COMPARISONS OF SOL–GEL-DERIVED THIN FILMS WITH MONOLITHS IN A MULTICOMPONENT SILICATE GLASS SYSTEM*

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A sol–gel process was used to produce glasses of the composition (wt.%) 66% SiO_2–18%B_2O_3–7%Al_2O_3–3%BaO–6%Na_2O. Monolithic samples of this composition were made by gelling concentrated solutions (12% equivalent oxides). Thin films were prepared by dipping soda–lime glass substrates into dilute solutions (2% equivalent oxides). The densification of both the monolithic gels and the thin films was investigated by thermal gravimetric analysis combined with dilatometry (monoliths) and ellipsometry (films). The pore structures and refractive indices of both films and monoliths were also investigated as functions of the gel-to-glass conversion temperature. Although for the same heat treatment most film properties showed trends similar to those for monolithic samples, film properties generally exhibited values which corresponded to a more compact structure, *i.e.* higher density, lower surface area and higher refractive index.

1. INTRODUCTION

In a previous paper[1] we reported on the preparation of multicomponent silicate gels of the composition (wt.%) 66%SiO_2–18%B_2O_3–7%Al_2O_3–6%Na_2O–3%BaO and the conversion of these gels to monolithic glasses at temperatures less than the glass softening point. In the present study thin gel films of the above composition were deposited on soda–lime glass substrates by a dipping process and converted to glass films by low temperature heat treatments. The purpose of this investigation was to characterize this gel-to-glass conversion for thin films.

In order to obtain a coating which might serve as a protective barrier, it is necessary that the pore structure be discontinuous. Therefore it is essential that the gel-to-glass conversion be characterized with respect to densification and specific surface area. The present study was conducted so that these parameters could be monitored as a function of the conversion temperature. The results are compared with those obtained previously for monolithic gels so that the differences between sol–gel preparations of thin films and monoliths could be established.

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2. EXPERIMENTAL PROCEDURE

2.1. Sample Preparation

A schematic representation of the sol gel process used to produce both monoliths and thin films is shown in Fig. 1 and reported in detail elsewhere[2]. The preparation method employed was essentially the same as those developed by Dislich[3] and Thomas[4,5] and reported on by other workers[5-8], in which metal alkoxides of network-forming oxides are partially hydrolyzed and then polymerized to form a gel network linked by bridging oxygen atoms. Network-modifying cations Ba^{2+} and Na^+ were added as acetates in aqueous solutions.

Bulk monolithic samples were prepared by casting concentrated solutions (12 wt.% oxide) in Teflon molds. Thin films were prepared by mechanically dipping soda-lime glass substrates into low concentration solutions (2.5 wt.% oxide) and withdrawing them vertically at a rate of about 1 cm min^{-1}. Samples were multiply dipped to obtain sufficient coating weights for weight loss and surface area measurements.

Heat treatments were performed in stagnant air atmospheres at a heating rate of 1 C min^{-1}. Weight loss, shrinkage and differential thermal analysis (DTA) measurements were made dynamically for monolithic samples. To obtain equivalent data for thin films, shrinkage measurements were made on samples heated to the temperatures indicated then immediately quenched to room temperature. Refractive index and surface area measurements for both monolithic and thin film samples were made on similarly quenched specimens.

2.2. Characterization methods

Linear shrinkage, specific surface area and weight loss of the thin films and monoliths were measured as functions of the conversion temperature. The characterization methods employed for the monolithic samples have been reported previously[1]. The shrinkage for thin films was determined by ellipsometry. The specific surface area was determined by the Brunauer–Emmett–Teller (BET) method[9] using krypton gas at liquid nitrogen temperatures. The weight loss was determined by suspending coated substrates from a Cahn model 1000 microbalance and heating in stagnant air to 600 C.

The refractive indices were determined for bulk samples by the Becke line method and by the method of minimum deviation[10] in which a monochromatic beam of light was passed through a 30° right prism machined from the gels. The angle of deviation ε, i.e. the angle which the emergent ray makes with the incident ray, was minimized and the refractive index of the bulk gel was determined from the relation

$$n = \frac{\sin\{(\varepsilon_{min} + \alpha)/2\}}{\sin(\alpha/2)} \tag{1}$$

where $\alpha = 30°$, the angle between the two prism faces. The refractive indices of the thin films were determined by ellipsometry and by reflectivity measurements using Fresnel's equation at normal incidence in air where

$$R = \left(\frac{n-1}{n+1}\right)^2 \tag{2}$$

3. RESULTS AND DISCUSSION

3.1. Removal of organic compounds and water

During the gel-to-glass conversion, chemically and physically bound water as well as residual organic compounds were removed by heating in air to approximately 400 °C. Figure 2 shows weight losses for films and monoliths and Fig. 3 shows the corresponding DTA trace. The weight loss curves for both films and monoliths have similar features. From room temperature to 150 °C a weight loss of approximately 10% was observed for both samples owing primarily to removal of physically bound water[11]. This corresponds to the endotherm observed in the DTA trace. Above 200 °C carbonization[12] and oxidation of residual organic compounds takes place. This resulted in an endotherm at 220 °C and a broad exotherm centered at 330 °C. Between 200 and 400 °C films showed an increased weight loss of approximately 8 wt.% in comparison with the monolithic samples. This was due to the increased amounts of acetic acid required to maintain solution stability at pH 4.5 after dilution with ethyl alcohol.
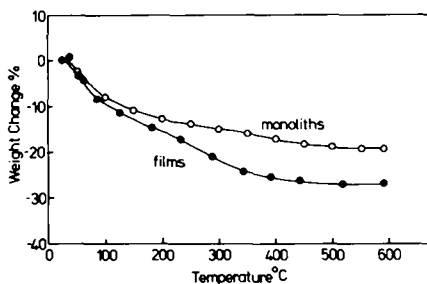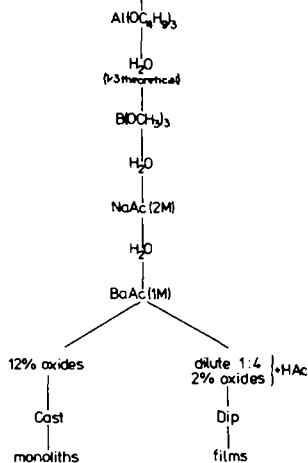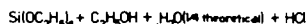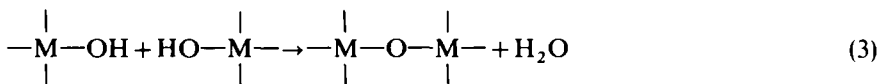

Fig. 1. Schematic diagram of sol–gel processes for films and monoliths.
Fig. 2. Percentage weight loss for monoliths and films.

Over the temperature range 25–500 °C water was slowly liberated, probably as the byproduct of condensation reactions of the type

$$-\overset{|}{\underset{|}{M}}-OH + HO-\overset{|}{\underset{|}{M}}- \longrightarrow -\overset{|}{\underset{|}{M}}-O-\overset{|}{\underset{|}{M}}- + H_2O \qquad (3)$$

as suggested by Yamane et al.[12] Most of the weight loss was completed by 400 °C which corresponded to the high temperature boundary of the oxidation peak.

3.2. Densification

Thin films, if adherent, shrink only in thickness during the gel-to-glass

conversion. Therefore the relation

$$t = \frac{\text{coating weight}}{\text{area} \times \text{density}}$$ (4)

should predict the coating thickness as a function of weight loss and densification.
Figure 4 shows a plot of the percentage of linear shrinkage for monoliths along with
the percentage of thickness shrinkage for films as a function of conversion
temperature. Both predicted and measured thickness shrinkages are plotted. The
predicted curve uses the weight loss data (Fig. 2) along with densification data
obtained previously for monoliths[1]. Differences arise between the predicted and
measured curves owing to differences in densification behavior between films and
monoliths. At temperatures above 525 °C ellipsometry data was uninterpretable:
525 °C corresponds to the glass transition temperature of the soda-lime glass
substrates. Heat treatments at or above 525 °C apparently caused significant
interdiffusion at the film-to-glass interface, resulting in a graded refractive index
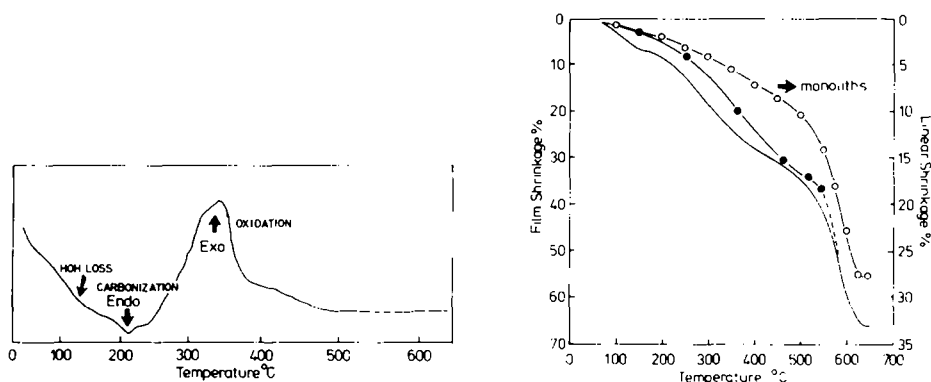rather than an abrupt step. Ellipsometry, therefore, could not be used to measure
thicknesses.

Fig. 3. DTA for powdered gels heated in stagnant air at 10 °C min⁻¹.

Fig. 4. Percentage linear shrinkage for monoliths (○) heated at 1 °C min⁻¹ and percentage thickness
shrinkage for films (●) heated at 1 °C min⁻¹ to the temperatures indicated and quenched. The lower solid
line was predicted from the weight loss (Fig. 2) and densification of monoliths (see ref. 1).

Weight loss (Fig. 2) and shrinkage data (Fig. 4) were combined to obtain the
density data shown in Fig. 5 for films and monoliths. Unheated films showed a 13%
increase in density compared with monoliths, which partially explains why
measured film shrinkages were less than predicted values (Fig. 4). The increased
density is believed to be due to either the adhesion mechanism existing between the
film and substrate in which bridging oxygen atoms are formed or to increased
amounts of residual organic compounds or absorbed water present in the films.
Heating to 200 °C caused the film density to decrease to a value slightly lower than
that for the monolithic samples, which suggests that physically bound water might
contribute to the initially high density. Further heating, however, resulted in the
reverse effect so that at all higher temperatures films showed higher densities
than monoliths. At approximately the glass transition temperature of the gel

composition, 550 °C, monolithic samples densified rapidly owing to viscous sintering[13]. Films behaved in a similar manner at even lower temperatures and densified rapidly with time when heated isothermally, as indicated by the arrows in Fig. 5. Above 525 °C, no film densification data were obtainable.

3.3. Pore structure

The BET surface area measurements shown in Fig. 6 indicate a major difference between the pore structure of films and monoliths. At all temperatures, films showed considerably lower surface areas than monolithic samples. Densities of films were generally greater than those of comparably heated monoliths (Fig. 5); however, the contribution of increased density alone probably does not explain all the differences observed in the surface area. Gel films might incorporate a larger proportion of isolated rather than continuous pores, which would result in lower values of surface area being obtained by the BET method.
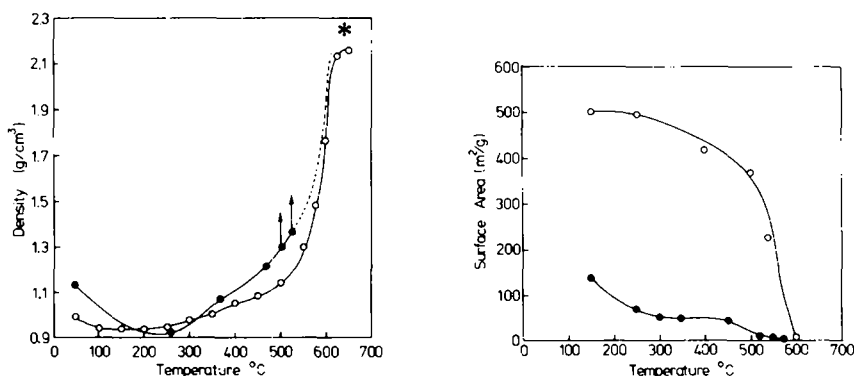

Fig. 5. Densification for monoliths (O) heated at 1 °C min⁻¹ and films (●) heated at 1 °C min⁻¹ to the temperatures indicated and quenched. The symbol * indicates the density of conventionally melted glass of this composition and ↑ indicates rapid densification with time.

Fig. 6. BET surface area for films (●) and monoliths (O).

Monolithic samples heated from 150 to 500 °C contained pores of very narrow size distributions, ranging from 30 to 40 Å in diameter[1]. If, for gel films with the same pore volume, the average pore diameter is larger, lower values of surface area would be obtained for the films. It is conceivable that the pore structure for films might also be affected by stresses set up in the film owing to the constraint that films can only shrink in one unrestrained direction.

Figure 7 shows transmission electron microscopy (TEM) micrographs of an unheated gel fragment scribed from a monolithic sample along with a gel fragment heated to 575 °C. Very fine continuous porosity is observed for the unheated sample. After 12 h at 575 °C the porous network was apparently completely collapsed for monolithic samples. The minimum temperature at which the pore structure becomes discontinuous has not yet been determined for gel films. This, however, is an important consideration with regard to the preparation of protective films.

3.4. Refractive index

Refractive indices for monoliths were determined by two different methods.

(a)   (b)

Fig. 7. Transmission electron micrographs of (a) unheated gel monolith fragments (surface area equals 400 m^2 g^{-1}) and (b) gel monolith fragments heated to 575 C for 12 h.

The minimum deviation method[10] requires that light be passed through a monolithic gel prism and thus measures the bulk refractive index. In the Becke line method, continuous pores are impregnated by an immersion oil so that the refractive index of only the condensed phase is measured.

Values of the refractive index measured by the Becke line method initially increased with time of immersion in the respective oils owing to the slow process of flow through the fine capillaries. Samples were immersed for periods sufficient that no further increase in index was observed with time. It was assumed that under these conditions all continuous pores were filled with oil.

Figure 8 shows the results for both measurement methods. The curves obtained were quite similar in shape but not in magnitude owing to the effect of porosity. The bulk refractive index can, however, be predicted from the Becke line data by the following relation:

$$n_p^2 = (n^2 - 1)(1 - P/100) + 1 \tag{5}$$

where n_p is the bulk refractive index, n is the refractive index of the condensed (non-porous) material and P is the volume percentage porosity. For a 400 C gel. P was determined to be 37.4% by a nitrogen desorption technique[14]. If the measured value, 1.437, is taken as the refractive index of the non-porous material at 400 C (Fig. 8), then a value of 1.300 is obtained for n_p, which corresponds well to the bulk refractive index measured (1.295).

The minimum in bulk refractive index corresponded to the temperature at which all the organic compounds were removed (approximately 400 C). At temperatures below this, organic compounds, porosity, absorbed water and polymer structure all contribute to the bulk refractive index, so that the material cannot be considered to be simply a porous glass. The Becke line data eliminated the effect of continuous porosity on the refractive index; however, values of the refractive index obtained were still significantly lower than that for the comparable

glass composition (1.48), even after the residual organic compounds were removed. This indicates that either the condensed phase contains isolated micropores formed as a result of removal of organic compounds[12] or that the gel structure contains a higher free volume. Recent work by Puyané et al.[15] suggests that the gel structure might be similar to that of a conventionally melted glass which had been rapidly quenched from well above the transformation range (i.e. with a high fictive temperature). The Becke line data reported here as well as previously reported pore volume data[1] might confirm this type of gel structure model.

The refractive index of thin films is shown in Fig. 9 along with the corresponding film thickness as measured by ellipsometry. The change in refractive index with temperature shows the same general trend as for monolithic samples; however, the measured index is in all cases higher than that measured for the bulk monoliths by the minimum deviation method. The higher refractive index may be due to the adsorption of water (the refractive index for films increased with time of exposure to a moist atmosphere) and the greater density of the films (Fig. 5).
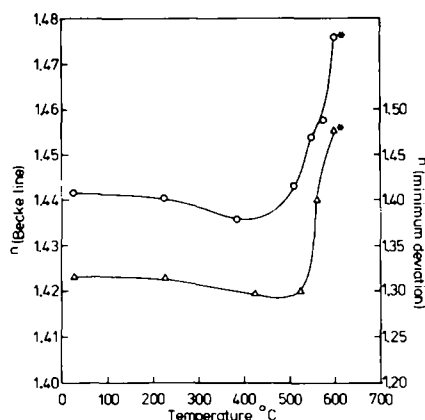

Fig. 8. Refractive index for monolithic gels measured by the Becke line method (○) and by the minimum deviation method (△). The symbol * indicates the refractive index of conventionally melted glass of this composition.
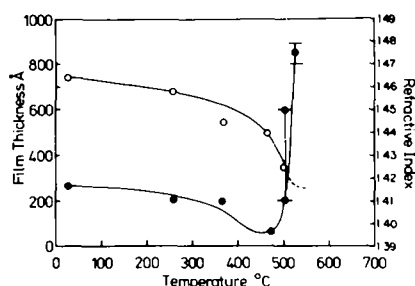
Fig. 9. Film thickness (○) and refractive index (●).

At temperatures above 500 °C, the refractive index was obtained using Fresnel reflection coefficients for polarized light reflected from a surface. This technique resulted in values ranging from 1.47 to 1.48, as expected for a borosilicate glass. Therefore, it is expected that films become fully dense at temperatures only slightly greater than 500 °C.

An unheated gel film of thickness 900 Å reduced the reflectivity of the glass surface by a factor of two at a wavelength of 5000 Å. Thus films could be used for antireflective coatings; however, they would be affected by environmental exposure if continuous porosity existed within the film.

4. CONCLUSIONS

Although as a function of conversion temperature most film properties showed

trends similar to those for monolithic samples, at any given temperature film properties consistently exhibited values which corresponded to a more compact structure, *i.e.* higher density, lower surface area and higher refractive index. The reasons for these differences have not yet been explained.

Films showed rapid densification at temperatures above 500 C; however, because both the glass corresponding to the film composition and the soda lime glass substrate approached their respective glass transition temperatures above 500 °C, some information concerning film densification was unobtainable. Refractive index measurements indicated that films were converted to dense borosilicate glasses at temperatures near 525 °C.

Refractive index results suggest that the gel structure is much more open than the comparable glass structure for temperatures less than the glass transformation temperature.

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