Ceramics International 30 (2004) 1843–1846
CERAMICS INTERNATIONAL
www.elsevier.com/locate/ceramint

Preparation and characterization of thick porous SiO_2 film for multilayer pyroelectric thin film IR detector

Liang Li*, Liangying Zhang, Xi Yao

Functional Materials Research Laboratory (FMRL), Tongji University, Shanghai 200092, China

Received 4 December 2003; received in revised form 18 December 2003; accepted 22 December 2003

Available online 30 April 2004

Abstract

Porous SiO_2 film is used as a thermal-insulation layer to block the diffusion of heat flow from the pyroelectric layer to the silicon substrate in multilayer pyroelectric thin film IR detector. It is important that porous SiO_2 film is uniform, smooth, crack-free, thick and high porosity in order to integrate other films to make IR detector having high specific detectivity (D^*). In this paper, thick porous SiO_2 film is prepared via sol–gel method with tetraethyl orthosilicate (TEOS), H_2O, $C_3H_5(OH)_3$, $NH_3{\cdot}H_2O$ as precursors. The thickness and refractive index of porous SiO_2 film are measured by Thin film Measurement System (Model: Filmetrics, F20). The surface condition is measured by Atomic Force Microscopy (Model: DI, Nano-scope III) and the Scanning Electron Microscopy (Model: JEOL, JSM-5510). Experiment results show that the thickness of porous SiO_2 film up to 3 μm can be obtained. Porosity of the film up to 59% and nanometer size pore can be achieved by one spin coating after annealed at 550 °C for 30 min. The surface roughness of porous SiO_2 thick film is about 7.25 nm. The thick porous SiO_2 film is smooth and crack-free. The electrical properties of thick porous SiO_2 film are also measured.

Keywords: B. Porosity; C. Electrical properties; Sol–gel; Porous SiO_2 film; Thermal-insulation layer; Thickness

1. Introduction

There is a great interest of porous SiO_2 film due to its many applications. Porous SiO_2 film is used in ultra large-scale integrated circuit (ULSI) as low dielectric layer to reduce the RC signal delay [1]. Porous SiO_2 film is also utilized as planar wave-guide film and low reflective coating where the refractive index is controlled by adjusting the porosity of film [2]. Porous SiO_2 film has potential applications in selective separation, adsorption of chemical or bio species as well as chemical sensing [3].

In this paper, we engaged porous SiO_2 film as a thermal-insulation layer to avoid the heat flow diffused from the sensing element to the substrate in a multilayer pyroelectric IR detector. Compared to the current thermal-insulation structures include cantilever or suspended air-gap structures and micro-bridge structures obtained using Si micro-machining, porous SiO_2 film thermal-insulation layer has many advantages such as simple fabrication process, high reliability, good packaging, cost-effective, compatibility with CMOS technology [4].

According to the heat conduction theory, the heat flow of material is inversely proportional to its thickness, i.e., the thicker the porous SiO_2 film, the better is the thermal-insulating effect. As a thermal-insulation layer, it is important that thick porous SiO_2 film must have high porosity to assure its low thermal conductivity.

We employed sol–gel method to prepare thick porous SiO_2 film with high porosity. Usually, both hydrolysis and condensation of TEOS in the sol–gel method may occur by acid- and base-catalysis reaction. As high shrinkage inherent in the acid-catalysis process produces tensile stresses, it is very difficult to fabricate crack-free films with high porosity beyond 1 μm in thickness [5]. The traditional base-catalysis process may obtain a film with a porosity of 25% and a thickness of 300 nm [6]. Only a few articles have reported the processing of porous SiO_2 films.

The objective of this paper is to fabricate thick porous SiO_2 film with high porosity, which is suitable to act as the thermal-insulation layer of multilayer pyroelectric thin film detector. The intrinsic properties of porous SiO_2 film is characterized.

* Corresponding author. Tel.: +86-21-65980544; fax: +86-21-65985179.
E-mail address: liliang@fmrl.ac.cn (L. Li).

0272-8842/$30.00 © 2004 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
doi:10.1016/j.ceramint.2003.12.059

2. Experimental

A sol–gel method was employed for the preparation of porous SiO_2 film with tetraethyl orthosilicate (TEOS), H_2O, $C_3H_5(OH)_3$, $NH_3{\cdot}H_2O$ as precursors. In first step, TEOS was mixed and strongly stirred with water and glyceryl alcohol at room temperature under $NH_3{\cdot}H_2O$ catalysis. After hydrolysis and condensation reactions for 3 h, a relatively stable sol solution was obtained. In the second step, porousifier was mixed with the above SiO_2 sol. Then the mixed sol and polymer solution was spun onto the p-type Si(1 0 0) wafer at 3500 rpm for 15 s. After coating, the film was annealed at 550 °C for 30 min.

The thickness and refractive index of porous SiO_2 film were measured by thin film measurement system (Model: Filmetrics F20, USA). F20 measured either reflecting or transmitting light through the thin film sample, and then analyzed this light over a range of wavelength. The characteristics of film can derived from analysis of light. A differential thermal analysis (DTA/TG) (Model NETZSCH STA449C) was also performed for the SiO_2 gels to investigate their thermal decomposition behavior. The TG measurements were carried out in flowing air with a heating rate of 10 °C/min up to 550 °C. The chemical species and chemical bonding state were investigated using a Fourier transform-infrared spectroscopy (FT-IR). Dielectric properties of porous SiO_2 film were checked by a HP4284a LCR meter. The surface condition was measured by an atomic force microscopy (Model: Nano-scope III) and a scanning electron microscopy (Model: JEOL, JSM-5510).

3. Results and discussion

Fig. 1 shows the reflectance spectrum of porous silica film measured and calculated by F20. The calculated reflectance spectrum matches as closely as possible with the measured spectrum. Analyzing those two spectrums, F20 determines that the thickness of porous SiO_2 film is 3070 nm. Fig. 2 shows that the refractive index of porous silica film is 1.189 when measured at wavelength 632.8 nm. According to the extended Lorenta-Lorenz effective medium equation, the porosity, P, of a film can be obtained by:

$$P = \frac{(n_{f0}^2 - n_b^2)(n_a^2 + 2n_b^2)}{(n_{f0}^2 + 2n_b^2)(n_a^2 - n_b^2)}$$

Where n_{f0}, n_b and n_a are refractive indexes of the film without adsorbed water, the dense film without pores and air (=1), respectively [7]. Using this formula, the porosity of 59% of the SiO_2 film has been achieved.

The using of porousifier is a predominant factor to get thicker SiO_2 film with higher porosity. The SiO_2 sol particles are coated by porousifier because of the existence of hydroxyl groups in both the porousifier and the SiO_2 sol particles. The porousifier forms a single molecular layer around the SiO_2 sol particles. This coating avoids further aggregation between particles and effectively restricts the growth of the sol particles. The coated particles also attract each other by Van der Waals forces. The interaction between the hydrogen bond and the Van der Waals force disperses uniformly the coated SiO_2 particles in the solution. This will create a uniform internal stress distribution. It will be possible to get a crack-free thicker film.

The TG curves of the SiO_2 gel solution with and without porousifier are shown in Fig. 3. It is can been seen from the curve that the SiO_2 gel solution with porousifier exhibits two steps weight loss. One distinct weight loss step occurs in the temperate range below 120 °C, and a shallow weight loss step follows in temperature range below 230 °C. The SiO_2

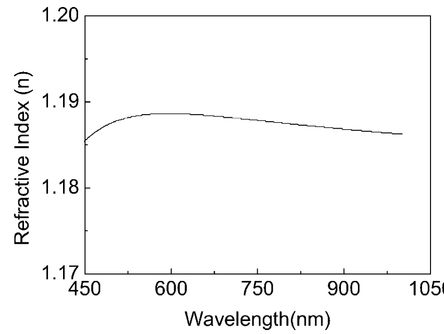

Fig. 2. Refractive index of porous SiO_2 film vs. wavelength.

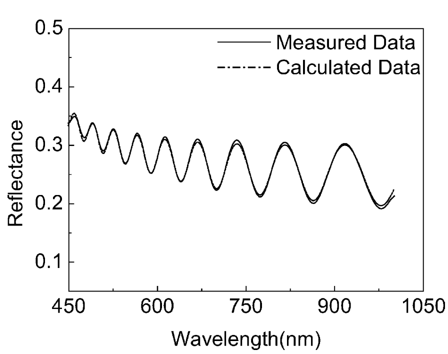

Fig. 1. Reflectance of porous SiO_2 film vs. wavelength.

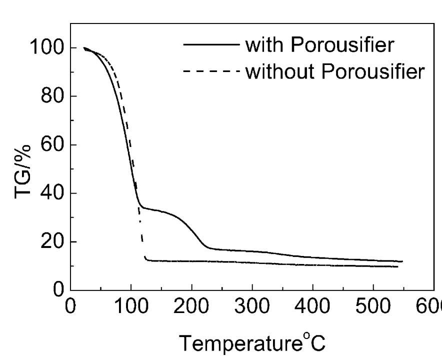

Fig. 3. TG curves of the SiO_2 gel solution.

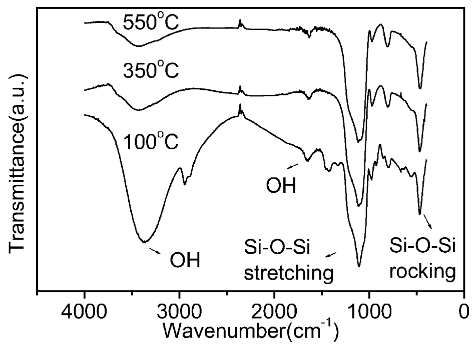

Fig. 4. FT-IR spectra of porous SiO_2 film with various annealing temperatures.

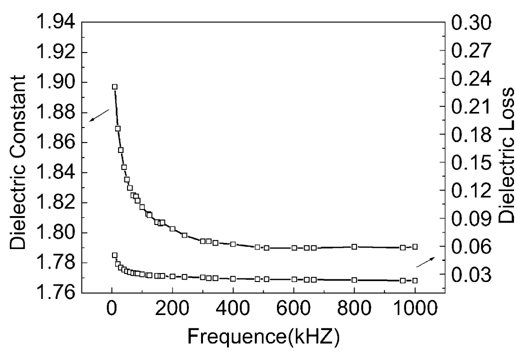

Fig. 5. Dielectric constant and dielectric loss of porous SiO_2 film.

gel solution without porousifier just has one sharp weight loss step in temperature range below 130 °C. So, porousifier enlarges the range of thermal weight loss of the SiO_2 gel solution, and effectively avoids the crack in film. The decomposition and oxidization of porousifier make the SiO_2 film with high porosity.

The evolution of the FT-IR spectra of porous SiO_2 film with various annealing temperatures is presented in Fig. 4. The Si–O stretching mode (1075 cm^{-1}), Si–O rocking vibration (470 cm^{-1}), and a broad O–H vibration peak centered at 3400 and 1620 cm^{-1} are observed in dry film heated at 100 °C. The peak at 2885 cm^{-1} is due to the $–CH_2–$ of the ethoxy group, and the peak at 2945 cm^{-1} is due to the $–CH_3$ of the ethoxy group [8]. This means that there is lots of ethoxy group in porous SiO_2 film caused by incomplete hydrolysis of TEOS. As can be seen, after annealed at 550 °C, the intensity of the –OH group absorption bands significantly decrease, suggesting that many of the hydroxyl groups have decomposed and have been removed while the intensity of Si–O bonds remain unchanged. It was also found that these C–H stretching peaks disappear due to thermally volatility of the ethoxy group.

Dielectric properties of porous SiO_2 film are shown in Fig. 5. Low relative dielectric constant of 1.79 is observed and the dielectric loss is about 0.02 at 1 MHz. Porous SiO_2 film can be regarded as a medium that is composed of dense SiO_2 film and air. Several models are offered to calculate the relative dielectric constant of a two phases medium. The simplest is that of Clausius–Mossotti which applied to a porous material gives:

$$\frac{\varepsilon_c - 1}{\varepsilon_c + 2} = (1 - p)\frac{\varepsilon_0 - 1}{\varepsilon_0 + 2}$$

Where ε_0 and ε_c are relative dielectric constant of dense SiO_2 film and porous SiO_2 film, P is the porosity of film [9]. Using this formula, the relative dielectric constant of porous SiO_2 film with porosity of 59% is 1.71. The theoretical result is similar with experimental result.

As a thermal insulation layer, surface of the porous SiO_2 film must be sufficiently smooth so that other functional overlying layers can be deposited onto it and also uniform

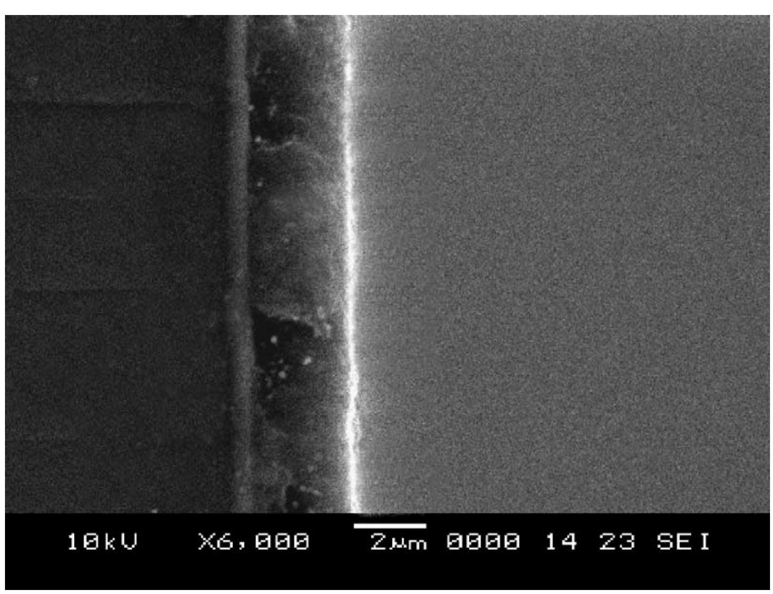

Fig. 6. SEM micrograph of a cross section of porous SiO_2 film.

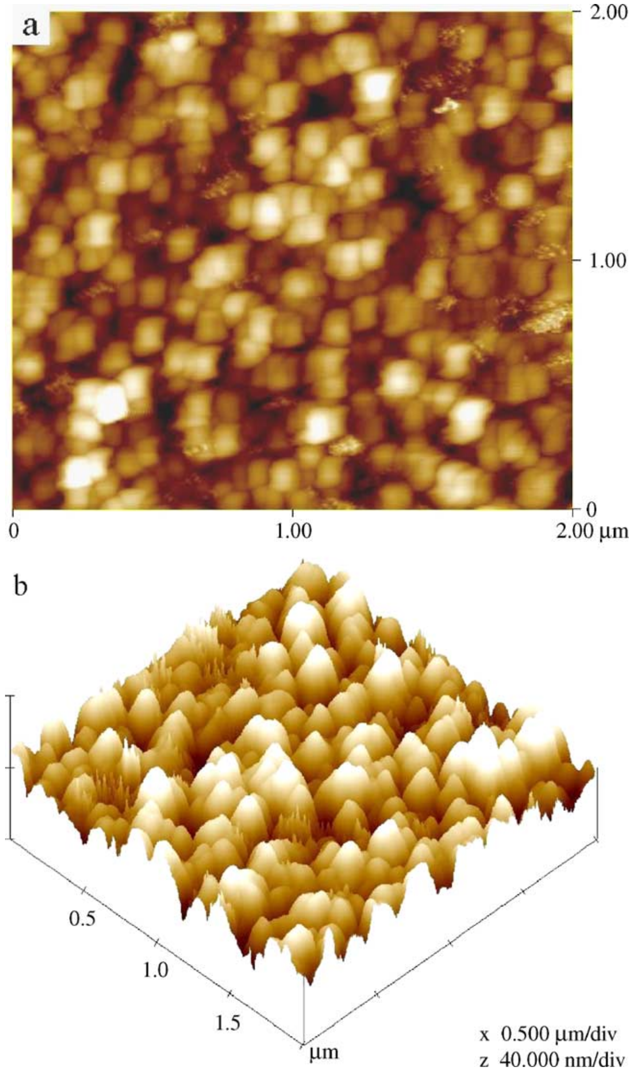

Fig. 7. (a) 2D and (b) 3D AFM micrographs for porous SiO_2 film.

across the thickness. Fig. 6 shows the SEM micrograph of a cross section of porous SiO_2 film. The SEM micrograph reveals that the porous SiO_2 film is uniform and smooth on the surface, as well as in the thickness of 3 µm. AFM images are shown in Fig. 7 for the purpose of analyzing the surface condition of porous SiO_2 film. The images indicate that there are some nanometer pores on the surface. The root mean square surface roughness of porous SiO_2 film is 7.25 nm.

4. Conclusion

Thick porous SiO_2 films with a 59% porosity and 3 µm thickness were successfully achieved by sol–gel method. Research results indicate that the additive, porousifier is a predominant factor to get thicker SiO_2 films with high porosity. The relative dielectric constant of porous SiO_2 films is as low as 1.79. Porous SiO_2 films are uniform, smooth, crack-free, thick and high porosity. It is very suitable to be the thermal-insulation layer of thin film IR detector and to integrate other functional films.

Acknowledgements

This work was supported by Shanghai Nano Fundamental Committee under Contract no. 0152NM038 and the university key studies project of Shanghai.

References

[1] A. Jain, S. Rogojevice, S. Ponoth, N. Agarwal, I. Matthew, W.N. Gill, P. Persans, M. Tomozawa, J.L. Plawsky, E. Simonyi, Porous silica materials as low-*k* dielectric for electronic and optical interconnects, Thin Solid Films 398–399 (2001) 513–522.

[2] G.C. Righini, S. Pelli, Sol–gel waveguide, J. Sol–Gel Sci. Technol. 8 (1997) 991–997.

[3] K. Jiang, Y. Wang, L. Gui, Y. Tang, Ordered porous films of organically-modified silica prepared by a two-step replicating process, Colloids Surf. A: Physicochem. Eng. Aspects 179 (2001) 237–241.

[4] L. Li, X. Yao, L. Zhang, Fabrication of thermal insulation structure for uncooled pyroelectric thin film IR detector, Chinese J. Semiconduct., in press.

[5] M.A. Fardad, E.M. Yeatman, E.J.C. Dawnay, M. Green, F. Horowitz, Effects of H_2O on structure of acid-catalyzed SiO_2 sol–gel films, Thin Solid Films 183 (1995) 260–267.

[6] W. Liu, Essential problems of ferroelectric thin films for pyroelectric detectors with thermal buffer layer, Ph.D. Thesis, Xi'an Jiaotong University, 1995.

[7] A. Matsuda, Y. Matsuno, M. Tatsumisago, T. Minami, Changes in porosity and amounts of adsorbed water in sol–gel derived porous silica film with heat treatment, J. Sol–Gel Sci. Technol. 20 (2001) 129–134.

[8] J.-K. Hong, H.-S. Yang, M.-H. Jo, H.-H. Park, S-Y. Choi, Preparation and characterization of porous silica xerogel film of low dielectric application, Thin Solid Films 308–309 (1997) 495–500.

[9] P. Mezza, J. Phalippou, R. Sempere, Sol–gel derived porous silica films, J. Non-Cryst. Solids 243 (1999) 75–79.