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Orientation dependent ferroelectric properties in samarium doped bismuth titanate thin films grown by the pulsed-laser-ablation method

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Samarium doped bismuth titanate thin films with the composition of $Bi_{3.25}Sm_{0.75}Ti_3O_{12}$ and with strong preferred orientations along the *c* axis and the (117) direction were fabricated on $Pt/TiO_2/SiO_2/Si$ substrate by pulsed laser ablation. Measurements on Pt/BSmT/Pt capacitors showed that the *c*-axis oriented film had a small remanent polarization ($2P_r$) of 5 $\mu C/cm^2$, while the highly (117) oriented film showed a $2P_r$ value of 54 $\mu C/cm^2$ at an electrical field of 268 kV/cm and a coercive field E_c of 89 kV/cm. This is different from the sol-gel derived *c*-axis oriented $Bi_{3.15}Sm_{0.85}Ti_3O_{12}$ film showing a $2P_r$ value of 49 $\mu C/cm^2$. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2221918]

Since Park *et al.* showed that fatigue-free La-doped bismuth titanate films ($Bi_{4-x}La_xTi_3O_{12}$, or BLT) on Pt electrodes exhibited high remanent polarization ($2P_r$=24 $\mu C/cm^2$) and required lower deposition temperatures (<750 °C) in comparison to other Bi-layered ferroelectrics (e.g., $SrBiTa_2O_9$) in 1999, bismuth layered ferroelectric oxides have attracted a lot of attention as prospective candidates to replace the toxic lead based material $Pb(Zr_{1-x},Ti_x)O_3$ for application in nonvolatile ferroelectric random access memory (FeRAMS).[1–3] Following this trend, many lanthanide elements besides La, such as Nd, Sm, and Pr, were tried.[4–8] Due to the size differences between Bi and the dopant ions, further structural distortion within the perovskite block will take place, and thus the remanent polarization is enhanced. Usually the structural distortion contributes to the enhancement of the polarization in specially oriented thin films in two different ways. One is to directly raise the intensity of the polarization, and the other is to shift the direction of the polarization vector towards the normal direction of the thin film. Actually, these two effects always take place simultaneously. In the undoped bismuth titanate (BT), the polarization vector almost lies in the *a-b* plane, which results in a large P_r along the *a* axis (or *b* axis) and almost negligible P_r along the *c* axis [for pure $Bi_4Ti_3O_{12}$, $2P_r$(//*a* axis)=36 $\mu C/cm^2$ and $2P_r$(//*c* axis)=4 $\mu C/cm^2$].[9] So, to achieve the highest performance in terms of a large sensing margin ($2P_r$) in bismuth titanate thin film, one way is to select dopant elements with large differences in their eightfold coordination ionic radii from bismuth, and the other is to fabricate thin films with preferred orientations. To compare the eightfold coordination ionic radii: Bi^{3+}, 0.117 nm; Nd^{3+}, 0.111 nm, and Sm^{3+}, 0.108 nm, so it can be expected that Nd and Sm doping in bismuth titanate will result in large P_r.[10] It has already been experimentally proved that sol-gel derived *c*-axis oriented Nd-doped BT films exhibit a $2P_r$ value of over 100 $\mu C/cm^2$.[4,5] This unexpected behavior was attributed to the tilting of the P_r vector towards the *c* axis of the film, while other authors showed a quite different result with a zero polarization for *c*-axis oriented Nd-doped BT film made by the pulsed-laser deposition method (PLD).[11] In the former report, the *c*-axis oriented $Bi_{3.15}Sm_{0.85}Ti_3O_{12}$ films obtained by the sol-gel method showed a polarization of 49 $\mu C/cm^2$.[6] In this letter, the PLD method was used to fabricate $Bi_{3.25}Sm_{0.75}Ti_3O_{12}$ thin films (abbreviated as BSmT hereafter) with different orientations, and their ferroelectric properties were studied in comparison with the results of the sol-gel method.

A target with the composition of $Bi_{3.41}Sm_{0.75}Ti_3O_{12}$, which is intended for the fabrication of $Bi_{3.25}Sm_{0.75}Ti_3O_{12}$ films, with 5% excess bismuth used to compensate for the loss of bismuth, was prepared by conventional solid state reaction at 1100 °C. The excimer laser is the third harmonic generation of a Nd:YAG (yttrium aluminum garnet) laser with a wavelength of 355 nm and intensity of 2–3 J/cm^2 at a repetition rate of 10 Hz. The deposition is in 200 mtorr dynamic oxygen at temperatures from 650 to 730 °C. A cooling rate of 15 °C/min was used to cool samples to room temperature after deposition. The preferred growth orientations of the films were realized through controlling the deposition temperatures, with the deposition temperatures of *c*-axis oriented and highly (117) oriented films of 710 and 650 °C, respectively. An upper electrode with dimensions of 0.007 85 mm^2 was covered with a shadow mask and coated by magnetron sputtering. The ferroelectric properties and dielectric properties of the Pt/BSmT/Pt capacitor were measured by an aixACCT EASY CHECH 300 system and an HP 4298A LCR meter, respectively. X-ray diffraction (XRD) of the films was measured by a JEOL JDX-3500 system with

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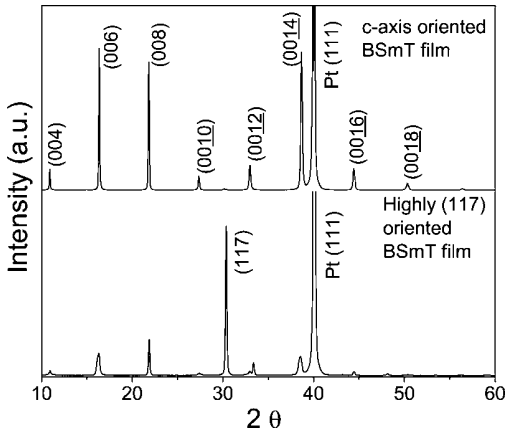

FIG. 1. XRD pattern of the *c*-axis oriented (top) and highly (117) oriented $Bi_{3.25}Sm_{0.75}Ti_3O_{12}/Pt/Ti/SiO_2/Si$ film (bottom).

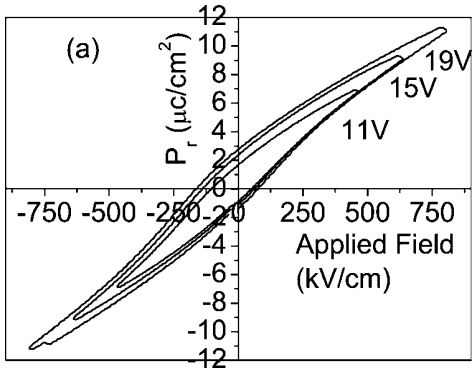

FIG. 3. Hysteresis loops of the highly *c*-axis oriented $Pt/Bi_{3.25}Sm_{0.75}Ti_3O_{12}/Pt$ capacitor measured at various applied voltages: 11, 15, and 19 V.

Cu $K\alpha$ radiation. The morphology of the films was scanned by a Digital Dimension™ 3100 atomic force microscope in the tapping mode. The thickness of the films was measured by an optical reflection method with a Filmtek™ 4000 system from Scientific Computing International, USA.

In Fig. 1, the XRD pattern shows that the degree of the (001)-type preferential growth, as estimated using the Lotgering orientation factor, is over 99% for the nominally *c*-axis oriented film, while the degree of (117) preferential growth is much lower. In Fig. 2, the morphology of the *c*-axis oriented BSmT film (a) shows flat layer structured grains with an average dimension of 700 nm, and the highly (117) oriented film (b) shows grains with a dimension of around 150 nm. At temperatures above 700 °C, bismuth titantate has a strong intensity to grow epitaxially on the Pt (111) face due to the small lattice mismatch between BT (00$\underline{1}$4) and Pt (111). However, at a lower deposition temperature, the tendency to grow epitaxially on the Pt (111) face is weak. BSmT film will thus show an XRD pattern similar to its ceramic bulk counterpart, of which (117) is the strongest diffraction peak.

Figure 3 shows the polarization-electrical field (*P-E*) hysteresis loops of a *c*-axis oriented BSmT thin film with a thickness of 234 nm. It should be noted that the electrical field applied on the samples during the measurement could not be high, for otherwise the films would be easily destroyed. It was found that the highly *c*-axis oriented thin film was very difficult to saturate. At an applied voltage of 19 V (or an electrical field of 812 kV/cm), the Pt/BSmT/Pt capacitor shows a remanent polarization $2P_r$ of 5 $\mu C/cm^2$, while the highly (117) oriented film with a thickness of 410 nm is easily saturated at an applied voltage of 11 V (268 kV/cm) with a remanent polarization $2P_r$ of 54 $\mu C/cm^2$, which is higher than the $2P_r$ of 27 $\mu C/cm^2$ for a highly *c*-axis oriented $Bi_{3.25}La_{0.75}Ti_3O_{12}$ capacitor.[1] At the same time, a low coercive electrical field (E_c) of 89.1 kV/cm was observed. Figure 4 summarizes the variations of $2P_r$ and E_c with applied electrical field for the BSmT capacitor. Structure refinement showed, in undoped BT film and La-doped BT film (BLT), that the polarization vector almost lies in the *a-b* plane. Thus the remanent polarization value of highly *c*-axis oriented pure BT and BLT films is less than that of the highly (117) oriented film. For the Nd-doped BT film (BNdT), the remanent polarization of a highly *c*-axis oriented film was much larger than that of the (117) oriented film, due to the shifting of the polarization direction to near the *c*-axis direction as well as further distortion of the Ti–O octahedra.[4] The small remanent polarization value of our *c*-axis oriented BSmT shows that the Sm doping in BT does not shift the polarization vector from the *a-b* plane to a direction near the *c*-axis, as occurred with Nd doping. This result is quite different from the previous result, where the highly *c*-axis oriented $Bi_{3.15}Sm_{0.85}Ti_3O_{12}$ films derived by the sol-gel method showed a $2P_r$ value as high as 49 $\mu C/cm^2$.[6] A small difference in the compositions cannot be responsible for the large difference in the properties (as the reported sample had the composition $Bi_{3.15}Sm_{0.85}Ti_3O_{12}$, and our sample has the composition $Bi_{3.25}Sm_{0.75}Ti_3O_{12}$). A possible reason for the contrary results might be differences in the microstructures caused by the fabrication methods and deposition temperatures. Higher deposition temperatures will

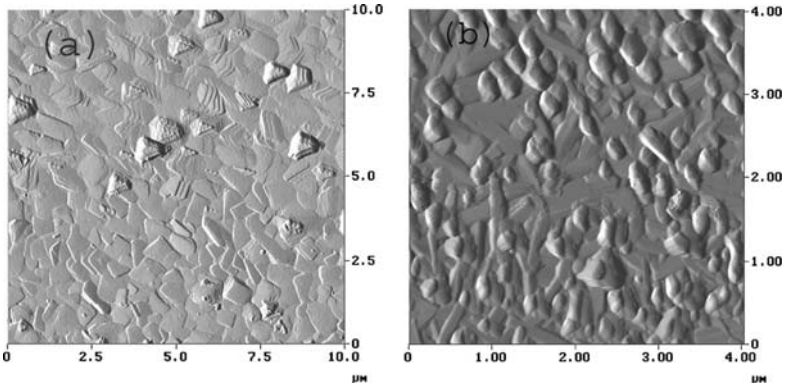

FIG. 2. Morphologies of the highly *c*-axis oriented film (a) and highly (117) oriented $Bi_{3.25}Sm_{0.75}Ti_3O_{12}/Pt/Ti/SiO_2/Si$ film (b) measured by an atomic force microscope in tapping mode.

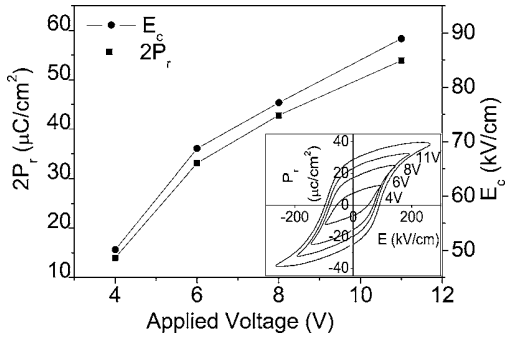

FIG. 4. Variations of $2P_r$ and E_c values of the $Pt/Bi_{3.25}Sm_{0.75}Ti_3O_{12}/Pt$ capacitor are plotted as a function of the applied voltage. The inset shows hysteresis loops measured at various applied voltages ranging between 4 and 11 V.

produce better crystallinity and larger grain sizes, thus decreasing the density of grain boundaries. The grain size of our sample is around 700 nm, which is much larger than that of films fabricated by the sol-gel method (usually less than 100 nm). PLD is a strongly nonequilibrium process, so large stresses always remain in the samples, which is favorable for large polarization. On the other hand, the sol-gel deposition process is an equilibrium crystal growth process, so strain relief can occur successfully. Though it is difficult to analyze the effect of each of the factors while ruling out the others, it is certain that microstructure and strain are the main reasons for the quite different performance of the two films derived from different methods. A similar difference was also observed in Nd-doped BT films.[11] A high P_r value was measured in sol-gel derived highly *c*-axis oriented BNdT film, while no P_r was measured in a sample with the same orientation that was fabricated by the PLD method.

The real part of the relative dielectric permittivity $[\varepsilon'(\omega)]$ and the dissipation factor $[\varepsilon''(\omega)/\varepsilon'(\omega)=\tan\delta]$ of the capacitor were measured at room temperature as a function of frequency [shown in Fig. 5(a)]. At a frequency of 1 MHz, $\varepsilon'(\omega)$ and $\tan\delta$ were 345 and 0.056, respectively. These values are comparable to those of PZT, SBT, and BLT capacitors.[1,12,13] Although both $\varepsilon'(\omega)$ and $\tan\delta$ decreased slightly with increasing frequency, there was no sudden change in their values up to 1 MHz. All these results indicate that the observed *P-E* hysteresis behavior of the highly (117) oriented BSmT capacitor originates from the ferroelectric polarization switching of bound charges, not from the response of freely moving charges.

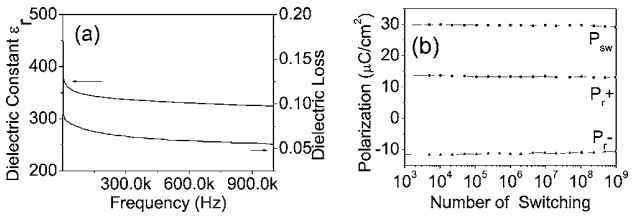

FIG. 5. Frequency dependence of dielectric constant and dielectric loss (a) and electrical fatigue characteristics (b) of $Pt/Bi_{3.25}Sm_{0.75}Ti_3O_{12}/Pt$ capacitor. The switching voltage during the fatigue test is ±3 V at a frequency of 5 kHz and the measurement voltage is 5 V.

The highly (117) oriented BSmT thin films also show a small leakage current of less than 10^{-6} A/cm^2. The fatigue-free characteristics of the highly (117) oriented BSmT capacitor are shown in Fig. 5(b). The capacitor shows little change either in the switching polarization (P_{sw}) or in the remanent polarization (P_r^+) for up to 10^9 write/read cycles at a switching voltage of ±3 V at a frequency of 5 kHz and a measurement voltage of ±5 V. The values of $2P_r=(P_r^+ - P_r^-)$ of the capacitor was 25.4 μC/cm^2 at room temperature and remained essentially constant during the fatigue testing, demonstrating an excellent fatigue-free behavior.

In summary, $Bi_{3.25}Sm_{0.75}Ti_3O_{12}$ films with different preferred orientations on platinized silicon were prepared by the PLD method. It was observed that highly *c*-axis oriented BSmT film had a very small remanent polarization, while highly (117) oriented film had a high remanent polarization of up to 54 μC/cm^2, which is much higher than that of La-doped BT film. These results are quite different from those for BSmT film derived from the sol-gel method, in which the highly *c*-axis oriented films show a high remanent polarization. The PLD derived BSmT film also shows a good fatigue resistance and small leakage current.

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