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Preparation of ferroelectric $Pb(Zr_{1-x}Ti_x)O_3$/Si films by laser lift-off technique

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Abstract

Materials characteristics and ferroelectric properties of thick xPb($Ni_{1/3}Nb_{2/3}$)O_3-(1-x)Pb($Zr_{0.52}Ti_{0.48}$)O_3 ($x=0.3$), PNN-PZT films, which were prepared by doctor-blade tape-casting and laser lift-off processes, were investigated. The underlying buffer materials were observed to influence significantly the densification behavior for the PNN-PZT sapphire layers. For PNN-PZT/sapphire films sintered without buffer layer, the substrates impose pronounced constraint on materials shrinkage, inducing the formation of porosity for the PNN-PZT layers. The proportion of pores is pronouncedly reduced when using a $Pb(Zr_{0.52}Ti_{0.48})O_3$ thin layer (<0.3 μm) prepared by metal-organic decomposition process as buffer layer. The PNN-PZT films transferred to silicon substrates by laser lift-off processes exhibit large electrical polarization characteristics ($Pr=41.9$ μC/cm^2), with small coercive field ($Ec=35.6$ kV/cm).

Keywords: PZT; Thick film; Laser lift-off

1. Introduction

Lead-based ferroelectric thin film materials, $Pb(Zr_{1-x}Ti_x)O_3$, possess high remanent polarization and large piezoelectric coefficient, which have found tremendous opportunity in device application, such as ferroelectric nonvolatile random access memories and pyroelectric detectors.[1,2] Moreover, these materials possess marvelous piezoelectric properties, which can be used in both strain sensors and electrical actuators. Thin films of $Pb(Zr_{1-x}Ti_x)O_3$-series materials are thus suitable for synthesizing microsensors. However, in order to apply these materials as microactuators, a critical component in micro-electro-mechanical system (MEMS), thick PZT films are required.[3–5] While the sputtering, sol–gel, MOD and laser ablation process[6–8] are suitable for synthesizing $Pb(Zr_{1-x}Ti_x)O_3$ films of sub-micron thickness, they have tremendously difficulty in growing the films with thickness ≧5 μm. The major problem is the accumulation of residual stress with film thickness, which easily induces the cracking for the films.

In this paper, we synthesized relatively thick PNN-PZT films in a totally different approach. We first modified the PZT materials with 30 mol.% $Pb(Ni_{1/3}Nb_{2/3})O_3$, so as to reduce the firing temperature necessary for the densification of materials, and then bonded the PNN-PZT tape prepared by doctor-blade technique[9,10] to a sapphire substrate, followed by sintering at high temperature to reach a high density. We then transferred the PNN-PZT films from sapphire to silicon substrates by using laser lift-off technique.[11,12] Relatively thick PZT films (≧20 μm) possessing good ferroelectric properties can thus be obtained.

2. Experimental

The xPb($Ni_{1/3}Nb_{2/3}$)O_3-(1−x)Pb($Zr_{0.52}Ti_{0.48}$)O_3 ($x=0.3$) materials, which were designated as PNN-PZT, were prepared by a conventional mixed oxide process using two-step calcination technique to circumvent the formation of undesired pyrochlore phase. NiO and Nb_2O_5 powders with 1:1 molar ratio were first mixed and calcined at 900 °C (1 h) to form Columbite phase, which were mixed with PbO, ZrO_2 and TiO_2 of nominal composition and then calcined at 900 °C (1 h). Thus obtained PNN-PZT powders were pulverized down to sub-micron size, mixed with PVB and disperse agent, in alcohol, and then tape-casted using a doctor-blade

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process to form PNN-PZT tapes about 40 μm in thickness.

The PNN-PZT tapes were bonded to a sapphire substrate, debindered at 550 °C for 2 h, and then fired at 1100 °C for 3 h, resulting in thick and dense PNN-PZT layer (~20 μm) on sapphire. The PNN-PZT layer was then transferred to Si-substrates by laser lift-off technique, which will be described shortly. The top electrode (Au-dots) was prepared by conventional lift-off technique. The ferroelectric properties of the films were measured by modified Sawyer–Tower circuits.

3. Results and discussion

3.1. Constraint sintering phenomenon

Typical microstructure for 1100 °C (3 h) sintered PNN-PZT/sapphire films, about 81 μm in thickness, is shown in Fig. 1a. The grains, about 1 μm in size, are not much different from the original particulate size for the PNN-PZT powders. There are a large number of pores on their surface. The proportion of pores decreases as the thickness of PNN-PZT layers increases. Presumably, the presence of pores results from the constraint imposed by the underlying sapphire substrates, which hinder the shrinkage of the PNN-PZT layers. To confirm such an assumption, ten layers of PNN-PZT tapes, were stacked together, about 200 μm in thickness, and were sintered without the substrate at the same conditions (i.e., 1100 °C—3 h). Fig. 1b indicates that the free standing PNN-PZT tapes can be fully densified and the grains grow to twice as large (~2.3 μm). Such a result supports the assumption that constraint sintering schematically illustrated in Fig. 1c is the prime mechanism inducing the formation of pores.

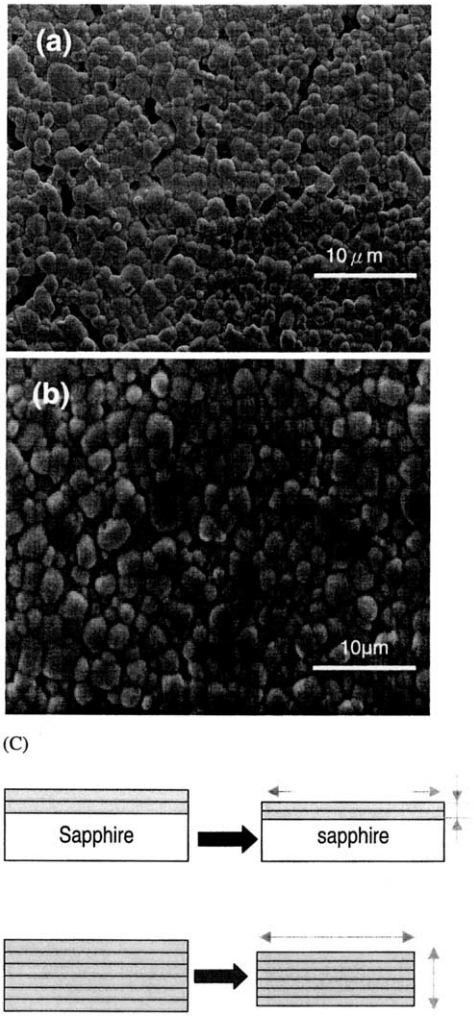

Fig. 1. SEM micrograph of (a) 5 layers of PNN-PZT tapes bonded on sapphire and (b) 10 layers of stacked PNN-PZT tapes without the sapphire substrates. The tapes were sintered at 1100 °C for 3 h; (c) schematic diagrams showing the constraint sintering process.

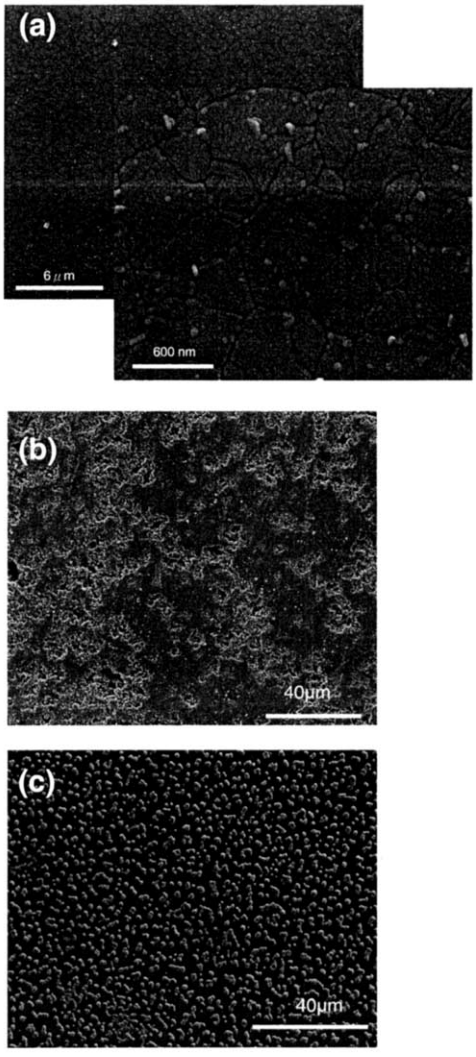

Fig. 2. Typical SEM micrographs of (a) PZT layer (~0.3 μm) synthesized by metal-organic-decomposition (MOD) process which were post-annealed at 650 °C for 1 h (b) PNN-PZT taped bonded on buffer sapphire and (c) thin MOD-derived PZT for serving as buffer layer, after sintering at 1100 °C for 3 h.

The above described phenomenon implies that the possible route to improve the sintered density of the PNN-PZT/sapphire films is to reduce the constraint of the underlying substrates on the shrinkage of the PNN-PZT layer. For this purpose, a thin layer of $Pb(Zr_{0.52}Ti_{0.48})$ materials was precoated on the sapphire substrate prior to the bonding of the PNN-PZT tapes. Fig. 2a shows the typical SEM microstructure of the thin PZT layer (~0.3 μm), which was spin-coated from metal-organic precursors of Pb, Zr and Ti, pyrolyzed at 450 °C for 1 h and crystallized at 650 °C for 1 h, indicating that the precursors behave very well. Thinner layer (~0.3 μm) of the same materials was then prepared to serve as buffer layer.

The buffer layers were observed to markedly influence the densification behavior of the PNN-PZT taped bonded on sapphire substrates. Fig. 2b indicates that the morphology of the PNN-PZT tapes is greatly improved, when PZT thin films were used as buffered layer. The small voids observed in Fig. 2(b) only present at the surface of the PNN-PZT tapes, such that the top and bottom electrodes are not short-circuited and the tapes exhibit marvelous ferroelectric properties, which will be further discussed shortly.

The densification behavior of the PNN-PZT tapes correlates intimately with the crystallization characteristics of the buffer materials. Fig. 2(c) indicates that PZT buffer layer form small clusters about 1 μm in size. In contrast, other kinds of buffer layers, such as PT or PZ films, coarsen rigorously after heat treatment (not shown) and induce in serious crack for the PNN-PZT thick films. These results infer that large aggregates in the buffer layer will still anchore the PNN-PZT tape materials, resulting in pronounced constraint on the densification of the materials. Only the small PZT clusters can effectively release the constraint of substrate surface during the sintering stage of PNN-PZT tapes.

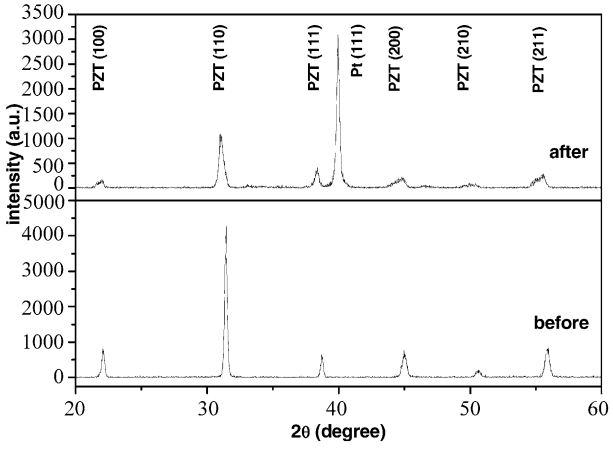

Fig. 3. X-ray diffraction patterns of (a) PNN-PZT tapes transferred to Si-substrate by laser lift-off (LLO) process, PNN-PZT/Si, and (b) PNN-PZT tapes bonded on sapphire before LLO process, PNN-PZT/sapphire.

3.2. Laser lift-off process

Laser lift-off (LLO) technique was then used to transfer the PNN-PZT layers from sapphire to silicon substrates. Both the PNN-PZT/sapphire films and Si-substrate were first precoated with In (1 μm) and Pd (100 nm) thin layers, followed by hot pressing at 200 °C for 30 min under 400 psi to result in hermetically bonding of Si/PNN-PZT/sapphire via the formation of $PdIn_3$ intermetallic layer. The sapphire substrate was then detached from the bonded layers by irradiating the UV laser (248 nm 800 mJ/cm^2) through the sapphire.

The laser irradiated PNN-PZT surface, which was detached from the sapphire substrate, labeled as PNN-PZT/Si, is of perovskite structure, and contains no secondary phases, as shown in Fig. 3. However, the X-ray diffraction peaks of the PNN-PZT/Si are much wider than the original PNN-PZT/sapphire surface. Such a phenomenon inferres the local melting of the buffer layer, which crystallized instaneously during cooling. The microstructure of the laser irradiated surface, shown in Fig. 4(a) and the inset, also confirm occurrence

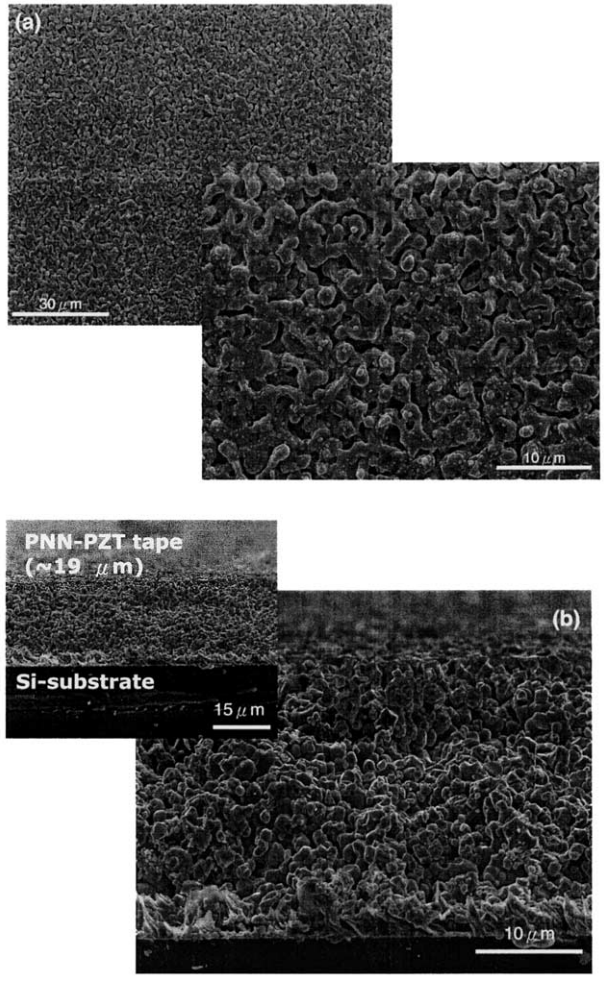

Fig. 4. Typical (a) top view and (b) cross-sectional SEM microstructure of PNN-PZT /Si films, after laser lift-off process.

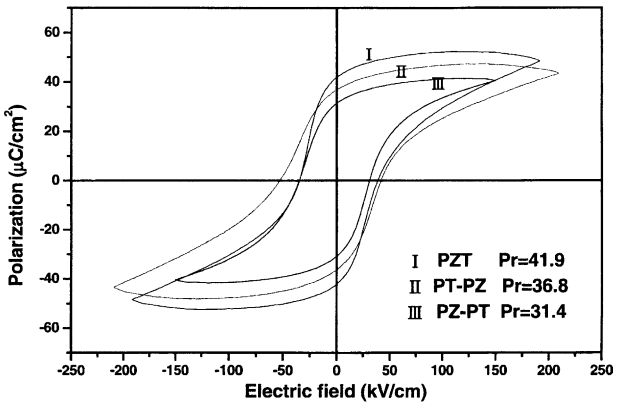

Fig. 5. Ferroelectric hysterics curves of PNN-PZT/Si films after laser lift-off process, using MOD-derived PZT, PT-PZ, or PZ-PT films as buffer layer.

of the partially melting phenomenon. This figure also indicates that the layer in adjacent to the buffered substrate still can not be fully densified, which is most probably owing to constraint mechanism and is in accord with the previous discussion. Such a microstructure does not vary with the nature of the buffer layer used. Cross-sectional micrograph of the LLO samples [Fig. 4(b)] reveals that the PNN-PZT/Si films thus obtained is about 19 μm in thickness and the grains are about 1μm in size. The $PbIn_3$ bonding layer is about 300 nm in thickness.

The ferroelectric properties of the LLO PNN-PZT/Si vary markedly with the buffer layer types. As shown in Fig. 5, the PNN-PZT bonded on PZT-buffered sapphire possess largest remanent polarization, $(Pr)_{PZT} = 41.9$ μc/cm^2, whereas those bonded on other kind of buffer layer show smaller remanent polarization. Apparently, the larger Pr-value for the PZT-buffered thick films can be ascribed to the larger density of the films. Leakage current density for all the LLO PNN-PZT films is very low, implying that porosity appearing on the up-most and bottom-most surface is not interconnected, such that the materials can still exhibit good ferroelectric properties.

4. Conclusion

Effect of buffer layers on the materials characteristics and ferroelectrical properties for relatively-thick (~20 μm) PNN-PZT layers, prepared by doctor-blade tape-casting and the laser lift-off process, were systematically investigated. A large proportion of porosity was observed on the film's surface, regardless of the buffer materials. The constraint on lateral shrinkage of the PNN-PZT layers by the underlying substrates induces the formation of pores on the film's surface. Fortunately, the induction of porosity didn't cause serious current leakage for the PNN-PZT films such that the films, after transferring from sapphire to silicon substrates still possess good ferroelectrical properties. The buffer materials impose marked influence on the ferroelectric behavior of the PNN-PZT layers. The PNN-PZT/Pt/Si thin layers possess larger remanent polarization ($Pr = 41.9$ μC/cm^2) when using MOD-derived PZT as buffer layer.

Acknowledgements

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