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# Influence of $SrTiO_3$ Buffer Layer on the Ferroelectric Properties of $Bi_2NiMnO_6$ Thin Film

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*Double perovskite $Bi_2NiMnO_6$ (BNMO) thin films with and without $SrTiO_3$ (STO) buffer layer have been prepared on Pt (111)/Ti/$SiO_2$/Si(100) substrates by a chemical solution deposition method. The microscopic surface morphology, ferroelectric, and leakage current have been investigated. It is shown that the STO buffer layer can improve the remnant polarization slightly, and reduce the coercive electric field from 100 to 36 kV/cm. When the positive voltage was applied on top Au electrode of the BNMO/STO/Pt thin film capacitors, the leakage current was controlled by ohmic conduction. When the negative voltage was applied on bottom Pt electron, the leakage current of BNMO/STO thin film was limited by the traps and the density of carriers at high electric field.*

**Keywords** Double perovskite; buffer layer; surface morphology; ferroelectric; leakage current.

## 1. Introduction

The multiferroic properties which show coexistence of ferromagnetic and ferroelectric property have received more and more attention due to their interesting fundamental nature and potentially wide applications [1]. An example of the interesting multiferroic materials is $Bi_2NiMnO_6$ with a double-perovskite structure. Du *et el.* have synthesized multiferroic $Bi_2NiMnO_6$ nanoparticles by a simple electrospray method and the particles crystallized in a monoclinic structure with a space group *C121* [2]. In recent years, a large number of $Bi_2NiMnO_6$ or $Bi_2NiMnO_6$)/$La_2NiMnO_6$ thin films on different substrates have been prepared by the pulsed laser deposition technique [3–7]. However, the polarization values of these thin films were relatively low. In order to enhance the polarization, a buffer layer such as $SrTiO_3$ has been taken into account. A lot of work devoting to calculation of lattice dynamics of perovskite thin film of $SrTiO_3$ indicated that ferroelectric instability arising in thin film of $SrTiO_3$ on the substrate [8,9]. Sadovskaya *et el.* proved that $SrTiO_3$ is an efficient barrier material [10].

In the present work, we fabricated the $Bi_2NiMnO_6$ single layer film and the $Bi_2NiMnO_6$ film with $SrTiO_3$ buffer layer. The microscopic surface morphology, ferroelectric property, and leakage current were investigated.

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## 2. Experimental Procedure

The double-perovskite $Bi_2NiMnO_6$ (BNMO) thin films were prepared by a chemical solution deposition method. The $SrTiO_3$ (STO) buffer layer was deposited via magnetron sputtering method. To produce the BNMO film, the precursor solution had been produced. High-purity bismuth nitrate $Bi(NO_3)_3{\cdot}5H_2O$, nickel acetate $Ni(CH_3COO)_2{\cdot}4H_2O$ and manganese acetate $C_4H_6MnO_4{\cdot}4H_2O$ were selected as starting materials for the preparation of precursor solution. Bismuth nitrate, nickel acetate and manganese acetate were accurately weighed corresponding to the $Bi_2NiMnO_6$ composition. Bismuth nitrate was dissolved in glacial acetic acid ($CH_3COOH$), meanwhile acetylacetone was added to prevent partial hydrolysis. Nickel acetate was dissolved in glacial acetic acid, manganese acetate was dissolved in 36% acetic acid, respectively. Then the solutions were mixed together, stirring at 60°C for more than half an hour, until the concentration of the final solution was adjusted to 0.2 Mol/L.

Before spin-coating, STO buffer layer was grown on Pt(111)/Ti/$SiO_2$/Si(100) substrates by rf-magnetron sputtering (China SKY Technology development Co. Ltd, CAS,JGP-450A) for 2 h. These STO target was prepared by a conventional solid state reaction. The deposition chamber was evacuated to a pressure less than $2 \times 10^{-3}$ Pa before preparing the thin films and then the gas mixture of Ar and $O_2$ was fed into the chamber to keep the total pressure to 9.2 Pa in the chamber during the deposition. The ratio of Ar:$O_2$ was kept to 4:1. The sputtering power was 420 W.The BNMO precursor solution was spin-coated directly on a Pt/Ti/$SiO_2$/Si substrate with and without STO buffer layer to form a uniform wet film at room temperature, respectively. Then the wet films were dried at 300°C for 30 minutes on drying platform. Finally, the films were annealed in ambient atmosphere at 650°C for 15 min by rapid thermal annealing (RTA). In order to measure the electrical properties of the films, Au dots were evaporated through a metal mask on the films' surface as the top electrodes.

The microscopic surface morphology of the BNMO and BNMO/STO thin films were analyzed by atomic force microscopy (AFM, Being Nano-Instruments Ltd., CSPM5500). The P-E hysteresis loops and leakage current of the film were observed by Radiant Technolies' Precision premier (USA). The thickness of the BNMO thin films grown Pt/Ti/$SiO_2$/Si substrate without and with STO buffer-layer were 100 and 238 nm, respectively, measured by a surface profiler (Ambios XP-2,USA).

## 3. Results and Disscussion

Figure 1 shows the 3D AFM images of (a) BNMO and (b) BNMO/STO thin films grown on Pt/Ti/$SiO_2$/Si substrates. The scan area was $5{\times}5$ $\mu m^2$. The root-mean-square (rms) roughness of BNMO film and BNMO/STO composite film are 15.2 nm and 33.4 nm, respectively. From the Fig.1, it is indicated that the BNMO thin film with STO buffer layer grew denser and the grain was smaller than that of BNMO thin film.

Figures 2 (a) and (b) show the *P–E* hysteresis loops of the BNMO thin film deposited on the Pt/Ti/$SiO_2$/Si substrates without and with STO buffer-layer. From Fig. 2, it can be observed that the remnant polarization and coercive electric field are 6.42 $\mu C/cm^2$ and 100 kV/cm, 8.24 $\mu C/cm^2$ and 36 kV/cm, respectively for BNMO and BNMO/STO thin films. The STO buffer layer improved the remnant polarization slightly and reduced the coercive electric field obviously. The curves first increased with the electric field to a maximum and then decreased. The distorted hysteresis loops may be owed to an effect of leakage current or the charge accumulation. Azuma *et el.* reported that the *C*2 symmetry of this compound allows a spontaneous polarization along the *b* axis, and a calculation

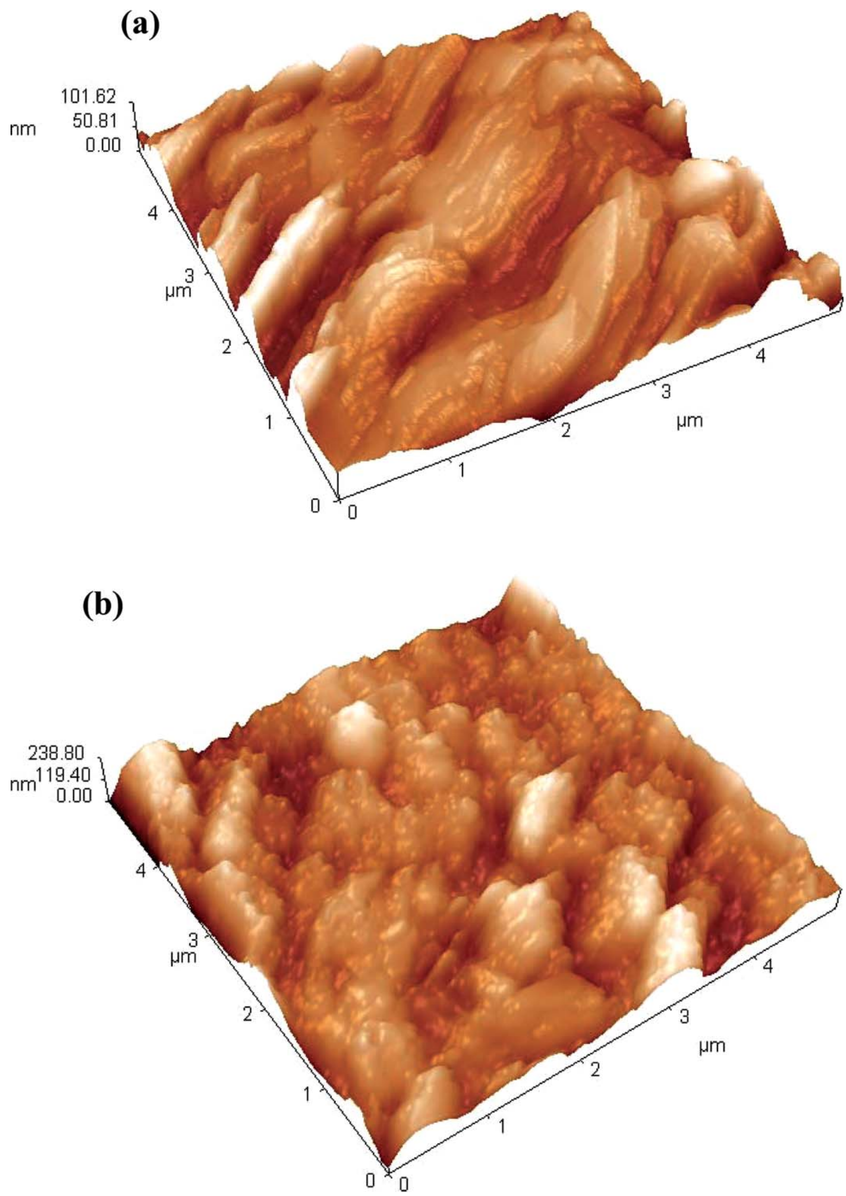


**Figure 1.** 3D AFM images of (a) BNMO and (b) BNMO/STO thin films grown on Pt/Ti/$SiO_2$/Si substrate and annealed at 650°C.

assuming a pointcharge model with the above structural parameters gave a polarization of 20 $\mu$C/cm$^2$ [11]. But the observed polarization is much smaller than the calculated value, because the observed ferroelectric polarization should be a projection along the out-of plane direction. Zhandun *et el.* reported that the $SrTiO_3$ (100) thin film had instable ferroelectric modes concerning with vibration atoms in plane parallel [12]. When voltages were applied to the (100)-oriented STO thin films, the in-plane orientation of the polar axis resulted in higher polarization.

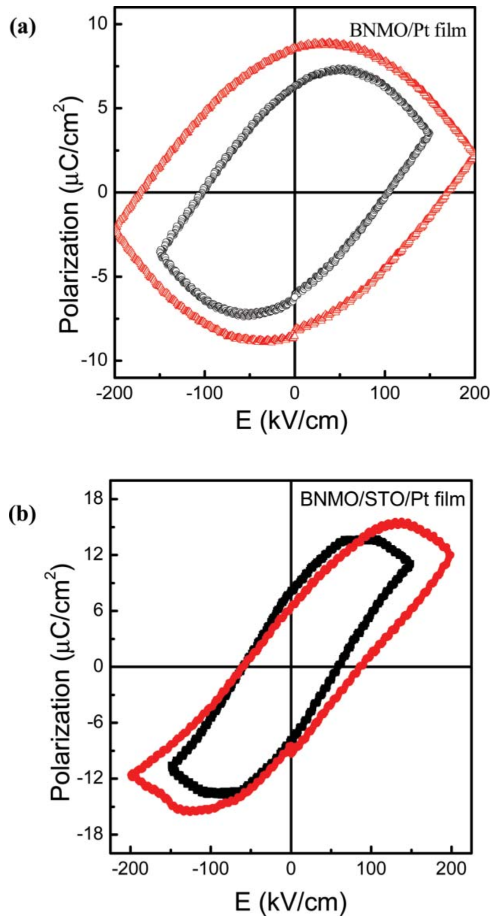


**Figure 2.** *P–E* hysteresis loops of (a) BNMO and (b) BNMO/STO thin films measured at different applied electric fields. (Figure available in color online)



Figure 3 shows the leakage current of the BNMO and BNMO/STO thin film deposited on the substrate Pt/Ti/$SiO_2$/Si at the electric field from 500 to −500 kV/cm. When the negative dc bias voltage was applied at the top Au electrode, the leakage current density of BNMO and BNMO/STO were less than $1.32\times10^{-2}$ A/cm$^2$ and $1.18\times10^{-2}$ A/cm$^2$. When the positive dc bias voltage was applied at the bottom Pt electrode, the leakage current density of BNMO thin film was lower than $1.28\times10^{-2}$ A/cm$^2$ over an applied field from 0 to 220 kV/cm; then increased to 0.16 A/cm$^2$. When the voltage was applied at BNMO/STO thin film, the leakage current density increased with the applied field, then reached to 0.187 A/cm$^2$. The negative leakage current was limited by the interface between the Pt bottom electrode and the thin films (the bottom interface), while the positive leakage current was limited by the interface between the Au top electrode and the thin films (the top interface) indicating an ohmic mechanism [13].

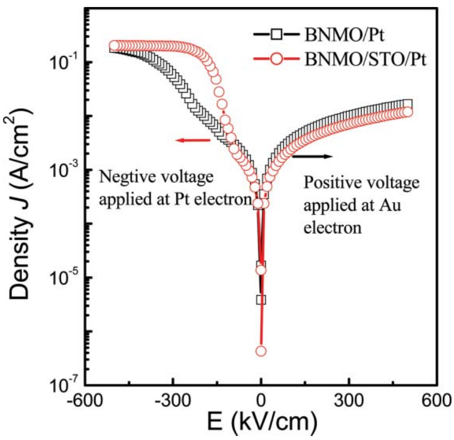


**Figure 3.** Leakage current density of the BNMO and BNMO/STO thin films deposited on the Pt/Ti/$SiO_2$/Si substrates at the electric field from 500 to −500 kV/cm. (Figure available in color online)



## 4. Conclusions

In summary, the BNMO film grown on Pt/Ti/$SiO_2$/Si substrates without and with STO buffer layer. The AFM images showed that the root-mean-square roughness of 33.4 nm for BNMO/STO thin film. The remnant polarization of and BNMO thin film the BNMO/STO thin film were 6.42 $\mu$C/cm$^2$ and 8.24 $\mu$C/cm$^2$, respectively. The STO buffer layer reduced the coercive electric field of BNMO thin films. The leakage current curves showed that the negative leakage current was limited by the interface between the Pt bottom electrode and the thin films (the bottom interface), while the positive leakage current was limited by the interface between the Au top electrode and the thin films (the top interface) indicating an ohmic mechanism.

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