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Fabrication and electrical properties of $Ba_{0.64}Sr_{0.36}TiO_3$ thin films by sol-gel on platinum coated silicon

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The $Ba_{0.64}Sr_{0.36}TiO_3$ thin films have been prepared by the sol-gel method on a platinum-coated silicon substrate. The structure and electrical properties of sol-gel derived Barium-strontium-titanate ($Ba_{0.64}Sr_{0.36}TiO_3$) thin films have been investigated. The as-fired thin films are found to be amorphous, and the films crystallize to a perovskite structure after a post deposition annealing at 700°C for 1 h in air. The dielectric constant and dissipation factor for $Ba_{0.64}Sr_{0.36}TiO_3$ thin film at a frequency of 200 Hz were 592 and 0.028, respectively. The temperature dependence of dielectric constant and dissipation factor exhibited a diffused ferroelectric to paraelectric phase transition at 40°C. The ferroelectric nature of this film at room temperature was confirmed by the existence of butterfly-shaped *C-V* curves caused by switching of the ferroelectric domains. The capacitance changed from 495 to 1108 pF with the applied voltage in the −5 to +5 V range at a frequency of 100 kHz. The pyroelectric coefficient at room temperature (25°C) is 1860 $\mu C/m^2K$, and the figure-of-merit of this film is 37.4 $\mu C/m^3K$. The high pyroelectric coefficients and the greater figures of merit of $Ba_{0.64}Sr_{0.36}TiO_3$ thin films make it possible to be used for thermal infra-red detection and imaging.

1. Introduction

High performance and inexpensive infrared sensors are required for various thermal detection and imaging of objects at near ambient temperature. Pyroelectric infrared sensors promise more convenient sensing system, because of the advantages of high sensitivity at long-wavelength and room-temperature operation without cooling systems. Materials being widely used as pyroelectric sensors are single crystals of $LiTiO_3$ [1] and Triglycine Sulphate (TGS) [2], ceramics and thin films of $PbTiO_3$ [3], $PbZr_{1-x}Ti_xO_3$ [4] and $Ba_xSr_{1-x}TiO_3$ [5], and organic films of polyvinylidene flucride (PVDF) [6], etc. Among these materials, barium strontium titanate (BST) is currently one of the most interesting ferroelectric materials due to its high dielectric constant and composition-dependent Curie temperature (from 30 to 400 K). The latter property makes an excellent infrared response obtainable at room temperature. In recent years, BST thin films have been produced by a variety of thin film deposition techniques that include sputtering [7], laser ablation [8], metal organic chemical vapor deposition (MOCVD) [9], and Sol-gel processing [10]. Compared to other deposition methods, the sol-gel process offers some significant advantages such as homogeneity, stoichiometry control, and the ability to coat large and complex area substrates. The low capital cost of the equipment and simplicity make it an excellent technique for formulating new compositions. In this paper, $Ba_{0.64}Sr_{0.36}TiO_3$ films were successfully fabricated by a sol-gel process. The structure of $Ba_{0.64}Sr_{0.36}TiO_3$ films was characterized by X-ray diffraction (XRD). The electrical properties were evaluated by the measurements on the $Ba_{0.64}Sr_{0.36}TiO_3$ films of the frequency and temperature dependence of dielectric constant and dissipation factor, the field dependence of capacitance, and the pyroelectric coefficient.

2. Experimental

Fig. 1 shows the flow chart for the fabrication of barium-strontium-titanate ($Ba_{0.64}Sr_{0.36}TiO_3$) thin films by the sol-gel method. Barium-ethylhexanoate ($Ba(C_8H_{15}O_2)_2$), strontium-ethylhexanoate ($Sr(C_8H_{15}O_2)_2$), and titanium(IV)-isopropoxide ($TiC_{12}H_{28}O_4$) were used as the starting materials for the synthesis of precursors for barium strontium titanate thin films. Barium-ethylhexanoate (0.64 moles), strontium-ethylhexanoate (0.36 moles) was first dissolved in ethanol under reflux condition. Then a stoichiometric amount of titanium(IV)-isopropoxide was added drop by drop under constant

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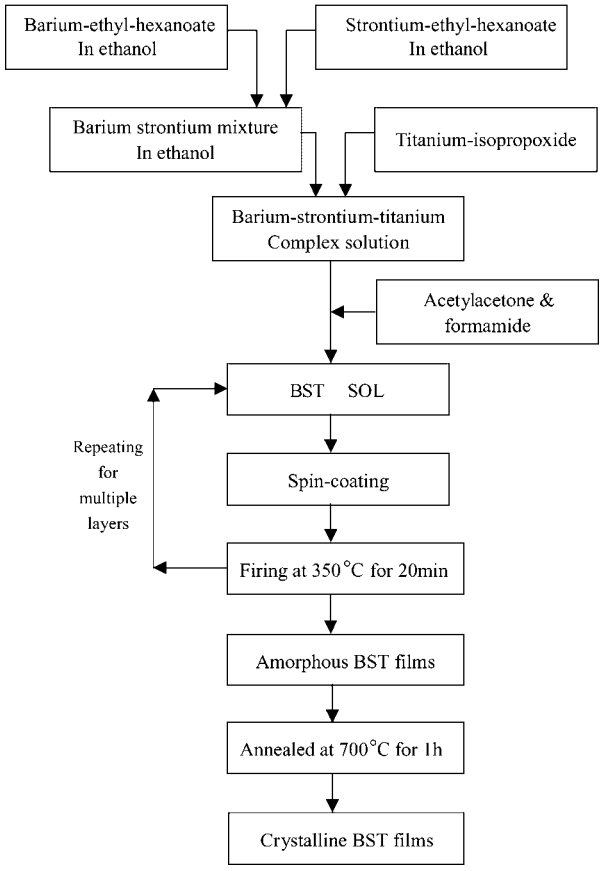

Figure 1 Flow-chart illustrating the procedure for the preparation of $Ba_xSr_{1-x}TiO_3$ ($x = 0.64$) thin films by the sol-gel method.

stirring to produce a Ba-Sr-Ti complex solution. To this solution 0.5 ml acetylacetone was added in order to increase the stability, and 0.4 ml formamide was also added to control the rate of pyrolysis. The mixture was finally filtered using a microglass fiber filter paper. The filtrate was used as the stock solution for the preparation of the films.

The substrates used for this study were platinized-silicon (100) wafers with 100-nm-thick thermally grown SiO_2. Prior to the deposition of the films, the substrates were cleaned by adopting a standard chemical procedure. The films were deposited by spin casting a single coating at 4000 rpm for 30 seconds using a spinner. After spin coating, the samples were baked at 150°C for 15 min to evaporate the solvent, and they were preannealed at 350°C for 20 min in dry air to eliminate organic components. Thicker films were prepared by repeating the deposition and pyrolysation cycle. Multiple coatings were required for building up the film thickness to the required value. The coated films were finally annealed in air at different temperatures (450–700°C) for one hour in a conventional furnace for achieving crystallization.

The structure of the film was analyzed by a Rigaku D/max-rA rotating target X-ray diffractometer. The dielectric properties of $Ba_{0.64}Sr_{0.36}TiO_3$ thin films were evaluated using a capacitor structure of Au/BST/Pt, where the Au top electrode was deposited by sputtering through a designed mask onto the film surfaces. The capacitance-voltage (C–V) properties were characterized using a Hewlett-Packard (4194A) impedance/grain phase analyzed, with the capacitance value measured using a small a.c. signal of 10 mV at 100 kHz. The dielectric constant and dissipation factor were measured as a function of frequency and temperature using a frequency range of 100 Hz–10 MHz and temperature range of −120°C to 80°C.

The pyroelectric currents were measured by the Byer and Roundy method [11]. The samples were poled at 3°C@5V/μm for 1 hour. The samples were then cooled down to approximately −75°C with the bias field on and then were short-circuited to neutralize any accumulated surface charge. The samples were heated at 2°C/min from −50°C up to 30°C and the pyroelectric current measured at a constant interval (2°C/min). This was repeated until the pyroelectric currents were similar in value at any given temperature. The pyroelectric coefficient was calculated from the following equation:

$$p = -\frac{IA}{\frac{dT}{dt}} \tag{1}$$

where I is the current in amperes, A is the metal contact area in m^{-2}, and $\frac{dT}{dt}$ is the temperature ramp rate in K/sec. Thus, the pyroelectric coefficient has a unit of C/m^2K.

3. Results and discussion

3.1. Crystallographic structure

The crystallographic structure of $Ba_{0.64}Sr_{0.36}TiO_3$ thin films was examined using the X-ray-diffraction techniques (XRD). Fig. 2 shows the X-ray diffraction patterns of the as-fired and annealed films deposited on platinum coated silicon substrate that were annealed in air at different temperatures for one hour. The as-fired films were amorphous. The film starts crystallizing on annealing at 550°C. The intensity and the sharpness of the peaks increase on annealing up to 700°C. However, no further improvement was noted with a further

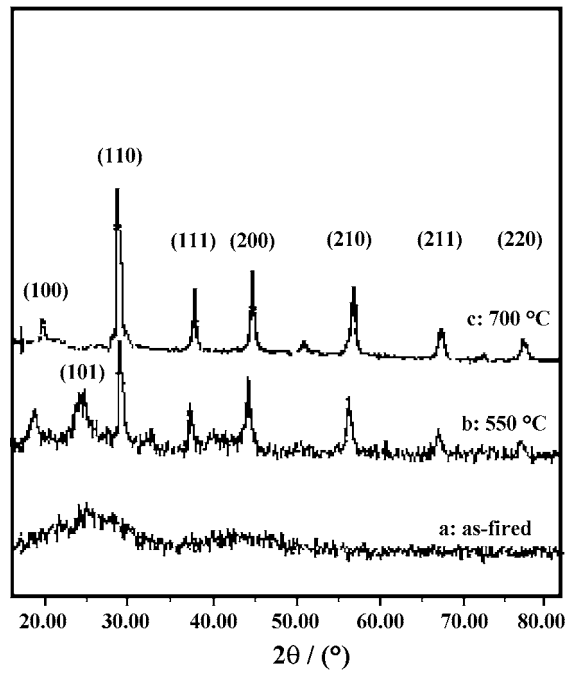

Figure 2 XRD patterns of the as-fired and films annealed at different temperatures on silicon substrate.

increase in the annealing temperature. In Fig. 2, trace-C represents a well-crystallized film; it is evident that the $Ba_{0.64}Sr_{0.36}TiO_3$ thin film was polycrystalline without preferential orientation and contained the perovskite phase only. The grain size, D, was calculated by using the full width at half maximum (FWHM) of the dominant (110) peak using Scherrer's formula [12]:

$$D = 0.94\lambda / B_0 \cos\theta \tag{2}$$

where B_0 is the FWHM of the peak. λ is the wavelength of the X-ray beam, and θ is the diffraction angle. The grain size for a film annealed at 700°C was 45.8 nm. The grain size of the film increased with increasing annealing temperature. The increasing in grain size with annealing temperature is expected as more defects are annealed out and the small grains coalesce to form larger grains.

3.2. Dielectric properties

The dielectric and pyroelectric behavior of $Ba_{0.64}Sr_{0.36}TiO_3$ thin films was measured in the metal-BST-metal configuration with the films sandwiched between the bottom platinum and top gold electrodes. The capacitance value of different spots varied by less than 3%, indicating a good degree of homogeneity in the thickness prepared by spin-coating techniques. The dielectric constant and dissipation factor for $Ba_{0.64}Sr_{0.36}TiO_3$ thin film at a frequency of 200 Hz were 592 and 0.028, respectively (Fig. 3). They showed no noticeable dispersions at frequency of up to 1 MHz, indicating the good quality of thin films prepared by spin-coating techniques. The high dielectric properties may be due to the good relationship between the electrode interface/film for this case. However, Fig. 3 show that there is a tendency for the dielectric constant to decrease and the dissipation factor to increase at frequency above 1 MHz, respectively. Several possible sources exist for such a dispersion, including the influence of the finite resistance of the electrodes, the presence of a barrier layer between the insulating film and the electrode surface, or leaky grain boundaries. These phenomena have also been reported for dielectric thin films prepared by other techniques [7, 8].

Fig. 4 shows the temperature dependence of the dielectric properties for the $Ba_{0.64}Sr_{0.36}TiO_3$ thin film.

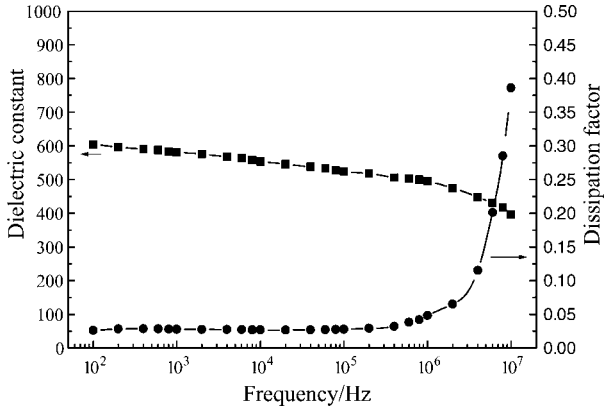

Figure 3 Dielectric constant and Dissipation factor of $Ba_{0.64}Sr_{0.36}TiO_3$ thin films as a function of frequency.

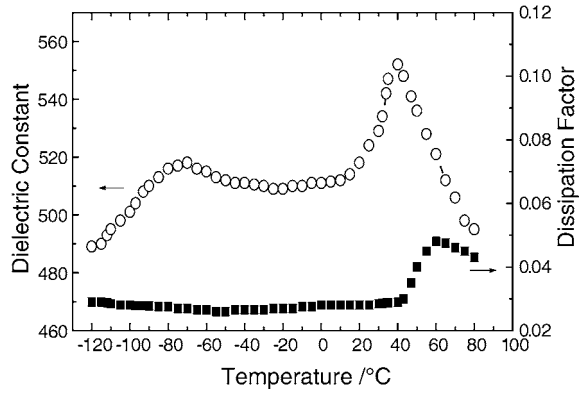

Figure 4 The temperature dependence of dielectric constant and dissipation factor for sol-gel derived $Ba_{0.64}Sr_{0.36}TiO_3$ thin films.

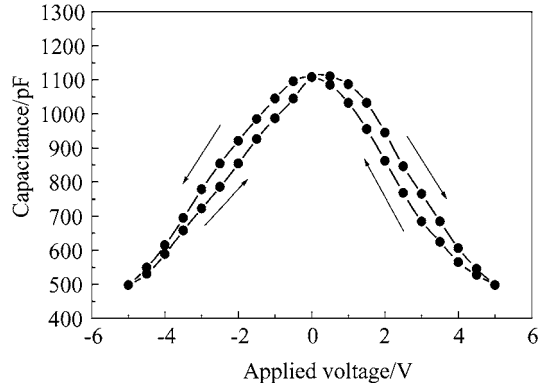

Figure 5 C–V curves of $Ba_{0.64}Sr_{0.36}TiO_3$ thin films at the frequency of 100 KHz.

The temperature range for ε_r–T and tg δ–T test was from −120°C to 80°C. As the temperature changed, two dielectric constant peaks appeared in the ε_r–T curve. The peak at about −70°C was broad, which is attributed to an orthorhombic to tetragonal phase transition. The peak located at about 40°C was relatively sharp, which corresponds to a tetragonal to cubic phase transition. The dissipation factor (tg δ) was less than 5% in the temperature range from −120°C to 80°C and showed a peak around 60°C. The relatively large separation (in temperature) between the peaks in the ε_r–T curve and tg δ–T curve are typical properties of ferroelectric materials with diffused phase transition [13].

The investigation of the bias voltage dependence of the capacitance is one of the most useful methods of gaining insight into the behavior of ferroelectric films and has been used to characterize ferroelectric thin films [14]. Fig. 5 shows the capacitance-voltage (C–V) characteristic of the $Ba_{0.64}Sr_{0.36}TiO_3$ thin film at room temperature. The capacitance was measured while a bias voltage was swept in an iteratively of $-5 \rightarrow 0 \rightarrow 5 \rightarrow 0 \rightarrow -5$, at 0.5 V increments with a step rate of 1 step/3s. The bias field E and the dielectric constant ε_r were calculated from the bias voltage V and the capacitance C using the following equations:

$$E = V/d \tag{3}$$

$$\varepsilon_r = Cd/\varepsilon_0 A \tag{4}$$

where ε_0 is the vacuum permittivity, d is the film thickness, and A is the area of a top electrode. In

TABLE I Dielectric and pyroelectric properties of $Ba_{0.64}Sr_{0.36}TiO_3$ thin film

Material	P_{RT} ($\mu C/m^2K$)	FOM ($\mu C/m^3K$)	T_c (°C)	ε_r	tan δ
$Ba_{0.64}Sr_{0.36}TiO_3$	1860	37.4	36	592	0.028

Fig. 5, the dependence of the capacitance as a function of the voltage shows a strongly non-linear character, and two peaks characterizing spontaneous polarization switching can be clearly seen in the figure. Therefore, the films' butterfly-shaped C–V curves indicate that the films have a ferroelectric nature. The capacitance changed from 495 to 1108 pF with the applied voltage in the −5 to +5 V range at a frequency of 100 kHz. The dielectric constant calculated from C_{max} is approximately 524 at a frequency of 100 kHz, which agrees with the value of the dielectric constant vs. frequency curve at a 100 kHz frequency (Fig. 3).

3.3. Pyroelectric properties

Dielectric material for pyroelectric detector applications should have a high pyroelectric coefficient and a low dielectric loss. This translates to a high material Figure-of-Merit defined as:

$$\text{FOM} = p/(d \cdot \varepsilon_r \cdot \tan\delta) \quad (5)$$

Where p is the pyroelectric coefficient ($\mu C/m^2K$), d is the thickness of the material (μm), ε_r is relative dielectric constant and tan δ is the dielectric loss.

Table I shows the pyroelectric coefficient at room temperature calculated from Equation 1, the FOM calculated from Equation 5, and the Curie temperature for the $Ba_{0.64}Sr_{0.36}TiO_3$ thin film specimens. The curie temperature T_c is 36°C, and the pyroelectric coefficient at room temperature (25°C) is 1860 $\mu C/m^2K$, and the figure-of-merit of this film (thickness = 3 μm) is 37.4 $\mu C/m^3K$. The figure-of-merit for $Ba_{0.64}Sr_{0.36}TiO_3$ thin film is greater than the $Ba_{0.64}Sr_{0.36}TiO_3$ ceramics due to reduced thickness [15], according to Equation 5. It has been observed by us that the BST compositions can be deposited in more epitaxial fashion on $SrTiO_3$ than Pt. The grain size of the films accompanied with orientation of the grains will contribute towards the pyroelectric behavior of the thin film. Further work on the C-axis-oriented BST and Mg-modified BST films deposited on $SrTiO_3$ and Pt-coated $SrTiO_3$ crystal to increase the pyroelectric coefficient are currently underway.

4. Conclusions

$Ba_{0.64}Sr_{0.36}TiO_3$ film has been successfully prepared by a sol-gel method. The as-fired films are amorphous, and a post deposition heat treatment in a conventional furnace at 700°C for one hour gives a polycrystalline film with perovskite structure. The grain size of this film was 45.8 nm. The electrical characteristics of the thin films showed good dielectric and pyroelectric properties. The dielectric constant and dissipation factor measured at 200 Hz were 592 and 0.028, respectively for $Ba_{0.64}Sr_{0.36}TiO_3$ thin film. They showed no noticeable dispersions at frequency of up to 1 MHz, indicating the good quality of thin films prepared by spin-coating techniques. The temperature dependence of dielectric constant and dissipation factor exhibited a diffused ferroelectric to paraelectric phase transition at 40°C. The dependence of the capacitance as a function of the voltage shows a strongly non-linear character, and two peaks characterizing spontaneous polarization switching can be clearly seen in this curve, indicating that the films have a ferroelectric nature at room temperature. The pyroelectric coefficient of $Ba_{0.64}Sr_{0.36}TiO_3$ thin film at room temperature (25°C) is 1860 $\mu C/m^2K$, and the figure-of-merit of this film is 37.4 $\mu C/m^3K$. These results show that BST thin films may be good candidate materials for thermal infrared detection and imaging.

References

1. C. B. ROUNDY, *Appl. Opt.* **18** (1979) 943.
2. H. BLACKBURN, H. C. WRIGHT, R. EDDINGTON *et al.*, *Radio Electron Eng.* **42** (1972) 369.
3. M. OKUYAMA and Y. HAMAKAWA, *Ferroelectrics* **118** (1991) 261.
4. R. KÖHLER, P. PADMINI and G. GERLACH, *Integrated Ferroelectrics* **22** (1998) 383.
5. J.-G. CHENG, X.-J. MENG, J. TANG *et al.*, *Appl. Phys.* A **70** (2000) 411.
6. N. NEUMANN, R. KÖHLER and G. HOFMANN, *Ferroelectrics* **118** (1991) 319.
7. T. HORIKAWA, N. MIKAMI, T. MAKITA *et al.*, *Jpn. J. Appl. Phys.* **32** (1993) 4126.
8. S. SAHA and S. B. KRUPANIDHI, *J. Appl. Phys.* **87** (2000) 849.
9. A. B. CATALAN, J. V. MANTESE, A. L. MICHELI *et al.*, *ibid.* **76** (1994) 2541.
10. S. LAHIRY, V. GUPTA, K. SREENIVAS *et al.*, *IEE Trans. Ultrason., Ferroelec., Freq. Contr.* **47** (2000) 854.
11. R. L. BYER and C. B. ROUNDY, *J. Appl. Phys.* **44** (1973) 929.
12. B. D. CULLITY, "Elements of X-ray Diffaraction," 2nd ed. (Addison-Wesley, Reading, MA, 1978) p. 102.
13. S. CHATTOPADHYAY, P. AYYUB, V. R. PALKAR and M. MULTANI, *Phys. Rev.* B **52** (1995) 13177.
14. M. E. LINES and A. M. GLASS, "Principles and Application of Ferroelectrics and Related Materials" (Oxford, Clarendon Press, 1997) p. 620.
15. J. H. YOO, W. GAO and K. H. YOON, *J. Mater. Sci.* **34** (1999) 5361.

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