

Electrical properties of the multilayered PZT/BaTiO₃/PZT thick films

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Multilayered PZT/BaTiO₃/PZT thick/thin/thick films were fabricated by two different methods-thick films of Pb_{1.1}(Zr_{0.52}Ti_{0.48})O₃ by a screen printing method on alumina substrate electrode with Pt, thin films of BaTiO₃ by a spin-coating method with PZT thick films and once more thick films of the PZT by a screen printing method on the BaTiO₃ layer. We investigated the effect of phase, composition, and interfacial state of the BaTiO₃ thin film layers at the interface between the PZT thick films. The structural and the dielectric properties were investigated for the effect of various stacking sequences of sol-gel-prepared BaTiO₃ layers at the interface of the PZT thick films. The insertion of the BaTiO₃ interlayer yielded PZT thick films with homogeneous and dense grain structures regardless of the number of the BaTiO₃ layers. These results suggested that there is coexistence of the PZT phase and the BaTiO₃ phase or the presence of a modified BaTiO₃ at the interfaces between the PZT thick films. The leakage current density of a multilayered PZT-7 film is less than 1.5×10^{-9} A/cm² at 5 V.

Key words: Pb_{1.1}(Zr_{0.52}Ti_{0.48})O₃, BaTiO₃, thick/thin film, multilayer, sol-gel.

Introduction

Studies on the application of ferroelectric materials have been very active for microsystem devices because of their wide range of useful properties, particularly high dielectric capacitors, non-volatile memories with low switching voltage, infrared sensors and electro-optic devices.[1-3] Development of high efficiency dielectric materials has helped to design and fabricate numerous novel devices for various applications. Among these materials, both lead zirconate titanate (PZT) and barium titanate (BT) have excellent dielectric properties. Although they have high dielectric constants, much research on heterolayered thin films tends to concentrate on superlattice structures.[4-7] Research concerning heterolayered thick films has almost not been reported. Thick-film technology has the merit of extensive production, convenient technology, lower cost, an ability to intermingle material design, thick-film integration technology compatibility and its advantages, limited tolerances (high or low temperature endurance, corrosion resistance, high-power, anti-radialization).[8-11] In this study, multilayered PZT/BaTiO₃/PZT thick/thin/thick films (hereafter multilayered PZT thick films) formed by inserting the BaTiO₃ thin film layers between the PZT thick film layers have been found to be another set of promising candidates. The purpose of this study is to investigate the role of the interface in PZT thick films in the crystalli-

zation of BaTiO₃ thin film during the number of the BaTiO₃ coating layers and the interfacial structure between the multilayered PZT thick films on the electrical properties. Further, by inserting the BaTiO₃ coating solution into a middle layer, it is possible to make an excellent thick film which is able to decrease the leakage current and the value of the loss in a thick film.

Experimental

Multilayered PZT thick films were fabricated by two different methods, as follows:

Method 1: PZT powder was prepared by a sol-gel method from Pb-acetate trihydrate [Pb(CH₃CO)₂·3H₂O], Zr n-propoxide [Zr(OCH₂CH₂CH₃)₄], Ti iso-propoxide {Ti(OCH(CH₃)₂)₄} as the starting materials: acetic acid (CH₃COOH) and 2-methoxyethanol (CH₃OCH₂CH₂OH) were used as solvents. The PZT powder precursors were dried and then calcined for 2 hours at 700 °C. The calcined powders were characterized using XRD and the particle size was analyzed using SEM. The thermal treatment conditions were selected through DTA/TGA analysis of the powder. These powders were used to make the slurries for processing to thick films. The screen-printable pastes were prepared by kneading the ground PZT powder with 30 wt% of an organic vehicle (Ferro. B75001) in a non-bubbling kneader (NBK-1, Kyoto Electro.).

Method 2: BaTiO₃ precursor solutions were prepared by a sol-gel method from Ba-acetate [Ba(CH₃CO)₂], Ti iso-propoxide {Ti(OCH(CH₃)₂)₄} as starting materials, and 2-methoxyethanol (CH₃OCH₂CH₂OH) as solvent. The BaTiO₃ precursor solution was passed through a

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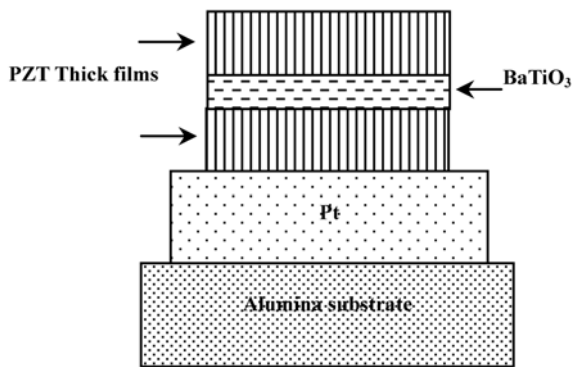


Fig. 1. Schematic diagram of the multilayered PZT thick film.

syringe filter and spin-coated on the PZT pastes using a spinner operated at 3000 rpm for 30 s to form the first layer. The BaTiO₃ precursor solution was then spin-coated and dried on the PZT layers to form the second layer using the same conditions. This procedure was repeated several times, and the multilayered PZT/BaTiO₃/PZT-*n* (*n* = number of BaTiO₃ coatings) thick films were sintered at 1200 °C for 2 h to crystallize them into a perovskite structure. A cross sectional schematic view of the laminated films is given in Fig. 1. The crystalline structures of the multilayered PZT/BaTiO₃ thick films were analyzed by XRD with Cu K α emission. The microstructure and chemical composition were analyzed using SEM coupled with an energy dispersive spectrometer (EDX). The dielectric constant and dielectric loss were measured by using an impedance/gain phase analyzer (HP4192A).

Results and Discussion

XRD patterns of the multilayered PZT thick films with the various numbers of the BaTiO₃ coating layers are shown in Fig. 1. This figure shows the typical XRD patterns of the perovskite polycrystalline structure while an impurity phase (i.e. pyrochlore) or preferred orientations were not observed. The intensity of the (110), (111) and (112) diffraction peaks of the multilayered PZT thick films increase with an increasing number of the BaTiO₃ coating layers. It can be assumed that the BaTiO₃ layers play an important role in nucleation or seeding sites at the interface. With an increase in the number of BaTiO₃ coating layers, the tetragonal phase in the films increases gradually, so the (101), (110) peaks are observed separately in the peaks from the multilayered PZT thick films. The mean lattice parameter *c* calculated from the main peak positions are shown in Fig. 3 as a function of the number of the BaTiO₃ coating layers at interfaces.

Figure 4 shows the surface and cross-sectional SEM micrographs of multilayered PZT thick films sintered at 1100 °C. A mixture of various grain sizes was evident for the multilayered PZT thick films sintered at 1100 °C, which that showed that very large grains

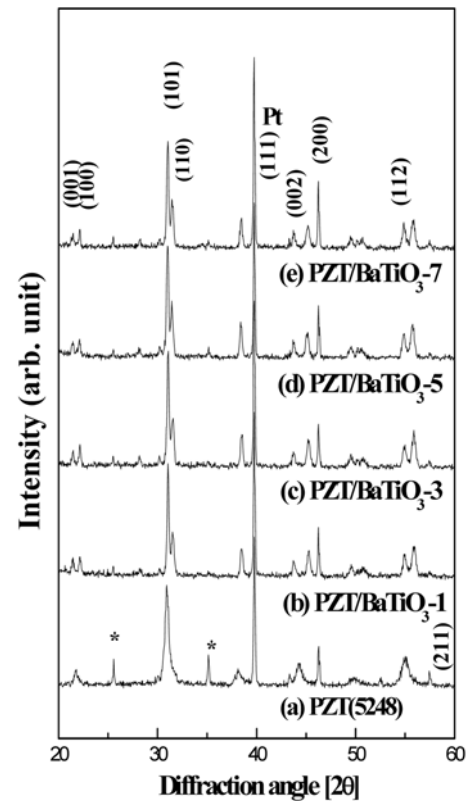


Fig. 2. XRD patterns of pure PZT thick films and multilayered PZT thick films with the number of BaTiO₃ coating layers.

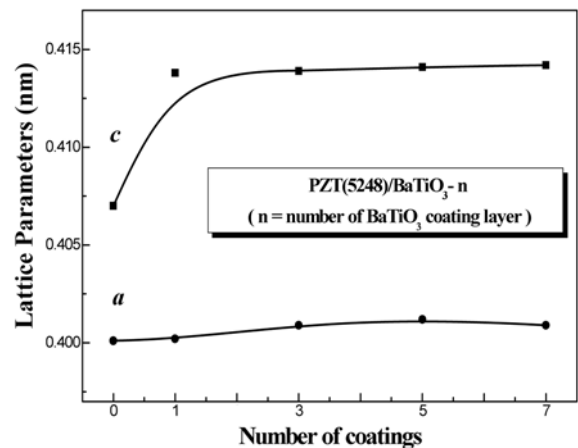


Fig. 3. Mean lattice parameter *c* of the multilayered PZT thick films with number of BaTiO₃ coating layer.

coexist with very small ones. It could be seen that the multilayered PZT thick films with a number of the BaTiO₃ coating layers were also effective in increasing the grain size and improving the microstructural homogeneity. All thick films showed large size pores due to the evaporation of the organic components. The adhesion between the Pt and the PZT layer is good, as shown in Fig. 4. Also, from the SEM cross sections of the multilayered PZT thick films, as shown in Fig. 4(b), (d), the boundary between the PZT and BaTiO₃ interlayer can not be seen. The porosity of the surface

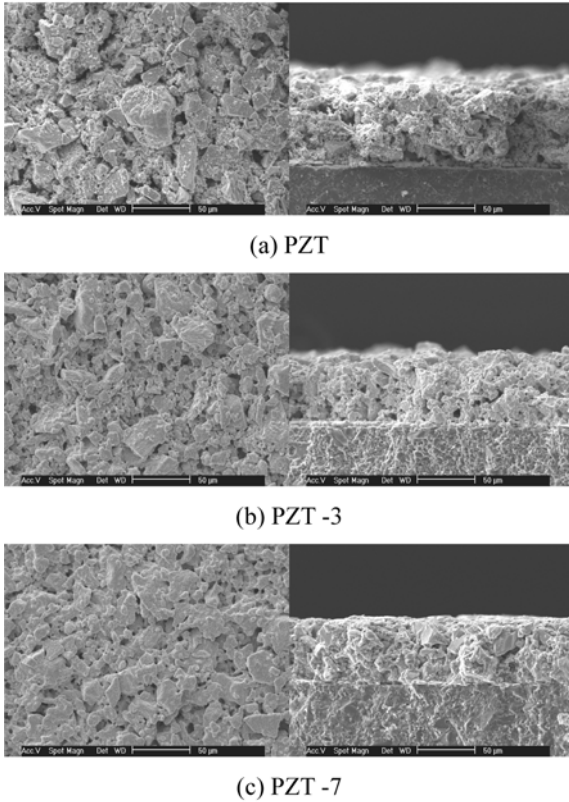


Fig. 4. SEM micrographs of thick films: surface morphologies and cross section of (a) pure the PZT thick film, (b) the multilayered PZT-3 and (c) the multilayered PZT-7 thick film.

increased with an increase in the number of BaTiO₃ coating layers and the PZT thick films coated with the BaTiO₃ layer exhibited densification and good surface flatness. And the PZT thick films coated with the BaTiO₃ layer exhibited a relatively dense cross-sectional microstructure. This result means that the BaTiO₃ precursor solution infiltrated between the particles and the agglomeration of particles increased with an increased treatment with the BaTiO₃ precursor solution. The average thickness of the multilayered PZT thick film sintered at 1100 °C was approximately 60 μm.

Figure 5 shows the dielectric constant and the dielectric loss of pure PZT and the multilayered PZT thick films as a function of coating layers at 1 kHz. The dielectric constant decreased with an increase in the number of coating layer and the multilayered PZT thick films showed typical dielectric dispersion properties. The dielectric loss decreased with an increase in the number of BaTiO₃ coating layers. These properties can be explained by the reduction of porosity and the increment of densification, as shown in the micrographs Fig. 4. The multilayered PZT-7 thick films exhibited superior dielectric loss compared with the single composition PZT thick films. We consider that there are there is a coexistence of the PZT phase and the BaTiO₃ phase or the presence of a modified BaTiO₃ phase at the interfaces between PZT thick films. The dielectric constant decrease and dielectric loss decrease with an

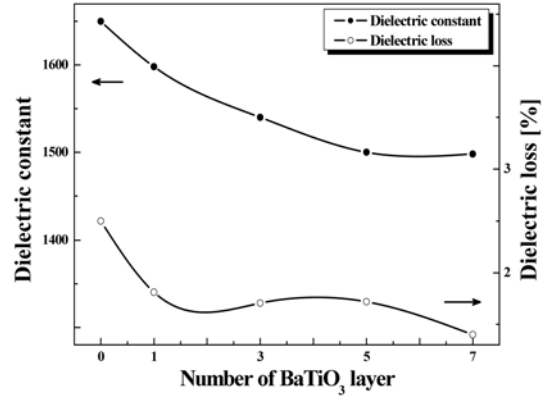


Fig. 5. Dielectric constant and loss of the multilayered PZT thick films at 1 kHz as a function of the number of BaTiO₃ coating layer.

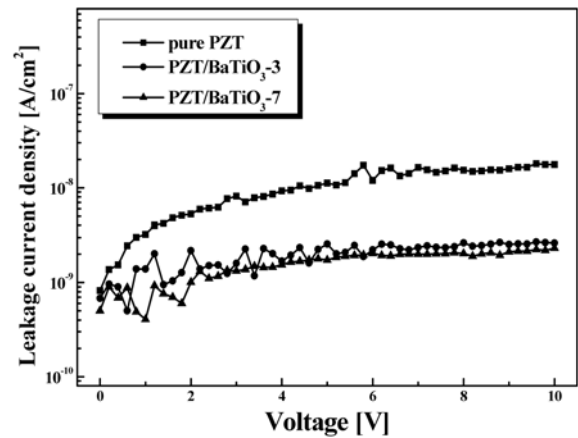


Fig. 6. Leakage current characteristics with the applied voltage for the multilayered PZT thick films.

increase in the number of BaTiO₃ coatings, and the multilayered PZT-7 thick shows good values, 1498 and 1.4% at 1 kHz, respectively.

Figure 6 shows the leakage current densities of the multilayered PZT thick films as a function of applied voltage. Leakage current densities decrease with an increase in the number of coatings, and there were lower values than those of single composition PZT thick films. These results suggest that trapping centers for carriers were formed at the interface between the PZT and BaTiO₃ layer, and these increased as the number of coating layer increased. The leakage current density of the multilayered PZT-7 film is less than 1.5×10^{-9} A/cm² at 5 V.

Conclusion

Multilayered PZT thick films were prepared by a sol-gel method and screen printing techniques on alumina substrate electrodes covered with Pt with thin films of BaTiO₃ by a spin-coating technique at the interfaces between the PZT thick films. The thickness of all thick films was about 60 μm. The dielectric properties such as dielectric loss of the multilayered PZT thick films

were superior to those of single composition PZT thick films, and dielectric constant and dielectric loss values for multilayered PZT-7 thick films were 1498 and 1.4%, respectively. The leakage current density of multilayered PZT-7 film is less than 1.5×10^{-9} A/cm² at 5 V. These results prove to us that the design of the multilayered structure can not only artificially control the ratio of different phases, but can also regulate the electric properties.

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