Growth of SiC and SiC$_x$N$_y$ films by pulsed laser ablation of SiC in Ar and N$_2$ environments

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Amorphous SiC and SiC$_x$N$_y$ films have been deposited by pulsed laser deposition on single crystal silicon substrates by KrF (248 nm) excimer laser ablation of a SiC sintered target in a vacuum system at room temperature using nonreactive, Ar, and reactive, N$_2$, background gases at different pressures. The pressure range in the growth chamber was from 4×10^{-8} Torr to 80 mTorr. The optical properties and stoichiometry of films were varied by the introduction of a background gas. The resulting films are inspected by spectroellipsometry in the photon-energy range of $1.5<h\nu<5.0$ eV. *In situ* high resolution x-ray photoemission spectroscopy characterization was performed on every film to obtain the atomic concentration and bonding constitution of the elements as a function of background gas pressure. The ideal stoichiometry for SiC films was obtained at Ar pressures higher than 30 mT. The existence of a new phase, given by SiCN$_2$, was suggested from surface techniques and ellipsometric data in the deposition of SiC$_x$N$_y$ films at N$_2$ pressures higher than 30 mTorr. © *1998 American Vacuum Society.* [S0734-2101(98)08603-5]

I. INTRODUCTION

Pulsed laser deposition (PLD) is now a well established technique to produce a wide variety of thin films.[1] High quality ceramic films can be processed by PLD at much lower temperatures than by other methods, like chemical vapor deposition (CVD) and rf sputtering. Films processed by PLD are usually accomplished by excimer lasers. The photon energy depends on the kind of gas mixture used to produce the excimers. For instance, photons with a 5 eV energy are produced when KrF is used. The interaction of intense laser pulses with the target generates particles which manifest nonequilibrium features, such as electronically and atomically excited species with high kinetic energies. These particles could lead to the formation and growth of films in metastable states with chemical control. These advantages have made PLD a unique technique to grow thin films of complex, multicomponent ceramics.

Thin films of ultrahard materials are of great technological interest. The synthesis of new ceramics with hardness as high as diamond is a challenge to materials scientists. Liu *et al.*[2] theoretically found a compound that can be compared to diamond in hardness. The proposed structure is similar to that of β-Si$_3$N$_4$, where the silicon atoms are replaced by carbon atoms. Since then, many groups have unsuccessfully tried to synthesize β-C$_3$N$_4$.[3–5]

Gómez *et al.*[6] suggested that if β-Si$_3$N$_4$ and β-C$_3$N$_4$ have the same structure, it might be expected that both should be miscible giving rise to SiCN alloys. Miyagawa *et al.*[7] have demonstrated that nitrogen-ion implantation in silicon carbide produces a surface layer with an intermediate state SiC$_x$N$_y$ or into Si$_3$N$_4$ under appropriate conditions. Bendedouche *et al.*[8] stated that the properties of this new material could be an interesting combination of silicon carbide, a semiconductor, and silicon nitride, a dielectric. In other words, it might be a hard material with a wide band gap having interesting optical and electronic properties.

One of the most technologically interesting wide band gap semiconductors is silicon carbide. The energy gap value depends on polytype and lies between 2.4 eV for 3C–SiC to 3.33 eV for 2H–SiC.[9] Conventional semiconductors like silicon (energy gap of 1.1 eV) and gallium arsenide (energy gap of 1.43 eV) are suited for ordinary circuitry, but fail at temperatures higher than 125 °C. Prototype semiconductor devices based on silicon carbide have shown remarkable performance at high temperatures, high powers, and high frequency applications.[10] Silicon carbide chips might go onto high-power microwave transmitters, automobile, and aircraft engines, etc. Zehnder *et al.*[11] and Balooch *et al.*[12] have successfully grown β-SiC (3C–SiC polytype) films by means of PLD. These two experiments were performed in vacuum and the resultant films were almost stoichiometric. According to the literature,[13] the films grown by PLD in vacuum do not necessarily preserve the target stoichiometry. For instance, an oxidizing environment is usually maintained during the deposition of high T_c superconducting films to help forming the desired composition. Venkatesan *et al.*[14] and Gonzalo *et al.*[15] have demonstrated that the interaction of the ablated species in the plume with a reactive or nonreactive background gas improves the morphology and modifies the stoichiometry of the deposited films. A naive conjecture of these investigations is that the composition of films can be altered by introducing a background gas during the deposition process. As the pressure of the background gas is raised, the collisions between the ablation plume species and the gas molecules become more frequent. The resultant films might be stoichiometric if the gas is nonreactive or new compounds if the gas is reactive. In the current work, this hypothesis is

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tested by growing SiC thin films in vacuum, Ar (nonreactive), and N_2 (reactive) gases.

The evolution and control of properties and stoichiometry of SiC and SiC_xN_y thin films by PLD in the 5 to 80 mTorr pressure range of Ar and N_2, respectively, has been investigated. The films deposited in a background gas atmosphere are compared to the one grown in vacuum, 4×10^{-8} Torr, under similar experimental conditions. Surface and optical spectroscopies are used to determine the bonding state and optical properties, respectively, of the as-grown films. The atomic concentration of each component and bond formation in the film were studied by *in situ* x-ray photoemission spectroscopy (XPS). The optical properties such as refractive index and optical band gap were determined by *in situ* spectroellipsometry at the end of the deposition. The experimental measurements were compared to data reported in the literature.

The experimental setup and procedure are explained in Sec. II. The experimental data and discussion of results are given in Sec. III; the XPS and ellipsometric measurements are shown in Secs. III A and III B, respectively. The conclusions of this work are summarized in Sec. IV.

II. EXPERIMENTAL PROCEDURE

The films were deposited in a custom made laser ablation system. This equipment consists of three vacuum chambers: sample loading, film growth, and analysis. Each chamber is independently evacuated by an ion pump, and isolated by UHV gate valves. The growth chamber is equipped with two fused silica viewports suitable for *in situ* ellipsometry and a UV transparent window. The target was a commercially available SiC sintered target, 99.9% purity, ablated by means of a KrF excimer laser ($\lambda=248$ nm, 30 ns pulse width) at a rate of 10 pulses per second and an energy of 800 mJ per pulse, corresponding to a fluence of 5 J/cm^2 at the target surface. The laser beam hits the target at an angle of 50° off the surface normal. The formation of craters on the target surface is minimized by a motorized X-Y scan. The substrates were Si(100) and Si(111) wafers, which have well documented optical properties,[16] degreased in acetone and isopropyl alcohol bath before being introduced into the growth chamber. All depositions were performed keeping the substrates at room temperature and facing the target at a distance of 10 cm, the laser parameters mentioned above were also maintained fixed for 10 000 laser pulses.

The growth chamber is evacuated to a base pressure of 10^{-8} Torr before the actual deposition process was started. The deposition is done at vacuum and in the presence of Ar for silicon carbide films; whereas, high purity molecular nitrogen is introduced for growing SiC_xN_y films. The ion pumps of the system are isolated when the background gases are introduced, and a turbo molecular pump is used to sustain a pressure in the 5 to 80 mTorr pressure range during deposition.

In situ spectroscopical ellipsometric analysis was performed with a phase modulated ellipsometer (Jobin–Yvon, UVISEL). The ellipsometric parameters (ψ,Δ) were measured in the 1.5 to 5 eV photon-energy range to determine the optical properties of the various films at the end of the deposition process. Kinetic ellipsometry was also done during deposition to qualitatively determine the films absorbance. Afterwards, the samples were transferred to the adjacent analysis chamber to characterize the films using *in situ* surface spectroscopies (CAMECA, MAC-3). XPS data were collected by means of Mg $K\alpha$ radiation, 1253.6 eV, calibrating the energy scale using the reference binding energies of Cu $2p_{3/2}$ at 932.67 eV and Ag $3d_{5/2}$ at 368.26 eV. The full width at half maximum value (FWHM) measured value of C_{graphite} $1s$ resulted to 1.2 eV, 1 eV being the nominal value for high resolution XPS. The film morphology was studied by scanning electron microscopy (SEM).

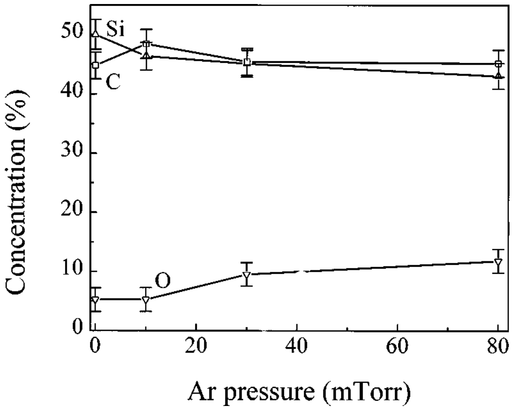

FIG. 1. Atomic concentration of the elements which form thin films grown when a SiC target is ablated in an Ar environment as a function of the gas pressure. The silicon, carbon, and oxygen concentration correspond to up triangle, square, and down triangle symbols.

III. EXPERIMENTAL RESULTS AND DISCUSSION

A. Surface analysis

The atomic concentration of each component in the films was obtained by integrating the peak area after linear subtraction from the XPS data for the N $1s$, C $1s$, Si $2p$, and O $1s$ core levels. Figure 1 shows the concentration of C, Si, and O as a function of argon pressure, p_{Ar}, for as-deposited SiC films, and Fig. 2 shows the concentration of C, Si, N, and O as a function of nitrogen pressure, p_{N_2}, for as-deposited SiC_xN_y films. The Ar signal was also present in the XPS measurements, but it was so small that it could not be quantified. It can be observed from Fig. 1 that the concentration of Si, C, and O are 50%, 45%, and 5%, respectively, for SiC films deposited in vacuum, 4×10^{-8} Torr. These values agree with the concentrations reported by Zehnder *et al.* for SiC films grown under the same conditions but sputtered clean prior to surface analysis.[11] The concentration of Si and C are slightly changed at higher pressures; in particular, these concentrations are practically the same, 45%, at $p_{\text{Ar}}\geqslant30$ mTorr. The concentration of oxygen kept constant and small, 10%, at $p_{\text{Ar}}\geqslant30$ mTorr, this is obviously an unwanted contaminant in the films.

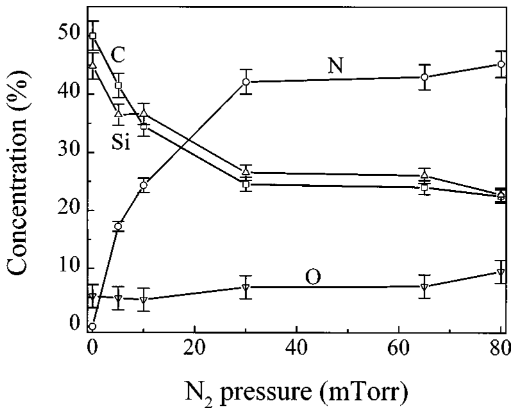

FIG. 2. Atomic concentration of the elements which form thin films grown when a SiC target is ablated in a N_2 environment as a function of the gas pressure. The silicon, carbon, oxygen, and nitrogen concentration correspond to triangle, square, inverted triangle, and circle symbols.

TABLE I. Experimental binding energies of different core levels as determined from this investigation for the growth of SiC and SiC$_x$N$_y$ films at different Ar and N_2 pressures, respectively, compared to values reported in the literature.

	Si 2*p*	C 1*s*	N 1*s*	O 1*s*
Si *n* type (Ref. 17)	99.3	⋯	⋯	⋯
C graphite (Ref. 17)	⋯	284.5	⋯	⋯
C diamond (Ref. 18)	⋯	284.8	⋯	⋯
SiC (Ref. 18)	100.5	283.4	⋯	⋯
Si_3N_4(Ref. 17)	101.8	⋯	397.4	⋯
N_2 physisorbed on graphite (Ref. 19)	⋯	⋯	404	⋯
SiO_2 (Ref. 17)	103.3	⋯	⋯	532.5
SiC-vacuum	100.8	283.6	⋯	negligible
30 mTorr Ar	100.5	283.3	⋯	532.5
SiCN - 5 mTorr N_2	101.5	284.1	398.1	532.5
- 10 mTorr N_2	101.6	284.2	398.1	532.5
- 30 mTorr N_2	102.1	284.9	398.3	532.5
- 80 mTorr N_2	102.8	285.9	398.3	532.5

Figure 2 shows that nitrogen content increases from 17% at $p_{N_2} \approx 5$ mTorr up to 43% at $p_{N_2} \approx 30$ mTorr, the nitrogen concentration keeps constant at $p_{N_2} \geqslant 30$ mTorr. At the same time, the concentration of C and Si decrease from 50% and 45%, respectively, at 4×10^{-8} Torr down to approximately 25% at $p_{N_2} \approx 30$ mTorr for both components, and remaining unchanged at $p_{N_2} \geqslant 30$ mTorr. A small oxygen contamination, never higher than 8%, is always present with the other elements in the films.

High resolution XPS spectra around the N 1*s*, C 1*s*, and Si 2*p* core levels are shown in Fig. 3 and the measured binding energies corresponding to these levels are given in Table I for as-deposited films as a function of nitrogen gas pressure. The reported values of binding energies of some single elements and compounds are included in Table I as a comparison.[17–19] As observed from Table I, the binding energies of C 1*s* and Si 2*p* of the film grown in vacuum are very similar to the binding energies of the one grown at $p_{\mathrm{Ar}} \approx 30$ mTorr, having these last values a better accordance with the reported values for pure SiC films.[18] In fact, this observation agrees with Fig. 1 because the ideal stoichiometry for silicon carbide resulted to be at $p_{\mathrm{Ar}} \approx 30$ mTorr. The binding energies of C 1*s* and Si 2*p* for the SiC$_x$N$_y$ film grown at $p_{N_2} = 10$ mTorr have shifted by 0.6 and 0.8 eV, respectively, referred to the deposition in vacuum. This result also agrees with those shown in Fig. 2. It can also be observed from Table I that the N 1*s*, C 1*s*, and Si 2*p* peaks for the SiC$_x$N$_y$ film grown at $p_{N_2} = 80$ mTorr have moved 0.2, 1.7, and 1.2 eV, respectively, with respect to the deposition at $p_{N_2} = 10$ mTorr. The shift of the core levels suggests that a new compound starts to be formed in the film when N_2 is introduced. However, this is not the only signal of the synthesis of a new compound. The FWHM values of the peaks shown in Fig. 3 became significantly broader at 80 mTorr relative to 10 mTorr; i.e., they grew from 1.8 to 2.6 eV for the N 1*s* peak, from 2.2 to 5.0 eV for C 1*s*, and from 2.0 to 2.6 eV for Si 2*p*. Therefore, the C 1*s* and Si 2*p* spectra of SiC$_x$N$_y$ films grown at $p_{N_2} = 80$ mTorr are composed of more than one peak.

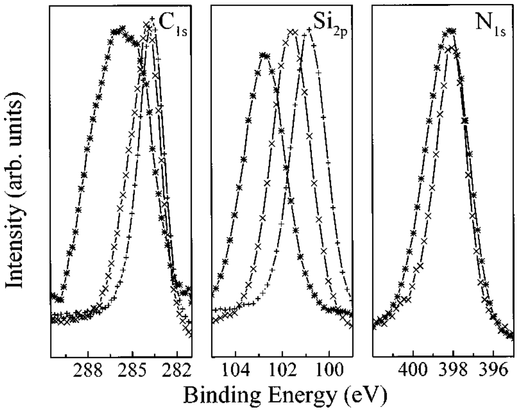

FIG. 3. High resolution XPS spectra around the N 1*s*, C 1*s*, and Si 2*p* peaks of SiC$_x$N$_y$ films deposited in vacuum at 4×10^{-8} Torr (+), and in a N_2 environment at 10 (×) and 80 mTorr (*).

The actual bonding state of the film constituents can be inferred by deconvoluting these spectra, as shown in Fig. 4. In particular, the C 1*s* peak is quite asymmetric and very broad, revealing the presence of at least three distinct bonds of carbon. The peaks were determined to be at 284.1, 286.0, and 287.7 eV, which correspond to the reported values for C–C, C–N, and C–O bonds,[6] respectively. The overlap of these three peaks fit well to the experimental data of C 1*s*, as observed in Fig. 4. The Si 2*p* peak was found to be composed of at least two distinct bonds of silicon. The peaks are located at 102.6 and 103.7 eV, which correspond to Si–N and Si–O, according to the literature.[6] The superposition of these two peaks are also in accord to the experimental measurements of the Si 2*p* spectrum. The absence of a Si–C bond in the deconvolution of the C 1*s* and Si 2*p* peaks is a clear indication that a new material is formed. The nonexistence of SiC in the SiC$_x$N$_y$ films is probably due to a local network of Si–N and C–N bonds in the films which inhibits the Si–C bond formation, as speculated by Gómez *et al.*[6]

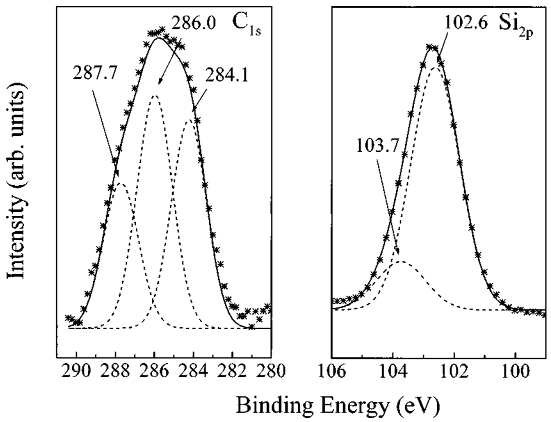

FIG. 4. Deconvolution of the C 1*s* and Si 2*p* transitions of the SiC_xN_y film deposited at $p_{N_2}=80$ mTorr. The deconvoluted peaks are shown as slashed lines, while their corresponding XPS peaks are shown as solid lines.

B. Ellipsometric analysis

The index of refraction, n, and extinction coefficient, k, of the deposited films were measured by *in situ* spectroscopic ellipsometry, the results are shown in Figs. 5 and 6. The experimental curves of (n,k) were fitted using the amorphous semiconductor model, implemented in the ellipsometer's software,[19] valid in the visible to near-UV range, and assuming the whole film has the same optical properties. A trial and error routine based on the Levenberg–Marquardt method complements the fitting procedure.[20]

Silicon carbide films grown in vacuum and at $p_{Ar}=10$ mTorr are highly absorbing as observed from Fig. 5. This is probably due to the nonideal film stoichiometry, see Fig. 1. The spectral response of pure Si shows a similar behavior to the n values for SiC films grown in vacuum, they decrease in the 3.5 to 5 eV photon energy range.[16] However, the n and k values decrease when the gas pressure is raised for silicon carbide films grown in an Ar atmosphere, as shown in Fig. 5 the films are less absorbent at $p_{Ar}=80$ mTorr. The values of k in the 2 to 5 eV photon energy range are very close to the reported values, but the n values are different.[6]

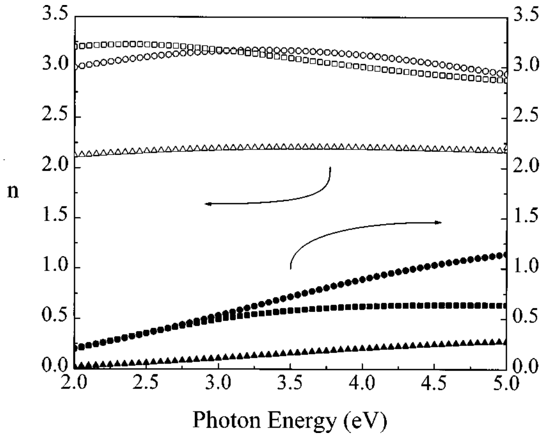

FIG. 5. Real and imaginary parts (n,k) of the refractive index vs photon energy of thin films grown when a SiC target is ablated in vacuum at 4×10^{-8} Torr (circles), and in an Ar atmosphere at 10 (squares) and 80 mTorr (triangles). The hollow and solid symbols correspond to n and k, respectively.

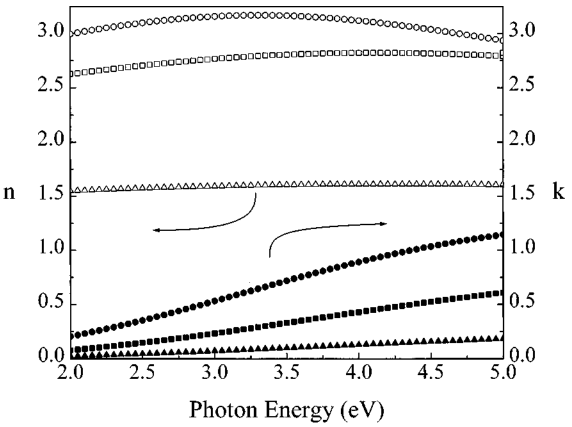

FIG. 6. Real and imaginary parts (n,k) of the refractive index vs photon energy of thin films grown when a SiC target is ablated in vacuum at 4×10^{-8} Torr (circles), and in a N_2 atmosphere at 10 (squares) and 80 mTorr (triangles). The hollow and solid symbols correspond to n and k, respectively.

Similarly, the n and k values decrease when the gas pressure is raised for SiC_xN_y films grown in an N_2 atmosphere. In particular, the values of n and k in the 2 to 5 eV photon energy range for SiC_xN_y films grown at $p_{Ar}=80$ mTorr are nearly the same to the values reported in the literature.[6] The films thickness was also determined from the ellipsometric measurements, and it was found to be in the 900 to 1000 Å range for all deposits.

IV. CONCLUSIONS

The deposition of SiC and SiC_xN_y films has been studied as inert (Ar) and reactive (N_2) gases are introduced into the growth chamber of a high vacuum system at various pressures when a SiC target was photoevaporated by an excimer laser. The evolution of the binding state of the various components and the optical properties of the films has been investigated by *in situ* ellipsometry and XPS. There is no gas incorporation into the films when they are grown in the presence of argon. Nearly stoichiometric and stoichiometric SiC thin films, thickness about 1000 Å, have been grown in vacuum and at $p_{Ar}\geqslant30$ mTorr.

However, nitrogen content is strongly increased into the SiC_xN_yfilms in the 5 mTorr$\leqslant p_{N_2}\leqslant30$ mTorr pressure range, as shown in Fig. 2. The SiC_xN_y films grown at $p_{N_2}\geqslant30$ mTorr resulted to have an almost constant stoichiometry, given by $SiCN_2O_{0.2}$. The oxygen is a nuisance in this experiment and can be attributed to residual water in our system.

The energy shift and the broadening of the XPS peaks shown in Figs. 3 and 4 are a clear indication that the film is not longer composed of SiC but a rather complex material is formed as nitrogen is incorporated into the film, as has been already reported.[6,7] Figures 2–4 show that nitrogen is bonded to silicon and carbon for SiC_xN_y films grown at $p_{N_2}\geqslant30$ mTorr, so a new SiCN alloy has been formed. In fact, the formation of this alloy cannot be attributed to the intermixing of two binary phases like Si_3N_4 and SiC because they have different binding energies, nor the presence of graphite immersed in a Si_3N_4 matrix, as observed from Table I. Neither can nitrogen be physisorbed to the film surface,[21] see Table I.

The mechanisms about how the Si–N and C–N bonding occurs are still uncertain, but some conjectures might be considered. The mass spectrum of material ablated from a SiC target shows that only atoms and ions of Si and C, no clusters, with kinetic energies of a few tens of eV are detected at fluence above 2.3 J/cm^2 and laser wavelength of 248 nm.[22] These highly energetic atoms and ions collide with the gas molecules as the plume expands in the background gas. Almost all these collisions are elastic because the masses of the colliding particles are similar and the gas molecules initially have a lower average kinetic energy than the ablated species.[23] Dissociation and dissociative ionization due to photon and electron impact with the gas molecules are rare because swarm electrons with energies above 24 eV are scant and the excimer photons have an energy of only 5 eV.[24] Ionization of the N_2 molecules might be possible because the threshold energy for this process is smaller, about 15 eV. Therefore, chemical reactions in the gas phase are highly improbable. Optical spectroscopy of the plume might help to clarify this hypothesis.

The ablated species in the plume transfer energy to N_2 molecules, and probably to N_2^+ molecular ions, gaining kinetic energy up to a few eV due to multiple elastic collisions. N_2 and N_2^+ with energies higher than 9 eV impinging on a surface are known to chemisorb and have a high probability of forming atomic nitrogen upon impact.[25] The high kinetic energy of plume constituents enhances surface mobility and chemical activity between Si and N, and C and N. Surface reactions are strongly enhanced in presence of highly reactive monoatomic species, forming Si–N and C–N bondings. If the kinetic energies of N_2 and N_2^+ are greater than 75 eV, they can also be trapped in the film as interstitials.[25]

The introduction of nitrogen gas during the ablation process is a means to enhance the nitrogen content in the films, but the deposition rate is reduced. As the gas pressure is raised, the number of collisions between the ablated species and the gas molecules becomes larger. The content of nitrogen in the films is increased because there are more N_2 and N_2^+ being chemisorbed, and more surface reactions with Si and C are produced; as a consequence, the film stoichiometry changes, as observed in Fig. 2. However, there is a pressure value, 30 mTorr, where the nitrogen content does not vary any longer, this corresponds to the saturation point of nitrogen in the film. At pressures higher than 30 mTorr, the number of collisions are so frequent that the plume constituents and the gas molecules get thermalized. In fact, it has been observed that the molecules do not react and just get trapped forming voids in the films.[26] The higher the pressure the greater the number of voids.

The effect of voids in the optical properties can be observed in Fig. 6, the n values of a film grown at $p_{N_2} = 80$ mTorr are drastically reduced as compared to the film grown at $p_{N_2} = 10$ mTorr in the 2 to 5 eV photon energy range. The films tend to become transparent at higher pressures. In general, Figs. 5 and 6 show that SiC and SiC_xN_y thin films become less absorbent as Ar and N_2 pressure, respectively, is raised.

SEM micrographs indicate the films are smooth, uniform with no inclusions. This is in contrast to Zehnder *et al.*[11] who observed splashing on the film. The background gas is assumed to improve the film homogeneity and uniformity.

In summary, the combination of PLD, surface spectroscopies, and ellipsometry are suitable to monitor and control metastable phases, like SiCN alloys.

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