Sol−Gel Synthesis of Nanocrystalline Magnesium Fluoride: Its Use in the Preparation of MgF_2 Films and MgF_2−SiO_2 Composites

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Thin, protective films of nanocrystalline MgF_2 were formed by spin-coating a sol that contained nanocrystalline MgF_2, which was formed by the action of HF on a sol prepared from methanolic H_2O_2 and $Mg(OCH_3)_2$. These thin films on Si(100) lost fluoride to form MgO when heated at 550 °C. When the films on two such substrates were placed together face to face and heated at 550 °C, rough, abrasion resistant MgF_2 films were obtained. To form composites, nanocrystalline MgF_2 sols were mixed with silicate sols prepared from the acid catalyzed hydrolysis and condensation of tetramethyl orthosilicate (TMOS). X-ray diffraction and TEM analysis of xerogels and films obtained from these biphasic sols indicated nanocrystals of MgF_2 dispersed in an amorphous matrix. On heating, fluoride loss and MgF_2 crystal growth were both greatly retarded in powders and thin films prepared from silicate−MgF_2 sols.

Introduction

Nanocrystals,[1] i.e., crystals with a mean size of ∼1−10 nm, possess a number of interesting optical and electrical properties. Since nanocrystals are smaller than wavelengths of visible light,[2] nanocrystalline materials (NCMs) behave as optically homogeneous solids. In addition, the dimensions of the wave functions of electron−hole pairs in nanocrystals are comparable in size to the crystals themselves. As a result, nanocrystals have a wider bandgap than that of the bulk parent material. In practical terms, such bandgap widening gives nanocrystals an optical absorption edge that is blue-shifted relative to that of the bulk material.[3,4] Two conventional methods of preparing nanocrystals and NCMs are vapor−solid−vapor cosputtering[1] and the solution sol−gel process.[2,3,5] The former requires the use of expensive, high-vacuum equipment, which may limit the size of the substrate that can be coated.

Magnesium fluoride has low chemical reactivity, low refractive index (1.38), is only mildly affected by high energy radiation, and is both scratch and weather resistant. It has been extensively used as an antireflective and protective coating on glass optics.[6,7] Since MgF_2 has an optical cutoff that begins at 132 nm, it has also been employed as an antireflective coating material on vacuum UV optics.[8] Blue-shifting of this optical cutoff to even shorter wavelengths might be expected if such coatings were prepared using nanocrystalline MgF_2.

The conventional method of producing durable MgF_2 coatings involves thermal evaporation of MgF_2 onto substrates heated at ∼300 °C. Vacuum evaporated MgF_2 films deposited on substrates at room temperature have low density (∼0.74 of the theoretical) and low abrasion resistance.[9] Recently, several wet chemical methods were used to form soft, porous MgF_2 films.[10−12] Such films might be useful as antireflective coatings if abrasion resistance were not needed, such as on the inner surface of a television tube.[11]

Since nanocrystalline composite materials behave as optically homogeneous solids, dispersing nanocrystals within an amorphous matrix might be one method of preparing new optical materials in systems that would otherwise not form glasses. A number of published reports have used vacuum evaporation techniques to prepare thin films of nanocrystals dispersed in amorphous SiO_2.[13−16] One report gave a novel method whereby ZnS nanocrystals were grown within nanometer size pores of aluminum borosilicate glass films prepared by sol−gel methods.[4]

The formation of glasses by hydrolysis and condensation of metal alkoxides in solution by "sol−gel" techniques has been extensively studied. Conceivably, a nanocrystal−glass composite might be prepared by

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condensing a glass-forming alkoxide within a solution containing a suspension of nanocrystals. For example, MgF_2 and SiO_2 will not melt to form a glass: Heating mixtures of these two compounds gives crystals of the clinohumite family of minerals.[17] Hydrolyzing a silicon alkoxide in a solution containing suspended MgF_2 nanocrystals might give a sol, which could be used to prepare coatings composed of nanocrystalline MgF_2 homogeneously dispersed in a matrix of SiO_2. By controlling the composition, the refractive index of the resultant films might by tailored between that of pure MgF_2 and SiO_2, as has been demonstrated with spin-on glass coatings in the SiO_2-TiO_2 system.[18]

This paper reports the preparation of a nanocrystalline MgF_2 sol and abrasion-resistant MgF_2 films prepared from it. In addition, the preparation of SiO_2-MgF_2 composites, both in bulk and in thin film form, produced by combining a silicon alkoxide sol with a nanocrystalline MgF_2 sol are described.

Experimental Section

Reagents and General Synthesis Techniques. Unless otherwise stated, all reactions were carried out under an atmosphere of dry, oxyge- free argon.[19] Round-bottom reaction flasks were equipped with a water-cooled condensor connected to an argon source and an oil bubbler using a three-way stopcock. Creased, round-bottomed flasks were the Morton type.[20] Magnetic stirring bars were Teflon coated. Ground joints were lubricated with a thin film of Krytox LVP grease.

Dry methanol used for sol preparations was obtained by distillation from $Mg(OCH_3)_2$ under argon. Electronic grade 2-propanol (<0.04% H_2O) was used as obtained from Fisher Scientific Co. Stock solutions of $Mg(OCH_3)_2$ were prepared from Mg turnings (Alfa, M4N or Cerac, 99.99%) and dry methanol as described previously.[28] In a typical preparation, a portion of a magnesium methoxide stock solution was transferred to a dry, 100 mL septum-sealed Schlenk reaction vessel (SRV) using a cannula. Through this septum was passed a needle that was connected to a 50 mL, ground-glass, argon-filled syringe whose barrel had been coated with a thin film of mineral oil. The syringe was mounted on a syringe pump: The argon injected into the SRV from the compression of the syringe caused the controlled displacement of the $Mg(OCH_3)_2$ solution from the SRV through a cannula into a reaction vessel.

Hydrofluoric acid (Mallinckrodt) was assayed at 48.8%. For synthesis, a portion of this acid was weighed into a 30 mL Nalgene bottle prior to quantitative transfer and dilution with dry methanol in a 60 mL Becton-Dickson plastic syringe to which was attached a length of polyethylene tubing. The syringe was mounted on a syringe pump, and the HF solution was added to a reaction solution through the polyethylene tubing that passed though a septum on the reaction flask. H_2O_2 (50%, Fisher) was assayed[21] at 49.4 ± 0.1%. Tetramethyl orthosilicate (TMOS, Aldrich, 99+%) was used as received.

Solvent was removed from sols by trap-to-trap vacuum distillation (TTVD).[22] Isolated xerogels were dried under vacuum for 12−72 h. For firing, a ~1 g portion of xerogel or a coated wafer was placed in an alumina boat, which was loosely covered with a lid made from fused silica tubing. The boat was heated in a silica tube in a flow of air, dried by passage through a column of Aquasorb. The tube furnace was heated at 100 °C h^{-1} to the desired temperature, held for 6 h and then allowed to cool to room temperature.

Silicon (100) substrates (Unisil) were twice cleaned in anhydrous methanol in an ultrasonic bath. Using profilometry, the surface roughness of such wafers was ~±10 Å. The silicon wafer pieces were coated on a Headway Research photoresist spinner. Wafers were spun at 3000 rpm and rinsed with 0.45 μm filtered anhydrous methanol immediately before coating. Approximately 4 drops of sol, filtered through a 0.45 μm Nylon syringe filter, was placed on the silicon wafer before spin-off at 3000 rpm for 40 s. This procedure was repeated for multiple coatings.

Characterization Techniques. Gas chromatographic analysis of headspace vapors was performed using a Hewlett-Packard 5880A series chromatograph equipped with a cross-linked methylsilicone capillary column.

X-ray diffraction (XRD) patterns were taken in air using a Scintag PAD X diffractometer with a Cu $K\alpha$ source and DMS software. Powders were placed on a low-background, single crystal quartz holder: $\theta-2\theta$ patterns were scanned at 2 or 5° (2θ) min^{-1}. Glancing-angle (2θ) patterns, taken at $\Omega = 2°$, were scanned at 1.5° (2θ) min^{-1}. Experimental XRD patterns were compared to the published patterns of MgO[23] and MgF_2.[24] For XRD analysis, solutions were contained in a poly(methyl methacrylate) cell (4 mm deep), which was covered with a thin PVC plastic window, sealed to the cell with Type T Apiezon grease. Diffraction patterns of solutions were scanned at a rate of 0.42° (2θ) min^{-1}.

IR spectra were taken at a resolution of 1 cm^{-1} with a Mattson Model IR-10410 FTIR spectrometer, which was purged with dry, CO_2-free air from a Balston Model 74-5071 Clean Air Package. KBr disks ground under N_2, were pressed under vacuum in a Perkin-Elmer Model 186−0025 die.[25]

Bright- and dark-field transmission electron microscope (TEM) imaging were taken using a JEOL 1200 EX TEM. Electron diffraction patterns were obtained with a JEOL 2000 CX TEM, using crystalline gold as a diffraction standard.[26] Copper grids coated with Formvar were used for TEM specimens.

Surface profilometry measurements were made on a Tencor Instruments Alfa-step thin film and surface profiler. Ellipsometry was done at 632.8, 546.1, and 405.0 nm using a Rudolph Research Auto EL II ellipsometer. Thin-film porosity was calculated using the Lorentz−Lorenz relationship.[8,18] Qualitative film hardness was determined by scratching with a steel razor blade.

Preparation of Nanocrystalline MgF_2 Sol (Sol B). A 0.66 M $Mg(OCH_3)_2$ stock solution was prepared using 3.344 g of Mg and 0.21 L of dry methanol. Over a 37 h period, 0.12 L (79 mmol) of this stock solution was added to a rapidly stirred solution prepared from 5.793 g of 49.4% H_2O_2 (84.1 mmol) diluted to 1.5 L with dry methanol in a 2-L, three-necked, creased flask equipped with a mechanical stirrer. The resultant sol, which showed a faint Tyndall effect, was heated at reflux for 25 h; it is called sol **I**. A 0.41 L portion of sol **I** (19 mmol of Mg) was transferred through a cannula to a 1-L, three-necked creased flask equipped with a magnetic stirring bar. Over a 10 h period, 1.6614 g (40.5 mmol) of 48.8% HF, diluted to 35 mL with dry methanol, was added to this rapidly stirred portion. During the HF addition, the sol's Tyndall effect became less apparent. The resultant sol (**B**) appeared unchanged after being heated at reflux for 23 h. Sols prepared in this way were stable at room temperature for several months, and could be concentrated to 0.38 M without gelling. The transparent xerogel, obtained by complete removal of the solvent, was easily ground into a fine white powder in a mortar and pestle.

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By concentrating sols prepared using the general technique outlined above, a sol with a 0.27 M Mg concentration was prepared for solution XRD analysis, and a sol with a 0.25 M Mg concentration was prepared for coating silicon substrates.

Preparation of MgF_2−Silicon Alkoxide Composite Sols. *(1) Magnesium Fluoride Sol (Sol M).* A sol, similar to **B**, was prepared as follows: A 0.66 M $Mg(OCH_3)_2$ stock solution was prepared using 3.344 g of Mg and 0.21 L of dry methanol. Over a 42 h period, a 0.21 L portion of this solution (0.14 mol) was added to a rapidly stirred solution of 9.82 g of 49.4% H_2O_2 (143 mmol) diluted to 0.95 L with dry methanol in a 2-L, three-necked, creased round-bottom flask equipped with a mechanical stirrer. After being heated at reflux for 19 h, 11.3 g (275 mmol) of 48.8% HF, diluted to 44 mL with dry methanol, was added to this sol over a 13 h period. The resultant sol (**M**) was unchanged after being heated at reflux for 8 h.

(2) Silicon Component Sol (Sol S). In a 2-L, three-necked, creased flask, equipped with a mechanical stirrer were mixed 0.65 L of dry, degassed methanol and 0.48 L of 2-propanol. Using a Gastight syringe, 19.7 mL (132 mmol) of TMOS was added. The solution was rapidly stirred for 3.5 h. Then, during a 2.5 h period, 0.13 g (1.3 mmol) of 37% HCl diluted with dry methanol (10.0 mL) was added via a syringe mounted on a syringe pump. The resultant sol was stirred for 2 h. Then using the procedure described above, 9.514 g (528 mmol) of distilled, deionized water, diluted to 45 mL with dry methanol in a 60 mL plastic syringe, was added in a 9 h period. The resultant sol, **S**, was clear.

(3) 80:20 (Mg:Si) Sol Mixture. A 0.32 L portion of sol **M** (39 mmol of Mg) was transferred via a cannula to a 500 mL, three-necked creased flask equipped with a magnetic stirring bar. Using a Gastight syringe, sol **S** (83 mL, 9.1 mmol of Si) was added to the rapidly stirred portion of sol **M**, giving a sol with a Mg:Si atomic ratio of 80:20, which will hereafter be referred to as the 80:20 sol. Using a Gastight syringe, 10 mL of dry methanol was added to this sol. The sol was heated at reflux for 16 h, giving a clear sol which showed a faint Tyndall effect. Analysis of the vapors in the head-space over this sol showed the absence of volatile silicon alkoxides.[27] Using a Gastight syringe, approximately 60 mL of the 80:20 sol was transferred to a dry 100 mL, septum-sealed round-bottom flask for use in coating wafers. Solvent was removed from the remainder of the sol by rotary evaporation at reduced pressure, yielding a xerogel which was white, slightly opaque, and was easily ground into a fine white powder with a mortar and pestle.

(4) 60:40 (Mg:Si) Sol Mixture. Using the above procedure, sol **S** (0.16 L, 18 mmol of Si) was added with rapid stirring to sol **M** (0.23 L, 28 mmol of Mg) in a dry, 500 mL, three-necked flask equipped with a magnetic stirring bar and a septum. Over a 2.5 h period, a solution of 3.48 g (193 mmol) of H_2O diluted to 9.0 mL in methanol was added from a syringe on a syringe pump to the sol mixture through thin polyethylene tubing. The resultant sol, which showed a faint Tyndall effect, was heated at reflux for 16 h. This sol had a Mg:Si atomic ratio of 60:40, and is referred to as the 60:40 sol. A portion of this sol was reserved for use in coating wafers. Solvent was removed from the remainder giving a white, opaque xerogel, which was easily ground into a fine white powder.

In both the 80:20 and 60:40 sols, the final R value (mol of H_2O/mol of −OR)[18] was 21 with respect to silicon, and the final concentration with respect to all metals (Mg + Si) was 0.11 M. The xerogel from a 44 mM MgF_2 sol, prepared after the method of sol **B**, was used as a nanocrystalline MgF_2 reference sample.

Results and Discussion

Nanocrystalline MgF_2. Recently we described a process by which nanocrystalline MgO_2 and $Mg(OH)OCH_3$ were prepared.[28a] Although the precursor sol, **I**, which formed on addition of $Mg(OCH_3)_2$ to an equivalent of aqueous H_2O_2 in methanol, was stable, X-ray diffraction and Raman spectral analyses were inconclusive as to its composition, especially regarding the question of whether it contained MgO_2.[28b] In the present work, this sol is converted to nanocrystalline MgF_2 by reaction with 2 equiv of HF, and the resulting stable sol is used to form thin films and composites. The reaction of HF with either MgO_2 or $Mg(OH)OCH_3$ has not been reported, but its reaction with magnesium acetate to give a monodispersed, colloidal (∼20−30 nm) suspension of MgF_2 has been described.[10]

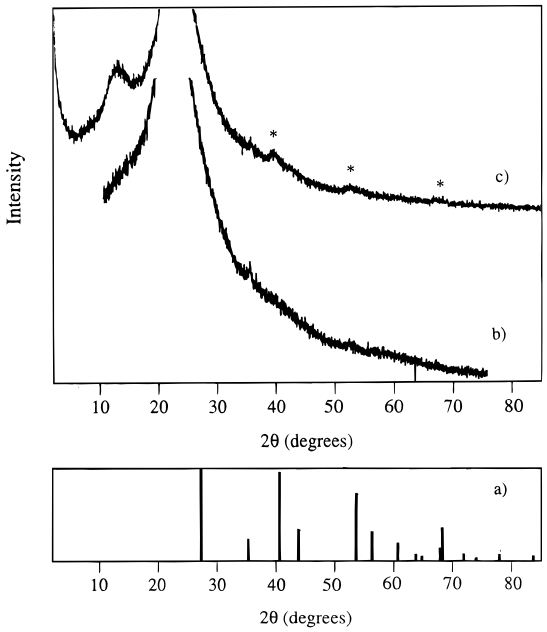

Figure 1. Representation of the XRD pattern of (a) randomly oriented MgF_2,[24] compared to the XRD pattern from (b) dry methanol, and (c) a 240 mM MgF_2 sol. Peaks from MgF_2 are denoted with an asterisk. The large peak at ∼25° (2θ) is due to solvent or the sample holder.

The XRD pattern of a sol, **M**, prepared by slow addition of 2 equiv of HF to sol **I**, is presented in Figure 1. The XRD pattern shows weak peaks at 39.6, 52.4, and 65.1° (2θ). By comparison, the strongest diffraction peaks (with their relative intensities) of MgF_2 have been reported at 27.3 (100) 40.4 (96), 53.5 (73), 67.7 (14), and 68.1 (35)° (2θ).[24] Assuming that XRD peak broadening due to the solvent and the plastic sample holder was negligible, the mean size of the MgF_2 crystallites in this sol was calculated to be ∼4 nm, using the full width at half maximum[30] (fwhm) of the MgF_2 (111) peak at 39.6°. The XRD pattern of the xerogel isolated from such a sol is presented in Figure 2. This pattern also shows diffraction from crystalline MgF_2. From the pattern in Figure 2, the mean crystallite size, based on the fwhm of the MgF_2 (110) peak at 27.2° (2θ), was calculated[30] to be ∼5 nm. The similar size of nanocrystals in the sol and the xerogel suggests that nanocrystalline MgF_2, which formed in solution, remained unchanged during removal of the solvent.

The slow addition or release of a soluble reactant is one reported method used to grow monodisperse nano-

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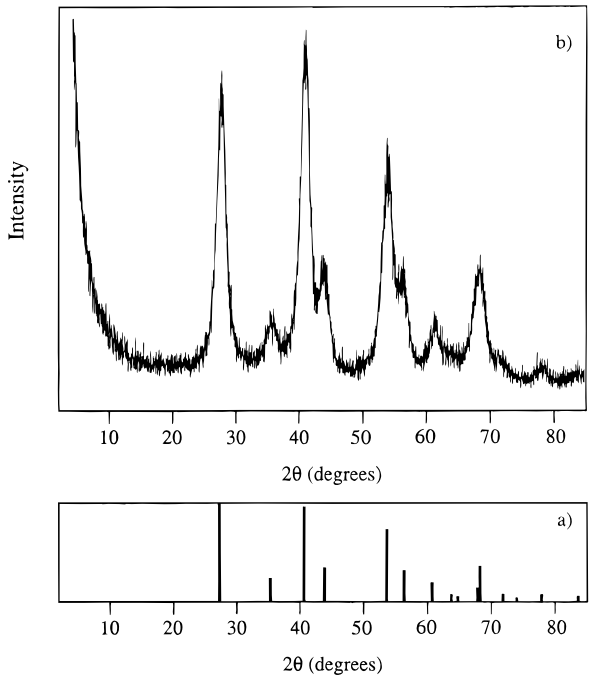

Figure 2. Representation of the XRD pattern of (a) randomly oriented MgF_2,[24] compared to (b) the XRD pattern from a xerogel recovered from a MgF_2 sol. From the (110) reflection at 27.2° (2θ), the mean crystallite size was calculated to be ~5 nm.[30]

or microcrystalline particles in solution. In this technique, when a critical reactant concentration is reached, nucleation occurs followed by the slow growth of the nuclei as reactant addition or release continues. Sols composed of monodispersed, nanocrystalline particles of a number of materials have been prepared using this synthesis approach.[5] The solution sol−gel method for forming nanocrystalline MgF_2 in the present study differs in that a stable intermediate sol was formed prior to fluoridation with HF. As previously stated, the XRD diffraction pattern of the xerogel recovered from sol **I** showed the presence of a mixture of nanocrystals of MgO_2 and $Mg(OH)OCH_3$, both with a mean size of ~4−5 nm.[28] The similar sizes of these nanocrystals and those in the MgF_2 sol suggest that each nanocrystal of MgF_2 may have formed from the reaction of HF with a like-sized nanoparticle of $Mg(OH)OCH_3$ or MgO_2 in sol **I**. Such a conversion mechanism would not be without precedent. For instance, roasting an intimate mixture of $MgCO_3$ and NH_4HF_2 between 150 and 400 °C gives MgF_2 particles with a size approximately the same as those of the starting carbonate.[6]

Thin films of nanocrystalline MgF_2 were prepared by spin coating the nanocrystalline MgF_2 sol onto Si(100). The film's thickness could be built up through successive coating, but films thicker than ~1000 Å generally showed haziness caused by "islands" on the surface, as seen by optical microscopy. Coated silicon wafers were heated either uncovered or cleaved in two with one half placed on the other so that the two films faced each other in a "sandwich" configuration.[29] Figure 3 presents the glancing-angle XRD patterns of MgF_2 films on Si(100), heated uncovered in dry air. The trace in Figure 3c shows the presence of nanocrystalline MgF_2 on the surface of these wafers prior to heating, as indicated by broad, weak reflections at 26.9, 40.3, and 53.0° (2θ). After heating to 550 °C, however, conversion of these

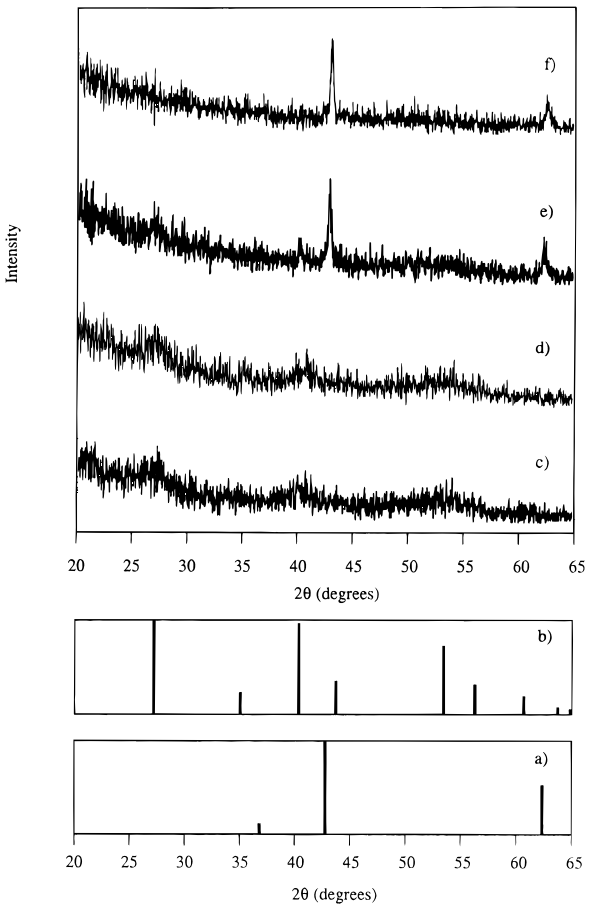

Figure 3. Representations of the powder XRD patterns of randomly oriented MgO (a),[23] and MgF_2(b),[24] compared to glancing-angle (2θ) XRD patterns, taken at $\Omega = 2°$, of ~1000 Å thick coatings made on Si(100) using a MgF_2 sol. Patterns are from coated wafers that were (c) unfired, and heated, uncovered, at (d) 300 °C, (e) 550 °C, and (f) 650 °C.

films to MgO is nearly complete (Figure 3e). In all cases, these heated films were easily scratched by a steel blade.

Figure 4 shows XRD patterns of comparable MgF_2 films fired in a "sandwich" configuration. These patterns show an increase in MgF_2 crystallite size with firing temperature, as indicated by narrowing of fwhm of the XRD peaks.[30] These diffraction patterns also show that substantial conversion of the films to MgO only occurred at temperatures above 550 °C. The film fired to 550 °C in the "sandwich" configuration could not be scratched with a steel razor blade. Using the Lorentz−Lorenz equation, the porosity of this film was estimated to be 21%, based on its refractive index of 1.294.

Densification of sol−gel prepared films usually occurs through vertical collapse of an open film network.[18] This densification process occurs most readily when films are composed of materials that readily form a glass (e.g., SiO_2), since such films can collapse and densify through viscous flow before crystallization begins. When films are crystalline prior to heating, densification must occur through diffusive sintering, which is orders of magnitude slower than viscous flow.[18] Figure 5 presents film thickness as a function of firing temperature for MgF_2 films heated in both the open and "sandwich" configurations. In both cases, very little structural collapse occurred when the films were fired at temperatures as

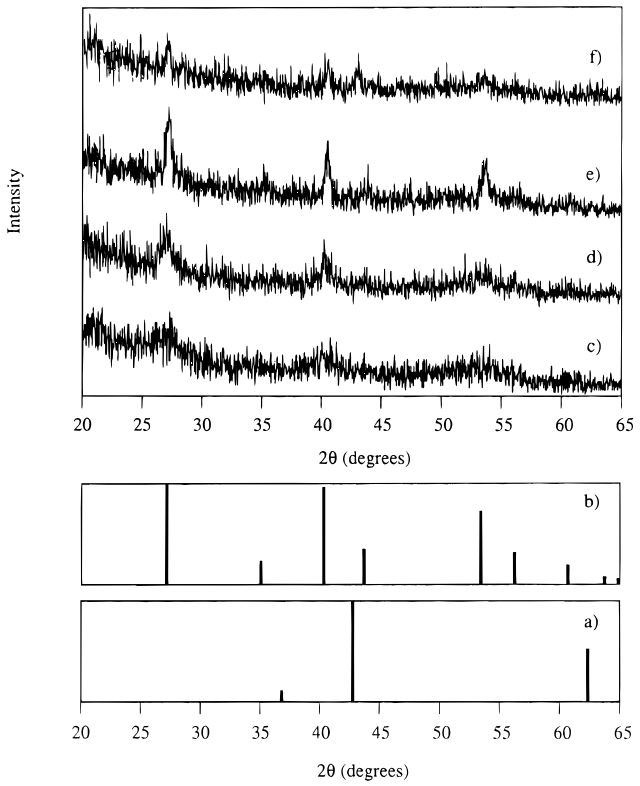

Figure 4. Representations of the powder XRD patterns of randomly oriented MgO (a)[23] and MgF_2 (b),[24] compared to glancing-angle (2θ) XRD patterns, taken at $\Omega = 2°$, of ~1000 Å thick coatings made on Si(100) using a MgF_2 sol. Patterns are from coated wafers that were (c) unfired, or heated at (d) 300 °C, (e) 550 °C, and (f) 650 °C. Wafers were fired with one coated substrate covering the other in a "sandwich" configuration.

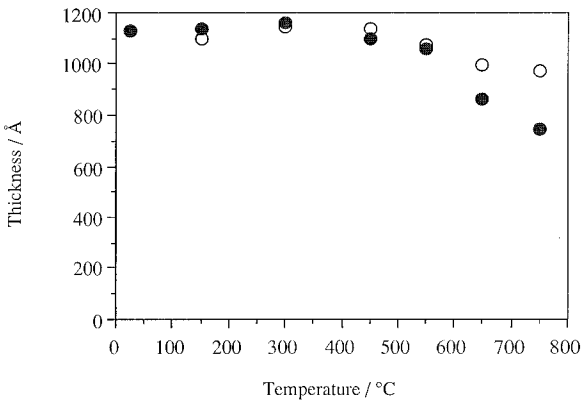

Figure 5. Thickness, measured using ellipsometry, of films deposited on Si(100) using a MgF_2 sol, plotted as a function of firing temperature. Open circles represent samples that were fired, uncovered, whereas filled circles represent samples that were fired in a "sandwich" configuration.

high as 550 °C. This lack of structural collapse with heating is attributed to the slowness of diffusive sintering of crystalline films.

SiO_2–MgF_2 Composites. The sol–gel formation of a glass–ceramic composite composed of amorphous SiO_2, which alone can be made into dense thin films using sol–gel methods,[18] and nanocrystalline MgF_2 was investigated as a way to make a dense coatings that have a low refractive index and may have antireflective properties. In principle, such optically homogeneous, two-component films could have their refractive indexes tailored between those of MgF_2 and SiO_2 by varying the ratios of Mg and Si in the sols used for coating. A similar strategy has been used for the sol–gel prepared, amorphous TiO_2–SiO_2 thin films.[18] The SiO_2 component of a SiO_2–MgF_2 composite thin film might also undergo viscous sintering during heating, causing the entire film to densify and harden at low temperatures.

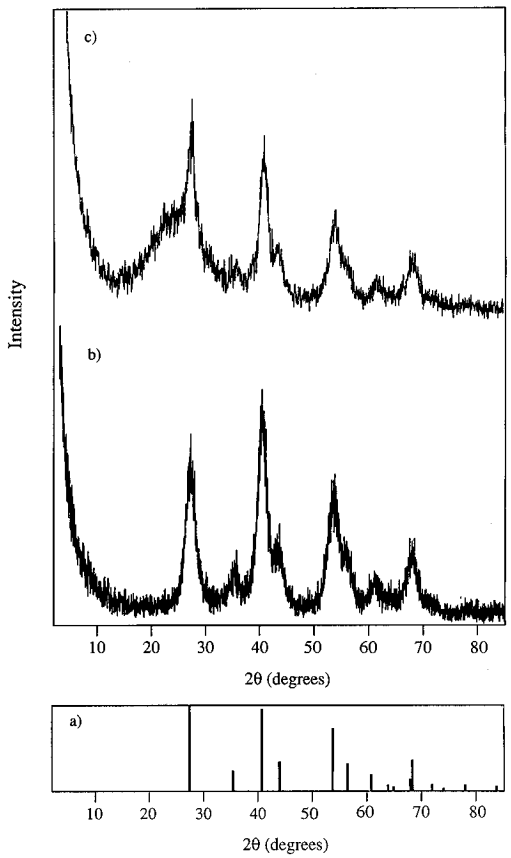

Figure 6. Representation of the XRD pattern of randomly oriented MgF_2 (a),[24] compared to XRD patterns of xerogels from a MgF_2 sol (b), and a composite sol prepared by mixing hydrolyzed TMOS with a MgF_2 sol (c). The Mg:Si ratio in this sol was 60:40.

Sols with MgF_2 to SiO_2 mole ratios of 80:20 and 60:40 were prepared by mixing appropriate amounts of a silicate sol, produced from acid-catalyzed hydrolysis of tetramethyl orthosilicate (TMOS), and a nanocrystalline MgF_2 sol. Acid catalysis of the silicate sol was chosen for this preliminary experiment because dense SiO_2 films have been obtained from the two-stage, acid catalyzed hydrolysis of metal alkoxides.[18] Figure 6 compares the powder XRD patterns of the unfired xerogel from the 60:40 sol, and the unheated xerogel from a nanocrystalline MgF_2 sol. Both of these patterns contain the peaks expected for nanocrystalline MgF_2. The broad feature centered at 24° in the pattern of the 60:40 gel is is assigned to diffraction from amorphous SiO_2.[31,32] Figure 7 shows the diffraction patterns of these two xerogels after being heated at 700 °C for the same length of time. These patterns indicate that both powders contain crystalline MgF_2, but the largely unchanged widths of the peaks in Figure 7d show that crystal growth in the composite has been dramatically slowed in comparison with that of pure MgF_2.

(31) Searle, A. B.; Grimshaw, R. B. *The Chemistry and Physics of Clays*; Interscience: New York, 1959.
(32) West, A. R. *Basic Solid State Chemistry*; John Wiley: New York, 1988.

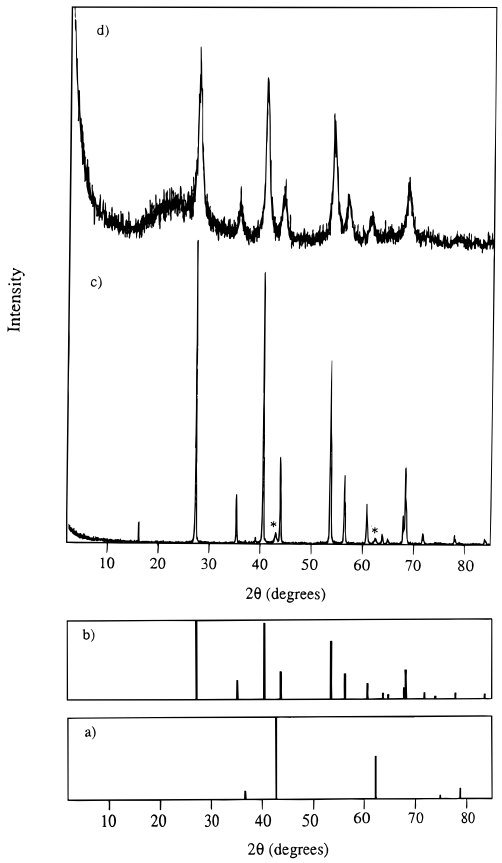

Figure 7. Representations of the XRD patterns of randomly oriented MgO (a)[23] and MgF_2 (b),[24] compared to XRD patterns of xerogels from a MgF_2 sol (c), and a MgF_2-SiO_2 composite sol with a Mg:Si atomic ratio of 60:40 (d). Xerogels were heated for 12 h under dry air at 700 °C. Peaks assigned to MgO are denoted by an asterisk.

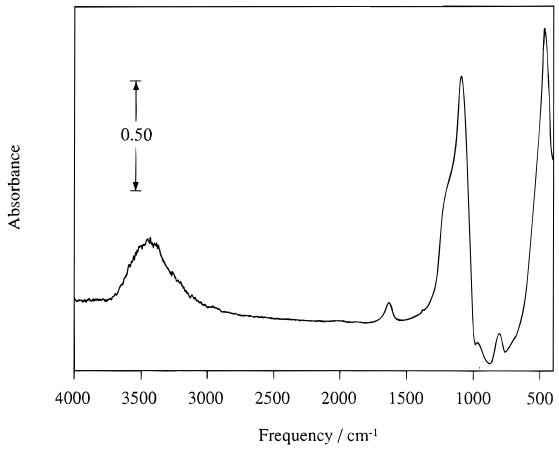

Figure 8. The IR spectrum of a xerogel from a sol with a Mg:Si atomic ratio of 60:40, prepared by mixing a MgF_2 sol with hydrolyzed TMOS. The xerogel was calcined at 700 °C for 12 h under dry air. Peaks at 3435 and 1638 cm^{-1} are assigned to adsorbed water.[34]

The IR spectrum of the xerogel, calcined at 700 °C after isolation from the 60:40 sol, is presented in Figure 8. Peaks at 3435, 1638, 1210, 1096, 971, 812, and 468 cm^{-1} are assigned to amorphous silica on the basis of their similarity to reported values (3413, 1630, 1220, 1099, 970, 809, and 470 cm^{-1}):[33] peaks at 3435 and 1638 cm^{-1} are assigned to adsorbed water.[34] The Mg-F stretching vibration of MgF_2, which occurs at 435 cm^{-1},[35] may be a part of the intense band at 470 cm^{-1}.

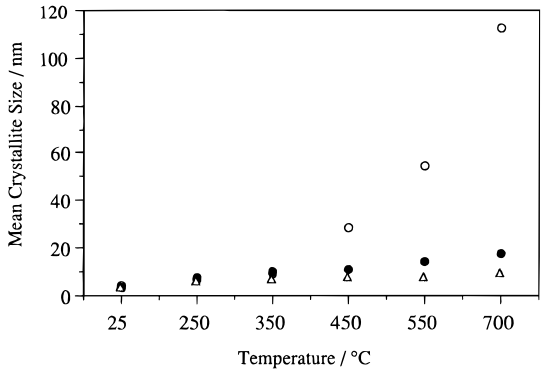

Figure 9. Mean crystallite size of MgF_2 in calcined xerogels versus firing temperature. Open circles represent the xerogel from a MgF_2 sol, filled circles represent xerogels from a sol with a Mg:Si ratio of 80:20, and triangles represent xerogels with a Mg:Si ratio of 60:40. Crystallite sizes were calculated using the fwhm of the MgF_2 (110) reflection,[30] at 27.3 °(2θ).[24]

Figure 9 presents the mean crystallite size in the xerogels from MgF_2 and from the biphasic sols (80:20 and 60:40), plotted as a function of firing temperature. These crystallite sizes were calculated[30] using the fwhm of the MgF_2 (100) peak at 27.3° (2θ), taken from the XRD patterns of these materials. It is noteworthy that the presence of as little as 20% SiO_2 in the composite considerably retarded the crystallization of MgF_2.

The bright-field transmission electron microscope (TEM) image of the 60:40 xerogel fired at 700 °C is presented in Figure 10a. This image implies that the xerogel is fairly homogeneous. On the basis of the similarity of the well-known XRD pattern (see Table 1), the electron diffraction pattern of this material, presented in Figure 11, is assigned to MgF_2. The dark-field image of this xerogel, taken using the MgF_2 (111) diffraction circle, is shown in Figure 10b. The image contains evenly distributed bright spots ascribed to MgF_2 nanocrystals dispersed in an amorphous matrix. The largest of these diffracting regions is ~5−10 nm, which is in good agreement with the ~10 nm mean crystallite size of MgF_2 in this xerogel, calculated from its XRD pattern (see Figure 9).

Using multiple coatings, ~1500 Å thick films were prepared on Si(100) from sols that had Mg:Si ratios of 80:20 and 60:40. These films had surface roughness of approximately ±50 Å after being heated, uncovered, at 550 °C. Figure 12 presents XRD patterns of these heated films. Diffraction from the 80:20 film (Figure 12c) indicates the presence of crystalline MgO and MgF_2, whereas the pattern from the 60:40 film shows diffraction from crystalline MgF_2 only. As described above, the XRD pattern of a film, formed from the nanocrystalline MgF_2 sol, showed diffraction from MgO after being heated, uncovered, at 550 °C (see Figure 3e). We conclude that the presence of SiO_2 inhibits loss of fluoride from the MgF_2-SiO_2 composite films during firing, possibly by excluding water. The large fwhm of the MgF_2 diffraction peaks in the patterns of these films

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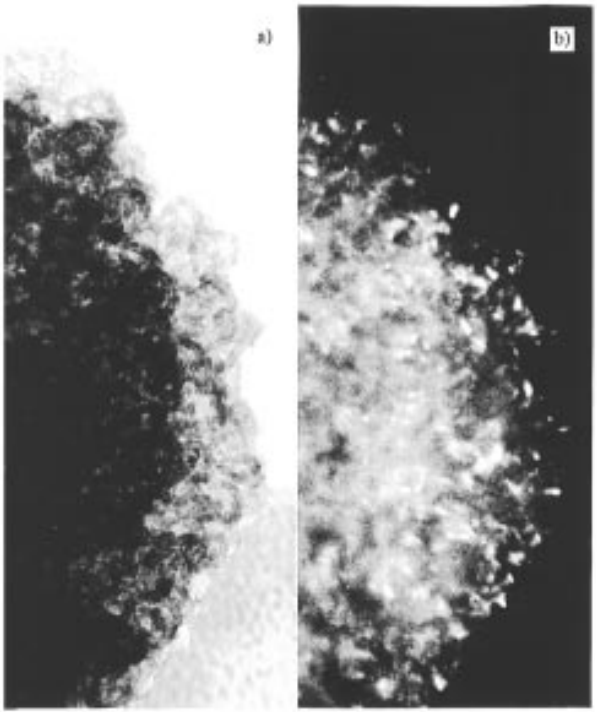

Figure 10. Bright-field (a) and dark-field (b) TEM images of the xerogel, heated to 700 °C in dry air, after isolation from the 60:40 Mg:Si sol. The dark-field image was taken using the MgF_2 (111) diffraction circle (see Figure 11 and Table 1). Bright areas in (b), especially those at the right side of the specimen, are ~5−10 nm (50−100 Å) wide.

Table 1. Lattice Spacings[a] from the Electron Diffraction Pattern (See Figure 11) of a Xerogel, Heated to 700 °C under Dry Air, after Isolation from a MgF_2−SiO_2 60:40 Sol

Mg:Si = 60:40 (700 °C)		MgF_2[a]	
d/Å	rel intensity	*d*/Å	rel intensity
3.12−3.21	s	3.275	100
2.44−2.55	w	2.545	22
		2.310	<1
2.15−2.24	m	2.231	96
2.00−2.08	vw	2.067	34
1.66−1.73	m	1.711	73
1.61−1.66	vw	1.635	31
1.47−1.50	vw	1.526	19
		1.462	6
		1.441	4
		1.382	14
1.32−1.35	m	1.375	35

[a] Crystalline gold was used as a calibration standard.[26] [b] X-ray diffraction data.[24]

indicates that the SiO_2 component may also have acted to retard the growth of the MgF_2 nanocrystals, as was seen in the bulk xerogels from the sols used to prepare these films. The refractive index of the 60:40 film fired at 550 °C was 1.43 at 4040 nm. The refractive index of a 60:40 molar mixture of MgF_2 and amorphous SiO_2 is expected to be ~1.41.

The composite films heated to 550 °C showed moderate abrasion resistance. Since the ability to tailor the morphology of a sol−gel prepared SiO_2 film through reactions in the sol is well established,[36] it may be possible to prepare scratch-resistant, antireflective MgF_2−SiO_2 films by modifying the silicate sol chemistry prior to combination with the MgF_2 sol.

(36) Brinker, C. J.; Hurd, A. J.; Ward, K. J. In *Ultrastructure Processing of Advanced Ceramics*, Mackenzie, J. D., Ulrich, D. R., Eds.; John Wiley: New York, 1988; pp 223−240.

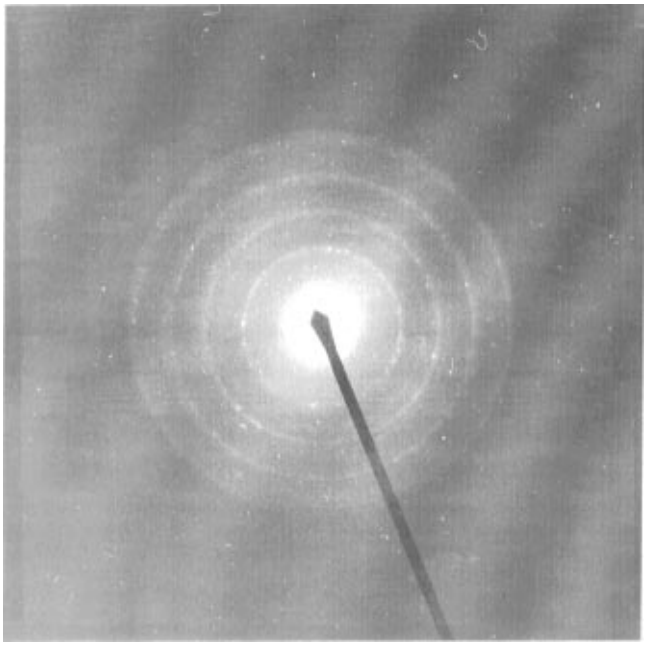

Figure 11. Electron diffraction, TEM pattern of a xerogel, heated to 700 °C under dry air, after isolation from the 60:40 Mg:Si sol. Measured *d* spacings are assigned to MgF_2 (see Table 1).

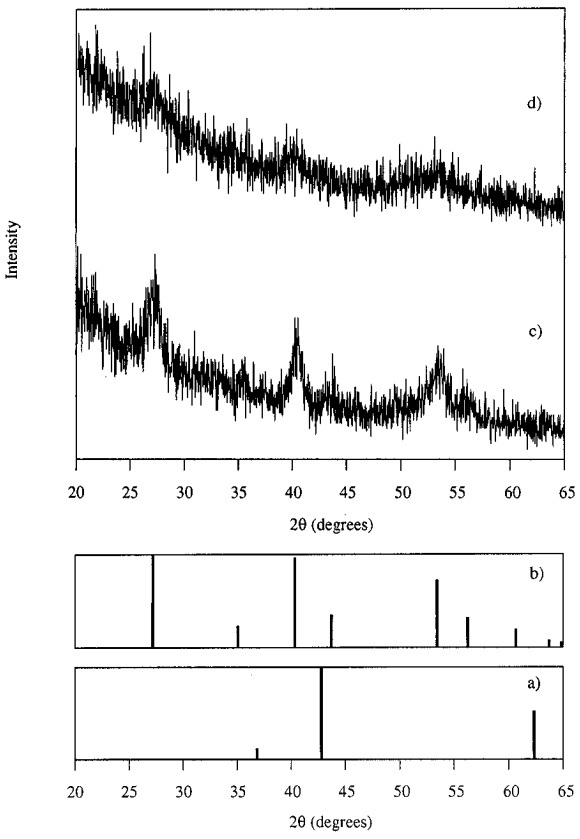

Figure 12. Representations of the XRD patterns of randomly oriented MgO (a),[23] and MgF_2 (b),[24] compared to glancing-angle (2θ) XRD patterns, taken at $\Omega = 2°$, of ~1500 Å thick films on Si(100) prepared using composite sols with Mg:Si molar ratios of (c) 80:20 and (d) 60:40. Coated substrates were heated for 6 h at 550 °C in dry air.

Summary and Conclusions

Nanocrystalline MgF_2 was produced from the reaction of HF with a sol prepared from methanolic aqueous H_2O_2 and $Mg(OCH_3)_2$. Soft, rough thin films of nanocrystalline MgF_2 spin cast on Si(100) lost all fluoride when heated in dry air at 550 °C. When a MgF_2 film was placed in contact with another and heated under the same conditions, fluoride loss occurred only above 550 °C. Such a film was resistant to scratching with a steel razor blade.

XRD and TEM analysis of biphasic xerogels prepared by combining a nanocrystalline MgF_2 sol with a silicate sol showed the presence of MgF_2 nanocrystals dispersed in an amorphous matrix. TEM showed that such a xerogel, heated to 700 °C was composed of ~5−10 nm MgF_2 grains evenly dispersed in an amorphous matrix. IR spectroscopic analysis indicated that the matrix was amorphous SiO_2. Fluoride loss and MgF_2 crystal growth were greatly retarded in biphasic xerogels and in thin films prepared from silicate−MgF_2 composite sols, presumably due to the exclusion of water vapor by the silicate network in these glass−ceramic composite materials.

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