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Synthesis and basic properties of lead-free bismuth titanate thin films for piezoelectric microsensing device

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Piezoelectric and ferroelectric properties were studied in a $Bi_4Ti_3O_{12}$ (BIT) thick film (0.9 μm thickness) synthesized from chemical solution. To make unconstraint from the film-substrate interface clamping and eliminate bending motion of substrate, an array of disk-shape BIT capacitor cells with Pt top electrode layers were fabricated by photolithography (80, 50, 30, 20 μm in diameter). Longitudinal piezoelectric elongation was measured by an AFM with application of ac electric field at 1 kHz between the conductive cantilever tip contacted to the top Pt electrode and the bottom Pt electrode. Positive piezoelectric displacement response of 1 nm was measured. The maximum strain was about 0.1 % under bipolar drive (amplitude of 400 kV/cm or $4E_c$). From the unipolar driven piezoelectric displacement, piezoelectric coefficient AFM-d_{33} was measured. The value of AFM-d_{33} increased with decreasing the cell diameter and approached to a constant value of 12-13 pC/N. Considering the crystalline orientation, this value well corresponded to that of 20 pC/N which were reported previously in a single crystal. Ferroelectric property measurement was carried out simultaneously and the remnant polarization of P_r=6-7 μC/cm^2 was found. This value was much poorer than that in single crystal because of the mixed orientation of (117) and nonpolar (020).

Key words: Bi-layer ferroelectrics, piezoelectric coefficient, ferroelectric polarization, AFM, chemical solution deposition, photolithography, micro fabrication

1. INTRODUCTION

La-modified $Bi_4Ti_3O_{12}$ (BIT) have attracted much interest as a candidate of ferroelectric random access memory device in thin film form due to the high fatigue endurance and relatively low processing temperature [1]. In concern with the basic properties and applications, BIT and related compounds have been studied substantially [2-5]. Because of the strong anisotropic nature of its crystalline structure, in most cases, polycrystalline BIT bulk bodies and thin films showed rather poor ferroelectric character resulted from preferential c-axis orientation or random orientation, although its intrinsic ferroelectric property is superior. Therefore, in BIT the orientation control is one of the significant part of better ferroelectric property [6] as well as the enhancement of spontaneous polarization [7, 8], our primal interest is the relationship between orientation and ferroelectric property in polycrystalline BIT thin film. In our second interest, BIT can be regarded as a model material of piezoelectric property investigation because the ferro- and dielectric properties can easily be controlled by Bi-site substitution [5, 7, 8]. Piezoelectric property is strongly related to ferroelectric domain switching and dielectric property [9]. We have succeeded in orientation control process and revealed intrinsic ferroelectric property of BIT in thin film form [10]. For the next step, we investigated the local piezoelectric properties by an AFM for the measure of the possibility of piezoelectric microdevice application. In this study we present synthesis and ferro- and piezoelectric properties of polycrystalline BIT thick films having preferential orientation as well.

2. EXPERIMENTAL

As for coating solutions, starting materials of Bi-acetate and Ti-iso-propoxide (99.99 % and 99.999 %, respectively, Aldrich) were dissolved in 2-methoxyethanol (anhydrous, 99.8 %, Aldrich). The nominal composition was BIT + 5 % excess Bi to compensate the possible Bi loss from the volatility. The solutions were spin-coated on RF-sputtered $Pt(111)/Ti/SiO_2/Si(001)$ substrates and heated at 450-600 °C for pyrolysis and crystallization for 5-10 times. Then the film was heated at 600 °C for post crystallization annealing. The final film thickness was in the range of 300-900 nm determined from the cross sectional observation by an FE-SEM (S-5000, Hitachi, Japan). Crystallization and orientation behavior were studied by an X-ray diffractometer (X'Pert Pro, PANalytical, Netherlands). Since a regular 2θ-θ scan only gives diffraction from the planes parallel to the film, but none from the tilted planes, distribution of 2θ-θ scan intensity by varying the inclination angle Ψ of the film surface normal with respect to the 2θ-θ diffraction plane in the range of 0-90°; Ψ=0° corresponds to a regular 2θ-θ scan configuration.

A disk-shape capacitor cell array of BIT microdots with Pt top electrodes standing on a Pt bottom electrode layer were fabricated by photolithography. The Pt top layer was deposited on whole surface of BIT film by RF-sputtering prior to the photolithography process. After the photoresist masking, Pt top layer and BIT film were removed in the unmasked region by dry etching and reactive ion etching, respectively. The cell diameters of 80, 50, 30, and 20 μm were fabricated to reduce the clumping and bending effects of the substrate. The cell array was annealed at 575 °C after the etching to cure the plasma damage. By AFM (Nano-R, Pacific Nanotechnology, USA) operations, the cantilever tip was contacted on a Pt top electrode and under the application of ac electric field at 1 kHz, the longitudinal piezoelectric displacement of BIT was calculated from Z-error signal. This signal detects the change of the tip position by bending the cantilever. Using the sensitivity of each cantilever, the displacement at the tip of the cantilever by bending motion was calculated. The polarization-electric field (P-E) hysteresis curve was measured simultaneously at the frequency by ferroelectric testing system (FCE, Toyo Corporation, Japan). Figure 1 shows schematics of photolithography process and AFM measurements.

3. RESULTS AND DISCUSSION

Figure 2 shows the distribution of 2θ-θ scans with the variation of inclination angle Ψ between the film surface normal and 2θ-θ diffraction plane. The figure indicated that at the film surface (Ψ=0°), (117) reflection at 2θ=30° was dominant with the FWHM of about 12°. The minor polarization axis (c-axis) component migrated at Ψ=53° corresponding to the angle between (117) and (001). From the crystallographic relation, (117) at Ψ=0° gives a pair of (200) peak at Ψ=60° and perpendicular (020) peak at Ψ=35° (truncated). Another set of (200)* at Ψ=90° (020)* at Ψ=0° and (117)* at Ψ=60° indicates that mixed orientation from (117) axis and nonpolar (020) axis was formed normal to the film surface.

From an FE-SEM cross-sectional observation, film thickness of 900 nm was found. Dielectric constant ε_r=210 and tanδ=0.01 were measured under the application of 5 mV at 1 kHz.

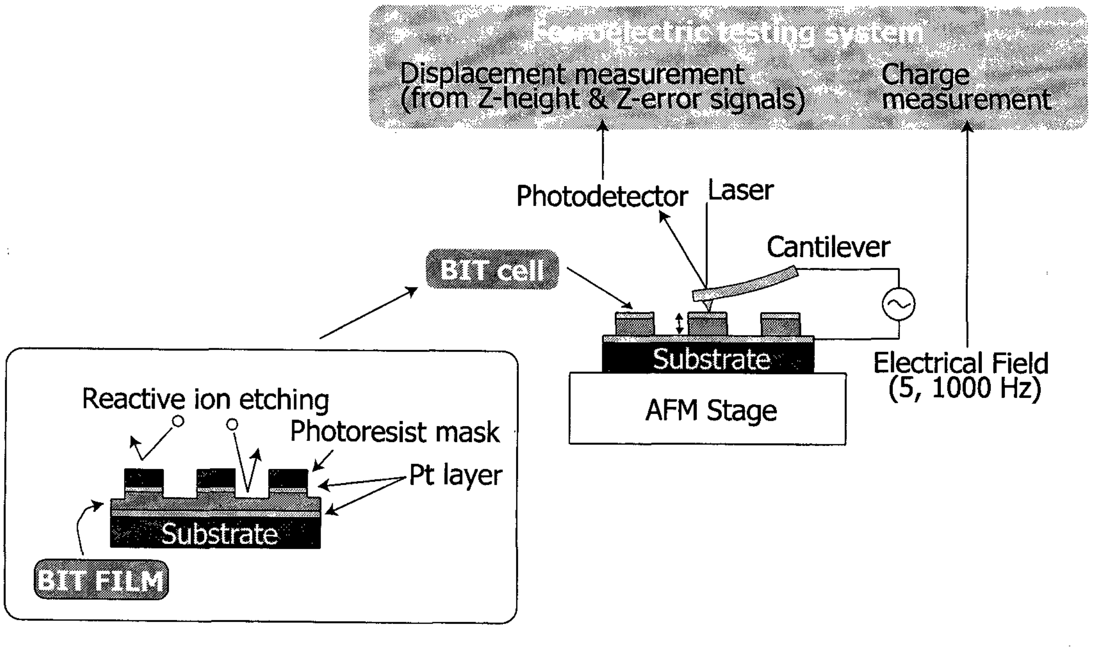

FIG. 1 Schematic view of sample micro fabrication by photolithography and simultaneous measurement of piezoelectric and ferroelectric response in BIT capacitor cell array.

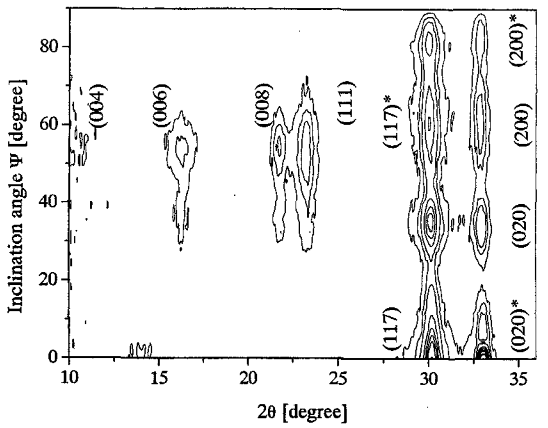

FIG. 2 Contour map of 2θ-θ diffraction intensity with the variation of inclination angle Ψ from the diffraction plane for 900-nm-thick BIT thick film pyrolyzed at 550 °C and annealed at 600 °C.

Figure 9 shows *P-E* hysteresis curves for 900-nm-thick BIT thick film measured by a contact-mode AFM operation at 1 kHz. Since no particular cell size dependence of P-E curves (both in P_r and E_c) was observed, the ferroelectric polarization response of 20-μm-cell was shown. The observed polarization was poor with the values of remnant and saturation polarizations P_r=7-8 and P_{sat}=18 μC/cm^2 in compare to the reported spontaneous polarization along a-axis P_s=50 μC/cm^2 in single crystalline sample. [2] Considering the angle between (117) and a-axis of 58°, P_{sat}=27 μC/cm^2 could be expected for the perfect (117) preferential orientation. As discussed earlier, the film surface was formed with grains having (117) and nonpolar (020) orientation, and only the (117)-oriented grains give ferroelectric polarization response. Therefore, the volume fraction of (117)-oriented grains was estimated as 60%.

Figure 4 shows piezoelectric responses measured simultaneously with ferroelectric response by a contact-mode AFM under the application of ac electric field with the amplitude of 400 kV/cm at 1 kHz. This result was the first reported piezoelectric response in BIT-based film. Since positive piezoelectric response was observed even in the 80-μm-cell, the removal of substrate bending displacement was successful. The total displacement of 1.1 nm was measured in 20-μm-cell and the values showed slight decrease with increasing cell diameter.

During the measurement, feedback of piezoscanner head position was inactive at this high frequency (1 kHz) and the curvature of cantilever was not constant (that's why the piezoelectric displacement could be measured by the change of the cantilever tip position), therefore, the value of indentation force was not constant. At low frequency of < 10 Hz, on the other hand, feedback of piezoscanner head becomes active and

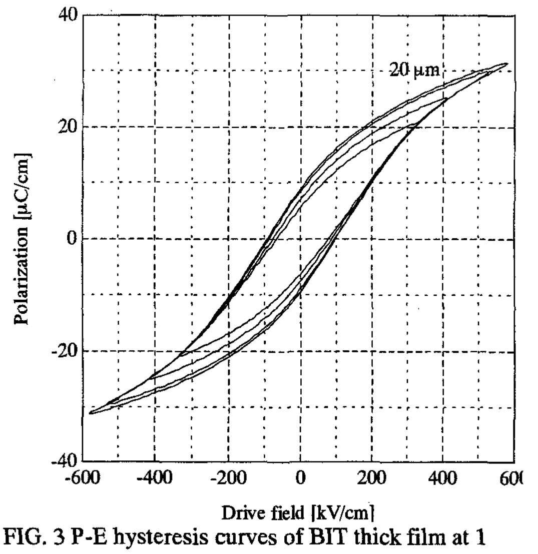

FIG. 3 P-E hysteresis curves of BIT thick film at 1 kHz.

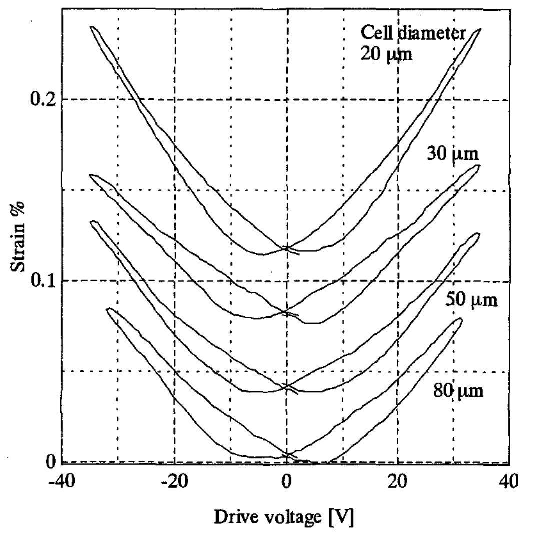

FIG. 4 Piezoelectric strain of 900-nm thick BIT film at 1 kHz. Positive piezoelectric responses with the cell diameter below 80 μm indicate that the bending motion of substrate was suficiently reduced.

indentation force can be maintained at constant value, so that the effect of indentation force variation can be eliminated by low frequency piezoelectric measurements. The measurement, however, at frequency lower than 100 Hz was not successful yet, because of the poor insulating property in BIT films. To decrease the defect so to improve insulating property, substitution of higher valence ions for Ti ions may be needed [11].

Figure 5 shows unipolar-driven longitudinal piezoelectric displacement with the amplitude of 100 kV/cm at 1 kHz. From the slope in this figure, longitudinal piezoelectric coefficient AFM-d_{33} was evaluated. Figure 6 shows capacitor cell size dependence of AFM-d_{33}. The value of AFM-d_{33} increased first with decreasing cell diameter, and may approach to a constant value of 12-13 pC/N by extrapolation. The cell

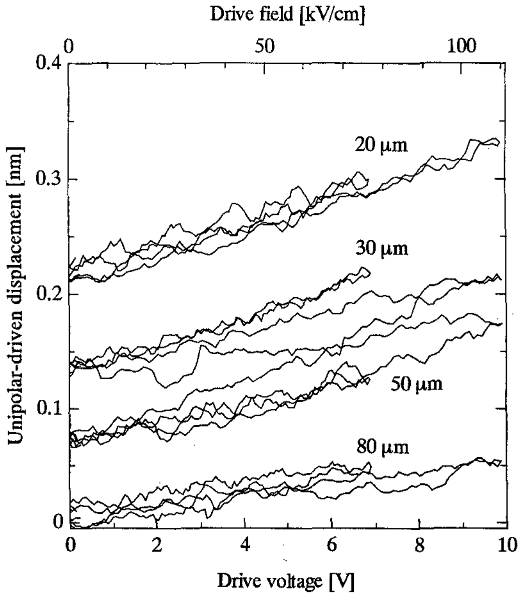

FIG. 5 Piezoelectric displacement of BIT thick film under unipolar electric field.

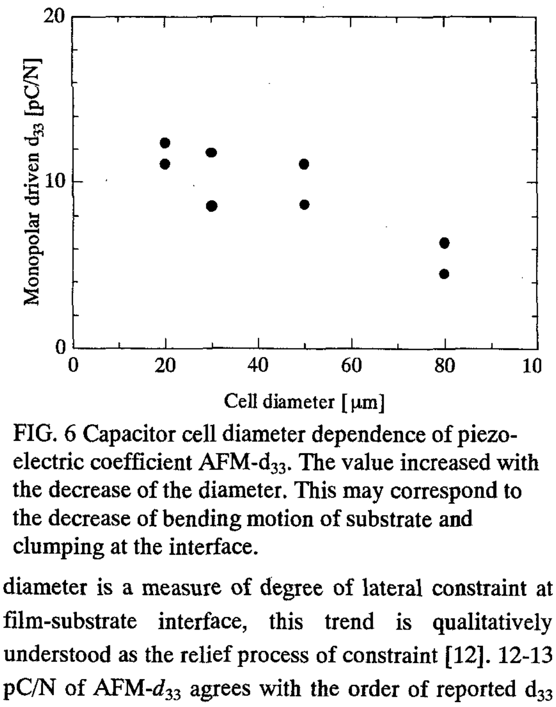

FIG. 6 Capacitor cell diameter dependence of piezoelectric coefficient AFM-d_{33}. The value increased with the decrease of the diameter. This may correspond to the decrease of bending motion of substrate and clumping at the interface.

diameter is a measure of degree of lateral constraint at film-substrate interface, this trend is qualitatively understood as the relief process of constraint [12]. 12-13 pC/N of AFM-d_{33} agrees with the order of reported d_{33} in single crystalline experiment [13], the difference may be resulted from the mixture of orientation, substrate bending and constraint at the film-substrate interface.

The reason for that reasonable piezoelectric coefficient was measured while poor ferroelectric polarization was measured in 900-nm-thick BIT film may be as follow: As shown in Fig. 7, in film surface (Ψ=0°) not only (117) but also nonpolar (020) were observed. In ferroelectric measurement, total charge on the Pt top electrode was measured, therefore, average polarization on whole area of Pt top electrode became poor. In case of piezoelectric measurement, on the other hand, displacement measurement might be performed on a single grain and not averaged the area of Pt top electrode.

4. CONCLUSIONS

900-nm-thick $Bi_4Ti_3O_{12}$ (BIT) films on conventional Pt substrates were successfully synthesized at 600 °C with the mixed orientation of (117) and (020). Disk-shape BIT capacitor cells were fabricated successfully by photolithography with the diameter of 20, 30, 50, and 80 μm. Ferroelectric polarization measurement indicate the volume fraction of (117) grain was 60%. Longitudinal piezoelectric displacement was measured for the first time by contact mode AFM at 1 kHz. Total strain: 0.1 % under 400 kV/cm (or 4 E_c), AFM-d_{33}: 12 pC/N (unipolar drive).

Acknowledgment

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