

Sol–Gel Synthesis and Characterization of Magnesium Silicate Thin Films

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An H₂O₂-assisted, sol–gel synthesis route to precursors to magnesium silicate thin films is described. Films having ratios of Mg to Si from 1 to 3 were prepared by spin-coating. On substrates such as silicon, aluminum, steel, glass, and fused silica, repeated coatings were applied, without intermittent treatment, to give ~0.5 μm thick films. Crack-free consolidation was achieved by conventional or microwave heating. Densification of the films on silicon was studied by IR spectroscopy, ellipsometry, and microhardness measurements; IR analysis indicated that these films were amorphous to at least 750 °C. At high enough temperatures, durable films were obtained that exhibited antireflective properties.

Introduction

Over the past several years, sol–gel technology has been used extensively to prepare coatings. These coatings, typically made from SiO₂, Al₂O₃, TiO₂, and others, have a variety of applications.^{1–4} In particular, anti-scratch^{5–7} and antireflective coatings^{8–14} are common uses.

Recently, novel routes to preparing sols as precursors for enstatite,¹⁵ forsterite,¹⁶ and Cr-doped forsterite¹⁷ were developed using hydrogen peroxide. Sols for enstatite were used to prepare clear, crack-free coatings on various substrates such as silica, polystyrene, and polycarbonate. Sols for forsterite were dried and fired

to prepare crystalline powders. While much has been learned about some of the early intermediates in the formation of the sols,^{18,19} little is known about the coating process. How does viscosity of the sol depend on concentration? Can stable sols be made to give reproducible coatings over a long time? What thicknesses can be obtained? If several coats were applied successively, would heat treatment be necessary between coats? The properties of the coatings, such as refractive index, adhesion to substrates, and hardness have not been investigated. How will these properties be affected by heat treatments? Hardnesses can be measured by continuous microindentation, which over the past few years, has become a powerful tool in the characterization of the mechanical properties of thin films.^{20–26} In particular, the variation of hardness with depth in thin films has been studied effectively by this technique.^{22,25,26}

In this paper we describe the synthesis and characterization of stable magnesium silicate sols that were used to coat various substrates. Coatings on silicon, glass, steel, aluminum, and fused silica were processed in conventional furnaces and in a microwave oven. The resulting thickness, index of refraction, IR spectra, hardness, and antireflection properties are discussed in terms of coating composition and heat treatments.

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Table 1. Experimental Details of Sol Preparations

sol ^a	Mg:Si	TEOS (g)	Mg (g)	MeOH (mL)		30% H ₂ O ₂ (g)	in MeOH (mL)	H ₂ O (g)	in MeOH (mL)	R3 ^c
				for Mg	for rinsings ^b					
1	1:1	15.59	1.83	175	331	1.99	150	3.38	84	4.0
2	2:1	15.91	3.71	350	322	8.135	150			6.0
4	1:1	10.67	1.24	110	60	2.725	155	1.209	20	4.6
5	1:1	9.99	1.16	125	62	2.568	164	2.592	25	6.0
6	2:1	11.07	2.58	200	115	5.721	100	1.803	20	8.0
7	2:1	10.33	2.41	200	115	5.28	100	1.798	100	8.0
8	3:1	11.11	3.89	320	128	7.56	139			8.0

^a Sols **3** and **9** were made by dilution of sols **2** and **8**, respectively. ^b This volume includes methanol used for any dilutions. ^cR3 is the ratio of total equivalents of potentially reactive hydrogens to moles of silicon.¹⁹

Experimental Section

Starting Materials and General Comments. Magnesium chips (99.99%) and tetraethyl orthosilicate (TEOS) 99+% were obtained from Johnson-Matthey and Aldrich, respectively. Methanol was dried and distilled from Mg(OMe)₂ before use. All glassware was vacuum-dried before use, and all syntheses were carried out under argon.²⁷ Particle size analysis was done in methanol on a Brinkmann Model 2010 instrument. Coatings were applied with a Headway Research Model PM101D-R485 spin-coater except when the 10 × 15 cm substrates were coated, for which a Model PM101D-CB12 was used. Ellipsometry measurements were done at 6328 Å with a Rudolph Research AutoEL Ellipsometer with Phi0 set at 70°; calculations were done with DAFIBM software. Powders were calcined and fired in a Lindberg Model 51848 box furnace. The microwave oven used was a Model KSA-8007A from Montgomery Ward. Sample temperatures were measured with an Omega surface temperature probe. IR measurements were made on a Mattson Galaxy 4020 FT-IR spectrophotometer using FIRST software. For metal substrates, a Baseline specular reflectance accessory by Spectra-Tech was used. The XRD patterns were obtained on a Scintag PAD X diffractometer using DMS2000 software. Viscosity measurements were taken on a Brookfield Model RVTDV-IICP cone/plate viscometer. Carbon resonance RBS was preformed at Cornell University's Ion Beam Facility. Physical properties of coatings were evaluated with military specification MIL-C-675C. These tests include severe abrasion: 40 strokes of an erasure with a force of 2–2.5 lbs; adhesion: quick removal of cellophane tape; humidity: 24 h at ~48 °C and near 100% humidity; and salt spray: 24 h in spray. Transmission and reflection were determined by specular reflectance utilizing a spectrophotometer.

For the following preparations, the general procedures used are similar to those described for sol **1**; the amounts of reagents used are summarized in Table 1. Vessel sizes were also scaled for the volumes used. For hydrolysis method 1, a stoichiometric quantity of potentially reactive protons, "H⁺" (assuming that, at most, two come from H₂O₂ and one from H₂O) was added to the alkoxides.¹⁹ Hydrolysis method 2 refers to a situation where less than the stoichiometric amount of "H⁺" was used; usually, enough "H⁺" was present to react with 75% of the alkoxide groups. Slow additions of the solutions of H₂O₂ and H₂O were made with a Sage Instruments Model 341B syringe pump with a B-D Yale 50 mL glass syringe. Sols were made with different magnesium-to-silicon ratios and will be denoted as 1Mg:Si, 2Mg:Si, and 3Mg:Si.

Preparation of 1Mg:Si Precursor Sol 1. A small Schlenk storage vessel (SSV) was charged with 15.59 g (0.0749 mol) of TEOS. To a 250 mL Schlenk reaction vessel (SRV) that contained 175 mL of methanol and a Teflon magnetic stir bar was added 1.835 g (0.0749 mol) of magnesium chips. The SRV was fitted with a water-cooled condenser topped with a three-way gas adapter connected to a source of purified argon and to an oil bubbler. The mixture was cooled in an ice bath to reduce the rate of gas evolution. After 12 h, the evolution of gas stopped. The gray, slightly cloudy solution was transferred

quantitatively via cannula into a medium-porosity fritted filter tube and was filtered into a 2 L 3-necked creased flask (Ace Glass Co., Morton type). The SRV was rinsed with methanol (6 × 30 mL), and the rinsings were added to the flask. The flask was also equipped with a water-cooled condenser (connected to a source of argon and to an oil bubbler with a three-way gas adapter) and a mechanical stirrer with a Teflon paddle. The TEOS was quantitatively transferred into the flask via a cannula; the SSV was rinsed with methanol (3 × 5 mL). Methanol (136 mL) was added to dilute the mixture. A solution of 1.99 g of 30% H₂O₂ (0.0176 mol of H₂O₂ and 0.0774 mol of H₂O) in 150 mL of methanol was added to the flask at 3.4 mL/h. Then H₂O (3.38 g, 0.188 mol) in 83.5 mL of methanol was added at 1.67 mL/h. During additions, mixing was fast enough to foam the solution without causing splashing. The resulting sol, **1**, was clear, and GC analysis of the head space detected no volatile silicon alkoxides.¹⁸ A portion (~20 mL) of **1** was transferred to a SSV to check the long-term stability of the sol. The viscosity was visually estimated to be similar to that of methanol.

Preparation of 2Mg:Si Precursor Sols 2 and 3. The procedure described above was used to prepare sol **2** with these differences: (1) the amount of TEOS used was 15.91 g (0.0764 mol), and the Mg(OMe)₂ was prepared from 3.71 g of Mg (0.153 mol) in 350 mL of methanol in a 500 mL round-bottom flask; (2) methanol (157 mL) was used for the dilution; (3) hydrolysis was done with 8.135 g of 30% H₂O₂ (0.0718 mol of H₂O₂ and 0.316 mol of H₂O) in 150 mL of methanol added at 13.3 mL/h. A GC analysis of the headspace showed no volatile silicon alkoxides were present.¹⁸ The sol was clear and had a low viscosity (estimated). Sol **3** was prepared by diluting **2** to 74.4% of the original concentration as follows: to a 100 mL graduated SRV was transferred 59.5 mL of **2** followed by 20.5 mL of distilled methanol by means of a cannula. The mixture, **3**, was magnetically stirred for about 6 h.

Preparation of 1Mg:Si Precursor Sol 4. This sol was hydrolyzed by method 2 and was based on 10.67 g (0.0512 mol) of TEOS. The first half of the H₂O₂ solution was added at 5.1 mL/h, and the second half was added at 1.67 mL/h. The first half of the H₂O was added at 0.34 mL/h, and the rest was added at 0.51 mL/h. The sol was hazy with a bluish tinge.

Preparation of 1Mg:Si Precursor Sol 5. The procedure was similar to that for **4** and is based on 9.987 g (0.0479 mol) of TEOS and hydrolyzed by method 1 with a different ratio of H₂O₂ and H₂O (see Table 1). The H₂O₂ solution was added at 1.67 mL/h, and the H₂O was added at 0.38 mL/h. The sol was hazy with a bluish tinge.

Preparation of 2Mg:Si Precursor Sol 6. This sol, hydrolyzed according to method 1, is similar to **2** based on 11.1 g (0.0531 mol) of TEOS. The first third of the H₂O₂ solution was added at 20 mL/h, the second third being added at 8.4 mL/h, followed by 20 mL/h for the rest. The H₂O was added at 20 mL/h. The sol was hazy with a bluish tinge.

Preparation of 2Mg:Si Precursor Sol 7. This sol is similar to **6** and is based on 10.3 g (0.0496 mol) of TEOS. The H₂O₂ solution was added at 20 mL/h, and the H₂O was added at 20 mL/h. The sol was hazy with a bluish tinge.

Preparation of 3Mg:Si Precursor, Sols 8–10. The procedure described for **2** was used to prepare **8** with 9.27 g (0.0445 mol) of TEOS. The sol was clear and had low viscosity. A portion (20 mL) was saved in an SSV. After 3 days, **9** was

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made by diluting of 42.3 mL of **8** with 37.7 mL of methanol in 100 mL of SRV. A similar dilution was made after about 1 month when **8** became more viscous. In a 500 mL flask, 208 mL of **8** was diluted with 185 mL of methanol to produce **10**. The remainder of **8** later gelled but stayed clear.

Viscometry. All the viscosity measurements were carried out at 25 °C using a Model CP-40 cone, which has an angle of 0.8° and a radius of 2.4 cm. To control evaporation of methanol during the measurement, the instrument housing was sealed with tape and purged with argon that had been bubbled through methanol.

Coating and Drying. The substrates used included glass cut from microscope slides into 2.5 × 2.5 cm squares, silicon wafers (Unisil) cleaved into 2 × 2 cm pieces, household aluminum foil glued to 2.5 × 2.5 cm glass slides, 1.5 cm diameter fused silica disks (Meller Optics), 1 cm² fused silica cut from a spectrophotometric cuvette (Heraeus Amersil or NSG Precision Cells), and 10 × 15 cm steel substrates obtained from Union Carbide Corp. Enough sol was applied dropwise through a 0.45 μm syringe filter to completely cover the substrate. If filtration was difficult, the sol was treated with ultrasound for 5–10 min to break up coagulated particles. The coated substrate was spun at 2500 rpm for 60 s. Multiple coats were applied in rapid succession.

For "furnace drying", substrates with coatings, which may or may not have been air-dried for about 12 h, while resting on alumina boats in a box furnace, were heated to 150 °C at 25 °C/h and held for 3 h. For higher temperatures, the furnace temperature was increased in 150 °C steps at 25 °C/h and held 3 h to the following: 150, 300, 450, 600, 750, 900, and 1050 °C. The heating rate for further heating during hardness studies was 1 °C/min. "Microwave drying" was done with the following four-stage procedure in which water was placed inside the oven along with the sample: (1) 2 min on medium high with 200 mL of deionized water in a 400 mL beaker, (2) 2 min on medium high with 25 mL of water in a 400 mL beaker, (3) 2 min on high with 25 mL of water in a 400 mL beaker, (4) 2 min on high with 25 mL of water in a 200 mL beaker. Each time the substrates and the beakers were placed in the same location inside the oven, and the water was at room temperature before each stage. The power level of the fourth stage, in which the minimum amount of water was used, was the highest permissible to avoid sparking.

IR Spectra of Coatings on Silicon. Since a silicon wafer is partially transparent in the IR region, absorbance spectra were taken of the coatings.^{28–30} Each uncoated silicon wafer was supported perpendicular to the beam with the polished side toward the source while the spectrum was taken. After a coating was applied, the silicon substrate was placed in the same orientation and another spectrum was taken. The spectrum of the coating was obtained by subtraction, using the software. The IR spectrum of a coating on silicon had peaks at 3420, 2955, 2849, 1653, 1194, 1036, 899, 802, and 446 cm⁻¹.

Hardness Measurements. The hardnesses of thin films were measured with a continuous microindenter built around a PZT stack which was capable of performing both indentation and scratch tests.^{31,32} The instrument has a depth resolution of 5 nm and a load resolution of 16 μN. During a hardness test, a Berkovich indenter, a three-sided pyramid, was driven into the sample at a rate of 15 nm/s until a predetermined load was reached, and then withdrawn at a rate of 20 nm/s. The load and depth of penetration were monitored continuously using a leaf spring load cell and sensitive capacitance probes.

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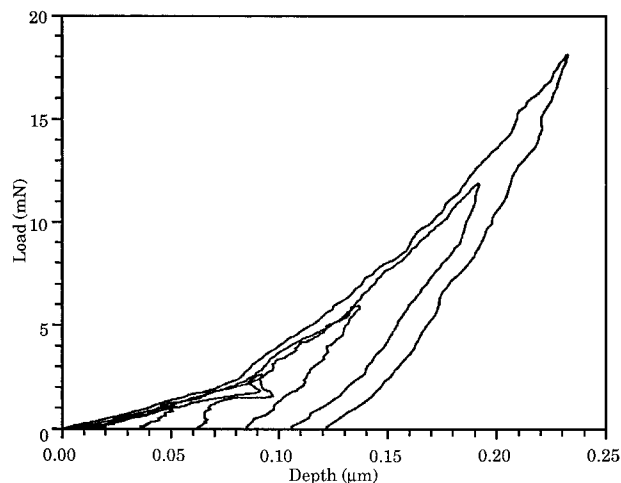


Figure 1. Load vs depth of penetration of the microindenter in a 2Mg:Si magnesium silicate coating on silicon.

Five indentations were made by the above procedure to loads of 1.2–18 mN in each of the samples. Figure 1 is a typical plot of load versus indentation depth obtained from an experiment in which the sample was indented five times, each time to a load higher than that used in the previous cycle.

The hardness, H , is calculated using the relation $H = P/A$, where P is the maximum load applied and A is the projected area of the indenter in contact with the sample at the maximum load.^{23,24} The contact area is determined from the contact depth obtained from the slope of the unloading portion of the load–depth of penetration curve and the shape function of the indenter. The shape function of the indenter was calibrated by imaging indentations made on annealed brass. By indenting the sample to a number of different loads, hardness was evaluated as a function of the depth of penetration.

Thickness Estimation for Coatings on Steel. A steel plate and a silicon wafer were each coated with 3 and 10 coats of **1**, and 3 and 10 coats of **3**, then dried for 4 h at 100 °C. Thickness of the coats on the silicon substrates was measured by ellipsometry, and IR spectra were taken of all the heated films. Thicknesses of the coatings on steel were estimated using ellipsometric data for the silicon substrates combined with the IR data and the thicknesses of films on silicon as illustrated below.

The thickness of coatings was estimated from Beers law, $A = abc$ in which A is the integrated area of the peak from Si–O absorbance, and b is the path length of the IR beam in the film. The absorptivity, a , and concentration, c , are constants. The IR spectra of films on silicon are taken straight through the film, so the path length is the thickness of the film. Using typical data from a 4606 Å thick coating of **1** on silicon, ac is given as

$$ac = A/b = 11.897/4606 \text{ \AA} = 2.583 \times 10^{-3} \text{ \AA}^{-1}$$

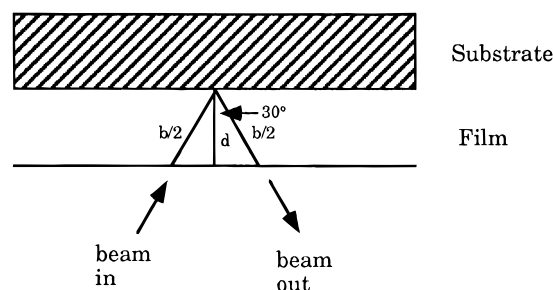
Assuming ac is constant, the path length for a beam in the coating on steel can then be calculated:

$$b = A/ac = 36.994/2.583 \times 10^{-3} \text{ \AA}^{-1} = 14\,322 \text{ \AA}$$

The relationship between the path length b and the film thickness d is shown schematically below:

For a path length b of 14 322 Å, the film's thickness is $d = (b/2)\cos 30^\circ = 6202 \text{ \AA}$.

Gel Drying. A sample of sol, typically 30 mL, was placed in a 500 mL Nalgene beaker that was loosely covered by aluminum foil. A glass tube was placed through a hole in the center of the foil, and supported a few centimeters above the sol; it was connected to a water aspirator to draw out the evaporating solvent fumes. A heat lamp was directed at the bottom of the beaker. When dry, the pieces of xerogel were



scraped into a mortar and ground to a fine powder. The powder was further dried by the heat lamp overhead for a few hours.

Firing. The stoichiometries of sols were checked by XRD of dried and fired crystalline materials. Xerogels of **1** (1Mg:Si), **2** (2Mg:Si), and **8** (3Mg:Si) were prepared by evaporation and were fired in alumina boats in a box furnace, by heating to 500 °C at 50 °/h and holding for 4 h, then heating to 1000 °C at 50 °/h and holding for 3.75 h.

Xerogel from sol **1** was heated only to 800 °C and then further fired to 1250 °C for 6 h in the tube furnace.

Results and Discussion

Synthesis. Magnesium silicate sols were prepared by hydrolysis of a solution of $\text{Mg}(\text{OMe})_2$ and TEOS in MeOH with H_2O_2 and H_2O . The H_2O_2 was used to prevent the precipitation of $\text{Mg}(\text{OMe})(\text{OH})$.¹⁵ Several compositions of magnesium silicate sols were prepared with different ratios of magnesium and silicon signified by 1Mg:Si, 2Mg:Si, and 3Mg:Si. The compositions of the sols are listed in Table 1.

The stoichiometry for hydrolysis using 30% H_2O_2 and H_2O was based on the assumption that each H_2O_2 yields at most two reactive protons and each H_2O yields one. The overall mol ratio of "H⁺" to silicon is termed R3.¹⁹ In hydrolysis method 1, enough "H⁺" was added to react with all of the alkoxide groups. Practically, however, since there was no evidence for formation of MgO_2 ,¹⁹ there is probably insufficient "H⁺" to react with all OR groups. For a 1Mg:Si sol with one $\text{Mg}(\text{OMe})_2$ and one $\text{Si}(\text{OEt})_4$, R3 was 6, and for 2Mg:Si with two $\text{Mg}(\text{OMe})_2$ and one $\text{Si}(\text{OEt})_4$, R3 was 8. Method 2 has even less "H⁺" added; for a 1Mg:Si sol, R3 was 4, while for a 2Mg:Si sol, R3 would be 6. In both schemes though, it is unlikely that all of the "H⁺" added actually reacted. Evidence for this is shown by the existence of the Si–O–Me peak in the IR at 1194 cm^{-1} (see more below).

Viscosity of Sols. Viscosity measurements were carried out on 1Mg:Si sols **4** and **5** and 2Mg:Si sols **6** and **7**; sols of each composition had different concentrations of silicon. In all cases, non-Newtonian, pseudoplastic behavior was observed, that is, the viscosity depended on the shear rate: the higher the shear rate the lower the viscosity, as illustrated in Figure 2. Moreover, at high concentration of silicon, the change in viscosity with change in shear rate was greater than that at a lower concentration.

The viscosity of sols **6** and **7** (2Mg:Si), which were synthesized under the same conditions, depended on the concentration of TEOS. The concentration of **6** (0.099 mol Si/L) was higher than that of **7** (0.090 mol Si/L), and the viscosities were 1.80 and 1.41 cP, respectively. This dependence of viscosity on concentration was further supported by measuring the viscosities after concentrating the sol by rotary evaporation. The viscosity did not increase linearly with concentration as shown

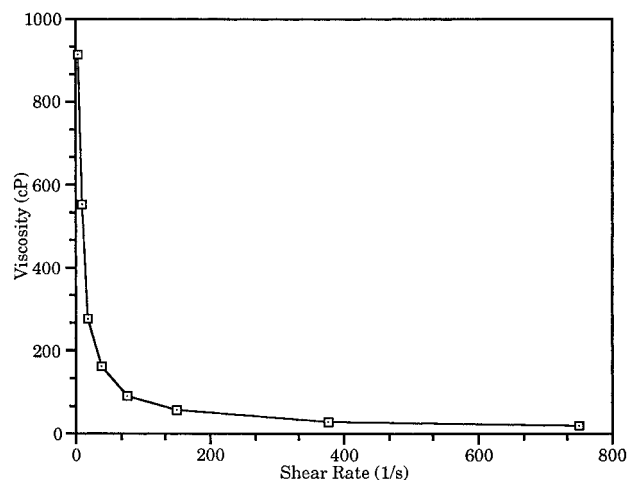


Figure 2. Plot of the change of viscosity with shear rate for 2Mg:Si sol **6** concentrated to 0.198 M, showing non-Newtonian behavior.

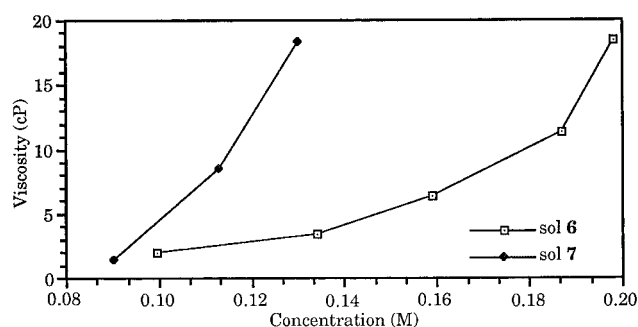


Figure 3. Plot showing the change of viscosity with concentration of 2Mg:Si sols **6** and **7** at fixed shear rate of 100 rpm.

in Figure 3. The viscosities of the concentrated sols increased substantially upon standing, which indicated that condensation reactions occurred during this time.

When the concentrated **7** was diluted from 0.130 to 0.0868 M, the viscosity was about 1.29 cP, compared to 1.41 cP for the 0.0902 M sol. This result demonstrates that the viscosity of a sol depends on concentration and that a concentrated sol can be diluted to restore its original viscosity.

Despite higher concentrations and more hazy appearance, 1Mg:Si sols exhibited lower viscosities (0.68 cP for **4** and 0.98 cP for **5**) than the 2Mg:Si sols. Hence, the rheological structure of the 1Mg:Si precursors was different from that of 2Mg:Si precursors.

Particle Size Analyses of Sols. Particle size analysis of 1Mg:Si sol **1** showed that there were particles larger than $0.5\ \mu\text{m}$, the detection limit of the instrument. The observed distribution was between 0.5 and $5\ \mu\text{m}$, with most particles being less than $1.5\ \mu\text{m}$. To determine what percentage of the sol passed through the $0.45\ \mu\text{m}$ filter used prior to the preparation of thin films, the mass of the dried gel from an aliquot of filtered **1** was compared with that of unfiltered **1** (see section on powders below). Since the two masses were the same within experimental error, the amount of sol lost during filtration was insignificant. After 14 days, **1** became hazy, and a particle size analysis revealed that a small percentage of particles was as large as $8\ \mu\text{m}$. Gravimetric analysis of a filtered aliquot gave the same value for solids content. After 38 days, **1** could not be filtered through a $0.45\ \mu\text{m}$ syringe filter, and particle size analysis revealed that the fraction of particles

greater than 1.5 μm had increased. Treatment of the aged **1** with ultrasound for 5 min enabled filtration. After 140 days, the sol was quite hazy but there was no gel formation; the viscosity still seemed to be low. The sol was unchanged in appearance over 22 months.

The initial particle size analysis of **2** indicated some particles up to 4 μm , with most less than 1.5 μm . After 80 days the sol had only a very slight haze and very low apparent viscosity. A comparison of the masses of the dried gels from filtered and unfiltered aliquots showed that the percentage of particles over 0.5 μm in diameter was insignificant. The sol was unchanged in appearance after 19 months.

Powders. A portion of **2** was evaporated to dryness. The resulting xerogel was fired at 1000 $^{\circ}\text{C}$ to make pure forsterite. The XRD pattern matched all the peaks of forsterite (JCPDS Card No. 34-189).³³ The IR spectrum of fired **2** in KBr had peaks at 1001, 885, 841, 613, 509, 469, and 422 cm^{-1} (lit.³⁴ 985, 884, 839, 609, 507, 475, and 420 cm^{-1}).

A sample of **2** was also dried then heated to 800 $^{\circ}\text{C}$ to yield a gray powder. After firing to 1250 $^{\circ}\text{C}$, the resulting white powder had only two major enstatite XRD peaks at ~ 28.2 and 31.1° (2θ) that is either orthoenstatite (JCPDS Card No. 19-768)³⁵ or protoenstatite (JCPDS Card No. 11-272).³⁶ The pattern also shows other not well-formed peaks of protoenstatite. The IR spectrum of enstatite in KBr had peaks at 1078, 1013, 945, 893, 856, 723, 691, 646, 548, 505, 484, 459, 434, and 405 cm^{-1} (lit.³⁷ 1074, 1017, 951, 900, 860, 690, 642, 572, 511, 458, and 420 cm^{-1}). The IR spectrum has all the peaks in the Si-O region that match the previously reported peaks of clinoenstatite, the only polymorph found, within 6 cm^{-1} but the peaks in the Mg-O region do not match. This difference is understandable if one considers the fact that the enstatite produced above at 1250 $^{\circ}\text{C}$ is mostly a mixture of the protoenstatite and orthoenstatite polymorphs and that the structural differences for all of the polymorphs can affect the spectra. Between phase changes, the Si-O-Si bonds remain unchanged while the Mg-O bonds have to be broken and re-formed.³⁸ Therefore, the three polymorphs could have similar IR absorption spectra in the Si-O region and different spectra in the Mg-O region.

Some xerogel, prepared by evaporating sol **8**, was fired to 1000 $^{\circ}\text{C}$. The XRD pattern contained peaks attributable to forsterite and to periclase (MgO) with peaks at 42.9 and 62.3° (2θ).³⁹ The IR spectrum shows a broad peak due to MgO⁴⁰ centered at 500 cm^{-1} superimposed on the expected forsterite peaks.³⁴ The spectrum was essentially identical with that of an equimolar mixture of forsterite and MgO.

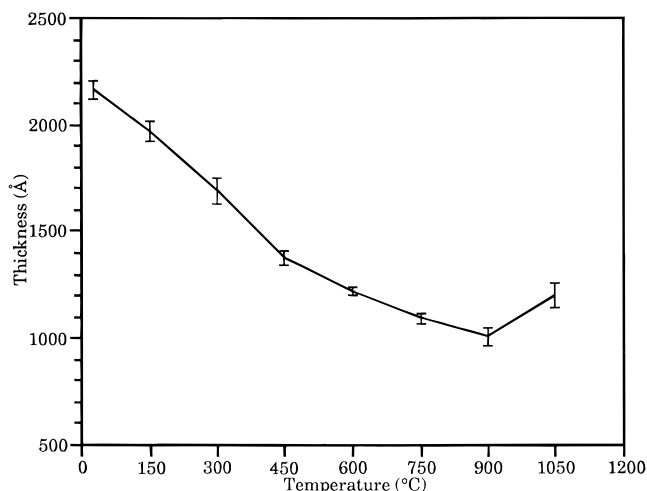


Figure 4. Thickness of five coats of 1Mg:Si sol **1** on silicon as measured by ellipsometry after being heated to the temperatures shown (bars show the ranges).

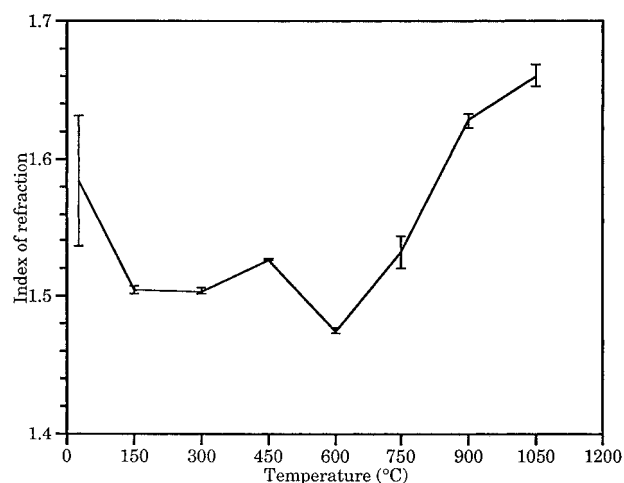


Figure 5. Index of refraction of five coats of 1Mg:Si sol **1** on silicon as measured by ellipsometry after being heated to the temperatures shown (bars show the ranges).

Coatings on Silicon. Six silicon substrates were coated with five coats of **1** and were heated in stages to 1050 $^{\circ}\text{C}$. All six coatings have roughly the same thickness and index of refraction as illustrated in Figures 4 and 5. The thicknesses decrease as the films densify with increasing heat treatment temperature, at least up to 900 $^{\circ}\text{C}$. The initial drop in index of refraction is attributed to porosity that results from removal of solvent. The initial scatter in the data may be caused by different amounts of solvent remaining in these pores at room temperature; after most of the solvent is removed by heating to 150 $^{\circ}\text{C}$, the values are about the same for all six films. The drop at 600 $^{\circ}\text{C}$ is probably caused by an increase in porosity due to burn off of carbon. With increasing heat-treatment temperatures, the film densifies, and the index of refraction reaches the theoretical value of 1.65 (the value reported for enstatite) after heating at 900 $^{\circ}\text{C}$.⁴¹ At this point the film is probably nearly fully dense. The increase in thickness after 1050 $^{\circ}\text{C}$ may be due to some reaction with the substrate. Similar results were obtained using a silicon substrate that had a 1000 \AA layer of SiO_2 between the substrate and the film.

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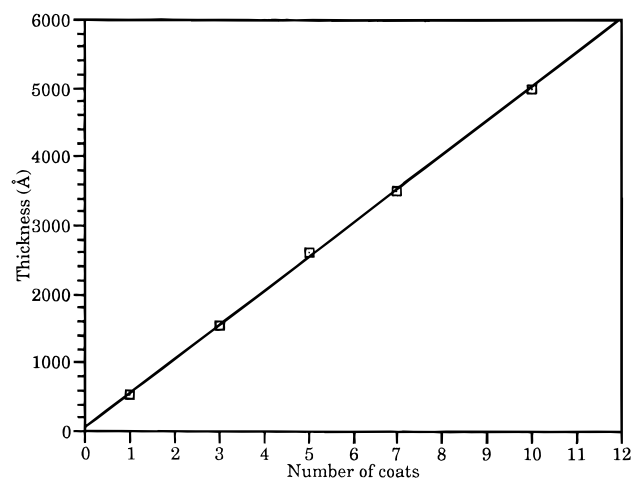


Figure 6. Thickness as a function of the number of coats for 1Mg:Si sol **1** on silicon without heating.

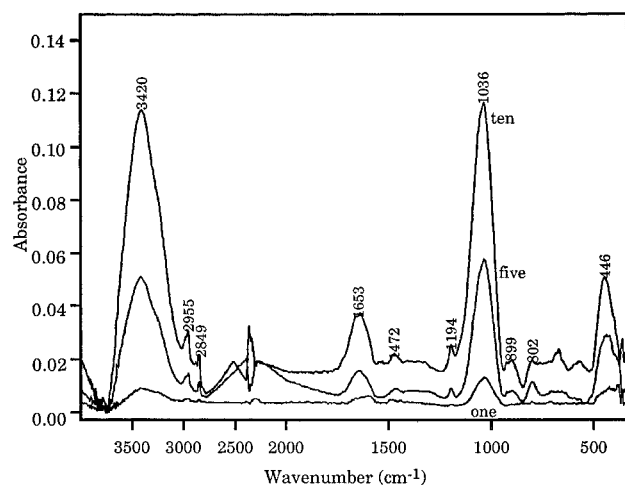


Figure 7. IR spectra of 1, 5, and 10 coats of 1Mg:Si sol **1** on a silicon wafer before heating.

Ellipsometry measurements (Figure 6) showed that the thickness increased linearly with the number of coats for five silicon substrates coated with various amounts of **1**.

An IR spectrum was taken after each coat of **1**; the spectra of 1, 5, and 10 coats are shown in Figure 7. The integrated area of the peak at 1036 cm⁻¹ (Si–O stretching)^{42,43} increases linearly with the number of coats, corroborating the conclusions made on the basis of ellipsometry. This linear relationship has previously been used to measure thickness of SiO₂ films on silicon.^{44,45}

To investigate the effects of heat-treatment on film thickness and IR peak area, five silicon substrates were coated with various number of coats of **1** and heated in stages to 1050 °C. The area under the IR peaks obtained at room temperature also increased linearly with number of coats, showing that reproducibility is quite good. The IR peak area is also linearly related to the film thickness. Ellipsometry data demonstrate that thickness and index of refraction follow the same basic trend seen in Figures 4 and 5, respectively.

Table 2. Room Temperature Thickness (Å) for Magnesium Silicate Coatings on Silicon of Various Sols (Sol **1**: 1Mg:Si; Sols **2** and **3**: 2Mg:Si; Sols **8** and **9**: 3Mg:Si)

coats	sol				
	1	2	3	8	9
1	509	656	527		
3	1483	1861	1481		
5	2437	3132	2552	4728	2436
7	3462	4281	3403		
10	4819	6142	4880		4604

Changes were seen in the IR spectra after the coatings were heated. After 3 h at 150 °C, peaks from O–H and C–H stretching (at 3420 and 2955, 2849 cm⁻¹, respectively)⁴⁶ decreased and the Si–O stretching peak broadened and shifted to 1015 cm⁻¹. After 300 °C, all C–H peaks disappeared, and the O–H stretching peak decreased further while the Si–O stretching peak broadened and shifted to 991 cm⁻¹. Drying at 450 °C resulted in a further decrease of the O–H stretching peak with the Si–O stretching peak staying basically unchanged. After heating at 600 °C for 3 h, the O–H stretching band was gone and only peaks attributed to Si–O and Mg–O stretching vibrations remained (at 999 and 463 cm⁻¹, respectively). These changes are interpreted as follows: first water and methanol were removed, then at higher temperatures Si centers on the predominantly linear –Si–O–Si– chains were linked by –O–Mg–O– groups as the films densified.⁴⁷ The broad bands indicated that the films were amorphous; no sharp peaks, which are typical of crystalline silicates,^{34,37} were observed in films heated to 750 °C. Chromium-doped forsterite films, prepared by electron-beam evaporation, have been observed to start to crystallize around 700 °C.⁴⁸

The linear relationship between IR peak area and thickness holds only up to 750 °C. The deviation from linearity at higher temperatures is believed to be due to thermally grown SiO₂, as indicated by the blue color that developed on the back of the silicon substrate. The thermal oxidation of silicon, which occurs by oxygen diffusion, is apparently not significant for 3 h below 700 °C.⁴⁹ It is also possible that the SiO₂ formed between the film and the silicon wafer; this film would account for the apparent increase in thickness of the coating after heating to 1050 °C as seen in Figure 4. This increase in the thickness occurred at 900 °C for the single coat, possibly because oxygen could permeate the thin coating more easily.

Sol **2** (2Mg:Si) was coated to various thicknesses onto five silicon substrates then heated to 750 °C. The thicknesses of the as-prepared coatings (Table 2) are greater than those of similarly prepared coatings of **1** (1Mg:Si). Since 10 coats of **2** was 1.27 times thicker than 10 coats of **1**, and the mass of forsterite obtained from **2** was 1.42 times the mass of enstatite from an equal volume of **1**, sol **2** was diluted to 74.4% of its original concentration to make **3**. Note that the molar

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mass of forsterite is 1.40 times that of enstatite. Silicon substrates were then coated with **3** yielding as-prepared thicknesses (Table 2) comparable to those of **1**. Hence, the films of both enstatite and forsterite precursors produce the same thickness for the same coating conditions. The drying and ellipsometry measurements were done as before up to 750 °C, and trends in thickness and index of refraction similar to those from **1** were observed.

Sol **8** (3Mg:Si) was repeatedly coated onto silicon wafers. After five coats had been applied, cracks were apparent when viewed by an optical microscope. Cracks could be seen with the unaided eye after seven coats, and pieces flaked off after 10 coats. The cracks were orientated 45° to the cleavage directions. Sol **8**, whose coats were 1.94 times thicker than those for **1**, was diluted to 52.9% of its initial concentration to bring the thickness of five coats to around 2500 Å as obtained for sol **1**. Note also that the molar mass of Mg₃SiO₅ is 1.80 times that of MgSiO₃. Thicknesses of coatings from the diluted sol (see sol **9** in Table 2) were similar to those of **1**, and they exhibited similar changes in thickness, index of refraction, and IR spectrum after heating to 750 °C.

Microwave Processing. Since silicon absorbs microwave energy, coatings on silicon wafers were heated in a microwave oven as a means of rapid thermal annealing.^{50–53} Coated substrates were heated in four stages as described in the Experimental Section; a container of water placed inside the oven was used to regulate the power absorbed by the wafer. The temperature of the silicon wafer reached at least 373 °C (but probably higher) after the final stage. Significant changes occurred in thickness and index of refraction after each heating stage, but not if a stage was repeated. On a Si wafer with 10 coats of **3**, which was 4787 Å thick and had an index of refraction of 1.415, the thickness decreased to 2129 Å and the index of refraction increased to 1.549 after the four-step process. The overall densification of the microwave-treated film was similar to that achieved in a furnace at 750 °C; after heating to 750 °C, another wafer with 10 coats of **3** (4880 Å thick and RI of 1.462) had a thickness of 1795 Å and an RI of 1.591. The IR spectra of the above coatings at room temperature were similar to those in Figure 7. The IR spectrum of the microwave-dried coating looked like that of the coating that was dried to 600 °C in a conventional furnace. Since the properties of the microwave-treated coatings were similar to furnace-dried coatings over 600 °C, the temperature of the silicon in the microwave oven probably reached a temperature considerably higher than that measured, namely, 373 °C. Microwave processing is an effective means for rapid thermal annealing of these coatings.

A typical limitation of sol-gel thin films is the production of thick films (>1 μm) due to thermal

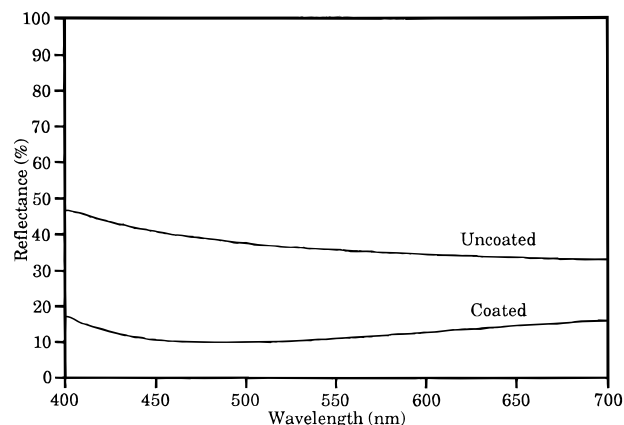


Figure 8. Comparison of the antireflection behavior of a 696 Å thick 1Mg:Si coating on silicon compared to an uncoated silicon wafer.

stresses. The microwave processing, which may heat the film more than the substrate, may be able to avoid thermal problems and allow thicker films. Ten coats of sol **3** were applied to a silicon substrate and then dried in the microwave oven using the four-stage procedure. This process was repeated three times for a total of 40 coats, yielding thicknesses of 1846, 3658, 5604, and 6995 Å after each 10 coats. After 40 coats, parallel cracks formed as described above. With about 5000 Å of fresh coating on the 5604 Å thick coat already there, the coating was over 1 μm thick before the final treatment. Even with the aid of heating the coating, using a microwave oven, coatings over 1 μm thick cracked.

Antireflection. Silicon solar cells typically reflect about 36% of incident solar radiation, and antireflective (AR) coatings of various metal oxides have been used to reduce this reflection.⁵⁴ To investigate magnesium silicates as AR coatings, a silicon substrate was coated with four coats of **1**, then heated directly to 450 °C, and held for 3 h. The antireflective properties of the resulting coating (thickness = 696 Å, $n = 1.55$) are compared to uncoated silicon in Figure 8. The reduction of reflection at 475 nm from 38% to 10–15% is typical for single-layer films.^{13,55,56} Although no attempt was made to optimize the coatings (e.g., by variation of thickness or index of refraction), the potential for such applications is clearly shown.

Residual Carbon in Coatings. Although no absorption peaks from organic groups were observed in the IR spectrum of a coating that had been heated above 300 °C or given microwave treatment, it was not known if residual carbon was present. Three samples having 10 layers of **1** on silicon were prepared. One was heated to 750 °C in 150 °C steps, another was heated directly at 100 °C/h to 750 °C, and the third was given the four-stage microwave treatment described above. Carbon resonance RBS showed that the carbon content was less than 0.1% for all three.

Hardness of Coatings. Hardness was measured by continuous microindentation for coatings on silicon.³¹ Two wafers were coated 10 times each with **3** (2Mg:Si).

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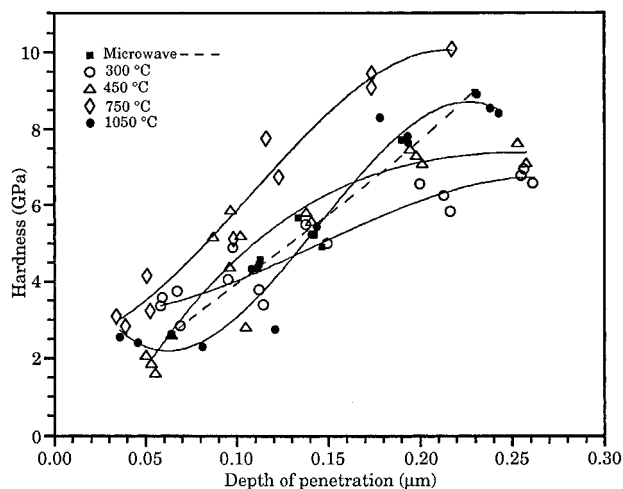


Figure 9. Continuous microindentation data for 2Mg:Si coatings on silicon heated in a furnace from 300 to 1050 °C and also heated in a microwave oven.

One was dried at 300 °C, and the other microwave-treated. The hardness versus depth plot for the films is plotted in Figure 9. Upon heat treatment to 450, 750, and 1050 °C, the hardness generally increased with each treatment. The hardness increased more significantly at larger depths than at small depths of penetration. The cause for the decrease in the hardness at 1050 °C may be due to the SiO₂ film that grows during treatment at 1050 °C. The hardness of the sample treated in the microwave oven was between those of the samples heated in a furnace at 450 and 750 °C. It showed a similar increase with increasing depth of penetration. It is therefore likely that the microwave produced an effective temperature between 450 and 750 °C.

The hardness may increase or decrease with depth depending on the hardness of the substrate relative to that of the film.^{22,31} For soft films deposited on hard substrates, the depth of penetration must be less than about one-quarter of the film thickness for the substrate to have negligible influence on the hardness measurement.³¹

Coatings on fused silica were prepared to further extend the hardness measurements. A fused silica disk was coated 10 times with **1** (1Mg:Si). A second disk, coated 10 times with **1**, was dried in a furnace at 300 °C. The coating procedure used for the second disk was repeated three times on a third disk for a total of 30 coats. Coatings using **3** (2Mg:Si) were prepared similarly.

The hardness values are generally lower than those involving silicon substrates, because the hardness of a thin film varies with depth of penetration due to the presence of a substrate. This behavior can be attributed to the fact that the hardness of fused silica is less than that of silicon (10 and 14.2 GPa, respectively).

A comparison of the hardness values for the 10 coats of **1** at 300 °C to 10 coats at room temperature indicates that heating the sample at 300 °C increases the hardness of the film from 1–3.5 to 3.5–6 GPa. The hardness of the furnace-dried coating is higher than that of the coating dried at room temperature, possibly because of the removal of some of the pores that are present in sol-gel coatings. As shown in Figure 10, the hardness of these coatings on fused silica also increased with increasing heat-treatment temperature. Ten coats on

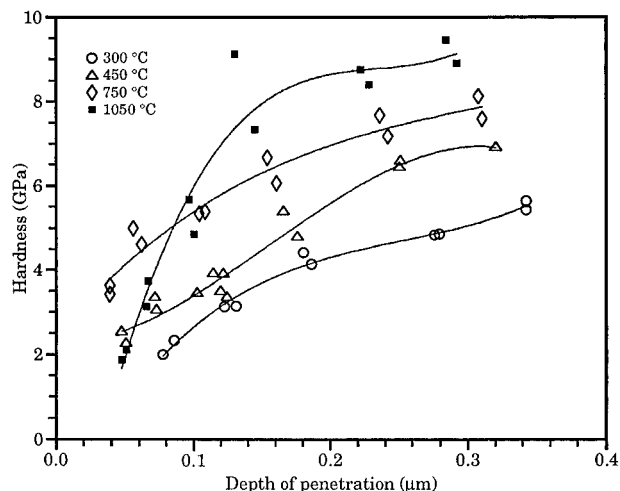


Figure 10. Variation of hardness with depth for 10 coats of 1Mg:Si on fused silica heated from 300 to 1050 °C in a furnace.

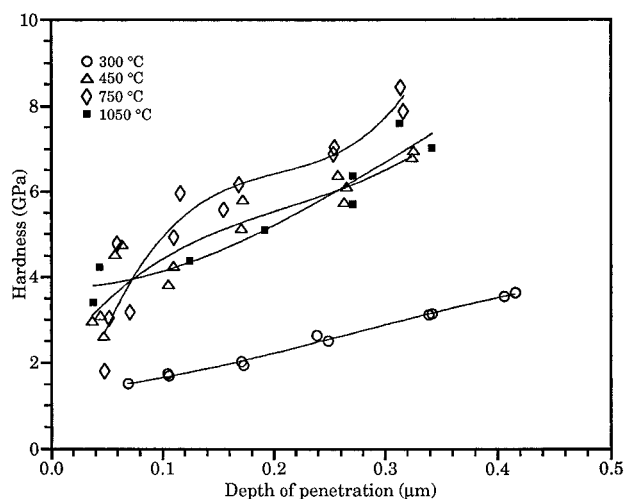


Figure 11. Variation of hardness with depth for 30 coats of 1Mg:Si on fused silica heated to different temperatures in furnace.

a fused silica disk (about 3100 Å thick) showed an increase similar to 10 coats on silicon after heating at 450 °C. The increase was significant at large depths. After heat treatment at 750 °C, the hardness was almost independent of depth at a value of ~7.5 GPa. The hardness increased to about 9 GPa after the treatment at 1050 °C. This value is close to the hardness of fused silica. These observations suggest that the effect of the interface and substrate are important at low depths, especially for a coating that was only about 0.23 μm thick.

As shown in Figure 11, the hardness of 30 coats of **1** increased after the first heat-treatment, but did not increase after subsequent treatments. It is interesting to note that the hardness is much smaller than that of the sample having only 10 coats and also dried at 300 °C. As stated earlier, the interface and the substrate significantly affect the hardness as the indenter penetrates deeper. However, when the film is thick compared to the depth of penetration, as in this case, at low depths of penetration, the influence of the substrate and interface is very small. Consequently, the hardness values obtained for this sample (1.8–3.6 GPa) have minimal contribution from either the interface or the substrate. These hardness values are more indicative of the film's hardness than of the net hardness of the

film-substrate composite. These hardness values are lower than that measured for a single crystal of enstatite (7–12 GPa) probably because of the amorphous nature of the coatings.

Direct comparisons of the hardness of the 1Mg:Si coatings to that of the 2Mg:Si coatings indicated that both responded to heat treatments in about the same manner. The only differences between them occurred in the 10-coat sample, for which the hardness of the 2Mg:Si coating was much greater than that of the 1Mg:Si coating (6.5 vs 3.5 GPa at 0.1 μm). After 1050 $^{\circ}\text{C}$ for both 10 and 30 coats, the 2Mg:Si coating was harder down to 0.13 μm than the 1Mg:Si coating. Again, the hardness of the amorphous 2Mg:Si coatings were lower than that measured for crystalline forsterite (10–14 GPa).

The effect of microwave processing of coatings has been described for silicon substrates. Since SiO_2 is a very poor absorber of microwaves, using silica substrates is a way to demonstrate how effective microwaves are in densifying the coatings. Two pieces of fused silica were coated with 10 coats of **1**. One was given a four-stage microwave treatment. The hardnesses of the treated and untreated samples are not significantly different, suggesting that the microwaves either did not interact with the coating or did not cause consolidation. At the highest power level, a fused silica substrate reached only 36 $^{\circ}\text{C}$ with the temperature of the glass plate on the bottom of the microwave oven. Alternatively, the energy used to densify the coatings on silicon may have come from the heated substrate rather than from absorption of the microwave energy by the coating material. Unfortunately, neither ellipsometry nor IR data could be obtained for coatings on fused silica.

Coatings on Glass. Coatings of **1** (~ 1500 \AA) were spun-cast on glass to determine their properties in the context of optical coatings. With 92% transmission, the coatings were as clear as the glass itself. After standard tape pull-off test, a cheesecloth rub test, and a humidity test, the films appeared unchanged. An erasure rub test scratched the films; the damage was more severe for the coating dried at room temperature than for those that were heated in a furnace to 300 $^{\circ}\text{C}$. The heated sample also had less cloudiness caused by the salt spray test. When coatings on glass were dried using the four-stage microwave process, they were not scratched by the erasure rub test. The hardness of coatings of **1** on glass were measured by the continuous microindentation method and are shown in Figure 12. The hardness of the coating on the microwave-treated sample is greater than that of either the unheated or heated (300 $^{\circ}\text{C}$) samples. Apparently, the microwave treatment hardened the coating material by other than a thermal process, as the glass substrate reached only 37 $^{\circ}\text{C}$ in the microwave oven. Again, ellipsometry and IR data could not be obtained. It is not known why there is this difference in properties after microwave treatment between silica and glass.

Coatings on Metals. As described above, the integrated area of the Si–O stretching peak in the FTIR spectra of coatings on silicon correlates with the thickness of the coating. To extend this technique to coatings on metals, aluminum foil substrates were coated with **1** and were examined by FTIR spectroscopy. The

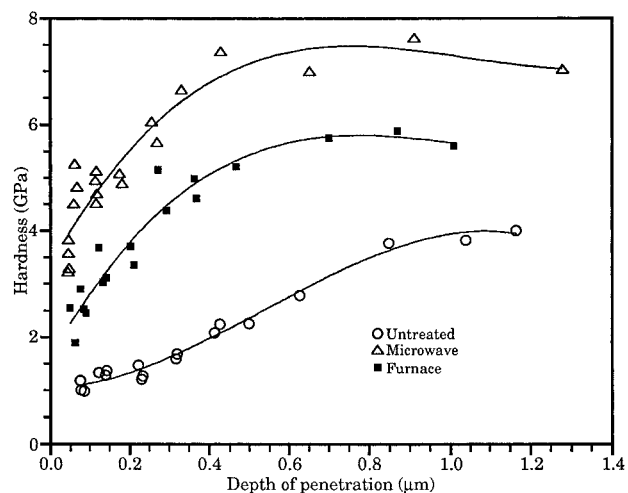


Figure 12. Variation of hardness with depth of 1Mg:Si coatings on glass, treated in various ways: room temperature, 300 $^{\circ}\text{C}$ in a furnace, and heated in a microwave oven.

Table 3. Calculated Thicknesses for Magnesium Silicate Coatings on Steel

sol	Mg:Si	no. of coats	thickness on silicon (\AA)	on steel (\AA)
1	1	3	1305	2335
1	1	10	4606	6202
3	2	3	1320	2459
3	2	10	4441	16441

integrated peak areas of the Si–O stretching peak at ~ 1030 cm^{-1} increased linearly with the number of coats. Ellipsometry could not be used to measure the thickness of the coatings; the coefficient of extinction for Al is too high, and the surface roughness of the steel plates scattered the laser beam (pits ranged from 1 to 50 μm in diameter). To circumvent these limitations, a combination of data and methods gleaned from the IR spectra of coatings on silicon and aluminum was used.

The thicknesses quoted in Table 3 are estimates because of an assumption made in the calculations, viz. that ac in Beer's law expression, $A = abc$, is the same on steel as it is on silicon. Also, the background spectrum (from the uncoated substrate) may not be properly subtracted from the spectrum of the coating since it contains other peaks, presumed to be from a phosphate coating, in the region of the Si–O stretching peaks. If bonding occurred between the silicon and the phosphorus (peaks from Si–O–P vibrations are likely to be within the range 1030–1050 cm^{-1}),⁵⁷ interferences from incompletely subtracted substrate peaks may contribute to the integrated areas and affect the calculated thickness.

The results, shown in Table 3, indicate that the coatings on steel are thicker than those on silicon, as would be expected since the rough surface of steel should retain more of the sol. Optical microscopy revealed that the larger pits partially filled with sol creating thicker areas that average into the IR peak.

Summary and Conclusions

Two sol preparations were modified to increase the stability so they could be used for coatings over a long time. Coatings could be formed on many substrates such as glass, silicon, aluminum, and steel. To increase

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thickness, multiple coatings could be applied in succession without any treatment in between. The thickness built up linearly with the number of coats applied, which is useful for applications such as antireflection. The integrated IR peak areas increased linearly with the number of coats, as well as the thickness. The relationship between IR peak area and thickness was used to estimate the thicknesses on the steel plates for which ellipsometry could not be used.

Heating densified the coatings as shown by the decrease in thickness and the increase in index of refraction. Changes in functional groups upon heating were observed by IR spectroscopy, which also showed that the films remained amorphous below ~ 750 °C. Heating also increased the hardness of coatings. The substrate has a significant effect on the measurement of the hardness of coatings by the microscratch technique. Microwave treatment was used as a rapid (mainly thermal) process for densification of magnesium silicate coatings on silicon; after microwave treatment,

the coatings' thickness, index of refraction, IR spectrum, and hardness were comparable to thermal treatments of 600 °C. With proper heat treatment, coatings on silicon and glass were shown to be durable, though softer than bulk crystalline materials. Coatings on silicon were shown to have anti-reflective properties typical for single-layer coatings.

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