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## Enhanced electrical polarization and ferromagnetic moment in a multiferroic BiFeO<sub>3</sub>/Bi<sub>3.25</sub>Sm<sub>0.75</sub>Ti<sub>2.98</sub>V<sub>0.02</sub>O<sub>12</sub> double-layered thin film

Z. Cheng

*University of Wollongong, [cheng@uow.edu.au](mailto:cheng@uow.edu.au)*

Xiaolin Wang

*University of Wollongong, [xiaolin@uow.edu.au](mailto:xiaolin@uow.edu.au)*

C. V. Kannan

*National Institute for Materials Science, Japan*

Kiyoshi Ozawa

*National Institute for Materials Science, Japan, [ozawa@uow.edu.au](mailto:ozawa@uow.edu.au)*

H. Kimura

*National Institute for Materials Science, Japan*

*See next page for additional authors*

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**Authors**

Z. Cheng, Xiaolin Wang, C. V. Kannan, Kiyoshi Ozawa, H. Kimura, T. Nishida, S. Zhang, and T. R. Shrout

# Enhanced electrical polarization and ferromagnetic moment in a multiferroic $\text{BiFeO}_3/\text{Bi}_{3.25}\text{Sm}_{0.75}\text{Ti}_{2.98}\text{V}_{0.02}\text{O}_{12}$ double-layered thin film

Zhenxiang Cheng and Xiaolin Wang<sup>a)</sup>

*Spintronic and Electronic Materials Group, Institute for Superconducting and Electronic Materials, University of Wollongong, Northfields Avenue, New South Wales 2522, Australia*

Chinna Venkatasamy Kannan, Kyoshi Ozawa, and Hideo Kimura

*National Institute for Materials Science, 1-2-1 Sengen, Tsukuba, Ibaraki, 305-0047, Japan*

Takashi Nishida

*Graduate School of Materials Science, Nara Institute of Science and Technology, 8916-5 Takayama-Cho, Ikoma, Nara 630-0101, Japan*

Shujun Zhang and Thomas R. Shroud

*Materials Research Institute, Pennsylvania State University, University Park, Pennsylvania 16802*

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Multiferroic  $\text{BiFeO}_3/\text{Bi}_{3.25}\text{Sm}_{0.75}\text{Ti}_{2.98}\text{V}_{0.02}\text{O}_{12}$  double-layered thin films on  $\text{Pt}/\text{Ti}/\text{SiO}_2/\text{Si}$  were fabricated using the pulsed-laser deposition technique. The films showed greatly enhanced ferroelectric and ferromagnetic properties. The values of the remanent polarization ( $2P_r$ ) and coercive field ( $E_c$ ) were  $71.8 \mu\text{C}/\text{cm}^2$  and  $148 \text{ kV}/\text{cm}$  at a maximum applied voltage of  $13 \text{ V}$ , respectively. The value of the magnetic moment was found to be  $17.5 \text{ emu}/\text{cm}^3$ . The enhancement of the polarization originated from the  $\text{BiFeO}_3$  with  $\text{Bi}_{3.25}\text{Sm}_{0.75}\text{Ti}_{2.98}\text{V}_{0.02}\text{O}_{12}$  working as a barrier layer. The enhancement of the magnetization is from the structural distortion of  $\text{BiFeO}_3$ , due to partial epitaxial growth on the bismuth titanate surface. © 2006 American Institute of Physics.

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Ferroelectromagnets, which display simultaneous magnetic and dipolar electrical ordering, have recently stimulated much scientific and technological interest.<sup>1</sup> The coexistence of magnetic and electric subsystems endows materials with the “product” property, thus allowing an additional degree of freedom in the properties of actuators, sensors, and storage devices.<sup>2–7</sup> However, the choice of single-phase materials exhibiting coexistence of strong ferro-ferrimagnetism (FM) and ferroelectricity (FE) is limited.<sup>8</sup> Therefore, multiferroic composites comprised of a mixture of two different types of materials with separate or combined ferromagnetic and ferroelectric properties have been proposed. These composites could be in the form of multilayers or nanocomposites. Magnetoelectric coupling could then take place through an elastic interaction.<sup>9</sup>

$\text{BiFeO}_3$  (BF), with a rhombohedrally distorted perovskite structure (space group  $R3c$ ,  $a=b=c=5.63 \text{ \AA}$ ,  $\alpha=\beta=\gamma=59.4^\circ$ ), is the only known perovskite oxide that exhibits both antiferromagnetism (weak magnetism from canted spins or parasitic ferromagnetism such as  $\alpha\text{-Fe}_2\text{O}_3$ ) and ferroelectricity at room temperature (with  $T_N \sim 643 \text{ K}$  and  $T_C \sim 1103 \text{ K}$ ). This material has recently attracted significant attention from the viewpoint of both fundamental research and the potential for practical applications involving mutual control of magnetization and polarization. Nevertheless, it has a serious electrical leakage problem, most likely as a result of sample defects and nonstoichiometry. Recently, to enhance the remanent polarization ( $P_r$ ) and reduce the leakage problem, a BF epitaxial thin film heterostructure was

fabricated on  $\text{SrTiO}_3$  with  $\text{SrRuO}_3$  as the bottom electrode. Results revealed an enhanced polarization and magnetization after the structure of  $\text{BiFeO}_3$  changed to tetragonal from rhombohedral.<sup>9</sup>

$\text{Bi}_4\text{Ti}_3\text{O}_{12}$  (BT), as one of the prospective candidates to replace  $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$  (PZT), for nonvolatile ferroelectric random access memory (FeRAM), has also been widely investigated. Many trivalent rare earth elements have been introduced into the  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  lattice in place of bismuth, as well as ions with +5 valence to substitute for Ti, with the aim of enhancing the remanent polarization, while reducing susceptibility to fatigue, and reducing leakage current, respectively.<sup>10–14</sup> It has been shown that doping BT with samarium can enhance  $2P_r$  from 4–8 up to  $54 \mu\text{C}/\text{cm}^2$ .<sup>14</sup> Bismuth titanate has a complicated pseudo-orthorhombic structure with the lattice parameters  $a=5.4444 \text{ \AA}$ ,  $b=5.4086 \text{ \AA}$ , and  $c=32.8425 \text{ \AA}$ . The structure of rare earth element doped BT can be described as a stack of alternating layers of bismuth oxide ( $\text{Bi}_2\text{O}_2$ )<sup>2+</sup> and perovskite ( $\text{Bi}_2\text{Ti}_3\text{O}_{10}$ )<sup>2-</sup> units containing Ti–O octahedral, with a rare earth element substituting for Bi in the perovskite units.<sup>15</sup>

In this letter, we report our study on the fabrication of double-layered films with the structure of  $\text{BiFeO}_3/\text{Bi}_{3.25}\text{Sm}_{0.75}\text{Ti}_{2.98}\text{V}_{0.02}\text{O}_{12}$  (BF/BSVT) on  $\text{Pt}/\text{Ti}/\text{SiO}_2/\text{Si}$  substrates using the pulsed laser ablation technique and the corresponding changes that occur in both the magnetic and ferroelectric properties. It was expected that both the FE and FM properties would be enhanced in a composite containing BF if BSVT was used as a barrier layer and that an engineered lattice mismatch would result in a tensile stress in BF, creating a favorable environment for large polarization and magnetization.

<sup>a)</sup> Author to whom correspondence should be addressed; electronic mail: [xiaolin@uow.edu.au](mailto:xiaolin@uow.edu.au)

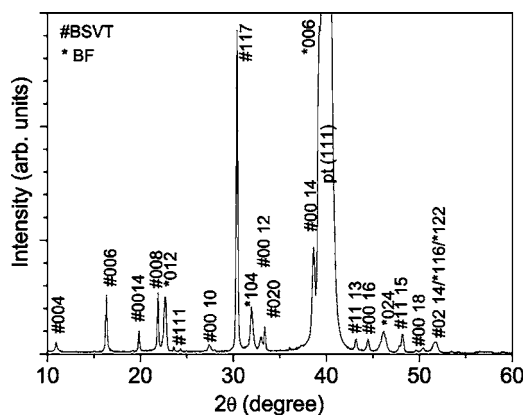


FIG. 1. Conventional  $\theta$ - $2\theta$  measurement of  $\text{BiFeO}_3/\text{Bi}_{3.25}\text{Sm}_{0.75}\text{Ti}_{2.98}\text{V}_{0.02}\text{O}_{12}$  (BF/BSVT) double-layered film on Pt/Ti/SiO<sub>2</sub>/Si at room temperature.

The thin film samples in this work were deposited using a pulsed-laser deposition (PLD) system described elsewhere.<sup>14</sup> Solid-state reaction sintered  $\text{Bi}_{3.25}\text{Sm}_{0.75}\text{Ti}_{2.98}\text{V}_{0.02}\text{O}_{12}$  and  $\text{BiFeO}_3$  ceramics, both with 5% excess bismuth, were used as targets. A  $\text{Bi}_{3.25}\text{Sm}_{0.75}\text{Ti}_{2.98}\text{V}_{0.02}\text{O}_{12}$  film first deposited at 680 °C to a Pt/Ti/SiO<sub>2</sub>/Si substrate, then cooled down to room temperature following rapid thermal processing (RTP).  $\text{BiFeO}_3$  was subsequently deposited on the BSVT film at 660 °C. For a comparison, single-layered BSVT and BF films on Pt/Ti/SiO<sub>2</sub>/Si were also prepared under the same deposition conditions as in the preparation of the individual layers of BF/BSVT. The phase and structure of the films were determined by x-ray diffraction (XRD). The morphology was studied with an atomic force microscope (AFM). A Pt upper electrode with an area of 0.007 85 mm<sup>2</sup> was deposited by magnetron sputtering. The thickness of the films was obtained through observation of the cross section of the film under a high resolution scanning electronic microscope (SEM). The ferroelectric properties were measured by an aixACCT EASY CHECH 300 system. dc magnetic hysteresis loops were determined by a superconducting quantum interference device (SQUID) magnetometer.

Figure 1 illustrates the XRD pattern of a BF/BSVT double-layered film deposited on a Pt/Ti/SiO<sub>2</sub>/Si substrate. The BF and BSVT films were both found to be polycrystalline in nature. The BSVT layer, with a thickness of 290 nm, showed strong crystallization along its  $\langle 117 \rangle$  direction. The BF film, with a thickness of 200 nm on BSVT, showed a certain degree of preferred growth along its  $\langle 012 \rangle$  direction, as the diffraction intensity of the (024) face is half that of the (104), while the ratio is 1.3% for the ceramic sample (PDF 71-2494).

Figure 2 shows the surface morphologies of the BF surface of the BF/BSVT film. A smooth and uniform surface with vertical roughness of 30 nm was observed, which reveals the potential for reproducing films with the same intrinsic physical properties.

Figure 3 shows the room temperature polarization hysteresis loops ( $P$ - $E$  loop) measured at different applied voltages. At an applied voltage of 12 V,  $2P_r$  and the coercive field ( $E_c$ ) were found to be 71.8  $\mu\text{C}/\text{cm}^2$  and 148 kV/cm, respectively. The  $2P_r$  value measured was found to be greatly enhanced in comparison with the value of 54  $\mu\text{C}/\text{cm}^2$  for a single layer BSVT film on Pt/Ti/SiO<sub>2</sub>/Si

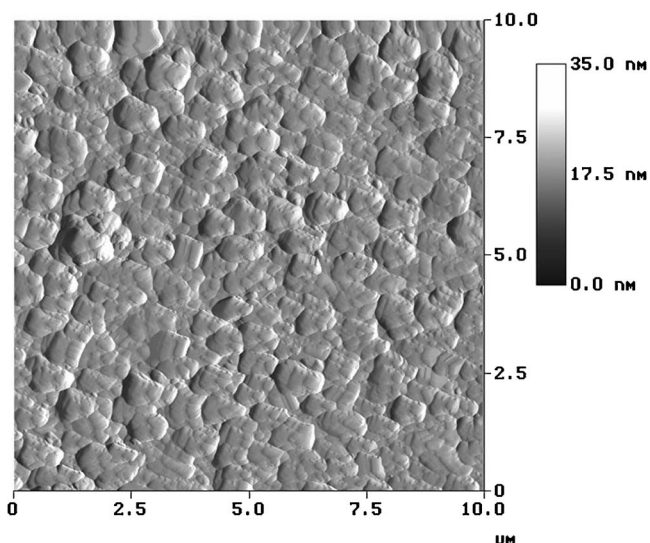


FIG. 2. AFM image of the surface of the  $\text{BiFeO}_3/\text{Bi}_{3.25}\text{Sm}_{0.75}\text{Ti}_{2.98}\text{V}_{0.02}\text{O}_{12}$  film.

substrate at an applied voltage of 268 kV/cm (shown in the inset of Fig. 3), while the coercive field ( $E_c$ ) increased from the value of 84 kV/cm for a single layer BSVT film.<sup>14</sup> In the double-layered film, BSVT was directly grown on Pt substrate, whose structure changed little in comparison with the single-layered BSVT film. So these changes in polarization could not be due to the BSVT layer but are from the contribution of the BF layer. Reference 16 gives the  $P_r$  value of BF bulk as only 6.1  $\mu\text{C}/\text{cm}^2$ . The  $P$ - $E$  loop of the single-layered BF film on Pt/Ti/SiO<sub>2</sub>/Si reveals a small  $P_r$  value about 3  $\mu\text{C}/\text{cm}^2$ , which failed to get saturated due to the large leakage current (shown as the inset of Fig. 3). The enhancement of polarization is most likely the result of interaction between the two layers. One reason for this is because the strain resulting from the small degree of epitaxial growth has tilted the structure of the BF, making it favorable for the large polarization. The XRD pattern of the BF layer revealed that the preferred growth was along its  $\langle 012 \rangle$  direction, which would definitely change the performance of the BF film. Another possibility is that BF perhaps originally had a large polarization, while the high leakage current in the bulk samples and single layer film caused by the multivalent nature of Fe prevented observation of the large value of spontaneous polarization. However, in the BF/BSVT double-layered film, BSVT plays a role as a good insulating barrier

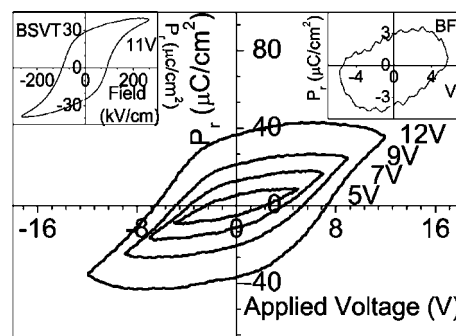


FIG. 3.  $P$ - $E$  hysteresis loops of a Pt/ $\text{BiFeO}_3/\text{Bi}_{3.25}\text{Sm}_{0.75}\text{Ti}_{2.98}\text{V}_{0.02}\text{O}_{12}$ /Pt capacitor measured at various applied voltages ranging between 5 and 12 V. The insets show the  $P$ - $E$  hysteresis loops of Pt/ $\text{Bi}_{3.25}\text{Sm}_{0.75}\text{Ti}_{2.98}\text{V}_{0.02}\text{O}_{12}$ /Pt (upper left) and Pt/ $\text{BiFeO}_3$ /Pt (upper right) capacitors.

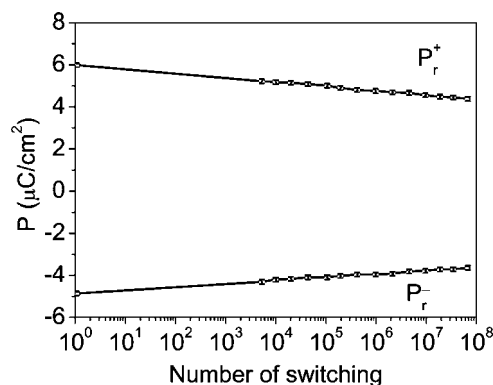


FIG. 4. Electrical fatigue characteristics of the Pt/BiFeO<sub>3</sub>/Bi<sub>3.25</sub>Sm<sub>0.75</sub>Ti<sub>2.98</sub>V<sub>0.02</sub>O<sub>12</sub>/Pt capacitor, with the fatigue test results determined using a switching (fatigue) voltage of 3 V and a measuring voltage of 5 V at a frequency of 5 kHz.

layer in stopping charge movement from the BF layer to the bottom electrode. This helps the observation of large polarization. The  $E_c$  of this double-layered film, 158 kV/cm, is very close to that of the separate BF layer, which is 150 kV/cm for the epitaxial film on SrTiO<sub>3</sub>.<sup>16</sup>

Figure 4 shows the fatigue characteristics of the Pt/BF/BSVT/Pt capacitor. The capacitor shows a decrease in both  $P_r^+$  and  $P_r^-$  at a measuring voltage of 5 V after being subjected to  $10^8$  write/read cycles at a switching voltage of  $\pm 3$  V.  $P_r^+$  decreased by 26% from 6 to 4.4  $\mu\text{C}/\text{cm}^2$ , and  $P_r^-$  decreased by 25% from 4.9 to 3.65  $\mu\text{C}/\text{cm}^2$ . The fatigue resistant properties of the double-layered film were decreased in comparison with the monolayered film with the structure of Pt/BSVT/Pt/Ti/SiO<sub>2</sub>/Si, which shows little fatigue. It is well established that ferroelectric fatigue is essentially related to the diffusion of defects and charges (typically oxygen vacancies). However, the stable perovskitelike slabs and/or (Bi<sub>2</sub>O<sub>2</sub>)<sup>2+</sup> layers in BSVT act as natural barriers to long-range diffusion, which causes it to have a different defect diffusion profile from those in other ABO<sub>3</sub>-type films.<sup>17,18</sup> Thus, the fatigue must originate from the BF layer, which is in accordance with the BF layer contribution to the polarization than that of the BSVT layer.

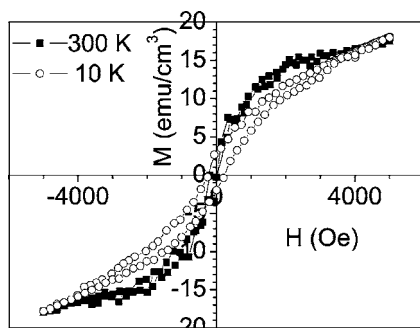


FIG. 5. Magnetic hysteresis loops of BiFeO<sub>3</sub>/Bi<sub>3.25</sub>Sm<sub>0.75</sub>Ti<sub>2.98</sub>V<sub>0.02</sub>O<sub>12</sub> film measured at 10 and 300 K.

Magnetic hysteresis curves of the film measured at 10 K and room temperature are shown in Fig. 5. At room temperature, the saturated magnetic moment is 17.5 emu/cm<sup>3</sup>. This value is greater than the value of the BiFeO<sub>3</sub> film on SrTiO<sub>3</sub> with a thickness of 400 nm (5 emu/cm<sup>3</sup>) and the value of BF on Pt/Si (3 emu/cm<sup>3</sup>). However, note that the sample does not get fully saturated at a magnetic field of 5000 Oe and 10 K.

In summary, double-layered BF/BSVT films on Pt/Ti/SiO<sub>2</sub>/Si substrate were fabricated by the PLD method. The thin film showed enhancements in both the ferroelectric properties and magnetic polarization. The enhancement of ferroelectric polarization could be due to the BF together with BSVT as a barrier layer, and the ferromagnetic properties might be from the small amount of epitaxial growth. The double-layered structure with bismuth titanate as a barrier layer, which shows significantly enhanced ferroelectric and ferromagnetic properties, could represent a promising solution to the problem of easily unmasking the ferroelectric and ferromagnetic properties of BF and realizing the coupling of these properties.

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