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Room-Temperature Synthesis of *a*-SiO_2 Thin Films by UV-Assisted Ozonolysis of a Polymer Precursor

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A room-temperature synthesis route for thin films of amorphous silica (*a*-SiO_2) based on irradiation of a silicon-containing polymer by UV light in pure O_2 atmosphere has been developed. The chemical conversion of spin-coated films of poly(pentamethyldisilylstyrene) (pPMDSS) to silicon oxycarbide and finally to amorphous silica is achieved by UV-assisted ozonolysis. The conversion process has been followed by Fourier transform infrared spectroscopy (FTIR), ellipsometry, and X-ray photoelectron (XPS) and Auger electron spectroscopies (AES). The control of the irradiation time allows for control of the chemical composition of the converted films ranging from that of a silicon oxycarbide for short exposure times to that of *a*-SiO_2 after 18 h of exposure. The surface composition of the fully converted films obtained by XPS is characterized by an atomic ratio O/Si = 2.00 ± 0.07. Auger electron depth profiles reveal a uniform chemical composition of the *a*-SiO_2 films with a residual carbon content in the bulk of the films below 1%. Converted *a*-SiO_2 films of thicknesses up to 150 nm were achieved. Ellipsometry shows that the conversion of the films in *a*-SiO_2 is accompanied by a progressive decrease of the film thickness and evolution of the refractive index to an asymptotic value of 1.44. The film surface of the converted films probed by optical microscopy over large areas and by atomic force microscopy (AFM) does not show any cracks and is atomically flat with a RMS roughness below 0.4 nm.

I. Introduction

There is an increasing interest in the development of new low-temperature synthesis routes for silicon oxide thin films, especially from the perspective of designing low-cost all-organic electronic devices on flexible plastic substrates.[1] Amorphous silica also attracts interest for the design of optoelectronic devices such as on-chip optical waveguide structures,[2] antireflection coatings for optical applications,[3] or membranes of controlled permeability for gas separation.[4] Typical elaboration methods for etch-resistant SiO_x and silicon oxycarbide thin films include chemical vapor deposition (CVD) and sol−gel processes using standard spin-on technology.[5,6] Both of these preparation methods involve organosilicon precursors such as siloxanes, i.e., silicon-containing polymers (SCP), which have also attracted much interest for their application as lithographic photoresists.[7] However, on one hand, CVD synthesis of *a*-SiO_2 involves either toxic tetraethylorthosilane (TEOS) or silane gas and requires expensive vacuum equipment and high annealing temperatures to remove water and residual organic byproducts such as alcohol. Sol−gel solution processing, on the other hand, is based on either TEOS or organosilicates, and high-temperature annealing is usually required to remove residual alkyl groups. Moreover, sol−gel processing usually causes unwanted cracking and shrinkage of thick films (thickness of around 1μm) because of the release of water and alcohol during condensation of polysiloxanes by hydrolysis.[8]

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(1) Crone, B.; Dodabalapur, A.; Lin, Y.-Y.; Filas, R. W.; Bao, Z.; LaDuca, A.; Sarpeshkar, R.; Katz, H.-E.; Li, W. *Nature* **2000**, *403*, 521.
(2) Yang, P.; Wirnsberger, G.; Huang, H. C.; Cordero, S. R.; McGehee, M. D.; Scott, B.; Deng, T.; Whitesides, G. M.; Chmelka, B. F.; Buratto, S. K.; Stucky, G. D. *Science* **2000**, *287*, 465.
(3) Uhlmann, D. R.; Suratwala, T.; Davidson, K.; Boulton, J. M.; Teowee, G. *J. Non-Cryst. Solids* **1997**, *218*, 113.
(4) Bhave, R. R. In *Inorganic Membranes: Synthesis and Applications*; Van Nostrand Reinhold: New York, 1991; p 1.
(5) Pierson, H. O. In *Handbook of Chemical Vapor Deposition. Principles, Technology and Applications*; Noyes Publications: Park Ridge, NJ, 1993; p 1.
(6) Brinker, C. J.; Scherer G. W. In *Sol−Gel Science*; Academic Press: San Diego CA, 1990; p 1.
(7) Hartney, M. A.; Hess, D. W.; Soane, D. W. *J. Vac. Sci. Technol. B* **1989**, *7*, 1.
(8) Sakka, S. In *Sol−Gel Processing of Advanced Materials*; The American Ceramic Society; Westerville, OH, 1991; pp 201−208.

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Recently, several groups have also demonstrated the possibility of converting nanostructured block copolymer thin films into periodic arrays of nanodomains from the perspective of one-step lithographic processes by reactive ion etching (RIE) using oxygen plasma.[9] Chan et al. proposed a new method for yielding nanoporous and nanorelief silicon oxycarbide materials by ozonolysis of block copolymers based on polyisoprene and pPMDSS.[10] More recently, Ouyang et al. demonstrated that various linear and cross-linked polysiloxanes can be transformed into silicon oxide (SiO_x) by a simple UV/ozone conversion process.[11] However, to the best of our knowledge, the previous studies dealing with silicon oxycarbide or oxide synthesis from SCPs, copolymers, and siloxane precursors[11−13] have not demonstrated that smooth inorganic coatings of uniform chemical composition, e.g., with a low residual carbon concentration, can be obtained without a high-temperature pyrolysis or annealing step.

In this study, we have focused on the conversion of thin films of pPMDSS by UV-assisted ozonolysis over a broad range of converted film thicknesses (10−150 nm), which constitutes an interesting alternative to O_2-RIE processing. O_2-RIE-treated films of pPMDSS exhibit a very rough reticulated morphology when etched at plasma temperatures; however, when etched at 0 °C using wafer cooling, the RMS roughness is only 0.7 nm.[14] Here, we demonstrate that the exposure of pPMDSS thin films to UV irradiation under an O_2 atmosphere results in an efficient conversion to atomically flat *a*-SiO_2 films at room temperature. In addition, this synthesis route employs currently available ultraviolet radiation used in lithography technology.

II. Experiment

Thin films of anionically polymerized pPMDSS (M_n = 30 000, M_w/M_n = 1.06) have been prepared by spin-coating 2 wt % solutions in toluene onto as-received Si(100) wafers with their native oxide (Silicon Inc.). Solutions were first filtered using 0.2-μm filters, and spin-coating was performed at 500−1500 rpm for 30 s, yielding films of thicknesses in the range 50−500 nm. Irradiation was performed by using a UV pencil lamp (UVP Pen-Ray Lamp, λ = 254 nm) mounted in a quartz tube that provided a power of approximately 20 mW/cm^2 at 1-cm distance. The generation of ozone by the UV lamp radiation in the O_2 flux (5 SCFH) was ascertained by iodometric titration. The substrate temperature during irradiation was measured using liquid crystal temperature indicators. The indexes and thicknesses of the films were measured by ellipsometry using a Greatner ellipsometer equipped with a He−Ne (643 nm) laser source. FTIR spectroscopy on spin-coated films was performed using a Nicolet MAGNA800 spectrometer equipped with a Nic-Plan IR microscope in reflection mode. Films were flushed with dry N_2 gas during sampling (typically 250−300 acquisitions per spectra). Atomic force microscopy using Si cantilevers (60−80 kHz frequency) in tapping mode was used to visualize the morphological changes during UV irradiation (Digital Instrument Nanoscope III instrument). Auger electron spectra were obtained on a Physical Electronics scanning auger microscope (model 660), and XPS spectra were collected on a Perkin-Elmer X-ray photoelectron spectrometer equipped with a monochromatic Al Kα X-ray source (1486.6 eV). Spectra were recorded for a spot size of 700 μm and a takeoff angle of 40°, and the peaks were corrected to the C 1s peak at 284.6 eV. AES depth profiling was achieved by etching the film surface with an argon ion beam (2 keV, 20 μA/cm^2). Static contact angles were measured by using a VCA2000 video contact angle system on sessile water droplets.

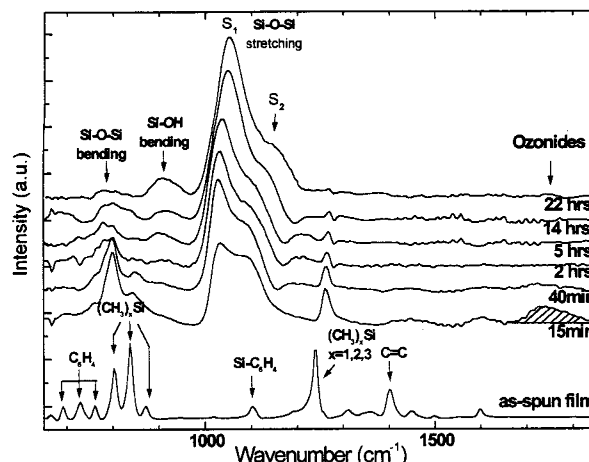

Figure 1. Kinetics of the conversion of pPMDSS thin films (initial film thickness = 220 nm) by UV irradiation in pure O_2 followed by FTIR spectroscopy. The spectra have been shifted along the intensity axis in order to clarify the figure. Identification of the main IR bands is based on previous works on polymethylphenylsiloxanes.[15]

III. Results and Discussion

The evolution of the FTIR spectra of pPMDSS thin films (initial film thickness = 220 nm) during UV irradiation is shown in Figure 1. The treatment of the films by UV radiation in a flow of pure O_2 results in the following major modifications of the FTIR spectrum: (i) a strong decrease in intensity of all of the peaks related to hydrocarbons and aromatic moieties in the 670−800 cm^{-1} range; (ii) the emergence of the Si−O−Si stretching peaks between 1025 cm^{-1} and 1060 cm^{-1}; (iii) the appearance of a broad band at approximately 1740 cm^{-1}, which tends to disappear after longer irradiation times; and (iv) a change in the shape, position, and relative intensity of the peaks around 800 cm^{-1}.

These observations demonstrate that UV irradiation under O_2 flow causes a significant chemical modification of the polymer film. Razumoskii et al. investigated the general degradation scheme of various polymers containing double bonds by ozonolysis.[16] Generally speaking, the degradation of such polymers involves the generation of primary degradation products (so-called molozonides), which fragment to ozonides and other

(9) Chan, V. Z.-H.; Hoffman, J.; Lee, V. Y.; Iatrou, H.; Avgeropoulos, A.; Hadjichristidis, N.; Miller, R. D.; Thomas, E. L. *Science* **1999**, *286*, 1716.
(10) Lammertink, R. G. H.; Hempenius, M. A.; van den Enk, J. E.; Chan, V. Z.-H.; Thomas, E. L.; Vancso, G. J. *Adv. Mat.* **2000**, *12*, 98.
(11) (a) Ouyang, M.; Yuan, C.; Boulares, A.; Koberstein, J. T. *Chem. Mater.* **2000**, 12, 1591. (b) Mirley, C. L.; Koberstein, J. T. *Langmuir* **1995**, *11*, 1049. (c) Ouyang, M.; Muisener, R. J.; Boulares, A.; Koberstein, J. T. *J. Membr. Sci.* **2000**, *177*, 177.
(12) (a) Liu, Q.; Shi, W.; Babonneau, F.; Interrante L. V. *Chem. Mat.* **1997**, *9*, 2434. (b) Soraru, G. D.; Liu, Q.; Interrante, L. V.; Apple, T. *Chem. Mat.* **1998**, *10*, 4047.
(13) Awazu K.; Onuki, H. *Appl. Phys. Lett.* **1996**, *69*, 482.
(14) Chan, V. Z.-H.; Thomas, E. L.; Frommer, J.; Sampson, D.; Campbell, R.; Miller, R.; Hawker, C.; Lee, V.; Miller, R. D. *Chem. Mater.* **1998**, *10*, 3895.
(15) Pawlenko, S. In *Organosilicon Chemistry*; Walter de Gruyter & Co.: Berlin, Germany, 1986; p 137.
(16) a) Razumowskii, S. D.; Kefeli, A. A.; Zaikov, G. E. *Europhys. Polym. J.* **1971**, *7*, 275. (b) Ho, K. W. *J. Polym. Sci. A*, **1986**, 24, 2467.

organic fragments involving carbonyl groups. In the specific case of polystyrene, it has been demonstrated that ozonolysis yields mainly radicals of the type R−C_6H_4−O· (R is an alkyl chain) and fragments containing C=O bonds.[16] Accordingly, we assign the broad peak at 1740 cm^{-1} to either the ozonide byproducts or the carbonyl ylides and carbonyl derivatives generated by ozonolysis of pPMDSS. As suggested by the disappearance of the 1740 cm^{-1} peak for $t > 1$ h, these organic byproducts are progressively evacuated in the flow of O_2 during UV irradiation. It must be stressed that atomic oxygen is generated by photodissociation at 185 nm of O_3 and can be considered as an alternative oxidizing agent responsible for the chemical degradation of pPMDSS.[11]

The key roles of both UV radiation and ozone in the chemical transformation of the films is ascertained by the fact that UV irradiation of the films under N_2 does not lead to the typical carbonyl peak. Treatment of the films by ozone without UV light does not lead to amorphous thin films of oxycarbide that adhere to the Si wafer: rather, a simple rinse in water or any organic solvent removes the films. These results clearly show that the conversion mechanism of pPMDSS by UV radiation plus O_2 involves the combination of different physicochemical processes: (i) the generation of ozone on the film surface by UV irradiation, which subsequently diffuses into and reacts with pPMDSS, yielding volatile ozonide byproducts; (ii) the photolysis of the polymer backbone, generating reactive sites such as radicals and dangling bonds, which favor rebonding in the overall network by reacting with ozone; and (iii) the densification of the silica network by local heating induced by nonradiative dissipation of the UV light energy.[17] In the present case, no significant increase of the surface temperature was observed during UV irradiation, as the overall temperature of the films remained below 60 °C.

The emergence of the Si−O−Si stretching peaks (in-phase and out-of-phase stretching modes S_1 and S_2, respectively) and the evolution of their characteristics (position, shape, and intensity) during irradiation reflect the modifications of the chemical environment of the silicon and especially the substitution of carbon by oxygen. The time evolution of the peaks related to CH and/or Si−$(CH_3)_x$ (x = 1, 2, or 3) bonds (around 1270 and 3000 cm^{-1} for aliphatic C−H) and Si−O−C bonds (around 800 cm^{-1}) confirms this tendency. The absence of the characteristic Si−H peak (around 2250 cm^{-1}) indicates that hydrogen is present mainly in the form of C−H bonds. After 18 h of irradiation, all of the peaks related to bonds involving carbon atoms have vanished, whereas other peaks typical of Si−OH (930 and 3400 cm^{-1}) are observed. As seen in Figure 1, the resulting FTIR spectrum obtained for $t > 18$ h is very similar to that of *a*-SiO_2 grown by conventional CVD or sol−gel processes at elevated substrate temperatures.

Additional information on the chemical conversion of SCP into *a*-SiO_2 can be obtained from an analysis of the characteristics of the S_1 peak, which is highly sensitive to the chemical composition, stoichiometry, and porosity/density of the silica matrix.[18] In the present case, we

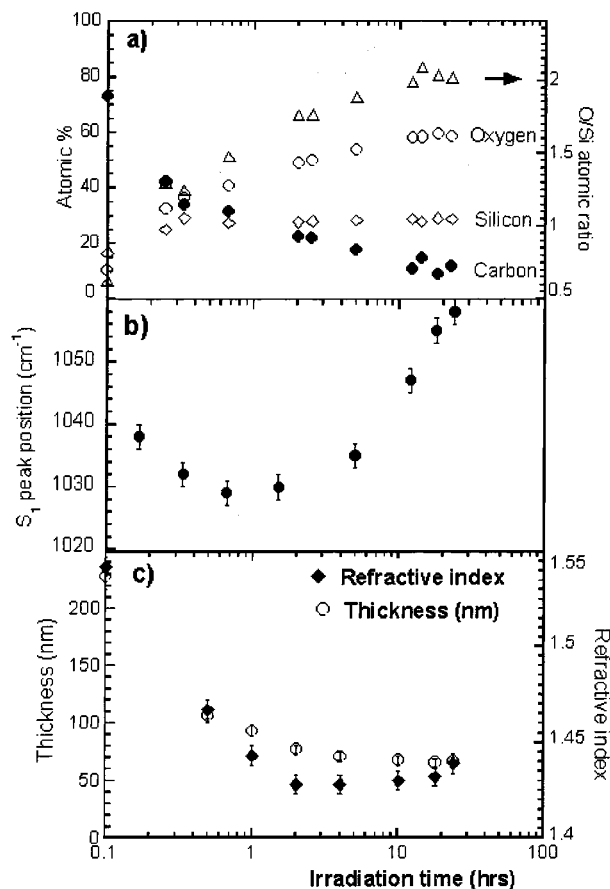

Figure 2. (a) Evolution of the surface composition for Si, O, and C as a function of UV exposure time as obtained from X-ray photoelectron spectroscopy. (b) Variation of the S_1 band position related to the in-phase stretching mode of the Si−O−Si bond. (c) Evolution of the refractive index at 633 nm and film thickness during ozonolysis as obtained from ellipsometry. All data were obtained on thin films of pPMDSS (initial thickness = 220 nm) spin-coated onto a Si(100) substrate covered by a native SiO_2 layer.

first observe a shift of the S_1 peak to lower wavenumbers (see Figure 2b) which coincides with the C → O substitution. After 40 min of irradiation, we observe an increase in the energy of the S_1 peak to a saturating value of around 1060 cm^{-1}, i.e., a value close to that of typical low-temperature thermal oxides (1060−1075 cm^{-1} [18]). Nevertheless, the full width at half-maximum (fwhm) value of 65 cm^{-1} for the S_1 peak is particularly narrow in the final *a*-SiO_2 material (a typical fwhm of approximately 80 cm^{-1} is observed in thermal oxides obtained at low temperature[18]). Furthermore, the S_2 peak located at around 1140 cm^{-1} is significantly shifted to lower wavenumbers with respect to the corresponding peak for thermal oxides (1200 cm^{-1}). Differences in the microstructure, density, and porosity of the converted films with respect to those of films grown by CVD at high temperature are most likely responsible for these observations.

The C → O substitution mechanism is confirmed by results obtained from the XPS analysis of the surface composition. The evolution of the surface composition depicted in Figure 2a shows that carbon is progressively

(17) Joubert, O.; Hollinger, G.; Fiori, C.; Devine, R. A. B.; Paniez, P.; Pantel, R. *J. Appl. Phys.* **1991**, *69*, 6647.

(18) (a) Pai, P. G.; Chao, S. S.; Takagi Y.; Lucovsky, G. *J. Vac. Sci. Technol. A* **1986**, 4, 689. (b) Lucovsky, G.; Mantini, M. J.; Srivastava, J. K.; Irene, E. A. *J. Vac. Sci. Technol. B* **1987**, *5*, 530.

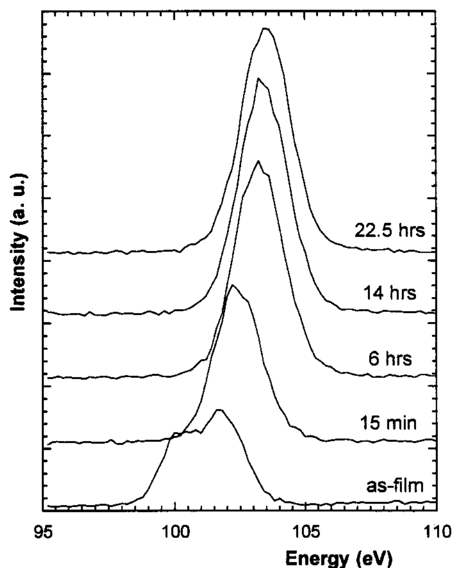

Figure 3. Evolution of the Si 2p X-ray photoelectron spectrum during UV-assisted ozonolysis of pPMDSS thin films spin-coated onto Si(100) substrates (thickness = 220 nm).

removed and replaced by oxygen, with the atomic concentration of silicon remaining essentially unchanged. The steady-state surface composition of the converted films is characterized by a surface atomic concentration of carbon of around 9%. As expected for conversion to *a*-SiO_2, the ratio of the atomic concentrations of oxygen and silicon tends clearly toward an asymptotic value of 2.00 ± 0.07. As seen in Figure 3, the Si 2p XPS spectrum of pPMDSS consists of at least two overlaping peaks located at approximately 99.5 and 101.8 eV. From the chemical composition of pPMDSS, we expect the presence of two Si 2p peaks at 99.2 ± 0.2 and 100.5 ± 0.1 eV, corresponding to Si−Si and Si−C bonds, respectively.[19] However, in the present case, these two peaks cannot be clearly distinguished. The peak at 101.8 eV very likely corresponds to some oxidized species such as O−Si−C bonds (101.8 ± 0.2 eV from ref 19). From a previous study on the O_2-RIE of pPMDSS, it was found that the oxidized species are mainly located at the surface of the spin-coated thin films,[14] in agreement with the fact that polysiloxanes are characterized by a very low surface tension.[20] The evolution of the Si 2p peak during UV-assisted ozonolysis of pPMDSS confirms the change in the chemical environment of silicon. We observe that the Si 2p peak progressively shifts to higher energy during conversion and levels off at around 103.5 eV, a value close to that observed for *a*-SiO_2.[19] These results illustrate that a silicon oxycarbide with increasing oxygen and decreasing carbon concentration is formed by combination of ozonolysis and UV irradiation of the pPMDSS thin films. Correspondingly, the film surface becomes increasingly hydrophilic, with the contact angle decreasing from a value of ~105° for pPMDSS to ~37° after 24 h of irradiation.

To probe the uniformity of the chemical composition throughout the film thickness, we performed depth

(19) Choi, W. K.; Tan, L. S.; Loh, F. C.; Tan, K. L. *J. Appl. Phys.* **1998,** *83*, 4968.
(20) Brandrup, J.; Immergut, E. H. *Polymer Handbook*; John Wiley & Sons: New York, 1989; pp IV−423.

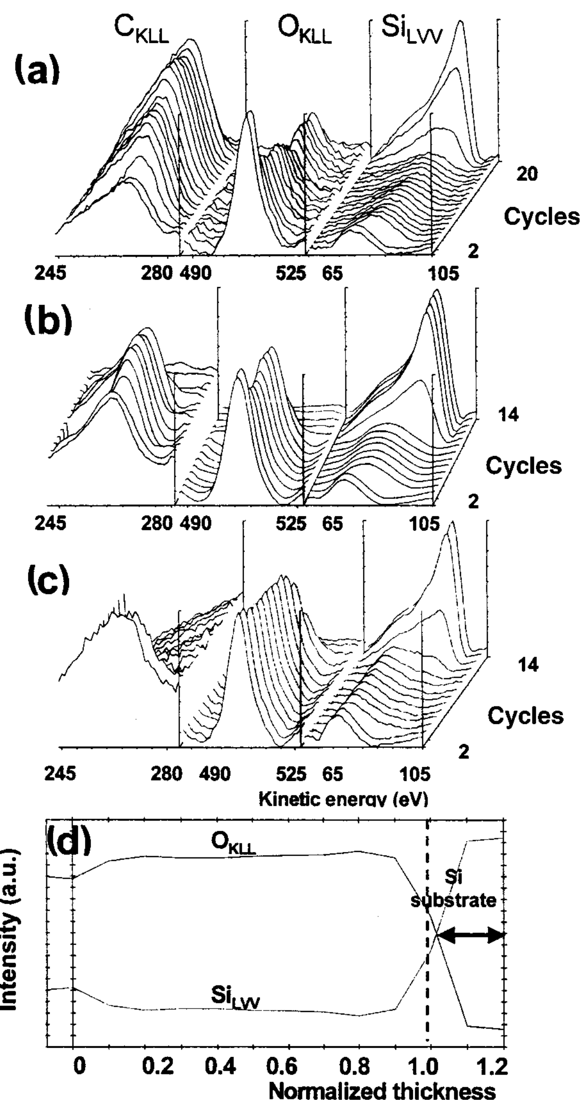

Figure 4. Evolution of the Auger electron depth profile for a pPMDSS thin film (220 nm) spin-coated onto Si(100) substrate during UV irradiation (λ = 254 nm, 20 mW/cm^2): (a) 40 min, (b) 4 h, and (c) 18 h. (d) Depth profile of the Si_{LVV} and O_{KLL} Auger electron peak intensities after 18 h of UV irradiation.

profiling using AES during the conversion process (see Figure 4). After about 1 h of UV−ozone treatment, the O_{KLL} signal shows a clear decrease in intensity with increasing film depth, whereas the C_{KLL} signal increases. With increasing exposure time to UV−ozone, we observe that the O_{KLL} signal becomes more intense in the bulk of the film, whereas the C_{KLL} peak clearly loses intensity. These observations are in agreement with the C → O substitution mechanism evidenced by XPS.

We also observe that after 4 h of UV−ozone treatment (see Figure 4b), the Si_{LVV} signal still shows a shift in position for the first two sputtering cycles with respect to the bulk of the film. These observations show that (i) the conversion mechanism proceeds from the surface of the pPMDSS film that is most exposed to UV−ozone into the bulk of the film and (ii) the chemical surface composition probed by XPS for UV irradiation times below 4 h is different from the overall composition in the bulk of the films. After 18 h of UV irradiation (see Figure 4c and 4d), we observe that the O_{KLL} and Si_{LVV} peaks are almost unchanged throughout the film thick-

ness in both position and intensity until the Si_{KLL} signal of the Si wafer becomes apparent after approximately 12 sputtering cycles (see Figure 4c). The Auger depth profile of the fully converted film (see Figure 4d) demonstrates that the atomic concentrations of silicon and oxygen are essentially constant throughout the film thickness. A C_{KLL} signal of very small intensity is observed before the two first sputtering cycles. It is most likely due to the presence of a surface contamination by hydrocarbons, which is also responsible for the 9 atom % carbon detected by XPS on the surface of the fully converted films. In the bulk of the converted films, no C_{KLL} Auger electrons are detected. This indicates that the residual carbon concentration in the bulk of the thin films is below the resolution limit of the spectrometer, i.e., below 1%, which is in agreement with the absence of any detected Si−CH_3 peaks in the corresponding FTIR spectra around 1275 cm^{-1}.

Modifications in the composition also affect the refractive index at 633 nm (n_f) of the material and the film morphology. As seen in Figure 2c, n_f decreases from its initial value of 1.530 for pPMDSS to 1.425 after 1 h of irradiation. For longer irradiation times, the index increases very slightly to a plateau value at around 1.43−1.44, which is slightly below the value obtained for silica made by high-temperature CVD (1.46).[18]

Strong correlations exist among the chemical composition of the oxycarbide, the refractive index of the films, and the characteristics of the S_1 peak (intensity, position, and shape) for irradiation times below 2 h. Such correlations are not unexpected and have previously been reported in the case of nonstoichiometric SiO_x.[18] For $t > 5$ h, the chemical composition of the silica has almost reached the steady-state composition. We therefore interpret the increase in n_f and the spectral shift of the S_1 peak in terms of a densification of the ceramic matrix, as proposed by Lucovsky et al.[18] A similar densification of a silica matrix accompanied by an increase in refractive index and a decrease in film thickness has been observed in sol−gel-derived silica films as a consequence of UV irradiation.[21]

The chemical conversion of the polymer films into silicon oxycarbide and *a*-SiO_2 is accompanied by a strong decrease in film thickness, which coincides with the decrease in the intensity of the C 1s peak observed by XPS (see Figure 2a). The ratio between the final and initial film thicknesses lies in the range of 0.25−0.28. From the value of this ratio, we can estimate the density of the converted material to be approximately 1.87 g/cm^3, as compared with 2.20 g/cm^3 for fused silica.[18] This low density of the converted *a*-SiO_2 films is consistent with a refractive index of around 1.43 and the characteristics of the FTIR spectrum (S_1 peak position) and suggests an amorphous silica of high porosity.

The surface morphology was probed during the UV−ozone treatment of the films by AFM (see Figure 5). The pPMDSS thin films show a featureless surface with a RMS roughness in the range of 0.27−0.30 nm (12 × 12 μm^2) (Figure 5a) The flatness of the films is maintained after treatment, and the film surface is found to be essentially atomically flat with a RMS roughness of about 0.4 nm over a surface of 12 × 12 μm^2 and with no significant increase in roughness being observed over a larger area. Films obtained after 18 h of UV irradiation show good thermal stability; no changes in the FTIR spectrum are observed after the films are annealed in ambient air for several hours at 400 °C. In contrast to this, the partially converted pPMDSS films obtained after 40 min of UV irradiation show a clear decrease in the intensity of the Si−O−C peaks in the FTIR spectrum, as well as a decrease in thickness after annealing at 400 °C in ambient. Both of these effects are related to the thermal oxidation and densification of the oxycarbide material.

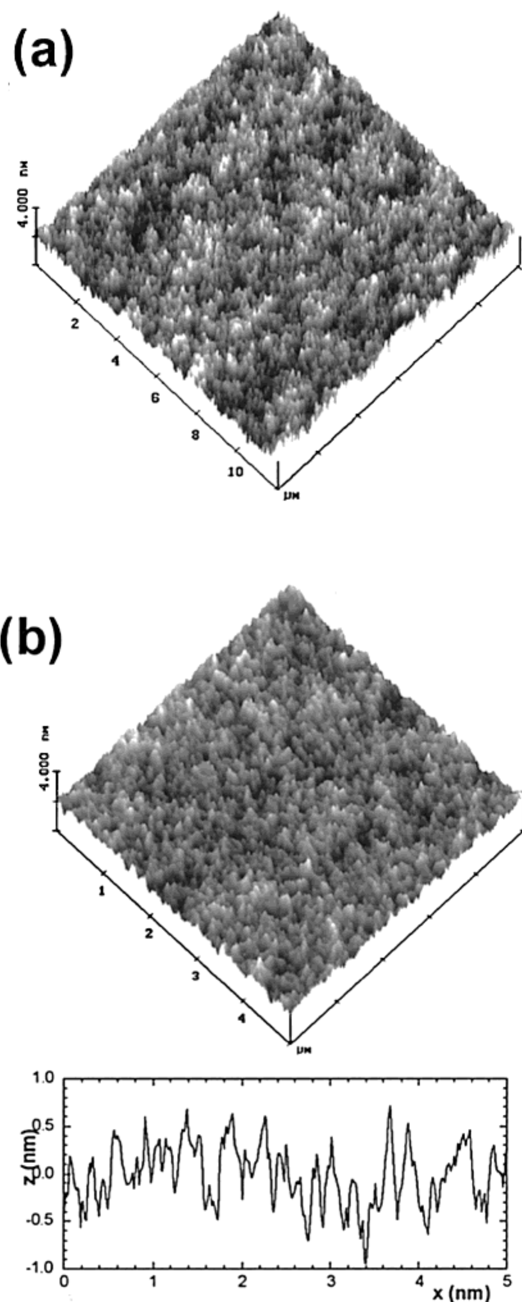

Figure 5. AFM topographic images of (a) an as-spin-coated thin film of pPMDSS (220 nm) and (b) a converted *a*-SiO_2 film after 18 h of UV irradiation in O_2 with the typical AFM section profile of the converted film showing a RMS roughness of less than 0.4 nm over an area of 12 × 12 μm^2.

(21) (a) Imai, H.; Yasumori, M.; Hirashima, H.; Awazu, K.; Onnuki, H. *J. Appl. Phys.* **1997**, *79*, 8304. (b) Maekawa, S.; Ohishi, T. *J. Non-Cryst. Solids* **1994**, *169*, 207.

IV. Conclusions

We have demonstrated the possibility of synthesizing essentially atomically flat *a*-SiO_2 thin films with low residual carbon contamination (below 1 atom %) from pPMDSS by exposure to UV irradiation in a flow of O_2. Optimization of this process, e.g., by shortening the required UV exposure times, can be achieved by increasing the intensity and/or decreasing the wavelength of the UV source or by using an additional ozone generator. Extension of this conversion process to self-assembling silicon-containing block copolymers in order to achieve nanoporous *a*-SiO_2 thin films is in progress. The possibility of converting pPMDSS into *a*-SiO_2 by simple UV-assisted ozonolysis opens some interesting potential applications, especially in the area of soft-printing processing of silicon-containing polymers and their subsequent conversion into *a*-SiO_2 optical waveguide circuits on a silicon substrate.

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