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# Effects of water content and sol viscosity on morphology of porous silica thermal insulating layer

Xiaoqing Wu*, Xi Yao, Minqiang Wang, Lumei Gao

*Electronic Materials Research Laboratory, Key Laboratory of the Ministry of Education, Xi'an Jiaotong University, Xi'an 710049, China*

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**Abstract**

Amorphous porous silica thin films as a thermal insulating layer in pyroelectric infrared (IR) detector were prepared by a modified sol–gel method. These silica films possessed sponge-like disordered pore structure. The effects of water content and sol viscosity on morphology of the films were investigated. The results shown: with decreasing water content and increasing sol viscosity, the pore size, root-mean-square surface roughness (RMSSR), and thickness of the films increased obviously. However, the porosity did not change greatly. While the values of the water content and the sol viscosity changed from 91.69 to 79.58 wt.% and 5.59 to 59.37 cP, respectively, the thickness of single layer film increased from 0.34 to 1.50 μm, and the values of porosity just fluctuated between 45 and 50%. A crack-free, uniform porous silica films with porosity of 45% and thickness of 15 μm also could be obtained by repeating coating procedure easily.


*Keywords:* Porous silica films; Modified sol–gel method; Water content; Sol viscosity

## 1. Introduction

Porous silica thin films possessing high specific surface area, low dielectric constant, and low thermal conductivity have a variety of potential applications, such as catalysis, microelectronics, host–guest chemistry, and so on. In our research, we use porous silica film as a thermal insulating layer in pyroelectric film infrared (IR) detector arrays [1]. High porosity and greater thickness for one coating are necessary for many purposes. However, by a conventional sol–gel method, the fabrication of the films is not easy, because high shrinkage inherent in the process produces a large capillary force and tensile stress, which can make collapse of pores and cracking of the films. Using other two ways based on sol–gel solution precursors, porous silica films with a larger thickness and extremely high porosity can be synthesized.

First way is aerogel process in which wet films are dried at a supercritical state. Since above critical point, no liquid–vapor interfaces exist in wet films, capillary force equals to zero so that pores can be preserved in the films. But the supercritical process is expensive and time consuming, especially dangerous and not easily adaptable to continuous thin film forming operations [2]. Second way is xerogel process. For this process, the films are fabricated by a surface modification technique in which the wet films are treated with some chemical reagents. The drying shrinkage of the films at ambient pressure is almost completely reversible [3], so that pores can be released. Xerogel process is not carry out at a higher pressure, but the samples must be emerged in solution containing chemical agents for a long time in order to complete diffusion of the agents. Furthermore, aerogel films or xerogel films also show a lower mechanical strength.

Our research group has developed a modified sol–gel techniques for making porous silica films with a high porosity and a greater thickness of the films. This process is very easy for operation, and do not use ethanol as a solvent [4]. As we know, the characteristics of porous silica films are related to a large number of factors. In this work, we will investigate the effects of water content and sol viscosity on the properties of porous silica films further. More research results will be reported in other papers.

## 2. Experimental

Tetraethylorthosilicate (TEOS) was mixed in a larger amount of water with $NH_4OH$. The volume ratio of TEOS:

* Corresponding author. Fax: +86-29-82668794.
*E-mail address:* xqwu@mail.xjtu.edu.cn (X. Wu).

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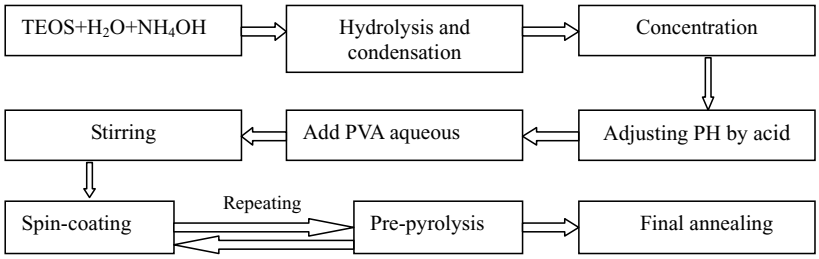


Fig. 1. Flow chart for preparation of silica sol and films.

$H_2O$:$NH_4OH$ was 5 ml:20 ml:2 ml. After the hydrolysis reaction of TEOS and condensation reaction of silanol groups ($Si(OH)_4$) finished, the solution was concentrated at 60 °C for the evaporation of water. Through different concentration time, silica sol solutions with different water content and viscosity were obtained. Then, PH of the solutions was adjusted to 2.5 with acid. An aqueous containing additive PVA and the silica sol solutions were mixed together by magnetic stirring. The wet silica films were prepared by spin-coating techniques, and were heated at 400 °C for 30 min. The spin-coating and heating process were repeated for several times according to required thickness of the film. The final films were heated at a temperature of 550 °C for 30 min. Fig. 1 shows the

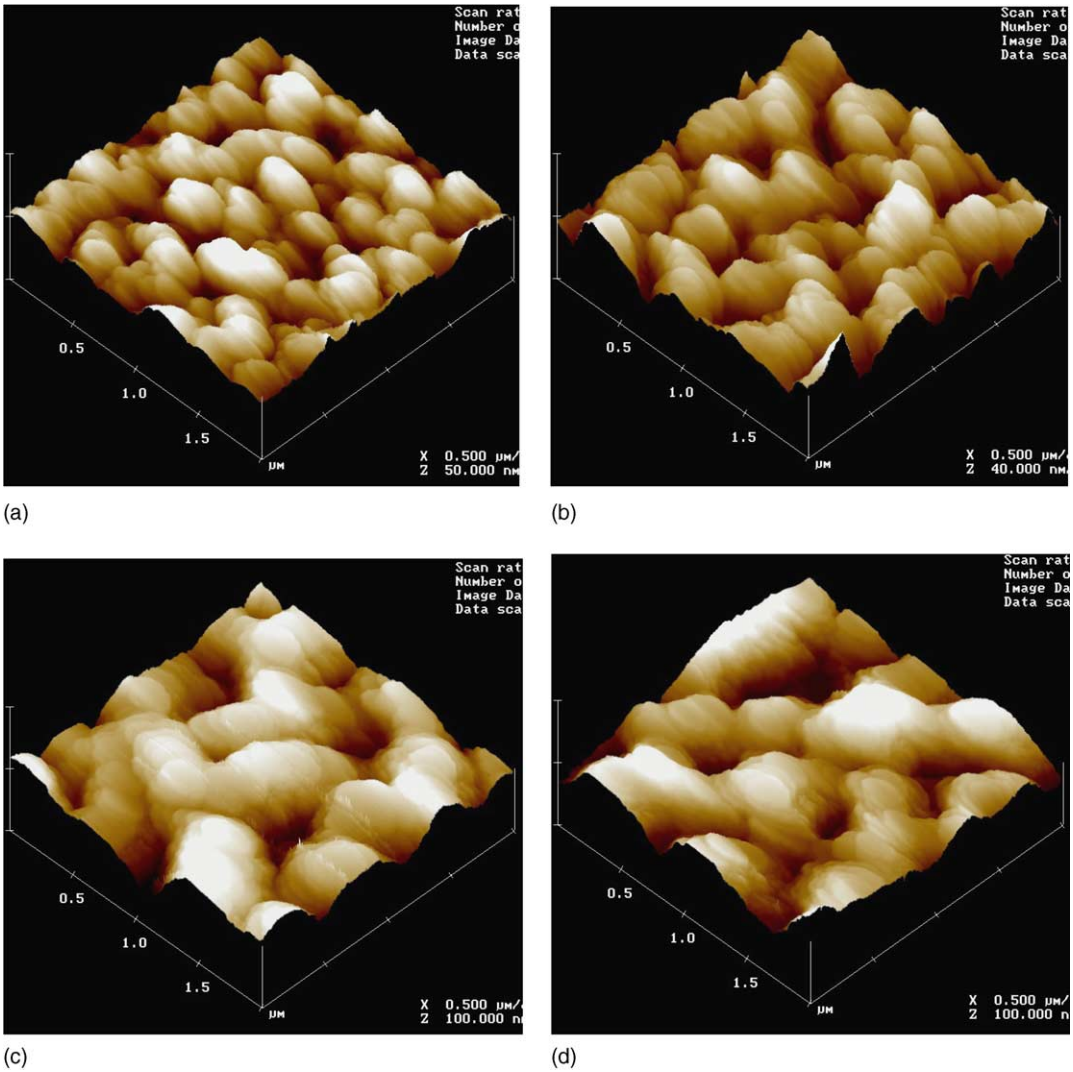


Fig. 2. Effects of water content on morphology of silica films: (a) water content of 91.69 wt.%, (b) water content of 89.79 wt.%, (c) water content of 84.88 wt.%, (d) water content of 79.58 wt.%.

preparation flow chart of the silica sol solution and the silica films.

The morphology and the root-mean-square surface roughness (RMSSR) of the porous silica films were obtained by Dimension 3100 Atomic Force Microscope (AFM) with tapping mode. The refractive index of the films was measured by Filmetrics F20, the porosity was calculated using the formula $P = 3(n_s^2 - n^2)/(n_s^2 - 1)(n^2 + n)$, here $n_s$ and $n$ are the refractive indices of dense and porous silica films, respectively. The thickness of the porous silica films was measured by Dektak[3] ST Surface Profiler. The phase structure of the films determined by DMAX-2400 X-ray Diffractometer.

## 3. Results and discussion

Fig. 2 shows the AFM patterns of single layer porous silica films made by the solutions with different water content and different sol viscosity. The relative data of various porous silica films are summarized in Table 1. All of the films have amorphous phase structure (the XRD patterns were not shown). The microstructure of the porous silica films seems to be a sponge-like network, and disordered pore structure is very obvious. With decreasing water content and increasing sol viscosity, the thickness of single layer film increases greatly, and RMSSR also becomes larger correspondingly. While the values of water content and sol viscosity change from 91.69 to 79.58 wt.% and 5.59 to 59.37 cP, respectively, the thickness of single layer film increases from 0.34 to 1.50 μm, the RMSSR of the films changes from 4.68 to 13.66 nm. However, the values of porosity just fluctuate between 45 and 50%. From Fig. 2, we can also see: while water content are higher, the pore of the three-dimensional (3-D) framework is smaller. While water content decrease, the pore of 3-D framework becomes larger and deeper, so the films have larger RMSSR. Meanwhile, width of the pore walls also widens, and the framework seems to be more regular.

In summary, lower water content results in larger pore size and higher RMSSR. In addition, Fig. 2c and d possess similar surface morphology and close values of RMSSR. It means that when the value of water content is less than 84.88 wt.%, the morphology of the films is no longer changing obviously. Although the films have different thickness, pore size, and RMSSR, the values of the porosity are close. This is because total pore volume in these films is close probably.

Table 1
Relative data of silica porous films

| | Water content (wt.%) | Viscosity (cP) | RMSSR (nm) | Thickness (μm) | Porosity (%) |
|---|---|---|---|---|---|
| a | 91.69 | 5.59 | 4.68 | 0.34 | 46.8 |
| b | 89.78 | 8.27 | 5.65 | 0.41 | 47.7 |
| c | 84.88 | 32.16 | 12.32 | 0.96 | 50.7 |
| d | 79.58 | 59.37 | 13.66 | 1.50 | 45.3 |

Usually, repeating coating and pre-pyrolysis procedure are necessary to obtain thicker films in sol–gel process. For a greater thickness of single layer film, it allows us getting a thicker film by less repeating times. Decrease of the repeating times can reduce opportunity of atmospheric contamination and pre-pyrolysis times of the films, as well as can increase compatibility of the films with existing microelectronic procedure. In a word, we can make a crack-free, uniform porous silica film with porosity about 45% and thickness of 15 μm by repeating coating procedure easily. Usually, we use porous silica films with a thickness of 3 μm in pyroelectric film IR detector arrays. This thickness just need repeating process for two times.

## 4. Conclusions

Amorphous porous silica films with higher porosity and greater thickness for one coating have fabricated by a modified sol–gel method, and they have been used as the thermal insulating layer in study of pyroelectric thin film IR detector arrays. The porous silica films have a sponge-like network. The effects of water content and sol viscosity on morphology of the porous silica films were investigated. With decreasing water content and increasing sol viscosity, the pore size, the RMSSR, and the thickness of the single layer films increased obviously. However, the porosity did not change greatly. While the values of the water content and the sol viscosity changed from 91.69 to 79.58 wt.% and 5.59 to 59.37 cP, respectively, the thickness of single layer films increased from 0.34 to 1.50 μm, and the values of porosity just fluctuated between 45 and 50%. In particular, a crack-free, uniform porous silica film with porosity of 45% and thickness of 15 μm could be obtained by repeating spin-coating procedure.

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