PROPERTIES OF FILMS PREPARED FROM LOW SURFACE AREA/DENSITY ALUMINA-SILICA

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ABSTRACT

A sol-gel method was used to prepare bulk, closed pore, amorphous alumina-silica. Films prepared from this 47wt% Al_2O_3-SiO_2 composition were examined by SAW, elipsometry and electrical measurements. The films were found to have a surface area of 1.1 cm^2/cm^2, a refractive index of 1.44 at 633 nm, and a relative permittivity of 6.2 at 200 KHz. These properties indicate potential applications as hermetic seals, barrier coatings, dielectric layers for capacitors and passivation coatings for electronic circuits.

INTRODUCTION

An amorphous alumina-silica material prepared via sol-gel routes was found to have an anomalously low surface area and density in a composition of approximately 47 wt% alumina [1]. From various techniques, it was determined that these properties were due to closed porosity in the material [2]. If closed porosity can be maintained in the films, they would be ideally suited for hermetic, thermal, and chemical barriers. The large amount of porosity also suggests it as a candidate for reasonably low relative permittivity ceramic coatings for electronic applications.

EXPERIMENTAL

The 47wt% alumina-silica sol was prepared using alkoxide precursors. Ethanol was added to TEOS in a round bottom flask. A solution of ethanol and HCl (molar ratios 1 EtOH: 1 conc. HCl: 0.8 TEOS) was added to the flask, then an appropriate amount of aluminum tri-sec butoxide (ASB) was added. This was allowed to react (with slight agitation) for several minutes, then diluted with ethanol, and refluxed at 353K overnight. The gel was formed by adding water (molar ratios 100 H_2O:Si) to the sol and allowing the gel to start forming. Films were prepared by spin coating at 2000 rpm.

Dynamic light scattering was performed on a series of gelling mixtures using a Wyatt spectrometer equipped with the autocorrelation option. The two components of each sample were filtered through a 0.2 μm filter into a clean, dust-free scintillation vial where they were gently mixed then place in the spectrometer. Temperature was controlled to 37.0 ± 0.5 °C. Focussed HeNe light (633 nm) was scattered at a fixed angle of 92° and collected by a SelFoc optical fiber, which fed the scattered light to a Hamamatsu photomultiplier tube. The intensity autocorrelation function $\langle I(0)I(t)\rangle$ was obtained by feeding the photocurrent to a Langley-Ford 1096 digital autocorrelator via a preamplifier. The data were taken at 20 minute intervals continually from the time of mixing until the gel time, which was (crudely) determined by observing an aliquot.

To characterize porous films using surface acoustic wave (SAW) devices, the solution was cast onto a quartz substrate then placed in a brass test case with a stainless steel lid for gas inlet and outlet. The devices were cooled to liquid N_2 temperatures (77K, by immersion) and a gas mixture of He and N_2 was passed over the film. The frequency of the device was monitored as the N_2 concentration (p/p_o where p is the N_2 partial pressure and p_o is the N_2 saturation vapor pressure) in the gas stream is varied from zero up to about 0.95 and then back to zero by adjusting the relative flow rates of a N_2 stream and a He mix-down stream. The frequency shifts are used to determine the mass of N_2 adsorbed on the surfaces or condensed in the pores of the films as a function of the

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N_2 concentration (N_2 adsorption isotherm). If the SAW device is used as the feedback element of an oscillator circuit, relative changes in frequency (f) can be related to relative changes in wave velocity (v) which can then be related to changes in the film mass per area (m) by :

$$\frac{\Delta f}{f_o} = \frac{\Delta v}{v_o} = c_m f_o m \qquad (1)$$

where c_m is the mass sensitivity of the device (1.3×10^{-6} cm^2 s/g for quartz) and f_o and v_o are the unperturbed frequency and velocity . For the 97 MHz devices used in this study, a 10 Hz frequency change (typical noise level) is due to mass change of only 0.8 ng/cm^2. The N_2 adsorption isotherm was used to calculate the surface area of the film using the BET analysis and the pore size distribution by accounting for capillary condensation. Additional details on the experimental system and this characterization technique are given in reference [3].

The 47% sol-gel alumina-silica films, spin-coated on silicon, were analyzed by null elipsometry. The home-built elipsometer is in the "PCSA" configuration, i.e. polarizer, (quarter-wave) compensator, sample, analyzer. The compensator was set at 45° and the angle of incidence was 67.5°. An unfocussed beam from a HeNe laser was first passed through a depolarizer then into the system optics. Two-zone measurements were made by finding nulls in the reflected intensity while varying the analyzer and polarizer angles. Two measurements were made at different spots in the central region. In each case the beam average over approximately 2 mm^2 of area and the two measured spots were at least 2 mm apart. Since reproducible results were obtained, defects and inhomogeneities apparently had no effect on the results.

The electrical properties of the Al_2O_3-SiO_2 films were characterized by the fabrication of simple parallel-plate capacitors from the film. A silicon wafer was used as a mechanical substrate onto which a 2000Å thick aluminum layer was e-beam evaporated to form the bottom electrode of the capacitors. The alumina-silica gel was then spin coated on this aluminum coated silicon wafer. The sample was heated to 325°C for 2 hours in an UHP Argon environment, which was found to greatly improve the films electrical properties. To form the individual test capacitors, a second aluminum evaporation (2000Å) with a shadow mask was used to form metal dots of approximately 300 μm diameter.

The capacitors were tested for electrical performance by using an HP4145A Semiconductor Parameter Analyzer and an HP4275A Multi-Frequency LCR Meter. The dielectric constant was determined from the measured capacitance by assuming an ideal parallel-plate model:

$$\varepsilon_r = \frac{t}{A\varepsilon_o} C, \qquad (2)$$

where ε_r is film's relative permittivity (dielectric constant), t is the measured film thickness, A is the metal dot's area, ε_o is the free-space permittivity, and C is the measured capacitance. Fringing fields were safely neglected due to the thinness of the coating in relation to the test capacitors' diameters (over 3000 to 1). The test capacitors' areas were determined with an optical microscope. The films thickness was measured using elipsometry and found to be relatively uniform over the sample and about 875 Å thick.

RESULTS AND DISCUSSION

In the light scattering experiment (Figure 1), the correlation functions were nonexponential decays that appeared to be the sum of two or more exponentials. The data were analyzed by fitting second-order cumulant to the early and late times in order to bracket the decays.

$$\ln\langle I(0)I(t)\rangle = \mu_o - \mu_1 t + (\mu_2/2)t^2 \qquad (3)$$

Thus the above formula was applied for $t \to 0$ and $t \to \infty$ separately. The first cumulant was related to a hydrodynamic radius R_h through the relation,

$$\mu_1 = 2 D q^2 = 2 \frac{kT}{6\pi\eta R_h} q^2 \qquad (4)$$

where D is the diffusivity, $q = \left(\frac{4\pi n}{\lambda}\right)\sin\left(\frac{\theta}{2}\right)$ is the scattering wavevector, n is the sample index of refraction, θ is the scattering angle, η is the viscosity, and T is the temperature.

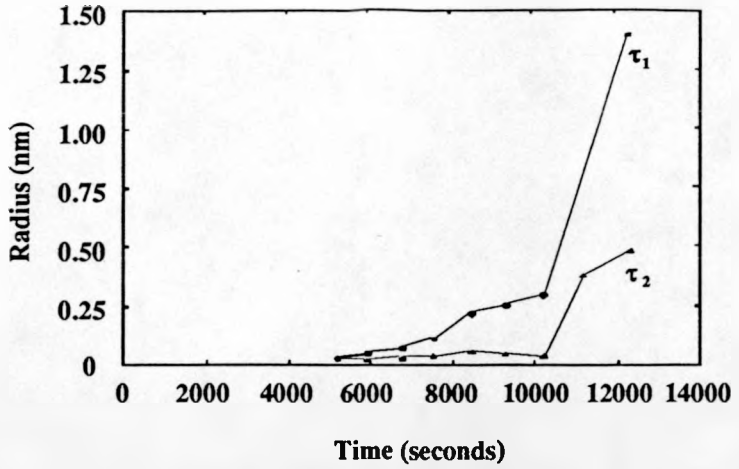


Figure 1. Light scattering results of 47% Al_2O_3-SiO_2 ASB (molar ratio 100H_2O:Si).

The relatively smooth and featureless films were spun at $t/t_{gel} \approx 0.5$, which corresponds to ≈7200 seconds in Figure 1. ^{29}Si NMR by Pouxviel showed that even under slow hydrolysis conditions, the Si and Al reactions had proceeded sufficiently by this time [4]. Films made from solutions before $t/t_{gel} \approx 0.5$ were found to be quite thin, while films made at later times were found to have a varying degree of waviness, presumably due to the large variation in the features of the gel.

A SAW device was coated with the 47% alumina-silica to determine whether the low surface (and presumably the closed porosity) remain in the films. From Figure 2, it is show that the 47% alumina-silica film is found to have a surface area of 1 cm^2/cm^2, compared to a silica gel having a surface area of 46 cm^2/cm^2. These measurements would indicate that the low surface area, and thus the closed porosity remains in the film material.

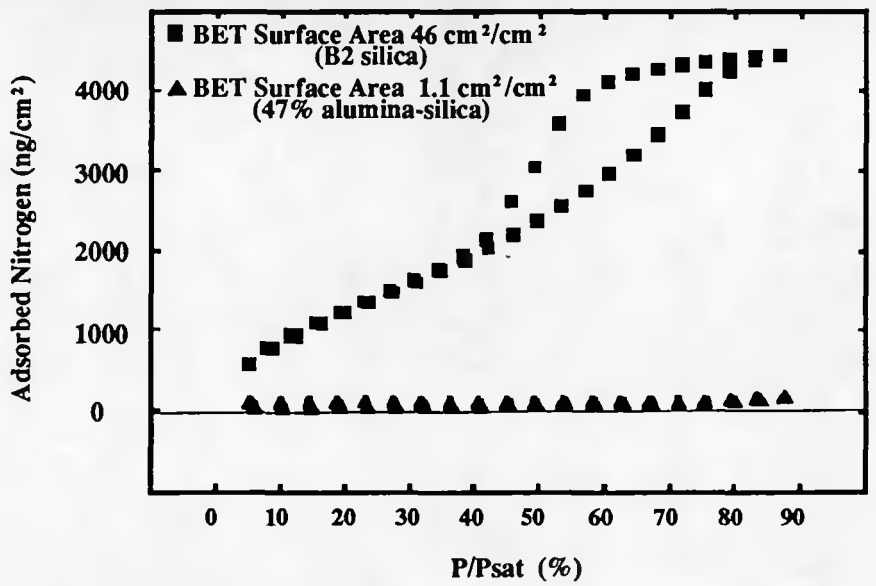


Figure 2. SAW measurements for 47% Al_2O_3-SiO_2 and silica films.

The refractive index (n), as measured by elipsometry, was 1.44. Using a refractive index for the solid matrix as 1.55, the porosity is calculated to be 20%. In principle, the porosity and refractive index can be varied and still maintain closed porosity by proper selection of processing conditions.

Figure 3 shows a plot of density as a function of wt% Al_2O_3 for the bulk material. From the rule of additive densities the expected density of the 47% composition should be 2.65 g/cm^3, from the graph the density would be ≈2.52 g/cm^3. The measured density was 2.2 g/cm^3, which gives a porosity in the range of 15% to 20%. Theoretical porosity is similar to that obtained from elipsometry (20%), whereas the measured (15%) is probably the result of the greater time available for morphological rearrangement during drying in the bulk as compared to films.

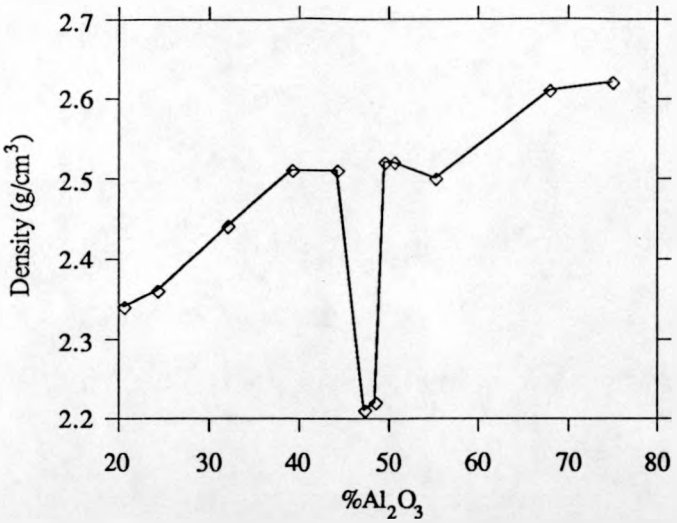
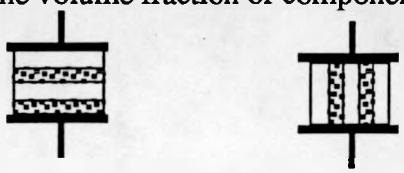


Figure 3. Density as a function of weight% alumina in 47% alumina-silica

Theoretical models for relative permittivity calculations (Figure 4) show two extremes which should bound the actual values obtained [5,6,7]. The series model (a) would bound the relative permittivity on the low side, and the parallel model (b) would bound the measurement on the high side. The general equation for the models is:

$$\varepsilon_r^n = \Sigma v_i \varepsilon_i^n \qquad (5)$$

where k is the relative permittivity of the composite material, k_i is the relative permittivity of the individual components and v_i is the volume fraction of components.



a. series model b. parallel model

Figure 4. Theoretical models for dielectric constant calculations.

An intermediate value between the series and the parallel models, is found by the "log" equation:

$$\log(\varepsilon_r) = \Sigma v_i \log(\varepsilon_i) \qquad (6)$$

These three equations are plotted versus porosity in Figure 5, assuming a homogeneous mixture of alumina-silica with relative permittivity of 5.7.

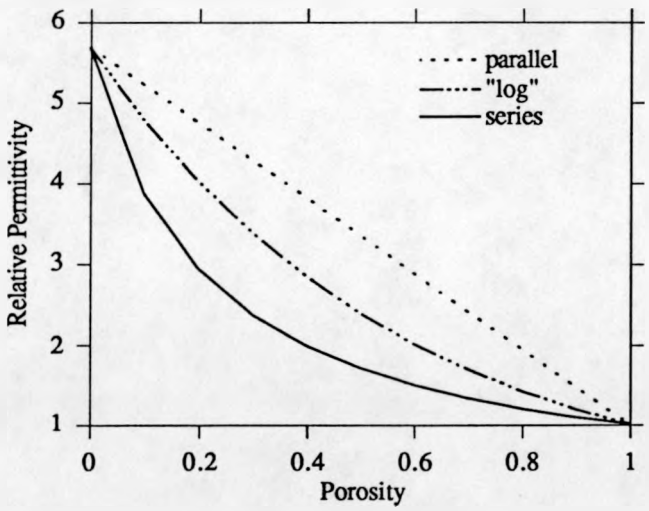


Figure 5. Theoretical dielectric constant as a function of porosity (equations 5,6).

For the range of porosity calculated from elipsometry and density data, the relative permittivity is expected to be in the range of 2.6 to 5.0. For crystals and glasses:

$$\varepsilon_r = n^2 \qquad (7)$$

From the measured refractive index, if this were crystalline or glassy, we would expect a relative permittivity of 2.1.

The test capacitors were first tested with the Semiconductor Parameter Analyzer for leakage current. Virtually all of the capacitors tested (randomly over several cm^2) where seen to be leakage free at low test voltages. This gives a good indication of the pin-hole free nature of the film. The test capacitors' breakdown voltage was measured to be approximately 2 Volts. This corresponds to an electric field of approximately 230 KV/cm. The dielectric constant was measured to be virtually constant 6.2 ± 0.2 over a frequency range of 10 KHz to 4 MHz. The measured quality factor (1/ loss-tangent) was found to be about 85 at 100 KHz.

CONCLUSIONS

The 47% alumina-silica films are relatively simple to process. Films of various thicknesses and homogeneity may be obtained in different stages of the process, dependent on the size of the polymers at various stages in gelation. The low surface area measured by SAW indicate that the closed porosity has been retained in the films. From the capacitance measurements, the spin-coated film was seen to be void of pin-holes and relatively uniform in thickness. The films relative permittivity was determined to be approximately 6.2 ± 0.2 with a reasonable quality factor. This value was much greater than that predicted from elipsometry measurements, possibly due to difficulty in measuring film thickness, the hydroxides space charge polarization, or high ionic compared to electronic contributions to the relative permittivity.

This film has potential use in two important electrical applications: dielectric for capacitors, passivation coating for microelectronic circuits. For these applications the film's primary benefit would be in the predicted low permeability which would provide excellent stability from possible environmental contaminants. For capacitors, the measurements presented give a direct indication of expected performance. The quality factor was observed to be dependent on the drying conditions. For a passivation coating, the film can be applied with low-temperature processing, which would allow for the passivation of temperature sensitive circuits (i.e. GaAs). With the film's predicted low permeability, a thin coat should be adequate for passivation. The dielectric constant is somewhat higher than desired, but a thin coating of the film should have little effect on a circuit's operation.

The possible future use of this film in these applications will depend on further studies of the film's electrical and mechanical properties and studies on film quality verses drying conditions.

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