Thermally Induced Porosity in CSD MgF_2-Based Optical Coatings: An Easy Method to Tune the Refractive Index

John D. Bass, Cédric Boissiere, Lionel Nicole, David Grosso,* and Clément Sanchez

Laboratoire de Chimie de la Matière Condensée de Paris, Université Pierre et Marie Curie−Paris 6 and CNRS, 4 place Jussieu, 75252 Paris 05, France

Received April 10, 2008. Revised Manuscript Received June 10, 2008

A very simple and robust method is described to prepare MgF_2-based optical thin films exhibiting refractive indices ranging from 1.08 to 1.2. These coatings were deposited on solid substrates through chemical solution deposition from a single and extremely stable (up to few years old) sol−gel solution composed of magnesium acetate and trifluoroacetic acid dissolved in a mixture of ethanol and water. The present work shows that the generation of the porosity responsible for the ultralow refractive indices of these materials is triggered by the thermal decomposition of the metallic precursor ligands. The resulting nanobubbles of gas are then frozen-in by the thermally induced condensation and partial crystallization of the mineral network around them. We demonstrate that such a process is governed, and can be perfectly controlled, by the heating rate and the atmospheric water content applied during calcination, through which nanobubble size, quantity, and the material's chemical makeup are tuned. The resulting vesicle-like porous materials demonstrate a range of tunable compositions with varying refractive indices and combine good mechanical properties with high chemical and thermal resistance. This work is supported by a novel thermal ellipsometry analysis (TEA) method that allows for in situ monitoring of the films' optical constants, structure, and thickness during thermal treatment. This is the first time, to our knowledge, that this technique has been used in the dynamic characterization of evolving unstructured porosity, allowing valuable insight into the thermal decomposition, condensation, crystallization, and sintering processes occurring during calcination.

Introduction

Highly porous optical coatings are attractive materials that can be used in sensing, optics, and microelectronics as a result of their high accessible surface area, low dielectric constant, and adjustable refractive index. MgF_2-type coatings are interesting systems for optics and electronics because the poor polarizability of the Mg-F bond results in materials with some of the lowest refractive indices and dielectric properties. When porous, the combination of the latter extreme optical properties with that of insulating air enables further reduction of these optical constants.[1,2] Unlike analogous SiO_2 systems, it is insensitive to water, allowing for better environmental stability and longer life-times. Additionally, it is stable up to 700 °C, whereas its intrinsic mechanical properties are characteristic of hard crystalline materials. A promising route toward these materials involves chemical solution deposition (CSD) (e.g., spin or dip coating) of a magnesium perfluoroacetate solution on selected substrates followed by thermal calcination of the as-made hybrid layers. However, tuning the porosity in such materials cannot be done by conventional approaches, such as micellar templating,[3,4] because of rapid crystallization at moderately low temperatures that favor the formation of nanoparticules instead of interconnected solid frameworks. Recently we reported the preparation of magnesium oxyfluoride vesicle-like porous coatings with extremely low refractive indices down to 1.08 and low dielectric constants ($\kappa_{100\ \mathrm{kHz}} = 1.6$). These materials were obtained upon applying a rapid thermal treatment to the wet intermediate layer.[5] The present work is dedicated to understanding the mechanisms that are responsible for the porosity creation and controlling the critical parameters governing this transformation. Our conclusions are mainly supported by dynamic in situ investigations of the thermal treatment using a novel, non destructive, ellipsometry-based technique called thermal ellipsometry analyses (TEA) that has recently proven very useful in investigating the crystallization of mesostructured TiO_2 films.[6] Applied for the first time on materials with evolving unstructured porosity, we show that thermal treatment conditions (ramp rate) and the calcination atmosphere (water content) are critical parameters and can be adjusted to perfectly tune the refractive index of the MgF_2-based layers.

---

* Corresponding author. E-mail: david.grosso@upmc.fr.

(1) Fujihara, S.; Tada, M.; Kimura, T. *Thin Solid Films* **1997**, *304* (1−2), 252–255.

(2) Fujihara, S.; Tada, M.; Kimura, T. *J Sol−Gel Sci. Technol.* **2000**, *19* (1−3), 311–314.

(3) Grosso, D.; Cagnol, F.; Soler-Illia, G. J. D. A.; Crepaldi, E. L.; Amenitsch, H.; Brunet-Bruneau, A.; Bourgeois, A.; Sanchez, C. *Adv. Funct. Mater.* **2004**, *14* (4), 309–322.

(4) Sanchez, C.; Boissiere, C.; Grosso, D.; Laberty, C.; Nicole, L. *Chem. Mater.* **2008**, *20* (3), 682–737.

(5) Grosso, D.; Boissiere, C.; Sanchez, C. *Nat. Mater.* **2007**, *6* (8), 572–575.

(6) Bass, J. D.; Grosso, D.; Boissiere, C.; Sanchez, C. *J. Am. Chem. Soc.* **2008**, *130*, 7882–7897.

10.1021/cm8010106 CCC: $40.75

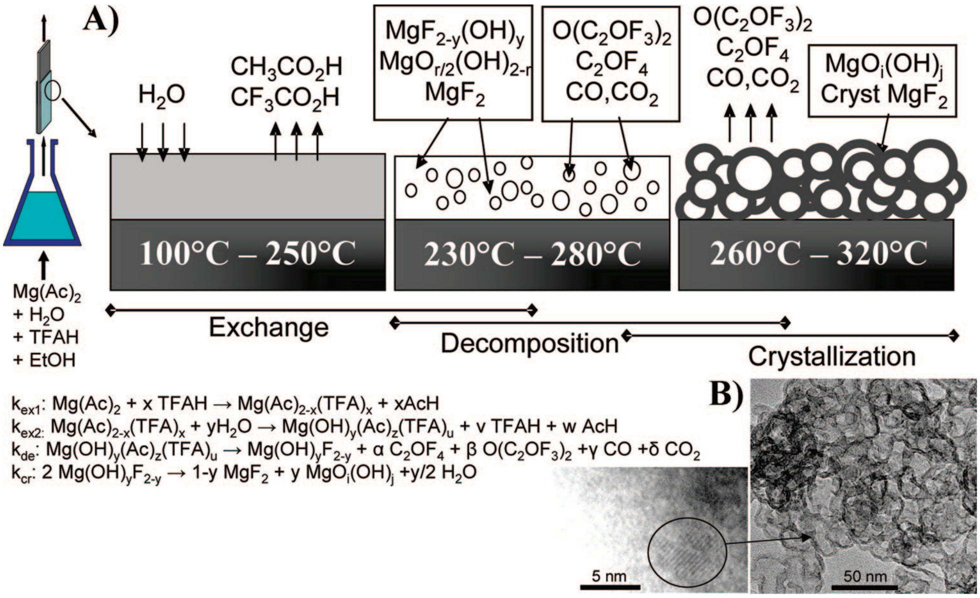

Figure 1. (A) Scheme representing the various thermally driven steps involved in material formation and the 4 main reactions susceptible to occur (k_{ex1}, exchange between acetate and trifluoroacetate ligands in solution; k_{ex2}, substitution of organic ligands by hydroxyl groups from atmospheric water at moderate temperature; k_{de}, thermal decomposition of organic ligands at high temperature; k_{cr}, crystallization of MgF_2 at high temperature. (B) TEM images of a typical vesicle-like structure characteristic of the material (film prepared at 10 °C/min under a dry atmosphere).

Ex situ FTIR investigations have been performed to assess the Mg chemical environment within the coating at different steps of the thermal treatment. Structural characteristics have been deduced by AFM and TEM investigations. The result is a class of MgF_2-based optical coatings with tunable compositions and optical properties.

Results and Discussion

Description of the Process. We recently reported the synthesis of magnesium oxofluoro thin films[5] beginning with the deposition of a $Mg(CF_3CO_2)_{2-x}(CH_3CO_2)_x$ precursor solution prepared by mixing $Mg(CH_3CO_2)_2$ with trifluoroacetic acid (TFA) in a water−alcohol solution. Deposition leads to evaporation of the solvent, acid, and water, leaving a fluoroacetate enriched precursor at the surface of the substrate. A thermal treatment is then used to drive the phase transition from the magnesium salts to a 3D magnesium oxofluoro network.[2] Figure 1 illustrates the various steps involved in the formation of the porous layer together with the dominate chemical reactions[1,2] believed to be taking place along the process. After deposition of the initial solution, thermal treatment triggers three physicochemical processes: k_{ex2} corresponds to the exchange and removal of labile functional organic ligands by hydroxyl groups; k_{de} is associated with the decomposition of the perfluoroacetate; and k_{cr} corresponds to the condensation and partial crystallization into MgF_2 of the network. These processes take place successively but can more or less overlap depending on the applied conditions. Indeed, we will show that they are affected by two key variables during the thermal treatment, the heating rate and the relative environmental content of water.

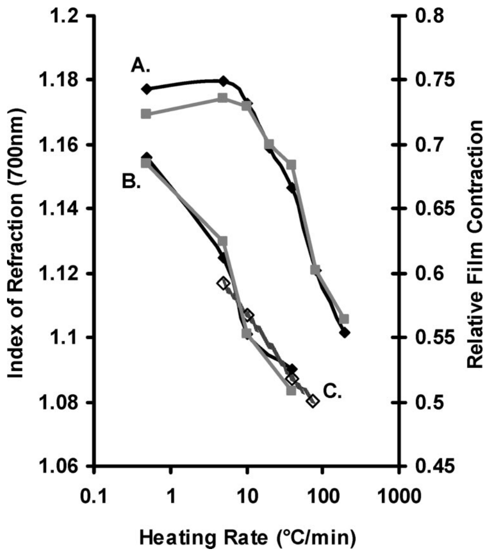

Figure 2. Influence of the heating rate on (♦) the final index of refraction and (gray square) the relative contraction upon calcination for films calcined to 450 °C under (A) wet air (1 vol % H_2O), (B) argon, and (C) dry air (20% O_2/80% N_2, $RH_{25\,°C} = 0.0$) as measured by ellipsometry.

Film Structure, Porosity, and Optical Properties. Initial hybrid films were 500 nm thick before calcination and were prepared as described in the Experimental Section. Thermal treatment involves three physicochemical processes: the exchange and removal of labile functional groups, the thermal decomposition of the organic ligands, and the condensation and partial crystallization of the network. These processes are affected by two key variables during thermal treatment, the heating rate and the calcination environment. This is illustrated in Figured 2, which shows the influence of the heating rate and the water content of the calcination environment on the final index of refraction and thickness of the films calcined to 450 °C. First, one observes that oxygen appears to play no role, because equivalent results are observed under argon and dry air. Second, the degree of contraction of the materials is seen to be directly correlated with the final index of refraction because both types of curves are almost overlapping. This aspect will be discussed later.

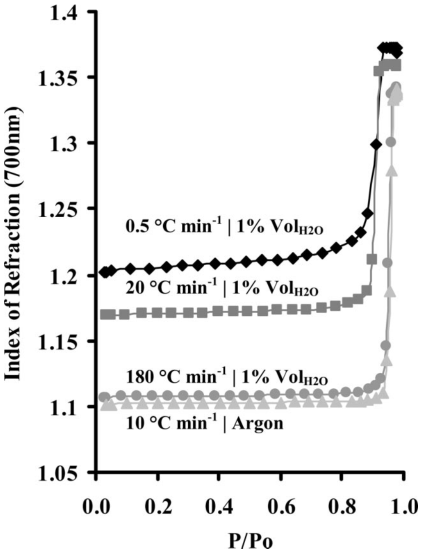

Figure 3. Index of refraction as a function of water partial pressure (adsorption branch) for films heated at (♦) 0.5 °C/min, (■) 20 °C/min, (●) 180 °C/min under wet air (1 vol %), and (▲) 10 °C/min under argon. Data for the 0.5 °C/min material was obtained after exposure to a high RH environment, because this material is initially slightly hydrolytically unstable (and hence the higher index of refraction compared to above in situ data).

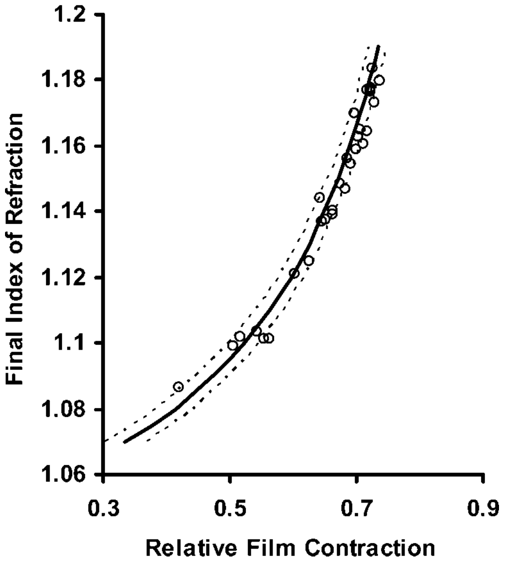

Figure 4. Correlation between the final index of refraction (at 700 nm) and the relative film contraction upon calcination up to 450 °C. Data are shown for the four series presented above in Figure 2 and below in Figure 7. The black line is the expected correlation from an effective media approximation on the basis of the formation of a fixed amount of matrix material with a given index of refraction (quantitative values for these two parameters cannot be uniquely determined). Dotted lines are theoretical changes in the index of refraction based on changing the quantity of magnesium hydroxide type species from 0% (upper) to 25% (lower).

Finally, the plots show that the final index of refraction can be tuned between 1.08 and 1.18, from the same initial solution, by controlling the heating rate and the atmospheric water content during calcination. High heating rates and a water-free environment favor the production of thicker films with lower indices of refraction. The degree of contraction of the materials is seen to directly correlate with the final index of refraction (see below). The final index of refraction can be tuned by controlling the heating rate, a reduction of which reduces the release rate and temperature (thus volume) of gaseous porogens that drive the foaming process (see Figure 1). Greater film contraction follows, reducing the porosity and increasing the final index of refraction. For both dry and wet conditions, a linear dependence of the index of refraction with respect to the log of the heating rate is observed over most of the heating range investigated. For the wet system, linearity is observed at high heating rates, whereas below 10 °C/min, at which point the index of refraction reaches a maximum of 1.18, it gradually declines.

All thermal conditions produce materials with open structures and accessible void space as characterized by water adsorption−desorption investigation by environmental ellipsometry porosimetry,[7] Figure 3. In this technique, water from the atmosphere is adsorbed at the pore interface while capillary condensation eventually occurs at a specific relative pressure that can be correlated to the pore dimension for a given surface energy. The pore water filling is monitored by the variation of refractive index as the global density of the layer increases. For all four samples, the index of refraction remains relatively flat at low relative humidity until capillary condensation is finally seen to occur just below a partial pressure of 0.9 for high index of refraction materials and just above 0.9 for a low index of refraction materials. This indicates a porous structure characterized by pores with internal dimension between 10 and 15 nm and between 20 and 30 nm, respectively. No precise values of the pore sizes are provided because their morphology cannot rigorously be described as sphere or cylinder. However, lower values were estimated using a model corresponding to cylindrical pores while higher value correspond to spherical pores.[7]

Correlation between Refractive Index, Porosity, and Film Contraction. As before, the relative film contraction upon calcination follows nearly identical trends as the index of refraction. The correlation between these two film properties is shown in Figure 4 based on the data series presented in Figures 2 and 7. Also shown is the expected correlation from a Bruggemann effective media approximation based on the formation of a fixed amount of matrix material with a given index of refraction.[7]

Although the quantitative values for these two parameters cannot be uniquely determined, the ability to describe the index of refraction from the Bruggman effective media approximation (BEMA) based solely on the contraction strongly suggests that it is the porosity that is largely governing the index of refraction. The present films are composed of MgF_2 and MgO-based domains, which may be surface hydroxylated.[5] The relative abundance of these domains, and thus the material composition, is dependent on the thermal treatment conditions (see below). However, for this system, the specific identity of the magnesium species has very little influence on the simulated index of refraction. This is due to a particularity between the properties of MgF_2 and MgO, where the former has a much lower index of refraction (1.376 for MgF_2 compared with 1.73 for MgO at 700 nm) but also much lower molar density (0.051 compared with 0.089 mol/ml). A fixed molar quantity of either in a

---

(7) Boissiere, C.; Grosso, D.; Lepoutre, S.; Nicole, L.; Bruneau, A. B.; Sanchez, C. *Langmuir* **2005**, *21* (26), 12362–12371.

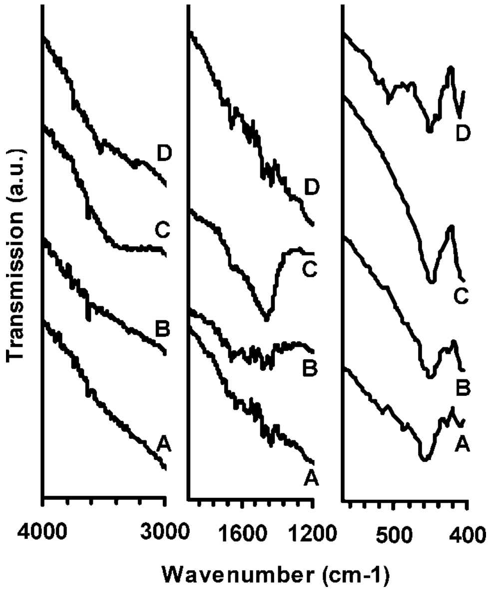

Figure 5. Effect of heating rate and atmosphere: FTIR spectra of films heated at (A) 180 °C/min, (B) 20 °C/min, and (C) 0.5 °C/min under wet air (1 vol %) and (D) 10 °C/min under argon. (Inset) All materials show bands at ∼450−460 characteristic of ν(MgF) in MgF_2.

fixed volume modeled with an effective media approximation yields virtually the same composite index of refraction. Thus a differentiation cannot be made between the two species from ellipsometry alone and only the volume of space occupied, as defined by the contraction of the film, is of importance for determining the index of refraction. Although this is less true with any potential magnesium hydroxide type species, varying their quantity from 0 to 25% still has only a marginal impact on the index of refraction (based on a Bruggemann model using the properties of $Mg(OH)_2$ as a reference). This is shown with the dotted lines in Figure 4. Previous XPS investigation[5] gave a global formula of $MgF_{1.43}O_{0.15}(OH)_{0.27}$ for the matrix under flash heating conditions, or 72 ± 5% MgF_2.

Chemical Composition of the Films after Calcinations. Figure 5 shows FTIR spectra of films calcined at 450 °C under different conditions. The low intensity of the signals, due to the presence of the substrate and the low quantity of matter analyzed, does not allow quantitative analysis but is of great utility in deducing the global chemical environment of the Mg species in the films. The EEP isotherms that correspond to films prepared at high heating rates (Figure 3) show reversible optical properties that suggests that they are hygroscopically stable. However, for materials obtained at low heating rates, a slight contraction of the network is observed upon water loading cycling. Such a slight instability of materials calcined at slow heating rates is in part explained by the different chemical makeup of the network, as accessed by IR in Figure 5. Although all materials show a main band at 450 cm^{-1} and a sharp but weaker band at 410 cm^{-1} characteristic of MgF_2,[8,9] slower heating rates and wet atmospheres led to materials exhibiting bands assigned to the absorption of water and bridged hydroxyl groups at 3750−3000 cm^{-1} and strong absorption bands recorded at ∼1460 cm^{-1} corresponding to CO_2 adsorbed on basic MgO-type surfaces.[10] The latter bands thus reveal the presence of oxide-based phases in the material, responsible for the higher water sensibility observed by EEP in Figure 3. However, no peaks characteristic of $Mg(OH)_2$ (3700 cm^{-1}) are visible for any of the materials, suggesting that OH groups found by XPS in the previous work are likely to be due to chemisorbed water located at the surface of the materials. Regardless of the heating rate, XRD measurements (see the Supporting Information) detect solely the MgF_2 crystalline phase.

Spectra of materials heated under argon resemble those produced at the fastest heating rates in moderately wet atmospheres, with no bands characteristic of bicarbonate, water, or bridged hydroxyl groups, suggesting that the chemical composition is mainly represented by MgF_2. The IR data show that water presence in the calcinations atmosphere can promote the formation of a basic MgO type surface over MgF_2, especially when slow heating rates are used. Similar results, displaying a more MgO-type structure, can be obtained by reducing the initial quantity of TFA in the deposition solution (data not shown). Once more, oxygen appears to play no role, with equivalent FTIR spectra recorded under argon and dry air.

Film Surface Topography. AFM images corresponding to the surface topographies of films prepared at 10 °C/min under wet air (1%vol), 10 °C/min and 72 °C/min under a dry atmosphere are displayed in Figure 6. Their final corresponding index of refraction values were 1.176, 1.103, and 1.08, whereas rms roughness values are 3, 20, and 37 nm, respectively. As expected from EEP investigations, denser films are composed of smaller features, whereas less dense films are composed of larger features. Films obtained at 10 °C/min under a dry atmosphere (Figure 5 middle) exhibit characteristic features that are close to 20 nm in dimension, which is in agreement with the size of the vesicle-like structure seen in the TEM image in Figure 1.

Influence of Water in the Initial Calcinations Atmosphere. In general, the presence of moderate quantities of water results in more contracted structure as observed by AFM and EEP. The presence of water in the calcination environment is therefore seen to be a crucial parameter, both in terms of the final index of refraction and the final makeup of the inorganic network. Although a dry atmosphere is conducive to highly porous MgF_2-rich materials, a wet atmosphere is shown to result in MgO-rich materials with lower porosity, the latter exacerbated at slow heating rate. The total effect of water, however, is more nuanced. Figure 7 shows the final index of refraction (450 °C) as a function of the volume fraction of water in the calcination environment for films heated at 10 °C/min and 165 °C/min. At low water concentrations the index of refraction of the final material increases linearly with the water content in the atmosphere. The dependence is higher at slower heating rates, indicating that longer exposure time is detrimental. This trend

---

(8) Wojciechowska, M.; Zielinski, M.; Pietrowski, M. *J. Fluorine Chem.* **2003**, *120* (1), 1–11.

(9) Murthy, J. K.; Gross, U.; Rudiger, S.; Kemnitz, E.; Winfield, J. M. *J. Solid State Chem.* **2006**, *179* (3), 739–746.

(10) Mekhemer, G. A. H.; Halawy, S. A.; Mohamed, M. A.; Zaki, M. I. *J. Phys. Chem. B* **2004**, *108* (35), 13379–13386.

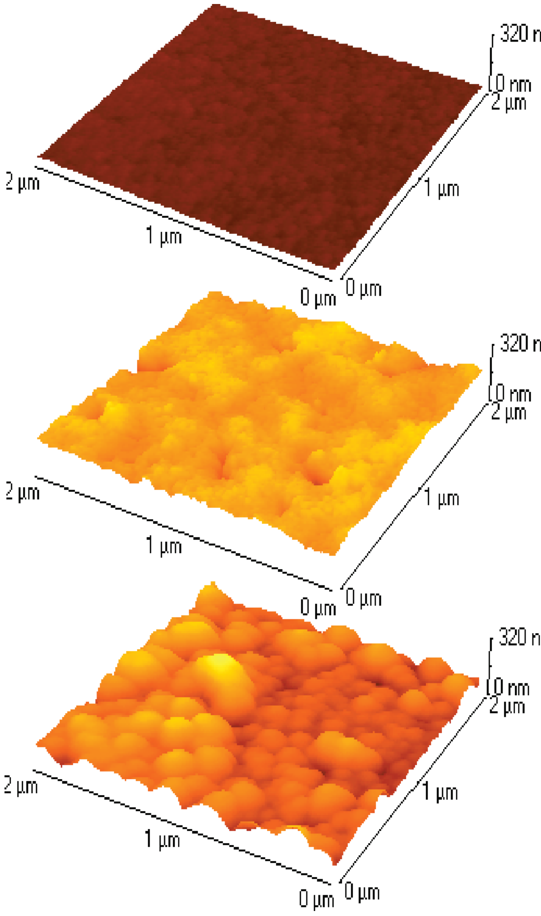

Figure 6. AFM images of film surface topographies. Samples heated at (top) 10 °C/min under wet air (1 vol %), (middle) 10 °C/min, and (bottom) 72 °C/min under a dry atmosphere.

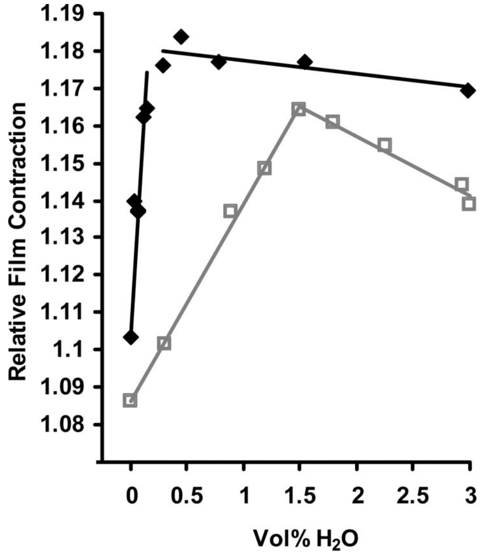

Figure 7. Final index of refraction (at 700 nm) shows a large dependence on the quantity of water in the calcination environment. Even very low quantities of water in the atmosphere result in a significant increase in the index of refraction. Data are shown for films calcined at (♦) 10 °C/min and (☐) 165 °C/min under a 20% O_2/80% N_2 environment. Lines are linear guides for the eye.

reaches a maximum of ∼1.18 at ∼0.2 vol % water heating at 10 °C/min and ∼1.16 at 1.5 vol % water heating at 165 °C/min. At higher concentrations, the index of refraction of the final material decreases linearly with the water content in the atmosphere, with a lower dependence at slower heating rates. Since it is the film contraction that largely governs the observed index of refraction, Figure 7 indicates that water effects film contraction by two distinct, time-dependent pathways.

Low quantities of water increase the observed index of refraction while at higher quantities the index of refraction goes through a maximum and then decreases. The increase likely results from water exchange, liberating fluoroacetic acid prematurely and thus reducing the quantity of fluoroacetate available to drive the foaming mechanism. The second effect is likely due to the promotion of inorganic oxyhydroxide condensation at low temperatures, stabilizing the network against contraction. This condensation is preceded by TFA ligand exchange by water, resulting in MgO-rich films that are more water sensitive and fragile. These processes are further detailed using in situ ellipsometry coupled with ex situ IR.

In situ TEA Investigations and Formation Mechanism. In situ thermal ellipsometry analysis allows the index of refraction and the contraction of the film to be monitored in real-time during calcination.[6] For a such analysis, the sample lies on a heating plate inside a chamber where a flux of gas with controlled composition is maintained. Figure 8 shows in situ thermal ellipsometry data coupled with ex situ IR measurements for a film calcined at 10 °C/min under a wet atmosphere (1.5 vol % H_2O). The final refractive index of the film is 1.18, which corresponds to a low porosity system. At low temperature (T < 250 °C, point A), steady film contraction culminates in a loss of some 35% of the thickness of the film along with a weaker decline in the index of refraction. This is followed (T > 260 °C, point B) by a dramatic drop in the film thickness and a concurrent small spike in the index of refraction.

During this period, film collapse more or less conserves the optical density of the material, without the creation of porosity. At slightly higher temperatures between points B and C (∼275 to 320 °C) the index of refraction undergoes a distinctive drop in two steps. The first is a precipitous drop synchronous with arrested contraction of the film. The second is less precipitous and is accompanied by a small resumption in film contraction. These large decreases in the index of refraction are characteristic of porosity generation. Above ∼325 °C (point C), the film stabilizes in terms of both the index of refraction and contraction, both decreasing only slightly up to 450 °C, the duration of the experiment (point D). Corresponding chemical information on the processes observed by in situ thermal ellipsometry is obtained by ex situ IR. Between points A and B the majority (∼ 84%) of the signal corresponding to the organic species is lost. These organic bands are predominately associated with the presence of TFA in the deposition solution, as they are not present for films deposited without TFA (data not shown). The IR spectra for point A, at 170 °C, is taken well above the boiling point of fluoroacetic acid (72.4 °C) to eliminate the influence of potentially noncoordinated species. The large loss of organic species between points A and B occurs before any significant generation of porosity in the material. Between points B and C, where porosity is generated, most of the

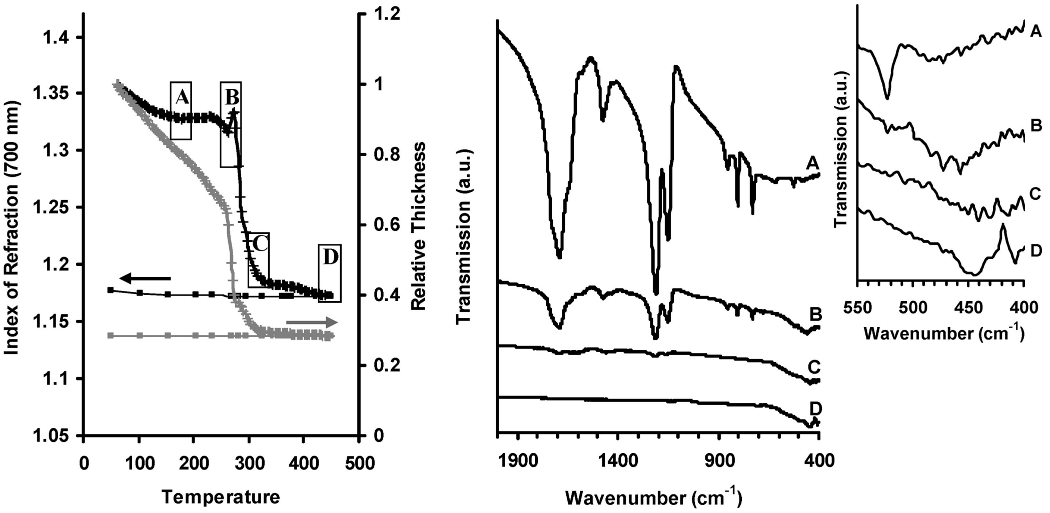

Figure 8. (Left) In situ thermal ellipsometry of a film calcined at 10 °C/min in wet air (1.5 vol %) showing (black) the index of refraction and (gray) the relative thickness during (+) heating and (□) cooling. (Right) Ex situ IR data taken at points corresponding to A−D. (Inset) Expansion of the low-frequency data.

remaining organic is lost, with only about 2% remaining relative to point A. Thus, in the presence of water, only a relatively small fraction (<14%) of the organic fluoroacetate ligand participates in the porosity generating process, as most of it is previously liberated. The remaining organic is lost by the final measurement at 450 °C, point D.

Porosity is generated only as the contraction of the film slows, corresponding to a point in which the inorganic network has sufficiently rigidified. At low wavenumbers, the evolution of the film matrix can be seen, Figure 8 right inset. Point D at 450 °C shows bands characteristic of crystalline MgF_2, with a main band at 450 cm^{-1} and a sharp but weaker band at 410 cm^{-1}.[8,9] Point C, just after the drop in the index of refraction, shows similar, but broader bands over the same region, consistent with a mostly amorphous MgF_2 material.[9] Broad structure is also seen at point B, though centered at higher frequency. This broad structure, and its absence in point A, indicates that the contraction in the film thickness is accompanied by new bonding at the metal center, most likely as part of network formation, but that this bonding has a different characteristic structure than at later times.

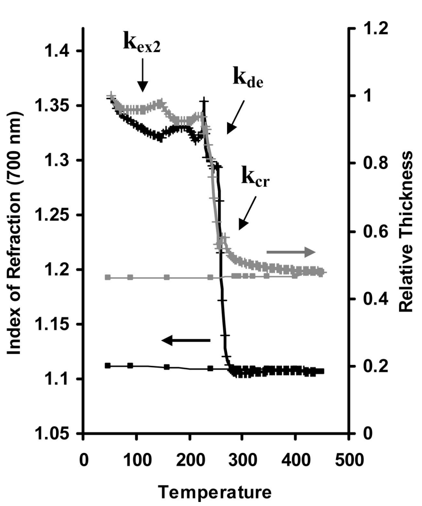

Figure 9. In situ thermal ellipsometry of a film calcined at 10 °C/min under argon showing (black) the index of refraction and (gray) the relative thickness during (+) heating and (□) cooling.

Under dry conditions, the in situ thermal ellipsometry analysis (TEA) behavior is considerably different (see Figure 9). No significant film contraction is seen at low temperatures, other than a small feature involving ~5% contraction seen just above 150 °C, likely the removal of weakly coordinating species such as water or acetate groups.[2] Features broadly similar to that in the wet systems are observed but these occur at temperatures that are 20 to 50 °C lower and they overlap to a greater extent. The drop in film thickness (T > 225 °C) again occurs accompanied by an initial spike in the index of refraction followed closely followed by a two-stage drop in the index of refraction. The first (225−253 °C) is quite small and overlaid by a large contraction of the film. The second (253 to 271 °C) is a dramatic decrease in the index of refraction marking the creation of porosity. Porosity is again seen to synchronize with an arrestment of the film contraction. There is even a small expansion in the film thickness, indicating that the liberated gaseous species upon decomposition of the magnesium fluoroacetate salts can partially inflate the film. Beyond this point, the film rigidifies and rests relatively stable, with only small changes in the index of refraction and the film thickness up to the conclusion of the measurement at 450 °C. Arresting the contraction of the film and stabilizing a more open, inflated state is thus essential in synthesizing low index of refraction materials. Stabilization occurs upon formation of the inorganic network as polymerization drives up the viscosity and finally rigidifies the network. Under conditions where the network resists contraction, the liberation of species associated with the original magnesium salts creates porosity in the materials. The network will resist contraction at high heating rates for three reasons: the time available for relaxation is shorter, the high rate of evolving gaseous species generates inflationary pressure against collapse, and the temperature of formation is higher. Higher temperatures place more available energy into the system, so that the consolidation of the network occurs with greater facility upon ligand decomposition. The decrease in the index of refraction at high water contents may also be facilitated by this, as the temperatures marking the phase transitions increase with water content. At lower concentrations, the negative effect of ligand loss through exchange dominates, yielding materials with high indices of refraction and greater MgO character.

Conclusions

The thermally activated synthesis of low index of refraction magnesium oxyfluoro materials is seen to be strongly dependent on the heating rate and calcination environment. These parameters affect the overall contraction of the materials during calcination, which in turn almost wholly determines the final index of refraction. Unlike under slow heating, where physicochemical processes are coupled and where thermodynamic control is dominant, rapid or flash heating is controlled by kinetic processes, giving access to higher-energy metastable states.[4] In the present system, rapid heating and the associated energy oversaturation inside the coating, triggers the liberation of gaseous species originating from the organic ligands[2] and the nucleation and limited growth of MgF_2-based crystalline nanoparticles. A highly viscous network and gaseous species from liberated ligands forms a foam-like structure of inorganic matrix surrounding nanobubbles. The final stabilized structure is a partially nanocrystalline inorganic network with an open-celled vesicular texture, or nanopumice. The resulting void space from the interconnected cavities can comprise up to ~80% of the film volume and is the origin of the extremely low indices of refraction in these materials.

These processes are followed in situ by thermal ellipsometry, providing fine-scale details on the thermal evolution of the contraction and the index of refraction during calcination. Porosity generation is only observed after polymerization of the inorganic network arrests contraction. At high heating rates the degree of contraction is reduced via faster polymerization kinetics, an inflationary pressure caused by quickly evolving gaseous species, and higher synthesis temperatures. At low concentrations, the presence of water strongly increases the final index of refraction of the films by reducing, through ligand exchange, the quantity of fluoroacetate species. At higher concentrations, especially coupled with high heating rates, water decreases the observed index of refraction. The presence of water also affects the final composition of the materials, producing materials with greater MgO-based character in lieu of MgF_2.

Here again, processing conditions are shown to be of utmost importance in the nanostructuration of nanoporous thin inorganic thin films. The present approach allows the precise tuning of the porosity of inorganic films without using shape and/or dimensionally predefined templates and without changing the composition of the (highly stable) initial solution.

Experimental Section

All products were purchased from Sigma/Aldrich and used as furnished. Typical initial solutions were prepared by mixing 3.58 g of $Mg(CH_3COO)_2 \cdot 4H_2O$ with 25 g of ethanol, 0.75 g of H_2O, and 3.68 g of TFA (giving respective molar ratios of 1:33:2.5:2) and heating for 5 min at 60 °C. After complete dissolution and homogenization, a layer of this solution was deposited on silicon wafers by dip-coating at a constant relative humidity of 10% and at a fixed velocity of 2.5 mm s^{-1}. After 5 min of drying in the latter conditions, films were immediately calcined under a controlled heating schedule (controlled ramp and atmosphere water content) up to 450 °C. Typical film thicknesses were 260 to 125 nm after calcination with refractive index values of 1.08 to 1.18.

Ellipsometry measurements were performed on a UV−visible variable angle spectroscopic ellipsometer (VASE) from Woollam, and the data analysis was performed with the WVase32 software. Measurements were fitted over the transparent range (400−1000 nm). A single Cauchy layer was used to model the deposited films, asymmetric optical properties, possibly originating by gradients in the thickness or caused by stress gradients due to film contraction were not observed and therefore no correction was applied. For in situ ellipsometric analysis,[6] the Ellipsometer was fitted with a home-built covered heating unit connected to a programmable temperature regulator (now being developed in conjunction with SOPRA). Small holes were present to allow a thermocouple and beam access to the sample as well as gas flow. The calcination environment was adjusted by flowing between 2.5 and 5 L min^{-1} of gas through the sample stage at controlled RH (0−100% at 25 °C). For environmental porosimetry measurements the ellipsometer was fitted with a small, variable humidity flow chamber (SOPRA) flushed with 2.5 L of air per min. The humidity was adjusted using a mass flow controller and monitored using a relative humidity probe held in the environmental chamber.[7] In this case, ellipsometry was conducted at room temperature (25 °C) using the adsorption−desorption isotherm of water analyzed with an isotropic inorganic pore contraction model (IIC) and a modified Kelvin equation for ellipsoidal pores.[7]

Acknowledgment. This material is based on work supported in part by the National Science Foundation under the International Research Fellowship Program, Grant OISE-0505786. The authors also acknowledge funding provided by CNRS and UPMC.

Supporting Information Available: X-ray diffractograms (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

CM8010106