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Studies on the spin coating process of silica films

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Abstract

Silica xerogel films with good uniformity and various thicknesses were successfully prepared by a two-step acid-base catalyst procedure and spin coating. After the addition of ammonia catalyst, the sol changes gradually from a Newtonian fluid to a shear-thinning one due to the progress of polymerization reactions. An empirical equation using the relative ratio of reaction time to gel time can give successful prediction of sol viscosity. Our systematic study of the coating process indicates the existence of a process window in terms of t/t_{gel} and spin speed can be defined for obtaining uniform and defect-free films. It is difficult to obtain films with good quality when the viscosity of the sol is either too high or too low. Another parameter that also exhibits strong influence on film thickness is the concentration of TEOS in the starting solution. Finally, the film thickness was found to correlate well with sol viscosity and spin speed as $h = A\ \eta^{0.45}\ \varpi^{-0.62}$.

Keywords: Silica film; Spin coating; Process window

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1. Introduction

As the feature dimension of ultra large-scaled integration technology continues to shrink, interconnection delay, generally termed resistance-capacitance (RC) time delay, dominates most attention over the basic gate delay in the deep submicron devices [1]. Therefore, insulating materials with low dielectric constants are needed to mitigate this problem of RC delay and cross talk between metal interconnects. Sol-gel derived porous SiO_2 xerogel film is particularly attractive among various low k dielectric candidates in advanced semiconductor devices, because of its inherent ultra-low permittivity and high thermal stability through the incorporation of micropores into the SiO_2 skeletal network [2].

One of the basic requirements for a spin-on material for use as an interlayer dielectric is that it must be uniform. The requirement is generally met for most spin-on materials because they are Newtonian fluids. However, the sol-gel precursors used to fabricate spin-on xerogel films may be Newtonian or non-Newtonian fluids depending on how close to the gel point [3,4]. Yet, in the literature, very few studies were devoted to the coating process of this xerogel films, with most focus on the properties of final films only [5–7].

In the early days, a series of mathematical models considering spin coating on a flat substrate have been published. For example, Emslie et al. [8] proposed a simple model of the spin-coating process predicting film thickness as a function of a number of physical parameters as follows:

$$h = \frac{h_0}{(1 + \frac{4\omega^2 h_0^2 t}{3\eta})^{1/2}} \tag{1}$$

where h_0 is initial film thickness, ω the spin speed, and η the viscosity. Yet, in reality, the various operating conditions rarely satisfy the assumption required by this equation, thus limiting its applications to real situations.

In this work, we hope to provide a very systematic study on the spin coating itself. The viscosity change of sols will be followed and correlated with time. We will also provide a process window in terms of relative reaction time to gel time and spin speed for obtaining uniform films. Defects are easily observed when the films are coated outside this process window. The film thickness will then be correlated in terms of sol viscosity and spin speed as implied by the equation by Emslie et al. [8].

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2. Experimental

The flow chart for synthesizing silica sol is shown in Fig. 1. The typical two-step acid/base catalyst procedure was used here [7]. In the first step, tetraethylorthosilicate (TEOS), ethanol, water and HCl were refluxed at 70 °C for 90 min in the following molar ratios:1:10:3.5:0.003. In the second step, a certain amount of the base catalyst (0.1 M NH_4OH) was added to 10 ml of the previous solution, which was then used for spin coating and rheological measurements after various periods of reaction. The reaction beaker was covered during this period to avoid loss of solvent.

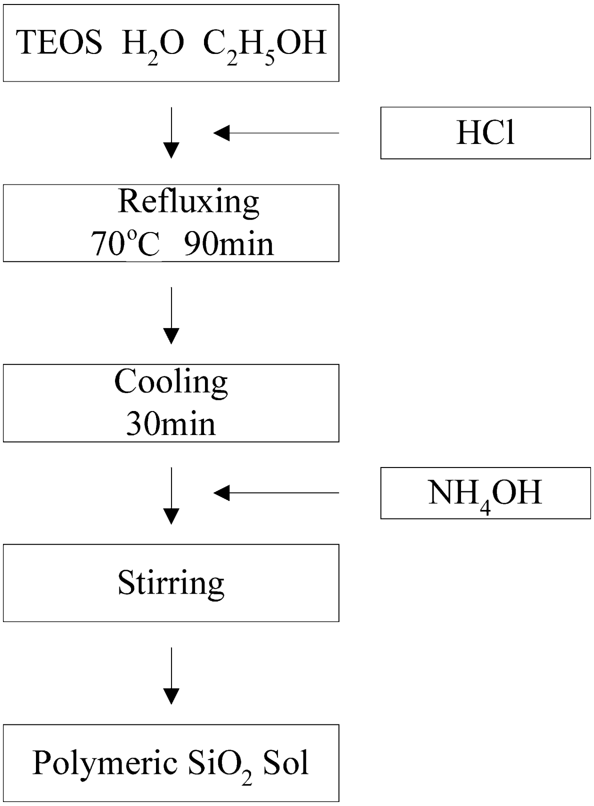

Fig. 1. Experimental flow chart for preparing silica sols.

The rheological measurement was made using viscometer (Brookfield LV- CV III$^+$) at a shear rate of 100 s^{-1} unless otherwise specified. Xerogel films were prepared in a spin coater (PM- 490, Synrex Spinner, Taiwan) using various rotation speeds. P-type Si (100) of size 4×4 cm^2 was used as the substrate. Standard cleaning procedure of Si substrate was adopted before coating. 1 ml sol was used for each coating and the spin time was kept at 30 s throughout this work. To avoid excessive loss of solvent, the coating was conducted in an ethanol atmosphere and the spun-on film was aged under the same atmosphere for 10 min before taken out and dried in the ambient. Finally, film thickness was measured by surface profiler (Dektak, IIA).

3. Results and discussion

3.1. Changes of sol viscosity and gelation time

Once ammonia was added to the solution, the polymerization reaction was accelerated and the solution viscosity increased accordingly due to either cross-linking, sol formation and/or solvent evaporation. The viscosities were measured for a number of experimental

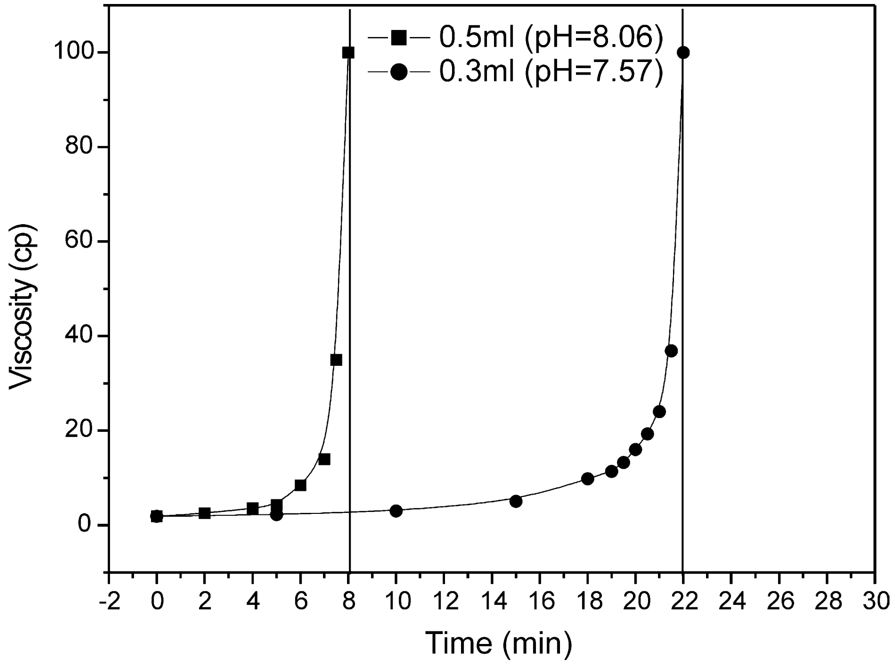

Fig. 2. Changes of sol viscosity with time for different amounts of base addition.

conditions as a function of time up to the point of gelation. In Fig. 2 shows the change in viscosity with time for two different amounts of base addition. In general, the viscosity would increase at first gradually and then more rapidly to very large values, meaning a loss of fluidity of the solution. From this figure, a gel time (t_{gel}) can be estimated by drawing a tangent to the final portion of viscosity versus time curve. Here $t=0$ was defined as the time when the base catalyst was added.

In the literature, there have been quite a number of equations describing the relationship between viscosity and colloidal concentration, such as [9]:

$$\frac{\eta}{\eta_s} = \left(1 - \frac{\varphi}{\varphi_{\max}}\right)^{-n} \tag{2}$$

By substituting t and t_{gel} for φ and $\varphi_{\max}$, we found very good fitting of experimental data with predictions from the following equation:

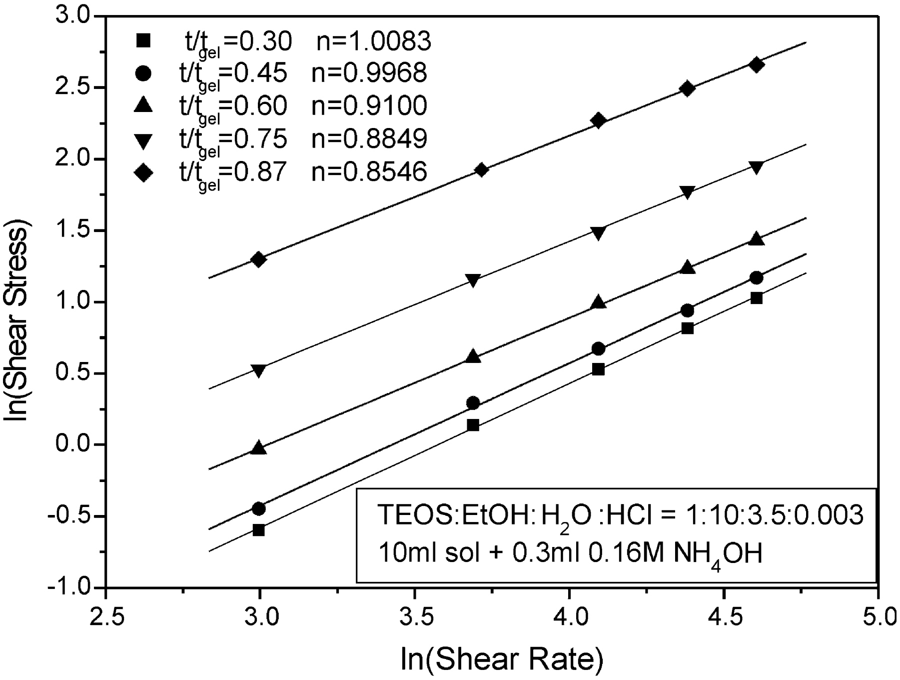

Fig. 3. Rheological behavior development of sols as they approach gelation.

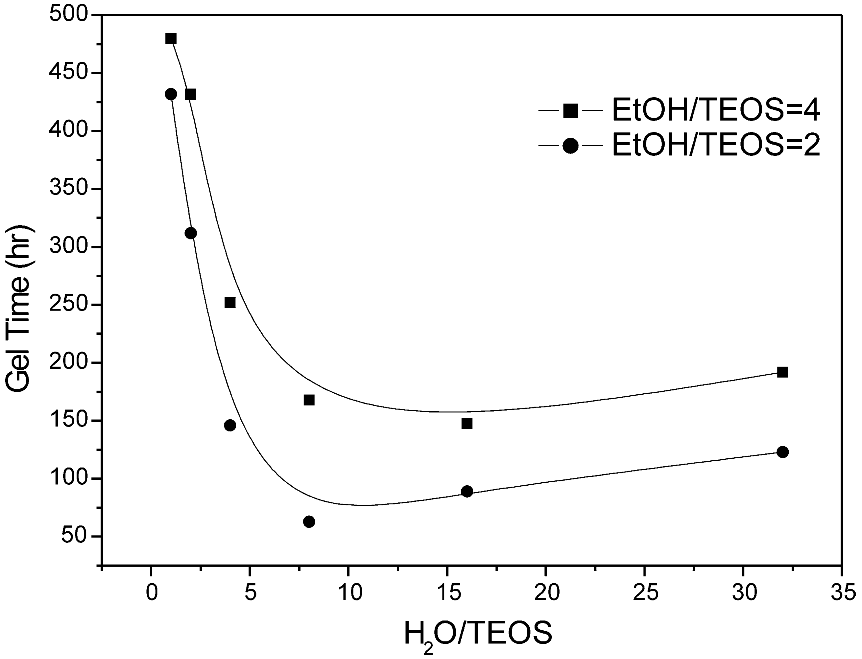

Fig. 4. Gelation time as a function of H_2O:TEOS molar ratio for two EtOH/TEOS ratios.

$$\frac{\eta}{\eta_s} = \left(1 - \frac{t}{t_{gel}}\right)^{-1.2} \qquad (3)$$

Here η is the viscosity at time t, η_s is the viscosity of solvent (i.e. mixture of water and ethanol, $\eta_s = 1.41$cp for this case), and t_{gel} is the experimental gel time. The similarity between reaction time and sol concentration suggests that the sol concentration probably increase linearly with time, reaching maximum packing at the gel point. This equation is very helpful in estimating the solution viscosity once we learned of the gel time for that specific solution. In general, knowledge of viscosity is necessary for successful coating operations.

Another rheological property that may be of concern about the solution is its viscosity dependence upon shear rate. The general equation that relates shear stress to shear rate is $\tau = \mu\gamma^n$, where τ is shear stress, μ the viscosity, and γ the shear rate. In Fig. 3 the dependence of τ on shear rate was shown of a specific solution aged for different times. Clearly, the silica sol changed gradually from Newtonian fluid ($n = 1$) at the early stage of aging to shear-thinning fluid ($n < 1$) as time progressed.

In order to apply Eq. (3), we need to know the gel time for each synthesis condition. In Figs. 4 and 5, the variation of gel time as functions of either H_2O/TEOS molar ratio or amount of base catalyst (0.1 M NH_4OH) added was exhibited. In theory, any synthesis parameter that has some effects on the reaction rate would exhibit influence on gel time. Increase of water (a reactant) would increase the hydrolysis rate and hence decrease the gel time. However, when water was in excess, further increase of water would lower the reactant concentration and therefore has an adverse effect on reaction rate. As

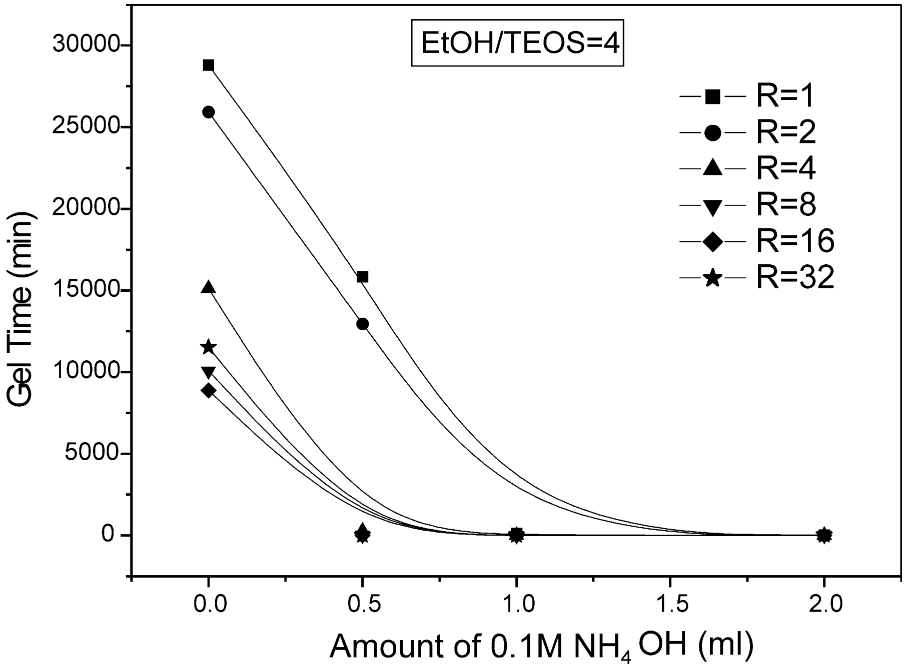

Fig. 5. Gelation time versus different amounts of base.

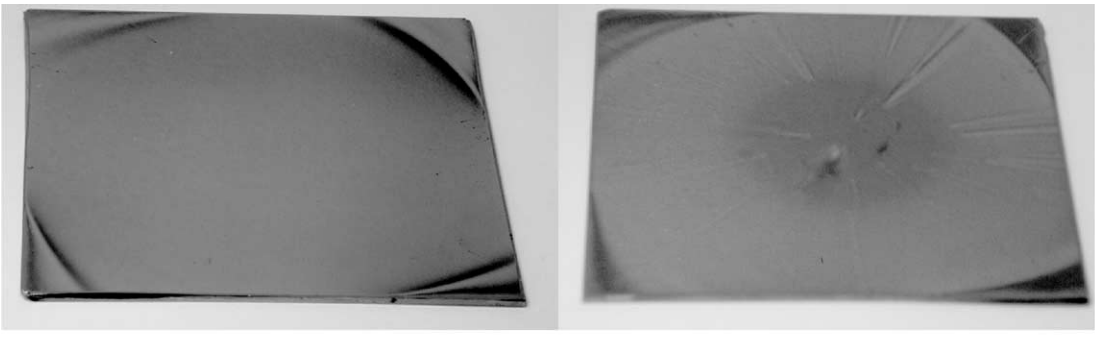
(a) (b)

Fig. 6. Representative film surface appearance (a) uniform film; (b) non-uniform film.

a result, the gel time increased slightly. As for the amount of base catalyst, its increase would accelerate the reaction rate and decrease the gel time. Nevertheless, there seemed to exist an upper limit for the quantity of NH_4OH to be effective in reducing the gel time.

3.2. Film morphology and uniformity

Fig. 6 shows the pictures of two representative film surfaces obtained from sols having different viscosities. Uniform films would exhibit a uniform color corresponding to its thickness, while the color of a non-uniform film would change from the center to the edge of the film, suggesting a non-uniform thickness distribution in the film. In theory, the film thickness is mainly determined by the shear forces from spinning and viscosity of sols. In Fig. 7, the film thickness distributions in the radial direction were reported for films obtained under different spin speeds and for sols having different viscosities. In general, the less viscous sol would produce thinner, but

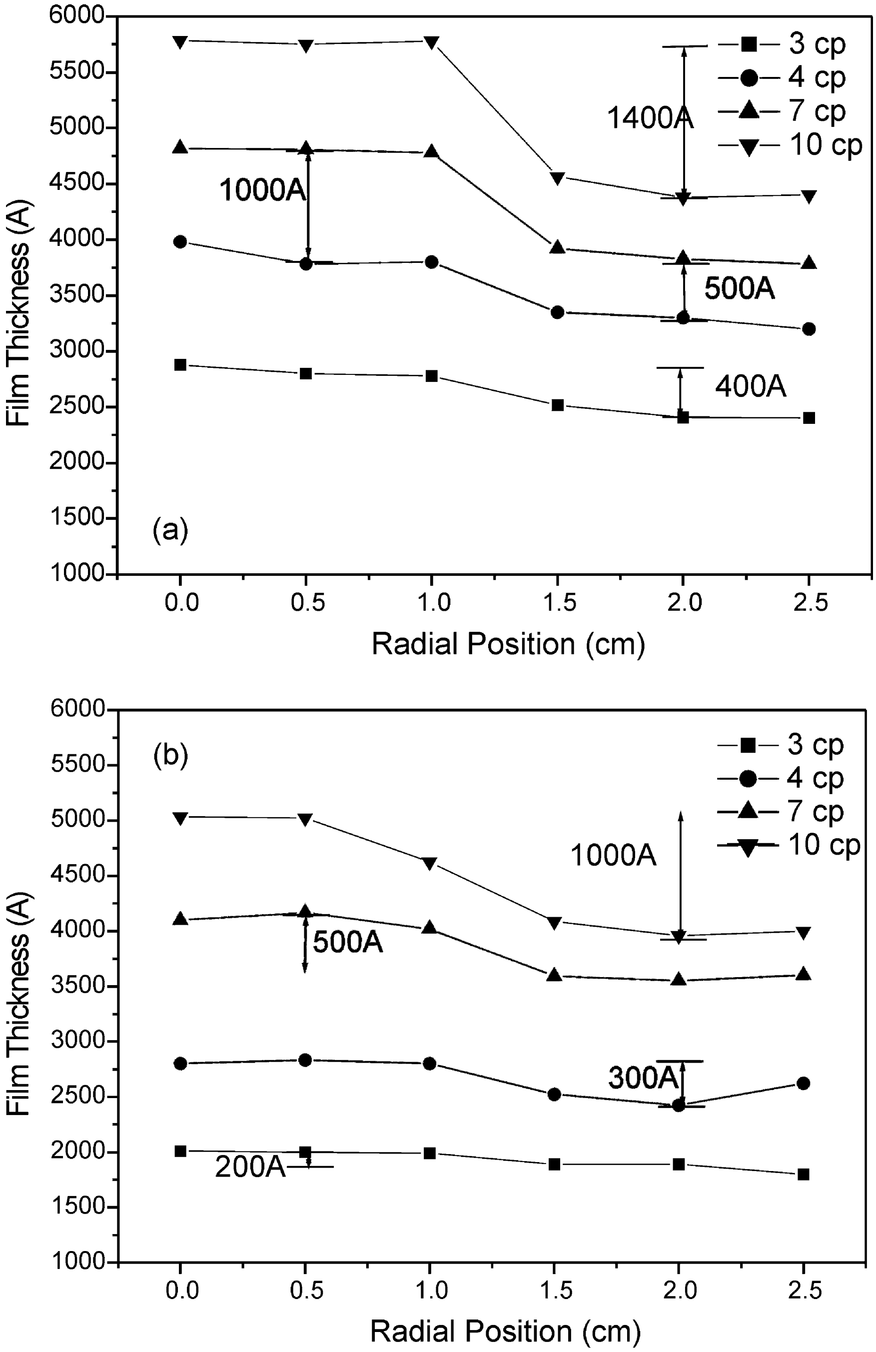

Fig. 7. Film thickness profile of films obtained for sols of different viscosity; spin speed was (a) 1000; (b) 2000; (c) 3000 and (d) 4000 rpm.

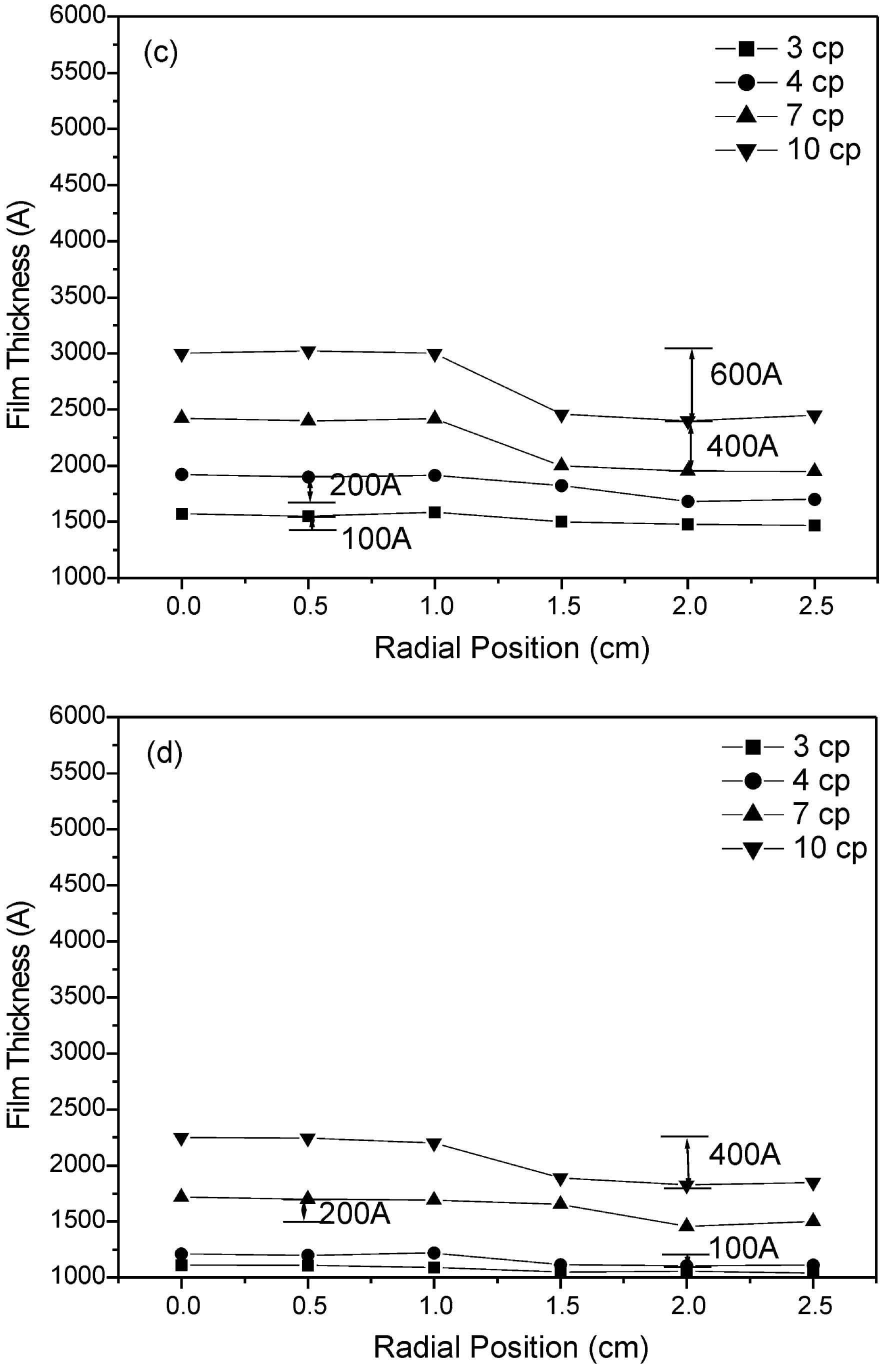

Fig. 7. (*continued*).

more uniform films. However, the non-uniformity can be somewhat remedied by applying higher spin speeds. Summarizing these results, we can conclude that it is better to conduct the coating before $t = 0.7\ t_{\mathrm{gel}}$. After that time, the sols would deviate too much from Newtonian fluid to produce uniform xerogel films. The shear-thinning characteristic is obviously not favored when considering film uniformity.

3.3. Correlation for film thickness

Based on the above results, one can easily understand the importance of sol viscosity and spin speed on film thickness. Using the Emslie equation (Eq. 1) as a model, the following empirical correlation was found to fit our experimental data quite successfully as shown in Fig. 8.

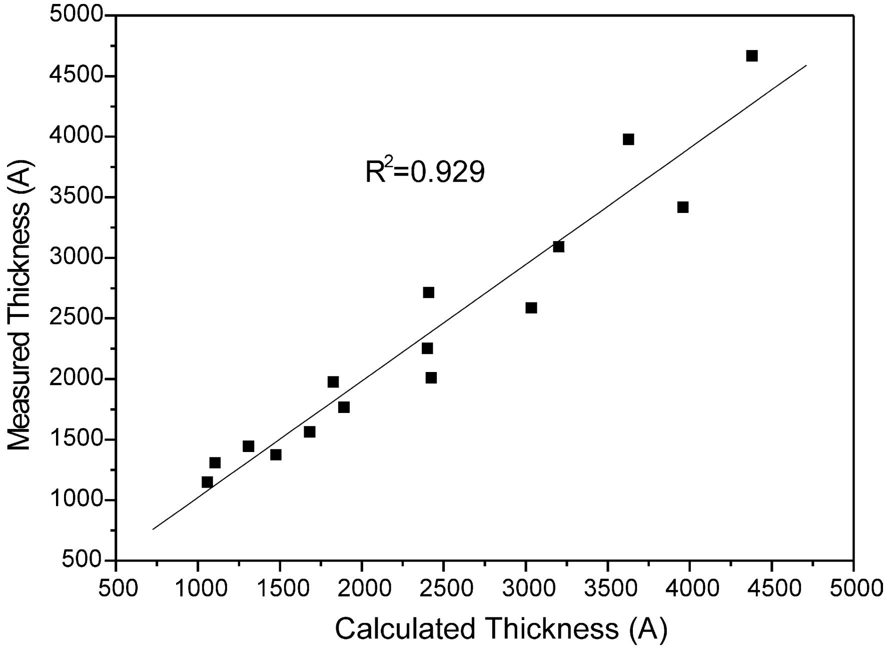

Fig. 8. Comparison of calculated thickness versus measured thickness.

$$h = A\eta^{0.45}\varpi^{-0.62} \qquad (4)$$

Here h is the film thickness in Angstroms, η is the viscosity in cP and ϖ is the spin speed in rpm. If the film is not very uniform, we used the averaged thickness at the outer edges for correlation work. The fitted constant A is 1.2×10^5 and the square of correlation coefficient (r^2) is 0.929. The dependence of thickness on spin speed is in general: $h \propto \varpi^{-b}$. The value of exponent b would be equal to 1 if only centrifugal force is important [8]. On the other hand, b would be 0.5 when evaporation of solvent is dominant in the coating process [10]. In the literature, b was reported to be between 0.45 [5] and 0.6 [6]. In our case, the evaporation is probably more important than the centrifugal action due to the longer spin time of 30 s.

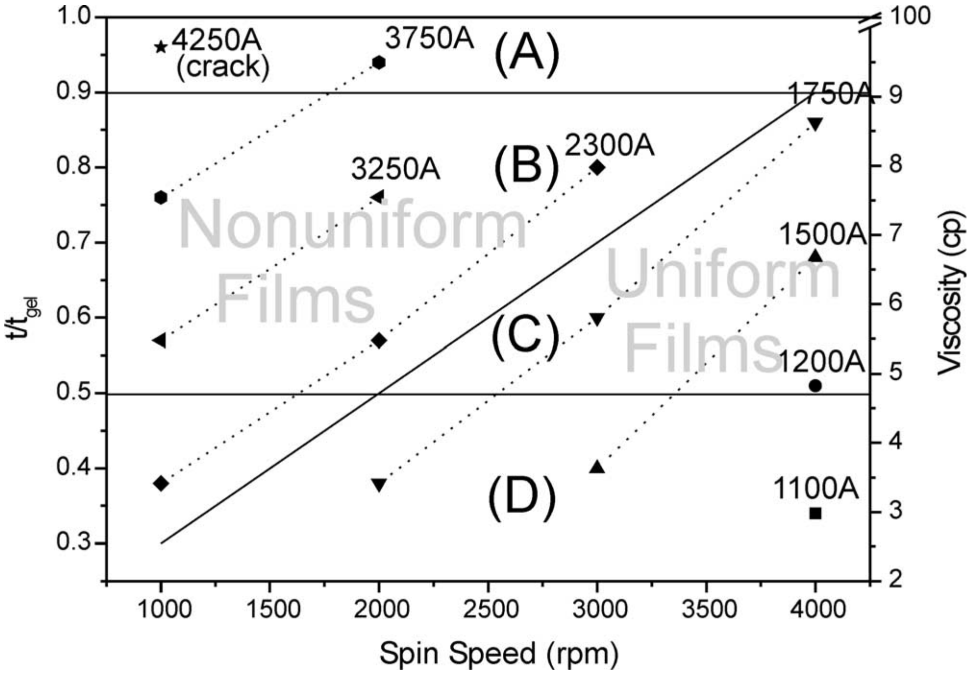

Fig. 9. Process windows for spin coating of xerogel films.

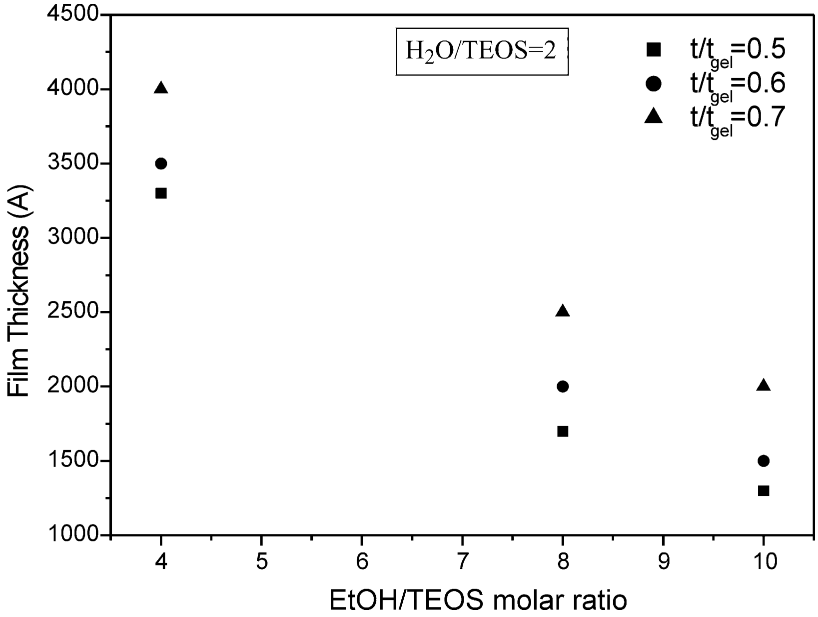

Fig. 10. Effect of starting concentration on film thickness; the sols were reacted for various times before coating.

3.4. Process window

In Fig. 9, the two most important process parameters, i.e. relative time of reaction to gel time and spin speed are divided into four regions, representing conditions that produce films easily cracked (region A), non-uniform films (region B), uniform films (region C) and incomplete-coverage films (region D) respectively. Also shown in this figure are lines of constant thickness. In region A, the sols are viscous and the resulting films are therefore rather thick. As a result, after drying, the shrinkage often leads to cracks in the films. In region B, the films are non-uniform mostly due to the shear-thinning nature of sols. In region C, the films are made uniform and defect-free by applying high spin speeds. At last, in region D, although it is Newtonian, the sol contains too much solvent. After evaporation of solvent and shrinkage effect, the films often cannot cover the whole substrate.

Because the starting concentration of TEOS was fixed in this study, the manipulation of reaction time and spin speed can only produce films with a certain range of thickness as indicated in Fig. 9. If we want to get thicker films with good uniformity and defect-free, we then have to use a higher concentration of TEOS in the starting solution. Shown in Fig. 10 are representative results. By reducing EtOH/TEOS molar ratio, we are actually increasing the TEOS concentration. The film thickness increases correspondingly. The spin speed adopted for this series of experiments was fixed at 3000 rpm.

4. Conclusions

Based on the results presented above, the following conclusions about the coating process of silica xerogel films can be drawn:

1. The silica sol starts from a Newtonian fluid after the addition of base catalyst and changes gradually to shear-thinning fluid when the aging process continues. The viscosity of the sol can be conveniently predicted by Eq. (3) in terms of the relative ratio of reaction time to gel time, implying a positive correlation between reaction time and sol concentration.
2. Film thickness can be conveniently correlated with sol viscosity and spin speed as shown by Eq. (4). The dependence of thickness on spin speed suggests that evaporation of solvent is very important for this coating procedure.
3. In order to obtain uniform and defect-free films, spin coating must be performed within a certain process window defined by the relative ratio of t/t_{gel} and spin speed. The films become either non-uniform or contain too many defects to be useful when the coating was conducted outside this window. In addition to the above two process parameters, the starting concentration of TEOS also exhibits strong influence on film thickness.

Acknowledgements

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