

Characterization of PT ferroelectric thin films on porous silica for pyroelectric IR detectors

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Abstract Ferroelectric PbTiO_3 thin films were deposited on Pt/DS/PS/ SiO_2 /Si substrates by sol–gel technique. Porous silica (PS) thin film was used as thermal-insulation layer and dense silica (DS) thin film was a buffer layer to reduce surface roughness of PS layer. Root mean square surface roughness can be effectively reduced from 9.7 to 3.5 nm after PS buffer layer was prepared. The average grain size of PT thin films decreased slightly with increasing thickness of porous silica. Dielectric constant of PT increased from 107 to 171 at 1 KHz as thickness of PS layer increased from 0 to 2,000 nm. PT thin film prepared on 2,000 nm porous silica exhibited good dielectric property. The leakage current density was less than 1.6×10^{-6} A/cm² when the applied electrical field was 200 kV/cm. The composite film is suitable for preparing pyroelectric IR detectors.

Keywords Ferroelectric · Pyroelectric IR detector · Porous silica · Thermal-insulation

1 Introduction

Pyroelectric infrared (IR) detector is based on the temperature-induced change of spontaneous polarization. Compared with photon IR detector, pyroelectric thermal detector can be used under room temperatures and is sensitive in the 8 to 14 μm far infrared wavelength band. Therefore, studies on ferro-

electric materials for pyroelectric detection of IR radiation have become an attractive technological activity in the past decade. Lead titanate (PT) is a very good candidate of pyroelectric material. And PT thin films are more attractive than PT ceramics because they are possible to be integrated into standard silicon chip fabrication process [1–4].

However, the low detectivity of the thin film IR detectors due to the heat conduction from the pyroelectric thin film to Si substrate is a big problem. To solve this problem, many thermal-insulation structures such as suspended air-gap structures, micro-bridge structures and porous silica layers have been proposed and studied [3–6]. Porous silica film as a thermal insulation film has a lot of advantages compared with other thermal-insulation structures [7], including simple fabrication, high reliability, and compatibility with CMOS technology.

In this paper, a multilayer PT pyroelectric thin film with porous silica as thermal-insulation layer and dense silica as a buffer layer reducing surface roughness and improving dielectric response has been studied. Sol–gel method was employed to fabricate porous silica, dense silica, and PT layers. Platinum and gold electrodes were deposited by DC-sputtering. The dielectric response and leakage current of PT prepared on porous silica with various thicknesses have been investigated.

2 Experimental

The composite multilayer samples were prepared on SiO_2 /Si substrate and consist of five layers, including porous silica (PS) thin film, dense silica (DS) thin film, Pt bottom electrode, PbTiO_3 (PT) ferroelectric thin film and

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Au top electrode, which were deposited layer by layer using sol–gel method.

Porous silica thin film was prepared by sol-gel method with tetraethyl orthosilicate (TEOS), deionized water (H_2O), and glycerol alcohol ($C_3H_5(OH)_3$) as raw materials and ammonia ($NH_3 \cdot H_2O$) as catalyst. Those raw materials were mixed together by magnetic stirring. An aqueous solution of poly-vinylacetate (PVA) was added into the silica precursor solution to promote the formation of porous structure. In order to achieve thick porous films, the PVA solution was concentrated at $60^\circ C$ to adjust its viscosity. The thickness of the porous film can be effectively controlled by the viscosity of precursor solution. The silica sol was spin-coated onto Si wafer at 3,000 rpm for 30 s. After coating, the film was annealed at $550^\circ C$ for 1 h. Porosity of the porous silica thin films fabricated by this method was about 60% [7].

Dense silica film was fabricated in the same way with TEOS, H_2O , C_2H_5OH as raw material but using HCl as catalyst.

PT thin films were fabricated by sol–gel method where the precursor solution was prepared by reacting lead acetate trihydrate with tetrabutyl titanium using ethylene glycol monomethyl ether as a solvent, and acetylacetonate as a stabilizing agent. PT sol was spin-coated on Pt/DS/PS/SiO₂/Si substrate at 3,000 rpm for 20 s. Then the wet film was pyrolyzed at $500^\circ C$ for 20 min to remove organics. To get required thickness, the deposition process was repeated for ten times. Then, the resultant film was annealed at $600^\circ C$ for 1 h.

In order to test the dielectric properties of PT films, Pt bottom electrode and Au top electrode (1 mm diameter) were deposited by DC-sputtering.

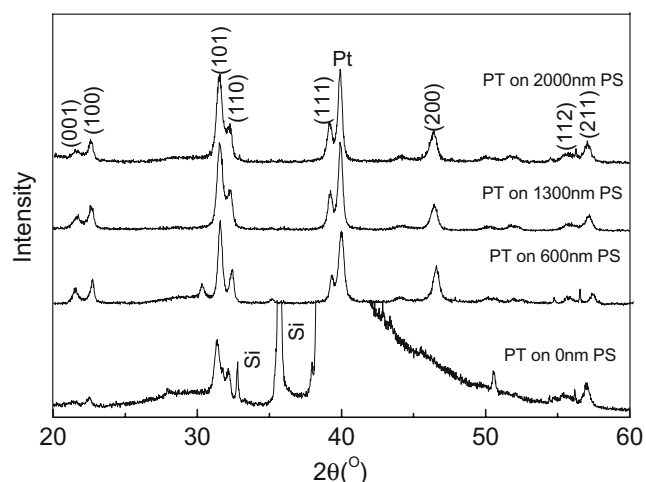


Fig. 1 XRD patterns of PT thin films on 0, 600, 1,300 and 2,000 nm porous silica films

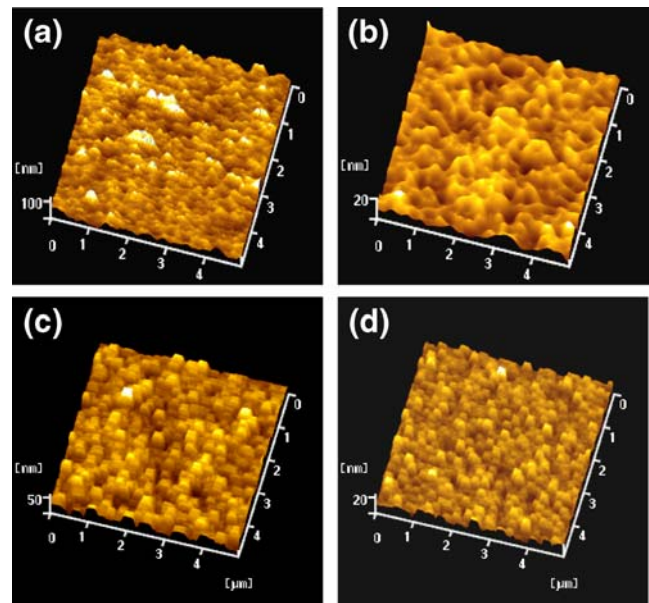


Fig. 2 AFM surface morphology of different functional layers: (a) porous silica on SiO₂/Si; (b) dense silica on PS/SiO₂/Si; (c) Pt on DS/PS/SiO₂/Si; (d) PT on Pt/DS/PS/SiO₂/Si

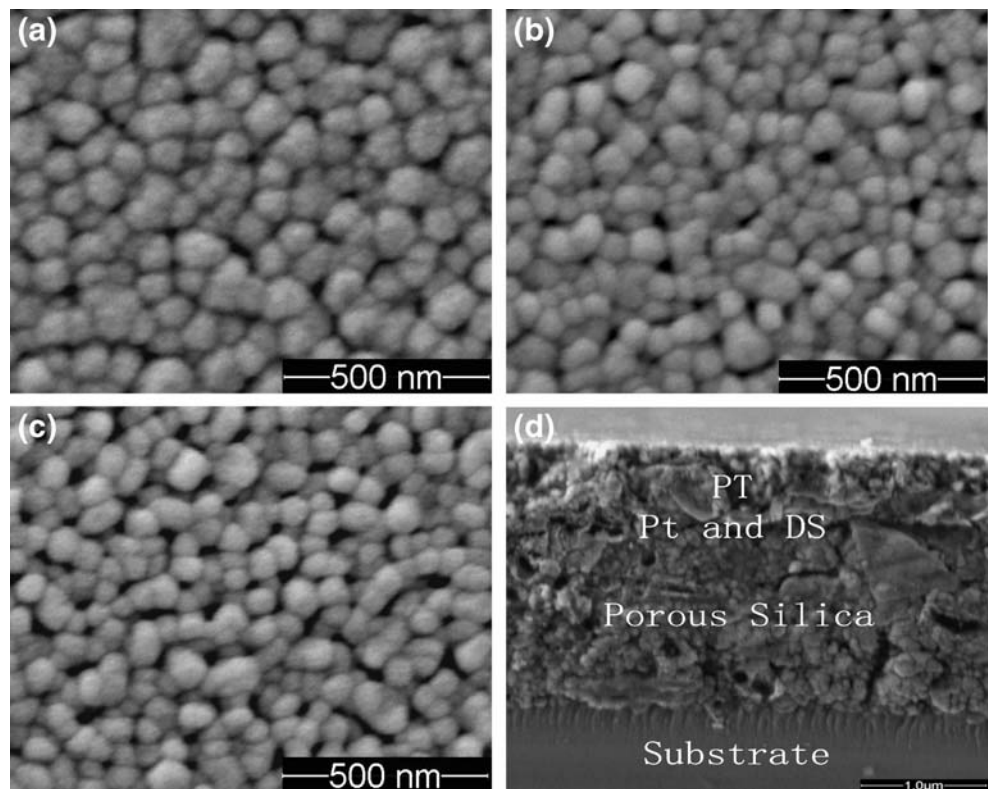
An optical interferometer (F20 filmetrics) was employed to measure the thicknesses of porous silica, dense silica, and PT films. Samples with various thicknesses of porous silica, 0, 600, 1,300, and 2,000 nm, were prepared for investigation. The thickness of dense silica and PT films were 170 and 500 nm, respectively. The crystal structure of thin films was studied by a D8 advanced X-ray diffractometer (XRD) with Cu K α radiation. Atomic force microscope (AFM) and field emission scanning electron microscope (FESEM) were used to investigate the surface morphology and cross section of the films. A HP4284A LCR meter was used to measure dielectric properties of PT thin films. Leakage current was measured by a Keithley 6517A picometer.

3 Results and discussions

Figure 1 shows XRD patterns of PT thin films deposited on porous silica of various thicknesses. All the four samples are characterized as pure perovskite phase with no detectable pyrochlore phase. The doublets of (100)/(001) and (101)/(110) peaks revealed the tetragonal structure of the films [8, 9]. It suggests that the PT thin films are ferroelectrics as well as pyroelectrics at room temperature.

The surface morphology of different functional layers is shown in Fig. 2 revealing the very rough surface of porous silica. In order to deposit other functional layers overlaying on it, a 170 nm-thick dense silica thin film was prepared

Fig. 3 FESEM micrographs of PT thin films (a) on 0 nm; (b) 1,300 nm; (c) 2,000 nm porous silica films and (d) cross section of PT thin films on 2,000 nm porous silica film



as a buffer layer. The root mean square (RMS) surface roughness decreased from 9.7 to 3.5 nm after DS layer was deposited. However, RMS surface roughness of Pt deposited on DS/PS/SiO₂/Si increased to 6.4 nm. It may be attributed to the cluster formation of Pt during sputtering. After ten-layer PT films deposited, RMS surface roughness was 3.1 nm and it was larger than other reports [10].

Figure 3(a–c) shows the FESEM micrographs of PT prepared on 0, 1,300 and 2,000 nm PS films respectively. The average grain size decreased slightly with increasing thickness of porous silica thin film. All the three films were crack free, dense and smooth. Nevertheless, PT prepared on 0 and 1,300 nm PS were denser and smoother than on 2,000 nm PS. Figure 3(d) shows the cross section of PT prepared on 2,000 nm PS indicating a well-crystallized, dense and void-free structure composed of granular grains in PT thin film and there were pores of different sizes in porous silica layer. Pt and dense silica layer cannot be seen clearly due to the diffusion among different layers.

Frequency dependence of dielectric constant and dielectric loss of PT thin films prepared on 0, 600, 1,300 and 2,000 nm porous silica is shown in Fig. 4. Dielectric constant of PT increased from 107 to 171 with an increase of the thickness of porous silica from 0 to 2,000 nm at 1 kHz. Since the PT layer was very rough, which was confirmed by AFM and FESEM, the area of Au electrode

may become larger compared with electrode prepared on even PT layer. Dielectric constant of PT thin films was calculated from

$$\epsilon_r = \frac{Cd}{\epsilon_0 A} \tag{1}$$

Where ϵ_0 , A , d , and C were the vacuum dielectric constant, electrode area, film thickness and measured

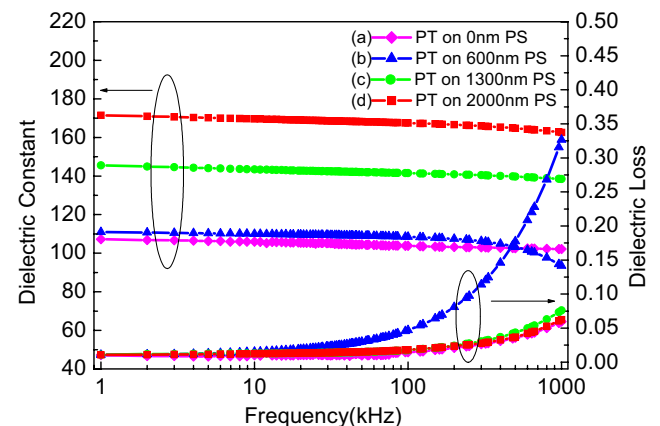


Fig. 4 Dielectric constant and dielectric loss as functions of frequency for PT thin films on 0, 600, 1,300 and 2,000 nm porous silica films

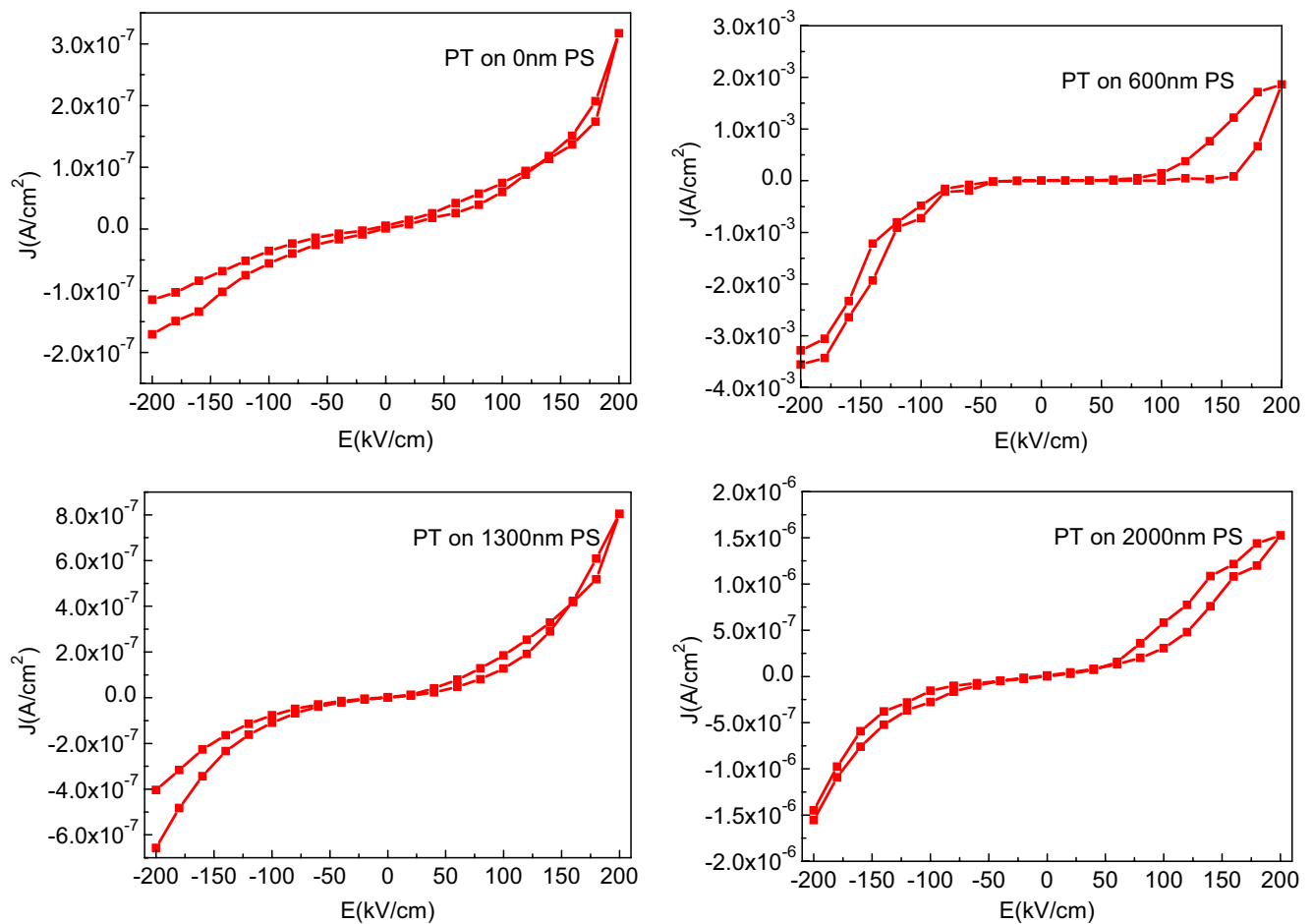


Fig. 5 J–E characteristics of PT thin films on 0, 600, 1,300 and 2,000 nm porous silica films

capacitance, respectively. Therefore improvement in dielectric constant may be caused by the larger electrode area which was supposed to be 1 mm in diameter. Furthermore, stress due to lattice and thermal misfit between PT film and substrate can influence dielectric constant as well [11–13]. Further studies were needed. The dielectric loss of PT prepared on porous silica layer is in the range of 0.02 at room temperature and 10 KHz, which is a little higher than that of the films deposited on silicon substrates.

Figure 5 shows the leakage currents of the four samples. The reverse currents in the negative voltage region were different from the forward currents in the positive bias region especially for PT on 600 nm PS. It may be due to the top Au/PT interface and the bottom PT/Pt interface [14, 15]. Except for PT on 600 nm PS, the leakage current density were lower than 1.6×10^{-6} A/cm² under an applied electrical field of 200 kV/cm and decreased as the thickness of porous silica decreased. The leakage current of samples deposited onto 600 nm PS was much higher than that of the

other three. This is probably due to macro preparation defects of the sample.

4 Conclusion

PT ferroelectric thin films were fabricated on Pt/DS/PS/SiO₂/Si substrates with various thicknesses of porous silica films. It can be summarized that PT thin films are pure perovskite phase with no secondary phase. Dense silica prepared on porous silica can effectively reduce the RMS surface roughness from 9.7 nm to 3.5 nm. The average grain size of PT thin films decreased slightly with increasing thickness of porous silica layer. Dielectric constant of PT thin films increased from 107 to 171 at 1 kHz as thickness of porous silica increased from 0 to 2,000 nm. Leakage current density of PT on 0, 1,300 and 2,000 nm porous silica is below 1.6×10^{-6} A/cm² under electrical field of 200 kV/cm. PT thin film prepared on 2,000 nm porous silica exhibited good dielectric property

and low leakage current and this makes it suitable for the preparation of pyroelectric IR detectors.

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