

Formation of silicon oxynitride by laser ablation of a silicon target in a nitrogen atmosphere

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Abstract— Studies during the last ten years have demonstrated that it is difficult to deposit pure silicon nitride by Pulsed Laser Deposition (PLD) without oxygen contamination even using a pure nitrogen atmosphere and a pure silicon target. The difference in the reactivity of nitrogen and oxygen means that there is always a certain amount of oxidation during the film growth from the residual oxygen in the vacuum system; the oxygen content can be more than 20 at.%. The aim of this work was to study the deposition of silicon nitride thin films under different experimental conditions to determine whether oxidation during, or posterior, to the deposition where the principal processes. We used optical emission spectroscopy (OES) and Langmuir probe measurements to study the plasma species and the parameters of the plasma. The chemical composition and the deposition rate of the films were measured by Rutherford Back Scattering (RBS), x-ray photoelectron spectroscopy (XPS) and profilometry, respectively. The OES results showed that the signal from nitrogen reached a maximum at 0.4 Pa (N_2^+ , 391.4 nm) and decreased if the nitrogen pressure was increased further. The maximum nitrogen concentration in the deposits was ~21 at.% at 1 Pa, with an oxygen content of 28 at.%. For lower pressures the coatings were rich in silicon and the coatings deposited at higher pressure (>1Pa) were rich in oxygen up to 50 at.%.

Keywords— Laser ablation, oxidation, plasma, silicon nitride.

I. INTRODUCTION

Silicon nitride is an attractive material for a large number of applications in microelectronics, optoelectronics and NEMS devices because of its high band gap, thermal, chemical and mechanical properties and stability. Silicon nitride coatings are commonly deposited by Plasma Enhanced Chemical Vapor Deposition (PECVD) [1], and magnetron sputtering [2, 3]. There are also many reports of silicon nitride deposition by Pulsed Laser Deposition (PLD) using different configurations such as a silicon target in a reactive nitrogen[4-6] or an ammonia atmosphere, or from a silicon nitride target in an Ar/N₂ gas mixture. Using the first configuration I. Umezu, et al.[6] studied the effect of the nitrogen pressure on the FTIR spectra and the optical band gap of the deposited films. They found that when the pressure was increased from 5 to 25 Pa the main FTIR peak shifted from 835 to 920 cm⁻¹ and that this was related to the transformation of the silicon nitride into silicon oxynitride. This result implied that the group could deposit pure silicon nitride at low pressure, but unfortunately they did not report the composition of the film. However, the band gap of the films deposited at 5 Pa was 3 eV which is considerable lower than the 5.5 eV value normally accepted for silicon nitride [7]. The gap increased as the pressure was increased, but this was probably due to the increased amount of oxygen in the films, and the authors suggested that the oxidation occurred after the deposition. J.D. Wu [8] combined PLD with a nitrogen plasma produced in a microwave electron cyclotron resonance system (ECR) to increase the concentration of reactive nitrogen species, since molecular nitrogen was not effective for the formation of the nitride [9]. Auger Electron Spectroscopy (AES) measurements showed that the nitrogen content increased from 6 to 48 at.% when the ECR system was used, but the oxygen content was approximately 15 at.% [8]. Silicon nitride has been deposited in ammonia [9] with the idea that atomic nitrogen could be more easily produced from the decomposition of the ammonia. The group of E. D` Anna[10] deposited silicon nitride in an ammonia atmosphere using an excimer laser, and based on the X ray diffraction measurements they obtained a mixture of Si, Si₃N₄ and SiO₂. Chemical analysis showed that when the gas pressure was increased the nitrogen concentration increased from 8 to 21.6 at.%, but that the oxygen content also changed from 36.5 to 43.4 at.%.

The deposition of silicon nitride by PLD using a silicon nitride target has also been studied. In that case it was concluded that it was necessary to use high nitrogen pressures (≥ 10 mtorr) in order to obtain a N/Si ratio of greater than 1.3, but the thin films had a void volume fraction close to 50%. The band gap of the films was seen to increase from 2.8 eV to 4.6 eV as a function of the nitrogen pressure. Similarly, E.C. Samano [11] found a clear relationship between void formation and background gas pressure, and they concluded that the voids were due to the trapping of the gas.

The aim of the present research was to study the chemical reactions occurring in the PLD plasma of ablated silicon in nitrogen, at different working gas pressures, to determine the relation between the nitrogen and oxygen incorporation in the deposits, and to establish if the included nitrogen was present as silicon nitride or trapped nitrogen gas.

II. MATERIALS AND METHODS

Fig. 1 shows a schematic representation of the laser ablation system used in this work. It consisted of a turbomolecular pumped vacuum chamber which was baked at 80 °C for 30 min, this gave a base pressure of 1.0×10^{-4} Pa. For the deposition the chamber was backfilled with pure nitrogen (99.99%) to the required gas pressure. The laser ablation was performed using a Nd:YAG laser with emission at 1064 nm, a 5 ns pulse duration and a 10 Hz repetition rate with a deposition time of 60 minutes. The laser output energy was kept constant (200 mJ) and the fluence (J/cm^2) on the silicon target was changed by varying the focusing lens position outside the chamber. The substrate holder was placed 6 cm in front of the silicon target.

The plasma parameters, mean kinetic ion energy and plasma density, were calculated from the time of flight (TOF) curves, obtained using a 6 mm diameter planar Langmuir probe biased at -50 V using the procedure described elsewhere [12, 13], and the maximum value of the ion current in the TOF curves, respectively. For these measurements the planar probe was placed in the same position as the substrate for the deposits. The probe current was obtained by measuring the voltage drop across a 15 ohm resistor using a Tektronix 500 MHz digital oscilloscope. Optical emission spectroscopy (OES) of the discharges was performed using a 0.5 m spectrograph (Spectra Pro 500i) equipped with a fast intensified charge-coupled detector (Princeton Instruments ICCD). The light emitted by the plasma at the substrate position was collected by a system of lenses and focused on a quartz optical fiber bundle connected to the spectrograph. The OES measurements were used to determine the type of excited species generated during the ablation of the targets; using standard references of the wavelengths [14, 15]. The coating thickness was measured using a Tenkor profilometer and the reported values are the average of at least 8 measurements of each sample. The X-ray photoelectron spectroscopy (XPS) analysis was performed using a Thermo Scientific K-Alpha system with monochromatic Al $K\alpha$ X-ray radiation ($h\nu=1486\text{nm}$). In the high resolution mode, after 90 seconds of pre-analysis sample etching using a 3 keV argon ion beam, the data was acquired using a pass energy of 15 eV and a step size of 0.025 eV. The binding energy was calibrated using sputter cleaned Cu foil ($\text{Cu}2p^{3/2}$ 5932.7 eV, $\text{Cu}3p^{3/2}$ 575.1 eV) from ASTM E2108-00. The XPS atomic profile was obtained during 3 keV argon ion beam erosion by taking spectra every 5 seconds using a pass energy of 20 eV and a step size 0.163 eV. The composition was calculated from the area of the peak for silicon, oxygen, nitrogen, carbon and gold.

A vertical High Voltage Engineering Co. Van de Graaff 5.5 MV CN accelerator [16] was used for the Rutherford Back Scattering (RBS) analysis of the samples. The samples were bombarded with 4He^+ beams with energies from 1.4 to 1.8 MeV, at normal incidence and using a 1 mm diameter collimator. The backscattered 4He^+ ions were measured using a 500 μm thick silicon surface barrier detector with a resolution of 30 keV, located at 150° with respect to the beam direction and at about 10 cm from the sample. The signals were recorded by means of a UCS30 SPECTECH multichannel in the form of energy spectra, and then analyzed using the SIMNRA[17] computer code, in this way generating depth profiles of the elements of interest.

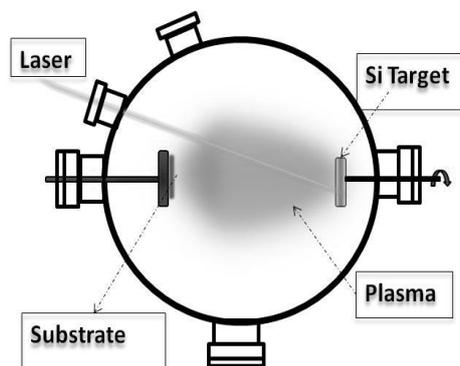


FIG. 1. A SCHEMATIC DRAWING OF THE TOP VIEW OF THE EXPERIMENTAL SETUP.

III. RESULTS AND DISCUSSION

The figures 2a and b show the data obtained from the TOF measurements of the plasma plume at the different working pressures with a laser fluence of $4.73 \pm 0.21 \text{ J}/\text{cm}^2$. Fig. 2a shows the TOF curves obtained during the ablation of the Si target at different pressures. The relatively larger distribution of the curves show that there was more dispersion of the flux of ions

as the gas pressure was increased. Fig. 2b shows the plasma density and the average kinetic ion energy, calculated from the TOF curves. As the pressure was increased the ion-gas molecule collision rate also increased and this produced a reduction in the ion energy from 120 to 98 eV, and the plasma density was reduced from $3.3 \times 10^{13} \text{ cm}^{-3}$ to $4.9 \times 10^{11} \text{ cm}^{-3}$ as the pressure was changed from vacuum to 6 Pa.

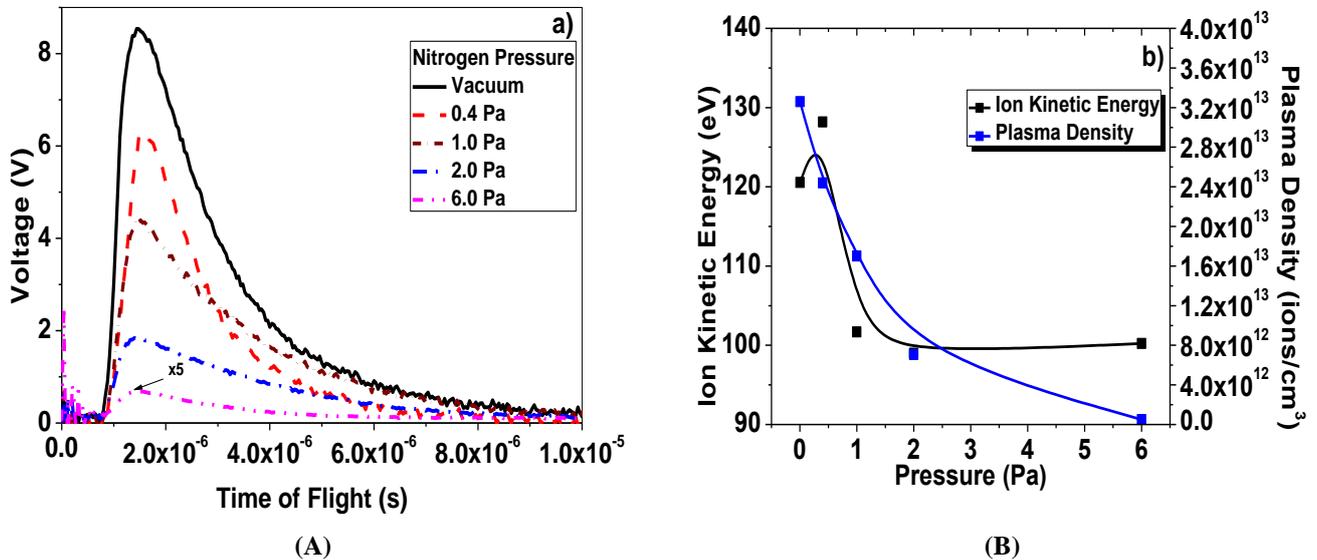


FIG.2. A) THE DATA FROM THE TOF MEASUREMENTS USING THE LANGMUIR PROBE AS THE DETECTED CURRENT AS A FUNCTION OF TIME AFTER THE LASER STRUCK THE TARGET AND B) THE VALUES OF THE AVERAGE ION ENERGY AND PLASMA DENSITY AS A FUNCTION OF THE NITROGEN PRESSURE.

The figure 3a presents optical emission spectra obtained for a laser fluence of 4.73 J/cm^2 and a nitrogen pressure of 1 Pa. As has been reported by other authors [5, 18] the presence of Si^* , Si^{+1} , Si^{+2} and N_2^+ was detected. Except for the case of when an external ECR nitrogen excitation source was used [8], other groups have not reported the observation of N_2^+ . In the present experiment the laser fluence of 4.73 J/cm^2 was sufficient to produce ionized molecular nitrogen. Nevertheless, we did not observe either the presence of atomic nitrogen (neutral or ionized) or signals from of any form of oxygen.

The figure 3b shows the effect of the pressure on the intensity of the different plasma species. The ionized silicon and nitrogen peaks decreased in intensity as the pressure was increased, possible due expansion of the plasma plume due to collisions. The maximum emission from ionized nitrogen was observed at 0.4 Pa.

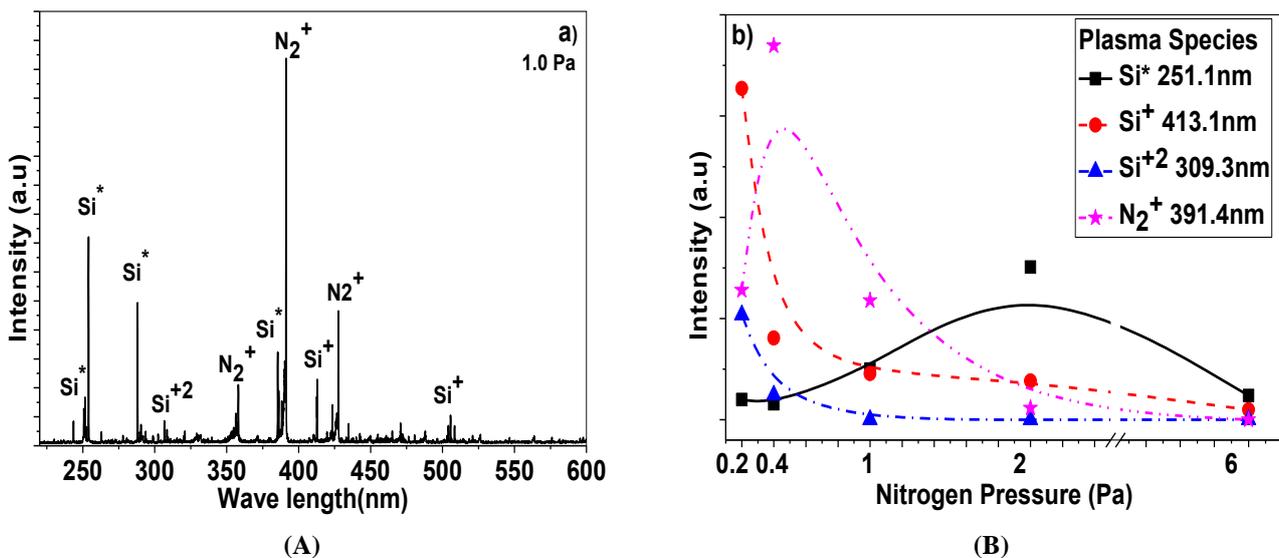


FIG. 3. A) OPTICAL EMISSION SPECTRA OF THE PLASMA PRODUCED DURING THE LASER ABLATION OF THE SI TARGET AT 1 PA AND (B) THE VARIATION OF THE INTENSITY OF THE OES SIGNALS FROM THE EMITTING SPECIES, AT CONSTANT FLUENCE (4.73 J/cm^2) BUT AS A FUNCTION OF THE NITROGEN GAS PRESSURE.

To study the effect of the plasma characteristics on the coatings, the chemical composition and the deposition rate were measured and the results are given in figures 4a and 4b, respectively. It was observed that the nitrogen content of the films had no direct relation with the intensity of the OES signal from the excited ionized molecular nitrogen. The maximum nitrogen content in the films was obtained at 1 Pa (22 at.%) whilst, as mentioned above, the maximum of the OES signal for the excited ionized molecular nitrogen was observed at 0.4 Pa. The deposition rate rapidly increased for pressures up to 1 Pa, but then the increase was lower for higher pressures. It is important to remember that the deposition rate was in reality the variation of the thickness of the film produced under the different conditions, and therefore changes in the film density could strongly affect the thickness-deposition data.

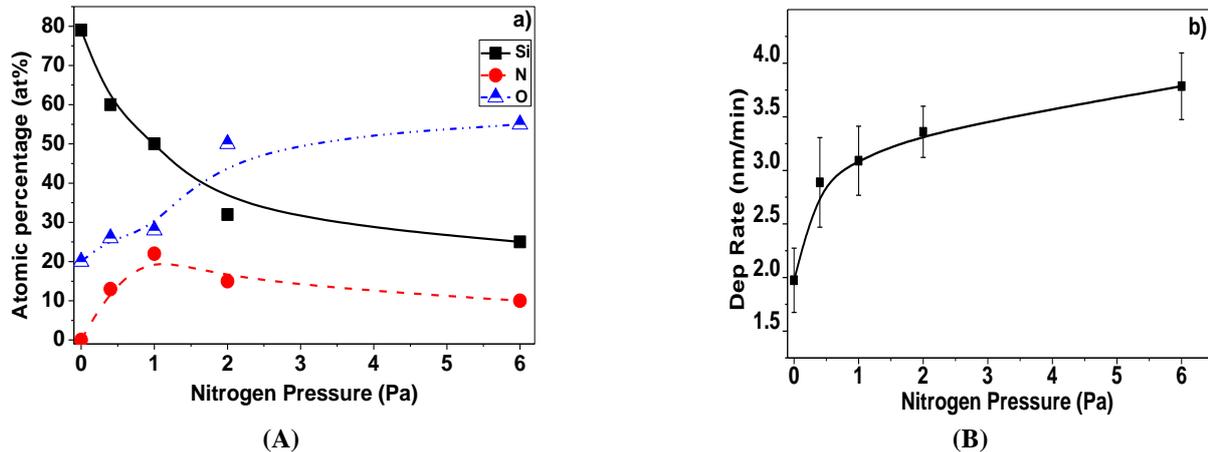


FIG. 4. EFFECT OF THE NITROGEN PRESSURE: A) ON THE CHEMICAL COMPOSITION DETERMINED BY RUTHERFORD BACK SCATTERING AND B) DEPOSITION RATE.

XPS analysis was performed to determine the bonding between the atoms present in the films. According to the random bonding model for silicon oxynitride, there are five tetrahedral structures for $\text{SiO}_v\text{N}_{4-v}$ (where $v = 0, 1, 2, 3$ and 4), and the chemical shift of the Si 2p level for each of the five structures is proportional to the partial charge on the Si atom, resulting in a broad peak [19].

The figure 5 shows the effect of the nitrogen pressure on the silicon peak position confirming the formation of silicon oxynitride, with different silicon oxidation states related with the silicon, oxygen and nitrogen content. This result is in agreement with the RBS results where the sample grown at 6 Pa had an oxygen content that was probably related to the formation of silicon dioxide. In the random bonding model all the silicon is bonded to nitrogen and/or oxygen (there are no silicon-silicon bonds), however, the thin films deposited in this study showed a contribution of silicon (Si^0 -99.7eV) in all the samples [19]. For example, the coatings deposited at the base pressure (10^{-4} Pa) showed a mixture of pure silicon (Si^0) and silicon monoxide (Si^{+2} at 101.6eV) [20], the thin films deposited using a nitrogen atmosphere showed a broad peak with a mixture of pure silicon and oxynitrides with different amounts of nitrogen corresponding to various of the five structures.

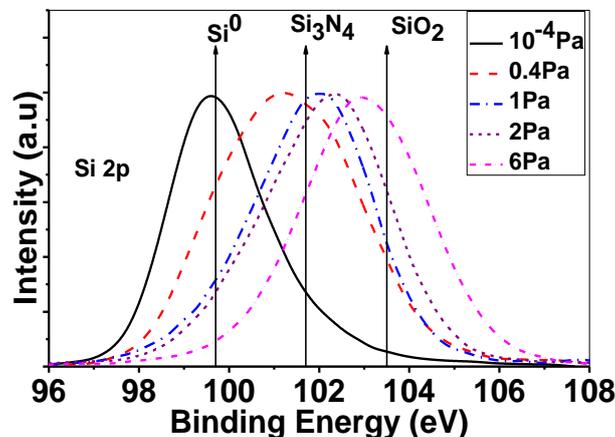


FIG. 5. Si 2p XPS spectra of SiO_xN_y with different compositions

The oxygen content reached values between 20 at.% and 55 at.% for vacuum of 10^{-4} Pa and N_2 pressure of 6 Pa, respectively.

The inclusion of oxygen in the films is principally related to two factors, that the oxide formation is exothermic whilst the nitride formation is endothermic [21], and that the nitrogen molecule is more stable than the oxygen molecule, and therefore a silicon atom will preferentially react to form the oxide rather than the nitride [22]. The residual oxygen in the chamber is the most probable source of the partial oxide formation. It is well known, that at a residual oxygen pressure $\sim 10^{-4}$ Pa the time to form a monolayer of oxide is approximately one second, assuming a sticking coefficient of one [23]. Therefore, if the deposition rate of the metal layer is one monolayer per second the resulting deposit is of metal oxide. For magnetron sputtering where the deposition rate is often 10 monolayers per second the oxygen content can be less than 10%. [3, 19]. For our study the residual oxygen pressure is $\sim 3 \times 10^{-5}$ Pa and a deposition rate of about a tenth of a monolayer per second explains the high oxygen content of the films. It has been reported that high nitrogen pressures produce more voids and a porous film structure,²⁰ and this may be related to direct inclusion of molecular nitrogen in the deposits or a porous structure.

To determine whether the oxidation of the film occurred during the deposition or was due to post-deposition oxidation, we deposited a SiN_x film under the normal conditions at 1 Pa and then a 20 nm gold thin film was deposited as a barrier layer, before the chamber was vented to atmosphere. The XPS composition profiles with and without the gold barrier layer are shown in the figures 6a and b, respectively. It can be seen that the oxygen content throughout the majority of the thickness of the film was ~ 30 at.% in both cases. The shape of the oxygen, nitrogen and silicon profiles in the outer most layers of the film indicate there is little or no diffusion or accumulation of oxygen from the atmosphere posterior to the deposition. This result appears to confirm that, for the conditions used in this study, the oxidation of the film occurred during deposition due to the reaction of the residual oxygen in the vacuum systems with the new surface of the layer produced by each laser pulse.

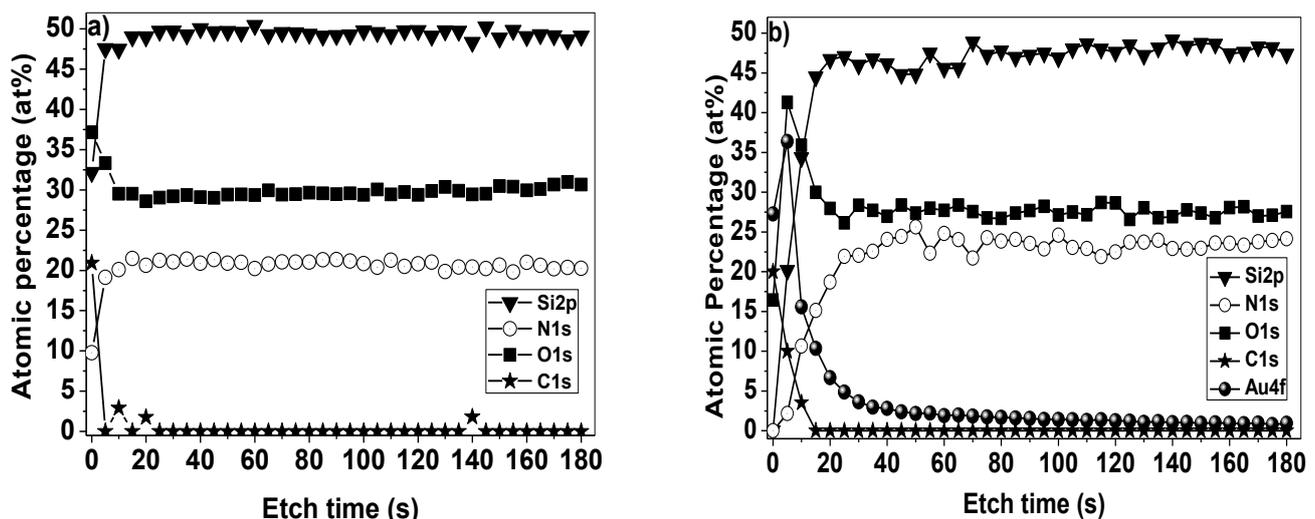


FIG. 6. ATOMIC PROFILE OF THE FILMS DEPOSITED AT 1 Pa, A). WITHOUT THE GOLD TOP LAYER, B). WITH A GOLD TOP LAYER.

IV. CONCLUSION

Using pulsed laser deposition we deposited silicon oxynitride coatings from a pure silicon target in a flow of pure nitrogen. The measurements of the composition showed that the oxygen and nitrogen content were comparable with experiments performed with an ammonia atmosphere and an external nitrogen ion source. The plasma characterization showed that it was possible to ionize silicon and molecular nitrogen, but neither atomic nitrogen ions nor any excited species of oxygen were observed. Based on our results we propose that the oxidation of the deposit occurred after each laser pulse, when the fresh film surface reacted with the residual oxygen in the chamber. For the gas pressures greater than 1 Pa this process was probably enhanced by the formation of a less dense, more porous deposit with the greater surface area leading to films with higher oxygen and lower nitrogen concentrations. The XPS results showed that the obtained thin films consisted of a mixture of silicon oxynitrides and pure silicon, and that the ratio of these phases was determined by the nitrogen pressure used.

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