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Piezoelectric Properties of (K,Na)NbO₃ Thin Films Deposited on (001)SrRuO₃/Pt/MgO Substrates

Isaku Kanno, Takuya Mino, Shuichiro Kuwajima, Takaaki Suzuki, Hidetoshi Kotera, and Kiyotaka Wasa

Abstract—(K_x,Na_{1-x})NbO₃ (KNN) thin films were deposited on (001)SrRuO₃/(001)Pt/(001)MgO substrates by RF-magnetron sputtering, and their piezoelectric properties were investigated. The x-ray diffraction measurements indicated that the KNN thin films were epitaxially grown with the *c*-axis orientation in the perovskite tetragonal system. The lattice constant of the *c*-axis increased with increasing concentrations of potassium. The KNN thin films showed typical ferroelectric behavior; the relative dielectric constant ϵ_r was 270 ~ 320. The piezoelectric properties were measured from the tip displacement of the KNN/MgO unimorph cantilevers; the transverse piezoelectric coefficient e_{31}^* ($= d_{31}/s_{11}^E$) of KNN ($x = 0$) thin films was calculated to be -0.9 C/m². On the other hand, doping of potassium caused an increase in the piezoelectric properties, and the KNN ($x = 0.16$) films showed a relatively large transverse piezoelectricity of $e_{31}^* = -2.4$ C/m².

laser deposition (PLD) [6], [7]. However, the piezoelectric properties of the KNN thin films are still unclear.

In this study, we have grown epitaxial KNN thin films by RF-magnetron sputtering and examined their crystal structure and piezoelectric properties. The KNN thin films are one of the promising materials to realize lead-free piezoelectric microelectromechanical systems (MEMS). Furthermore, understanding of the relationship between the crystal structures and the piezoelectric properties of the KNN thin films would lead to creation of new lead-free materials with simpler compositions. In this paper, we describe the epitaxial growth of KNN thin films and their piezoelectric properties.

II. EXPERIMENTAL

I. INTRODUCTION

ALKALI metal-based ferroelectric perovskite materials have attracted attention as promising substitutes for lead-based piezoelectric materials which are widely used for piezoelectric sensors and/or actuators. Among the alkali-based perovskite materials, it is known that the bulk solid solution of KNbO₃ and NaNbO₃, (K_x,Na_{1-x})NbO₃ (KNN), shows a high electromechanical coupling at about $x = 0.5$ [1], [2]. Furthermore, it has been reported that doping of Li, Ta, and/or Sb, as well as orientation control, leads to further elevation of the piezoelectricity [3], and these materials are now provided in a form of bulk ceramics. On the other hand, KNN in the epitaxial thin-film form is useful not only for the practical micro-device applications, but also for the fundamental understanding of ferroelectricity and/or piezoelectricity of the alkali-based thin films by intentional control of the crystal structure. Several deposition processes have been employed for the hetero-epitaxial growth of the KNN films, including sputtering [4], chemical vapor deposition (CVD) [5], and pulsed

KNN thin films with a composition of K/(K+Na) from 0 to 0.6 were deposited using an RF-magnetron sputtering technique. The sputtering target we used was a mixture of stoichiometric KNbO₃ and NaNbO₃ powders to prepare the KNN films with a variety of K/Na compositions. The deposition was conducted in an Ar/O₂ mixed atmosphere on (001)MgO single-crystal substrates covered with a (001)Pt electrode and a (001)SrRuO₃ (SRO) buffer layer. The substrate temperature was 580 ~ 650°C for the epitaxial growth of the KNN films, and we did not conduct a post annealing treatment for the deposited films. In this study, we prepared two types of thickness variation, 0.5 ~ 0.7 μ m and 2.0 ~ 2.5 μ m. The KNN films with the thickness of 0.5 ~ 0.7 μ m was for measurements of crystal structure, while the thicker KNN films of 2.0 ~ 2.5 μ m were used for electric measurements to avoid unexpected leaks or shorts due to the pin holes. Typical sputtering conditions are shown in Table I.

The chemical compositions of the thin films were evaluated by energy dispersive spectroscopy (EDS), and we confirmed that the (K+Na)/Nb ratio of the resulting films was around 1. The surface morphology of the film was observed by a scanning electron microscopy (SEM). The crystal structure was measured by $2\theta/\theta$ x-ray diffraction (XRD; MultiFlex; Rigaku Japan, Tokyo, Japan) with a high resolution x-ray diffractometer (ATX-G; Rigaku Japan). For examination of electric properties, Pt upper electrodes 0.3 mm in diameter were deposited on the films, and the relative dielectric constant ϵ_r and the dielectric loss $\tan \delta$ were measured by an LCR meter (ZM2353; NF Corp.,

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TABLE I
SPUTTERING CONDITIONS.

Target	mixed powder: $x\text{KNbO}_3$ and $(1-x)\text{NaNbO}_3$ ($x = 0 \sim 0.7$)
Substrates	(001)SRO/(001)Pt/(001)MgO
Sputtering gas	0.5 Pa (Ar/O ₂ = 20/1)
Growth temperature	580 ~ 650°C
Growth rate	2.5 ~ 5 nm/min
Film thickness	0.5 ~ 2.5 μm

Fig. 1. An SEM image of a KNN ($x = 0$) thin film on (001)SRO/Pt/MgO substrate.

Yokohama, Japan). P - E hysteresis loops were measured using a Sawyer-Tower circuit. The transverse piezoelectric properties of the KNN thin films were evaluated using KNN/MgO unimorph cantilevers (length: 10–15 mm; width: 1–2 mm; thickness: 0.3 mm). Then Pt upper electrodes were deposited over the surface of the KNN film except for one end of the beam, where the cantilever beam was clamped as a unimorph actuator. Application of sine wave voltage between the upper and bottom electrodes generates a deflection by the transverse inverse piezoelectric effect; the tip displacement was measured using a laser Doppler vibrometer (AT-3500; Graphtec Corp., Yokohama, Japan). The electric and piezoelectric measurements were conducted at room temperature.

III. CRYSTAL STRUCTURE

Fig. 1 shows an SEM image of the surface of a KNN thin film ($x = 0$) 0.5 μm in thickness. The surface of the KNN thin film exhibits high density and a smooth and homogeneous structure. Fig. 2 shows the XRD patterns of KNN films ($x = 0$ and 0.16) with a thickness of 0.5 ~ 0.7 μm . The $\theta/2\theta$ XRD patterns show that these KNN films were

Fig. 2. XRD patterns of KNN thin films on (001)SRO/Pt/MgO: (a) KNN ($x = 0$), (b) KNN ($x = 0.16$). The inset in (a) is a reciprocal space map of (004)KNN ($x = 0$).

highly oriented along the [001]-direction in a pseudo-cubic system of perovskite structure [Fig. 2(a) and (b)]. The KNN films with the other compositions also showed the c -axis orientation. The inset in Fig. 2(a) is the reciprocal space map of (004)KNN ($x = 0$). The clear spotty diffraction peak of (004)KNN was obtained, indicating that the KNN thin films were grown with an epitaxial relationship to the (001)MgO substrate. However, the diffraction peak is very broad and therefore suggests that many defects would exist in the films.

The lattice parameters were calculated by the (004)-peaks of the KNN thin films of 0.5–0.7 μm thickness; the dependence on the K/(K+Na) ratio is shown in Fig. 3. The length of the c -axis of bulk KNN in the orthorhombic phase ($a = c > b$) is also plotted in Fig. 3 [8]. The lattice parameters of the c -axis increased with increasing potassium concentration in the films, like those of the bulk KNN; however, the KNN thin films show longer c -axes than bulk ones. The reason for the difference in elongation of the c -lattice parameters between thin films and bulk materials is unclear; however, the same phenomena have been reported for epitaxial PZT films with a thickness of 2.5 ~ 3.0 μm [9]. So that the dependence on thickness might be examined, lattice constants of the KNN films ($x = 0$ and 0.16) with a

Fig. 3. The lattice constant as a function of the K/(K+Na) composition of the KNN films (0.5 ~ 0.7 μm).

thickness of 2.0 ~ 2.5 μm were also measured, and the films showed 3.95 Å ($x = 0$) and 3.98 Å, respectively. Considering lattice constants of the KNN thin films of 0.5 ~ 0.7 μm , we could say that the thickness dependence of the lattice constant is small, and stress from the substrate would be relaxed when the thickness is more than 0.5 μm . In the case of the PZT thin films, Nagarajan *et al.* reported that the PZT films with a thickness of more than 300 nm were fully relaxed [10]. Thickness dependence of KNN thin films has not been reported yet; however, our result is consistent with that of PZT thin film.

IV. ELECTRIC PROPERTIES

Dielectric and ferroelectric properties of the (001)KNN ($x = 0$ and 0.16) thin films 2.0 ~ 2.5 μm in thickness were measured. The values of the relative dielectric constant (ϵ_r) of KNN films of $x = 0$ and 0.16 were 270 and 320, and those of the dielectric loss ($\tan \delta$) were 0.09 and 0.15, respectively. However, further increase of potassium concentration in the films ($x > 0.16$) resulted in an abrupt increase of $\tan \delta$ and it was difficult to measure proper electric properties. The large dielectric loss might be attributed to the existence of the lattice defects or the interstitial atoms which would also cause the relatively broad diffraction peak of the KNN thin films shown in Fig. 2.

Fig. 4 shows the P - E hysteresis loops of the KNN ($x = 0$ and 0.16) thin films. The P - E hysteresis loop shows typical ferroelectric behavior for both KNN thin films. Compared with the hysteresis loop of the KNN ($x = 0$) film, that of the KNN ($x = 0.16$) thin film shows a larger remanent polarization (P_r) of about 20 ~ 25 $\mu\text{C}/\text{cm}^2$ and smaller coercive electric field (E_c) of 30 ~ 45 kV/cm, respectively. Although bulk KNN ($x = 0.16$) ceramics show larger remanent polarization (30 $\mu\text{C}/\text{cm}^2$) and smaller coercive electric field (12 kV/cm) [2], the difference is attributed to the single-crystal structure as well as the (001)-preferred orientation, which is different from the polar direction of orthorhombic KNN.

Fig. 4. P - E hysteresis of KNN epitaxial thin films ($x = 0$ and 0.16; 2.0 ~ 2.5 μm).

Fig. 5. Tip displacement of a KNN/MgO unimorph cantilever as a function of applied voltage.

V. PIEZOELECTRIC PROPERTIES

So that the piezoelectric properties of the KNN thin films ($x = 0$ and 0.16; 2.0 ~ 2.5 μm) might be evaluated, the tip displacement of the unimorph cantilever of KNN/MgO was measured by applying unipolar sine wave signals at 300 ~ 500 Hz. The tip displacement increased proportionally with increasing the magnitude of applied voltage, as shown in Fig. 5. From the result of Fig. 5, we evaluated the transverse piezoelectric properties. The transverse piezoelectric coefficient d_{31} is calculated from the tip displacement of the cantilever [11],

$$d_{31} = -\frac{\delta K}{3s_{11,p}^E s_{11,s} h_s (h_s + h_p) V L^2},$$

$$K = 4s_{11,p}^E s_{11,s} h_s (h_p)^3 + 4s_{11,p}^E s_{11,s} (h_s)^3 h_p + (s_{11,p}^E)^2 (h_s)^4 + (s_{11,s}^E)^2 (h_p)^4 + 6s_{11,p}^E s_{11,s} (h_s)^2 (h_p)^2, \quad (1)$$

where δ , V , L , h , and s_{11} are the tip displacement, applied voltage between top and bottom electrodes, length of the

Fig. 6. The transverse piezoelectric coefficient e_{31}^* as a function of applied voltage. A 16% doping of potassium in NaNbO₃ thin films caused enhancement of piezoelectricity.

cantilever, thickness, and the elastic compliance, respectively. The subscripts of 's' and 'p' denote the substrate and the piezoelectric film, respectively. When $h_s \gg h_p$, (1) can be simplified as [12]

$$d_{31} \cong -\frac{h_s^2}{3L^2} \frac{s_{11,p}^E}{s_{11,s}^E} \frac{\delta}{V}. \quad (2)$$

Although mechanical properties of substrates are stable and easy to measure because of the large volume of the materials, those of thin films are difficult to estimate precisely due to their small volumes as well as the existence of a substrate. In this study, to eliminate the ambiguity of the mechanical properties of the KNN thin films, we define the transverse piezoelectric coefficient e_{31}^* as follows,

$$e_{31}^* = \frac{d_{31}}{s_{11,p}^E} \cong -\frac{h_s^2}{3s_{11,s}^E L^2} \frac{\delta}{V}. \quad (3)$$

This equation is equivalent with the following equation:

$$e_{31}^* = e_{31,f} \frac{s_{11,p}^E + s_{12,p}^E}{s_{11,p}^E} = \left(e_{31} - \frac{c_{13}^E}{c_{33}^E} e_{33} \right) \left(1 + \frac{s_{12,p}^E}{s_{11,p}^E} \right), \quad (4)$$

where c_{ij} is the elastic stiffness of the piezoelectric thin films, and e_{31} and $e_{31,f}$ are the transverse piezoelectric coefficient and the effective transverse piezoelectric coefficient, respectively [13]. Eq. (4) means that the e_{31}^* neglects the effects of the deformation along thickness and width of the cantilever; however, we could evaluate the transverse piezoelectric properties of the thin film by simple calculation and, furthermore, we can obtain e_{31} and $e_{31,f}$ from e_{31}^* , if we know all of the mechanical properties of the film. For example, if we consider s_{12}^E/s_{11}^E of the KNN thin film the same as that of bulk KNN ($x = 1$: $s_{12}^E/s_{11}^E = 0.27$) [14], e_{31}^* becomes $0.73 \times e_{31,f}$.

Fig. 6 shows the e_{31}^* of the c -axis-oriented epitaxial KNN thin films as a function of the applied electric field. For calculation of the e_{31}^* , we use the elastic properties of the MgO substrate ($1/s_{11} = 248$ GPa) from the literature [15]. The transverse piezoelectric properties of KNN

films are stable and almost independent of the applied electric field. The piezoelectric properties of the KNN films with the composition of $x = 0$ and 0.16 were -0.9 and -2.4 C/m², respectively. These results indicate that the 16% doping of the potassium in NaNbO₃ thin films causes a large enhancement of piezoelectric properties. Egerton *et al.* reported that KNN ceramics ($x = 0.5$) had a transverse piezoelectric coefficient d_{31} of -31×10^{-12} C/N and Young's modulus of 1.04×10^{11} N/m², representing an e_{31}^* of -3.2 C/m² [16]. This result indicates that the epitaxial KNN thin films ($x = 0.16$) have a compatible piezoelectricity with KNN ceramics ($x = 0.5$).

VI. CONCLUSION

Epitaxial KNN thin films were grown on (001)SRO/Pt/MgO substrates by RF-magnetron sputtering. The KNN thin films showed highly c -axis orientation, and the lattice parameter of the c -axis increased with increasing the potassium concentration in the resulting films. The KNN thin films ($x = 0$ and 0.16) showed the typical ferroelectric P - E hysteresis loop, and the values of the relative dielectric constant ϵ_r were 270 and 320, respectively. The piezoelectric properties were measured from the tip displacement of the KNN/MgO unimorph cantilevers. The transverse piezoelectric coefficient e_{31}^* ($= d_{31}/s_{11}^E$) of the KNN ($x = 0.16$) thin films was -2.4 C/m², which is almost compatible with that of bulk KNN ceramics.

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