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Journal of the European Ceramic Society 26 (2006) 2143–2146
www.elsevier.com/locate/jeurceramsoc

Effect of seeding layer on orientation control of potassium niobate thin film by CSD

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Available online 21 November 2005

Abstract

This paper focuses on the orientation control of the KN thin film on Si wafer by chemical solution deposition (CSD). We selected the PbO layer and PZT layers as the seeding layer in order to control the crystal orientation of the resulting KN thin film. Crystalline phase in KN thin film was identified by XRD, and the degree of *c*-axis orientation was calculated from XRD analysis. The resultant KN thin film was orthorhombic perovskite single phase. As a result, highly *c*-axis oriented thin film (about 90%) was deposited by using PbO seeding layer. The dielectric constant of the resultant KN thin film was measured by impedance analyzer. The dielectric constant of highly *c*-axis oriented KN thin film was compared with that of the *c*-axis of KN single crystal.

Keywords: Sol–gel process; Dielectric property; Niobates; Interfaces; Orientation control

1. Introduction

Recently, the demand for high frequency and wide band surface acoustic wave (SAW) devices, such as wide band filter, wide band voltage controlled oscilator (VCO) and high efficiency non-linear devices has increased for the requirement of high density electrical communication system.[1] For these devices, a high electromechanical coupling material is very important. Thin film of potassium niobate ($KNbO_3$, KN) have been investigated over the past 10 years due to their large electro-optic coefficient,[2] non-linear optical coefficients[3] and electromechanical coupling factor for various electronic device applications. The electromechanical coupling factor (κ^2) of the *c*-axis oriented KN is theoretically 10 times larger (53%)[4,5] than that of the lithium niobate (5.5%).[6,7] Therefore, orientation control of the thin film on a silicon wafer is essential to develop the high performance SAW devices in microwave region at low cost. Various deposition techniques, such as epitaxial growth from melt, chemical vapor deposition (CVD), sputtering and CSD,[8–10] have been used for the deposition of KN thin films. In our previous work, (1 1 0)-oriented KN thin film was deposited on strontium titanate (ST) single crystal substrate and highly *c*-axis oriented KN thin films were deposited on a Si wafer by controlling the processing parameter such as the film thickness and substrate.[10] However, for the commercial use, low cost fabrication process is expected. Therefore, in this paper, we discuss on the effect of the seeding layer for the orientation control of the alkoxy-derived KN thin film.

2. Experimental procedure

In this study, KN thin film was deposited on Si wafer by CSD. The starting reagents for KN precursor solution were penta-ethoxy niobium and potassium ethoxyde. Excess amount of penta-ethoxy niobium was added to the precursor solution to compensate the potassium loss during processing. Penta-ethoxy niobium and potassium ethoxyde were refluxed in 2-methoxyethanol for 6 h to prepare the KN precursor solution. KN thin film was deposited by spin coating method. The obtained thin film was dried at 115 °C for 10 min, pre-annealed at 420 °C for 10 min to pyrolyze the residual organic compounds and finally annealed at 700 °C for 5 min by rapid thermal annealing (RTA) process.

In this study, PbO and PZT seeding layer was selected to deposit the highly *c*-axis oriented KN thin film. Highly (0 0 1)-oriented PbO seeding layer was deposited from 0.15 M PbO precursor solution, pre-annealed at 420 °C and annealed at 600 °C.

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0955-2219/$ – see front matter © 2005 Published by Elsevier Ltd.
doi:10.1016/j.jeurceramsoc.2005.09.073

On the other hand, highly (0 0 1) or (1 1 1) oriented PZT seeding layer was deposited according to our previous works.[11,12]

Crystal structure was determined by XRD analysis, and the microstructure of the resultant thin film was observed by the scanning electron microscope (SEM). The Raman spectra were measured using JASCO Co., NR-1800, Rev. 1.00 Raman spectrometer in back scattering geometries. The 488 nm line of an argon ion laser was used as the excitation source at a power level of 100 mW. Each spectrum was the result of the addition of several scans. The dielectric behavior of the film was measured by LCR meter.

3. Results and discussion

3.1. Deposition of perovskite-type KN thin films

At first, KN precursor powder was prepared from KN precursor solution by evaporating the solvent to investigate the crystallization behavior. From the result of TG-DTA measurement, this precursor powder crystallized at around 550 °C into the single-phase perovskite. Therefore, The obtained precursor powder was calcined at 550 and 700 °C. Fig. 1 shows the XRD patterns for the resultant KN powders. From this figure, the KN powder annealed at 550 °C was identified to be an orthorhombic perovskite phase. However, the crystallinity of this powder was not so good. Therefore, in this study, KN thin film was annealed at 700 °C to deposit the high quality KN thin film.

Fig. 2 shows the XRD pattern for the KN thin film annealed at 700 °C. In this case, only the KN (1 1 1) peak of a perovskite KN phase was identified in the thin film, indicating no preferred orientation. To confirm the crystallization of the perovskite type KN thin film, Raman spectra of this film and the powder were measured at room temperature (Fig. 3). The Raman analysis indicated that the Raman spectrum for the resultant KN thin film exhibited very similar to that of the KN powder. Therefore, the alkoxy derived KN thin film on Si-substrate crystallized into polycrystalline film if a seed layer were not used.

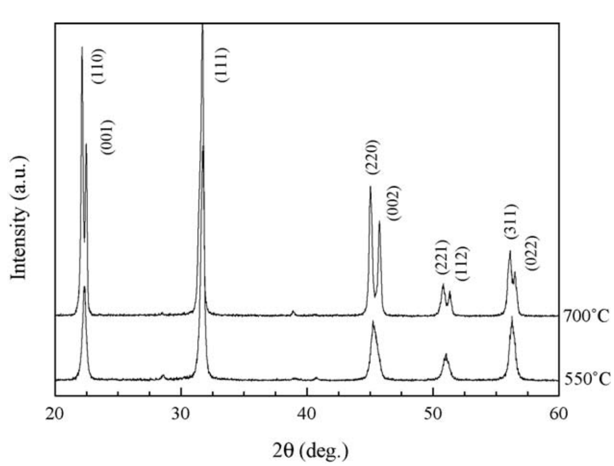

Fig. 1. XRD pattern for KN powders calcined at different annealing temperatures.

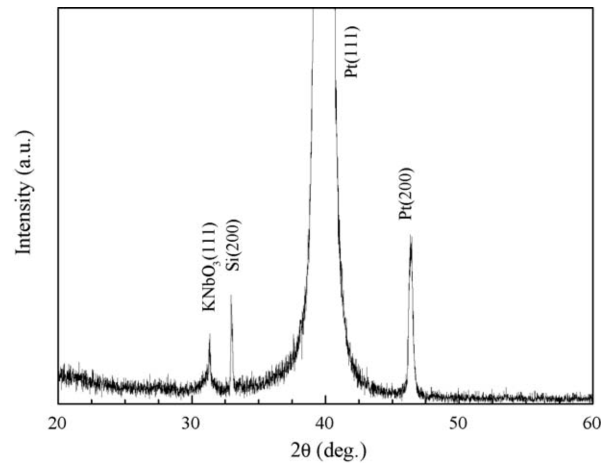

Fig. 2. XRD pattern for the KN thin film annealed at 700 °C.

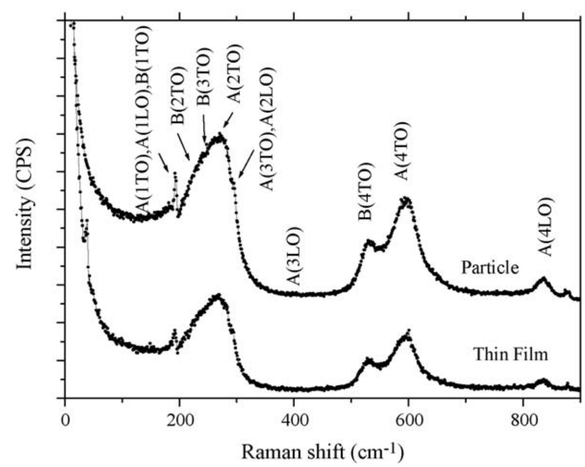

Fig. 3. Raman spectra for KN thin film, together with that for the KN powder calcined at 700 °C.

3.2. Orientation control

The resultant KN thin film without seeding layer did not exhibit the preferred orientation. Therefore, we tried to control the orientation of the KN thin films by using a seeding layer, because the orientation of a KN film with the highest electromechanical coupling factor (κ^2) was (0 0 1)-direction. The lattice parameters of the orthorhombic unit cell for a perovskite KN at room temperature are, $a = 0.5696$ nm, $b = 0.5721$ nm and $c = 0.3974$ nm,[13] respectively. Therefore, (0 0 1)- or (1 1 1)-oriented lead zirconate titanate (PZT) thin layers and (0 0 1)-oriented PbO layer were used as a seeding layer because of the better lattice misfit (Table 1 and Fig. 4). Fig. 5 exhibits the

Table 1
Lattice constant of seeding layer, and lattice matching

	Lattice constant	Lattice match (%)
KN	$a = 5.695$, $b = 5.721$	–
PbO (0 0 1)	3.960	98.3
PZT (0 0 1)	4.036	99.8
PZT (1 1 1)	2.853	99.8

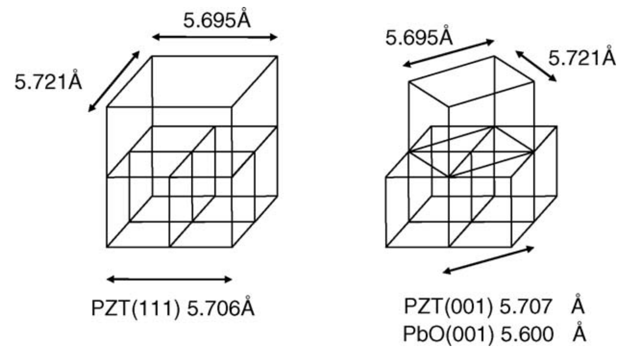

Fig. 4. Schematic illustration for the orientation mechanism by lattice matching.

effect of the seeding layer on the orientation of the resultant KN thin films. As a result, the seeding layer was very effective to control the film orientation towards to the *c*-axis. The degree of *c*-axis orientation (D_c) was calculated by the following equation,

$$D_c = \frac{I_{(0\,0\,1)} + I_{(0\,0\,2)}}{I_{(0\,0\,1)} + I_{(0\,0\,2)} + I_{(0\,1\,1)} + I_{(0\,2\,2)}}$$

where $I_{(0\,0\,1)}$, $I_{(0\,0\,2)}$, $I_{(1\,1\,1)}$ and $I_{(0\,2\,2)}$ are the intensity of the XRD peaks for the (0 0 1)-, (0 0 2)-, (1 1 1)- and (0 2 2)-planes of the perovskite KN phase, respectively. D_c for the resultant KN thin films with a seeding layer of (0 0 1) PbO, (0 0 1) PZT and (1 1 1) PZT were 77.9, 90.1 and 84.7%, respectively. Fig. 6 shows the cross-sectional SEM image for the resultant KN thin film with PbO seeding layer. From the cross-sectional SEM images, the resultant KN thin film with a PbO seeding layer showed dense and columnar microstructure. The film thickness was estimated to be about 800 nm. On the other hand, PZT thin layer will have the large effect on the electrical properties of the resultant thin films, whereas the degree of *c*-axis orientation was very high. Therefore, we selected PbO layer as a seeding layer. To increase the film quality and therefore, the electrical properties of the resultant KN films, final annealing temperature was increased to 800 °C. Fig. 7 shows XRD pattern for the resultant KN thin film annealed at 800 °C with PbO seeding layer. As a result, D_c was improved from 84.7 to 94.0% by increasing the annealing temperature from 700 to 800 °C.

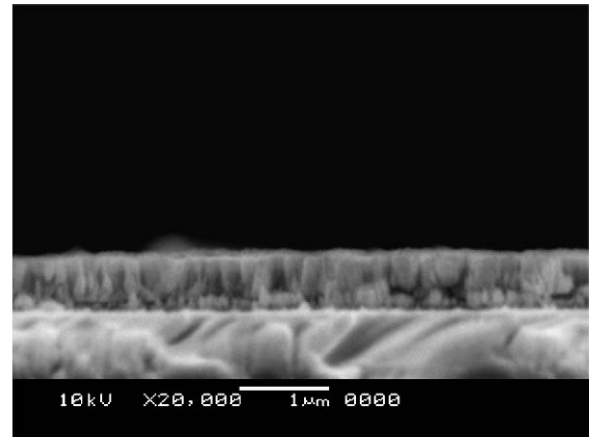

Fig. 6. Cross-sectional SEM image for the KN thin film on PbO seeding layer.

3.3. Dielectric property

The dielectric constant for the resultant KN thin film was measured by LCR meter. For the dielectric measurement, the resultant KN thin film with high D_c was dip-coated and post-annealed in an oxygen atmosphere to improve the surface roughness (RMA of AFM) from 15.8 to 4.9 nm. Fig. 8 shows the dielectric behavior of the resultant KN thin films with a PbO seeding layer. The dielectric constant of the film annealed at 800 °C (D_c = 94.0%) showed a high value of 1050 at 1 kHz (dielectric loss was less than 10%). On the other hand, the dielectric constant of the film annealed at 700 °C (D_c = 84.7%) showed 660 at 1 kHz. This result suggests that the degree of *c*-axis orientation has significant effect on the electrical properties of the KN thin film. In the case of the KN single crystal, the dielectric constants are reported to be $\varepsilon_a = 140$, $\varepsilon_b = 40$ and $\varepsilon_c = 1200$.[14] Therefore, it was concluded that the dielectric constant of the resultant KN thin film with high *c*-axis orientation compared with that of the *c*-axis of KN single crystal. These results indicated that the PbO seeding layer was very effective to control the

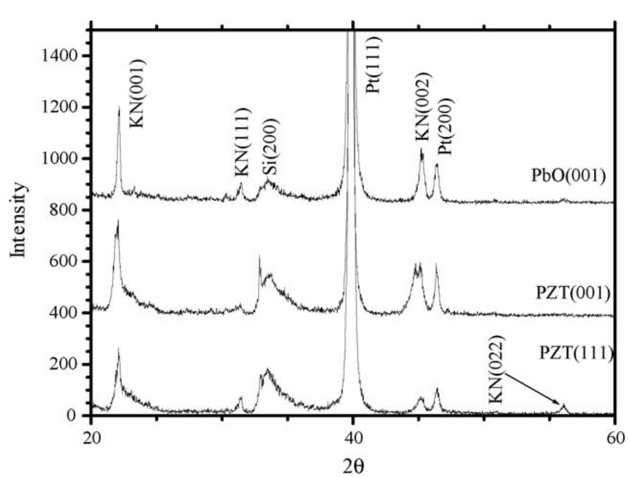

Fig. 5. XRD pattern for KN thin films on different seeding layers.

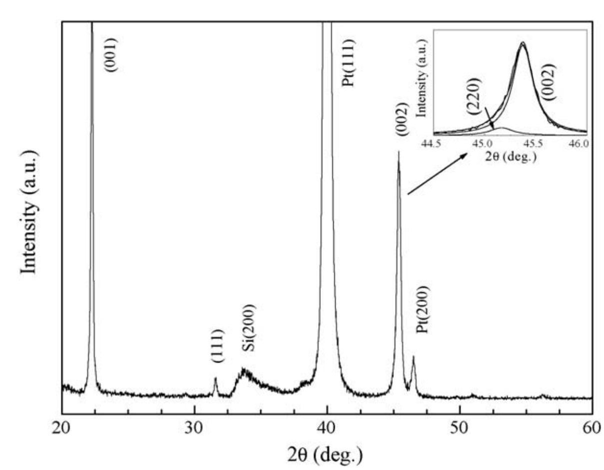

Fig. 7. XRD pattern for the KN thin film on PbO seeding layer annealed at 800 °C.

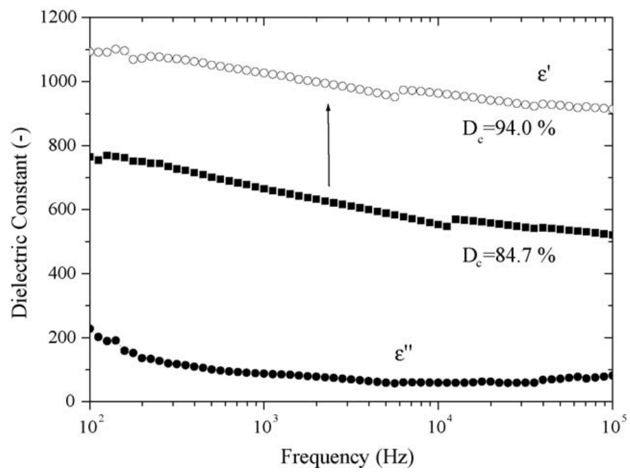

Fig. 8. Change in the dielectric constant with frequency for the KN thin films on PbO seeding layer with different degree of *c*-axis orientation.

film orientation of the alkoxy-derived KN thin film with good electrical properties at high frequencies in microwave region, which was expected to be used as a SAW filter.

4. Conclusion

This paper described the effect of a seeding layer on the orientation of alkoxy-derived KN thin film. Highly *c*-axis oriented KN thin film was successfully deposited with a CSD on a Si wafer by using PbO and PZT thin films as seeding layers. In this study, we obtained the 94% *c*-axis oriented KN thin film by control the experimental parameters and by using the effective seeding layer. The resultant highly *c*-axis oriented KN thin film exhibited similar dielectric property as that of KN single crystal along *c*-axis.

Acknowledgement

This work was supported in part by Grants-in-Aid for Scientific Research (B) (No. 16360325) from Japan Society for the Promotion of Science.

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