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Effects of annealing temperature on structure and electrical properties of sol–gel derived 0.65PMN-0.35PT thin film

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ABSTRACT

0.65Pb($Mg_{1/3}Nb_{2/3}$)O_3-0.35$PbTiO_3$ (0.65PMN-0.35PT) thin films were deposited on Pt/Ti/SiO_2/Si substrates annealed from 550 to 700 °C using sol-gel process. The effects of annealing temperature on microstructure, insulating, ferroelectric and dielectric properties were characterized. The result reveals that 0.65PMN-0.35PT thin films possess a polycrystalline structure, matching well with the perovskite phase despite the existence of a slight pyrochlore phase. The film samples annealed at all temperatures exhibit relatively dense surfaces without any large voids and the grain size increases generally with the increase of the annealing temperature. Meanwhile, pyrochlore phase is considerably generated because of the deformation of perovskite phase caused by volatilization of Pb at an excessive high-temperature. The film annealed at 650 °C exhibits superior ferroelectricity with a remanent polarization (P_r) value of 13.31 μC/cm^2, dielectric constant (ε_r) of 1692 and relatively low dielectric loss (tanδ) of 0.122 at 10^4 Hz due to the relatively homogeneous large grain size of 130 nm and low leakage current of approximately 10^{-6} A/cm^2.

1. Introduction

Relaxor ferroelectrics (FEs), such as Pb($Mg_{1/3}Nb_{2/3}$)O_3 (PMN) materials, have attracted much attention since they were first discovered in 1950's [1]. Relaxor FEs, in contrast to conventional Fes like $PbTiO_3$ (PT), are characterized by the suppression of long-range ordering of the spontaneous polarization and the dielectric behaviors are derived from localized polar nano-regions [2]. In the vicinity of morphotropic phase boundary (MPB), where relaxor-based FEs undergo a structural transition induced by changes in chemical composition, large dielectric responses and exceptional electromechanical properties can be observed. For solid-solutions single crystal of the prototypical relaxor FE, such as Pb($Mg_{1/3}Nb_{2/3}$)O_3 with the normal FE $PbTiO_3$ (PMN-PT), superior electrical properties including a high piezoelectric coefficient (d_{33}) of 2800 pC/N, electromechanical coupling coefficient of 90% and large dielectric permittivity of over 8000 have been reported [3]. These remarkable electrical properties show maximum values around MPB with the composition of 33-35% $PbTiO_3$ at room temperature [4]. As reported that, many researchers have found the superior electrical properties of PMN-PT thin film with the composition around MPB. Zhu et al. [5] prepared a 12-μm PMN-PT(65/35) thick film on Pt/Ti/SiO_2/Si substrates at 650 °C by spin-coating. With this technique, a high quality PMN-PT thick film was obtained, showing a dielectric constant (ε_r) of 3300 and dielectric loss (tanδ) of 0.02 at 1 kHz. Arai et al. [6] deposited a layer of PMN-PT(65/35) thin film on $LaNiO_3$/Si substrate and a high d_{33} of about 200 pm/V has been obtained.

As known to all, PMN-PT thin film can be prepared by various methods including sputtering deposition [7], pulsed laser deposition [8], metalorganic chemical vapor deposition [9], as well as chemical solution deposition [6]. Among these techniques, chemical solution deposition, especially for sol-gel processing, offers some advantages over other methods in terms of low-temperature preparation, uniform structure, ability to coat large area and complex-shaped substrate, as well as cost effective and simple [10]. This in turn lead to an appropriate method of obtaining PMN-PT thin film on Si substrate as industrial uses. Especially, in the process of thin film preparation, annealing temperature is an important parameter for the layer-by-layer

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rapid thermal annealing method and an appropriate annealing temperature can reduce the porosity and internal stress of thin film, which can therefore promote the growth of crystal nucleus and improve the quality of the crystalline [11].

In this paper, on the base of the previous working results, $0.65Pb(Mg_{1/3}Nb_{2/3})O_3$-$0.35PbTiO_3$ (0.65PMN-0.35PT) thin film was selected to be prepared under the annealing temperatures of 550, 600, 650 and 700 °C on Pt/Ti/SiO_2/Si substrates. The effects of annealing temperature on crystallinity, surface morphology, leakage current, ferroelectric and dielectric properties of PMN-PT thin films are investigated systematically.

2. Experiment

0.65PMN-0.35PT precursor solution was prepared by sol–gel method. The 0.65PMN-0.35PT sol-gel solution was synthesized from starting materials of lead acetate trihydrate [$Pb(CH_3COO)_2{\cdot}3H_2O$], magnesium acetate tetrahydrate [$Mg(CH_3COO)_2{\cdot}4H_2O$], niobium ethoxide [$Nb(OCH_3CH_2)_5$] and tetrabutyl titanate [$Ti(C_4H_9O)_4$]. 10 mol% excess Pb solution was added to compensate for Pb loss and 5 mol% excess Mg solution was added to promote the formation of perovskite phase [12]. 2-methoxyethanol and glacial acetic acid are taken as solvent and catalyst, respectively. Acetyl acetone as a stabilizing agent was mixed in the Pb–Mg–Nb–Ti solution. The concentration of the 0.65PMN-0.35PT solution was diluted to 0.4 mol/L. Subsequently, the 0.65PMN-0.35PT layers were firstly deposited by spin coating on Pt/Ti/SiO_2/Si substrates at 2000 rpm for 9 s and then the speed of spin coating was increased to 4000 rpm for 30s. After each spin-on deposition, the film was dried at 220 °C for 3 min to evaporate the solvent in the solution, and then pyrolyzed at 450 °C for 5 min. The 0.65PMN-0.35PT films were finally annealed at 550, 600, 650, and 700 °C, respectively for 5min in air by rapid thermal annealing (RTA), respectively. All these processes were repeated 5 times to obtain the film thickness of around 470 nm. Au top electrodes were deposited on the films using a sputtering system through a shadow mask with a diameter of 500 μm for the electrical measurements [13]. The crystal structure of the films was characterized by X-ray diffraction (XRD) using a Bruker D8 diffractometer with Cu-Kα radiation in the 2θ range of 20-60° with step size of 0.05 at RT. The surface morphologies of the films were examined by a scanning electron microscope (SEM)(JSM-6380LA). A standard ferroelectric tester (Precision Pro. Radiant Technologies) was used to measure the polarization–electrical field (P–E) hysteresis loops and leakage current. The Impedance Analyzer (HP4294A) was used to test the dielectric properties of film samples.

3. Results and discussion

Fig. 1 shows X-ray diffraction patterns of 0.65PMN-0.35PT thin films annealed at temperatures ranging from 550 to 700°C scanned in the range of 2θ=20-60°, respectively. It can be noted that all the film samples possess similar structure without any preferential orientation, indicating the polycrystalline nature. Along with perovskite phase, a certain pyrochlore peak around 2θ=30° can be noticed. This can be partly attributed to the fact that the bottom electrode-Pt has a large lattice mismatch with 0.65PMN-0.35PT, which may lead to the generation of pyrochlore phase along with perovskite structure. With the annealing temperature increasing from 550 to 650 °C, the samples exhibit pyrochlore intensity with an obvious reduced tendency while the intensity is increased till 700 °C. As further increasing from 550 to 650 °C, enough energy can be provided for pyrochlore phase to be transformed into perovskite phase. However, till 700 °C, the intensity of the pyrochlore peak is considerably increased again because of the deformation of perovskite phase caused by volatilization of Pb and Mg during the high-temperature thermal treatment.

For clarity, the XRD patterns in the 2θ ranges of 21-23° were shown in Fig. 1(b) to explore the effects of annealing temperature on the crystallinity of 0.65PMN-0.35PT thin film. With the annealing temperature increasing, the intensity of (100) peak is considerably increased while the full width at half maximum (FWHM) is decreased. It indicates that higher temperature can improve the crystallinity and favors the grain growth of 0.65PMN-0.35PT thin film.

An evident change of surface morphology for 0.65PMN-0.35PT thin films annealed at various temperatures (550-700 °C) are investigated as shown in Fig. 2. Through all the SEM images, it can be observed that the film samples annealed at all temperatures exhibit relatively dense surfaces without any large voids and the grain size increases generally. With the increase of temperature from 550 to 650 °C, the grain size exhibits an obvious tendency of increase. The phenomenon that big grains are surrounded by a certain amount of small grains, which can be related to the non-uniformity of nucleation and grain growth with the annealing temperature increasing disappears gradually [14]. Meanwhile, the surface tends to possess homogeneous feather. Whereas, for the film annealed at 700 °C, along with the grain growth, large cracks come into our sight, which can leave bad effects on its performance.

In order to evaluate the grain size distribution quantitatively, we

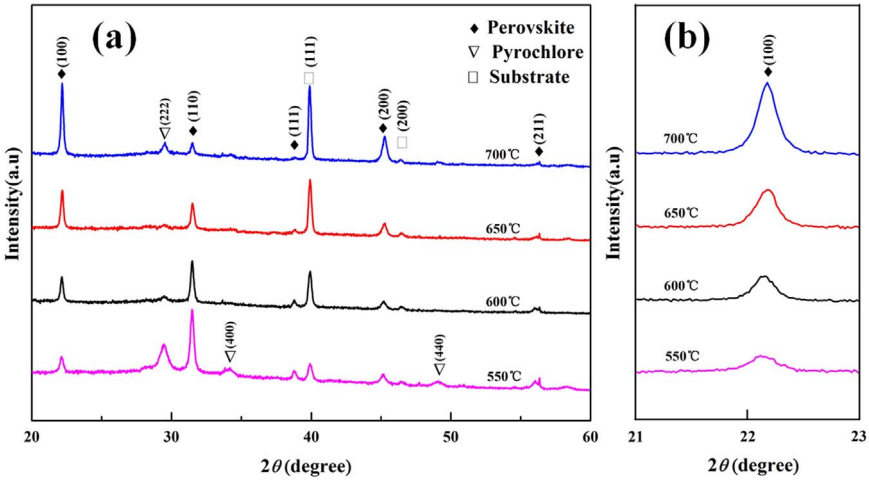

Fig. 1. (a) XRD patterns of 0.65PMN-0.35PT thin films annealed at temperatures ranging from 550 to 700 °C. (b) Magnified XRD patterns of 0.65PMN-0.35PT thin films in the vicinity of 2θ=21-23°.