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Highly (1 1 1)-oriented and pyrochlore-free PMN–PT thin films derived from a modified sol–gel process

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ABSTRACT

Ferroelectric PMN–PT (68/32) thin films, about 250 nm in thickness, have been successfully grown on Pt/Ti/SiO_2/Si substrate by a modified sol–gel process. Pure perovskite phase with highly (1 1 1)-preferred orientation, determined by X-ray diffraction, was formed in the PMN–PT thin films when annealed at 650 °C. The pyrochlore phase has been effectively avoided through a variation of the processing parameters such as Mg content, Mg precursor and annealing temperature during thin film deposition. FE-SEM investigation showed that the films have a smooth and crack-free surface with densely packed grains after annealed at 650 °C. The annealed films exhibited well-defined hysteresis loops, with a respective remanent polarization P_r of 16.1 μC/cm^2 and coercive field E_c of 71.2 kV/cm at an applied electric field of 400 kV/cm at room temperature.

1. Introduction

Over the past few decades, ferroelectric thin films ($(1-x)Pb(Mg_{1/3}Nb_{2/3})O_3$–$xPbTiO_3$, PMN–PT) have received special attention due to many fascinating properties such as their large electric-optic coefficients, longitudinal coupling coefficients, piezoelectric constants and high dielectric constants coupled with low loss [1–3]. It had been proven to be promising materials for high-*k* capacitors, actuators and non-linear optical devices [4,5]. Various techniques, such as rf magnetron sputtering [6], pulsed laser deposition [7,8], sol–gel [9–11] and metalorganic chemical vapor deposition [12], have been used to obtain the PMN–PT film on different substrates. Among these, sol–gel process is an attractive one, with the merits of atom-level homogeneity, easy composition control, good film uniformity and low capital investment. However, as starting materials, alkoxides would make the whole fabricating process more susceptible to temperature and ambient humidity, and must be handled under inert atmosphere. Therefore, the alkoxides of some metals such as Mg and Nb were coordinated using pyridine, alcohol-amine, and metal complex compound became stable. But the addition of complex agent makes it difficult for the control gelation. In order to overcome these problems, we used new raw materials and solvent, thus stable PMN–PT precursor solution can be prepared to allow their handling in air, which makes the operation more convenient.

From the viewpoint of practical application, it is more desirable to fabricate highly oriented and pyrochlore-free PMN–PT thin films on Si substrates than on oxide single crystal substrates in order to fully exploit the well-developed Si semiconductor processing when we consider a new functional device with ferroelectric films. The main problem in PMN–PT on a Pt/Ti/SiO_2/Si substrate is the occurrence of parasitic pyrochlore phase with perovskite phase [8] and the orientation of the film is not easy to control [13], which results in a degradation (pyrochlore) or potentially non-optimal (random orientation) physical performances [14]. Our work has been made to grow highly (1 1 1)-oriented and pyrochlore-free PMN–PT thin films for the purpose of using their superior ferroelectric properties.

In this paper, we explored the formation of 68%$Pb(Mg_{1/3}Nb_{2/3})O_3$–32%$PbTiO_3$ thin film which is close to morphotropic phase boundary (MPB) on Pt/Ti/SiO_2/Si substrates at the room temperature using a modified sol–gel process. The effects of subsequent annealing at temperatures in the range of 550–750 °C on the crystallized phase are investigated. The pyrochlore phase has been effectively avoided by using such a modified sol–gel process and, meanwhile, highly (1 1 1)-preferred orientation has been obtained in the PMN–PT (68/32) thin film. It is important to note that the PMN–PT thin film achieve excellent ferroelectric properties.

2. Experimental

PMN–PT (68/32) films were grown on Pt/Ti/SiO_2/Si substrates with a modified solution method using inorganic magnesium precursor and spin-coating processing. Chemically homogeneous PMN–PT (68/32) sol was synthesized using lead acetate trihydrate, magnesium acetate tetrahydrate, niobium ethoxide, and tetrabutyl titanate as starting materials, 2-methoxyethanol as a as solvent and glacial

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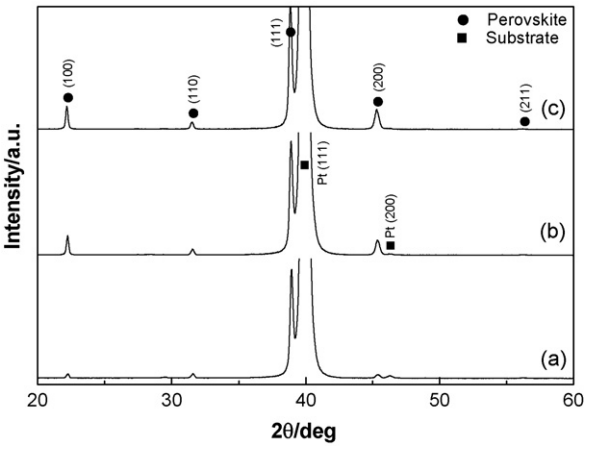

Fig. 1. XRD patterns of PMN–PT (68/32) films as a function of temperature: (a) 550 °C, (b) 650 °C, and (c) 750 °C.

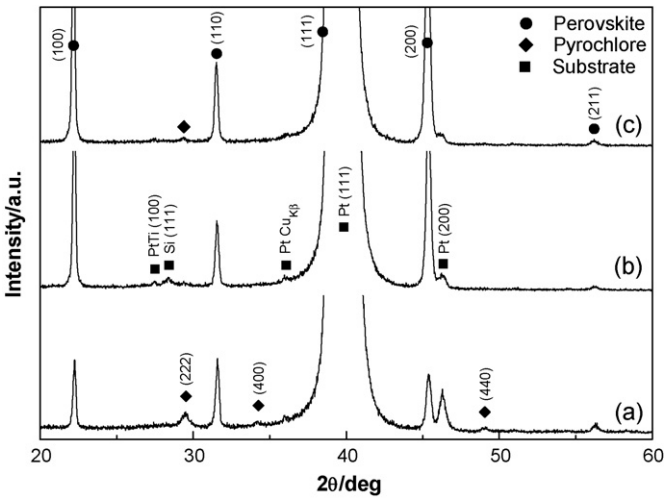

Fig. 2. High-resolution (HR) XRD of PMN–PT (68/32) films as a function of temperature: (a) 550 °C, (b) 650 °C, and (c) 750 °C.

acetic acid as a catalyst. Acetyl acetone as a stabilizing agent was mixed in the Pb–Mg–Nb–Ti solution at 80 °C and stirred for 2 h. Magnesium acetate rather than alkoxide of magnesium [15] was used as magnesium source to prepare stable PMN–PT sol. Thus, the hydrolysis and polymerization reaction is easier to control. A 10 mol% excess Pb solution was added to compensate for any Pb loss, and a 5 mol% excess Mg solution was added to promote the formation of perovskite phase of PMN–PT film. The final concentration of the solution was diluted to 0.4 M. The whole preparation of the precursor solution was preformed in the air. Then PMN–PT layers were deposited by spin coating on $Pt/Ti/SiO_2/Si$ substrates at 4000 rpm for 30 s. After each spin-on deposition, the film was dried at 200 °C for 3 min, and then pyrolyzed at 450 °C for 5 min. The pyrolyzed thin film was received by repeating above processes for 5 times, and finally annealed at 550 °C, 650 °C, 750 °C for 5 min in pure oxygen atmosphere by rapid thermal annealing (RTA), respectively.

The phase of the film and its orientation were analyzed by X-ray diffraction (XRD, Rigaku, D/max-2500/PC). An atomic force microscope (AFM, Digital Instruments, Multi Mode TM SPM) was employed to measure the surface morphology of the PMN–PT thin film. The SEM observations of the thin film were carried out using a field emission scanning electron microscopy (FE-SEM, CamScan, MX-2600). The hysteresis loops of thin film were measured by ferroelectric tester (Precision LC, Radiant Technologies). The 200-μm diameter Pt top electrodes were deposited by electron-beam evaporation methods to characterize the ferroelectric properties.

3. Results and discussion

Fig. 1 shows the XRD patterns of PMN–PT (68/32) film annealed for 5 min at temperatures ranging from 550 °C to 750 °C. The sharp and narrow XRD peaks indicate that the films are highly crystalline and consist of only one PMN–PT compositional phase. The peak at about $2\theta = 38.92°$ is very strong as compared with other peaks, indicating a highly preferential crystal growth along the [1 1 1] orientation.

For the lotgering factor methods the preferential orientation parameter, α_{hkl}, can be calculated by the following formula [16]:

$$\alpha_{hkl} = \frac{I_{hkl}}{\sum I_{hkl}} \quad (1)$$

where I_{hkl} is the relative intensity of the corresponding hkl-diffraction peaks, α_{111} represents the degree of (1 1 1) texture. According to the XRD results in Fig. 1, α_{111} of 550 °C RTA-treated PMN–PT film was about 92%; after being annealed at 650 °C and 750 °C, α_{111} changed from 82% to 80%, revealing the highly (1 1 1)-textured structure in film when deposited on platinized silicon substrate. It was reported that the (1 1 1)-oriented PMN film was preferentially formed due to low interfacial energy, which resulted from the fact that the lattice parameters of Pt(1 1 1) matched closely with those of PMN(1 1 1) [17].

We investigate more precisely the structure of our films by magnifying y-scale in Fig. 1. The spectrum we obtained is shown in Fig. 2, relative to PMN–PT films deposited on $Pt/Ti/SiO_2/Si$ substrates at the annealing temperature range of 550–750 °C. It can be seen that PMN–PT film was mainly perovskite phase and a parasitic pyrochlore phase when annealed at 550 °C, and was crystallized to pure perovskite phase without pyrochlore phase after annealed at 650 °C. However, in the patterns of film annealed at 750 °C, the peaks of a pyrochlore phase appeared again. The presence of a pyrochlore phase in the film annealed at 750 °C is attributable to the more lead loss at an increased temperature. When this volatilization of lead occurs, the deviation on the stoichiometry favors the formation of pyrochlore phase [18].

Fig. 3 shows the surface and cross-section FE-SEM micrographs of PMN–PT (68/32) film. In Fig. 3(a), some small grains are found distributed around other large grains annealed at 550 °C. The microstructure was characterized by a bimodal grain size distribution, containing larger and smaller sized grains, approximately 150–450 and 40 nm, respectively. SEM investigation of surface revealed that the smaller grains were more prevalent on the surface and often covered larger grains. The smaller sizes grains disappeared when annealed at 650 °C, suggesting that the two grain sizes annealed at 550 °C did denote two distinct crystalline phase, i.e. with the temperature increased, the pyrochlore phase gradually transformed into the perovskite phase. The PMN–PT film is smooth and dense after annealed at 650 °C. However, we annealed the thin films at 750 °C, resulting in the smaller sized grains observing again and leading to degradation of the perovskite phase. This is due to further lead loss as annealing temperature increased to 750 °C, resulting in the lead-deficient pyrochlore phase appearing. The cross-section view of the film in Fig. 3(d) shows that the film thickness is quite uniform along the film length, and it was measured to be ~250 nm. As shown in the cross-sectional image, the PMN–PT film exhibited a smooth and crack-free surface, which is composed of densely packed grains. The clear columnar grain growth also demonstrates that the film is well crystallized.

The 2D and 3D AFM images of the (1 1 1)-oriented films annealed at 650 °C are shown in Fig. 4. The shape of grains of the PMN–PT thin film is square or rounded square-like in the (1 1 1)-oriented film as shown in Fig. 4(a). The grain size of this PMN–PT (68/32) film is about 150–450 nm, in agreement with that of the FE-SEM observation. The root mean square roughness (R_{rms}) over scan areas of $5 \times 5\ \mu m^2$ was found to be ~10.7 nm. Fig. 5 shows the typical P–E hysteresis loop for PMN–PT (68/32) film annealed at 650 °C on $Pt/Ti/SiO_2/Si$ substrate with different applied voltages. The polarization and coercive field increase with increasing applied voltage. From this figure it is obvious that the hysteresis loop has good

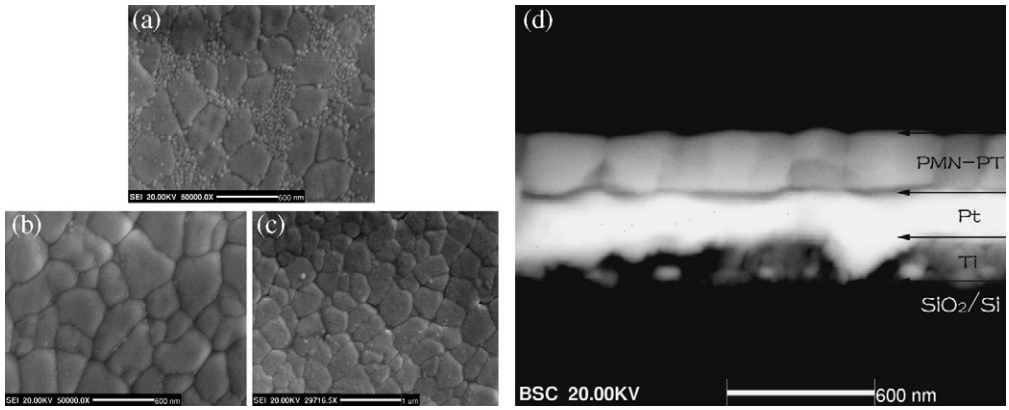

Fig. 3. Surface images of PMN–PT (68/32) film annealed at (a) 550 °C, (b) 650 °C, (c) 750 °C, and (d) cross-section view of film annealed at 650 °C.

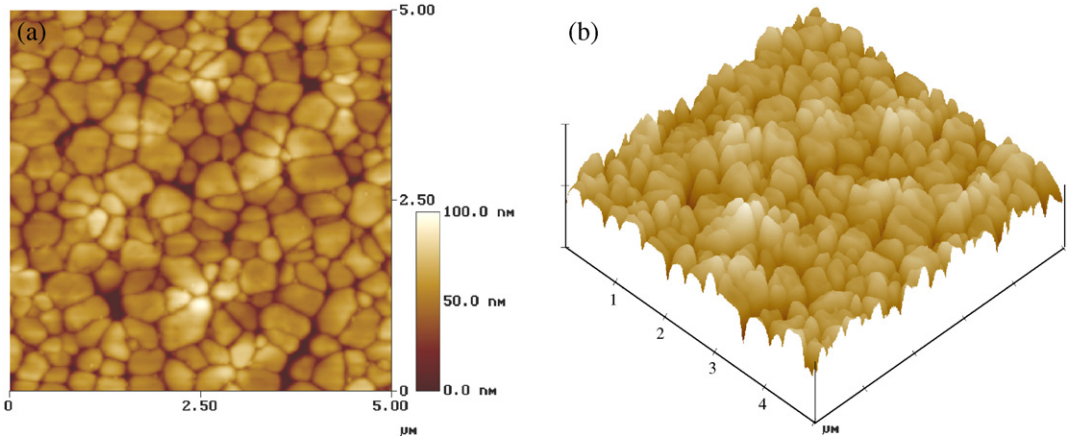

Fig. 4. The (a) 2D and (b) 3D AFM images of the (1 1 1)-oriented films annealed at 650 °C.

symmetry and square shape, with a remanent polarization P_r of 16.1 μC/cm^2 and a coercive field E_c of 71.2 kV/cm at an applied electric field of 400 kV/cm. Compared with the film prepared previously by sol–gel process, the remnant polarization P_r is about twice as that of Shyu et al. [19], who reported P_r = 8.0 μC/cm^2. The remnant polarization P_r is comparable with that of Laha et al. [8], who reported P_r = 16.9 μC/cm^2 for the film prepared by pulsed laser deposition. The remnant polarization P_r of (1 0 0)-oriented PMN–PT films is 3 μC/cm^2 on Pt/Ti/SiO_2/Si substrates [20], and 2 P_r of 29.8 μC/cm^2 annealed at 700 °C on LSMO/LAO single crystal substrates while on Pt/Ti/SiO_2/Si substrates with a very small switchable polarization by chemical solution deposition [21]. This implicated that the proposed sol–gel technique using inorganic magnesium precursor had considerable potentiality in fabricating highly (1 1 1)-oriented PMN–PT films with improved properties.

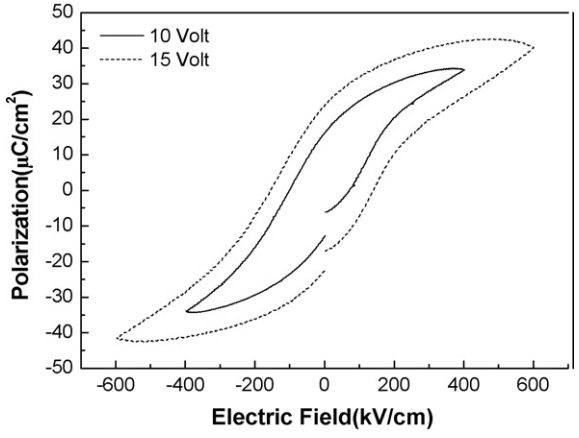

Fig. 5. Polarization vs. electric field (*P*–*E*) hysteresis loops for PMN–PT (68/32) film annealed at 650 °C on Pt/Ti/SiO_2/Si substrate with different applied voltages.

4. Conclusions

We have grown high quality and highly oriented single perovskite PMN–PT (68/32) thin film by a modified sol–gel process on Pt/Ti/SiO_2/Si substrates using inorganic magnesium precursor with magnesium acetate rather than the costly magnesium ethoxide. The post-annealing temperature was found to show great impact on the phase impurity and surface morphology of PMN–PT film. The PMN–PT films of 250 nm thick were well crystallized to perovskite phase, and exhibited highly (1 1 1)-preferred orientation (texture degree α > 82%) when annealed at 650 °C. The PMN–PT films showed a smooth and dense surface after annealed at 650 °C. The ferroelectric hysteresis loop has good symmetry and square shape, with a remanent polarization P_r of 16.1 μC/cm^2 and a coercive field E_c of 71.2 kV/cm.

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