Paper

Hydrothermal Deposition of KNbO_3 Films on Metal Substrates having Three-Dimensional Structure

Takahisa SHIRAISHI^{1,2*}, Noriyuki KANEKO¹, Minoru K. KUROSAWA³, Hiroshi UCHIDA⁴ and Hiroshi FUNAKUBO¹

¹Department of Materials Science and Engineering, Tokyo Institute of Technology, 4259-J2-43 Nagatsuda-cho, Midori-ku, Yokohama 226-8502, Japan.

²Institute for Materials Research, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan.

³Department of Electrical and Electronic Engineering, Tokyo Institute of Technology, 4259 G2-32 Nagatsuda-cho, Midori-ku, Yokohama 226-8502, Japan.

⁴Department of Materials and Life Sciences, Sophia University, 7-1 Kioi-cho, Chiyoda-ku, Tokyo 102-8554, Japan.

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ABSTRACT

In this study, KNbO_3 films were deposited on Ni-based metal coils with different curvature by hydrothermal method. The deposition of KNbO_3 films was hardly observed directly on metal coils. However, the growth of well-adhered KNbO_3 films was promoted by using LaNiO_3 -surface layers on Ni-based metal coil. Film thickness increased with increasing deposition time above 1 h and reached to 12.5 μm at 2.5 h. X-ray diffraction measurements revealed that the crystal structure did not depend on the average curvature radius. The dielectric constant and the remanent polarization were respectively 105 and 11 $\mu\text{C}/\text{cm}^2$, which were almost the same with flat films. This means that these are almost independent of the radius of curvature. These results indicate that the hydrothermal method is an effective way as a deposition technique for the piezoelectric films onto metal substrates having a three-dimensional structure.

KEY WORDS

hydrothermal method, piezoelectric film, LaNiO_3 -buffer layer, three-dimensional structure

1 Introduction

The vibration energy harvesting technique using piezoelectric films has been extensively studied in order to realize the battery-less sensor devices for applications in the fields of medical, public works, and automobile industry¹⁻⁵. This is because the piezoelectric films can act as a converter between electrical energy and vibration energy.

$\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$ -based films are one of the piezoelectric films practically used for various sensors and actuators because of their superior piezoelectric properties. However, the toxicity of the lead is recognized to be a serious issue from the viewpoint of environmental friendliness. Therefore, various lead-free piezoelectric films have been investigated⁶. KNbO_3 -based films have much paid attention as one of the prospective lead-free piezoelectric films because of their excellent electrical properties as well as the environmental friendliness⁷.

Since the vibration energy harvesting technique are applied to various locations where environmental vibration exists, the expansion of the structure of piezoelectric films, such as bimorph, multilayer, moonie, rainbow, symbal, and ribbon structures, is being considered⁸. In addition, these structure lead to increase the output power because of the increasing an area of piezoelectric films compared with standard unimorph structure. To expand the

structure of piezoelectric films, it is necessary to deposit films onto substrates having three-dimensional structure processed into various shapes⁹. However, many deposition methods, such as sputtering, Sol-gel, chemical solution deposition, and pulsed-laser deposition methods, are specialized for film formation onto flat substrates¹⁰⁻¹⁴. Therefore, it is not easy to expand the structure of piezoelectric films.

Hydrothermal method is the simple wet processes with autoclave and have been applied to fabricate the piezoelectric ceramic powders¹⁵⁻¹⁷. However, by setting the substrate in the autoclave, it is also possible to manufacture the film at the same time¹⁸. The most significant feature is that the piezoelectric materials are synthesized in the raw material solution. This means that raw materials are uniformly supplied onto substrate surface regardless of the substrate shape. In our previous reports, we successfully deposited KNbO_3 -based films on the flat metal substrates and clarified the importance of controlling the surface layer of substrates^{19,20}.

On such back ground, we have paid attention to deposit KNbO_3 -based films onto metal substrates having three-dimensional structure by using hydrothermal method. In this study, KNbO_3 films deposited on metal foil processed into coil shape by hydrothermal method. In addition, the crystal structures and electrical properties for those films were investigated.

* Corresponding author, E-mail: takahisa.shiraishi@imr.tohoku.ac.jp

2 Experimental procedures

Ni-based alloy foil with a 50 μm thickness (Inconel 600, hereafter designated as “Inconel foil”) was used as a substrate. 50 nm-thick LaNiO_3 -surface layers which are the conductive perovskite oxide were deposited at 350°C on Inconel foil by radio frequency magnetron sputtering method. This is because we have already demonstrated that the KNbO_3 film can be deposited on various substrates by using the conductive perovskite oxide surface layer¹⁹⁻²¹. After that, LaNiO_3 /Inconel foil was molded into a coil shape. In this study, the molded substrate described as LaNiO_3 /Inconel coil.

KNbO_3 films were deposited at 240°C by hydrothermal method. The raw materials used for hydrothermal synthesis were Nb_2O_5 powder (0.0037 mol) and KOH solution (12 mol/L, 20 mL). These source materials and substrates were sealed in an autoclave, which was set in a thermostat bath. After synthesis, KNbO_3 films were ultrasonically washed in distilled water, ethanol, acetone, and methanol, and then dried at 150°C for 1 h in air.

The film thickness was measured using a surface profile meter (Veeco DEKTAK 3ST). The average curvature radius, R , was estimated from $1/r$ where r is the distance between the curved surface and the center of curvature. The microstructure was observed by scanning electron microscope (SEM). The crystal structure was investigated by X-ray diffractometry (XRD, Philips X'Pert MRD system). A pseudocubic index denoted as $\{hkl\}_c$ was used to indicate the diffraction peaks.

Pt top electrodes with 100 μm in diameter were deposited by an electron beam evaporation to fabricate the capacitor structure of Pt/ KNbO_3 / LaNiO_3 /Inconel coil. The dielectric and ferroelectric properties were measured using an impedance analyzer (Agilent 4194A) and ferroelectric tester (Toyo Technica, FCE fast).

3 Results and Discussion

Fig. 1 shows the change in the film thickness with deposition time for KNbO_3 films prepared on Inconel foil and LaNiO_3 /Inconel foil. The deposition time was measured from the time when the autoclave was put in an oven. Although the deposition of KNbO_3 was hardly observed up to 2.5 h on Inconel foil, KNbO_3 films were deposited after 1 h on LaNiO_3 /Inconel foil. The deposition time dependence of film thickness can be divided into two regions. Deposition was hardly observed until the critical time (1 h). The first region, known as the incubation time, is the time required for the Nb_2O_5 powder to dissolve in the KOH solution²². Film thickness was ascertained to increase almost linearly as the deposition time increased up to 2.5 h. However, the film thickness did not increase at above 2.5 h because Nb_2O_5 powder converted to KNbO_3 film and powder completely. This indicates that LaNiO_3 -surface layer is an effective for promoting the growth of KNbO_3 films under the hydrothermal condition. Goh et al. reported the deposition process of hydrothermally-synthesized KNbO_3 films as follows; Firstly, K^+ are adsorbed on the substrate surface. Secondly, NbO_6^{7-} monomers

Fig. 1 (a) Film thickness versus deposition time for KNbO_3 films prepared on various substrates: (▲) Inconel foil and (●) LaNiO_3 /Inconel foil. (b) SEM image of surface of KNbO_3 film deposited on LaNiO_3 /Inconel foil.

which are made by dissolving Nb_2O_5 powder in KOH solution react with K^+ and the nucleuses of KNbO_3 is generated on the substrate surface. Finally, film is formed by growth of these nuclei²³⁻²⁵. Based on this consideration, K ions adsorption on the surface layer is the key point, and it is considered that LaNiO_3 assisted K^+ to adsorbed on the substrate surface. Fig. 1 (b) shows the surface SEM image for KNbO_3 films deposited on LaNiO_3 /Inconel foil. The shape of the grain was a rectangle and its size were below 3 μm .

Fig. 2 (a) and (b) show the photographs of KNbO_3 films deposited for 2.5 h on LaNiO_3 /Inconel foil and LaNiO_3 /Inconel coil, respectively. In order to estimate the curvature radius, KNbO_3 / LaNiO_3 /Inconel coil was cut in each section (Coil-1 to -4) as shown in Fig. 2 (c). Coil-1 to -4 indicate the places with different curvature, and Table 1 summarizes the average curvature radius, R , estimated from each place. Films were deposited uniformly on either substrate, and the film thickness was about 12.5 μm regardless of the shape of substrate. It is noticeable that the cracking and peeling were not observed under the bending condition.

Fig. 3 (a) shows the XRD 2θ - ω patterns of KNbO_3 films deposited on LaNiO_3 /Inconel foil and LaNiO_3 /Inconel coil prepared for 2.5 h. The pattern of LaNiO_3 /Inconel foil is also shown as reference. On all patterns, the diffraction peaks derived from perovskite phase were observed. In addition, KNbO_3 films had random orientation because LaNiO_3 -surface layers were polycrystalline characteristics. Fig. 3 (b) shows the enlarged XRD 2θ - ω patterns at $2\theta = 40$ – 50° .

Fig. 2 Photographs of KNbO_3 films deposited on (a) $\text{LaNiO}_3/\text{Inconel}$ foil and (b) $\text{LaNiO}_3/\text{Inconel}$ coil. Coil-1 to -4 indicate the places with different radius of curvature. (c) Image of Coil-1 to -4 with different curvatures.

Table 1 Average curvature radius, R , for KNbO_3 films deposited on $\text{LaNiO}_3/\text{Inconel}$ foil and $\text{LaNiO}_3/\text{Inconel}$ coils.

	Foil	Coil-1	Coil-2	Coil-3	Coil-4
R (mm)	0	1.2	2.3	4.1	6.2

There were two series of peaks (labeled $P1$ and $P2$) derived from KNbO_3 $\{200\}_c$ peaks. Fig. 3 (c) shows the average curvature radius dependencies of the out of-plane lattice spacings estimated from $P1$ and $P2$ from Fig. 3 (a). For all the film thicknesses, the lattice spacings of $P1$ and $P2$ were almost the same at 0.403 nm and 0.398 nm, respectively, and these values are in reasonable agreement with those reported for KNbO_3 bulk²⁶⁾. This result suggests that $P1$ and $P2$ are originated from 002_c and 020_c diffraction peaks due to the domain structures²⁷⁾.

Fig. 4 shows the relative dielectric constant, ϵ_r , and the dielectric loss, $\tan \delta$, measured at 10 kHz as functions of the average curvature radius for KNbO_3 films shown in Fig. 3. ϵ_r and $\tan \delta$ are about 105

Fig. 3 (a) XRD 2θ - ω patterns for KNbO_3 films deposited on $\text{LaNiO}_3/\text{Inconel}$ foil and $\text{LaNiO}_3/\text{Inconel}$ coils and (b) enlarged view between $2\theta = 40$ - 50° in (a). The pattern of $\text{LaNiO}_3/\text{Inconel}$ foil is also shown as reference. (c) Radius of curvature dependence of the out-of-plane lattice spacing estimated from $P1$ and $P2$ in (a) originated to KNbO_3 $\{200\}_c$ peaks.

Fig. 4 Average curvature radius dependence of the relative dielectric constant, ϵ_r , and dielectric loss, $\tan \delta$.

and 0.12, respectively, and these values did not markedly change with increasing the average curvature radius.

Fig. 5 (a)-(c) show the polarization (P) - electric field (E) hysteresis loops measured at 10 kHz for KNbO_3 films deposited on $\text{LaNiO}_3/\text{Inconel}$ foil and $\text{LaNiO}_3/\text{Inconel}$ coil shown in Fig. 3. The shape of hysteresis loop measured on $\text{LaNiO}_3/\text{Inconel}$ coil was very similar to that of $\text{LaNiO}_3/\text{Inconel}$ foil. Fig. 5 (d) shows the remanent polarization, P_r , and the coercive field, E_c , estimated from P - E hysteresis loops as function of the average curvature radius. P_r and E_c are about $11 \mu\text{C}/\text{cm}^2$ and $99.5 \text{ kV}/\text{cm}$ respectively, and R

Fig. 5 (a)-(c) Polarization (P) - electric field (E) hysteresis loops measured at 10 kHz for KNbO₃ films deposited on LaNiO₃/Inconel foil and LaNiO₃/Inconel coils. (d) Average curvature radius dependence of the remanent polarization, P_r , and coercive field, E_c .

dependence was hardly observed as shown in Fig. 5 (b).

From these results, it was found that KNbO₃ films with same quality were prepared regardless of the shape of substrate. This is a great advantage in forming a film onto substrates having three-dimensional structure. In addition, the dielectric constant and remanent polarization values were similar with those of KNbO₃ films deposited on single crystal substrates by hydrothermal method^{28,29)}. Therefore, an increasing in shape freedom of piezoelectric films is expected.

4 Conclusion

We prepared polycrystalline KNbO₃ films with thickness of 12.5 μm on LaNiO₃-covered Inconel foils with different radius of curvature by hydrothermal method. The growth of film was accelerated by using LaNiO₃-surface layer. Films were formed uniformly on curved surface without peel off. From XRD analysis, the average curvature radius dependence of crystal structure was hardly observed. In addition, dielectric and ferroelectric properties were also almost the same regardless of the average curvature radius. The present study thus demonstrated that hydrothermal method is one of the effective techniques to prepare piezoelectric films on substrates having three-dimensional structure.

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