1P3-6

Proceedings of Symposium on Ultrasonic Electronics, Vol. 34 (2013) pp. 141-142
20-22 November, 2013

Growth of Epitaxial KNbO3 Thin Films by Hydrothermal Method for Ultrasonic Transducers.

水熱合成法を用いたKNbO3薄膜の製膜と超音波トランスデューサーへの応用

Seiya Ozeki1[1†], Makoto Hosaki2[1], Daisuke Kameyama3[1], Satomi Ishida4[1], Takahisa Shiraishi5[2], Hiroshi Funakubo6[2], Minoru Kurosawa7[2], Mutsuo Ishikawa8[1] ([1] Toin Univ. of Yokohama1; [2] Tokyo Institute of Technology)

大関　誠也１[1†], 保崎　誠２[1], 亀山　大輔３[1], 石田　智美４[1], 白石　貴久５[2], 舟窪　浩６[2], 黒澤　実７[2], 石河　陸生８[1] ([1]桐蔭横大１, [2]東工大２)

1. Introduction

$KNbO_3$ is a candidate lead-free piezoelectric material for each application owing to its excellent piezoelectric properties. Moreover deposition methods of $KNbO_3$ films were recently reported. However the films of $KNbO_3$ and $KNbO_3$-based materials have not been utilized as ultrasonic transducers because it is difficult to deposit $KNbO_3$ thin films with superior electrical-mechanical properties. Therefore, we tried to fabricate 100nm thin films of $KNbO_3$ using hydrothermal method[1)2)3)] without high temperature such as annealing process.

2. Experimental Procedure

The $KNbO_3$ thick films were grown at 240 ºC on $(100)_c$ $SrRrO_3$ // $SrTiO_3$ substrates by the hydrothermal method. The $(100)_c$-oriented $SrRrO_3$ layers used for bottom electrodes were epitaxially grown on the (100) $SrTiO_3$ substrates by a sputtering method. An autoclave (PARR, 4748) that contained an inner vessel made of Teflon to resist high alkali solutions was utilized for the hydrothermal growth. A 20 m*l* solution of KOH (Kantokagaku) and 1.0 g of niobium oxide powder (Nb_2O_5, purity 99.95%, Kantokagaku) were used as source materials of K and Nb, respectively. The $(100)_c$ $SrRrO_3$ // $SrTiO_3$ substrate was kept facing down with a Teflon folder in the inner vessel, and the above-mentioned source materials were mixed and placed in the autoclave. The autoclave was shut tight and placed in a constant-temperature oven (Yamato DS-400) maintained at 240 ºC for a hydrothermal chemical reaction.

The thickness of the obtained films grown on $(100)_c$ $SrRrO_3$ // $SrTiO_3$ substrates was determined by a surface profilometer (Veeco DEKTAK 3ST). The crystal structure and the orientation of the films were characterized by X-ray diffraction analysis using a four-axis diffractometer (HRXRD; Philips X'Pert MRD system) with $CuK\alpha_1$ radiation. The dielectric and piezoelectric properties were measured using $Pt/KNbO_3/SrRuO_3$ capacitors at room temperature; after Au or Pt deposition by evaporation method. The needle-type electrode was connected to the top electrode and the $SrRuO_3$ bottom electrode was grounded through the Ag paste. The dielectric properties and the piezoelectric properties were measured with an impedance analyzer (HP HP4194A) and a laser Doppler velocimeter (Polytec OFV-3001). Figure 1 shows the system used to measure the electrical mechanical characteristics of piezoelectric $KNbO_3$ films.

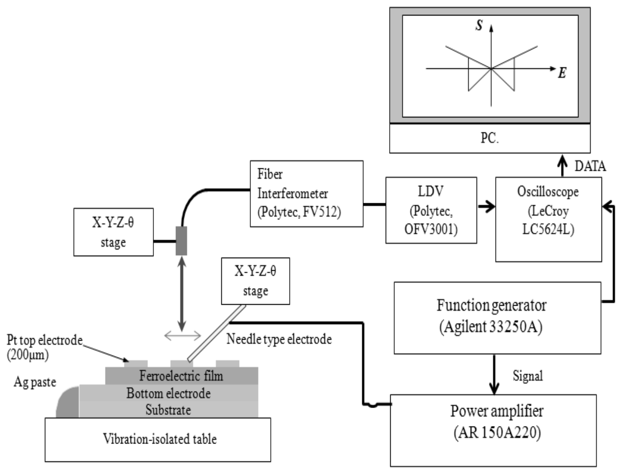

Fig.1 Measurement setup for piezoelectric displacement of $KNbO_3$ films.

3. Results and Discussion

Figures 2 shows logarithmic scale XRD patterns for the films deposited from 1 *mol*/*l* to 11 *mol*/*l*. {*h00*} peaks of the perovskite phase were observed from using 6 *mol*/*l* KOH solution. Figure 3 shows the change of the thickness of the obtained films with the concentration of the KOH solution from 6 *mol*/*l* to 11 *mol*/*l*. The thickness was approximately 100nm in 6 *mol*/*l* KOH solution.

Therefore, the $P-E$ relationships measured at 100 kHz at room temperature is shown in Fig. 3 for the Pt/(100nm-$KNbO_3$)/$SrRrO_3$/ capacitor. Clear hysteresis loops originated from their ferroelectricity were observed. Observed remanent polarization, P_r, was 20μC/cm^2 at the maximum electric field of 1000 kV/cm. Figure 3 shows the relationship between the piezoelectric strain and the driving electric field versus strain measured at 100 kHz. The effective longitudinal piezoelectric constant, $d_{33}{}^{eff}$, calculated from the linear region indicated in Fig. 3 from 0 to 100 V in the butterfly loops was estimated to be 35 pm/V. Additionally, dielectric constant ε_r at 100 kHz was 50. Our present results indicate that the hydrothermal method enables the excellent $KNbO_3$ thick film without any doping or solid solution, which might be related to the low process temperature of the hydrothermal method.

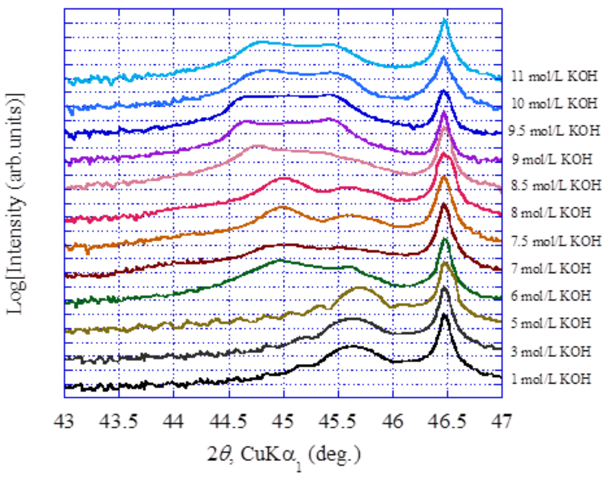

Fig. 2 Logarithmic scale XRD patterns of obtained films prepared.

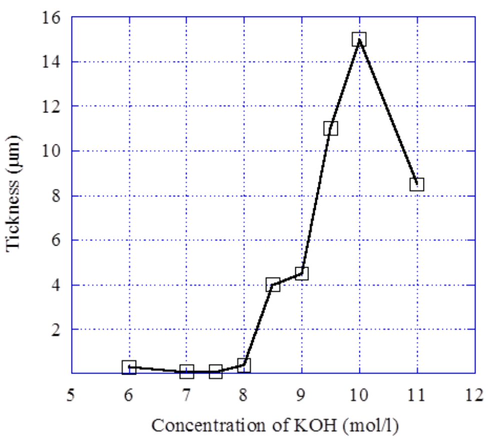

Fig.3 Change of the thickness of the obtained films with the concentration of the KOH solution

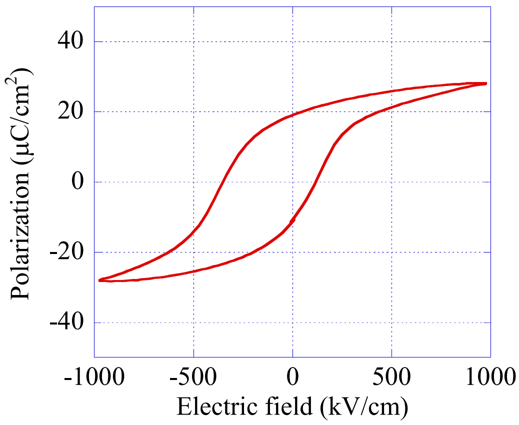

Fig.4 Polarization and electric field (*P-E*) relationships measured at 100 kHz for Pt/($KNbO_3$)/$SrRrO_3$ capacitor.

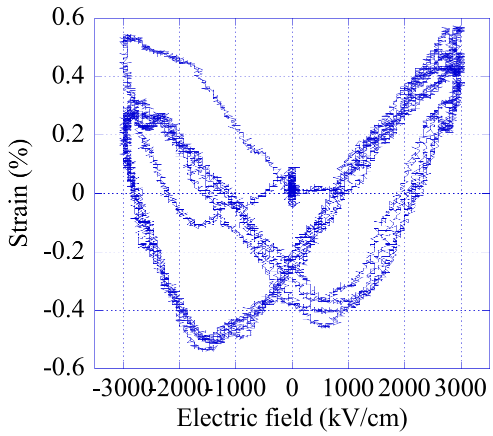

Fig.5 Displacement versus driving voltage butterfly loop of $KNbO_3$ thick film grown on (100)c $SrRuO_3$//(100) $SrTiO_3$ substrate at 100kHz.

4. Conclusions

The epitaxially-grown 100nm-$KNbO_3$ thin films were successfully obtained on the $(100)_c SrRuO_3$//$SrTiO_3$ substrates. The dielectric constant ε_r was 50. The clear hysteresis loops and the butterfly-shape curve were observed. These results indicate that the hydrothermal method enables the excellent $KNbO_3$ thin films for ultrasonic transducers applications.

References

1) T. Morita, *et al.*, J. Mater. Res. 19 (2004)
2) M. Ishikawa *et al.*, Mater. Res. Soc. Symp. Proc, 1139, 1139-GG03-52 (2009).
3) T.Shiraishi *et al.*, Jpn. J. Appl. Phys., 50, 09ND11-1-4 (2011)