Piezoelectric Properties and Microstructure of BaTiO₃ Films on Heat-Resistant Stainless-Steel Substrates Deposited Using Aerosol Deposition

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Lead (Pb)-free piezoelectric films formed on metallic substrates are of interest for advanced piezoelectric devices. BaTiO₃ films with a thickness of 10 μm were deposited on Fe-Cr-Al based heat-resistant stainless-steel substrates using aerosol deposition at room temperature. The BT film annealed at 1473 K for 1h had 1.2 μm-diameter grains, of which crystal phase was the perovskite single phase of the tetragonal crystal system. The dielectric constant was 2200, and the dielectric loss was 0.02. Piezoelectric displacement of the cantilevers with annealed BT films on stainless-steel substrates improved with increased annealing temperature. The piezoelectric constant d_{31} of film annealed at 1473 K was -56 pm/V.

Key words: lead free piezoelectric material, thick film, stainless steel, aerosol deposition, diffusion barrier layer

1. INTRODUCTION

It is possible to downsize and integrate sensor and actuator devices using piezoelectric films, because piezoelectric ceramic materials enable the design of devices with a simple configuration. Piezoelectric film devices have been actively developed and have already been put to practical use (e.g., inkjet print-heads and gyro sensors) [1]. However, most current piezoelectric ceramic devices in practical use contain highly toxic lead (Pb), which is regulated by RoHS in the EU market, along with other hazardous substances. Currently, piezoelectric ceramics containing Pb are excluded from regulation, due to the lack of alternative materials.

Due to social demand and environmental considerations, it is desirable to use Pb-free piezoelectric ceramic materials for novel piezoelectric devices. Pb-free piezoelectric materials have been actively studied in recent years [2-4]. BaTiO₃ (BT), a typical Pb-free piezoelectric material, enables the improvement of piezoelectric properties through control of microstructures such as grain size and domain structure by applying advanced ceramic process technology [5-10]. For example, Karaki et al. reported that bulk ceramics of BT prepared using two-step sintering have a piezoelectric constant d_{31} of -185 pC/N and d_{33} of 460 pC/N [10], which are almost same as those of common Pb-based piezoelectric ceramic materials.

Recently, R&D on thick-film technology for BT-based materials has also been carried out [11-13]. Since BT-based ceramic materials generally require high sintering temperatures (above 1573 K), zirconia substrates are usually used for BT-based thick film preparation, due to their excellent heat resistance and chemically stable characteristics. Nakaiso et al. reported that the piezoelectric constant d_{31} of BT-based film annealed at 1473 K on a yttria partially-stabilized zirconia (YSZ) substrate is -140 pm/V [14]. Aerosol deposition (AD) enables the formation of dense ceramic thick films at room temperature, due to

collision of accelerated fine particles onto substrates. The microstructure of AD films consists of fine crystal grains with the diameters of several tens of nanometers, which form as a result of fracture of collided fine particles during deposition. Preparation and physical properties of AD films on various piezoelectric materials such as BT and (K_{0.5}Na_{0.5})NbO₃ based ceramics have been evaluated [15-20]. The piezoelectric constant d_{31} of BT film annealed at 1373 K formed using AD was found to be -138 pm/V [20]. High temperature annealing (above 1273 K) is required to obtain available piezoelectric properties.

As mentioned above, ceramic substrates are usually used for BT-based piezoelectric films. However, the brittleness of ceramic substrates is an obstacle for device applications that require flexibility in shape. Metallic substrates may be useful to extend the scope of device applications using Pb-free piezoelectric films such as BT films. Metals have excellent fracture toughness compared to ceramics, flexible mechanical characteristics, and a high degree of shape freedom; therefore, it is possible to design novel piezoelectric devices utilizing metals.

However, to use metals as substrates for BT-based films, it is necessary to solve some problems such as the interdiffusion of elements between film and substrate and the cracking or delamination of film during high-temperature annealing, due to the difference in thermal expansion coefficients. We have been studying the availability of Fe-Cr-Al based stainless steel as a substrate for BT films, due to its excellent heat resistance at high temperature and its thermal expansion coefficient, which is close to that of ceramics. As a result, we confirmed that high-quality BT films can be formed using AD on Fe-20Cr-5Al (mass%) heat-resistant stainless-steel substrates without interdiffusion of elements and delamination during high-temperature (1473 K) annealing [21].

In this study, we evaluate the piezoelectric properties of BT films formed on heat-resistant stainless-steel substrates.

2. EXPERIMENTAL

2.1 Sample Preparation

To evaluate characteristics of piezoelectric films formed on a heat-resistant stainless-steel substrate, samples were prepared as follows. Stainless-steel sheets with the composition of Fe-20Cr-5Al (mass%) (Nippon Steel & Sumitomo Metal Corp, YUS205M1), processed into the size of 25×2×0.1 (mm), were used for substrates. To prevent interdiffusion of elements on piezoelectric films and substrates during annealing, an Al thermal oxide layer was preformed on the substrate surface by annealing for 1h at 1473 K in air. A Pt/Ti bilayer was formed using sputtering as an electrode on the Al thermal oxide layer of the annealed stainless-steel substrate, because the Al oxide layer provides electrical insulation.

Source BT powder for AD was prepared by calcination of BT01 (Sakai Chemical Industry Co., Ltd.) powder for 3h at 1373 K, with subsequent dry-milling using planetary ball milling. The average particle size of the prepared BT powder was 1 μ m, as determined using a laser diffraction particle size analyzer (Japan Laser, HELOS & RODOS).

BT films with 10 μ m thickness were formed using AD on the substrate in the deposition conditions detailed in Table I. The deposited samples were annealed at 1073, 1273, 1373, and 1473 K for 1h in air. Au as an upper electrode was subsequently formed by sputtering on the surface of BT films.

Table I. Conditions of aerosol deposition

Deposition temperature	Room Temperature
Carrier gas	O ₂
Gas flow rate	4 L/min
Orifice size of the nozzle	5 × 0.5 mm ²
Scanning rate	25 mm/s

2.2 Evaluation

Microstructural observations and composition analysis on the microscopic region of BT films were conducted using a scanning electron microscope (SEM) (JEOL, JSM-7001F) with energy dispersive spectroscopy (EDS) (Oxford Instruments, INCA x-act). The grain size of the BT films was estimated using the line-cross method from SEM images of the film surface. Crystal structural analysis was carried out using X-ray diffraction (Rigaku, Mini Flex600). Capacitance and dielectric loss of the films were measured at 1 kHz on 1 V using an LCR meter (NF Co. Ltd., ZM2375). The dielectric constant of films was calculated using the measured capacitance. To evaluate the ferroelectric properties, the polarization electric (*P-E*) field hysteresis curve was measured with ac applied voltages at 100 Hz and ± 100 V using a ferroelectric tester (Radiant, Precision LC). The piezoelectric constant was evaluated by measuring the tip displacement of films using a laser displacement meter (KEYENCE, LK-G30) when unipolar voltages were applied to films in the state of cantilever. The piezoelectric constant d_{31} was calculated using the equation reported by Q. M. Wang and L. E. Cross [22], substituting the measured values of tip displacement, thicknesses of films and substrate, and Young's modulus of films and substrate. The applied values of Young's modulus of BT film and substrate were 77 GPa for measured BT bulk

ceramics and 169 GPa for a stainless steel of YUS205M1.

3. RESULTS AND DISCUSSION

3.1 Thermal Oxide Layer of Stainless-Steel Substrate

Figure 1 depicts the X-ray diffraction pattern of the thermal oxidation layer formed on the surface of Fe-20Cr-5Al (mass%) stainless-steel substrate by annealing at 1473 K for 1h in air. Analysis using X-ray diffraction indicated that the thermal oxide layer was α -Al₂O₃ phase. Cross-sectional SEM observation confirmed that the Al₂O₃ layer was 1 to 2 μ m in thickness.

Fig.1 XRD patterns of heat-resistant stainless steel substrate before and after annealing at 1473 K in air.

3.2 Cross-Sectional Analysis

Figure 2 presents the cross-sectional SEM image (Fig. 2a) and depth profile of major elements through the interface between BT film and Fe-20Cr-5Al stainless-steel substrate with a Pt/Ti electrode (Fig. 2b). This sample was annealed at 1473 K. A multi-layer structure was clearly observed: BT film, Pt electrode, Al₂O₃, and stainless-steel layers. In addition, no Fe or Cr elements were detected in the BT layer (analysis positions 1, 2, and 3), and no Ba or Ti elements were detected in the substrate (analysis positions 7, 8, and 9). These results indicate that the thermally oxidized Al₂O₃ layer formed on the surface of a stainless-steel substrate suppresses interdiffusion of elements between the stainless steel and the BT film.

3.3 Crystallinity and Microstructure of BT Films

Figure 3 depicts a typical XRD pattern of BT film annealed at 1473 K. It was confirmed that annealed BT films formed on stainless-steel substrates exhibit a single perovskite crystal structure for all prepared samples. Figure 4 presents plane view SEM images of the surface of annealed BT films. The grain size of BT film annealed at 1073 and 1273 K was 1 μ m or less, and those of annealed films at 1373 and 1473 K were confirmed to have grown drastically above 1 μ m. Figure 5 indicates the annealing temperature dependence of the lattice constants of annealed BT films calculated from (200) and (002) lattice planes measured using XRD. The values of the lattice constant of the a-axis and c-axis of tetragonal BT (ICDD, PDF# 05-0626) are denoted as dotted lines. The film annealed at 1073 K exhibited a pseudo-cubic crystal structure. The separation of XRD peaks became notably clear on films annealed above 1373 K, and their crystal structure became tetragonal. The lattice constant of BT films annealed above 1373 K

(2a) Cross-sectional SEM image and analysis positions for EDS.

(2b) Results of composition analysis at each position.

Fig.2 Results of cross-sectional analysis on the interface between BT film and stainless steel substrate.

Fig.3 XRD pattern of BT film annealed at 1473 K.

Fig.4 Surface SEM images of annealed BT films.

converged to that of the tetragonal BT reported in the ICDD database. However, the c -axis lattice constants are slightly smaller than the database values, and those of the a -axis are slightly larger than the database values, which implies remaining internal stress in the annealed BT films.

Fig.5 Lattice constant of annealed BT films.

3.4 Electric Properties of BT Films

Figure 6 depicts P - E curves of annealed BT films with high resistivity ($> 10^{10} \Omega\text{cm}$). The maximum polarization (P_{max}) when the highest voltage of 100 V was applied increases with increasing annealing temperature. The dielectric constant was 2200, and the loss was 0.02 on the film annealed at 1473 K.

Fig.6 P - E hysteresis curves of annealed BT films.

Figure 7 illustrates the relationship between the grain size and the coercive field of BT films, based on the P - E curves. The ferroelectric domain walls in grains become easy to move because internal stress is reduced by grain growth on BT films; thus, the coercive field of BT films becomes smaller with increasing grain size. These results indicate that the ferroelectric properties of BT films improves with increasing grain size.

Figure 8 illustrates the tip displacement of annealed BT films on stainless-steel substrates. Displacement increased

with increasing annealing temperature. Improvement in piezoelectric response is assumed to be caused by grain growth, like the ferroelectric behavior discussed above. Furthermore, displacement significantly improved on the film annealed at 1473 K.

Fig.7 Relationship of coercive field and grain size of BT films.

Fig.8 Tip displacement of cantilevers of annealed BT films on stainless steel substrates.

We consider the reason for this result as follows. Figure 9 compares (002) and (200) X-ray diffraction peaks for BT films annealed at 1073, 1273, 1373, and 1473 K. The diffraction peak intensity of the (200) plane for BT film annealed at 1473 K is greater than that of the other samples. This result indicates that the volume fraction of *a*-domains (with their *c*-axis parallel to the XRD planes) in BT film exceeds that of *c*-domains (with their *c*-axis perpendicular to the XRD planes). It has been reported that the piezoelectric properties of Pb(Zr_{0.52}Ti_{0.48})O₃ film formed by AD improves with increasing volume fraction of the *a*-domain [17]. Because of the reversible response of *a*-domain without the disappearance of the domain wall in a high-electric field, a large volume fraction of the *a*-domain is generally believed to improve the piezoelectric properties. This is also assumed to be the reason for the BT film's improved piezoelectric properties with increasing volume fraction of the *a*-domain. The maximum value of the

piezoelectric constant d_{31} in this study was confirmed to be -56 pm/V on the film annealed at 1473 K.

Fig.9 XRD peak of 002 and 200 plane on annealed BT films.

Table II summarizes the properties of the BT film annealed at 1473 K that formed on the heat-resistant stainless-steel substrate. The d_{31} value of -56 pm/V obtained in this study is less than previous studies' values of -138 pm/V [13] and -140 pm/V [20], which were obtained for BT-based films formed on YSZ substrates. We consider that internal stress, caused by thermal stress resulting from differences in the coefficients of thermal expansion between stainless-steel and YSZ substrates, affects piezoelectric properties. The coefficient of thermal expansion, at a temperature range of RT to 1000 °C, of YSZ is 10.0 [23], that of BT is 14.7 [23], and that of Fe-20Cr-5Al stainless steel is 15.4×10^{-6} /K. In other words, the coefficient of thermal expansion of BT exceeds that of YSZ but is less than that of stainless steel. Therefore, after annealing of BT films, it is expected that tensile stress remains in films formed on the YSZ substrate and that compressive stress remains in those formed on the stainless-steel substrate. This suggests that compressive stress decreases the piezoelectric properties of BT film on stainless-steel substrates. To further improve piezoelectric properties, it is necessary to investigate the effect of residual stress in piezoelectric films.

Table II Piezoelectric property of BT film annealed at 1473 K on a stainless steel substrate.

Piezoelectric constant	d_{31}	-56 pm/V
Dielectric constant	ϵ_r	2200
Dielectric loss	$\tan\delta$	0.02

4. SUMMARY

In this study, we evaluated the microstructure and piezoelectric properties of BT films formed on Fe-Cr-Al based stainless steel. An α -Al₂O₃ layer forms on the surface of Fe-Cr-Al based heat-resistant stainless steel with annealing in air, and its layer suppresses the interdiffusion of elements between the BT films and the stainless steel during annealing. The grain size of BT films increases with increasing annealing temperature. The crystal structure of BT film annealed at 1373 and 1473 K indicates that the

tetragonal crystal structure and the lattice constant of BT films is close to that of tetragonal BT in the ICDD (PDF #05-0626). The piezoelectric properties also improved with increased annealing temperature and grain size. These results suggest that piezoelectric properties are affected by the microstructure (e.g., grain size and volume fraction of ferroelectric domains). The maximum value of the piezoelectric constant d_{31} in this study was -56 pm/V on the film annealed at 1473 K.

ACKNOWLEDGEMENTS

The authors acknowledge the technical contributions of Mr. A. Honma for his support in preparing the samples, and thank Professor H. Masumoto of Tohoku University for his help in measuring ferroelectric properties. This study was supported by NEC Tokin Corporation.

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(Received April 30, 2016; Accepted June 13, 2016;
Published Online September 1, 2016)