

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