Journal of Solid Mechanics and Materials Engineering

Vol. 3, No. 11, 2009

Synthesis and Characterization of Piezoelectric $(Bi_{1/2}Na_{1/2})TiO_3$ Films by a Hydrothermal Method*

Fangchao XU ** and Kazuhiro KUSUKAWA **

** School of System Engineering, Kochi University of Technology,
185 Miyanokuchi, Tosayamada-cho, Kami, Kochi, Japan
E-mail: kusukawa.kazuhiro@kochi-tech.ac.jp

Abstract

Thin films of lead-free piezoelectric ceramics $(Bi_{1/2}Na_{1/2})TiO_3$ (abbreviated as BNT) were prepared on pure titanium substrates by a hydrothermal method. The properties of BNT films synthesized from the reaction solution with various contents of bismuth and titanium were investigated using SEM, EDX, XRD and other instruments. Moreover, the effects of the concentrations of starting materials on permittivity and piezoelectric effect of deposited BNT films were discussed. The results showed that an impurity of Bi_2O_3 crystal was produced on the surfaces of all deposited films. With assumption of deposited films as an system of (1-x) $(Bi_{1/2}Na_{1/2})TiO_3$-xBi_2O_3, the BNT content was calculated from the Bi/Ti ratio of the EDX results. The optimized synthesis condition was determined on the evaluation target of the calculated BNT content. In addition, the unimorph cantilever type actuators were fabricated by BNT deposited samples, and their piezoelectric responses were measured at their resonance frequencies under AC field. It was noted that the piezoelectric effect of the deposited BNT film was greatly dependent on its crystallization level.

Key words: BNT, Piezoelectric Film, Hydrothermal Method, Lead-Free, Actuator

1. Introduction

Piezoelectric materials have been extensively used in smart devices such as sensors and actuators. Nowadays, lead zirconate titanate $Pb(Zr_x,Ti_{1-x})O_3$ (abbreviated as PZT) and PZT-based ceramics are the most commonly used piezoelectric materials due to their excellent piezoelectric properties [(1)]. However, because of the strong toxicity of lead oxide, the use of the lead-based ceramics has caused serious lead pollution and environmental problems [(2)]. Therefore, there is a great need to develop lead-free piezoelectric ceramics for replacing them. BNT, one of promising lead-free piezoelectric ceramics, belongs to the perovskite family (ABO3-type) with rhombohedral symmetry at ambient temperature [(3)]. BNT ceramics and some BNT-based ceramics have been studied extensively [(4) - (8)].

Recently, piezoelectric films have attracted more and more attentions in microelectronic and micromechanical systems, especially in the development of micro-sensors and micro-actuators [(9)]. Kanda et al. reported that PZT films were successfully deposited on pure titanium substrates by the hydrothermal method [(10)]. In the present study, we introduced the hydrothermal method to deposit BNT films on pure titanium substrates. Compared with other methods such as sol-gel method, chemical vapor deposition (CVD), or the sputtering method, the hydrothermal method has two outstanding advantages: [(11)] (1) films can grow on

*Received 7 July, 2009 (No. 09-0318)
[DOI: 10.1299/jmmp.3.1173]

the complex shaped or tiny substrates, allowing new kinds of micro-sensors and micro-actuators; (2) the deposited films require no post treatment (annealing or poling).

The hydrothermal synthesis of BNT powder was reported by Jing et al. [12] and Pookmanee et al. [13]. There were few reports on the hydrothermal synthesis of BNT films [14]. However, there has been no report on the optimization of hydrothermal synthesis conditions of BNT films. In this work, the characteristics of BNT films were investigated with varying the concentrations of starting materials.

2. Experimental

2.1. Hydrothermal Synthesis

In the hydrothermal synthesis of BNT films, hydrated bismuth nitrate [$Bi(NO_3)_3 \cdot 5H_2O$, hereinafter referred to as $Bi(NO_3)_3$] and titanium oxide(TiO_2) were used as bismuth precursor and titanium precursor respectively, and sodium hydroxide(NaOH) was used as sodium precursor and mineralizer.

The hydrothermal method utilizes the chemical reaction at high temperature and pressure to grow films on a substrate. Hence, the reaction vessel must be sealed to prevent the solution from evaporating. The reaction solution still exists as liquid in the process of hydrothermal synthesis. The schematic of experimental equipments is shown in Fig.1. During the hydrothermal synthesis process, the autoclaves were rotated at the speed of 12 rpm to stir the reaction solution. Figure 2 shows the process of the preparation of BNT films. Firstly, the starting solution was prepared by mixing 8 ml TiO_2 aqueous solution, 4 ml $Bi(NO_3)_3$ aqueous solution and 16 ml NaOH aqueous solution. Secondly, the prepared solution and pure titanium substrate (40×20×0.05mm) were put into an autoclave with a Teflon cup of 40 ml, and then the autoclave was kept in an oven at 150℃ for 24 hours. This process was called "nucleation". At the beginning of the hydrothermal synthesis, the titanium substrate reacted with the ions dissolved in the solution to form some nuclei on the substrate surface. This finally helps to increase the adhesion strength between deposited BNT film and the titanium substrate. After the "nucleation" step, the reaction solution was renewed as the starting solution, and the autoclave was kept at 120℃ for 24 hours. This process was called "crystal growth". BNT crystals were expected to grow in this step. In this study, we repeated the "crystal growth" step once more to obtain a thicker film.

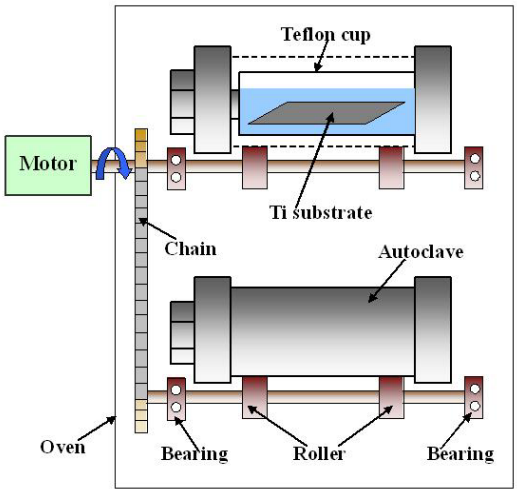


Fig.1 Schematic of the experimental equipments

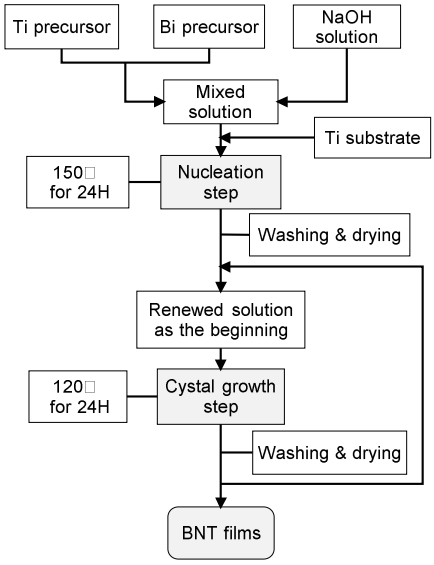


Fig.2 The process of the preparation of BNT films by the hydrothermal method

2.2. Characterization

BNT films were synthesized with varying the concentrations of starting materials. Table 1 shows the hydrothermal synthesis conditions of starting materials. In this study, the concentration of NaOH was kept constant at 10 mol/l for all of 16 conditions, which are represented by the symbols of A to P.

Table 1 Conditions of starting materials and symbols of samples

16 ml solution of NaOH(10mol/l)		4ml solution of $Bi(NO_3)_3$ (mol/l)			
		1.0	1.2	1.4	1.6
8 ml solution of TiO_2 (mol/l)	0.3	A	E	I	M
	0.4	B	F	J	N
	0.5	C	G	K	O
	0.6	D	H	L	P

The morphology and microstructures of deposited BNT films were observed by a scanning electron microscopy (SEM, Philips XL20) which is equipped with an energy dispersive X-ray spectrometer (EDX). The latter was used to make a quantitative analysis of element compositions of deposited BNT films. Crystal structures and crystallization levels of deposited BNT films were analyzed by X-ray diffraction (XRD, JEOL JDX-3500) at the detection range(2θ) of 10-90º with a step of 0.05º.

In order to evaluate the dielectric properties of deposited BNT films, punctiform conductive epoxies were laid on the film surface as electrodes. The dielectric loss and capacitance between the electrode and the titanium substrate (counter electrode) was measured at the frequency of 1 kHz using LCR Meter (Agilent 4284A). The piezoelectric constant d_{33} of deposited films was measured using a piezo-meter system (UK, Piezotest).

3. Results and Discussion

3.1. Observation of Synthesis Process

To study the evolution of the hydrothermal deposition of BNT films on titanium substrates, the procedure of deposition was stopped at various appointed time after the beginning of the synthesis of BNT films, and then SEM observations were performed on the substrate surface. Figure 3 shows that some crystal nuclei were found on the substrate surface after 15 minutes of deposition, and BNT crystals were generated all over the substrate surface after one hour of deposition. However, the film thickness was less than 1 μm after one hour of deposition.

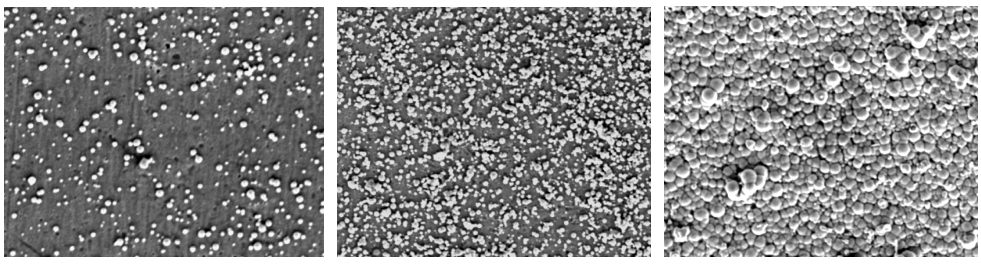


Fig.3 SEM observations of substrate surface in the process of BNT crystallization

3.2. Morphology and Microstructure

Figure 4 shows the variation of the film thickness with the $Bi(NO_3)_3$ concentration. It was found that the film thickness tended to be large in the case of high $Bi(NO_3)_3$ concentrations. Figure 5(a) shows the microstructure of as-deposited film surface of sample G. It was found that granular BNT crystals (approximately 2 μm grain size) and tetrahedral Bi_2O_3 crystals were generated on the substrate, and those Bi_2O_3 crystals were dispersed all over the film surface. The Bi_2O_3 impurity was more generated in the case of high $Bi(NO_3)_3$ concentrations. The generation of Bi_2O_3 increased the thickness of deposited films, and however it has no contribution to the piezoelectric property of deposited films. The Bi_2O_3 impurity can be removed by the immersion into concentrated nitric acid. The SEM image of sample G after the immersion is shown in Fig. 5(b). The thickness of etched BNT film was about 7 μm on each side regardless of the synthesis condition. The other properties of etched BNT films such as crystal structure, element composition, permittivity, piezoelectric constant etc. will be further investigated in our future research. In the present work, we focus on the characterization of as-deposited BNT films.

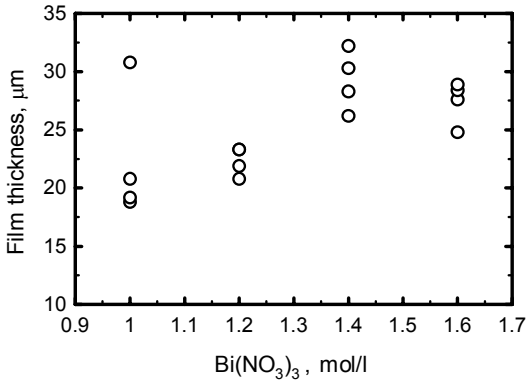
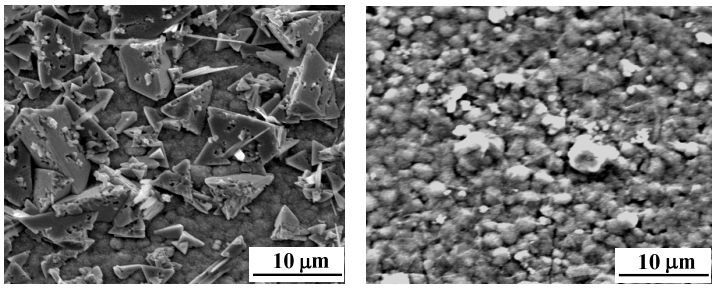


Fig.4 Variation of the film thickness with the $Bi(NO_3)_3$ concentration



(a) (b)

Fig.5 SEM images of BNT films (Sample G): (a) as-deposited BNT film; (b) etched BNT film after the treatment of concentrated nitric acid

3.3. EDX and XRD Analysis

Deposited BNT films were quantitatively analyzed by EDX for all the samples, and their element compositions were shown in Fig.6. It can be seen that the element composition ratio (Bi/Na/Ti/O) of deposited BNT films is different from the stoichiometric ratio of BNT (10/10/20/60). This is thought to result from the generation of Bi_2O_3. The content of Bi_2O_3 will be calculated from the result of element compositions in Section 3.4.

All the samples were measured using XRD. The generations of BNT and Bi_2O_3 crystals were confirmed for each sample. As examples of measured XRD patterns, those of sample G, K and O ($Bi(NO_3)_3$ concentrations of the starting solution were 1.2, 1.4 and 1.6 mol/l

respectively) are shown in Fig.7. The results show that sample G and K were nearly the same and more intense than sample O in the BNT diffraction peaks. Each diffraction peak of sample O was comparatively low, indicating that the crystallization level of sample O was not so high as that of sample G and K.

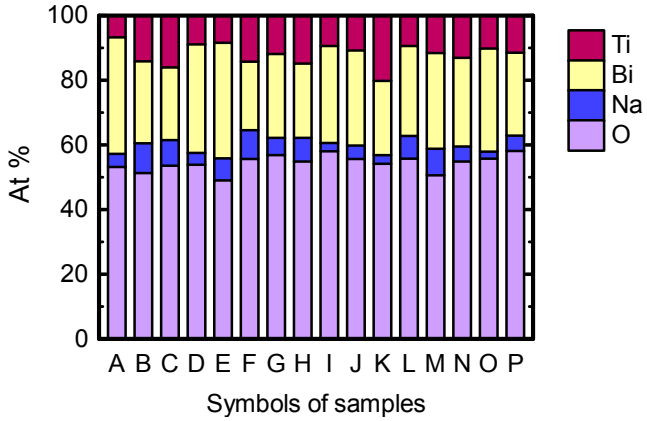


Fig.6 Quantitative analysis of films by EDX

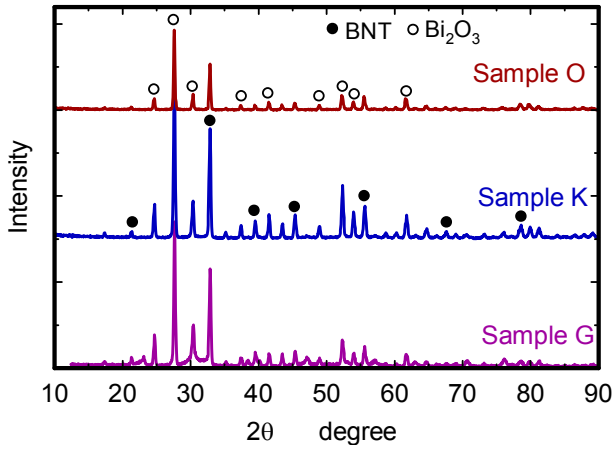


Fig.7 XRD patterns of sample G, K and O

3.4. Optimization of Synthesis Condition

It is evident that the homogeneity of deposited BNT films plays a vital role in determining their piezoelectric properties. However, the Bi_2O_3 impurity was found in deposited films from the results of XRD analysis and SEM observation. Without considering the other impurities of small quantity, we can assume deposited BNT films as a system of $(1-x)(Bi_{1/2}Na_{1/2})TiO_3$-$xBi_2O_3$. In other words, the element composition ratio (Bi/Na/Ti/O) of deposited BNT films is assumed to be (1+3x):(1-x):(2-2x):6. The value of x can be determined by the measured ratio of Bi/Na, Bi/Ti, Bi/O or etc. Since the change of the concentrations of Bi and Ti precursor is thought to directly affect the Bi/Ti ratio of deposited BNT films, the measured Bi/Ti ratio was used to calculate the values of x and 1-x, which indicate the contents of Bi_2O_3 and BNT. The optimized synthesis condition was determined on the evaluation target of the calculated BNT content.

Figures 8 and 9 show the correlation between the BNT content of deposited films and the $Bi(NO_3)_3$ and TiO_2 concentrations of starting solutions, respectively. In these two figures, fitting curves obtained by the least square method show that the BNT content reach a maximum at the $Bi(NO_3)_3$ and TiO_2 concentrations of 1.2 and 0.5 mol/l, respectively. This indicates that the synthesis condition of G is optimum in our current research.

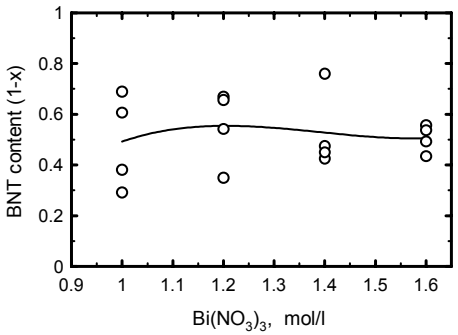


Fig.8 Correlation between the BNT content and the $Bi(NO_3)_3$ concentration

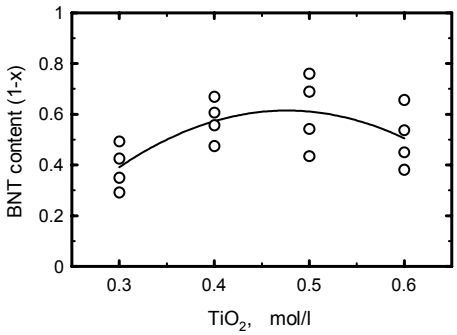


Fig.9 Correlation between the BNT content and the TiO_2 concentration

3.5. Permittivity and Dielectric Loss

The relative permittivity ε_r was calculated from the following equation:

$$\varepsilon_r = \frac{C_p \cdot t}{A \cdot \varepsilon_0} \quad (1)$$

where C_p is the capacitance(F), t is the film thickness(m), A is the top electrode area(m^2) , and ε_0 =8.85×10^{-12} F/m, which is the vacuum dielectric constant. Figure 10 shows the relative permittivity of deposited BNT films. It shows that the relative permittivity was much larger in the case of the $Bi(NO_3)_3$ concentration of 1.6 mol/l, comparing to the case of 1.4 mol/l. However, a small difference in the film thickness has been found between these two cases of 1.4 and 1.6 mol/l. The decrease in crystallization may be a factor to increase the relative permittivity of deposited films.

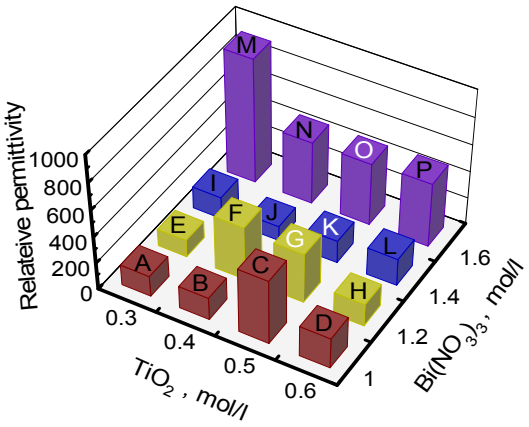


Fig.10 Relative permittivity of deposited films

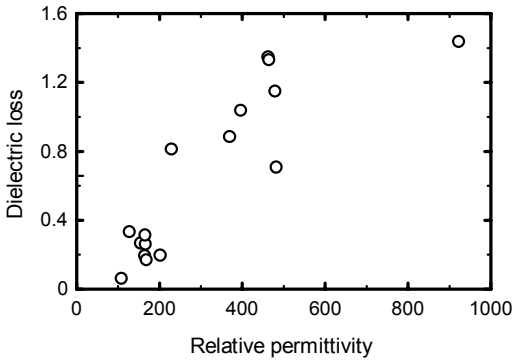


Fig.11 Correlation between the dielectric loss and relative permittivity

A correlation between the relative permittivity and dielectric loss was investigated and shown in Fig.11. The dielectric loss was positive correlated with the relative permittivity.

3.6. Piezoelectric Performance

Figure 12 shows the piezoelectric constant d_{33} of deposited BNT films. It indicates that the piezoelectric constant may tend to be large in the case of low concentration of $Bi(NO_3)_3$. In contrast to the results of XRD patterns, the results of piezoelectric constant indicate that the BNT crystallization level can affect the piezoelectric constant of film, and high crystallization of BNT leads to large piezoelectric constant. For example, sample G and K were almost the same and larger than sample O in the piezoelectric constant. This is in agreement with their BNT crystallization levels. In addition, the correlation between the relative permittivity and piezoelectric constant of deposited films can not be found by comparing Fig.10 with Fig.12.

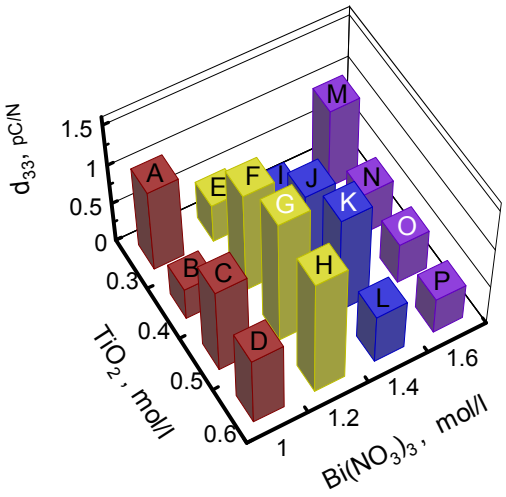


Fig.12 Piezoelectric constant of deposited films

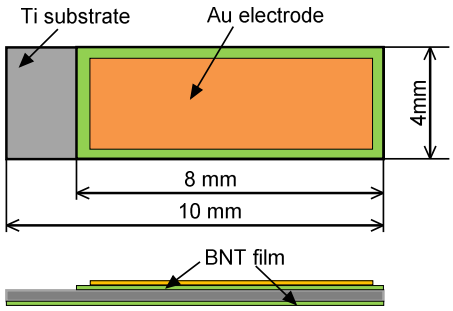


Fig.13 Dimensions of unimorph cantilever type actuator

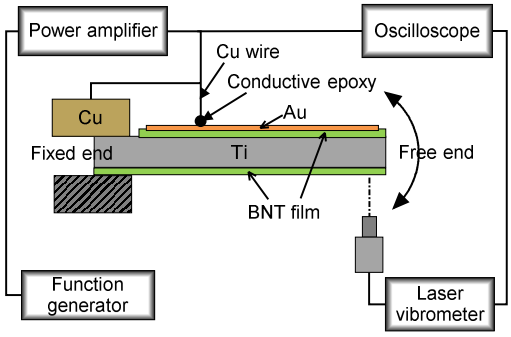


Fig.14 Measurement system of the unimorph cantilever type actuator

The converse piezoelectric effect of BNT was examined by the actuation testing. Figure 13 shows the unimorph cantilever type actuator used in the testing. Gold (Au) was sputtered on the film surface as an electrode, and the titanium substrate was used as the other electrode. The measurement system is shown in Fig.14. A thin copper wire was bonded to the gold electrode with conductive epoxy. A sinusoidal AC voltage was applied on the actuator through the function generator, and then we monitored the vibration of the tip of its free end on the oscilloscope by using a laser vibrometer (Melectro, V100). The resonance amplitude was obtained by adjusting the input frequency using the function generator. The

unimorph cantilever type actuators were made from three different samples (G, K and O). Figure 15 shows the variation of resonance amplitude with applied peak-to-peak voltage $V_{p\text{-}p}$ for sample G, K and O. It can be seen that the resonance amplitude was almost linear to the applied voltage for each sample, and the relatively large resonance amplitudes were obtained for sample G and K. This is considered to be in good accordance with their results of crystallization level.

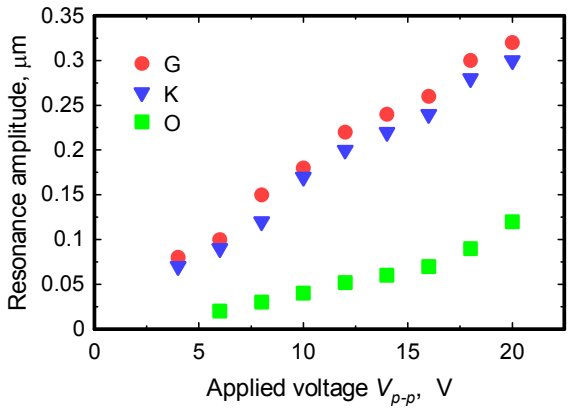


Fig.15 Variation of resonance amplitude with applied voltage $V_{p\text{-}p}$

4. Conclusions

BNT films were hydrothermally synthesized on pure titanium substrates with varying the $Bi(NO_3)_3$ and TiO_2 concentrations of the starting materials. The impurity of Bi_2O_3 was found in the deposited films. With the evaluation target of the calculated BNT content of deposited films, the optimized synthesis condition was determined as the condition of G, which is as follows: $Bi(NO_3)_3$ of 1.2 mol/l and TiO_2 of 0.5 mol/l. The relative permittivity tended to increase greatly in the case of the $Bi(NO_3)_3$ concentration of 1.6 mol/l. In addition, the actuation test confirmed the piezoelectric activity of deposited BNT films. The piezoelectric property of deposited BNT films greatly depended on the crystallization level of BNT, and so the piezoelectric response of the tested unimorph actuator was stronger in the case of higher BNT diffraction peaks.

References

(1) Demartin Maeder, M., Damjanovic, D. and Setter, N., Lead Free Piezoelectric Materials, *Journal of Electroceramics*, Vol.13, No.1-3(2004), pp.385-392.

(2) Xiao, D. Q., Lin, D. M. and Zhu, J. G., Investigation on the Design and Synthesis of New Systems of BNT-Based Lead-Free Piezoelectric Ceramics, *Journal of Electroceramics*, Vol.16, No.4(2006), pp.271–275.

(3) Prasad, K., Lily, Kumari, K. and Chandra, K. P., Electrical Properties of a Lead-Free Perovskite Ceramic: $(Na_{0.5}Sb_{0.5})TiO_3$, *Applied Physics A: Materials Science & Processing*,Vol.88, No.2(2007), pp.377-383.

(4) Wu, Y., Zhang, H., Zhang, Y., Ma, J. Y. and Xie, D. H., Lead-Free Piezoelectric Ceramics with Composition of $(0.97-x)Na_{1/2}Bi_{1/2}TiO_3$-$0.03NaNbO_3$-$xBaTiO_3$, J*ournal of Materials Science*, Vol.38, No.5(2003), pp.987-994.

(5) Choy, S. H., Wang, X. X. and Chan, H. L. W., Electromechanical and Ferroelectric Properties of $(Bi_{1/2}Na_{1/2})TiO_3$-$(Bi_{1/2}K_{1/2})TiO_3$-$(Bi_{1/2}Li_{1/2})TiO_3$-$BaTiO_3$ Lead-Free Piezoelectric Ceramics for Accelerometer Application, *Applied Physics A: Materials Science & Processing*,Vol.89, No.3(2007), pp.775-781.

(6) Wang, X. X., Chan, H. L. W. and Choy, C. L., $(Bi_{0.5}Na_{0.5})_{0.94}Ba_{0.06}TiO_3$ Lead-Free Ceramics with Simultaneous Addition of CeO_2 and La_2O_3, *Applied Physics A: Materials Science & Processing*, Vol.80, No.2(2005), pp.333-336.

(7) Huang, Y. Q., Gao, L. F. and Hu, Y., Compositional Effects on the Properties of $(1-x)BaTiO_3$-$xBi_{0.5}Na_{0.5}TiO_3$ Ceramics, *Journal of Materials Science: Materials in Electronics*, Vol.18, No.6(2007), pp.605-609.

(8) Lee, D. S., Jeong, S. J. and Park, E. C., Characteristic of Grain Oriented $(Bi_{0.5}Na_{0.5})TiO_3$-$BaTiO_3$ Ceramics, *Journal of Electroceramics*, Vol.17, No.2-4(2006), pp.505-508.

(9) Tressler, J. F., Alkoy, S. and Newnham, R. E., Piezoelectric Sensors and Sensor Materials, *Journal of Electroceramics*, Vol.2, No.4(1998), pp.257-272.

(10) Kanda, T., Morita, T., Kurosawa, M. K. and Higuchi, T., Sensitivity of a Miniaturized Touch Probe Sensor Using PZT Thin Film, *Ultrasonics,* Vol.40, No.1-8(2002), pp.61-65.

(11) Euphrasie, S., Daviero-Minaud, S. and Pernod, P., PZT Films Deposited by a Hydrothermal Method and Characterizations, *Material Science and Engineering B*, Vol.104, No.3(2003), pp.180-184.

(12) Jing, X. Z., Li, Y. X. and Yin, Q. R., Hydrothermal Synthesis of $Bi_{0.5}Na_{0.5}TiO_3$ Fine Powders, *Material Science and Engineering B*, Vol.99, No.1-3(2003), pp.506-510.

(13) Pookmanee, P., Uriwilost, P. and Phanickpat, S., Hydrothermal Synthesis of Fine Bismuth Powders, *Ceramics International*, Vol.30, No.7(2004), pp.1913-1915.

(14) Hasegawa, T., Kawashima, N., Ishikawa, M., Kurosawa, M. and Takeuchi, S., Development of Bimorph Vibrator Using Lead Free BNT Piezoelectric Film Deposited by Hydrothermal Method, *Proceedings of the 14th IEEE International Symposium on Applications of Ferroelectrics* (2004-8), pp.241-245.