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Effects of thickness on structures and electrical properties of $K_{0.5}Na_{0.5}NbO_3$ thick films derived from polyvinylpyrrolidone-modified chemical solution

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Abstract

Lead-free ferroelectric $K_{0.5}Na_{0.5}NbO_3$ (KNN) films with different thicknesses were prepared by polyvinylpyrrolidone (PVP)-modified chemical solution deposition (CSD) method. The KNN films with thickness up to 4.9 μm were obtained by repeating deposition-heating process. All KNN thick films exhibit single perovskite phase and stronger (1 1 0) peak when annealed at 650 °C. The variation of dielectric constant with thickness indicates that there exists a critical thickness for the dielectric constant in the KNN films which should lie in 1.3–2.5 μm. The similar trend is observed for the ferroelectric and piezoelectric properties of KNN films. Both the remnant polarization P_r and the piezoelectric coefficient d_{33} of KNN thick films increase with the film thickness and become saturated after the critical thickness.

Keywords: A. Films; C. Electrical properties; D. Perovskites; Chemical solution deposition

1. Introduction

Lead-free ferroelectric $K_{0.5}Na_{0.5}NbO_3$ (KNN) has attracted great attention due to its large piezoelectric coefficients [1,2]. A number of KNN based ceramics and films have been extensively studied to improve their electrical properties [2–6]. However, because of the serious volatility of alkali ions during thermal process, the severe leakage current appears in the KNN materials, especially in the KNN films derived from chemical solution deposition (CSD) method [7–9]. This large leakage current greatly deteriorates KNN films' piezoelectric and ferroelectric properties. In our previous study, we have succeeded in preparing KNN thick films with the improved performance by using the polyvinylpyrrolidone (PVP)-modified CSD method [10–13]. However, the electrical properties of films are also strongly dependent on the film thickness [14,15], so the thickness dependence of the structures and electrical properties of KNN thick films has been investigated.

2. Experimental

For the preparation of KNN precursor solution, potassium acetate, sodium acetate and niobium ethoxide were used as the starting chemicals. 2-methoxyethanol was selected as the solvent. The synthesis procedure of KNN precursor solution has been reported elsewhere [10,11]. Polyvinylpyrrolidone (PVP) with a molecular weight of 360,000 was added in the precursor solution subsequently with the molar ratio of PVP monomer to KNN at 1:1. The solution was spin-coated onto Pt/Ti/SiO_2/Si substrates. The gel films were dried for 2 min at 100 °C, and then pyrolyzed for 3 min at 400 °C. After the second spin coating, drying and pyrolysis process, the films were annealed at 650 °C for 10 min. This procedure was repeated until the desired film thickness was obtained.

The crystalline phases and morphologies of the KNN films were examined by X-ray diffraction (XRD, D8-Advance, Bruker) and field-emission scanning electron microscopy (FESEM, JSM-6700F, Jeol), respectively. The dielectric properties were measured using an impedance analyzer (HP4194A, Agilent). Polarization–electric field (*P–E*) hysteresis loops were characterized using a standard ferroelectric test unit (Premier II, Radiant). The piezoelectric dilatations of the

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films were determined with a laser scanning vibrometer (LSV, OFV-056, PolyTech).

3. Results and discussion

The XRD patterns of the KNN films with different thicknesses are shown in Fig. 1. It can be seen that all the films exhibit a single perovskite phase and that the intensity of (1 1 0) peak for all films is higher than (1 0 0) peak. In our previous study [10], it was found that the KNN films annealed at 600 °C show obviously (1 0 0) preferential orientation. However, the (1 0 0) orientation becomes weaker with increasing of the annealing temperature. While the intensity of (1 1 0) peak becomes stronger than that of (1 0 0) peak for the KNN films annealed above 600 °C. In this study, the films were annealed at 650 °C, so all the films show strong (1 1 0) peaks. When comparing the intensity ratios of (1 1 0) peak to (1 0 0) peak, it is found that they increase from 1.154 (1.3 μm) to 1.198 (2.5 μm) and then 1.306 (3.3 μm) with increasing the film thickness. However, the ratio decreases to 1.229 when the thickness is 4.9 μm, which might be attributed to the porous morphology.

It can be seen from Fig. 1 that the intensity of the XRD peaks increases with the film thickness. This is attributed to the increasing of the film thickness [16]. Further inspection reveals that the (1 1 0) diffraction peak for the KNN film with the thickness of 1.3 μm is in a lower 2θ angle of 32.10°. While other KNN films with the thickness of 2.5–4.9 μm are all in 32.14°. This was attributed to the Ti diffusion into KNN films [17]. With the anaysis in Ref. [17], the thicker the films, the weaker the effect of Ti diffusion on films. As a result, the (1 1 0) peak shifts to higher angle when increasing the thickness.

The surface morphologies of the KNN films with different thickness are shown in Fig. 2(a)–(d). It can be seen that the 2.5 μm-thick film shows the densest surface, but there are many

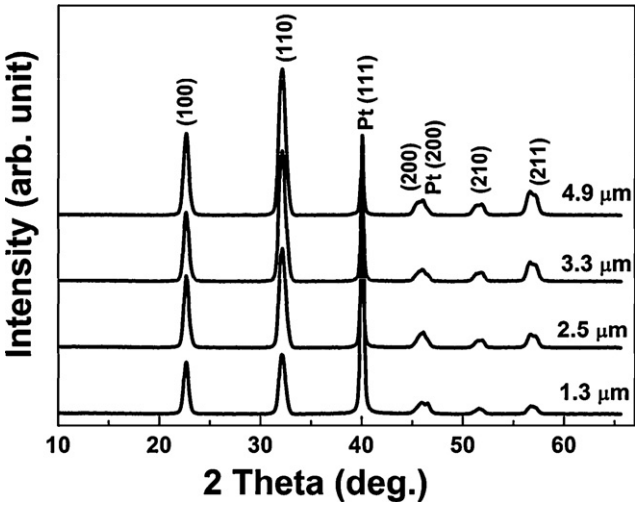

Fig. 1. XRD patterns of $K_{0.5}Na_{0.5}NbO_3$ films with different thickness.

pores in other films with the thicknesses of 1.3 μm, 3.3 μm and 4.9 μm. The cross-sectional FESEM images of the KNN films with the thicknesses of 2.5 and 3.3 μm are shown in Fig. 2(e) and (f), respectively. There are districted interfaces between KNN films and Pt layers. No obviously columnar growth is found in the KNN films as observed in the PZT thick films [15].

Fig. 3 gives the frequency dependence of dielectric constant and loss tangent of the KNN films with different thickness. It can be seen that the increase of the dielectric constant becomes saturated with further increasing the thickness. The highest dielectric constant of 907 and the lowest dielectric loss of 7.6% at 1 kHz are obtained for the 2.5 μm-thick KNN film. The degraded dielectric properties for the KNN films with the thicknesses of 3.3 μm and 4.9 μm are attributed to the porous morphologies as shown in Fig. 2(c) and (d). The inset in Fig. 3 shows the variation of dielectric constants of the KNN films

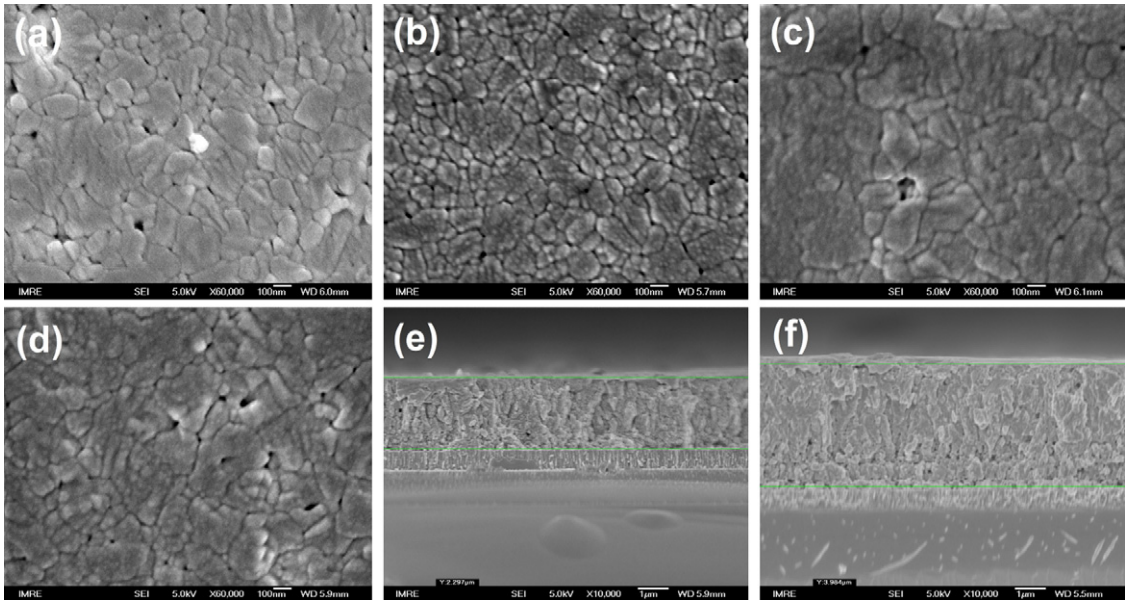

Fig. 2. FESEM images of $K_{0.5}Na_{0.5}NbO_3$ films with different thicknesses. (a), (b), (c) and (d) are the surface morphologies for the KNN films with the thicknesses of 1.3 μm, 2.5 μm, 3.3 μm and 4.9 μm, respectively; (d) and (e) are the cross-sectional morphologies for the KNN films with the thicknesses of 2.5 μm and 3.3 μm.

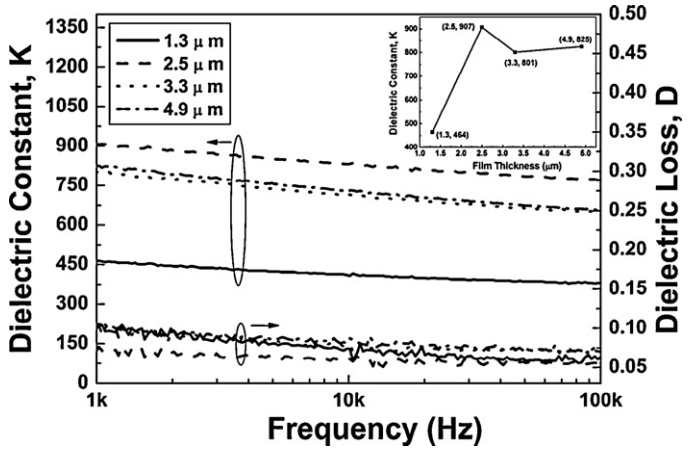

Fig. 3. Frequency dependences of dielectric constant and loss tangent of $K_{0.5}Na_{0.5}NbO_3$ films with different thickness. The inset shows the variation of dielectric constants with thickness. The first values in the parentheses are the thicknesses of KNN films, and the second values are the dielectric constants.

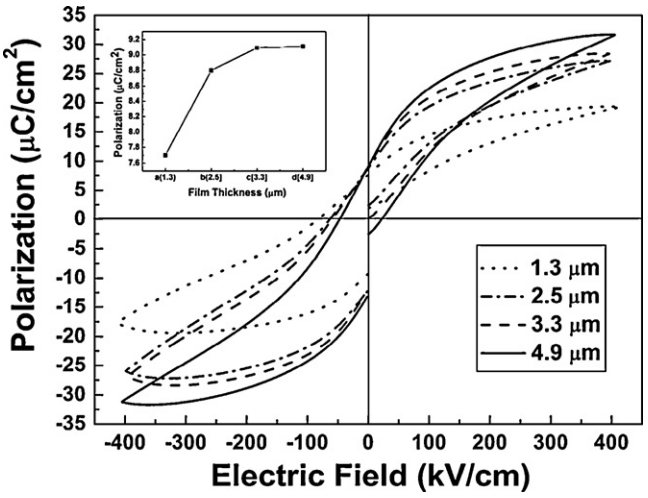

Fig. 4. *P–E* hysteresis loops of $K_{0.5}Na_{0.5}NbO_3$ films with different thickness.

with thickness. The dielectric constants for the KNN films with the thickness higher than 2.5 μm are significantly larger than that of 1.3 μm-thick film, although the dielectric constant decreases when the thickness is over 2.5 μm. This indicates that there exists a critical thickness for KNN films, which lies in 1.3–2.5 μm.

Fig. 4 shows the effect of film thickness on the ferroelectric properties of the KNN films. The remnant polarization P_r increases with thickness, as shown in the inset of Fig. 4. It can also be observed that there exists a critical thickness in the KNN films. The *P–E* loops for the films become saturated after the critical thickness. The highest P_r for the KNN film with the thickness of 4.9 μm is 9.1 μC/cm^2.

The variation of piezoelectric coefficients d_{33} for the KNN films with thickness is shown in Fig. 5. The insets show the three-dimensional drawings of the instantaneous vibration data when the displacement magnitude reaches the maximum under sine wave electrical driving for the films with the thicknesses of

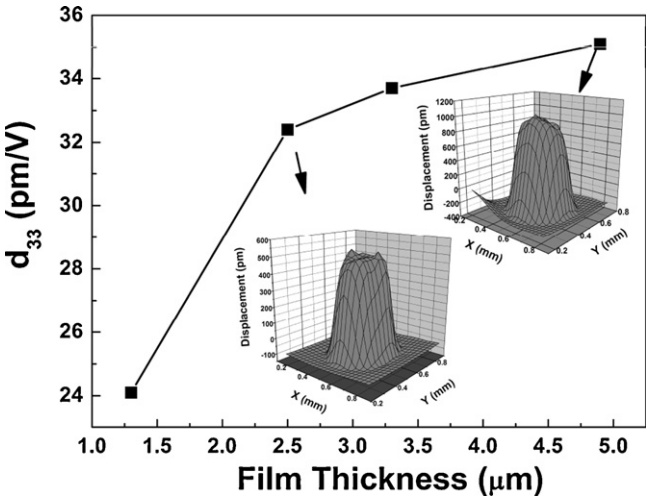

Fig. 5. Variation of piezoelectric coefficient d_{33} of the KNN films with thickness. The insets are the three-dimensional drawings of the instantaneous vibration data when the displacement magnitude reaches the maximum under sine wave electrical driving for the films with corresponding thickness.

2.5 and 4.9 μm. The dilatation magnitude of the films divided by the driving voltage gives the effective d_{33}. It can be seen that the calculated effective d_{33} for the KNN films increases with thickness. The largest d_{33} value is obtained in the 4.9 μm-thick KNN films and is 35 pm/V. This value is smaller than that of KNN films reported in Ref. [10]. The reason is that the KNN films in Ref. [10] were annealed at the optimized temperature. Like the dielectric costant and ferroelectric remnant polarization, there also exists a critical thickness for the d_{33}. Thickness dependence of dielectric, ferroelectric and piezoelectric properties in this study suggests that to obtain decent electrical properties in the KNN films, it is desired to have the films with the thickness over the critical thickness.

4. Conclusions

Lead-free KNN films with different thicknesses were prepared by PVP-modified chemical solution deposition method. All the films exhibit single perovskite phase and stronger (1 1 0) peak. There exists a critical thickness in the films which lies in 1.3–2.5 μm. When the films are thicker than this critical value, the KNN films exhibit decent dielectric, ferroelectric and piezoelectric properties.

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References

[1] G. Shirane, R. Newhnam, R. Pepinski, Dielectric properties and phase transitions of $NaNbO_3$ and $(Na,K)NbO_3$, Physical Review 96 (1954) 581–588.

[2] Y.P. Guo, K. Kakimoto, H. Ohsato, Structure and electrical properties of lead-free $(Na_{0.5}K_{0.5})NbO_3$-$BaTiO_3$ ceramics, Japanese Journal of Applied Physics Part 1 43 (2004) 6662–6666.

[3] M. Matsubara, T. Yamaguchi, W. Sakamoto, K. Kikuta, T. Yogo, S. Hirano, Processing and piezoelectric properties of lead-free (K,Na)(Nb,Ta)O_3 ceramics, Journal of the American Ceramic Society 88 (2005) 1190–1196.

[4] Y.P. Guo, K. Kakimoto, H. Ohsato, $(Na_{0.5}K_{0.5})$ NbO_3-$LiTaO_3$ lead-free piezoelectric ceramics, Materials Letters 59 (2005) 241–244.

[5] C.R. Cho, A. Grishin, Self-assembling ferroelectric $Na_{0.5}K_{0.5}NbO_3$ thin films by pulsed-laser deposition, Applied Physics Letters 75 (1999) 268–270.

[6] F. Söderlind, P.O. Käll, U. Helmersson, Sol–gel synthesis and characterization of $Na_{0.5}K_{0.5}NbO_3$ thin films, Journal of Crystal Growth 281 (2005) 468–474.

[7] Y. Nakashima, W. Sakamoto, T. Shimura, T. Yogo, Chemical processing and characterization of ferroelectric $(K,Na)NbO_3$ thin films, Japanese Journal of Applied Physics Part 1 46 (2007) 6971–6975.

[8] F.P. Lai, J.F. Li, Sol–gel processing of lead-free $(Na,K)NbO_3$ ferroelectric films, Journal of Sol–Gel Science and Technology 42 (2007) 287–292.

[9] K. Tanaka, H. Hayashi, K.i. Kakimoto, H. Ohsato, T. Iijimai, Effect of (Na,K)-excess precursor solutions on alkoxy-derived $(Na,K)NbO_3$ powders and thin films, Japanese Journal of Applied Physics Part 1 46 (2007) 6964–6970.

[10] L.Y. Wang, K. Yao, W. Ren, Piezoelectric $K_{0.5}Na_{0.5}NbO_3$ thick films derived from polyvinylpyrrolidone-modied chemical solution deposition, Applied Physics Letters 93 (2008) 092903.

[11] L.Y. Wang, K. Yao, P.C. Goh, W. Ren, Volatilization of alkali ions and effects of molecular weight of polyvinylpyrrolidone introduced in solution-derived ferroelectric $K_{0.5}Na_{0.5}NbO_3$ films, Journal of Materials Research 24 (2009) 3516–3522.

[12] L.Y. Wang, K. Yao, W. Ren, Effect of amount of polyvinylpyrrolidone introduced in solution-derived ferroelectric $K_{0.5}Na_{0.5}NbO_3$ thick films, Ferroelectrics 404 (2010) 192–199.

[13] L.Y. Wang, W. Ren, K. Yao, G.C. Goh, P. Shi, X.Q. Wu, X. Yao, Effect of pyrolysis temperature on $K_{0.5}Na_{0.5}NbO_3$ thick films derived from polyvinylpyrrolidone-modified chemical solution, Journal of the American Ceramic Society 93 (2010) 3686–3690.

[14] F. Xu, S. Trolier-McKinstry, W. Ren, B.M. Xu, Z.L. Xie, K.J. Hemker, Domain wall motion and its contribution to the dielectric and piezoelectric properties of lead zirconate titanate films, Journal of Applied Physics 89 (2001) 1336–1348.

[15] P. Lin, W. Ren, X.Q. Wu, P. Shi, X.F. Chen, X. Yao, Thickness effects on structures and electrical properties of lead zirconate titanate thick films, Ceramics International 34 (2008) 991–995.

[16] J.L. Van Heerden, R. Swanepoel, XRD analysis of ZnO thin films prepared by spray pyrolysis, Thin Solid Films 299 (1997) 72–77.

[17] P.C. Goh, K. Yao, Z. Chen, Titanium diffusion into $(K_{0.5}Na_{0.5})NbO_3$ thin films deposited on $Pt/Ti/SiO_2/Si$ substrates and corresponding effects, Journal of the American Ceramic Society 92 (2009) 1322–1327.