New Sol-Gel Solution with 45 Days Stability for Preparation Silica Thin Films

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ABSTRACT: *As we know sol-gel is one of the most important techniques for thin film preparation. In this paper, high transmission silica thin films have been prepared by dip-coating process from a new silicon-alkoxide solution. The prepared sol was stable for 45 days which is very important to characterize the coating process. The optical properties as a function of aging time, withdrawal rate, and heat treatment parameters (temperature and time) have been studied.*

KEY WORDS: *Silica, Sol-Gel, Solution stability, Thin film, High transmission coating*

INTRODUCTION

For a long time, several techniques have been applied to make optical thin films [1]. These techniques are, the physical vapor deposition (PVD) and the chemical etching (liquid or vapor). Each of these techniques have their own disadvantages such as high cost, limited substrate-area, utilization of environmentally harmful and toxic chemicals [2, 3].

In recent years, sol-gel process has been successfully employed to prepare optical thin films [1]. In comparison with other techniques, the sol-gel technique has several advantages; such as, wide possibility of varying the film properties, simple coating process, good homogeneity, large-area coating, and low equipment costs [4]. Sol-gel derived thin films have been used in the development of a wide range of optical coatings [1, 5]. Therefore sol-gel method is a rapidly advancing technology.

The sol-gel is a chemical synthesis technique for preparing thin films, glasses, and ceramic powders from metal alkoxide $(M(OR)_n$ M: Si, Ti, Zr, Hf, Ta, Nb, Al,

etc. and R: CH_3, C_2H_5, C_3H_7, etc.)[6]. In the sol-gel process, a system of colloidal particles in a solution (sol) becomes a network (gel), by linking of particles together. The basic sol-gel reactions that are shown in Fig. 1 consist of two steps: hydrolysis (1) and condensation reactions (2-a and 2-b). The hydrolysis reaction produces the sol and then condensation reactions lead to the formation of an oxide network (gel). Water and organic molecules remain trapped in the gel.

The hydrolysis and condensation reactions will start and continue after the raw materials are mixed. So sol-gel solutions are active systems. These reactions cause to change concentration and stability of solution. The optical properties of thin films are affected by the stability of sol-gel solution. Therefore the stability of solution is important and must be constant along a period of time. The hydrolysis and condensation reactions require either an acidic or basic catalyst. The catalyst (acid or base) affects the hydrolysis and condensation rate

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\begin{array}{l}
-\overset{|}{\underset{|}{Si}} - OH + HOH \xrightarrow{\text{Hydrolysis}} -\overset{|}{\underset{|}{Si}} - OH + ROH \qquad (1) \\[2em]
-\overset{|}{\underset{|}{Si}} - OH + -\overset{|}{\underset{|}{Si}} - OH \xrightarrow[\text{Condensation}]{\text{Water}} -\overset{|}{\underset{|}{Si}} - O - \overset{|}{\underset{|}{Si}} - + HOH \qquad (2\text{-a}) \\[2em]
-\overset{|}{\underset{|}{Si}} - OH + -\overset{|}{\underset{|}{Si}} - OR \xrightarrow[\text{Condensation}]{\text{Alcohol}} -\overset{|}{\underset{|}{Si}} - O - \overset{|}{\underset{|}{Si}} - + ROH \qquad (2\text{-b})
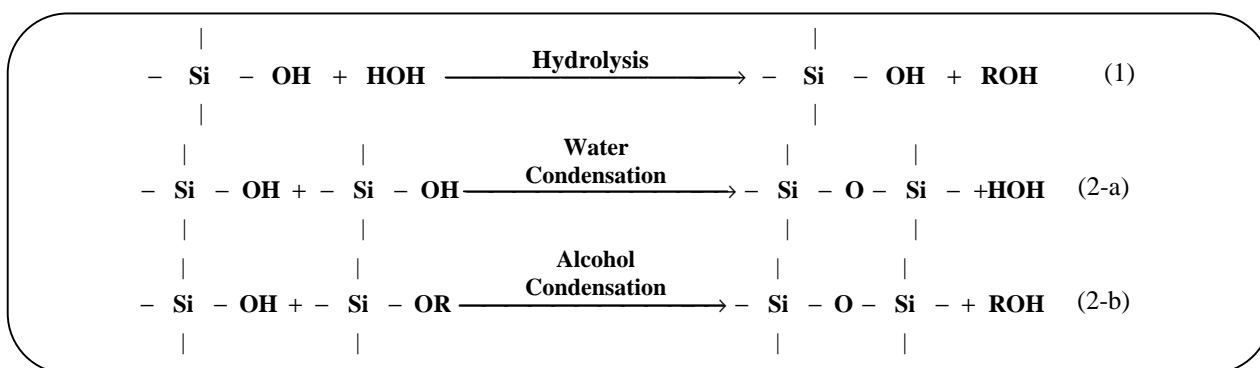\end{array}
$$

Fig. 1: The basic sol-gel reactions.

and therefore stability of solution [7]. For example in sol-gel solution catalysis with base (NH$_4$OH), stability of solution is about 107 hours [6].

Several methods can be used to make a coating by sol-gel process. Dip coating is one of them. In this process the substrate which should be coated, is immersed in sol-gel solution and then withdrawn. When sol deposits on substrate, thin film will be obtained after evaporation of solvent. This film has optical properties. Now for improvement of optical properties, good scratching resistance, and adhesion, the film requires heat treatment at temperature approximately 500 °C. The water and organic materials are removed form thin film by heat treatment. *Brinker* and *Scherer* have reviewed the details of sol-gel process [6]. The optical properties of thin film depend on thickness. The coating thickness is mainly defined by withdrawal rate. So in this method a well-defined withdrawal rate is very important [5].

In this paper we introduce new solution with long time stability and also preparation of SiO$_2$ thin film by sol-gel process. The optical transmission of SiO$_2$ thin films have been measured as a function of aging time, application withdrawal rate, and heat treatment. The structures of the films have been investigated.

EXPERIMENTAL

All solvents and reagents were analytical reagent grade. A new sol-gel solution was prepared using the base catalyst. The sol was prepared by mixing 10.5 ml of ammonia solution (25%) and a solution of tetra-ethyl silicate (33.2 ml) in 328 ml of anhydrous ethyl alcohol. It is necessary to stir the solution during mixing at room temperature. Then the mixture is allowed to stand at room temperature for one day. After this time hydrolysis and

sol formation will be completed. The final product consisted of a colloidal suspension of SiO$_2$ in substantially ethanol at a concentration of 3.0%.

Microscope slide glass-samples with dimensions 70×25×1 mm were cleaned and prepared for dip-coating process. Dip coating can be described as a process where the substrate is immersed perpendicular in a liquid (sol). After a few seconds, the substrate is withdrawn with a specific speed under controlled temperature and environmental conditions. Thin films entrain by evaporation of solvent and gravitational draining. During the process, the substrate is withdrawn from the sol at the rates between 10 and 15 cm/min at 25 °C. The heat treatment was performed at different temperatures between 25-500 °C for 60 and 120 minutes. At higher temperatures the glass deforms and complicates further analyses.

A HITACHI U-3410 spectrophotometer is used to obtain transmission spectra of SiO$_2$ film in the range of 400-800 nm. The spectral transmission curves of the films are obtained at a few number of withdrawal rates, and in different heat treatment temperatures.

A Sloan DekTak auto-leveling profilemeter is used to determine the thickness of thin film. We used an optical design and analysis program (Essential Macloed software, version 8.7) for the comparison of experimental results and theoretical data.

RESULTS AND DISCUSSION

Process stability

The hydrolysis and condensation reactions commence immediately after mixing raw materials. These reactions lead to formation of a system of colloidal particles in the solution (sol). Various equilibrium are set up in the

solution, where the size and number of particles vary with time. As condensation reactions (2-a and 2-b) proceed, the size of particles increases. This behavior is done by bonding monomers to particles, or joining particles together. So sol-gel solution is a "living system" [5].

In dip coating method (according to *Levich* equation) the thickness of the thin film depends on two fundamental parameters: solution factors and application rate (equation (3)) [5,6].

$$h = 0.9\,(\eta\,v)^{0.666}\,(\rho g)^{-0.5}\,\gamma^{-0.166} \qquad (3)$$

Where h is film thickness, v: rate of the substrate withdrawal, γ: surface tension of solution, η: solution viscosity, ρ: solution density, and g: gravity.

Following the hydrolysis and condensation reactions, the solution parameters such as solution viscosity vary. If solution parameters change with time, the control of coating thickness will be difficult or impossible. Without coating thickness controlling, transmission cannot be controlled. Thus, it is important to ensure that properties of sol-gel solution remain stable during a reasonable period of time (shelf life). The shelf life can be increased by adjusting pH of solution. *Nelson et al.* [8] and *J.A. Soutar et al.* [9] have shown that the solution is stable for long time at low pH. Another solution is used for thin films have a base catalyst. In contrast to acid catalyzed solution, the thin films obtained from high pH contains a minimum of organic contamination (organic residues and carbonaceous) [10]. So in our investigation, the base catalyzed system is used. The stability of coating solution, and thin film produced repeatedly from it, are studied during 45 days. Transmission curves of this thin film are shown in Fig. 2. Good agreement of different curves shows that the sol-gel solution is stable during this interval of time.

Effect of withdrawal rate

In *Levich* equation, as the solution parameters are constant, we can put $k = 0.9\,\eta^{0.666}\,(\rho g)^{-0.5}\,\gamma^{-0.166}$.

So we have:

$$h = k\,v^{0.666} \qquad (4)$$

In this case the film thickness will be affected only by withdrawal rate. The thickness of films as a function of withdrawal rate is determined by DekTak method and the result is shown in Fig. 3. The equation of line is

$h = 62.2\,v^{0.657}$. The experimental results are in good agreement with the *Levich* equation.

The effect of withdrawal rate on the spectral transmission curves are tested and shown in Fig. 4. The position of maximum transmittance (λ_{max}) depends on the thickness of the film, while the magnitude of the maximum is only determined by the refractive index of the film [1]. It can be observed from the results that the maximum wavelength (λ_{max}) of each curve is the rapidly varying function of the rate. *K. Cathro et al.* have reported the same effect of withdrawal rate on spectra curve [11]. In other words, the maximum wavelength of transmittance (which is controlled by the film thickness) can be adjusted by withdrawal rate. Also Fig. 4 shows the value of maximum transmittance is independent of withdrawal rate. This confirms that the refractive index (which controls the transmittance value) is nearly independent of withdrawal rate.

In Fig. 5, the experimental results and theoretical data (refractive indexes 1.46 and 1.32) of SiO_2 are shown and compared. There is a good agreement between the experimental and theoretical curve (refractive index 1.32) in λ_{max} and in the magnitude of transmittance. In the other theoretical curve (refractive index 1.46) the magnitude of transmittance is lower than experimental. As we mentioned, the magnitude of the maximum is only determined by the refractive index of the film. Thin films with low refractive indexes have higher transmittance [12]. In theoretical calculation, the refractive index of SiO_2 is supposed 1.46, but the higher transmittance of experimental data shows that the refractive index of SiO_2 is much lower. The experimental results and theoretical data for SiO_2 with n=1.32 are same. I.M. *Thomas* has reported the same result [13].

X-ray diffraction (XRD)

X-ray diffraction (XRD) is used in order to investigate the crystallinity of the film. In XRD graph of the films that are heated in the temperature range 100-500 °C, crystalline phase isn't observed and films are amorphous. *W. Que et al.* have reported the same result [14].

Heat treatment

Deposited films by sol-gel method, contain water and organic materials, and mechanical properties of the film are poor and must be improved. One way to overcome
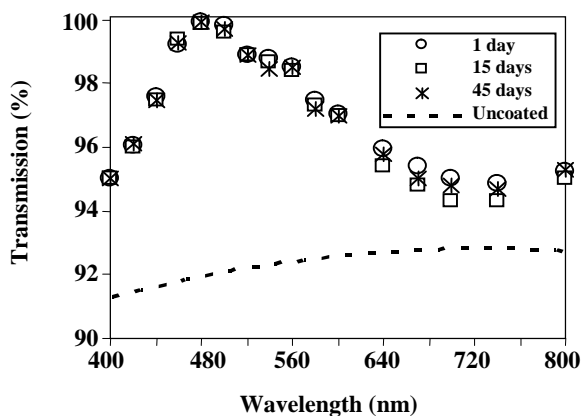
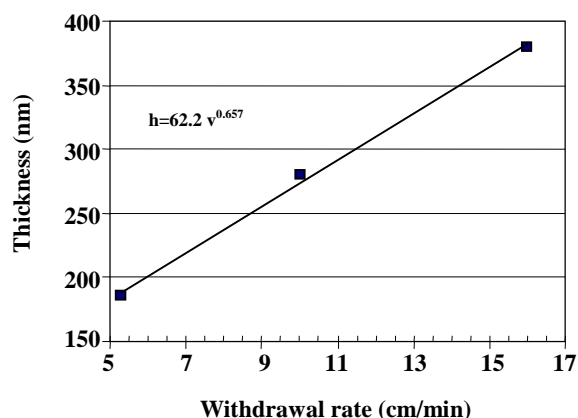*Fig. 2: Transmission spectra of thin films produced over the 45-days period.*

Fig. 4: The effect of withdrawal rate on the transmission spectra curves.

Fig. 3: The thickness of coating as a function of withdrawal rate.

Fig. 5: Comparison between experimental result and theoretical data.

these problems is heat treatment. So the sample should be put in an oven for a suitable time and temperature. This improves the optical and mechanical properties of thin film. Also removes water and organic materials from thin film.

Fig. 6 shows the optical transmittance curves between 400-800 nm of the film with different heat treatment temperatures. It can be observed that the transmission and λ_{max} of SiO_2 film are changed with heat treatment temperature. The increasing annealing temperatures displace the λ_{max} towards shorter wavelengths. This is in agreement with the fact that the film thickness is decreased with increasing the heat treatment temperature [15]. In other words, increasing the annealing temperature causes the film shrinkage. The reason of shrinkage is removal of water and organic materials form thin film [6, 16]. The shrinkage causes
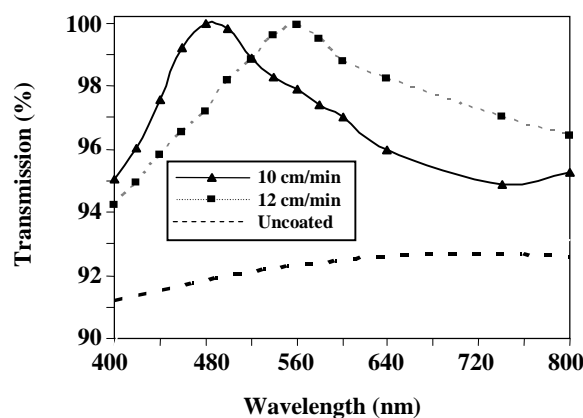
transfer of λ_{max} from 520 nm (at 100 °C) to 500 nm (at 300 °C) and to 475 nm (at 500 °C). The increasing of the temperature improves the maximum transmittance from %98.55 at 100 °C to %99.30 at 300 °C, and then %99.95 at 500 °C. This improvement of transmittance with temperature can be attributed to the increase of structure homogeneity, and a lower defect density [17]. Also increasing of heat treatment time has same effect on the λ_{max}.

Table 1 presents the λ_{max}, and the maximum transmission of a thin film (heat treatment at 500 °C for 60 and 120 minutes). The results show that, heat treatment causes improvement of the maximum transmission from % 98.45 at 25 °C to %99.95 at 500 °C. The increasing of heat treatment time, at 500 °C, causes the shift of the λ_{max} to shorter wavelengths and has no effect on the maximum transmission. In 500 °C

Table 1: The optical properties (λ_max & maximum transmission) of silica coating at different heat treatment time's.

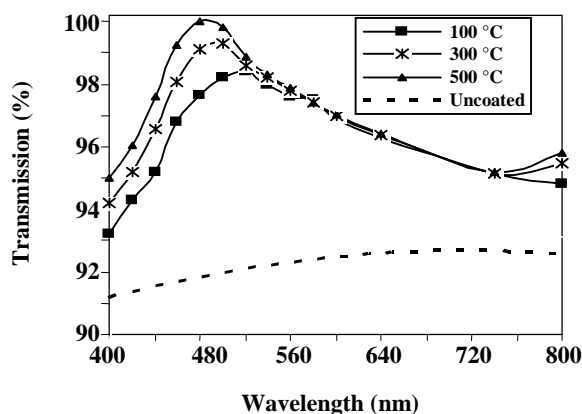|	As coated 25 °C	60 min 500 °C	120 min 500 °C	Theoretical
λ_{max} (nm)	580	475	460	480
T (%)	98.45	99.95	99.95	99.96

Fig. 6: Optical transmission spectra of SiO₂ thin films as a function of annealing temperatures.

temperature, the experimental data approaches to expected theory.

CONCLUSIONS

We have obtained a new solution to prepare SiO₂ thin films by sol-gel method. There is a good agreement between the film thickness and the *Levich* equation. This solution is stable during 45 days. The SiO₂ films have amorphous structure the annealing temperate of 500 °C. Increasing the annealing temperature improves the transmittance and the highest transmission is obtained at 500 °C (approximately 99.5%). The position of maximum transmission (λ_{max}) can be adjusted by withdrawal rate. The time of heat treatment has same effect on the λ_{max}.

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