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Constrained phase evolution in gel-derived thin films of magnesium oxide

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We investigate possible influences of substrate constraints on the phase evolution of thin films synthesized from liquid precursors. MgO films are formed on Si (111) substrates by spin casting an acetate-substituted magnesium ethoxide liquid precursor. The phase evolution and crystallinity of the films are tracked as a function of temperature by differential scanning calorimetric/thermogravimetric analyses (DSC/TGA) and X-ray diffraction. There are two major differences between the phase evolution of thin films and that of bulk powders formed from the same solution: (1) in the films, highly [010]-textured triclinic magnesium acetate forms at room temperature, while in the powders an orthorhombic polymorph of magnesium acetate is selected that transforms to the triclinic structure at 150–250 °C. Both films and powders undergo complete pyrolysis by 360 °C to form magnesium oxide. However, (2) although powders decompose to phase-pure periclase, thin films form both periclase *and* a rarely observed pseudo-spinel polymorph, both with strong $\langle 001 \rangle$ preferred orientation. Both selection of the triclinic acetate polymorph in films at room temperature and formation of the spinel-like MgO structure are consequences of interaction with the underlying substrate.

Pyrolytic decomposition of liquid precursors is a common method for synthesizing inorganic materials. Powder synthesis by this method can sometimes cause unexpected, perhaps undesirable, metastable phases to crystallize from the amorphous precursor, preempting formation of the thermodynamically stable structure.[1,2] Metastable phases can appear when a high free-energy phase (in this context, the precursor) is kinetically restricted from transforming to the state which globally minimizes its free energy.[2,3] In this respect, pyrolysis of supported thin film precursors might yield different products than that of bulk precursors because, for films, the approximately two-dimensional geometry and the presence of an underlying substrate may impose additional constraints on the evolution of phases.

In this paper, we investigate the possibility that precursor-derived thin films exhibit different phase evolution than the same materials in powder form. As a target material, MgO was selected because (1) it has only one thermodynamically stable solid phase (periclase), (2) that phase has a particularly simple rocksalt crystal structure, and (3) thin films of MgO are technologically important as chemically stable buffer layers for growth of textured superconducting or ferroelectric thin films on silicon.[4] Here we synthesize both bulk powders and thin films of MgO by the same sol–gel method and compare their phase development and crystallinity. An anomalous crystalline modification of MgO is observed in the films, the origins of which we trace to influences of the underlying substrate.

Experimental

MgO can be difficult to synthesize by hydrolysis and condensation of aqueous solutions because of the spontaneous precipitation of brucite ($Mg(OH)_2$) during hydrolysis. Therefore we adopt a procedure, used by several investigators, of using an acetate-substituted alkoxide precursor to form MgO at temperatures as low as 150 °C.

Precursor solutions were prepared by a procedure similar to that described by Van de Leest.[5] Magnesium ethoxide† ($Mg(OCH_2CH_3)_2$, which will hereafter be denoted as $Mg(OEt)_2$) was dispersed in absolute ethanol and was refluxed by adding acetic acid to bring the solution pH to 5.5 (molar ratio 27:3:1 of EtOH:AcOH:$Mg(OEt)_2$). The addition of acetic acid causes substitution of ethoxy groups by acetate groups,[5–7] and stabilizes the precursor against formation of $Mg(OH)_2$.[5,7] In some experiments, deionized water was added to the precursor solution in a molar ratio of 5:1 with $Mg(OEt)_2$, as prescribed by previous investigators.[5–7] Solutions both with and without water additions remained stable for several weeks. We will call them simply *precursor solutions*, and will distinguish the behavior of those with and without water when it is necessary to do so.

To form the films, boron-doped Si (111) wafers were washed in acetone and exposed to UV radiation to remove organic residue and to introduce –OH functionality to the surface. Precursor solution was then spin-cast onto a prepared wafer at 5000 rpm, during which time most of the ethanol evaporated. We will refer to these as-spun, evaporated films, as *precursor films* (either with or without water addition). To compare with the films, bulk powders were also formed by evaporating the free ethanol from the modified solution at 80 °C. The dried gel was in the form of a white powder, which hereafter will be referred to as *precursor powder*.

To estimate the temperatures at which pyrolysis and crystallization occur, simultaneous differential scanning calorimetric/thermogravimetric analyses‡ (DSC/TGA) were performed on the precursor powder (*i.e.*, the dried gel) using a constant heating rate of 10 °C min^{-1}. DSC/TGA could not be performed directly on the thin films because the resulting heat fluxes and mass changes were below the detection limit of the instrument.

Both precursor films and precursor powders were heated in ambient air atmospheres at 0.1 °C min^{-1} to 200, 360, 550, and 1200 °C. Scanning Auger electron spectroscopy revealed no impurities in the films to within the detection limit of the instrument.§ Crystallinity and phase composition of films and

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†Alfa Æsar, Ward Hill, MA, USA.

‡Netzsch STA 409, Germany.

§PHI 660, Scanning Auger Microprobe, Perkin Elmer, Norwalk, CT, USA.

powders, before and after heat treatment, were compared by X-ray θ–2θ diffraction.¶ X-Ray diffraction analysis of powders is straightforward and will not be described here. However, thin films present several complications that make diffraction analysis less straightforward. Therefore, we now describe several procedures that were used to ensure the accuracy of our diffraction analysis of films.

Because of the small sampling volume, X-ray diffraction patterns from thin films generally have low overall intensities and low signal-to-noise ratios. Therefore, for all of the diffraction scans made on the films, at least eight θ–2θ scans were performed and the diffraction intensities summed to obtain a pattern with acceptable intensity. However, although this summation resulted in higher overall intensities, the improvement in the signal-to-noise ratio was marginal. True peaks were tentatively identified as those with a higher intensity than the surroundings and with a finite width at half maximum. The validity of the peaks was further confirmed by repeating the X-ray diffraction experiments and accepting only those peaks which appeared in both patterns.

Preliminary X-ray diffraction scans were obtained on the Si (111) substrate to determine the miscut of the Si (111) surface—that is, the difference between the observed θ value for Si (111) and its known value of 14.24°. Two types of diffraction scan were then made on the films. The first type, hereafter called an *aligned* scan, was made by keeping the incident beam aligned with the Si [111] lattice direction. The second type, hereafter called a *surface* scan, was made with the incident beam fixed perpendicular to the substrate surface. Finally, rocking curve measurements were also made on the films to determine their degree of texturing and orientation relative to the Si substrate.

Results

Precursor powders

In all cases, the phase composition of as-evaporated precursor—whether in film or powder form—is dominated by one or more crystalline magnesium acetate ($Mg(OAc)_2$) compounds. Fig. 1 shows diffraction patterns obtained from precursor powders formed from solutions with and without added water. Both powders contain a considerable amount of α-$Mg(OAc)_2$; the primary difference between them is the additional presence of $Mg(OAc)_2 \cdot 4H_2O$ in powders prepared from solutions with water addition. Solutions prepared without water addition also contain a very small amount of $Mg(OAc)_2 \cdot 4H_2O$, which is presumably due to incorporation of moisture from the atmosphere. In addition, powders prepared from solutions with intentional water addition exhibit a small X-ray signal that does not correspond to any of the $Mg(OAc)_2$ phases, but which matches the most intense peak catalogued for crystalline $Mg(OEt)_2$. Therefore, a slight amount of this phase may be present in the precursor powders prepared from solutions with added water, although one cannot make a definite phase identification with only one relatively weak X-ray signal.

These X-ray diffraction data show that acetate groups (from acetic acid) completely convert solid $Mg(OEt)_2$ to $Mg(OAc)_2$ in solution. Furthermore, the only contribution of water is the partial hydration of $Mg(OAc)_2$. No direct Mg–OH bond formation occurs and, as we shall describe later, added water has no measurable effect on the phase evolution at higher temperatures. This conclusion contrasts with the speculations made in previous investigations of this system,[5–7] in which it was assumed that acetic acid only partially reacts with the alkoxide, providing enough stability to prevent brucite formation. Therefore, in those earlier reports water was assumed necessary to initiate hydrolysis of the remaining alkoxy groups.

When precursor powders are heated from room temperature at $0.1\,^{\circ}\mathrm{C\,min^{-1}}$ to 200 °C, two primary events occur: (1) complete structural transformation from α-$Mg(OAc)_2$ to β-$Mg(OAc)_2$ as residual ethanol is volatilized, and (2) dehydration, for those precursors prepared with added water. The lower X-ray scan of Fig. 2 confirms the conversion to β-$Mg(OAc)_2$ and the absence of any hydrated species. In addition, the simultaneous DSC/TGA curves in Fig. 3 exhibit an endothermic event accompanied by $\approx$70% mass loss in this temperature range, reflecting dehydration and loss of residual ethanol. The diffraction pattern in Fig. 2 also shows that some decomposition of $Mg(OAc)_2$ to MgO has begun by 200 °C. And according both to the X-ray diffraction data in Fig. 2, and to the DSC/TGA analyses (Fig. 3), most pyrolytic decomposition of β-$Mg(OAc)_2$ occurs at $\approx$300 °C, where both a fairly sharp endotherm and simultaneous mass loss are indicated.

As expected, the powder decomposes to the thermodynamically stable periclase MgO structure (see Fig. 2), and the conversion to periclase continues at higher temperatures until, by 360 °C, decomposition is essentially complete. The final mean particle diameter is $\approx$80 nm, and the specific surface area measured by nitrogen adsorption/desorption is

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¶D-Max, Rigaku, Japan.

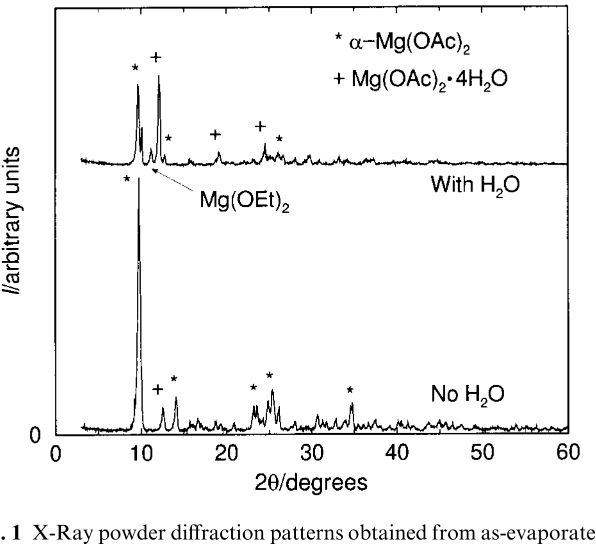

Fig. 1 X-Ray powder diffraction patterns obtained from as-evaporated precursor powders with and without water addition to the liquid precursor solution.

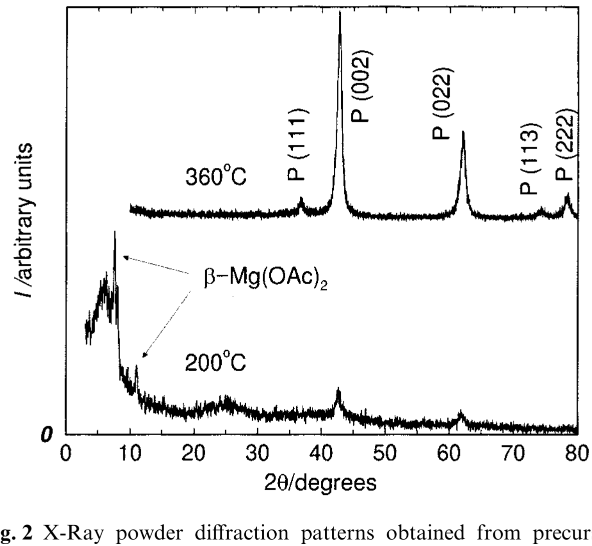

Fig. 2 X-Ray powder diffraction patterns obtained from precursor powders heated in air at a rate of $0.1\,^{\circ}\mathrm{C\,min^{-1}}$ to 200 °C (lower pattern) or 360 °C.

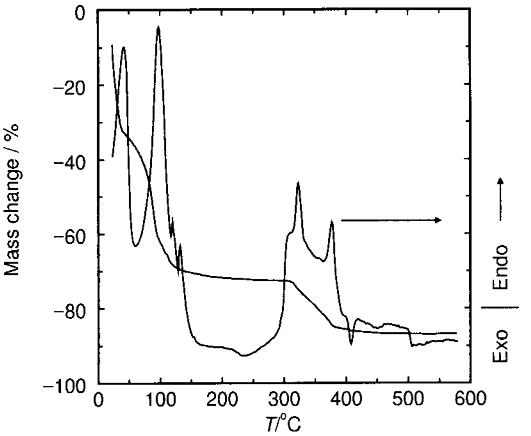

Fig. 3 Differential scanning calorimetric (DSC) and thermogravimetric (TG) measurements on the MgO precursor with water added to the liquid precursor solution before evaporation.

consistent with fully dense periclase crystals of this average size.[8]

Calorimetric measurements from 150 to 360 °C provide information about the relative stability of α-$Mg(OAc)_2$ and β-$Mg(OAc)_2$. Any reversible polymorphic transformation between two thermodynamically stable structures due to an increase in temperature must be endothermic.[9] But Fig. 2 indicates a rather broad, shallow *exothermic* signal from 150 to 250 °C. Based on comparison with the diffraction data—and on the fact that no mass loss is observed in this temperature range—we associate this exotherm with the α→β transformation of $Mg(OAc)_2$, which implies that bulk α-$Mg(OAc)_2$ is *metastable* relative to β-$Mg(OAc)_2$ at lower temperatures. The width and shallowness of the exotherm indicate that the driving force for the transformation is rather small, which is consistent with the fact that both variants of $Mg(OAc)_2$ are commonly observed at room temperature.

Precursor films

For precursor thin films, both the phase evolution and texture of the films were investigated. To determine texture relative to the underlying substrate, a rocking curve was obtained for each Si substrate, one example of which is shown in Fig. 4. For all the Si (111) substrates used, misalignment of the surface with the (111) lattice planes is indicated by a displacement of the (111) peak by ≈4.35° from its expected position of 14.24°. We use this 4.35° miscut to align the X-ray beam with the Si [111] lattice direction, as described in the Experimental section.

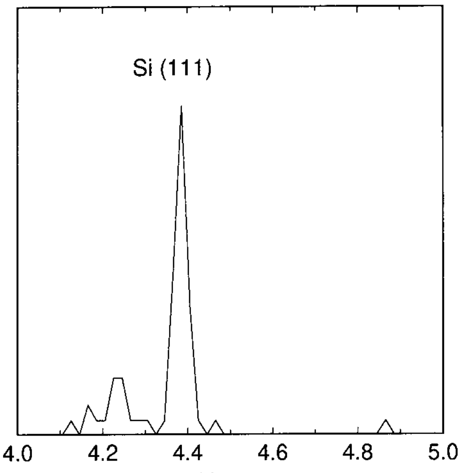

Fig. 4 Rocking curve obtained for the Si (111) lattice planes. The plot indicates a surface miscut of ≈4.35°.

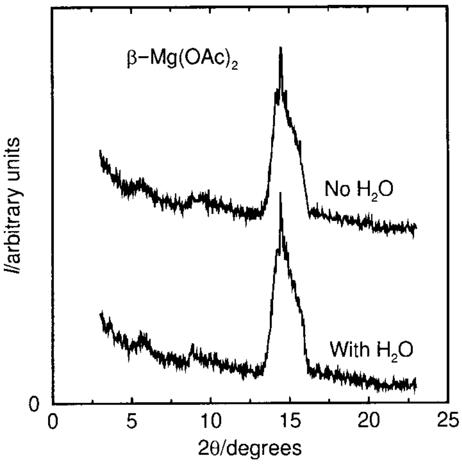

Fig. 5 X-Ray powder diffraction patterns obtained from as-spun precursor films with and without water addition to the liquid precursor solution.

Fig. 5 shows low-angle X-ray diffraction patterns, collected in the aligned mode, for as-spun precursor films formed from solutions with or without water addition. Both patterns again indicate predominance of a crystalline $Mg(OAc)_2$ compound. However, in contrast to bulk powders, the triclinic β phase is exclusively selected in the films. Moreover, its (100) diffraction peak, which normally appears at ≈8° (see Fig. 2) and which is the most intense peak catalogued for β-$Mg(OAc)_2$ powders,[10] is absent in these scans. Instead, the (010) and (020) are the strongest β-$Mg(OAc)_2$ reflections observed. Absence of a (100) peak, in addition to the exaggerated intensities of the (010) and (020) peaks, implies that the (010) lattice planes of β-$Mg(OAc)_2$ lie nearly parallel to the (111) planes of the underlying Si substrate.[‖]

In concurrence with bulk powders, decomposition of β-$Mg(OAc)_2$ in the films is complete by 360 °C, as indicated by the absence of its peaks in the diffraction patterns. Also in agreement with the powders, pyrolysis of β-$Mg(OAc)_2$ is accompanied by crystallization of MgO, as shown by the emergence of several new peaks in aligned X-ray diffraction patterns (see Fig. 7). The resulting oxide films are ≈100 nm thick.

At temperatures between 200 and 1200 °C, considerable differences emerge between the phase evolution of precursor-derived thin films and that of their powder counterparts. At 360 °C, only one of the four new peaks in the thin film can be attributed to periclase (see Fig. 7(B)). The other three peaks index to an uncommon variant of MgO having a pseudo-spinel cubic crystal structure (lattice parameter $a = 8.12$ Å,[10] roughly double the value of 4.23 Å for periclase[10]). We will refer to this phase as β-MgO. In Fig. 7 we label the periclase peaks with a 'P', and the peaks of β-MgO with a 'β'. The most intense peaks at 360 °C are (002) of periclase and (004) of β-MgO, both of which occur at 40–45°. In the Discussion, we consider reasons why β-MgO might be stabilized in gel-derived thin films but not in bulk powders.

In Fig. 6, the rocking curves obtained for periclase (002) and β-MgO (004) peaks at 1200 °C are overlayed on the rocking curve for Si (111). Both of these peaks are shifted from their expected position by ≈4.35°, which is identical to the peak shift observed for Si (111) due to miscut of the substrate. In addition, the full width at half-maximum

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[‖] We will refer to this preferred orientation of β-$Mg(OAc)_2$ as [010] texture, indicating that its (010) planes preferentially align with Si (111), even though for a triclinic unit cell the [010] lattice direction is not orthogonal to these (010) lattice planes.

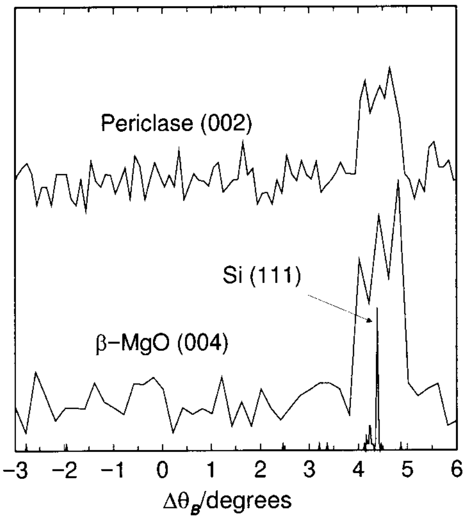

Fig. 6 Rocking curves for β-MgO (004) and periclase (002) of a thin film deposited on Si (111) and annealed by heating at 0.1 °C $\min^{-1}$ to 1200 °C. The rocking curve for Si (111) from Fig. 4 is shown for reference.

(FWHM) for both peaks is $\approx 1°$, which indicates an exceptionally sharp alignment of the cubic {100} planes of both MgO phases with Si (111). Further evidence of texturing is given by the fact that the (111) peak for β-MgO (at $2\theta = 82.01°$) is absent in the aligned scans on films (see Fig. 7), even though it is the strongest peak reported in the accepted powder diffraction pattern.[10] Finally, *surface* scans, collected with the beam oriented perpendicular to the surface rather than to Si (111), fail to resolve any MgO signals whatsoever. Therefore, both the periclase and β forms of MgO are strongly textured up to 1200 °C, with their {001} lattice planes parallel to Si (111).

Discussion

The X-ray diffraction data in Fig. 7 clearly demonstrate the presence of a low-temperature spinel-like phase in the thin films. Because no impurities were found in the film that could react with MgO to form a common spinel compound (see Experimental section), the evidence is compelling that the new phase is a spinel-like variant of pure MgO. MgO powders derived from the same precursor, however, contain none of this phase (see Fig. 2), nor do those MgO powders synthesized by other researchers using similar techniques.[6,7] To our knowledge, this is the first reported instance in which influences of a film geometry and/or substrate constraint cause formation of a MgO phase that is unstable in bulk form.

Freund[11] first observed a β-MgO structure as an intermediate phase occurring during slow, *in vacuo* thermal decomposition of $Mg(OH)_2$ to periclase at 400 °C. He proposed that the structure was composed of Mg^{2+} ions in a low oxygen-coordinated state. Bokhimi *et al.*[7] have used Rietveld refinement to conclude that MgO powders, formed from a liquid precursor similar to that used here, can form periclase with a Mg cation deficiency as high as 11%. And recently, Bokhimi *et al.*[12] reported formation of a highly Mg-deficient periclase structure during synthesis of Pt/MgO catalysts by a co-gelation method. Therefore, it is evident that synthesized MgO can be substantially non-stoichiometric, and that under certain conditions it may even adopt a structure other than periclase.

The simultaneous formation of both periclase and β-MgO in the thin film configuration, as well as the strong alignment of their {001} planes with Si (111), is dictated by the structure and orientation of their β-$Mg(OAc)_2$ parent phase. The triclinic β-$Mg(OAc)_2$ unit cell has lattice parameters $a = 10.34$ Å, $b = 12.95$ Å and $c = 7.726$ Å. The lattice parameter for β-MgO (8.12 Å) corresponds more closely with these values than does the lattice parameter of periclase (4.23 Å). If sufficient kinetic constraints are imposed to inhibit structural rearrangement during pyrolysis of β-$Mg(OAc)_2$, the product which requires the lesser amount of rearrangement—β-MgO in this case—could be stabilized even though periclase is thermodynamically favored in bulk form. The necessary constraints to block the formation of periclase must arise from bonding of β-$Mg(OAc)_2$ to the underlying substrate, because precursor *powders* form phase-pure periclase directly from β-$Mg(OAc)_2$ within an identical temperature range (see Fig. 2).

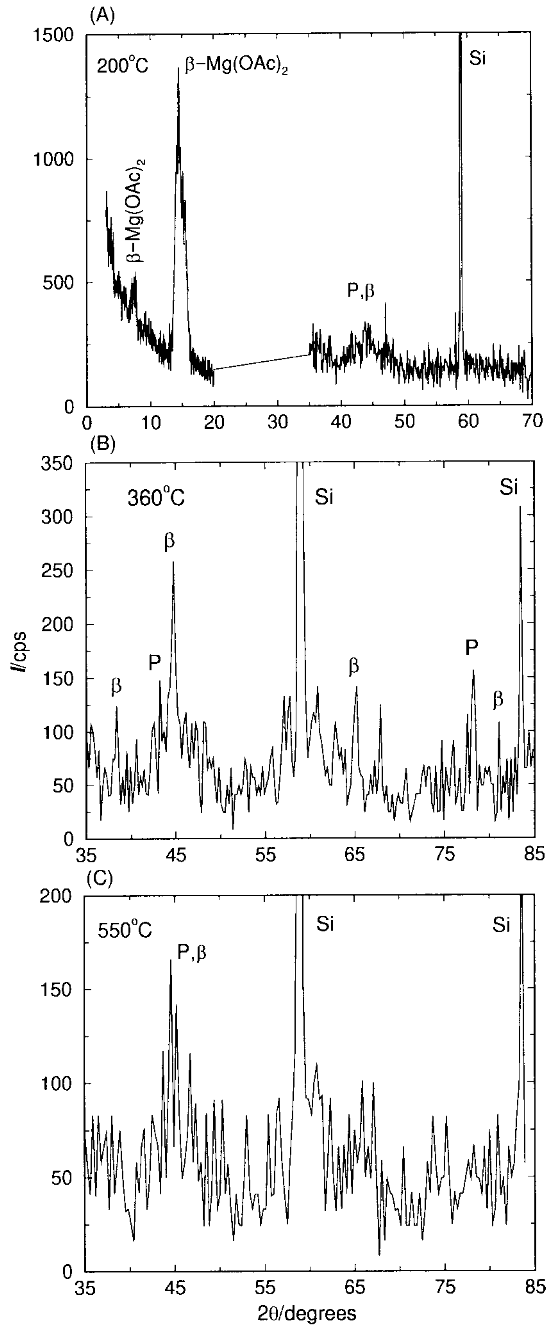

Fig. 7 θ–2θ X-Ray diffraction patterns of an MgO film annealed in air at 0.1 °C $\min^{-1}$ to a maximum temperature of (A) 200 °C, (B) 360 °C, and (C) 550 °C. Scans were obtained by orienting the incident beam perpendicular to the (111) lattice planes of Si. Phases are labeled as β-$Mg(OAc)_2$ (β-magnesium acetate), β (spinel-like, β-MgO) and P (periclase).

Strong texturing occurs within the films, both for β-$Mg(OAc)_2$, which has its (010) planes aligned with Si (111), and for the two MgO phases which both have their {001} planes aligned with Si (111). That texturing occurs at all seems remarkable, since no effort was made in these experiments to remove the native SiO_x layer from the substrate surface. The ⟨001⟩ texture of MgO, at least in its spinel-like form, is facilitated by the parent β-$Mg(OAc)_2$. Because β-MgO forms due to constraints provided by the underlying Si substrate during the decomposition, and because its lattice parameter closely matches the *c*-spacing of β-$Mg(OAc)_2$, which lies parallel to Si (111), we may also expect any one of the equivalent {100} β-MgO planes to lie approximately parallel to Si (111) after pyrolysis. Furthermore, the spinel-like unit cell can be viewed as a 'supercell' having nearly twice the edge length of periclase and its oxygen anions arranged in a cubic close packing. Subsequent periclase formation thus involves degeneration of this supercell into eight periclase subcells. The periclase subcells, each formed from one octant of the supercell, necessarily have their cube faces parallel to those of the β-MgO phase. Therefore, the β-MgO→periclase transformation preserves the ⟨001⟩ film texture.

We are still left with the questions of (1) why β-$Mg(OAc)_2$ forms at room temperature on the substrate while in bulk powders the α polymorph is favored, and (2) why β-$Mg(OAc)_2$ in films grows with its (010) plane parallel to Si (111). As for the first question, the native Si-oxide layer, upon which the β-$Mg(OAc)_2$ structure initially forms, may have a degree of atomic order with its terminating oxygens spaced to closely match the *a* or *c* lattice parameters of β-$Mg(OAc)_2$; the oxidized substrate may therefore provide local templates upon which that phase can grow heteroepitaxially. It is well documented that ultrathin (<10 Å) oxides form on Si (001) as heteroepitaxially oriented trydimite,[13] a stable hexagonal bulk form of crystalline SiO_2 having lattice parameters $a=5.067$ Å and $c=8.23$ Å. We do not know what, if any, crystalline form of the oxide forms on Si {111} planes. However, the fact that β-$Mg(OAc)_2$ is selected at room temperature in the films in contrast to the powders, in which the α structure appears first, strongly suggests that some oxide structure on the Si (111) surface provides favorable nucleation sites for β-$Mg(OAc)_2$.

As for the question of why β-$Mg(OAc)_2$ grows with such strongly preferred [010] orientation, the explanation probably may be traced to the anisotropy of its crystal structure. Triclinic structures can be highly anisotropic and, therefore, their surface energy densities, γ, may be strong functions of crystallographic orientation. In fact, for many oxides and low-symmetry organic crystals, a plot of γ *versus* orientation can have deep cusps that correspond to low-energy faceted surfaces.[14] Using these considerations, the observed preferred orientation of β-$Mg(OAc)_2$ in the films is energetically favored if the interface between the (010) β-$Mg(OAc)_2$ lattice planes and the vapor, or between the (010) β-$Mg(OAc)_2$ planes and the substrate,** has a particularly low energy density.

Summary

MgO can be formed by pyrolytic decomposition of a liquid precursor solution of $Mg(OEt)_2$, ethanol, and acetic acid. Acetate groups fully substitute for ethoxy groups to produce $Mg(OAc)_2$ in solution. Powders formed from evaporation of the liquid are mostly crystalline α-$Mg(OAc)_2$, with small amounts of $Mg(OAc)_2{\cdot}4H_2O$ and $Mg(OEt)_2$ also present if water is added to the solution prior to evaporation. Thin films on Si (111) substrates deposited from the same solution form highly oriented β-$Mg(OAc)_2$ at room temperature, with the triclinic (010) lattice planes lying essentially parallel to the Si (111) plane.

Increasing temperature causes bulk α-$Mg(OAc)_2$ powders to transform to β-$Mg(OAc)_2$ at 150–250 °C. Both in thin films and powders, with or without water additions, β-$Mg(OAc)_2$ decomposes to crystalline MgO during heating at a constant rate to 360 °C. In powders, the decomposition product is phase-pure periclase MgO. In thin films, however, decomposition results in two coexisting structural variants of MgO: periclase and a rarely observed spinel-like structure with nearly double the lattice constant of periclase. Both MgO structures exhibit a strong ⟨001⟩ preferred orientation with Si [111], which arises from the [010] texture of their parent β-$Mg(OAc)_2$ phase. Constraints imparted by the substrate are responsible both for the formation of oriented β-$Mg(OAc)_2$ before pyrolysis, and for the stabilization of the β-MgO phase.

The β-MgO structure is remarkably robust in films, and it only partially transforms to periclase at temperatures as high as 1200 °C. This structural transformation preserves the ⟨001⟩ orientation by a simple degeneration of the spinel-like unit cell into eight periclase unit cells.

The results for MgO raise the possibility of using substrate constraints to tailor unusual oxide phases in thin film form. Potential applications of this approach include novel ionic conductors, gas sensors, buffer layers, and dielectric components in integrated circuits. The crucial step in any such application will be the selection of a suitable substrate. As an example, we have obtained preliminary results indicating that, in comparison with the results found in this study using Si (111) substrates, the use of $MgAl_2O_4$ (001) substrates allows selection of β-MgO in phase-pure, single crystal form (100 nm thick) by the same processing method.[15]

Acknowledgements

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**A sharply cusped energy density between the film and substrate would lend further support to the argument in the preceding paragraph, that the substrate provides especially favorable sites for nucleation of β-$Mg(OAc)_2$.