

Plasma-enhanced chemical vapor deposition of SiO₂ from a Si(CH₃)₃Cl precursor and mixtures Ar/O₂ as plasma gas

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Silicon dioxide thin films have been prepared at room temperature by remote plasma-enhanced chemical vapor deposition in a downstream reactor by using Si(CH₃)₃Cl as a volatile precursor and a microwave electron cyclotron resonance external source. Experiments are done at constant pressure by changing the relative amount of Ar species *R* in the plasma gas. The aim was to obtain thin films with low density and, therefore, low refractive index. Characterization of the species of the plasma is carried out by optical emission spectroscopy. The changes of the plasma conditions are correlated with the growing rate and microstructure of the films, the latter determined by atomic force microscopy and infrared spectroscopy. It is found that the growing rate of the films decreases and their roughness increases as *R* increases. The optical properties of SiO₂ thin films are analyzed by optical ellipsometry. A decrease in the refractive index is found for the films grown with high values of *R*. The possible routes for activation of the precursor and the formation of the SiO₂ thin films are discussed. © 2003 American Vacuum Society. [DOI: 10.1116/1.1577134]

I. INTRODUCTION

Silicon dioxide thin films are prepared by a large variety of methods including plasma-enhanced chemical vapor deposition (PECVD). This technique is widely used for this purpose because it permits a low deposition temperature, high deposition rate, etc.¹ Traditionally, SiO₂ thin films have been deposited from SiH₄/O₂ or SiH₄/N₂O plasmas.^{1,2} Other silicon precursors used are SiCl₄,^{1,3} tetraethoxysilane [(TEOS) Si(O(C₂H₅)₄)],⁴ hexamethyldisiloxane [(HDMSO) O(Si(CH₃)₃)₂],⁵ and more recently, tetraethylsilane [(TMS) Si(CH₃)₄]^{6,7} and chlorotrimethylsilane [(TMSCl) Si(CH₃)₃Cl].⁸ These precursors have been utilized in pure form or mixed with oxygen or N₂O. There are some advantages in using organosilicon precursors, such as their safer handling, the fact that they yield a better step coverage, and the possibility to prepare inorganic SiO₂ as well as polymeric SiO_xC_yH_z thin films, depending on the

dilution degree of the precursor in the oxidizing gas.^{9,10} More recently, the use of TMS for preparing SiO₂ thin films by PECVD has been introduced because the films deposited with TMS+O₂ mixtures produce better water repellent layers than thin films deposited by using an ethoxide-like tetramethoxysilane+O₂.¹¹ Other authors have also shown that by using TMS+O₂, it is possible to deposit hydrophobic SiO_x thin films in a corona discharge plasma at atmospheric pressure.⁶ In addition, since TMS and TMSCl do not contain oxygen, it is possible to deposit SiC and polymeric SiC_xH_y thin films^{12,13} without adding to the plasma CH₄ or other hydrocarbons, as has to be done when using SiH₄. However, in contrast with the ample literature existing about the use of SiH₄, TEOS, or HDMSO, much less is known about the use of TMS or TMSCl. In previous works, we have employed the precursor TMSCl to obtain stoichiometric SiO₂ or SiO_xC_yH_z thin films in a remote microwave electron cyclotron resonance (ECR)-PECVD reactor working in a downstream configuration.^{8,14} Moreover, we showed that under our experimental configuration, the existence of a Si—Cl

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bond in TMSCl makes this precursor more susceptible than TMS to chemical attack by the excited species of the plasma.⁸

The use of SiO₂ thin films as an antireflective coating in, for example, photovoltaic cells,¹⁵ requires the fabrication of low refractive index porous coatings of this material. This can be done by increasing the total pressure of the plasma chamber during deposition. This parameter usually favors the condensation processes in the gas phase and, therefore, leads to an enhancement of porosity. However, as a drawback, this procedure usually has detrimental effects with respect to the mechanical stability of the layers because of the poor adhesion between the large aggregates formed in the gas phase.

The present article reports the preparation at room temperature of SiO₂ thin films by using the TMSCl precursor and mixtures Ar/O₂ as plasma gas in a remotely coupled PECVD system. It has been found that, for a constant working pressure, the roughness, growing rate, and other microstructural characteristics of the films depend on the ratio between the plasma gases and precursor. From this study, some clues are deduced about the reaction mechanism of the TMSCl precursor and the deposition processes leading to the formation of the SiO₂ thin film. The dependence of the optical properties of the films on their microstructural characteristics is also examined and discussed in relation with the parameters of the deposition process.

II. EXPERIMENT

Silicon dioxide thin films have been prepared at room temperature by a remote PECVD procedure. Si(CH₃)₃Cl has been used as volatile precursor of Si. The plasma reactor has a "downstream" configuration with an external microwave ECR source (SLAN) operated at 400 W. The source was separated from the reactor by a metallic grid preventing the microwave irradiation of the substrates. This grid allows easy control of the plasma ignition and the separation of the deposition area from the plasma region. Also, owing to the presence of the grid, it is expected that most activated species in the deposition zone are neutral, although it cannot be ruled out that some electrons and positively charged plasma species arrive at the sample position. The distance from the substrate and grid was 10 cm. Pieces of one side polished Si(100) wafers of 3 cm² were placed in the reactor, while the precursor was dosed on top of their surface through a dispersal ring placed 6 cm from the substrate to ensure its homogeneous spatial distribution. The base pressure of the system is lower than 10⁻⁶ Torr. A fully detailed description of the experimental setup has been presented elsewhere.^{8,16} Precursor and plasma gases were dosed by suitable mass flow controllers. Thus, fixed flow rates of 10 sccm for the oxygen and 5 sscm for the precursor were used, while the flow rate of Ar was varied in the range 0–5 sccm. Pure oxygen or mixtures Ar/O₂ were supplied to the source. A total pressure of $\sim 2 \times 10^{-2}$ Torr was maintained constantly in the chamber during deposition by adjusting the pumping capacity of the system with a throttle valve. We have shown previously that this pressure corresponds to the maximum in the depo-

sition rate when pure oxygen is used as plasma gas.⁸ The main parameter followed in this work is the ratio *R* between the Ar flow and the total flow of gases supplied to the reaction chamber (i.e., *R* is the mass flow of Ar divided by the addition of the mass flows of Ar, O₂, and TMSCl). This relative estimation of the Ar added to the plasma gas provides a more appropriate description of the process than the mere Ar/O₂ ratio.

Optical emission spectroscopy was carried out during thin film deposition. The light emitted by the plasma was collected by an optical fiber which was positioned 4 cm downstream from the source center through a hole in the SLAN air cooling ring. The fiber was joined to a monochromator Jobin–Yvon HR250 with a 1200 grooves/mm grating and equipped with a R928 Hamamatsu photomultiplier.

The growth rate was measured with a quartz-crystal monitor placed beside the substrate. The typical thickness of the studied samples was about 500 nm.

Atomic force microscopy (AFM) images were obtained in air by using a Topometrix Explorer microscope working in the noncontact mode. The cantilever (supplied by Topometrix) with a spring constant of 42.6 N m⁻¹ was oscillated at 130 kHz. Amplitude reduction was monitored while the surface is scanned at a typical rate of one line per second. The scanner was calibrated in the *X*, *Y*, and *Z* directions with gratings provided with the equipment. Both topographic (constant force) and direct signal (constant height) images were acquired.

Fourier transform infrared (FT-IR) spectra were collected in transmission mode at normal geometry in a Nicolet 510 spectrometer for samples deposited on Si(100) wafers. The thicknesses of the analyzed samples have been chosen to avoid the saturation of the infrared signal, thus enabling the comparison of the relative intensity of the bands.

Rutherford backscattering spectroscopy (RBS) measurements of the films were performed in the Ion Accelerator ARAMIS (Orsay, France) using 1.5 MeV α particles. The energy resolution of the detector used in the RBS measurements was 15 keV. The spectra were simulated using the RUMP code. The samples have been deposited on Si(100) and channeling was used to improve the sensitivity of the technique for the SiO₂ thin films.

Spectroscopic ellipsometry experiments were performed using a SOPRA commercially available system. The measurements of ellipsometric parameters were made within a wavelength range from 0.21 μ m to 1.2 μ m at different angles of incidence (65°, 70°, and 75°). These are the most sensitive angles, since they are close to the Brewster angle of a silicon substrate. For the studied films, the first step of the analysis procedure consists of a regression using a Cauchy law to simulate the refractive index $n(\lambda)$, the extinction coefficient $k(\lambda)$, and the thickness of the layer. In a second step, the layer thickness was fixed as determined herein and a point-by-point extraction of the complex refractive index was performed at each wavelength.

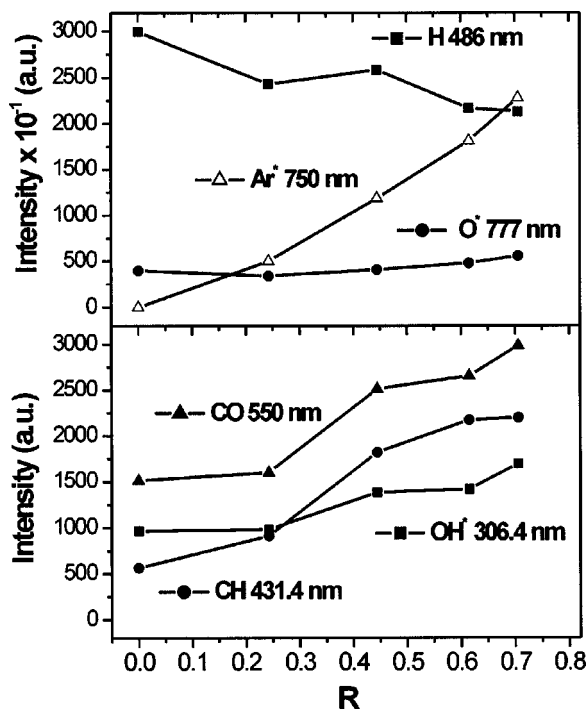


FIG. 1. Intensity of the indicated emission lines excited in the plasma reactor as a function of R .

III. RESULTS AND DISCUSSION

A. Plasma characterization and deposition process

Optical emission spectra of the plasma were recorded for increasing values of R . The spectra of oxygen/argon plasmas (without precursor) are dominated by sharp lines due to emission from atomic oxygen or argon and by several molecular bands resulting from transitions between low vibrational levels of the O₂⁺ species. The addition of the precursor to the reactor increases the emission from the lines of atomic hydrogen in detriment to those of oxygen or argon. Thus, the optical emission spectra of the Ar/O₂/TMSCl mixture, apart from the lines due to oxygen and argon, exhibit strong emission lines due to H* (lines of the Balmer series) and other excited species such as CH*, CO*, CO⁺, OH*, etc., the latter very likely coming from the fragmentation and oxidation of the precursor molecule. A systematic analysis of the variation in intensity of some selected lines can be used to understand some of the reaction pathways of species in the plasma. Figure 1 shows the variation of the intensity of emission lines/bands (Ar* at 750 nm, O* at 777 nm, H* at 486 nm, OH* at 306.4 nm, CH* at 431.4 nm, and CO* at 507.1 nm) with R . The assignments of these signals have been done in agreement with the Refs. 17 and 18. The plot of Fig. 1 shows a net increase in the intensity of the Ar* line as R increases, while the O* emission increases only very slightly and the H* emission decreases. On the other hand, the emissions corresponding to CH* and OH* bands increase as R increases. The intensity of the CO* remains practically constant when Ar is added to the discharge.

As a first approximation, the intensity of H* lines can be

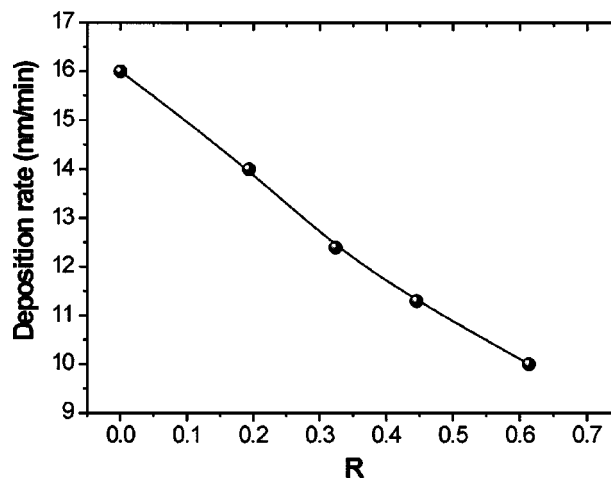


FIG. 2. Deposition rate of SiO₂ thin films as a function of R . The line is plotted to guide the eyes.

taken as a trace of the degree of fragmentation of the precursor molecule in the plasma (note, however, that this is not rigorously true because the electron density and/or temperature may also contribute to changes in the intensity of the H* emission). Figure 1 clearly shows that the yield of this process decreases as the Ar content in the plasma increases. It is also important to mention that, for a given value of R , the intensity of all emission lines increases with the microwave power.

The growth rate of the SiO₂ thin film was also determined as a function of R . Figure 2 shows that the deposition rate of the film diminishes almost linearly with R . We would also like to stress that no deposition was observed when only pure Ar was used as plasma gas or when TMS was used as a silicon precursor molecule instead of TMSCl. In the case of TMS, no deposition is observed either when O₂ or mixtures Ar/O₂ are used as plasma gas,⁸ while for TMSCl, the growth rate increases for increasing precursor flow.

B. Thin-film characterization

The thin-film samples prepared in this work were analyzed by RBS to determine their composition. All of them had a silicon dioxide stoichiometry (i.e., O/Si ratio equal to 2) and no traces of Cl or C were detected. Therefore, the samples, at least up to the sensitivity limit of the RBS spectroscopy (≤ 5 at. % for C and ≤ 1 at. % for Cl), can be considered as free from these elements present in the TMSCl precursor.

The microstructure of the deposited SiO₂ thin films was investigated by AFM and FT-IR. Figure 3 shows as an example two AFM images of the surface of SiO₂ thin films corresponding to $R=0$ [i.e., Fig. 3(a)] and $R=0.6$ [i.e., Fig. 3(b)]. These images clearly show that the roughness of the films increases with the relative concentration of Ar. A more quantitative evaluation of the roughness of the films is provided by the root-mean-square (rms) surface roughness values. Figure 4 shows the variation of the rms surface roughness for SiO₂ thin films prepared with increasing relative

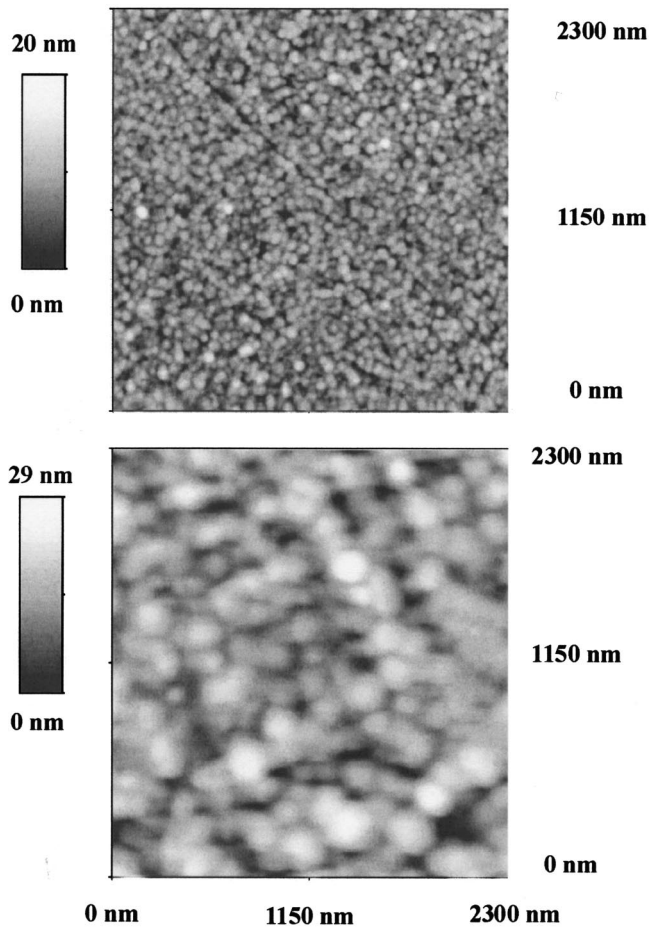


FIG. 3. AFM images of SiO₂ thin films prepared with $R=0$ (a) and 0.6 (b).

amounts of Ar in the plasma gas. It is found that the rms surface roughness increases as the Ar concentration in the plasma increases.

Figure 5 shows FT-IR spectra of SiO₂ samples prepared with increasing concentrations of Ar. It is important to note

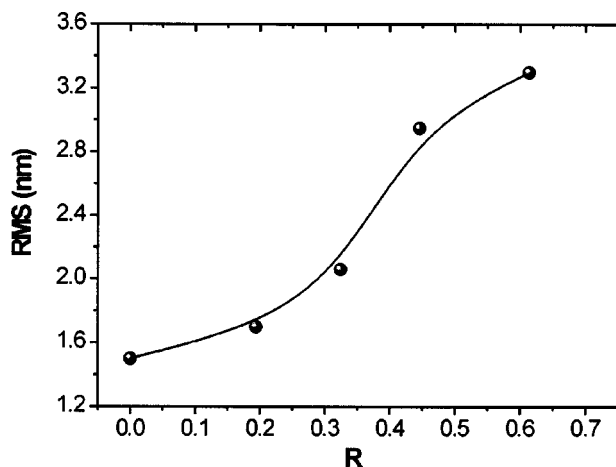


FIG. 4. rms surface roughness of SiO₂ thin films as a function of R . The line is plotted to guide the eyes.

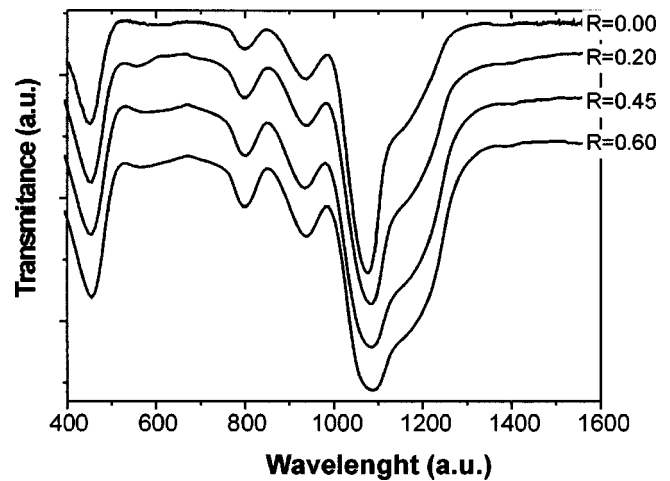


FIG. 5. FT-IR spectra of SiO₂ thin films prepared with different values of R .

that no signals from organic groups⁸ are detected in the FT-IR spectra for any of the deposited thin films, indicating that even if the investigated process is carried out at room temperature, the complete removal of organic groups takes place. The different peaks and shoulders in the 400–1500 cm^{-1} region have been attributed to the vibrational modes of elemental SiO₄ tetrahedral forming the structure of the SiO₂ thin films.^{14,19–21} They can be assigned to a transversal optical (TO₁) rocking mode (460 cm^{-1}), a TO₂ bending mode (800 cm^{-1}), an asymmetric stretching mode (the big band at ~ 1070 cm^{-1}), a TO₄ asymmetric mode (1170 cm^{-1}), and its corresponding longitudinal mode LO₄ (1200 cm^{-1}). These two latter bands give rise to the well defined shoulder at the right-hand side of the most intense band at ~ 1090 cm^{-1} . Si—OH and Si—O⁻ rocking (578 cm^{-1}) and stretching (960 cm^{-1}) modes can be also detected in the spectra. The 960 cm^{-1} peak increases with the value of R in agreement with an increase of the incorporation of OH⁻ groups in the less compact SiO₂ thin films. The relative intensity of the shoulder at 1200 cm^{-1} (due to the contribution of several elemental bands as has been mentioned herein) has sometimes been taken as a measure of the degree of porosity of the films (see Ref. 14 and references therein and Ref. 19). Although some other factors besides compactness may contribute to this intensity, the results obtained here show a parallel tendency of shoulder intensity, rms surface roughness values and, as it will be shown in the next subsection, decrease in the density of the films.

C. Optical properties

The optical properties of the SiO₂ thin films prepared under different conditions were determined by spectroscopic ellipsometry. Figure 6 shows the refractive index $n(\lambda)$ and the extinction coefficient $k(\lambda)$ as a function of the wavelength λ , for thin films prepared with different values of R . The plot shows that the refractive index of the films decreases as the relative amount of Ar in the plasma gas increases, for the entire wavelength range.

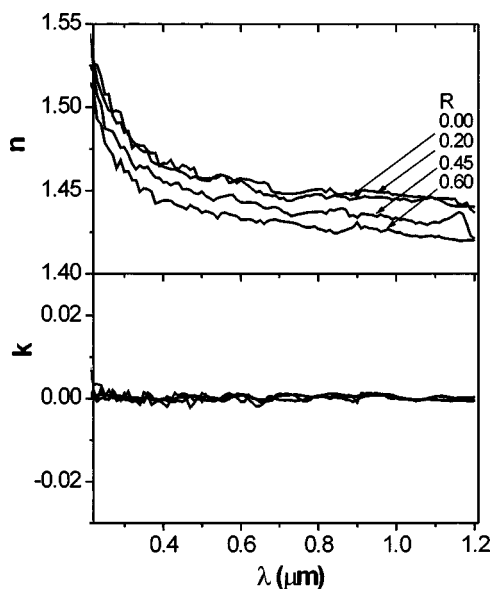


FIG. 6. Refractive index n and extinction coefficient k for SiO₂ thin films deposited with different values of R .

It is possible to estimate changes in the density ρ of the SiO₂ thin films from the variation of their refractive indices. It has been reported^{22,23} that in the case of SiO₂, $\Delta\rho=5 \times \Delta n \text{ g cm}^{-3}$. In the present case, a maximum change of 0.023 is found in the value of n for practically all of the visible region. This difference in n gives a maximum difference in density $\Delta\rho=0.11 \text{ g cm}^{-3}$, between the most and least compact SiO₂ thin films reported here. The less compact films are those prepared at high values of R . This tendency agrees with the higher degree of roughness and porosity deduced from the AFM and FT-IR characterization analysis of the samples (cf. Figs. 3–5).

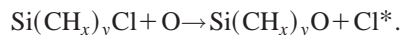
It is also worth noting that all of the samples were totally transparent (k values equal to zero on the whole spectral range) with independence of the R value, and that no light scattering was detected in any of the deposited films, as it would happen if the size of the aggregates were large enough to scatter visible light. The high transparency of the thin films supports the possible use of the less compact thin films as antireflective coatings for photovoltaic or similar applications.¹⁵

D. Plasma-enhanced chemical vapor deposition thin-film formation with TMSCl and mixtures Ar/O₂

The choice of TMSCl as volatile precursor of Si rather than TMS has been imposed, under our experimental conditions, by the fact that no thin-film deposition is found in this latter case either by using pure O₂ or mixtures O₂/Ar as plasma gas. This results contrasts with those reported by other authors showing the formation of SiO₂ thin films by using TMS in plasma microwave reactors with downstream configurations.^{13,24} Jauberteau *et al.*²⁵ have reported that an afterglow Ar plasma may yield a large fragmentation of the TMS molecule, mainly via Si—C bond breaking. This pro-

cess principally generates Si(CH₃) fragments. Radicals formed through the dissociation of C—H bonds [i.e., SiC_{*x*}H_{*y*} radicals ($y < 3x$)] may be also produced, though with smaller efficiency. In our system, a process similar to the first one does not seem to occur because there is no deposition with TMS under any condition or with TMSCl with an Ar plasma. However, we believe that the polymerization of intermediate radicals of silicon produced through an alternative mechanism could contribute to the formation of the film (see next).

The different behavior found in our experiment by using TMS or TMSCl precursors⁸ points to that a Si—Cl bond in the precursor molecule favors its decomposition by the plasma to produce SiO₂ thin films. The fact that no chlorine is detected in the films supports that this atom is removed during the first stages of the reaction mechanism and that no, or very few, fragments containing this atom arrive to the growing film surface. Thus, it is very likely that the first or one of the initial steps in the deposition mechanism of the films is the attack of the Si—Cl bond by some activated species of the plasma and/or free electrons. Since in our experimental configuration the concentration of free electrons and ionic species in the deposition zone must be rather small, we assume that oxygen species are most important for the activation of the precursor molecule. Thus, such activation could be written schematically as



With this process, we propose that activated oxygen species intervene in the initial activation steps of the precursor molecule leading to the removal of chlorine and the formation of Si-containing radicals, either in the gas phase or adsorbed on the surface. It has to be mentioned that the intensity of the O* emission line at 777 nm remains practically constant independently of the value of the parameter R , a feature that points to a complex nature of the whole deposition process and stresses the need of considering other parameters, like concentration and energy of free electrons, other radicals, the role of Ar, etc., which are not accessible in our experiment.

Although, we do not have enough evidence to propose a complete mechanism to account for the formation of the SiO₂ thin films, in line with the previous results by Jauberteau²⁵ and other authors,^{9,10} it is reasonable to assume that the formation of the oxide film from TMSCl is a process that involves the adsorption on the substrate of either the precursor molecule or some reactive fragments resulting from its activation and eventual fragmentation. On the surface, the competition between the polymerization of these fragments to yield SiO_{*x*}C_{*y*}H_{*z*} polymeric chains and the oxidation or etching of organic fragments of these films leading to the removal of organic components will control the formation of Si—O bonds. In fact, previous results of our laboratory using TMSCl and pure oxygen plasmas⁸ showed that it is possible to deposit SiO_{*x*}C_{*y*}H_{*z*} thin films when the flow of oxygen is lower than that of the precursor flow. In the present investigation, the increase with R of the intensity of the emis-

sion lines of OH* and CH* species (cf. Fig. 1) might indicate that the Ar addition favors the etching and oxidation at the surface of the organosilicon fragments, a process that has been reported previously by other authors.^{25,26,22}

Within this phenomenological description, it is possible to reconcile the high roughness with the low growing rate as well as the SiO₂ composition of the prepared thin films by assuming that intermediate siliconelike layers and/or fragments are being produced during the deposition of the films. Then, this polymeric material deposited on the surface is further oxidized by the plasma to yield gases (CO₂ and H₂O) that would be desorbed whereas SiC_xO_yH_z layers or fragments are being incorporated onto the surface. The release of volatile compounds is likely to yield films with a large roughness and porosity as has been actually observed here by AFM and FT-IR characterization.

IV. CONCLUSIONS

It has been shown that TMSCl is a suitable precursor for the deposition of SiO₂ thin films by PECVD using mixtures Ar/O₂ as plasma gas and a microwave ECR plasma system in a downstream configuration. Under these conditions, no deposition was found by using TMS, thus indicating that the existence of a C—Cl bond favors the plasma activation of the precursor molecule. SiO₂ with no traces of Cl was obtained in all cases. This supports that Cl is being removed during the first steps of activation of the precursor molecule. It has been found that the thin-film microstructure and growth rate depend on the plasma conditions. Increasing the relative concentration of Ar in the plasma gas at constant total pressure leads to a decrease in the growing rate by a factor of 0.6 and, unexpectedly, to an increase in the film roughness and porosity. As a consequence, the refractive index of the films can be tailored by controlling the relative concentration of Ar in the plasma gas. This technique could be very useful for the synthesis of antireflective SiO₂ thin films of interest in photovoltaic and similar applications.

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- ¹A. Grill, *Cold Plasma in Materials Fabrication* (IEEE, New York, 1994).
- ²C. Charles, G. Giroult-Matlakowski, R. W. Goswell, A. Goullet, G. Turban, and C. Cardinaud, *J. Vac. Sci. Technol. A* **11**, 2954 (1993).
- ³A. Ortiz, S. López, C. Falcony, M. Farias, L. C. Araiza, and G. Soto, *J. Electron. Mater.* **19**, 1411 (1990).
- ⁴A. Granier, C. Vallée, A. Goullet, K. Aumaille, and G. Turban, *J. Vac. Sci. Technol. A* **17**, 2470 (1999).
- ⁵J. Schwarz, M. Schmidt, and A. Ohl, *Surf. Coat. Technol.* **98**, 859 (1998).
- ⁶R. Thyen, A. Weber, and C. P. Klages, *Surf. Coat. Technol.* **97**, 426 (1997).
- ⁷Y. Inoue, H. Sugimura, and O. Takai, *Thin Solid Films* **345**, 90 (1999).
- ⁸A. Barranco, J. Cotrino, F. Yubero, J. P. Espinós, J. Benítez, C. Clerc, and A. R. González-Elipe, *Thin Solid Films* **401**, 150 (2001).
- ⁹*Plasma Processing of Polymers*, edited by R. d'Agostino, P. Favia, and F. Fracassi (Kluwer, Dordrecht, 1997), Chap. 5 (and references therein).
- ¹⁰C. Vallée, A. Goullet, A. Granier, A. van der Lee, J. Durand, and C. Marlière, *J. Non-Cryst. Solids* **272**, 163 (2000).
- ¹¹A. Hozumi and O. Takai, *Thin Solid Films* **334**, 54 (1998).
- ¹²D. S. Kim and Y. H. Lee, *Thin Solid Films* **283**, 109 (1996).
- ¹³A. Grill and V. Patel, *J. Appl. Phys.* **85**, 3314 (1999).
- ¹⁴A. Barranco, F. Yubero, J. Cotrino, J. P. Espinós, J. Benítez, T. C. Rojas, J. Allain, T. Girardeau, J. P. Rivière, and A. R. González-Elipe, *Thin Solid Films* **396**, 9 (2001).
- ¹⁵H. Nagel, A. Metz, and R. Hezel, *Sol. Energy Mater. Sol. Cells* **65**, 71 (2001).
- ¹⁶J. Cotrino, A. Palmero, V. Rico, A. Barranco, and A. R. González-Elipe, *J. Vac. Sci. Technol. B* **19**, 410 (2001).
- ¹⁷National Institute of Standards and Technology, <http://physics.nist.gov> (2002).
- ¹⁸R. W. B. Pearse and A. G. Gayden, *The Identification of the Molecular Spectra* (Chapman and Hall, London, 1976).
- ¹⁹C. T. Kirk, *Phys. Rev. B* **38**, 1255 (1988).
- ²⁰R. M. Almeida, T. A. Guiton, and C. G. Pantano, *J. Non-Cryst. Solids* **121**, 193 (1990).
- ²¹P. Lange, *J. Appl. Phys.* **66**, 2001 (1989).
- ²²L. Zajíčková, J. Janca, and V. Perina, *Thin Solid Films* **338**, 49 (1999).
- ²³R. A. B. Devine, *Trans. Mater. Res. Soc. Jpn.* **8**, 165 (1992).
- ²⁴A. M. Wróbel and Y. Hatanaka, in *Plasma Processing of Polymers*, edited by R. d'Agostino, P. Favia, and F. Fracassi (Kluwer, Dordrecht, 1997), p. 334.
- ²⁵J. L. Jauberteau, I. Jauberteau, and J. Auberton, *Chem. Phys. Lett.* **327**, 351 (2000).
- ²⁶C. E. Viana, N. I. Morimoto, and O. Bonnaud, *Microelectron. Reliab.* **40**, 613 (2000).