Scientific paper

Strain Engineering Effects on Electrical Properties of Lead-free Piezoelectric Thin Films on Si Wafers

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Dedicated to the memory of Prof. Dr. Marija Kosec.

Abstract

Using radio frequency – magnetron sputtering, calcium-doped barium zirconate titanate ($(Ba_{0.85}Ca_{0.15})(Zr_{0.1}Ti_{0.9})O_3$, BCZT) thin films were deposited on Si wafers with different bottom electrodes. The obtained BCZT thin film on a lanthanum nickel oxide (LNO) electrode had a highly c-axis preferred orientation, while the BCZT thin film on a Pt bottom electrode had (111) preferred orientation. Furthermore, the out-of-plane lattice constant of the BCZT on LNO/Si was 3.4% larger than that of the reported bulk material because of the compressive thermal stress from LNO with a large thermal expansion coefficient. This compressive thermal stress engenders an increase of the Curie temperature. The local piezoelectric response of the BCZT thin film on a LNO/Si structure was measured by piezoresponse force microscope.

Keywords: Lead-free piezoelectric material, thin film, chemical solution deposition

1. Introduction

Piezoelectric materials have been anticipated for use in applications such as sensors and actuators.[1–3] For these applications, lead zirconate titanate (PZT)-based materials have been widely used because of their excellent electrical properties. Nevertheless, it is necessary to prepare an integrated structure using lead-free piezoelectric materials with high Curie temperature (T_c) to meet environmental goals. Although many researchers have reported lead-free piezoelectric materials for substitution of PZT, almost all reported materials had lower electrical properties and/or lower T_c than PZT-based materials.

Fu *et al.* reported that calcium-doped barium zirconate titanate bulk ceramic has excellent piezoelectric properties. They examined the change in the piezoelectric constant (d_{33}) according to the material composition. The results show that d_{33} = 310 pC/N was attained at ($(Ba_{0.85}Ca_{0.15})(Zr_{0.1}Ti_{0.9})O_3$, BCZT) composition.[4] However, Cross *et al.* showed that these materials have low T_c of approximately 105 °C.[5] From the perspective of device design, T_c of the piezoelectric materials should be higher than 300 °C. Choi *et al.* recently reported the increased T_c under a huge compressive residual stress condition.[6] They examined this phenomenon using barium titanate thin film on a single-crystal substrate with a large thermal expansion coefficient. Therefore, we considered that the BCZT thin film under the large compressive residual stress condition shows good piezoelectric properties with high T_c.

In our previous study, we achieved control of the residual stress condition in piezoelectric thin films on a Si wafer by designing a buffer layer structure. Results show that $LaNiO_3$ (LNO) buffer layer is an effective buffer layer to apply the compressive thermal stress to piezoelectric thin film, even on a Si wafer.[7,8] Therefore, we deposited BCZT thin film on a LNO/Si and Pt/Si structure using RF-magnetron sputtering. The dielectric properties and T_c were examined to clarify the stress engineering effects in a lead-free piezoelectric thin film. In addition, some researchers had reported the dielectric and ferroelectric properties of BCZT thin films.[9,10] However, there is no data about the piezoelectric property of BCZT thin films. Therefore we also attempted to observe the local piezoelectric property (d_{33}) of BCZT thin film in this paper.

2. Experimental Procedure

An LNO layer for the buffer layer was deposited on a Si wafer using chemical solution deposition (CSD). The starting reagents for the LNO precursor solution with 0.3 M concentration were lanthanum nitrate, nickel acetate and 2-methoxy-ethonal. Experimental details are described elsewhere.[11] First, the LNO layer was deposited on a Si wafer by spin coating. The as-deposited LNO layer was dried, pre-annealed and annealed, respectively, at 150, 350, and 700 °C. Subsequently, the BCZT with the $(Ba_{0.85}Ca_{0.15})(Zr_{0.1}Ti_{0.9})O_3$ composition was deposited on LNO/Si and a commercial Pt/Si substrate using RF-magnetron sputtering. A sputtering target was prepared using the solid-state synthesis method. The film deposition was conducted at a substrate temperature of 700 °C in an Ar and O_2 mixed gas atmosphere ($Ar:O_2$ = 8:2) of 2 Pa. The RF power was adjusted to 150 W. The deposition time was 120 min. The BCZT film thickness was adjusted to 300 nm. Au top electrodes were prepared using DC sputtering with a metal mask (300 µmΦ).

The cross section microstructure was analysed by scanning electron microscope (SEM, with Carl Zeiss Supra 35 VP, JSM 5800; JEOL). The crystal phase was determined using X-ray diffraction technique (D8 Advance; Bruker AXS K.K.).

For this study, we measured the dielectric and ferroelectric properties of the obtained BCZT thin films using an impedance analyzer (HP-4194), and a ferroelectric test system (FCE-1; Toyo Corp.), respectively. The temperature dependence of the dielectric permittivity was estimated at 1 kHz using a heating plate, and the ferroelectric properties were also measured at 1 kHz. The local piezoelectric response was observed by an atomic force microscope (AFM, SPI3800N; SII Nano Technology Inc.) with a piezoelectric force mode (PFM). A Si tip coated with Rh was used (Hitach High-Tech Science Corp., Japan) for this measurement. The electric field was applied between the AFM tip and the bottom electrode of the thin film.

3. Results and Discussion

Figure 1 presents a cross-sectional SEM image of the obtained BCZT/LNO/Si structure. The film thicknesses of the obtained BCZT and LNO layers were estimated respectively as 300 and 200 nm. In addition, the obtained BCZT thin film had a dense microstructure, while the CSD derived LNO layer includes some nanopores.

Figure 2 shows the respective XRD patterns of BCZT thin films on a LNO/Si and on a Pt/Si substrate. The bulk BCZT material with the same composition was reported to crystallize in tetragonal phase at room temperature. Therefore, we assumed that the obtained BCZT thin film also had the tetragonal structure. The diffraction peaks of BCZT on a Pt/Si structure were very weak, however, we assume that the film was predominantly (111)-oriented.

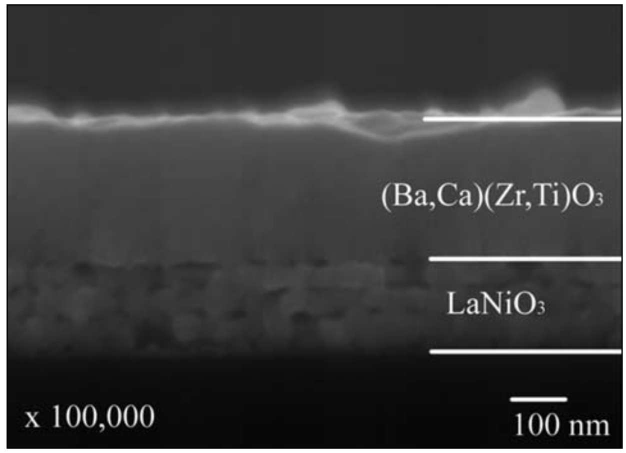

Figure 1. Cross-sectional SEM image of the BCZT/LNO/Si structure.

The results show that the BCZT thin film on a LNO/Si structure had highly c-axis preferred orientation. For BTO thin film deposited on the LNO/Si structure, the a-axis oriented LNO layer acted as a seeding layer for the c-axis preferred oriented BTO thin film because the lattice constants of LNO (*a* = 0.384 nm) and BTO (*a* = 0.399) are nearly equal.[12,13]

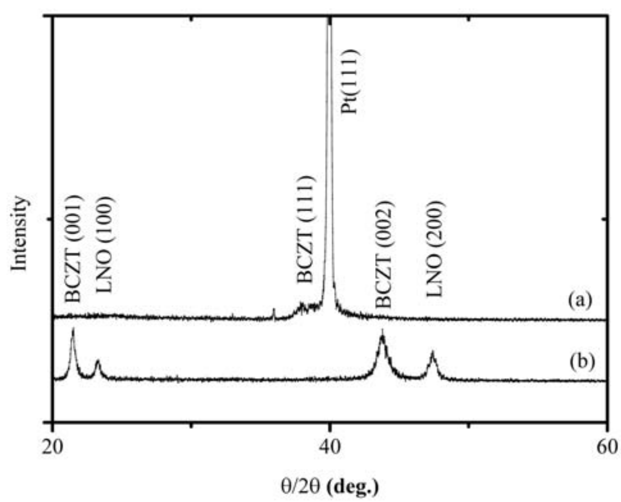

Figure 2. XRD patterns of BCZT film (a) on a Pt/Si and (b) on a LNO/Si structure.

In addition, the out-of-plane lattice constant of the obtained BCZT thin film on a LNO/Si structure was calculated as approximately 0.413 nm. This value was 3.4% larger than the lattice constant (i.e., the c-axis) of the reported bulk materials. In the case of the PZT and BTO thin films on LNO/Si structures, the lattice strain was compressive because the thermal expansion coefficient of

LNO (8.2×10^{-6}) [14] is greater than that of BTO and PZT[15]. Therefore, we concluded that the increase of the c-axis in the BCZT thin film on the LNO/Si structure also derived from the thermal compressive stress introduced by the substrate during deposition. Here, the polar axis of the tetragonal BCZT is the c-axis. Therefore, we considered that the expansion of the c-axis engenders enhancement of the ferroelectric property.

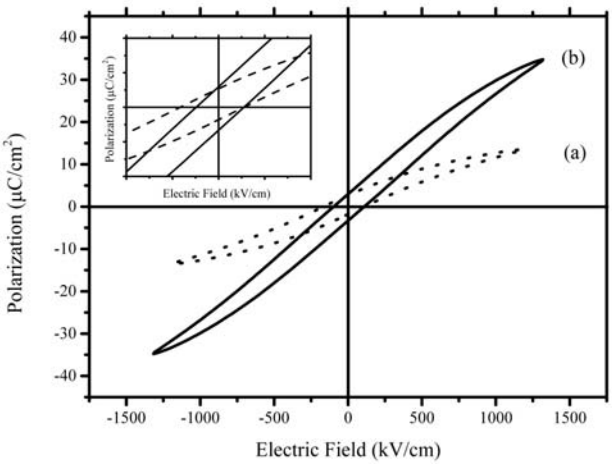

Figure 3. P–E hysteresis loops of BCZT film (a) on the Pt/Si structure and (b) LNO/Si structures.

Figure 3 shows polarization – electric field (P–E) hysteresis loops of the obtained BCZT thin films on the LNO/Si and on the Pt/Si substrates. Results show that the remanent polarization ($2P_r$) of the BCZT/LNO/Si was approximately 8.0 μC/cm^2, while that of BCZT/Pt/Si was approximately 4.0 μC/cm^2. Lin et al. reported the ferroelectric property of $(Ba_{0.835},Ca_{0.165})(Zr_{0.09},Ti_{0.91})O_3$ thin film on a Pt/Si substrate. Although the composition is a little bit different from our sample, the obtained remanent polarization was about $P_r = 1.73$ μC/cm^2.[10] Therefore, the reported value was nearly the same as that of our BCZT thin film on a Pt/Si. In contrast, the remanent polarization of the BCZT thin film on a LNO/Si was higher the reported value, so we assume that the strain in BCZT thin film was effective to enhance the ferroelectric property. Furthermore, the saturation polarization ($2P_s$) of BCZT on the LNO/Si structure was higher than that on the Pt/Si structure.

Figure 4 portrays the temperature dependence of the dielectric constant of the obtained BCZT thin film on the LNO/Si substrate. The reported T_c of BCZT with the same composition is 105 °C. However, the T_c of the obtained BCZT thin film on a LNO/Si was estimated as higher than 400 °C.

Figure 5 shows the local piezoelectric properties of the obtained BCZT thin film on a LNO/Si structure. We could observe that the local piezoelectric activity was detected in the BCZT thin film on the LNO/Si substrate.

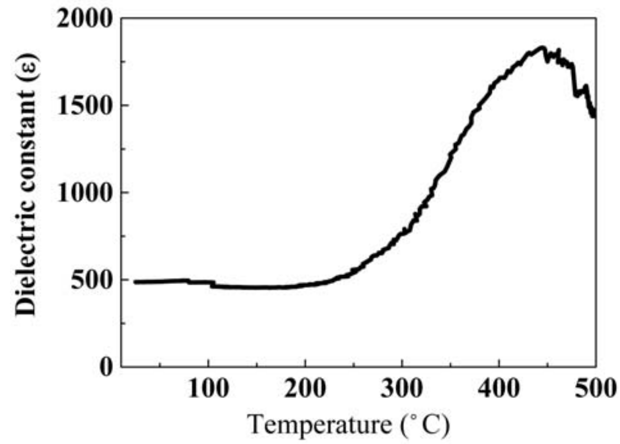

Figure 4. Change in the dielectric constant of BCZT/LNO/Si structure with temperature.

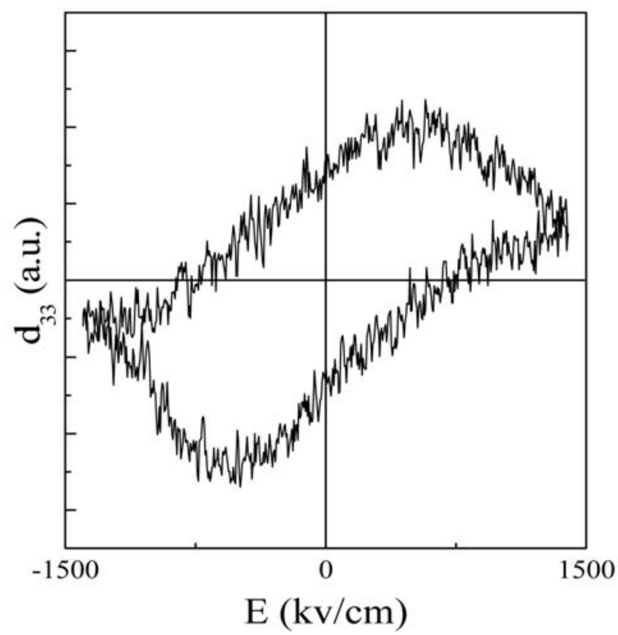

Figure 5. Local piezoelectric property of the BCZT thin film on a LNO/Si structure as measured by PFM.

4. Conclusions

The thin film with the $(Ba_{0.85}Ca_{0.15})(Zr_{0.1}Ti_{0.9})O_3$ (BCZT) composition was deposited on $LaNiO_3$(LNO)/Si and Pt/Si structures using rf-magnetron sputtering. The BCZT thin film with the (001) preferred orientation was obtained on the LNO/Si structure. Also, the out-of plane lattice constant was increased compared to the bulk value which was related to the compressive thermal stress introduced by the LNO/Si substrate. The Curie temperature was obtained from the change in the dielectric constant with temperature. Results show that the Curie temperature was higher than 400 °C, which is higher than that of the reported bulk material. In addition, the local piezoelectric response of the BCZT film on LNON/Si was analyzed by PFM.

5. Acknowledgement

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6. References

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Povzetek

Tanke plasti barijevega cirkonata titanata, dopiranega s kalcijem, ($(Ba_{0.85}Ca_{0.15})(Zr_{0.1}Ti_{0.9})O_3$, BCZT) smo pripravili na silicijevih rezinah z različnimi spodnjimi elektrodami z metodo radiofrekvenčnega magnetronskega naprševanja. Plast na silicijevi podlagi z elektrodo lantanovega nikelata (LNO) je izkazovala izrazito c-osno usmerjenost, medtem ko je bila plast na platinizirani podlagi (111) usmerjena. Nadalje je bil celični parameter BCZT v smeri pravokotno na podlago LNO/Si za 3,4 % večji od vrednosti, ki jo navajajo za volumensko keramiko z enako sestavo, kar smo pripisali tlačnim napetostim v plasti, ki so posledica velikega termičnega raztezka LNO. Slednje prispevajo tudi k povišanju Curiejeve temperature. Lokalni piezoelektrični odziv plasti BCZT na podlagi LNO/Si smo merili z mikroskopom na atomsko silo s piezoelektričnim modulom.