Ceramics International 30 (2004) 1539–1542

CERAMICS INTERNATIONAL

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$0.67Pb(Mg_{1/3}Nb_{2/3})O_3$–$0.33PbTiO_3$ thin films derived from RF magnetron sputtering

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Received 19 November 2003; received in revised form 17 December 2003; accepted 22 December 2003

Available online 6 May 2004

Abstract

Lead magnesium niobate–lead titanate ($0.67Pb(Mg_{1/3}Nb_{2/3})O_3$–$0.33PbTiO_3$, PMN–PT) thin films have been successfully deposited on Pt/Ti/SiO_2/Si substrates by RF magnetron sputtering. Annealing at 550 °C led to a well established perovskite structure. The annealed films exhibited well-defined hysteresis loops, with a respective remanent polarization ($2P_r$) of 27.4 μC/cm^2 and coercive field ($2E_c$) of 58.6 kV/cm at an applied electric field of 250 KV/cm at room temperature. A dielectric constant of 947 and a dielectric loss of 3.8% were measured for the PMN–PT thin film at 100 kHz. The annealed films were found to be little fatigue even after 10^{10} number of switching cycles. The ferroelectric properties of these PMN–PT thin films, which are compared favourably with those of PMN–PT thin films via other deposition routes, are accounted for by their structural features.

Keywords: PMN–PT; Ferroelectric thin films; RF magnetron sputtering

1. Introduction

Lead magnesium niobate–lead titanate ($(1-x)Pb(Mg_{1/3}Nb_{2/3})O_3$–$xPbTiO_3$, PMN–PT) thin films have attracted much attention as a candidate material for a number of applications in microelectronics and microelectromechanical systems (MEMS), such as multilayer capacitors, ultrasonic transducers, microsensors and microactuators, owing to their high electric-fields-induced strains, longitudinal coupling coefficients, piezoelectric constants and high dielectric constants coupled with low loss. Integrated microsensors and microactuators based on ferroelectric PMN–PT allow potential performance that is superior to the conventional nonferroelectric piezoelectrics.

Successful deposition of prochlore-free PMN–PT films has been one of the key challenges for PMN–PT thin film applications. Although the Columbite method can be used to prepare powders to obtain pure perovskite PMN–PT bulk ceramics, it is however quite difficult to apply it for PMN–PT thin films. Sol–gel process [1], metalorganic vapour deposition (MOCVD) [2] and physical vapour deposition (PVD) including sputtering [3] and pulsed laser ablation (PLD) [4,5], have been explored for fabrication of PMN–PT ferroelectric films on large-area substrates. Sol–gel processing, spinning on and pyrolyzing the multiple layers for each substrate is time consuming, making it generally unsuitable for large-scale production. Also, the precursors must be carefully selected to avoid toxicity and contamination. Problems may arise with residual stresses in these thin films due to densification and outgassing during annealing at temperature as high as 700 °C [1]. For MOCVD, thin films of PMN–PT were grown at 700 °C [2]. Such a high temperature employed in sol–gel and MOCVD is detrimental to the integration with silicon integrated circuits. Although PLD can lead to PMN–PT thin films of perovskite structure [4,5], it is more suitable for small sample. On the other hand, sputtering deposition is compatible with the standard IC technology and the processing temperature is often lower than those used in many other deposition techniques. Sputter deposition of complex perovskite films is challenging as far as the composition and phase controls are concerned. Few previous studies have been made with PMN–PT films. It is thus of

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doi:10.1016/j.ceramint.2003.12.093

interest to investigate the deposition of PMN–PT thin films with perovskite structure by RF magnetron sputtering and to study their ferroelectric behaviours. In this paper, we explored the formation $0.67Pb(Mg_{1/3}Nb_{2/3})O_3$–$0.33PbTiO_3$ which is close to the morphotropic phase boundary (MPB) on $Pt/Ti/SiO_2/Si$ substrates at room temperature using RF magnetron sputtering. The effects of subsequent annealing at temperatures in the range of 550–750 °C on the resulting electrical properties are investigated.

2. Experimental procedure

The sputtering target consisting of a single $0.67Pb(Mg_{1/3}Nb_{2/3})O_3$–$0.33PbTiO_3$ phase was prepared by the Columbite method from PbO (>99.0% in purity, Fluka), $(MgCO_3)_4\cdot Mg(OH)_2\cdot 5H_2O$ (99.0% in purity, AJAX Chemicals), Nb_2O_5 (99.9% in purity, Fluka), TiO_2 (99.0% in purity, Merck), with 15% excess PbO to compensate the likely PbO loss. Magnetron sputter (Leybold Univex 350) was carried out at an Ar working pressure 10.0–25.0 mTorr, power density of 50 W/cm^2. The deposition time was controlled at 5 h on $Pt/Ti/SiO_2/Si$ substrates. The films were subsequently annealed at various temperatures in the range of 550–750 °C with cover to minimise Pb loss at elevated temperatures. Crystallographic structure and surface morphology of thus derived PMN–PT films were characterised using X-ray diffractometer (X'pert, Philips) and scanning electron microscopy (SEM) (X'pert, Philips). A ferroelectric analyzer (Radiant Technologies) and an impedance analyzer (Solartron SI 1260, UK) were employed to characterize their respective ferroelectric and dielectric behaviours.

3. Results and discussion

3.1. Structure and morphology

Fig. 1 shows the XRD patterns of PMN–PT films annealed at temperatures in the range of 550–750 °C, which are matched with those of PMN–PT bulk. Pyrochlore phase appeared at temperatures greater than 650 °C. While the films annealed at <650 °C exhibited a predominant perovskite phase. The perovskite phase was formed at an annealing temperature as low as 550 °C. The formation temperature is lower than that observed in sol–gel as shown by Park et al. [1], who observed that pyrochlore phase was a dominant phase at a temperature of as low as 700 °C. The PMN–PT films derived from MOCVD by Lee et al. [2] also required a formation temperature of as high as 700 °C.

Fig. 2(a) shows the cross-section of 0.67PMN–0.33PT film annealed at 550 °C. The film thickness is quite uniform along the film length, and it was measured to be ~500 nm. Fig. 2(b) is a SEM micrograph showing surface morphology of the 0.67PMN–0.33PT film. The PMN–PT grains are ~100 nm in sizes and rounded in morphology.

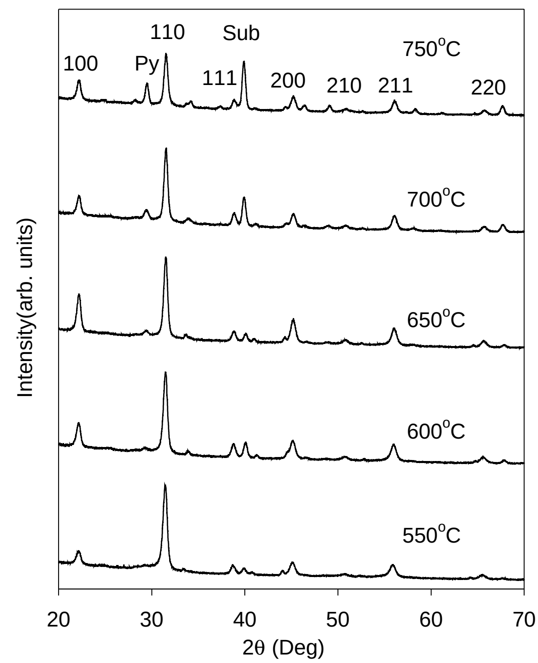

Fig. 1. XRD patterns of 0.67PMN–0.33PT films annealed at different temperatures.

3.2. Electrical properties

Fig. 3 shows the electrical polarization hysteresis loop of PMN–PT thin film at a measurement frequency of 200 Hz, where the polarization versus electric field (*P*–*E*) is plotted for the PMN–PT film annealed at 550 °C. At room

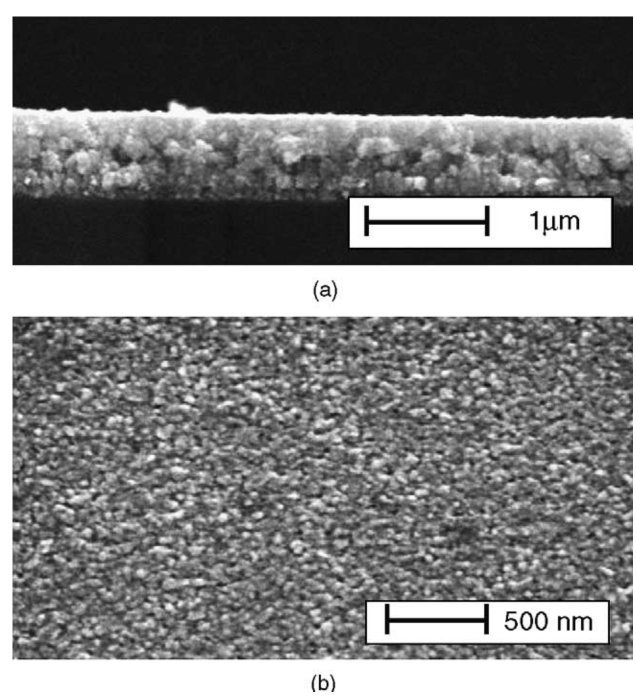

Fig. 2. Fracture cross-section (a) and surface view (b) of 0.67PMN–0.33PT film annealed at 550 °C.

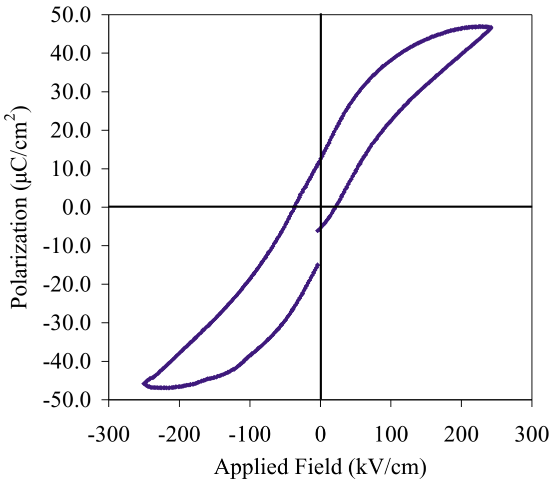

Fig. 3. Polarization vs. electric filed (*P*–*E*) hysteresis loop for 0.67PMN–0.33PT film annealed at 550 °C on $Pt/Ti/SiO_2/Si$ substrate, measured at 200 Hz.

temperature, a remnant polarization ($2P_r$) of 27.4 μC/cm^2 and a coercive field ($2E_c$) of 58.6 kV/cm were measured at 250 kV/cm. The applied electric field cannot be further raised due to the large leakage current at too high a field, while the hysteresis loop is about to saturate at 480 kV/cm. The remnant polarization (P_r) is comparable with that of Donnelly et al. [6], who reported $P_r = 18$ μC/cm^2 for the film prepared by pulsed laser deposition. Compared with the film prepared previously by RF magnetron sputtering, the remnant polarization ($2P_r$) is about twice as that of Jiang et al. [3], who reposted $2P_r = 17.0$ μC/cm^2. At the same time, the coercive filed ($2E_c$) for the PMN–PT film in the present work is about half as that reported by Jiang et al. [3], who reported $2E_c = 92$ kV/cm.

Fig. 4 plots the dielectric constant and dissipation factor for the 0.67PMN–0.33PT film with film thickness 500 nm as a function of frequency at room temperature. It shows that both dielectric constant and the dielectric loss steadily

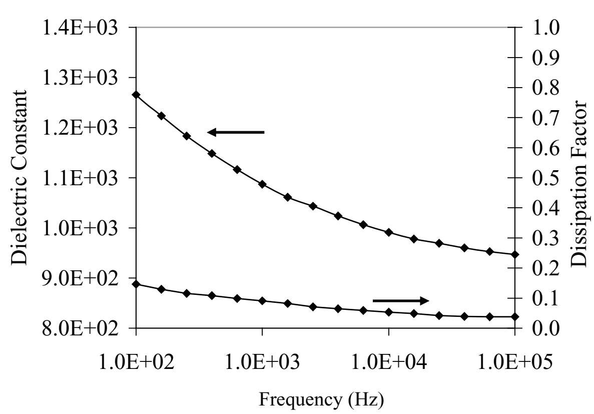

Fig. 4. Dielectric constant and dissipation factor of 0.67PMN–0.33PT film of 500 nm in film thickness as a function of frequency at room temperature.

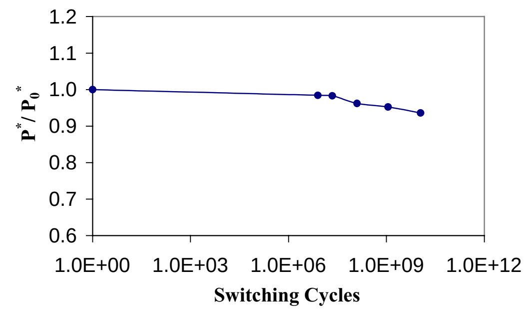

Fig. 5. Fatigue behaviour of PMN–PT thin film of 500 nm in thickness. P^* is the switchable polarization. P_0^* is the switchable polarization of first cycle. The applied voltage is 50 V.

decrease with the increase in frequency. The dielectric constant and loss factors are comparable with those of PMN–PT films prepared by MOCVD [2] and PLD [6]. It is higher than that of Lee et al. [2], who reported a dielectric constant of 600–800 and that of Donnelly et al. [6] who reported a dielectric constant of 500–700. At the same time, the loss factor is smaller than that of Lee et al. [2] (loss factor 0.2–0.4), and is comparable with that of Donnelly et al. [6] (loss factor 0.05–0.45).

The fatigue behaviour of the PMN–PT film annealed at 550 °C is shown in Fig. 5. There occurs a minimal degradation (∼6%) in polarization after 10^{10} number of cycles. When compared with PZT films, which exhibit an apparent fatigue (about 50% decrease in polarization) after 10^9 cycles (Feng et al. [7]), the fatigue resistance of PMN–PT films are much better.

4. Concluding remarks

Lead magnesium niobate–lead titanate ($0.67Pb(Mg_{1/3}Nb_{2/3})O_3–0.33PbTiO_3$) thin films have been successfully prepared by RF magnetron sputtering on $Pt/Ti/SiO_2/Si$ substrates followed by thermal annealing at 550 °C. They exhibit well-defined hysteresis loops, with a respective remanent polarization ($2P_r$) of 27.4 μC/cm^2 and coercive field ($2E_c$) of 58.6 kV/cm at an applied electric field of 250 KV/cm at room temperature. A dielectric constant of 947 and a dielectric loss of 3.8% were measured for the PMN–PT thin film at 100 kHz. PMN–PT thin films are also of little fatigue after 10^{10} switching cycles, which are compared favourably with PZT films.

Acknowledgements

This work is supported by the Science and Engineering Research Council—A*Star, Singapore, under Grant No: 022-107-0007 and the Institute of Materials Research and Engineering (IMRE), Singapore. Authors also acknowledge the support of the National University of Singapore.

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