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Electrical properties of lead-free KNN films on SRO/STO by RF magnetron sputtering

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Abstract

Highly (001) oriented (K,Na)NbO_3 lead-free piezoelectric films were fabricated on $SrRuO_3$ buffered $SrTiO_3$(001) single crystal substrates by RF magnetron sputtering. The films showed a stable frequency dependence of dielectric permittivity and loss tangent in the range of 1 kHz–1 MHz. A fairly high tunability of 69.7% (@400 kV/cm) was obtained in the films. Well saturated *P–E* hysteresis loops were obtained at $E=250$ kV/cm, the remnant polarization P_r was 8 μC/cm^2, and coercive field E_c was only 40 kV/cm. These films showed a fatigue-free behavior up to 10^{10} switching cycles. The decreased coercive field, improved dielectric and fatigue properties may be related to SRO bottom electrodes, which can efficiently suppress the "dead layer" near the ferroelectric-electrode interface. The leakage current density of the films was only 3.48×10^{-6} A/cm^2 at the electric field of 250 kV/cm, which is even lower than that of Mn-doped KNN films. In addition, the piezoelectric constant d_{33} was estimated to be 36 pm/V.

Keywords: Lead-free; Piezoelectric thin films; (K,Na)NbO_3; $SrRuO_3$

1. Introduction

Lead oxide-based piezoelectric materials such as Pb(Zr,Ti)O_3 (PZT) films are widely used for various actuators, sensors and transducers in the micro-electro-mechanical systems (MEMS) due to their excellent piezoelectric properties [1–3]. However, in recent years, lead-free piezoelectric films have received increasing attention for environmental protection. (K,Na)NbO_3 (KNN) is a promising lead-free candidate for piezoelectric applications owing to its high Curie temperature and excellent piezoelectric properties [4–6]. Great efforts have been made to fabricate KNN films using different growth techniques [7–10]. However, KNN films with high performance are difficult to fabricate, and many problems such as decreasing the leakage current, ensuring the stoichiometric composition, improving the piezoelectricity etc. need to be resolved before its commercial applications.

It is known that bottom electrodes have an obvious influence on the texture and the electric properties of the films [11,12]. In general, two types of electrodes are used in the ferroelectric heterostructures: metal Pt and Au, conductive oxide $LaNiO_3$ (LNO), $SrRuO_3$ (SRO), and La(Sr,Mn)O_3 (LSMO). It is common that metal electrodes possess high conductivity. Nevertheless, it is also believed that a depolarizing field will be produced at the ferroelectric-metal electrode interface, and the depolarizing field can suppress the polarization and the permittivity of the films [13]. By contrast, conductive oxide electrodes are usually perovskite structure, and their lattice constants match well with that of many ferroelectric perovskite oxides. Therefore, they have been used as bottom electrodes to improve the structural and electric properties of ferroelectric films [14,15]. As one of the highly conductive perovskite-type oxide, SRO has good thermal and chemical stabilities, it is

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recognized as the most attractive electrode material for growing epitaxial films [16]. In this work, highly (001) oriented KNN films were fabricated on SRO buffered $SrTiO_3$ (STO) by RF magnetron sputtering, and the electrical properties were investigated. These films were shown to exhibit the stable frequency dependence of permittivity, high tunability, lower leakage, well ferroelectric and fatigue properties.

2. Experimental details

SRO bottom electrodes were deposited on STO(001) single substrate by DC sputtering at 700 °C, and then in-situ annealed at 700 °C for 30 min. After that, KNN films were deposited on SRO/STO(100) using a K,Na-enriched $K_{0.55}Na_{0.55}NbO_3$ ceramic target. The controlled growth of KNN films have already been reported elsewhere, [11,14] but the thickness of KNN film here was about 1 μm by changing the Ar/O_2 ratio as 9:1. The average size of nanocrystalline particles of KNN films was about 150 nm. XRD pattern depicted that KNN films were highly (001) oriented, as shown in Fig. 1. Relative permittivity vs voltage and frequency characteristics were measured using HP4192A (Agilent Technologies, Santa Clara, CA). Polarization-field (*P*–*E*) hysteresis loops, electrical fatigue test, and the leakage current behaviors of the films were measured by TF 2000 analyzer (aixACCT Systems GmbH, Aachen, Nordrhein-Westfalen, Germany). An optical system was adopted to measure the d_{33} coefficient of the piezoelectric thin films at room temperature. The system has been developed upon a commercial Laser Doppler Vibrometer (Polytec OFV512/DFE650, Waldbronn, Germany), and combined with a Nikon (Tokyo, Japan) optical microscope [17].

3. Results and discussion

Fig. 2(a) shows the frequency dependence of dielectric permittivity and loss tangent of the KNN film. It is found that the KNN film exhibits a stable frequency dependence of dielectric permittivity and loss tangent in the range of 1 kHz–1 MHz. The dielectric permittivity and loss tangent of the film are 677 and 0.03, respectively, at 100 kHz. Fig. 2(b) shows the evolution of the relative permittivity and loss tangent of the KNN film as a function of DC bias electric field, applied with an AC small-signal voltage of 500 mV at 10 KHz. The KNN film showed a fairly high tunability of 69.7% (@400 kV/cm) and a loss tangent of 0.03 at room temperature, and the *K*-factor (K = tunability/tan δ_{0V}, tan δ_{0V} is the loss tangent at 0 kV/cm) was calculated to be 23.2. A value of 69.7% is high when compared to the previously reported value of 51.7% for KNN films on Pt, [18] and it is comparable to those of (Ba,Sr)TiO_3 and Pb(Sr,Ti)O_3 films, [19,20] which are popular materials used in tunable applications. The relative permittivity in this work is higher than that of KNN films grown on Pt metal electrodes, which may be contributed by the improved interface due to SRO bottom electrodes. In general, the decreased dielectric permittivity in ferroelectric films is thought to be caused by the "dead layer" near the interface between ferroelectric films and electrodes. According to Gerra et al. [13] perovskite metal oxides like SRO can essentially share the ionic displacements that are responsible for the polarization in ferroelectrics, which can efficiently suppress the occurrence of "dead layer", leading to the improved dielectric properties.

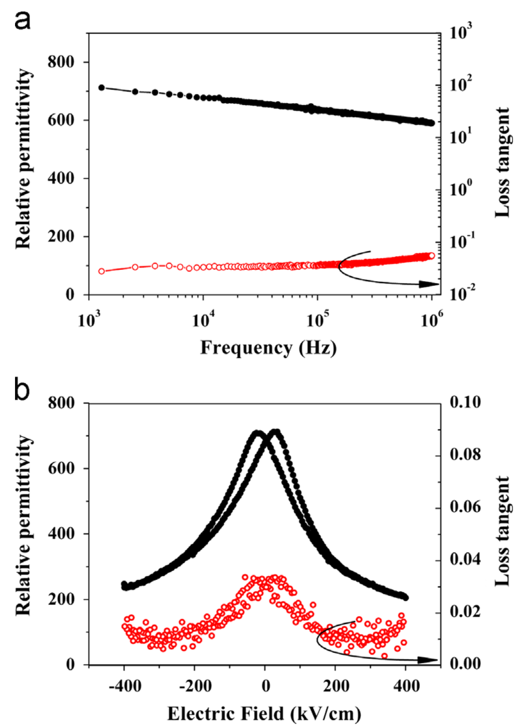

Fig. 2. (a) Frequency dependence of the relative permittivity and loss tangent for Pt/KNN/SRO/STO; (b) relative permittivity and loss tangent as a function of bias field with a frequency of 10 kHz.

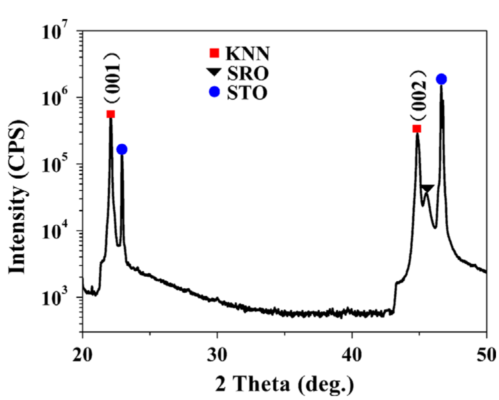

Fig. 1. The XRD pattern of KNN films deposited on SRO/STO(001).

The *P*–*E* hysteresis loops of the KNN film are shown in Fig. 3(a). Well saturated *P*–*E* hysteresis loops were obtained at E = 250 kV/cm. A desired remnant polarization P_r = 8 μC/cm^2 and lower coercive field E_c = 40 kV/cm were observed in the film. The coercive field here is lower than that of KNN films on Pt (E_c = 100 kV/cm), [18] which can be ascribed to the matched KNN/SRO interface, at which domains can reverse easier. The electrical fatigue characteristic of the KNN film is displayed in Fig. 3(b) measured at f = 1 MHz. The KNN film appears fatigue-free subjected to 10^{10} switching cycles, which is similar to other oxide bottom electrodes in improving the fatigue characteristics of the ferroelectric thin films. Generally, the degradation of switching ability in film is believed to be associated with the electrical overstress in the "dead layer" [13]. However, oxide electrodes like SRO can efficiently suppress the occurrence of "dead layer", resulting in the improved fatigue properties.

Fig. 4 shows the leakage behavior of Pt/KNN/SRO. The leakage currents were measured with a voltage step of 0.5 V, a step duration of 10 s. It is found that the leakage current density of the film is only 3.48×10^{-6} A/cm^2 at the electric field of 250 kV/cm, which is even lower than that of Mn-doped KNN films, [21] and about three orders of magnitude lower than that of previous reported KNN films on SRO [12]. In addition, the leakage current curve is asymmetry, which can be explained by the different barrier heights of the two interfaces in Pt/KNN/SRO. A similar asymmetric leakage behavior was observed in Au/KNN/Pt by Blomqvist et al. [22]. In order to further understand the leakage mechanism in Pt/KNN/SRO, the logarithmic plots of dependence of J as a function of E for the positive and negative fields were shown in inset of Fig. 4. The J–E curves under both directions of filed can be described on the basis of the space charge-limited current (SCLC) model. It was observed that Pt/KNN/SRO follows an Ohmic conduction ($J \sim E^{\alpha}$, $\alpha \sim 1$) mechanism in the low field region ($\alpha = 0.69$ for the positive filed, $\alpha = 0.66$ for the negative field). In the high electrical field region, Pt/KNN/SRO follows a SCLC conduction ($J \sim E^{\alpha}$, $\alpha \gg 1$) mechanism ($\alpha = 3.94$ for the positive filed, $\alpha = 3.73$ for the negative field). The transition field E_t separating the two conductive regions are different for the positive and negative field, which confirms the different barrier heights between the KNN/SRO and Pt/KNN interface. As shown in inset of Fig. 4, E_t under the positive field ($E_t = 105$ kV/cm) is higher than that under the negative field ($E_t = 49.8$ kV/cm).

Fig. 5 shows the d_{33} hysteresis loops of Pt/KNN/SRO/STO at room temperature. To obtain the characteristic piezoelectric hysteresis loop, a dynamic small signal voltage ($V_{ac} = 100$ mV at $f = 12$ kHz) and a variable DC bias voltage was applied to the KNN film. As shown in Fig. 5, the maximum $d_{33,max}$ and remnant $d_{33,rem}$ of the KNN film are 36 pm/V and 22 pm/V respectively. These values are desired for the lead-free undoped KNN films. In addition, the coercive fied can be confirmed to be 40 kV/cm in the piezoelectric hysteresis loops, which is consistent with that in the P–E loops.

4. Conclusion

In summary, highly (001) oriented KNN films were fabricated on SRO buffered STO by RF magnetron sputtering. A stable frequency dependence of dielectric permittivity and fairly high tunability of 69.7% (@400 kV/cm) was obtained in the film. Well saturated P–E hysteresis loops with desired

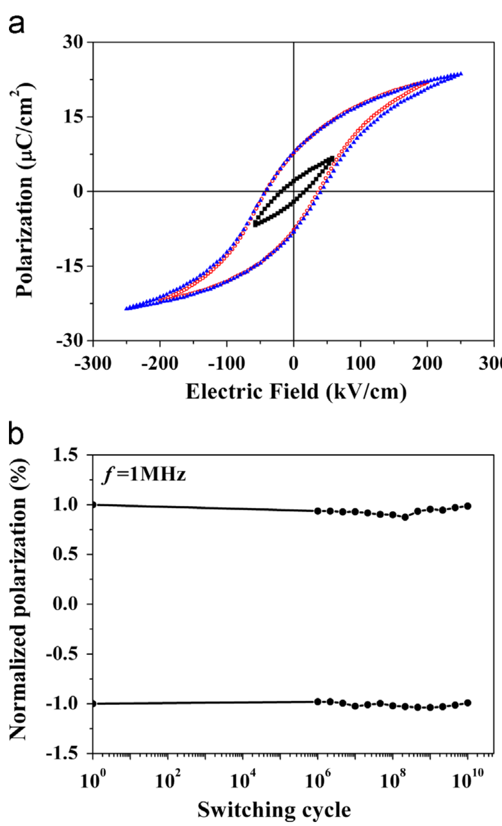

Fig. 3. (a) P–E hysteresis loops under various electric fields; (b) the fatigue behavior of Pt/KNN/SRO/STO.

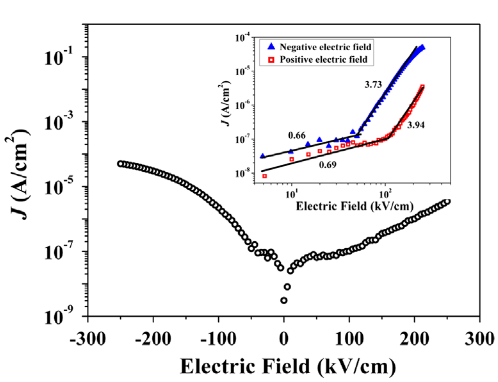

Fig. 4. Leakage current density as a function of applied field for Pt/KNN/SRO/STO; inset shows the logarithmic plots of dependence of J as a function of E under the positive and negative field.

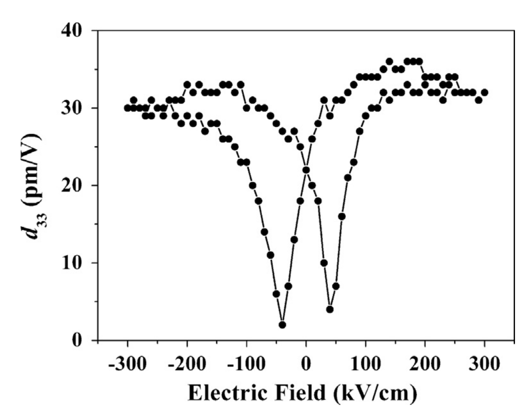

Fig. 5. The piezoelectric loop of Pt/KNN/SRO/STO at room temperature.

remnant polarization $P_r = 8\ \mu C/cm^2$ and lower coercive field $E_c = 40$ kV/cm were observed. The KNN film showed a fatigue-free behavior up to 10^{10} switching cycles. The leakage current density of the film is only 3.48×10^{-6} A/cm^2 even at the electric field of 250 kV/cm. An asymmetric leakage behavior of Pt/KNN/SRO was observed, which indicates the different barrier heights between Pt/KNN and KNN/SRO interface. Besides, the piezoelectric constant d_{33} was estimated to be 36 pm/V. The decreased coercive field, improved dielectric and fatigue properties were thought to be ascribed to SRO bottom electrodes, which can efficiently suppress the "dead layer" near the ferroelectric-electrode interface. High tunability, well fatigue behavior, low coercive field and leakage current are essential for microwave tunable devices and ferroelectric random access memories. Therefore, our results show that KNN film on SRO/STO is a promising candidate for applications of lead-free ferroelectric film devices.

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