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Properties of Chemical Solution Deposited Polycrystalline Neodymium-Modified $Bi_4Ti_3O_{12}$

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Abstract. Thin films of neodymium-modified bismuth titanate $Bi_{3.44}Nd_{0.56}Ti_3O_{12}$ (BNT) were grown on $Pt/TiO_2/SiO_2/Si$ substrates using chemical solution deposition method. The capacitors made by applying top Au electrodes on BNT films showed significantly improved values of the remanent polarization as compared to that using bismuth titanate $Bi_4Ti_3O_{12}$ (BT) films. The $2P_r$ value for the BNT capacitors was determined to be equal to 38 $\mu C/cm^2$ at an applied voltage of 24 V, whereas, for $Bi_4Ti_3O_{12}$ (BT) capacitors a value of 20 $\mu C/cm^2$ was measured at the same applied voltage. The maximum piezoelectric and pyroelectric coefficients of 22 pm/V and 112 $\mu C/m^2$ K respectively, were measured for the BNT thin films.

Keywords: ferroelectric, $Bi_{3.44}Nd_{0.56}Ti_3O_{12}$, pyroelectric, piezoelectric

1. Introduction

Bismuth containing ferroelectrics of the Aurivillius phases are in use in a number of recent applications: (a) $SrBi_2Ta_2O_9$ (SBT) is used in ferroelectric non-volatile memory. Its advantage in comparison with the competing Pb(Zr, Ti)O_3 (PZT) perovskite is very small polarization fatigue and imprint [1]. Its processing temperature however, is high, 750°C in comparison with the 600–650°C of PZT. In comparison with PZT (Zr/Ti = 45/55), SBT also has a lower remanent polarization, typically 25 $\mu C/cm^2$ versus 15 $\mu C/cm^2$, respectively. (b) Some of the bismuth containing Aurivillius ferroelectrics, such as $Na_{0.5}Bi_{0.5}Ti_4O_{15}$, have a high Curie temperature and therefore have recently been introduced in piezoelectric sensors for high temperature applications [2]. At room temperature, their piezoelectric voltage and piezoelectric coupling coefficients are moderate in comparison with the better performing PZT, and therefore they have not been investigated extensively in the past. In recent years, due to the wish for a cleaner environment, there is an increased interest in these materials [3].

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Bismuth titanate $Bi_4Ti_3O_{12}$ (BT), has neither been used in non-volatile memory nor in high temperature piezoelectric sensor applications due to its low remanent polarization, low piezoelectric coefficient and high losses [4]. The low remanent polarization of BT films stems from the fact that the large polarization vector lies few degrees of the a-axis in the monoclinic structure, while the films orient readily in the c-direction that has a small polarization component. Recently, Park et al. [5] showed that La-modified BT has a remanent polarization (P_r) and processing temperature comparable to those of PZT and high resistance to polarization fatigue. The work by Kojima et al. [6] also showed the advantages of other rare earth substituted BT. The Nd-modified BT films were shown to have a higher P_r than La-modified BT of a similar orientation. Sm-modified BT films were shown to have a strong polarization vector in the c-direction. The La-modified BT films were prepared recently with the (100) direction perpendicular to the substrate, showing P_r of 32 $\mu C/cm^2$ [7].

The piezoelectric properties of the rare earth substituted BT have not been reported so far. The high remanent polarization and the apparent shift of the polarization direction more strongly off the 'a' direction in the a–c plane could potentially result in a higher piezoelectric coefficient for these lead free

piezoelectric materials. Since various modifications have shown various directions of the resultant polarization vector, it may also be possible to find the compositions for which the anisotropic energy is low, thus electrically softening the material, which could be advantageous both in piezoelectric and in memory applications. Since the rare earth substitution reduces the Curie temperature, while maintaining a high remanent polarization, and relatively a low permittivity, it is also of interest to measure the pyroelectric response of these materials, which has not been reported so far to the best of the author's knowledge. The following report presents the initial analysis of the piezoelectric and pyroelectric properties of rare-earth modified bismuth titanate thin films.

2. Experimental

The precursor solutions were synthesized from bismuth acetate $Bi(CH_3COO)_3$, titanium diisopropoxide bis(acetylacetonate) Ti(bisAcAc), neodymium acetate $Nd(CH_3COO)_3$ and 2-methoxy ethanol $CH_3OCH_2CH_2OH$, (Aldrich Chemie, Buchs-CH). In order to synthesize bismuth titanate precursor solution, 0.04 mol of $Bi(CH_3COO)_3$ was dissolved in 300 ml of a mixture containing 2-methoxy ethanol and acetic acid in a ratio of 2:1 and the resulting mixture was refluxed at 115°C for 1 h, followed by the distillation at 124°C to remove two third of the mixture. The solution was cooled down to 50°C and 90 ml of acetic acid was added to it and the resulting mixture was refluxed at 110°C to get a clear solution. 0.03 mol of Ti(bisAcAc) was dissolved in 60 g of 2-methoxy ethanol separately. Bismuth and titanium precursor solutions were then mixed and refluxed at 124°C in nitrogen atmosphere for 6 h. After that the excess solvent along with other unwanted by-products were distilled off to obtain a concentrated precursor solution. In order to prepare a sol containing bismuth neodymium titanate, instead of taking 0.04 mol of bismuth acetate, a mixture of 0.0344 mol of bismuth acetate and 0.0056 mol of neodymium acetate was taken and the rest of the process was kept same as described above.

Thin films were deposited using a spin coater (Headway research Inc., Garland, TX, USA) at 4000 rpm for 30 s on in-house platinized silicon substrates with TiO_2 adhesion layer between SiO_2 and Pt. The substrates spin coated using the sols were pyrolyzed for 15 s at 350°C on a hot plate after each deposition. The substrates containing stacks of 4 layers were finally heat treated in air at temperatures from 550°C to 700°C, in a rapid thermal anneal apparatus using heating rate of 10°C/s (RTA apparatus from Process Product Corp., Andover, MA, USA). The final thickness of the films was measured approximately to be 0.6 μm.

A multi frequency LCR-meter (Hewlett Packard 4274A, Palo Alto, CA, USA) was used to determine dielectric loss ($\tan\delta$) and to measure capacitance in order to calculate permittivity of the films. The measurements reported in this work were carried out at 1 kHz. Pyroelectric currents were measured dynamically as a function of a 1 K temperature change, controlled by a waveform generator driven peltier element [8].

Hysteresis loop measurements were carried out with a Sawyer-Tower bridge. The piezoelectric coefficient d_{33} was determined with the help of an extremely sensitive double side interferometer described in [9]. X-ray diffraction (XRD) studies (Siemens, D500, Munich, Germany) were carried out to identify the phases and to study the crystallinity versus processing temperature and the orientation of the films. Scanning electron microscopic studies (SEM; JEOL, 6300 F Tokyo Japan, and Philips) were performed to observe the microstructure and the grain size of the films.

3. Results and Discussion

Figure 1 shows the XRD results of BT and BNT thin films annealed at 700°C for 15 min in air. For both the films only one phase was obtained, and the films produced were randomly oriented without any c-axis

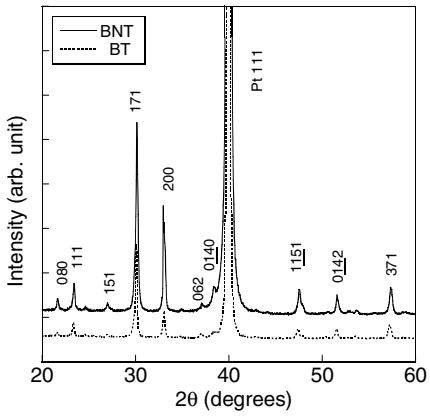

Fig. 1. XRD patterns of bismuth titanate (BT) and Nd-modified bismuth titanate (BNT) thin films deposited on $Pt/TiO_2/SiO_2/Si$ substrates and annealed at 700°C.

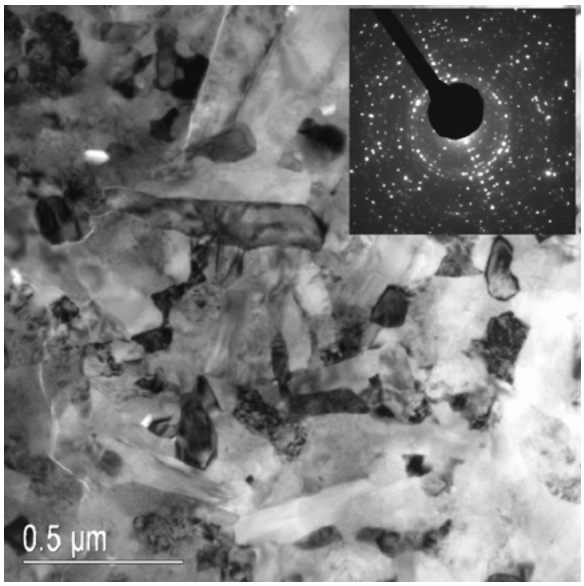

Fig. 2. TEM bright field image (planar view) and the corresponding selected area diffraction pattern (inset) of Nd-modified bismuth titanate thin films.

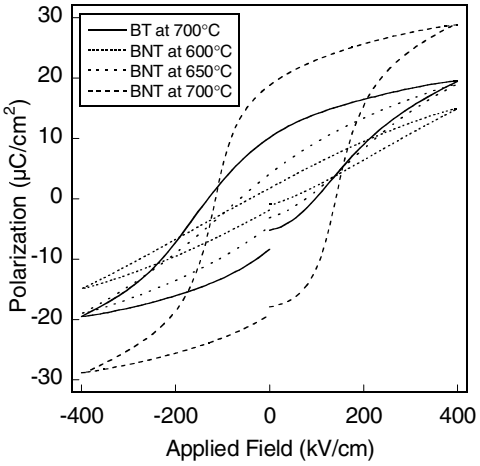

Fig. 3. P-E hysteresis loops of bismuth titanate and Nd-modified bismuth titanate capacitors. Films thickness is approximately 0.6 μm.

preferred orientation. Plane-view TEM bright field image of BNT sample is shown in Fig. 2. This figure shows a dense polycrystalline microstructure with platelet-like shape of the grains. No preferential orientation could be detected by selected area diffraction (inset in Fig. 2).

For electrical characterization, circular Cr/Au (10 nm/200 nm) top electrodes of 0.6 mm diameter were deposited by evaporation through a shadow mask (Edwards, West Sussex, GB). Profilometer thickness measurements (α-step 260, Tencore, Mountain View, CA, USA) and bottom electrode contact were facilitated by etching a part of BT and BNT layers in a $HF/HCl/H_2O$ mixture.

Polarization-electric field (P-E) hysteresis loops for $Bi_4Ti_3O_{12}$ (BT) and $Bi_{3.44}Nd_{0.56}Ti_3O_{12}$ (BNT) thin films annealed at 600°C to 700°C are shown in Fig. 3. On comparing the hysteresis loops of pure bismuth titanate with those of neodymium modified bismuth titanate, it can be seen that both P_r and E_c values of the BT films did not saturate and were found to be small. On the other hand, well-saturated hysteresis loops were obtained for the BNT films. The P_r and E_c values for BT films were measured equal to 10 μC/cm^2 and 110 kV/cm, whereas those for BNT films were 19 μC/cm^2 and 135 kV/cm, respectively. The hysteresis loop of BNT films annealed at 700°C is slightly shifted to positive voltages. This shift in the hysteresis loop can be due to the dipolar objects formed by $\ddot{V}_{O_2^-}$ and some $[Nd^{3+}_{Ti+4}]'$ or the defect states related to the electrode-film interface [10].

On comparing the P-E hysteresis loops of BNT films annealed at different temperatures, it can be observed that P_r and E_c values increase drastically on increasing the annealing temperature from 600°C to 700°C (Fig. 3). It is known from the previous studies on PT and PZT [11, 12] that when the grain size of the ferroelectric materials is <1 μm, the increasing grain size reduces the volume fraction of grain boundaries. Therefore, the coupling between the grain boundaries and the domain walls, which makes domain reorientation more difficult and severely constrains the domain wall motion, will decrease. This then results to an increase in the achievable domain alignment (which corresponds to an increase in the values of remanent polarization) and in domain wall mobility (which corresponds to an increase in dielectric constant).

To observe the change of grain size with respect to the annealing temperature, the SEM micrographs were recorded for the BNT thin films annealed at different temperatures. Figure 4 shows the SEM micrographs of two samples annealed at 600°C and 700°C. On comparing the grain size at two different annealing temperatures, it can clearly be seen that there is a drastic increase in the grain size on increasing the temperature from 600°C to 700°C. Therefore, the increased polarization for the samples annealed at high temperature can be attributed to the increased grain size.

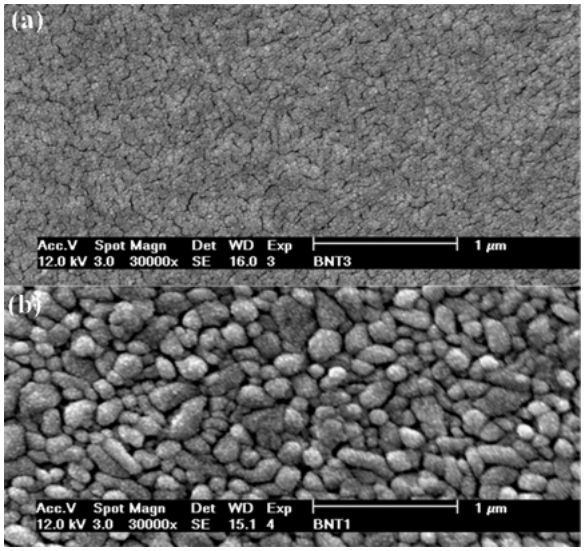

Fig. 4. SEM micrographs of Nd-modified bismuth titanate thin films annealed at different temperatures: (a) 600°C and (b) 700°C, for 15 min.

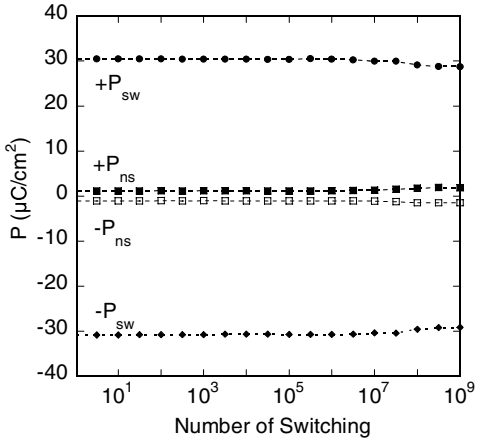

Fig. 5. Fatigue properties of Nd-modified bismuth titanate thin films, (film thickness is 600 nm, measuring voltage of 15 V and frequency of 20 KHz).

The fatigue-free characteristics of the BNT capacitors are shown in Fig. 5. The film showed little change both in the switching and non-switching polarization up to 1×10^9 read/write cycles. The value of non-volatile charge [i.e. $(+P_{sw}) - (+P_{ns})$] is approximately 28 μC/cm^2 and remains constant throughout the switching cycles. Which is considerably larger than that reported by Chon et al. [13] for the Sm-modified bismuth titanate films synthesized by sol-gel route.

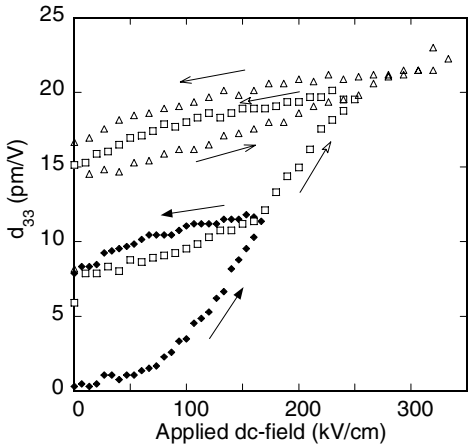

Fig. 6. Effective piezoelectric coefficient (d_{33}) of Nd-modified bismuth titanate thin films at different dc-fields.

The piezoelectric coefficient d_{33} of BNT thin films has been measured as small signal response to a small ac field as a function of a much larger dc-field. Figure 6 shows the variation of d_{33} coefficient as a function of applied field strength. The maximum piezoelectric coefficient was measured to be equal to 22 pm/V at an applied dc-field of 300 kV/cm.

In order to achieve high pyroelectric coefficient 'p' the films were poled on a hot plate for 10 min at temperatures between 50°C and 150°C and fields between 100 kV/cm and 300 kV/cm. The poling field necessary to achieve an optimized pyroelectric coefficient was determined experimentally by systematically increasing the field strength and temperature until no further improvement of p could be measured. For the electrical

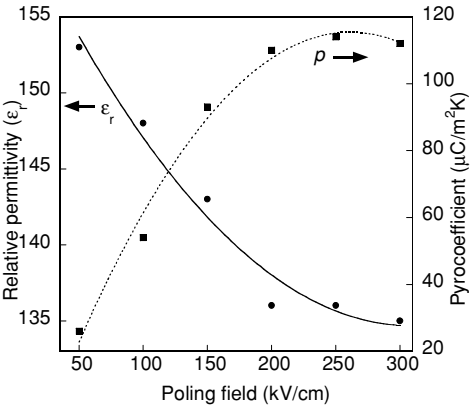

Fig. 7. Pyrocoefficient and relative permittivity of Nd-modified bismuth titanate thin films as a function of poling field, at a constant poling temperature of 120°C.

characterization, ε_r, tan δ and p were measured before and after poling of thin films. The dielectric losses for BT and BNT films at 1 kHz were 0.05 and 0.035, respectively, whereas the dielectric constants for BT and BNT thin films were calculated equal to 174 and 152, respectively.

Figure 7 shows the development of p and ε_r for the BNT thin films after poling for 10 min at a constant temperature of 120°C as a function of electric field strength. It can be observed that initially the pyroelectric coefficient increases with increasing poling field and after reaching to a maximum it becomes constant. The maximum pyroelectric coefficient of 112 μC/m^2 K was observed at the poling field of 250 kV/cm. Voltage figure of merit $f_v(f_v = p/\varepsilon)$ for BNT films was calculated equal to 0.85 μC/m^2 K, which is approximately same as that reported for PZT (Zr/Ti = 15/85, the best composition for pyroelectric applications) thin films [14].

Recently, AFM in a contact mode has drawn much interest as an emerging technique for the investigation on the complex nature of ferroelectric domains [15, 16]. In a contact mode AFM imaging, with a small ac voltage on the AFM cantilever at a frequency less than its mechanical resonance frequency, a measure of the electrostatic force modulation between the tip and the sample provides information about amplitude and phase changes, which indicate the magnitude and the directionality of local polarization in a ferroelectric film. A 35 nm SiC tip with an ac voltage signal of 1 Vpp (peak to peak voltage) was employed at a modulation frequency of 20 kHz to measure piezo response of the films, which is less than the resonance frequency of the tip (≈40 kHz). For d_{33} measurements, a dc field of −20 to +20 V was superimposed on the ac-modulating signal. Further experimental details can be found out in [16]. The phase and amplitude of the polarization for Nd-modified $Bi_4Ti_3O_{12}$ films are shown in Fig. 8(a) and (b), respectively. AFM topographic image shown in Fig. 8(c) revealed that the films have a surface roughness of the order of 30–40 nm. Figure 8(d) shows the

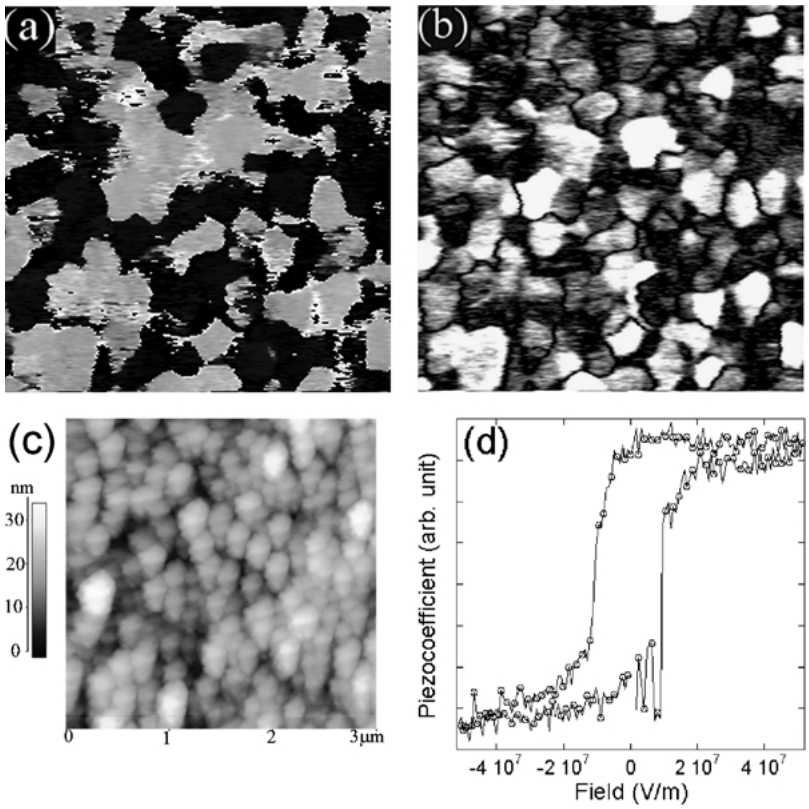

Fig. 8. AFM studies of Nd-modified bismuth titanate films: (a) phase and (b) amplitude of the polarization (c) surface topographic image and (d) d_{33} response versus applied field measured by AFM.

microscopic level d_{33} response vs. applied field, measured by AFM. The measured coercive field from the AFM piezo response was approximately 115 kV/cm, which is very close to the value from the polarization hysteresis measurements. Similar piezo-hysteresis was observed throughout the film, regardless of the orientation of the grains.

4. Conclusions

In conclusion, thin films of bismuth titanate and neodymium modified bismuth titanate have successfully been fabricated on platinized silicon wafers by chemical solution deposition method. The BNT capacitors using Au top electrode showed a well saturated P-E loop with remanent polarization of 19 μC/cm^2 at an applied voltage of 24 V. The maximum pyroelectric (p) and piezoelectric (d_{33}) coefficients for BNT thin films were measured to be equal to 112 μC/m^2 K and 22 pm/V, respectively.

Acknowledgment

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