Electrical properties of $Bi_{3.15}Sm_{0.85}Ti_3O_{12}$ thin films on Si for a metal-ferroelectric-semiconductor-metal structure

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As a typical perovskite layer structured ferroelectric material, bismuth titanate [$Bi_4Ti_3O_{12}$ (BTO)] has become a key candidate for memory storage capacitor, optical display, and electro-optical devices owing to its promising properties [1–3]. A metal-ferroelectric-semiconductor (MFS) hetero-structure with BTO as a gate electrode material for ferroelectric field effect transistor (FFET) in a nondestructive readout (NDRO) mode has been demonstrated [4]. However, BTO films show fatigue and an unexpectedly high leakage electric current, which are obstacles for further technological adoption [5].

The strong influence of a small amount of impurity on physical properties was shown recently. The studies suggested that the Bi ions affect fatigue characteristics and the failure characteristics of BTO could be improved if some Bi ions were substituted (with lanthanide ions) near the Ti—O octahedron layers [6, 7]. BTO doped with donors showed reduced electrical conductivity and enhanced the ferroelectric properties [8].

Thin films of BTO have already been prepared by rf sputtering [1], metal-organic chemical vapor deposition [9], pulsed laser deposition [10], and electron cyclotron resonance plasma sputtering [11]. Among the various techniques available for the fabrication of BTO thin films, the metal-organic decomposition (MOD) method employed in this study offers the advantages of precise control of composition and homogeneity along with the ability to coat a large film on a complex substrate. The main purpose of the present study was to develop BSmT ($Bi_{4-x}Sm_xTi_3O_{12}$, with $x = 0.85$) thin films on n-type Si (100) substrates by MOD and analyze the electrical properties.

Bismuth nitrate, samarium nitrate, and titanium butoxide were selected as starting materials. Glacial acetic acid was used as solvent and the solution was diluted with 2-methoxyethanol to adjust the viscosity and surface tension. To keep the precursor solution stable, it was necessary to add acetylacetone into the solution. Dust and impurities were removed by filtering through 0.2-μm syringe filters. BSmT films were fabricated on the Si (100) substrates by spin coating then heating. The wet films were heated at 400 °C in air for 20 min to remove residual organic material. The resulting films were annealed at various temperatures ranging between 500 and 800 °C for 1 h.

As-annealed films were specular, crack-free, dense, and adhered well to the substrates. The films were first examined by electron probe microanalysis to determine the composition and the obtained film compositions were in agreement with the nominal *one*. The film thickness, as measured using a Dektak II stepmeter, was approximately 500 nm. The cystallinity of the BSmT films was analyzed by X-ray diffraction (XRD) using a Rigaku D/Max-γA X-ray diffractometer. The current–voltage (I–V) measurements were conducted using a pA meter/dc voltage source (HP 4140B). The capacitance–voltage (C–V) characteristics and the dielectric properties were measured using an LF Impedance Analyzer (HP 4192A).

Fig. 1 shows the X-ray diffraction patterns of the $Bi_{3.15}Sm_{0.85}Ti_3O_{12}$ films prepared on Si (100) and annealed at various temperatures for 1 h. The higher annealing temperatures gave the stronger BTO peaks. The film annealed at 700 °C showed the highest peak intensity. However, the film annealed at 800 °C showed lower intensity, which might be due to the volatilization of Bi and Sm during annealing at a high temperature. The film was polycrystalline in nature and all the XRD patterns were essentially consistent with those given in Joint Committee on Powder Diffraction Standards

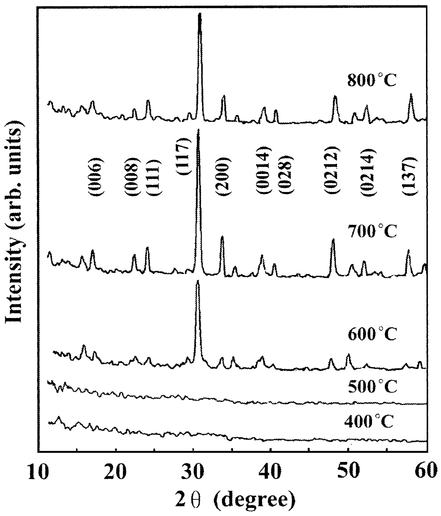

Figure 1 X-ray diffraction patterns of BSmT films annealed at various temperatures, as indicated.

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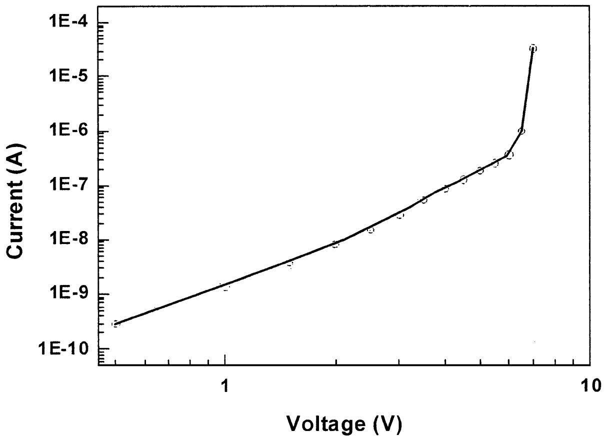

Figure 2 Typical log(I) vs log(V) curve for BSmT thin film annealed at 700 °C for 1 h.

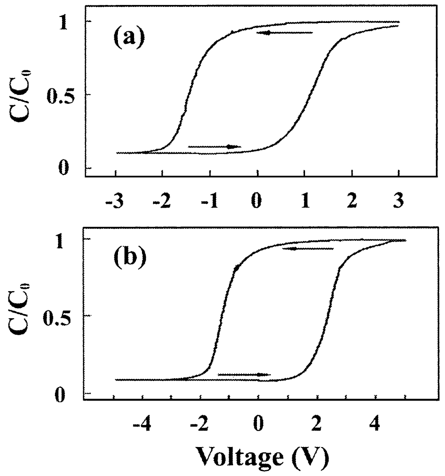

Figure 3 C–V characteristics of BSmT films. The curves are counterclockwise loops. The bias voltage ranges applied to the films in (a) and (b) are ±3 and ±5 V, respectively.

data cards for the perovskite $Bi_4Ti_3O_{12}$, implying that the BSmT film maintained a pseudotetragonal-layered structure similar to the perovskite BTO even under extensive modification by samarium.

Some electrical properties of the BSmT films were measured. Gold dots, 0.8 mm in diameter on the top of the BSmT film and gold film on the bottom of the silicon substrate were used to form a metal/ferroelectric/semiconductor/metal (MFSM) configuration.

Fig. 2 is a typical log(I) versus log(V) curve for the BSmT thin film annealed at 700 °C for 1 h. The BSmT film exhibited a resistivity in the range of 10^9–10^{11} Ω cm when a dc bias of 0–6 V was applied to the capacitor. In this voltage range, the maximum resistivity was up to 1.1×10^{11} Ω cm. The leakage current significantly increased thereafter and no breakdown occurred even if the dc bias was 25 V. The data above indicate that BSmT thin films directly deposited on the Si (100) substrates by the MOD technique have gold insulating properties and resistance to breakdown.

At low voltages (below 2.5 V), current I was linearly dependent on voltage V, i.e., the I–V curve exhibited ohmic behavior. At higher field (above 2.5 V), a nonlinear I–V relationship could be observed. It is proposed that current injection for highly resistive material is space-charge-limited [3]. According to space-charge-limited-current theory, as applied voltage is increased, the injection of charge carriers in the bulk of the film takes place. For stronger injection, the insulator traps fill up and a space charge appears. A square law region appeared in the voltage range of 2.5–6 V. At applied voltages higher than 6 V, a higher power law region could be observed.

Fig. 3 shows the C–V curves measured at 1 MHz for the MFSM structured BSmT films. The C–V characteristics exhibited clear regions of accumulation, depletion, and inversion. The counterclockwise C–V hystereses indicated by the arrows are attributable to ferroelectric polarization, which is the desired mode for memory operation [12]. When the bias voltage swept from −3 to 3 V and back to −3 V, the capacitances in the accumulation region did not coincide, indicating that the memory window was unsaturated. At a sweep voltage amplitude of ±5 V, the accumulation and depletion of the C–V curve coincided, and the memory window of the loop was around 3.6 V. Not only did the capacitance values saturate to the maximum and minimum values in both the accumulation and the inversion regions, but there were no features such as humps or valleys detectable in the C–V curves. The featureless C–V characteristics suggest that neither a large leakage current nor a significant carrier injection occurred. Besides, the memory window increased symmetrically with the sweep voltage, implying that it increased because of the ferroelectric polarization without charge injection. Furthermore, the hysteresis loops were relatively "square," indicating that the memory retention was very stable. The C–V curves showed that the capacitance varied from the depletion state to the accumulation state, and the direction of the hysteresis loop was consistent with ferroelectric polarization switching.

The consistent results of C–V and I–V measurement indicated that Sm substitution could improve the ferroelectric properties of metal/BSmT/Si structured materials, widen the memory window of the C–V loop, and after the insulating properties of thin films to satisfy the requirements of FFET devices.

Fig. 4 shows the dielectric constant and dissipation factor measured at room temperature as a function of frequency in the range from 1 kHz to 1 MHz. The

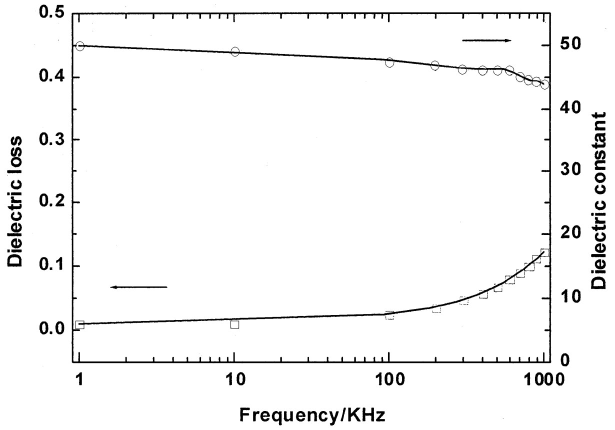

Figure 4 Dielectric constant and dissipation factor (loss) for the Au/BSmT/Si/Au films as a function of frequency.

dielectric constant of the BSmT capacitor slightly decreased with increasing frequency, but it was much more stable than that of BTO [13]. There were no sudden changes in the dielectric constant and the dissipation factor within the frequency range up to 1 MHz, indicating the compositional homogeneity and thickness uniformity of the film. Besides, the dissipation factor at 1 MHz was measured to be 0.14, which is much lower than values of BTO and BLT films [13, 14].

In summary, $Bi_{3.15}Sm_{0.85}Ti_3O_{12}$ thin films have been successfully produced on n-type Si (100) substrates by a MOD technique. BSmT films annealed at 700 °C for 1 h had good crystallinity. The I–V characteristics showed ohmic conductivity in the lower voltage range and space-charge-limited conductivity in higher fields. The dielectric properties and the C–V characteristic hysteresis curve showed that BSmT thin films obtained by MOD method are promising candidates for FFET memories.

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