Articles

Sol−Gel Preparation and Characterization of Magnesium Peroxide, Magnesium Hydroxide Methoxide, and Randomly and (111) Oriented MgO Thin Films

Anthony A. Rywak and James M. Burlitch*

Department of Chemistry, Cornell University, Ithaca, New York, 14853-1301

Thomas M. Loehr

Department of Chemistry, Biochemistry & Molecular Biology, Oregon Graduate Institute of Science and Technology, Portland, Oregon, 97291

A H_2O_2-assisted sol−gel method for the preparation of precursors for formation of thin films of MgO is described. Sols were prepared from the addition of $Mg(OCH_3)_2$ to methanolic H_2O_2. Two such sols, with Mg to H_2O_2 ratios of 1:1 and 1:10, were used to prepare, respectively, random or (111) oriented MgO thin films on Si(100). The xerogel from a sol with a 1:10 $Mg:H_2O_2$ ratio contained nanocrystalline $MgO_2 \cdot nH_2O$, whereas the xerogel from a comparable sol with a 1:1 $Mg:H_2O_2$ ratio contained nanocrystals of $MgO_2 \cdot nH_2O$, and $Mg(OH)(OCH_3)$. The latter compound was the hydrolysis product of methanolic $Mg(OCH_3)_2$ even when treated with up to 4 equiv of water. The thermal decomposition properties of this compound are reported. Using the published method of treating $Mg(NO_3)_2$ with excess 30% H_2O_2, $MgO_2 \cdot nH_2O$, with a $Mg^{2+}:O_2^{2-}$ ratio of 1:0.74, was prepared. Based on IR, TGA, and DTA results, it is proposed that the material also contained oxide, and possibly hydroxide ions for charge balance. These ions were present either in an amorphous phase, or possibly substituted for O_2^{2-} in the MgO_2 crystal structure.

Introduction

MgO is a dielectric ceramic material that, in thin-film form, has found increasing use in the semiconductor industry. High-quality MgO dielectric thin films, for instance, have been prepared on silicon.[1] Thin films of MgO have also been used as chemically stable "buffer layers" for separating films of oxide-based materials from underlying semiconducting substrates.[2−5] Epitaxial or oriented MgO films are preferred for such applications, since these films can be used as lattice templates for growing oriented overlayers. For example, the high temperature superconductor $YBa_2Cu_3O_7$ grows with *c*-axis orientation when crystallized on (100) oriented MgO films.[6,7] Also, films of the ferroelectric $LiNbO_3$ grow epitaxially on MgO(111),[8] due to the

excellent match of the MgO(111) atomic spacings with those in the *a*−*b* planes of $LiNbO_3$.

A number of methods have been reported for the preparation of oriented MgO thin films. Sputter-deposited MgO has been grown with (111) orientation on a number of substrates, including glass.[9] Chemical vapor deposition techniques have also been used[10,11] to grow (100) oriented MgO on the native oxide of Si(111). Henry reported that (111) oriented MgO films could be grown on dehydrated mica,[12,13] and Tarsa et al. used pulsed laser deposition techniques and GaAs as a substrate to grow MgO(111) oriented thin films.[5]

$Mg(OCH_3)_2$ solutions in MeOH have been used for the formation of high-strength, high-dielectric MgO films on nickel−iron wires, tapes, and laminations. The physical and electrical properties of the resultant coated materials made them ideally suited as low dielectric loss induction components in transformers.[14,15]

There is some disagreement in the literature regarding the compound formed from the hydrolysis of Mg-

[⊛] Abstract published in *Advance ACS Abstracts*, October 1, 1995.
(1) Hebard, A. F.; Fiory, A. T.; Nakahara, S.; Eick, R. H. *Appl. Phys. Lett.* **1986**, *48*, 520−522.
(2) Fork, D. K.; Nashimoto, K.; Geballe, T. H. *Appl. Phys. Lett.* **1992**, *60*, 1621−1623.
(3) Chang, L. D.; Tseng, M. Z.; Hu, E. L. *Appl. Phys. Lett.* **1992**, *60*, 1753−1755.
(4) Tanimura, J.; Takami, T.; Kuroda, K.; Wada, O.; Kataoka, M.; Kojima, K.; Ogama, T. *Jpn. J. Appl. Phys.* **1993**, *32*, L51-L53.
(5) Tarsa, E. J.; De Graef, M.; Clarke, D. R.; Gossard, A. C.; Speck, J. S. *J. Appl. Phys.* **1993**, *73*, 3276−3283.
(6) DeSisto, W. J.; Henry, R. L. *J. Cryst. Growth* **1991**, *109*, 314−317.
(7) Fork, D. K.; Ponce, F. A.; Tramontana, J. C.; Geballe, T. H. *Appl. Phys. Lett.* **1991**, *58*, 2294−2296.
(8) Nunomura, K.; Ishitani, A.; Matsubara, T.; Hayashi, I. *J. Cryst. Growth* **1978**, *45*, 355−360.

(9) Aboelfotoh, M. O. *Appl. Phys. Lett.* **1974**, *24*, 347−349.
(10) Kamata, K.; Shibata, Y.; Kishi, Y. *J. Mater. Res. Lett.* **1984**, *3*, 423−426.
(11) Fujii, E.; Tomazawa, A.; Fujii, S.; Torii, H.; Hattori, M.; Takayama, R. *Jpn. J. Appl. Phys. Part 2* **1993**, *32* (10A), L1448-L1450.
(12) Henry, C. R.; Poppa, H. *J. Vac. Sci. Technol. A* **1988**, *6*, 1113−1117.
(13) Henry, C. R.; Poppa, H. *Thin Solid Films* **1990**, *189*, 303−312.
(14) Lauriente, M. *Insulation* **1959**, *5*, 21−24.
(15) Suchoff, L. A. U.S. Patent 2796364, 1957; *Chem. Abstr.* 51: 12462c.

$(OCH_3)_2$. $Mg(OH)(OCH_3)$ has been reported to form from $Mg(OCH_3)_2$ in wet methanol.[16] Hydroxide methoxides of Mg have also been described from the hydrolysis of $Mg(OCH_3)_2$ in supercritical mixtures of MeOH and water,[17] and MeOH−water−toluene.[18] In contrast, Teichner reported that $Mg(OCH_3)_2$ in benzene, treated with 2 or more equivalents of water, formed $Mg(OH)_2$.[19] The difficulty of removal of methoxide groups from MgO powders prepared from $Mg(OCH_3)_2$ has been reported.[20,21]

One of the likely products to be formed from the reaction of H_2O_2 with $Mg(OCH_3)_2$ is magnesium peroxide hydrate,[22] $MgO_2 \cdot nH_2O$, where $n = 0.5$ to 2. A number of synthetic methods for making this compound are known. Published methods for preparing $MgO_2 \cdot nH_2O$ involve the treatment of a Mg salt with an excess of aqueous H_2O_2;[22−24] the mean crystallite size of MgO_2 has been very small, typically less than 200 Å.[25,26] During thermal decomposition under CO_2 free air, $MgO_2 \cdot 0.5H_2O$ lost its physisorbed water of hydration between 80 and 200 °C, giving anhydrous MgO_2.[24,25] MgO_2 disproportionated between 300 and 450 °C, forming MgO and dioxygen.[24] These results suggested that thin films of MgO_2, made using the sol−gel method, might provide a low-temperature means of preparing MgO coatings.

This paper describes the preparation of stable sols from the treatment of $Mg(OCH_3)_2$ with aqueous H_2O_2, and their use to form thin films of MgO; coatings of the sols on Si(100) gave thin films of MgO that were either randomly oriented or had preferred (111) orientation, depending on the precursor.

Experimental Section

Reagents and General Synthesis Techniques. Unless otherwise stated, all reactions were carried out under an atmosphere of dry, oxygen-free argon.[27] Round-bottomed reaction flasks were equipped with a water-cooled condenser connected to an argon source and an oil bubbler using a three-way stopcock. MeOH used for sol preparations was distilled from $Mg(OCH_3)_2$. H_2O_2 (30%) was used as obtained from Fisher. Fisher 50% H_2O_2 was assayed at $49.4 \pm 0.1\%$.[28] Unless otherwise stated, all chemicals were reagent grade. $Mg(OCH_3)_2$ was made from Mg turnings (Alfa, M4N or Cerac 99.99%) and dry MeOH under argon, and was filtered through a porosity-D fritted filter tube. For addition to methanolic H_2O_2, measured portions of $Mg(OCH_3)_2$

filtrates were transferred through a stainless steel cannula to 100 mL Schlenk reaction vessels (SRVs).[27]

Reactant solutions were transferred from SRVs to reaction vessels as follows: A needle from an argon-filled, 50 mL ground-glass syringe whose barrel had been coated with a thin-film of mineral oil was passed through the septum on a SRV that contained a reactant solution. This syringe was mounted on a syringe pump, and the argon injected into the SRV from the syringe slowly displaced the reactant from the SRV through a stainless steel cannula into a reaction flask.

Solvent was removed from sols using a trap-to-trap vacuum distillation (TTVD) apparatus,[29] with the condenser cooled with Dry Ice. Recovered xerogels were placed under a dynamic vacuum at room temperature until a pressure of 5 mmHg or less was reached, which typically took 14−72 h. Solids were kept in Schlenk storage vessels (SSVs) under an atmosphere of argon. Unless otherwise stated, solid products were handled in a N_2-filled glovebag.

Thin-Film Preparation. Silicon substrates used for thin-film experiments were prepared by cleaving Unisil Si(100) 3-in. diameter test wafers. These pieces were twice cleaned in anhydrous MeOH in an ultrasonic bath for approximately 2 min. Using profilometry, the surface roughness of such pieces was determined to be ~10 Å. The silicon wafer pieces were coated on a Headway Research photoresist spinner. Wafers were spun at 3000 rpm and were rinsed with 0.45 μm filtered anhydrous MeOH immediately before coating. Approximately 4 drops of sol, filtered through a 0.45 μm Nylon syringe filter, were placed on the silicon wafer before spinoff at 3000 rpm for 40 s. This procedure was repeated to form multiple coatings. For firing, wafers were held, film up, in 9 cm long alumina boats (Thomas Scientific Co.), which were loosely covered with fused silica lids. These boats were placed in a fused silica tube in a Lindberg Model 54233 tube furnace. Under an atmosphere of air, passed through a column of Mallinckrodt Aquasorb, the wafers were heated at 100 °C h^{-1} to the desired temperature and were held for 6 h before the furnace was turned off and allowed to cool to room temperature.

Characterization Techniques. IR spectra were taken using a Mattson Model IR-10410 FTIR spectrometer operating at a resolution of 0.5 or 1.0 cm^{-1}. KBr for IR samples was dried under dynamic vacuum at 200 °C for several days prior to use. In a nitrogen-filled glovebag, KBr disks (~1 mm thick, 13 mm diameter) were prepared by ball-milling for 30 s ~4 mg of sample with 400 mg of KBr. The resultant mixture was transferred to a Perkin-Elmer Model 186−0025 evacuable potassium bromide die.[30] Such mixtures were pressed with an 11 metric ton load for several min with the die under dynamic vacuum. The clear disks were quickly transferred to the spectrometer chamber, which was purged with dry, CO_2-free air purified with a Balston Model 74-5071 Clean Air Package. IR spectra of thin films on Si(100) were taken through the silicon substrate, using dry air as a background. Raman spectra of solids, taken at the Oregon Graduate Institute, were collected using a modified Jarrell-Ash 25-300 double-grating scanning spectrophotometer equipped

(16) Lutz, H. D. *Z. Anorg. Allg. Chem.* **1967**, *353*, 207−215.
(17) Kubo, T.; Uchida, K.; Tsubosaki, K.; Hashimi, F. *Kogyo Kagaku Zasshi* **1970**, *73*, 75−82.
(18) Utamapanya, S.; Klabunde, K. J.; Schlup, J. R. *Chem. Mater.* **1991**, *3*, 175−181.
(19) Teichner, S. J.; Nicalaon, G. A.; Vicarini, M. A.; Gardes, G. E. E. *Adv. Colloid Interface Sci.* **1976**, *5*, 245−273.
(20) Utamapanya, S.; Klabunde, K. J.; Schlup, J. R. *Chem. Mater.* **1991**, *3*, 171−181.
(21) Itho, H.; Utamapanya, S.; Klabunde, K. J.; Schlup, J. R. *Chem. Mater.* **1993**, *5*, 71−77.
(22) Vol'nov, I. I. *Peroxides, Superoxides, and Ozonides of Alkali and Alkaline Earth Metals*; Plenum: New York, 1966.
(23) Vannerberg, N. G. *Ark. Kemi* **1959**, *14* (10), 99−105.
(24) Allamagny, P. *Rev. Chim. Minerale* **1965**, *2*, 645−676.
(25) Vannerberg, N. G. *Prog. Inorg. Chem.* **1962**, *4*, 125−197.
(26) Hesse, W.; Jansen, M.; Schnick, W. *Prog. Solid State Chem.* **1989**, *19*, 47−110.
(27) Burlitch, J. M. *How to Use Ace No-Air Glassware: Bulletin 3841*; Vineland, NJ, 1984.
(28) Kolthoff, I. M.; Sandell, E. B. *Textbook of Quantitative Inorganic Analysis*; MacMillan: New York, 1946, p 630.

(29) Ace Glass Incorporated. *Catalog 1000*; Vineland, NJ, 1989.
(30) Farmer, V. C. *Spectrochim. Acta* **1957**, *8*, 374−389.

with an RCA C31034 PMT which was thermoelectrically cooled to −40 °C;[31] the excitation source was a Spectra-Physics Model 164 Ar ion laser operating at an excitation wavelength of 488.0 nm and a power of 200 mW. Solid samples were loaded in Pyrex capillaries in a N$_2$-filled glovebag. These capillaries were capped with type-T Apiezon grease before being sealed in air using a torch. Solutions for Raman spectroscopy were transferred to dry, septum-sealed Pyrex capillaries using a 10 mL Gastight syringe. Solutions in these tubes were frozen in liquid nitrogen, and the tubes evacuated before being sealed with a flame. Dry MeOH and a 0.25 M H$_2$O$_2$ solution, prepared by diluting 0.850 g (12.3 mmol) of 49.4% H$_2$O$_2$ to 50 mL with dry MeOH, were used as Raman solution standards. Spectra were collected with a DILOR Z24 triple-grating scanning spectrophotometer equipped with a Hamamatsu 943−02 photomultiplier which was thermoelectrically cooled to −40 °C. The excitation source was a Coherent Model INNOVA 90-6 argon ion laser operating at 488.0 nm.

All X-ray diffraction (XRD) was done using a Cu Kα source. Debye camera diffraction photographs were taken of potentially air-sensitive samples for comparison with comparable powder diffraction patterns taken in air. Samples for a Phillips Electronics Model 52056 Debye camera were loaded in glass capillaries in a N$_2$-filled glovebag, capped with T-type Apiezon grease, and sealed in air. All other diffraction patterns were done in air using a Scintag PAD X diffractometer and DMS software system; samples were placed on a low-background, single-crystalline, quartz holder. Typically, θ−2θ patterns were scanned at 2° or 5° (2θ) min^{-1}, and glancing-angle (2θ) patterns, taken at Ω = 2°, were scanned at 1.5° (2θ) min^{-1}. Solutions for XRD analysis were held in a machined PMMA cell (22 mm ID, 4 mm deep), which was covered with a thin PVC plastic window that was sealed to the cell with type-T Apiezon grease. Solutions patterns were scanned at a rate of 0.42° (2θ) min^{-1}. Experimental XRD patterns were compared to the published powder diffraction patterns of MgO[32] and MgO$_2$·nH$_2$O.[23]

Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) profiles were simultaneously collected using a Seiko Model SSC/5200 TG/DTA 320 thermal analysis system. Samples were heated at a rate of 2.5 °C min^{-1} under an atmosphere of nitrogen passed through a column of Mallinckrodt's Aquasorb and Aldrich's Ascarite.

Mg content of products was determined by titration.[33] Peroxide content of products was determined by iodimetric titration using sodium thiosulfate,[35,36] and by titration with KMnO$_4$.[35] Unless otherwise stated, all titration results represent an average of four measurements. Elemental analyses were done by Galbraith Laboratories, Knoxville, TN, and Desert Analytics, Tucson, AZ.

For thin-film characterization, surface profilometry measurements were made on a Tencor Instruments Alfa-step Thin-Film and Surface Profiler. Ellipsometry was done using a Rudolph Research Auto EL II ellipsometer operating at 632.8, 546.1, and 405.0 nm. Thin-film porosity was calculated using the Lorentz−Lorenz relationship.[14,37] Field emission scanning electron microscope (FESEM) images were taken on a Hitachi Model 4500 FESEM; coated silicon wafer pieces were cleaved and placed on double-sided carbon tape attached to 0.31 mm aluminum microscope stubs. These mounted samples were then coated with 20 Å of carbon.

Synthesis. *(1) Treatment of Mg(OCH$_3$)$_2$ with H$_2$O.* Methanolic Mg(OCH$_3$)$_2$ was prepared by treating 0.3156 g (12.98 mmol) of Mg turnings with ∼60 mL of dry MeOH in a 100 mL SRV. The Mg(OCH$_3$)$_2$ solution was diluted to 0.35 L in a 1-L, three-necked creased round-bottomed flask equipped with a magnetic stirring bar. To this rapidly stirred solution was added, over a 60 h period, 0.2336 g (12.97 mmol, R = 1) of distilled, deionized water diluted to 80 mL with dry MeOH. The Mg(OCH$_3$)$_2$ solution remained clear after the addition of the ∼20 mL but became cloudier as the addition progressed, forming a flocculent suspension after the addition of ∼40 mL. The resultant suspension appeared unchanged after being heated at reflux for 24 h. Solvent removal from a 250 mL portion of this cloudy suspension yielded a fine, white powder. Found: C, 16.01; H, 5.38; Mg, 31.18 ± 0.24%. Calcd for (see Results and Discussion) 0.936[Mg(OH)$_{0.97}$(OCH$_3$)$_{1.03}$]: C, 15.91; H, 5.26; Mg, 31.27%.

By the same method described above, Mg(OCH$_3$)$_2$, prepared from 0.9426 g (38.78 mmol) of Mg, was diluted to 0.70 L with dry MeOH in a 1-L, three-neck creased round-bottom flask equipped with a magnetic stirring bar. Over a 21 h period, 2.7857 g (154.6 mmol, R = 4) of distilled, deionized water, diluted to 50 mL with dry MeOH, was added to the rapidly stirred Mg(OCH$_3$)$_2$ solution, giving a white flocculent suspension. This suspension remained unchanged after being heated at reflux for 12 h. Solvent removal from this suspension gave a hard, white xerogel. Found: C, 14.88; H, 5.28; Mg, 32.59 ± 0.32%. Calcd for (see Results and Discussion) 0.964[Mg(OH)$_{1.08}$(OCH$_3$)$_{0.92}$]: C, 14.96; H, 5.24; Mg, 32.90%.

(2) Preparation of Magnesium Peroxide Hydrate.[24] In 0.50 L (4.9 mol) of 30% H$_2$O$_2$ placed in a 1-L Pyrex Erlenmeyer flask was dissolved 10.528 g (41.059 mmol) of Mg(NO$_3$)$_2$·6H$_2$O (Mallinckrodt). Using a piece of copper wire attached to the lip of the flask, 10 mL of 27% NH$_4$OH (Fisher) in a 20 mL glass vial was suspended over the solution. The flask was sealed with a rubber stopper through which ran a piece of Pyrex tubing, which was connected to an oil bubbler to prevent the entry of atmospheric CO$_2$. A large amount of white precipitate formed in the solution after it had stood for ∼18 h. The solution was left undisturbed for 108 days, after which time the product, which consisted of large white plates, was crushed and quickly transferred in air to a porosity D-fritted filter tube. The product was washed with several ∼10 mL portions of 30% H$_2$O$_2$ that had been degassed by bubbling argon through it for ∼30

(31) Loehr, T. M.; Keyes, W. E.; Pincus, P. A. *Anal. Biochem.* **1979**, *96*, 456−463.
(32) Swanson, H. E.; Tatge, E. *Nat. Bur. Stand. (U.S.) Circ.* **1953**, *539*(I), 37−39.
(33) Blaedel, W. J.; Knight, H. T. *Anal. Chem.* **1954**, *26*, 741−743.
(34) Skoog, D. A.; West, D. M. *Fundamentals of Analytical Chemistry*; Holt, Rinehart and Winston: New York, 1969.
(35) Kolthoff, I. M.; Sandell, E. B. *Textbook of Quantitative Inorganic Analysis*; MacMillan: New York, 1946; p 623.
(36) Hargis, L. G. *Analytical Chemistry: Principles and Techniques*; Prentice Hall: Englewood Cliffs, NJ, 1988.

(37) Roessler, D. M.; Huffman, D. R. In *Handbook of Optical Constants of Solids II*; Academic Press: San Diego, 1991; pp 919−955.

min. The product was then washed with several ~10 mL portions of diethyl ether, degassed as described above, before being transferred under argon to a SSV and placed under dynamic vacuum for ~14 h, after which time a pressure of 5 mmHg had been reached. The yield was 2.24 g (84% based on Mg). Found: Mg, 37.36 ± 0.85; O_2^{2-}, 36.61 ± 0.29; N < 0.5%. Calcd for (see Results and Discussion) [$Mg(O_2)_{0.72}(OH)_{0.33}O_{0.095}$· 0.32$H_2O$]: Mg, 39.92; O_2^{2-}, 38.89%.

(3) Treatment of Mg(OCH₃)₂ with 1 Equiv of H₂O₂: Preparation of a 1:1 Sol. In a 100 mL calibrated SRV was transferred 0.055 L (41 mmol) of 0.74 M Mg(OCH₃)₂ prepared previously from 16.506 g (679.12 mmol) of Mg in 0.920 L of dry MeOH. Over 33 h, the transferred solution was added to a rapidly stirred solution of 3.027 g (44.5 mmol) of 49.4% H_2O_2 diluted to 0.75 mL with dry MeOH in a 1-L, three-necked creased round-bottomed flask equipped with a magnetic stirring bar. The resultant sol showed a faint Tyndall effect, which became slightly stronger after being heated at reflux for 8 h. A portion of this sol appeared unchanged after being stored at room temperature for 17 months. Following reflux, a 250 mL portion of the sol was transferred to a 250 mL SRV for solvent removal. During concentration, the sol remained clear but displayed an increasingly stronger Tyndall effect as it became more concentrated. The sol gelled at a Mg concentration of ~500 mM. The white, opaque xerogel recovered after complete solvent removal was readily ground into a white powder in a mortar and pestle. Found: C, 8.77; H, 1.59; Mg, 35.58 ± 0.24; O_2^{2-}, 23.13 ± 0.48%. Calcd for (see Results and Discussion) [Mg(OH)(OCH₃)]$_{0.43}$-[$Mg(O_2)_{0.88}(OH)_{0.33}]_{0.57}$·0.087$H_2O$·0.057CH₃OH: C, 8.65; H, 3.44; Mg, 35.95; O_2^{2-}, 23.74%.

Sols, prepared by the general method described above, were concentrated to 250 mM in Mg for use in coating Si wafers and for solution Raman experiments, and to 310 mM for solution XRD analysis.

(4) Treatment of Mg(OCH₃)₂ With 10 Equiv of H₂O₂: Preparation of a 1:10 Sol. A solution of Mg(OCH₃)₂, prepared from the reaction of 0.8935 g (35.13 mmol) of Mg with dry MeOH, was diluted to 80 mL. Over 24 h, this Mg(OCH₃)₂ solution was added to a rapidly stirred solution prepared from 24.995 g of 49.4% H_2O_2 (363 mmol) diluted to 0.66 L with dry MeOH in a 1-L, three-necked, creased round-bottomed flask equipped with a magnetic stirring bar. The resultant sol, which showed a strong Tyndall effect, remained unchanged after being heated at reflux for 13.5 h. Solvent removal from this sol gave a white, dense xerogel. Found: Mg, 34.62 ± 0.24; O_2^{2-}, 34.63 ± 0.19%. Calcd for (see Results and Discussion) Mg(O₂)$_{0.80}$(CO₃)$_{0.054}$(OH)$_{0.28}$·(0.23H₂O· 0.20CH₃OH): Mg, 35.45; O_2^{2-}, 37.33%.

By the general method described above, 1:10 sols were prepared and concentrated to 250 mM in Mg for coating wafers and for Raman spectroscopic analysis of solutions.

Results and Discussion

Reaction of Mg(OCH₃)₂ with Water. In the present study, the hydrolysis products from two methanolic Mg-(OCH₃)₂ solutions were examined: One was prepared from the addition of 1 equiv of water to methanolic Mg-(OCH₃)₂, and the other from the addition of 4 equiv of water.
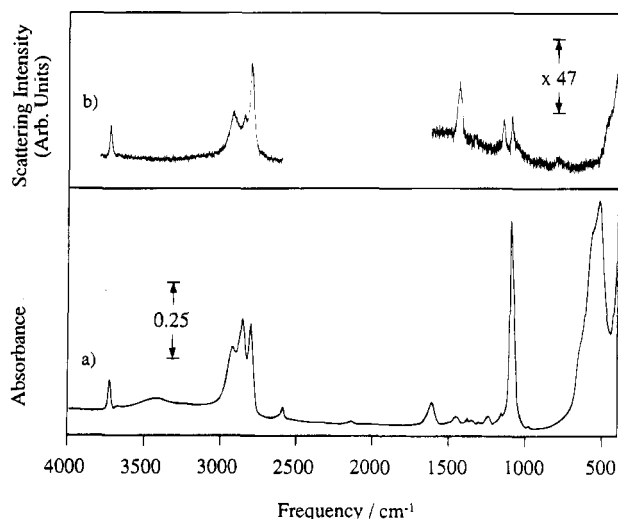

Figure 1. (a) IR and (b) Raman spectra of the xerogel isolated from methanolic Mg(OCH₃)₂ hydrolyzed with 1 equiv of water.

Figure 1 presents the IR and Raman spectra of the precipitate recovered from the suspension formed from the slow addition of 1 equiv of H_2O to methanolic Mg-(OCH₃)₂. The IR spectrum is identical to that reported for Mg(OH·OCH₃)₂,[17] which is essentially identical to the IR spectrum of nickel hydroxide methoxide, Ni[(OH)$_{2/3}$(OCH₃)$_{1/3}$]₂.[38] The sharp peak at 3729 cm⁻¹ in Figure 1a is assigned to MgO−H stretching and does not correspond to ν_{O-H} of Mg(OH)₂,[39] which occurs at 3697 cm⁻¹. In Mg(OH)₂, two OH groups are related by a center of symmetry, which causes coupling of their vibrational motions. This vibrational coupling gives rise to a symmetric −MgO−H vibration, seen in the Raman spectrum at 3655 cm⁻¹, which is 42 cm⁻¹ lower in frequency than the asymmetric ν_{O-H} seen in the IR spectrum.[39] The Raman spectrum of the product formed from methanolic Mg(OCH₃)₂ hydrolyzed with one equivalent of water showed ν_{O-H} occurring at 3726 cm⁻¹, only 3 cm⁻¹ lower in frequency than ν_{O-H} in the IR spectrum. On the basis of these results, it can be concluded that the −MgO−H groups in the hydrolysis product of Mg-(OCH₃)₂ reside in an environment where vibrational coupling is significantly smaller than in Mg(OH)₂.

The IR and Raman peaks at 2922, 2853, and 2802 cm⁻¹ in Figure 1 are assigned to a C−H bending overtone and two C−H stretching modes, respectively, of methoxy ligands.[17,20,21,38] Weak IR absorbance at 3422 and 1618 cm⁻¹ in Figure 1a is assigned to traces of adsorbed water,[40,41] possibly picked up during the short time the IR sample was exposed to the air.

With the exception of stronger absorbance at 3422 and 1618 cm⁻¹, the IR spectrum of the product obtained from the hydrolysis of methanolic Mg(OCH₃)₂ with 4 equiv of water was identical to Figure 1a and suggest that the two hydrolysis products were almost identical.

The thermal analysis profiles of the xerogel formed from the addition of 1 equiv of water to Mg(OCH₃)₂ showed that a weight loss of 6.4% occurred when the

(38) Lebihan, S.; Guenot, J.; Figlarz, M. *J. Solid State Chem.* **1976**, *17*, 15−25.
(39) Martens, R.; Freund, F. *Phys. Status Solidi A* **1976**, *37*, 97−104.
(40) Little, L. H. *Infrared Spectra of Adsorbed Species*; Academic Press: London, 1966.
(41) Socrates, G. *Infrared Characteristic Group Frequencies*; John Wiley: Chichester, 1980.

xerogel was heated to 270 °C. The powder XRD pattern of of the xerogel heated to this temperature was identical to the XRD pattern of the unheated material, indicating that the 6.4% weight loss was likely due to the loss of adsorbed species. A small portion of that weight loss may have come from the desorption of MeOH. When heated above 270 °C, the $Mg(OCH_3)_2$ hydrolysis product underwent a second weight loss with a coinciding endotherm at 370 °C. The DTA profile also showed a weak endotherm at 442 °C. The XRD pattern of this xerogel which had been heated to 600 °C showed that it had decomposed to form single-phase MgO. Assuming that the small weight loss below 270 °C was due to the desorption of gases that did not contain carbon or hydrogen, the elemental analysis values (see Experimental Section), divided by 0.936 to account for the initial 6.4% weight loss, gave values that corresponded to the formula $Mg(OH)(OCH_3)$. Results from thermal analysis profiles of the xerogel from the hydrolysis of methanolic $Mg(OCH_3)_2$ with 4 equiv of water were similar.

Layered hydroxide—methoxides of Mg with the formula $Mg(OH)_x(OCH_3)_{1-x}$ have been reported as products from the high-pressure treatment of either $Mg(OH)_2$ or $Mg(OCH_3)_2$ with supercritical MeOH-water solutions.[18] The powder XRD patterns of the xerogels from the treatment of methanolic $Mg(OCH_3)_2$ with 1 or 4 equiv of water were the same whether taken in air or under N_2. A rapid increase in scattering at 33° (2θ), followed by tailoff in intensity at higher angles, as illustrated in Figure 2a, is characteristic of diffraction from a layered lattice with extreme stacking disorder.[42] The X-ray diffraction pattern of $Mg(OH)(OCH_3)$ is remarkably similar to that of $Ni[(OH)_{2/3}(OCH_3)_{1/3}]_2$.[38] The pattern also had asymmetric, medium intensity peaks 33.7 and 59.2°, which showed intensity tailoff at higher angles, indicating disordered layer stacking. A weak peak of similar shape also occurred at 69.6°. The structure consists of ABC stacked sheets of octahedrally coordinated Ni cations; within each sheet, the OH^- and OCH_3^- ions are shared among three Ni^{2+} ions.[38] Assuming $Mg(OH)(OCH_3)$ is isostructural with $Ni[(OH)_{2/3}(OCH_3)_{1/3}]_2$, the XRD peaks from the hydrolysis products can be assigned as follows: 11.2 (00.3), 22.0 (00.6), 33.0 (10.1, 01.2, 00.9, 10.4, 01.5, 10.7, and 01.8), 59.3 (11.0, 11.3, 10.13, and 11.6), and 71° (02.1, 20.2, 11.9, 02.4, and 20.5) $(2\theta\ (hkl))$. Using the Scherrer equation,[43] and the full width at half-maximum (fwhm) of the symmetrical peak at 11.2°, the mean crystallite size in the basal direction of $Mg(OH)(OCH_3)$ was calculated to be ~60 Å. The overall mean crystallite size of was calculated to be 24 Å, using the two dimensional equation of Warren[42] and the fwhm of the broad peak centered at 35° (2θ).

Reactions of Magnesium Compounds with H_2O_2. *(1) $MgO_2 \cdot nH_2O$.* The powder XRD pattern of $MgO_2 \cdot nH_2O$, prepared by treating of $Mg(NO_3)_2$ with excess 30% H_2O_2,[24] is presented in Figure 2c. Except for the peak at 3.3° (2θ), this diffraction pattern is identical to that reported for $MgO_2 \cdot 2H_2O$.[23] Small-angle X-ray peaks are often seen in the diffraction patterns of ordered, monodisperse particles, which can diffract

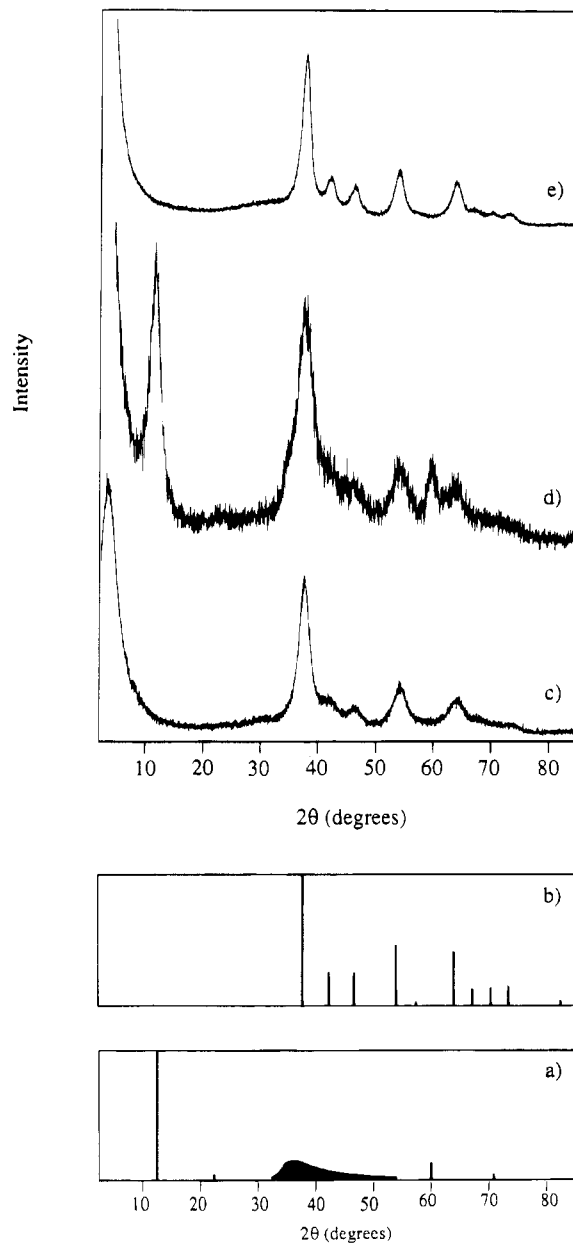**Figure 2.** Representations of the $\theta-2\theta$ powder XRD patterns of (a) $Mg(OH)(OCH_3)$ and (b) $MgO_2 \cdot 2H_2O$[23] and powder XRD patterns for (c) $MgO_2 \cdot nH_2O$[24] and xerogels recovered from methanolic $Mg(OCH_3)_2$ treated with (d) 1 equiv of H_2O_2, and (e) 10 equiv of H_2O_2.

X-rays like the ordered atoms in a crystal.[44-46]

The IR spectrum of $MgO_2 \cdot nH_2O$, prepared as described above, is similar to that reported by Vannerberg for $MgO_2 \cdot 2H_2O$,[47] except for the near absence of the reported peaks at 1490, 1410, and 1075 cm^{-1}, which may be attributed to carbonate ions formed from reaction of MgO_2 with atmospheric carbon dioxide.[48] Chemical analysis of $MgO_2 \cdot nH_2O$ gave a $Mg^{2+}:O_2^{2-}$ ratio of 1:0.74. The same ratio was obtained whether peroxide was assayed using iodimetric or potassium permanganate titration methods. The IR spectrum of this com-

(42) Warren, B. E. *Phys. Rev.* **1941**, *59*, 693–698.
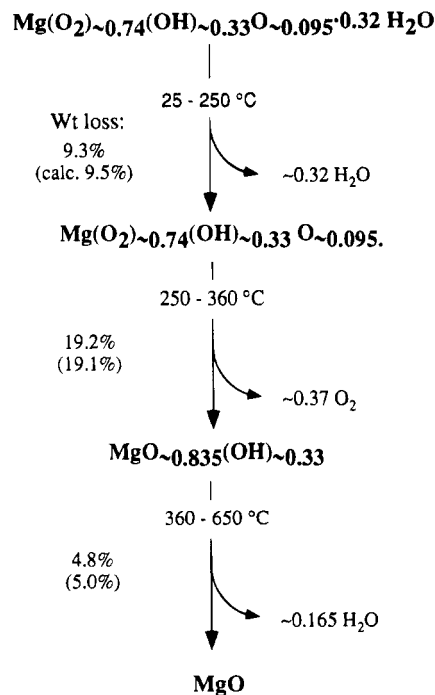(43) West, A. R. *Solid State Chemistry and Its Applications*; John Wiley: Chichester, 1989.

(44) Klug, H. P.; Alexander, L. E. *X-Ray Diffraction Procedures*; John Wiley: New York, 1954.
(45) Guinier, A. *Phys. Today* **1969**, *22* (11), 25–30.
(46) Yudowitch, K. L. *J. Appl. Phys.* **1951**, *22*, 214–216.
(47) Vannerberg, N. G. *Ark. Kemi* **1959**, *14*(11), 107–113.
(48) Rywak, A. A. Ph.D. Thesis, Cornell University, 1994.

(111) Oriented MgO Thin Films

Chem. Mater., Vol. 7, No. 11, 1995 **2033**

pound did not indicate the presence of ions other than peroxide which could account for charge balance, such as non-hydrogen bonded hydroxide[39,49] ($\sim$3600–3700 cm^{-1} (sharp)), carbonate or bicarbonate[41] ($\sim$1240–1580, 720–890 cm^{-1}) or nitrate[41] ($\sim$1340–1410, 800–860 cm^{-1}). It may be that the compound contained oxide ion (O^{2-}) or hydrogen-bonded hydroxide for charge compensation. A medium intensity peak (shoulder) at 3635 cm^{-1}, absent in the IR spectrum of $MgO_2 \cdot 2H_2O$,[47] may be due to ν_{O-H} of such hydrogen bonded hydroxide. These O^{2-} or OH^- ions could be present in amorphous material or possibly be substituted for O_2^{2-} in the MgO_2 structure. The possibility of O^{2-} substituting for O_2^{2-} in MgO_2 has been previously suggested[50] but has yet to be demonstrated. Allamagny[24] assayed only Mg in $MgO_2 \cdot 0.5H_2O$ and inferred peroxide and water contents from TGA results.

When heated to 250 °C, the compound underwent a 9.5% weight loss. Allamagny[24] attributed a weight loss between 80 and 200 °C in the TGA profile of $MgO_2 \cdot 0.5H_2O$ to loss of water from the $MgO_2 \cdot nH_2O$ crystals. A second weight loss, which occurred between 200 and 300 °C, was attributed to the formation of MgO and oxygen from the disproportionation of MgO_2.[24] An analogous 19.4% weight loss occurred between 250 and 360 °C, as well as a third 5% weight loss between 360 and 650 °C. As stated above, IR and elemental analyses implied that hydroxide ions may have been present in this xerogel. Since $Mg(OH)_2$ decomposes between 390 and 400 °C,[51] the slow weight loss between 360 and 650 °C may be caused by the decomposition of hydroxide. This conclusion is tentative, however, since crystalline $Mg(OH)_2$ decomposes endothermically,[51] whereas the thermal event associated with weight loss between 360 and 650 °C was exothermic. It is not known whether the hydroxide is crystalline or amorphous. When heated to 800 °C under dry, CO_2 free air, synthetic $MgO_2 \cdot nH_2O$ underwent a weight loss of 34 ± 3%, forming MgO. The weight loss expected for the conversion of the starting compound to MgO, based on Mg content, is 38 ± 3%. A possible pathway for the decomposition of the $MgO_2 \cdot nH_2O$ prepared in this study is presented in Scheme 1. Our results bring into question the proposed formula[24] of the product formed by this method.
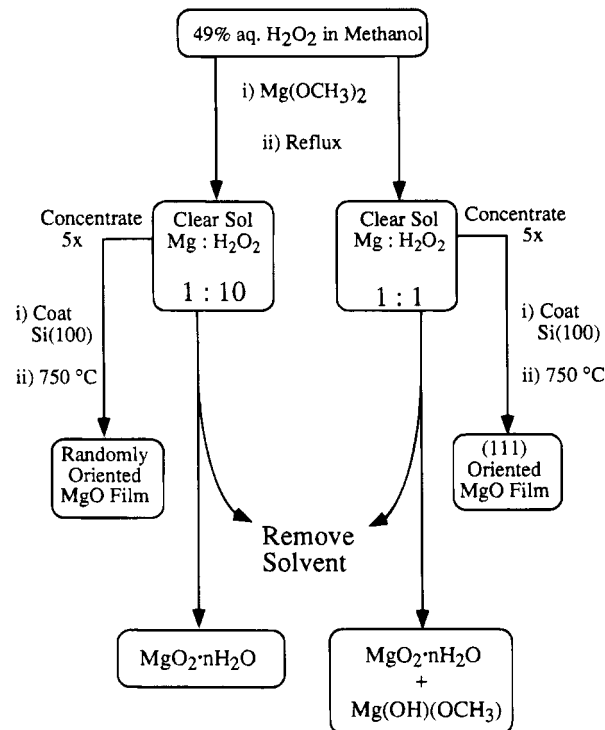
(2) Treatment of $Mg(OCH_3)_2$ with 50% H_2O_2. Sols were prepared from the slow addition of $Mg(OCH_3)_2$ solutions to methanolic H_2O_2. As outlined in Scheme 2, two such sols were prepared: One, with a $Mg:H_2O_2$ ratio of 1:1, is hereafter referred to as the 1:1 sol, and the other, with a $Mg:H_2O_2$ ratio of 1:10, is hereafter referred to as the 1:10 sol. Both sols were clear, although the 1:1 sol showed less Tyndall scattering than the 1:10 sol.

Raman spectra were taken of the 1:1 and 1:10 sols in an attempt to characterize the colloidal particles causing the Tyndall effect which these sols displayed. The Raman spectrum of a solution of 250 mM methanolic H_2O_2 showed a weak line at 869 cm^{-1}, close to the published[52] O–O fundamental Raman frequency of 880

Scheme 1. Proposed Decomposition Scheme for Magnesium Peroxide Prepared Using the Method of Allamagny[24] (Shown Are Calculated Weight Loss Values and, in Parentheses, Those Observed)

$Mg(O_2)_{\sim 0.74}(OH)_{\sim 0.33}O_{\sim 0.095} \cdot 0.32\ H_2O$

Wt loss:
9.3%
(calc. 9.5%)

25 - 250 °C

$\rightarrow \sim 0.32\ H_2O$

$Mg(O_2)_{\sim 0.74}(OH)_{\sim 0.33}O_{\sim 0.095}.$

19.2%
(19.1%)

250 - 360 °C

$\rightarrow \sim 0.37\ O_2$

$MgO_{\sim 0.835}(OH)_{\sim 0.33}$

4.8%
(5.0%)

360 - 650 °C

$\rightarrow \sim 0.165\ H_2O$

MgO

Scheme 2. Outline for the Preparation of Sols and Xerogels from the Treatment of Methanolic $Mg(OCH_3)_2$ with 1 or 10 mol equiv of H_2O_2

49% aq. H_2O_2 in Methanol

i) $Mg(OCH_3)_2$

ii) Reflux

Concentrate 5x

Clear Sol
Mg : H_2O_2
1 : 10

Clear Sol
Mg : H_2O_2
1 : 1

Concentrate 5x

i) Coat Si(100)

ii) 750 °C

i) Coat Si(100)

ii) 750 °C

Randomly Oriented MgO Film

(111) Oriented MgO Film

Remove Solvent

$MgO_2 \cdot nH_2O$

$MgO_2 \cdot nH_2O$
+
$Mg(OH)(OCH_3)$

cm^{-1} for liquid H_2O_2. The Raman spectrum taken of the 1:1 sol showed extremely weak scattering intensity from 750 to 950 cm^{-1}, possibly due to peroxide ions. The Raman spectrum of the 1:10 sol showed somewhat stronger Raman scattering from 800 to 900 cm^{-1}. Neither of the sol spectra showed sharp lines between 3600 and 3800 cm^{-1}, possibly indicating the absence of $Mg(OH)(OCH_3)$ in these sols. The XRD pattern of a 1:1

(49) Rosasco, G. J.; Blaha, J. J. *Appl. Spectrosc.* **1980**, *34*, 140–144.
(50) Wriedt, H. A. *Bull. Alloy Phase Diag.* **1987**, *8* (3), 227–233.
(51) Ramachandran, V. S.; Polomark, G. M. *Thermochim. Acta* **1978**, *25*, 161–169.
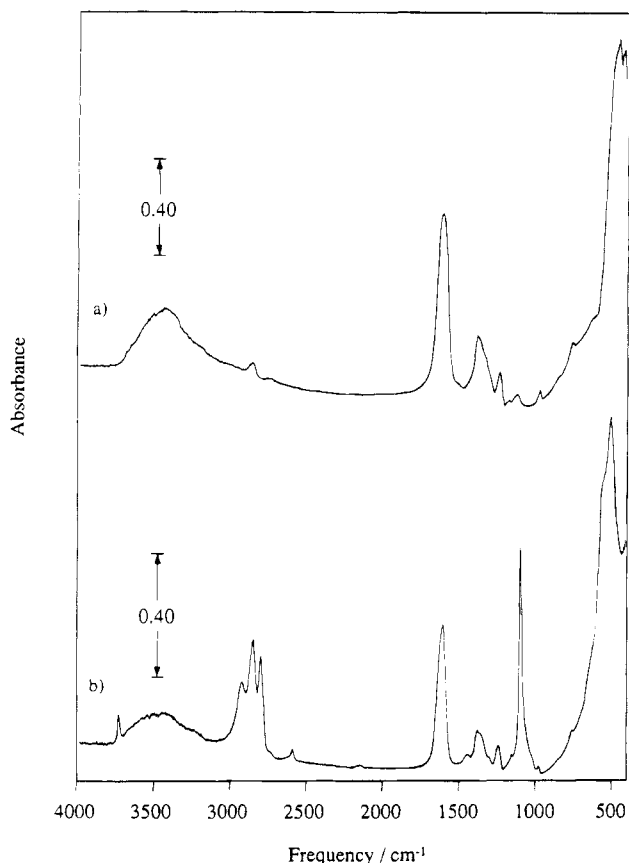(52) Evans, J. C. *Chem. Commun.* **1969**, 682–683.

Figure 4. DTA and TGA profiles of the xerogel isolated from the treatment of methanolic $Mg(OCH_3)_2$ with 10 mol equiv of H_2O_2. The sample was heated at 2.5 °C min^{-1} under dry, CO_2-free nitrogen.

Figure 3. IR spectra of xerogels isolated from sols prepared from the treatment of methanolic $Mg(OCH_3)_2$ with (a) 10 mol equiv of H_2O_2 and (b) 1 mol equiv of H_2O_2.

sol showed diffraction peaks attributed to solvent and the plastic sample holder only. The nature of the colloidal species in sols formed from $Mg(OCH_3)_2$ and H_2O_2 therefore remains to be determined.

Figure 2e presents the XRD pattern of the xerogel from a 1:10 sol, showing peaks consistent with crystalline $MgO_2{\cdot}nH_2O$.[23] The diffraction pattern of the xerogel from the 1:1 sol (see Figure 2d) showed peaks consistent with diffraction from a mixture of crystalline $MgO_2{\cdot}nH_2O$ and $Mg(OH)(OCH_3)$ (Figure 2a–c). The sizes of crystallites in the xerogels from both the 1:1 and 1:10 sols were calculated to be less than 50 Å.[43]

The IR spectrum of the xerogel from the 1:10 sol, presented in Figure 3a, is similar to the reported spectrum of $MgO_2{\cdot}2H_2O$.[47] The weak peaks at 1399, 1131, 991, and 770 cm^{-1} in Figure 3a, which are absent in the spectrum of $MgO_2{\cdot}nH_2O$, may be due to small amounts of carbonate or bicarbonate in the material, possibly formed from the reaction of xerogel with adventitious CO_2: Peaks at 1530–1470, 1370–1300, 1080–1040, 880–850, 820–750, and 690–670 cm^{-1} have been assigned to unidentate carbonate ion from the reaction of CO_2 with MgO.[53] The broad absorbance at 3426 cm^{-1} in Figure 3a is assigned to O–H stretching, possibly from water of crystallization, and the weak IR absorbances at 2860 and 1131 cm^{-1} may be caused by traces of methoxide or methanol.[54]
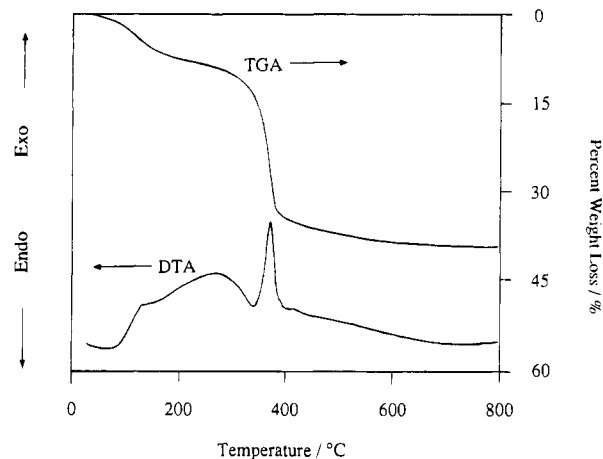
Figure 3b presents the IR spectrum of the xerogel from a 1:1 sol. Comparison with Figure 1a and ref 24 indicates that peaks in at 3730, 2921, 2852, 2800, 2594, 1452, 1384, 1366, 1308, 1105, 660, 571, and 516 cm^{-1} may be assigned to $Mg(OH)(OCH_3)$, whereas broad peaks at 3585 and 3443 cm^{-1} and a weak shoulder at 771 cm^{-1} may be caused by $MgO_2{\cdot}nH_2O$. This spectrum suggests that the xerogel from the 1:1 sol may be composed of a mixture of $Mg(OH)(OCH_3)$ and $MgO_2{\cdot}nH_2O$, which was also indicated by the XRD pattern of this xerogel.

Chemical analysis of the xerogel from the 1:10 sol gave a $Mg^{2+}{:}O_2{}^{2-}$ ratio of 1:0.80. As was the case for MgO_2 prepared by the method of Allamagny,[24] a less-than-stoichiometric ratio of O^{2-} to Mg implies that the xerogel contained anions other than O^{2-} for charge balance. These anions might possibly have been oxide, hydroxide, or possibly methoxide.

The simultaneous DTA and TGA profiles of the xerogel from the 1:10 sol are presented in Figure 4. The powder XRD pattern of the 1:10 xerogel heated to 800 °C showed peaks consistent with single phase MgO.[32] Examination of the DTA profile in Figure 4 shows that the decomposition of the xerogel from the 1:10 sol involved several thermal events that were not observed in the DTA profile of MgO_2 prepared using the method of Allamagny. In addition to an endotherm at ~98 °C, attributed to loss of water from the MgO_2 crystals, Figure 4 shows a broad exotherm between 140 and 340 °C, associated with an 8.6% weight loss. This weight loss may be caused by loss of MeOH or methoxide from the xerogel. The presence of methoxide or MeOH in this xerogel was implied by peaks in its IR spectrum at 2860 and 1131 cm^{-1} (see Figure 3a). The simultaneous DTA and TGA profiles of the 1:10 xerogel also showed a sharp exotherm with an associated 21.9% weight loss between 340 and 435 °C, likely due to the disproportionation of MgO_2.[24] This thermal event may have also involved the decomposition of carbonate in the xerogel, the presence of which was inferred from peaks at 1399, 1131, 991, and 770 cm^{-1} in its IR spectrum (see Figure 3a). Assignment of this thermal event to the decomposition of carbonate is tentative, however, since crystalline

(53) Evans, J.; Whateley, T. *Trans. Faraday Soc.* **1967**, *63*, 2769–2777.

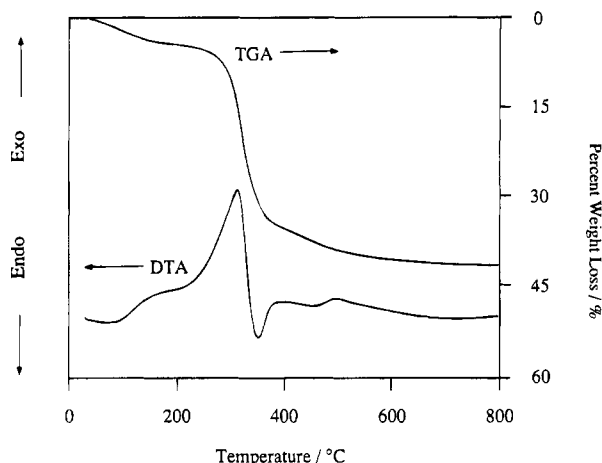(54) Zeitler, V. A.; Brown, C. A. *J. Phys. Chem.* **1957**, *61*, 1174–1177.

(111) Oriented MgO Thin Films

Chem. Mater., Vol. 7, No. 11, 1995 2035

Figure 5. DTA and TGA profiles of the xerogel isolated from the treatment of methanolic $Mg(OCH_3)_2$ with 1 mol equiv of H_2O_2. The sample was heated at 2.5 °C min^{-1} under dry, CO_2-free nitrogen.

$MgCO_3$ decomposes endothermically at 630 °C,[55] and it is not known whether the carbonate in the xerogel is crystalline or amorphous. As shown in Figure 4, an additional 3.5% weight loss occurred when the 1:10 xerogel was heated from 435 to 800 °C. This event may be caused by the decomposition of Mg−OH groups in the xerogel. This reaction was proposed for a similar weight loss event that occurred during the decomposition of $MgO_2 \cdot nH_2O$.

On the basis of IR spectra, simultaneous DTA, TG, and elemental analyses, the composition for the xerogel from the 1:10 sol might be the following:

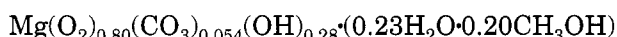$$Mg(O_2)_{0.80}(CO_3)_{0.054}(OH)_{0.28} \cdot (0.23H_2O \cdot 0.20CH_3OH)$$

Figure 5 presents the DTA and TGA profiles of the xerogel from a 1:1 sol. X-ray diffraction and IR spectral analysis strongly indicated that this xerogel was a mixture of nanocrystalline MgO_2 and $Mg(OH)(OCH_3)$ (see Figure 2d). The endotherm between 25 and 100 °C and broad and sharp exotherms with maxima at 160 and 310 °C, respectively, are similar to thermal events seen in the DTA profile of the xerogel from a 1:10 sol (see Figure 4). Figure 5 also shows sharp and broad endotherms at 350 and 451 °C, respectively, which are similar to those seen in the DTA profile of $Mg(OH)$-(OCH_3). The powder XRD pattern of the xerogel heated to 800 °C showed peaks consistent with the presence of single-phase MgO. The 1:1 xerogel, when heated to 800 °C, underwent a total weight loss of 42%. On the basis of the Mg content of the unheated xerogel, conversion to MgO should have resulted in a 41% weight loss.

On the basis of DTA, TG, IR, XRD and elemental analysis, the composition of the xerogel from the 1:1 sol, may be the following:

$$[Mg(OH)(OCH_3)]_{0.43}[Mg(O_2)_{0.88}(OH)_{0.33}]_{0.57} \cdot$$
$$0.087H_2O \cdot 0.72CH_3OH$$
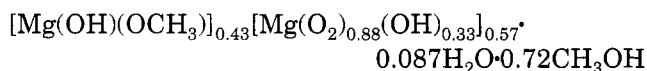
This composition is proposed, based on three assumptions: (i) weight loss between 100 and 235 °C was due to loss of MeOH, (ii) $Mg(OH)(OCH_3)$ was present in the xerogel, and (iii) weight loss above 500 °C was due to

(55) Warne, S. S. J.; Mackenzie, R. C. *J. Thermal Anal.* **1971**, *3*, 49−55.

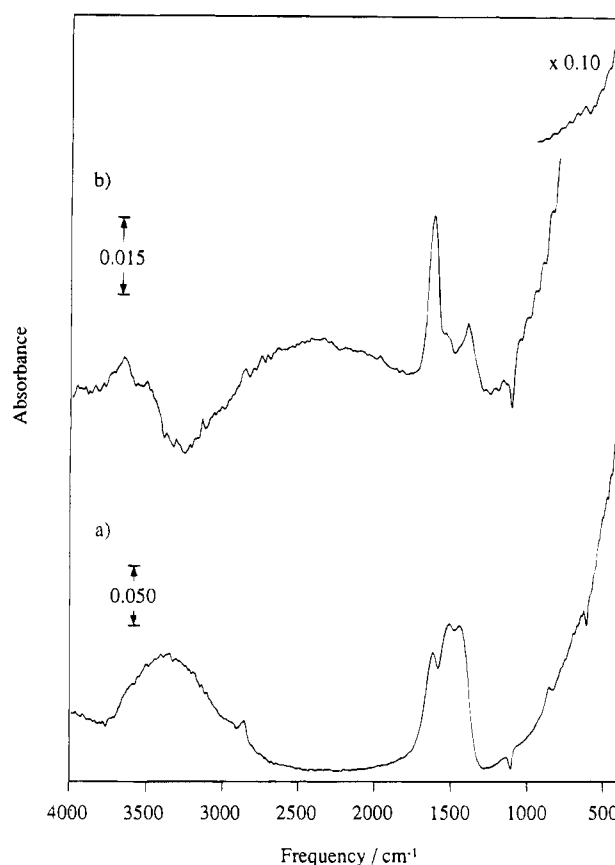**Figure 6.** IR spectra of thin films deposited on Si(100) using sols prepared from methanolic $Mg(OCH_3)_2$ and (a) 1 mol equiv of H_2O_2, or (b) 10 mol equiv of H_2O_2.

condensation of Mg−OH groups not associated with Mg-$(OH)(OCH_3)$. A proposed decomposition profile for the 1:1 xerogel is presented in Scheme 3.
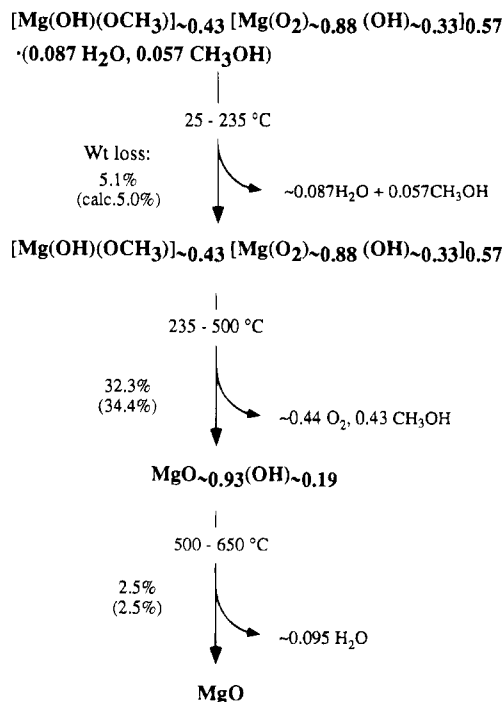
Thin Films. Portions of the 1:1 and 1:10 sols were concentrated and used to spin-coat films onto Si(100). The presence of nanocrystalline $MgO_2 \cdot nH_2O$ or $Mg(OH)$-(OCH_3) could not be detected in the XRD pattern of an unfired film on Si(100) prepared using the 1:1 sol. The IR spectrum of a 4300 Å thick unfired film on Si(100), prepared using the 1:1 sol, is presented in Figure 6a. Peaks at 3378 and 1620 cm^{-1} are assigned to adsorbed water,[40,41] and the weak absorbance at 2850 cm^{-1}, also seen in the IR spectrum of the 1:10 xerogel (see Figure 3a), is possibly due to C−H vibrations of methoxy groups within the film.[54] Absent from this spectrum is absorbance at ∼3700 cm^{-1}, which would be indicative of Mg-$(OH)(OCH_3)$ in the film (see Figure 1a). It might be expected that such unfired films would contain $Mg(OH)$-(OCH_3), since this compound was present in the xerogel recovered from the 1:1 sol. The strong peaks at 1514 and 1448 cm^{-1} are attributed to ν_3 vibrations from carbonate ions in the film. These ions were likely formed from the reaction of the film with atmospheric carbon dioxide.[48]

The IR spectrum of a 2500 Å thick film on Si(100), prepared using the $Mg:H_2O_2 = 1:10$ sol, is presented in Figure 6b. As in the spectrum of the film prepared using the 1:1 sol, peaks at 3585 and 1623 cm^{-1} may be assigned to adsorbed H_2O, and peaks at 1535, 1449, and 1398 cm^{-1} are assigned to the ν_3 vibrations from carbonate ions.[48]

Films deposited using the 1:1 and 1:10 sols could be built up linearly in thickness by multiple coating, as

Scheme 3. Proposed Decomposition Scheme for the Xerogel Recovered from the Treatment of $Mg(OCH_3)_2$ with 1 equiv of Hydrogen Peroxide (Shown Are Calculated Weight Loss Values and, in Parentheses, Those Observed)

$[Mg(OH)(OCH_3)]_{\sim 0.43} [Mg(O_2)_{\sim 0.88} (OH)_{\sim 0.33}]_{0.57}$

$\cdot (0.087\ H_2O,\ 0.057\ CH_3OH)$

|
25 - 235 °C

Wt loss:
5.1%
(calc.5.0%) $\sim 0.087 H_2O + 0.057 CH_3OH$

$[Mg(OH)(OCH_3)]_{\sim 0.43} [Mg(O_2)_{\sim 0.88} (OH)_{\sim 0.33}]_{0.57}$

|
235 - 500 °C

32.3%
(34.4%) $\sim 0.44\ O_2,\ 0.43\ CH_3OH$

$MgO_{\sim 0.93}(OH)_{\sim 0.19}$

|
500 - 650 °C

2.5%
(2.5%) $\sim 0.095\ H_2O$

MgO

shown by ellipsometry. A decrease in thickness of ~30% occurred when films prepared using both the 1:1 and 1:10 sols were heated between 150 and 300 °C. This decrease in thickness is consistent with the decomposition of $MgO_2 \cdot n H_2O$ and carbonate species thought to be present in such films prior to heating.[48] Very little additional decrease in film thickness occurred when coatings prepared using either the 1:1 or 1:10 sols were heated above 300 °C.

Crystallization of Randomly Oriented MgO Films from 1:10 Sol Coatings. The 2θ XRD pattern of a Si-(100) substrate, coated using a 1:10 sol before being heated to 750 °C, is presented in Figure 7. The broad, weak peaks at 43 and 62° (2θ) are assigned to the (200) and (220) reflections from poorly crystallized, randomly oriented MgO (lit.[32] 45.0 and 62.5° (2θ) respectively). The field emission scanning electron microscope image of this specimen (Figure 8a) shows that the MgO film is composed of small grains, and large 50–200 nm domed structures. The calculated porosity of this film was 37 vol %, based on its refractive index of 1.446 at 632.8 nm.

Crystallization of (111) Oriented MgO Films from 1:1 Sol Coatings. A Si(100) substrate was coated with a 1:1 sol and heated to 750 °C in dry air. Figure 9b presents the $\theta-2\theta$ XRD pattern taken of the resulting film. The strong peaks at 37 and 78.5° (2θ) occur at the same angles as the respective (111) and (222) reflections from MgO (lit.[32] 36.9 and 78.7° (2θ), respectively). The strongest diffraction peak in the XRD pattern of randomly oriented MgO, the (200) reflection, occurs at 42.9° (2θ).[32] Figure 10 presents a rocking-curve pattern of the MgO (111) reflection from the above described film, showing a fwhm of ~7° (Ω). There has been only one other published report of (111) oriented MgO grown on a semiconducting substrate.[5] In that
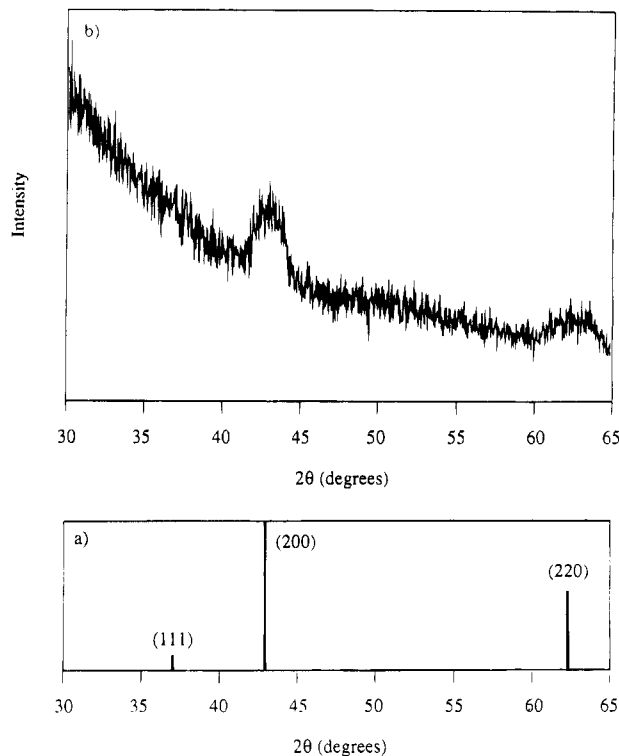

Figure 7. (a) Representation of the XRD pattern of randomly oriented MgO[32] and (b) the glancing-angle (2θ) XRD pattern, taken at $\Omega = 2°$, of a 1650 Å thick film on Si(100), coated eight times with a sol prepared from the treatment of methanolic $Mg(OCH_3)_2$ with 10 equiv of H_2O_2 before being heated to 750 °C in dry air.

study, MgO films, prepared using pulsed laser deposition, grew with (111) epitaxy when deposited on GaAs-(001) that had a portion of its native oxide layer removed. Rocking-curve profiles of unspecified reflections from such films had fwhm's that ranged from 1.8 to 2.1° (Ω).[5] Our XRD results are taken as evidence that MgO has grown with (111) preferred orientation on the wafer surface.

There have been several published reports of oriented crystalline films grown from sol–gel coatings on Si(100). Selvaraj et al. crystallized preferentially oriented TiO_2 from sol–gel coatings on[56,57] Si(100),[57] and Yamashita et al.[56] grew oriented $Li_2B_4O_7$ layers on Si(100) from films prepared using sols. It is surprising that such films crystallized with preferred orientation, since a 20–30 Å thick, randomly oriented layer of native silicon dioxide should have separated the single crystal silicon substrate from any overlying film.[58]

There have been a number of reports of preferentially oriented MgO growth on noncrystalline substrates. For instance, MgO films prepared using CVD methods showed (100) orientation when grown on either fused silica[11] or the native oxide of Si(111).[10,11] It has also been reported that evaporatively deposited MgO films thicker than ~500 Å showed (111) orientation when grown on glass: The first ~500 Å of such films, however, were randomly oriented.[59] The cause of orientated

(56) Yamashita, H.; Yoko, T.; Sakka, S. *J. Am. Ceram. Soc.* **1991**, *74*, 1668–1674.

(57) Selvaraj, U.; Prasadarao, A. V.; Komarneni, S.; Roy, R. *J. Am. Ceram. Soc.* **1992**, *75*, 1167–1170.

(58) Runyan, W. In *Kirk-Othmer Encyclopedia of Chemical Technology*; Mark, H. F., Ed.; John Wiley: New York, 1982; p 834.
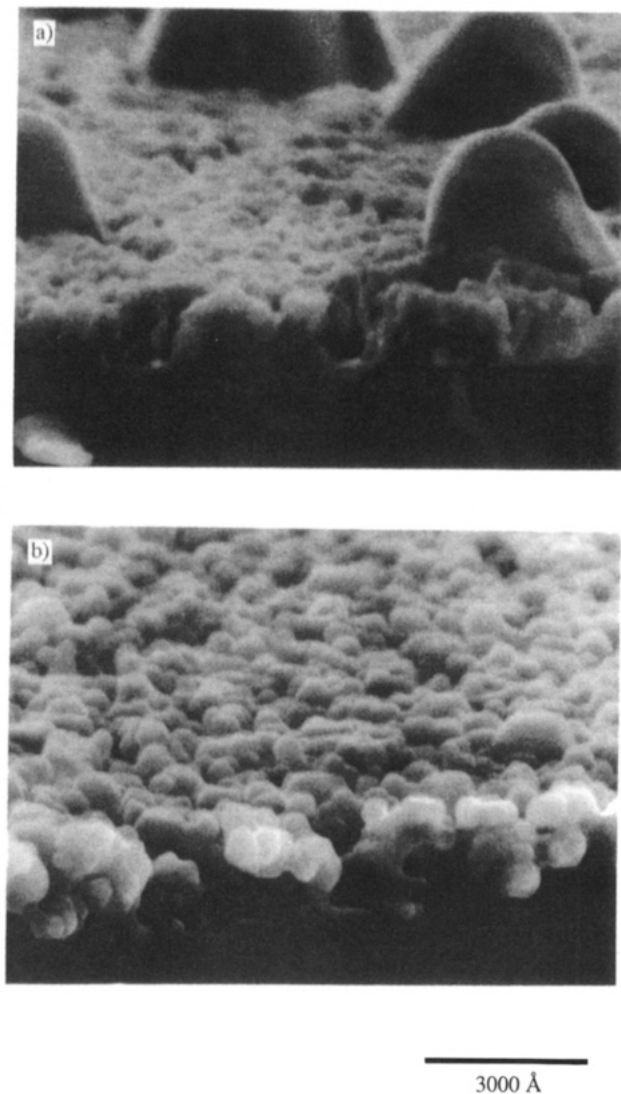
Figure 8. Field emission scanning electron microscope images of (a) the film described in Figure 7b and (b) the film described in Figure 9. Images were taken at 5.0 kV.

crystal growth in such films was not determined. As pointed out by Aboelfotoh,[59] the minimization of interfacial free energy between the film and the glass substrate could not be a driving force for oriented MgO growth, since the first 500 Å of such films had random crystallinity. However, the (111) surfaces of rock-salt type crystals such as MgO consist of two-dimensional sheets either of oxygen or Mg ions, and an interface where such a sheet of Mg^{2+} is commensurate with the terminal oxygens of an amorphous SiO_2 surface might be energetically favored.

As was discussed previously, XRD and IR analysis of the xerogel from a 1:1 sol, which could be used to prepare (111) oriented MgO films, contained both Mg-(OH)(OCH₃) and $MgO_2 \cdot nH_2O$. The xerogel from a 1:10 sol used to prepare randomly oriented MgO films contained only $MgO_2 \cdot nH_2O$. These observations suggest that Mg(OH)(OCH₃) may play a role in the growth of (111) oriented MgO from coatings made using a 1:1 sol. X-ray diffraction and IR results strongly suggest that Mg(OH)(OCH₃) is isostructural with the layered compound $Ni[(OH)_{2/3}(OCH_3)_{1/3}]_2$. This nickel compound decomposes topotactically to give NiO with (111) planes
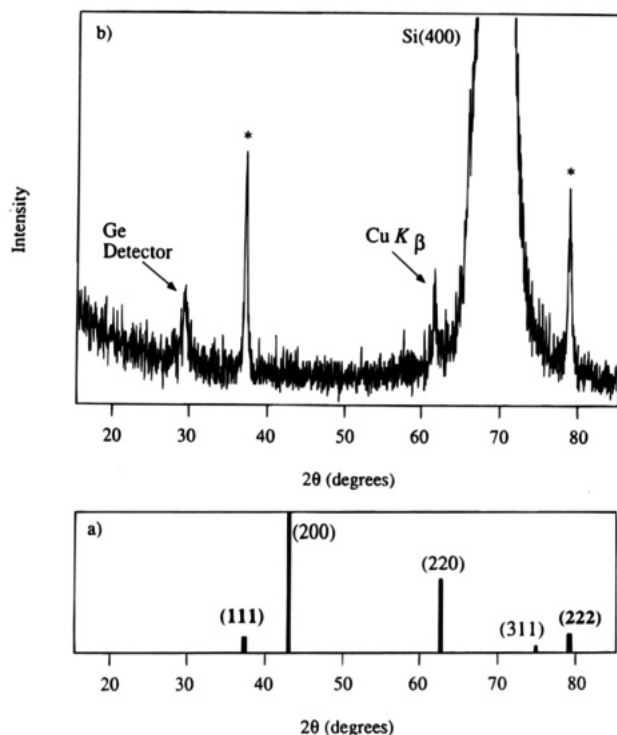
(59) Aboelfotoh, M. O. *J. Vac. Sci. Technol.* **1973**, *10*, 621–625.

Figure 9. (a) Representation of the XRD pattern of randomly oriented MgO,[24] and (b) the $\theta-2\theta$ XRD pattern of a 1800 Å thick film on Si(100), prepared by coating the substrate eight times with a sol made from the treatment of methanolic Mg-(OCH₃)₂ with 1 mol equiv of H_2O_2. The coated substrate was heated to 750 °C under dry air.
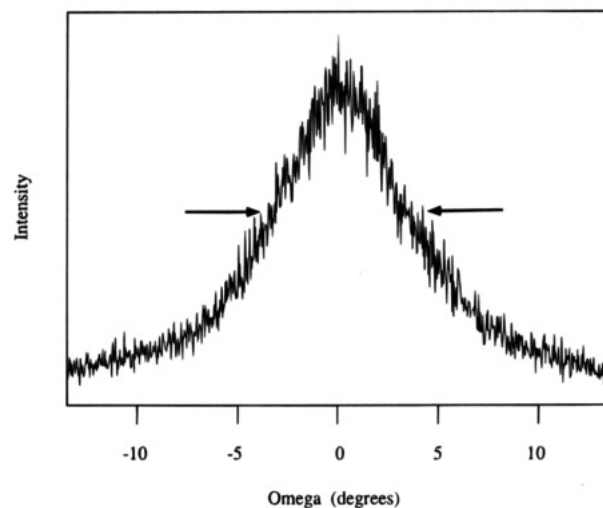

Figure 10. Rocking-curve XRD pattern of the film described in Figure 9. The pattern was taken at a fixed angle of 36.94° (2θ). Arrows indicate a full width at half maximum of ~7°.

in the same directions as the cationic sheets of the unheated nickel complex.[38] Since MgO and NiO have the same rock-salt crystal structure, oriented MgO may be expected to form topotactically from the decomposition of oriented Mg(OH)(OCH₃). However, the IR spectrum of an unfired film prepared using the 1:1 sol (see Figure 6a) showed no absorbances from Mg(OH)-(OCH₃). This spectrum did however show strong absorbances at 1514 and 1451 cm⁻¹, assigned to the ν_3 vibrations of carbonate ions, which likely formed from the reaction of this Mg compound with atmospheric CO_2.[48]

The reported topotactic formation of MgO from Mg-CO_3[60] suggested that oriented carbonate ions in films prepared using the 1:1 sol may have been involved in the growth of preferentially oriented MgO when such films were fired. To study the orientation of CO_3^{2-} ions in such films, IR spectra of an unfired film on Si(100), prepared using a 1:1 sol, were taken at different wafer orientations relative to the IR source. The combined area of IR peaks centered at 1451, 1514, and 1620 cm^{-1}, integrated from 1800 to 1200 cm^{-1}, was compared to the area of a peak centered at 1110 cm^{-1}, integrated from 1150 to 1025 cm^{-1}. This last-named peak is caused by the randomly oriented native SiO_2 layer on the silicon substrate.[61] These spectra showed no change in relative peak areas even when the film was tilted as much as 60° from the perpendicular, i.e., the direction of the IR beam. These results suggest that the CO_3^{2-} ions in the unfired film were randomly oriented[62] and not involved in the topotactic formation of the oriented MgO films.

Summary and Conclusions

As described by others, Mg(OH)(OCH$_3$) was formed from the hydrolysis of solutions of Mg(OCH$_3$)$_2$ in methanol. This compound resisted further hydrolysis, even when treated with up to 4 equiv of water. Elemental, IR spectroscopic, DT and TG analyses indicated that

$MgO_2 \cdot nH_2O$, prepared from the treatment of Mg(NO$_3$)$_2$ with excess H_2O_2, possibly contained O^{2-} or OH$^-$ ions. These ions may have been present either as an amorphous phase or substituted for peroxide in the MgO_2 structure.

Treatment of Mg(OCH$_3$)$_2$ with 1 equiv of H_2O_2 gave a sol, which was used to prepare (111) oriented MgO films on Si(100). The cause of this oriented film growth was not determined. IR and XRD analyses showed that the xerogel from such a sol contained nanocrystals of both MgO_2 and Mg(OH)(OCH$_3$). The IR spectrum of an unfired film, prepared on Si(100) using such a sol, showed no evidence of Mg(OH)(OCH$_3$) but did show absorbances attributed to randomly oriented carbonate ions. These ions were likely formed from the reaction of the film with atmospheric CO_2.

A sol prepared from the treatment of methanolic Mg-(OCH$_3$)$_2$ with 10 equiv of H_2O_2 was used to prepare randomly oriented MgO films on Si(100). Infrared spectroscopic and XRD analyses of the xerogel from such a sol showed the presence of nanocrystalline MgO_2 only.

CM950039G

(60) Dahmen, U.; Kim, M. G.; Searcy, A. W. *Ultramicroscopy* **1987**, *23*, 365–370.

(61) Grosse, P.; Harbecke, B.; Heinz, B.; Meyer, R.; Offenberg, M. *Appl. Phys. A* **1986**, *39*, 257–268.

(62) Stewart, J. E. *Infrared Spectroscopy: Experimental Methods and Techniques*; Marcel Dekker Inc.: New York, 1970.