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Surface modifications in diamond-like carbon films submitted to low-energy nitrogen ion bombardment

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Abstract

Amorphous hydrogenated carbon films (a-C:H) films deposited by plasma enhanced chemical vapor deposition in CH₄ atmosphere were submitted to nitrogen r.f.-plasma treatment. The influence of several parameters was investigated: the chamber pressure, ranging from 0.5 to 10 Pa, the self-bias voltage in the range between –50 and –500 V and the exposure time. The erosion rate was determined by profilometry. It increases as the self-bias increases and tends to saturate for higher pressures. The nitrogen incorporated in the films was measured by nuclear reaction analysis. The results indicate a decrease in the N content as the pressure or the self-bias increase. The chemical bonds were probed by XPS and two chemical environments can be identified, one with N atoms surrounded by C atoms and the other one with N atoms binding to H. Surface roughness and friction coefficient modifications were followed by atomic force and lateral force microscopies. The surface roughness is independent on the value of the self-bias voltage, while the friction coefficient decreases. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

In the last few years there has been a strong interest in the study of nitrogenated amorphous carbon films [1]. One of the main reasons of this research effort was the intent to synthesize the β -

C₃N₄ solid, proposed by Liu and Cohen [2] to have mechanical properties comparable to those of crystalline diamond. Despite this, no clear experimental evidence of the formation of β -C₃N₄ has been presented. An important fraction of this research effort was dedicated to the study of hydrogenated amorphous carbon–nitrogen films deposited by plasma enhanced chemical vapor deposition, PECVD. Nitrogen incorporation in a-C:H films was found to modify the structure and the mechanical properties [3–9] of these films, as

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well as their electrical and optical properties [9]. It results in a strong decrease of the fraction of carbon atoms in sp^3 hybridization state [5]. Concerning the mechanical properties, a strong reduction on the internal compressive stress was observed, with minor changes in the mechanical hardness [3]. Some authors reported a relative insensitivity of the hardness to nitrogen incorporation up to 15 at.% [3,4], while for films deposited with acetylene–nitrogen mixtures a remarkable hardness decrease was measured in nitrogen richer films (~ 20 at.%) [7]. The improvement in adhesion resulting from the stress reduction allowed the use of thick a-C(N):H films as antireflective coatings in Ge-based IR sensor [4]. Concerning the modification of electrical and optical properties, it was found that nitrogen could electronically dope a-C:H films, with the simultaneous reduction of the electronic defect density [9]. In addition, plasma-deposited a-C(N):H showed a promising performance as electron field-emitter [10]. Some of the potential applications of a-C(N):H films are critically dependent on the surface properties and the knowledge of the tribological and topological properties of the films is largely required.

One of the ways to modify surface properties in a controlled way is by low-energy ion bombardment, which can be achieved by plasma treatment. For example, argon plasma is used to increase the surface roughness of a-C(N):H films, thereby creating a more efficient electron emitter [10]. However, there are only a few studies about the surface nitrogen incorporation into a-C:H or a-C(N):H films by N_2 plasma treatment [11,12]. In this work, we investigate the effects of the N_2 r.f.-plasma treatment of a-C:H films deposited by PECVD. Ion beam analysis, atomic and lateral force microscopies (AFM and LFM, respectively) and X-ray photoelectron spectroscopy (XPS) have been used for the characterization of samples treated by varying several plasma parameters: exposure time, self-bias voltage and the total chamber pressure.

2. Experimental procedures

The a-C:H films studied in this work were deposited by PECVD in CH_4 atmosphere. The

$\langle 100 \rangle$ -Si single-crystal substrates were mounted on the r.f. powered (13.56 MHz) water-cooled electrode of a deposition chamber with large grounded-to-r.f. powered surface area ratio. The pressure in the deposition chamber was 10 Pa and the base pressure was lower than 10^{-3} Pa. The self-bias voltage was -300 V in all the depositions. The films studied in this work have thickness ranging from 0.3 to 1.0 μm . The films have typically 20 at.% of hydrogen and atomic density of 1.4×10^{23} atoms/cm³. Details of the film deposition and characterization can be found elsewhere [13].

The nitrogen r.f.-plasma treatments were performed in the same chamber. The total pressure in the chamber varied from 0.5 to 10 Pa, the self-bias voltage, V_b , was in the range between -50 and -500 V. Unless where indicated, the time treatment was 20 min. The samples were not submitted to any kind of sequential treatment. The film thickness and the erosion depth were measured by a stylus profilometer (DEKTAK 3, Veeco Instruments, Sloan Technology). The nitrogen content was measured using the reaction $^{14}N(d, \alpha_0)^{12}C$ at $E_d = 1.45$ MeV. For the NRA, a surface barrier detector (area 450 mm², positioned at 150° with respect to the beam direction) was covered with a 12 μm thick mylar foil for protection against the high flux of backscattered deuterons. A 4 MV Van de Graaff accelerator (High Voltage Engineering) provided the deuteron beam.

The AFM measurements were performed with a commercial microscope (Nanoscope III, Digital Instruments) operated in lateral force mode for the tribological studies and in contact mode for the analysis of the topography. During the measurements, the samples were kept at room temperature and with the relative air humidity in the range 35–40%. All the experiments were performed with a constant force of 100 nN. The RMS roughness was measured in an area of $0.1 \times 0.1 \mu m^2$ with a scan rate of 20 Hz. For the calculation of the friction coefficient, forward and reverse lateral force images were acquired. Before each image, the adhesion between the tip (V-shaped, Si_3N_4) and the surface of the film was measured in order to calculate the normal force exerted by the tip on the sample. The reverse image was subtracted from the forward one, and the result was exported as an

ASCII file to a computer code in order to obtain the absolute friction coefficients. The calibration method used to calculate friction coefficient values was the one proposed by Liu et al. [14].

XPS was employed to investigate the chemical state of the atoms at the film surface. It was performed using an Omicron UHV station based on a EA125 hemispherical analyzer. The photoelectron spectra of C 1s and N 1s core levels were monitored, excited by Mg-K α (1253.6 eV) radiation, with an overall resolution of 1 eV for 10 eV pass energy. The angle between surface normal and the electron energy analyzer axis was 45°. No surface cleaning procedure was carried out by means of argon sputtering in order to avoid hybridization changes of the carbon atoms or preferential sputtering due to Ar⁺ bombardment.

3. Results and discussions

In Fig. 1(a), we present the erosion depth as a function of the plasma treatment time ($V_b = -300$ V and $P = 3$ Pa). It shows a linear dependence with time indicating a uniform erosion rate even for long treatment times. The amount of nitrogen incorporated in the a-C:H film is shown in Fig. 1(b). This plot shows a constant behavior after an initial sharp increase. These results indicate that, for these plasma conditions, a steady-state condition is achieved after some few tens of seconds.

The erosion rates, as well as the total amount of nitrogen incorporated in the films as a result of the plasma treatment, are presented in Fig. 2 as functions of the self-bias voltage for a fixed treatment time of 20 min and a chamber pressure of 3 Pa. The observed increase of the erosion rate with self-bias may be at least partially ascribed to the increase of the N₂⁺ ion current, since self-bias increase is achieved by increasing the r.f. power fed to the substrate electrode. On the other hand, the self-bias increase also results in the increase of N₂⁺ ion energy, and this may also affect the erosion process since both chemical and physical sputtering of carbon films by N₂⁺ increase with the energy. As shown in Fig. 2(b), the surface nitrogen content decreases by about 40% for the overall self-bias variation. A similar result was obtained by XPS

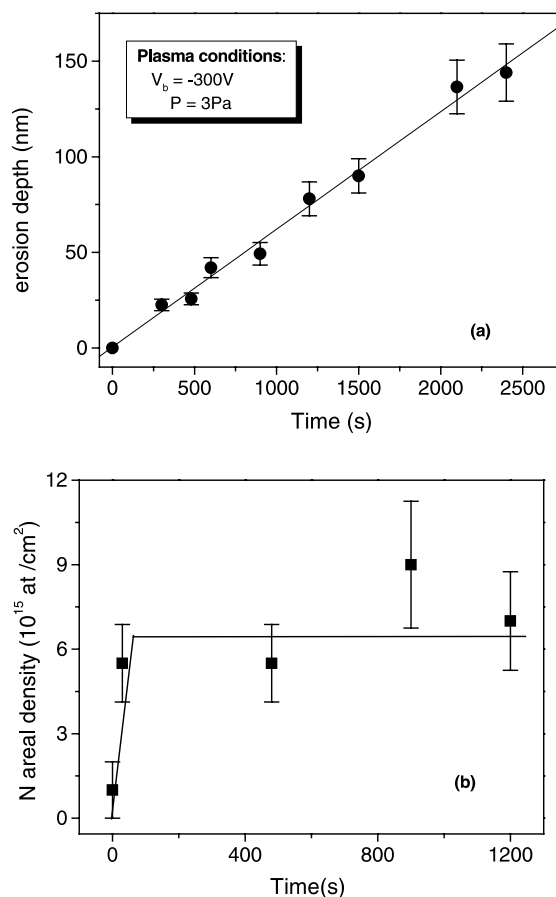


Fig. 1. Erosion depth (a) and nitrogen incorporated in a-C:H films (b) as a function of the treatment time. The treatment parameters are indicated in the figure. The lines are to guide the eye.

measurements. Since for the processing time that we adopted (20 min) the erosion process should occur in the stationary regime, we cannot regard this behavior as being caused by the increasing ion current. In fact, all the process affecting the surface film composition, such as chemical and physical sputtering and nitrogen incorporation, are proportional to the ion current. In this case, any variation of the ion current should lead to equally proportional changes on the mentioned processes, but no changes in the nitrogen content. Therefore, the observed decrease of the surface nitrogen content must be ascribed to an increase of the sputtering yield with the N₂⁺ energy. We do not

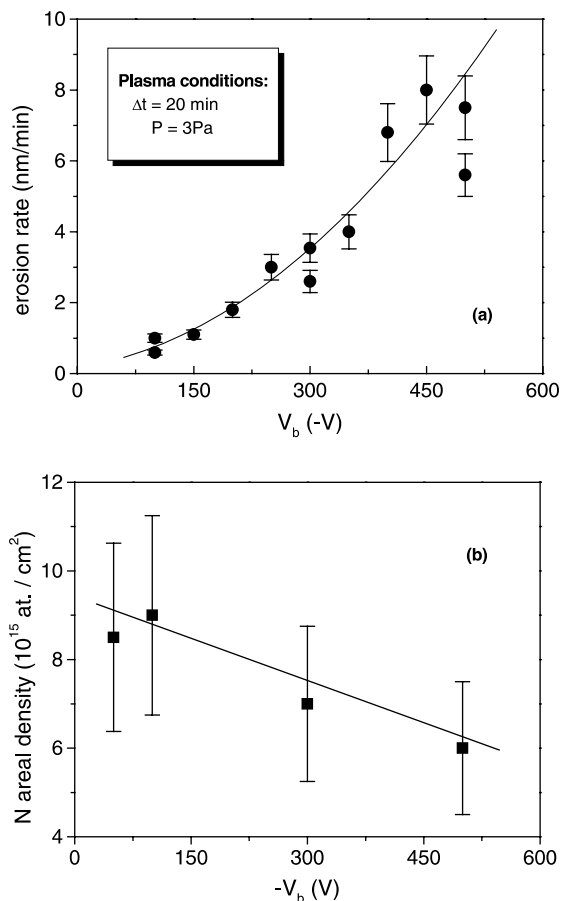


Fig. 2. Erosion rate (a) and nitrogen incorporated in a-C:H films (b) as a function of the self-bias voltage. The treatment parameters are indicated in the figure. The lines are to guide the eye.

expect an important energy dependence of the sticking factor of N_2^+ . If any exists, it must be in the direction of an increase of nitrogen incorporation since a deeper implantation was achieved when the bombardment energy increases. Hammer and Gissler [15] and Hammer et al. [16] previously studied the erosion of carbon films by low-energy N_2^+ ions. They found that the erosion process occurs as a chemical sputtering process, mainly by the evolution of CN and C_2N_2 molecules. The sputtering yield (about 0.5 C atom per N_2^+ ion) was found to be much higher than that shown by the physical sputtering induced by ion beams of noble gases in the same energy range. In addition, they

found that the sputtering yield increases with the ion energy [16]. In the present work, the observed decrease in the surface nitrogen content may be explained by the enhancement of the sputtering processes upon self-bias increase.

The variation of the erosion rate as a function of the pressure is shown in Fig. 3(a). This plot shows an initial sharp increase in the erosion rate, which may be ascribed to the increased r.f. power needed to maintain a constant self-bias upon pressure increase. For higher pressures, the erosion rate saturates. For this process, the surface nitrogen content decreased as the pressure decreases. We have no clear explanation for these variations. But it must be

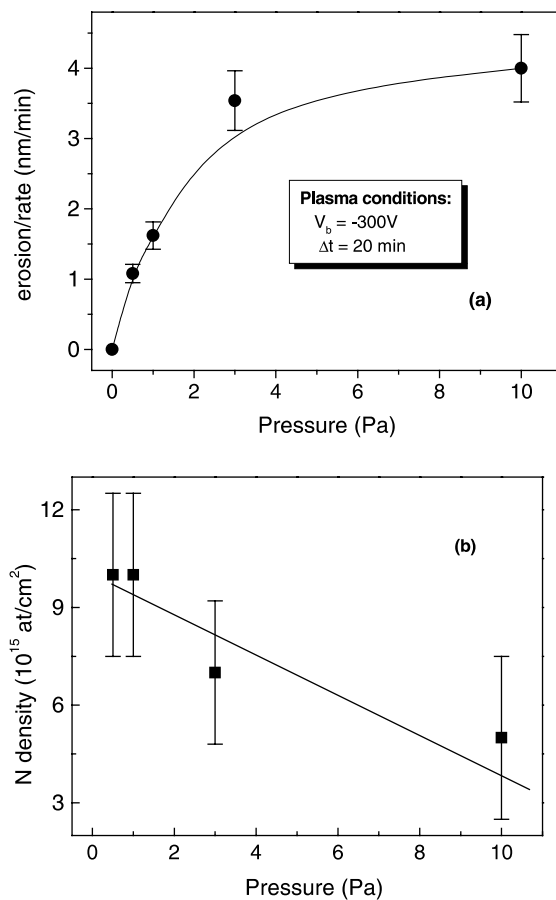


Fig. 3. Erosion rate (a) and nitrogen incorporated in a-C:H films (b) as a function of the self-bias voltage. The treatment parameters are indicated in the figure. The lines are to guide the eye.

noted that pressure variation in this range must certainly lead to strong changes, despite the constant self-bias, in the bombarding ion energy, due to the decrease on the collisional mean free path within the plasma ion sheath. This factor can also affect the collisional processes within the N_2 plasma itself, altering the concentration of the different plasma species, thus affecting the surface erosion process.

In Fig. 4, we present the C 1s and N 1s core-level XPS spectra obtained from a sample treated during 20 min at -250 V and 3 Pa. The spectra taken from samples treated at -150 and -450 V are identical to those presented in the figure, except by the relative intensity of the peaks. Comparing the C 1s spectra obtained from an untreated sample with those obtained from plasma-treated films, we observed a broadening and a higher asymmetry in the line shape towards high binding energies. This asymmetry suggests the existence of at least two different carbon environments: C–C/C–H and C–N. The small peak at

around 288 eV is attributed to oxygen contamination due to exposure to the atmosphere before the XPS analysis. On the other hand, the nitrogen binding energy and the line width of the N 1s core-level remained constant for the entire range of the self-bias voltage. All binding energy values fall within 399.5 ± 0.5 eV and the full width at half-maximum remains at 2.4 eV. These results are identical to those obtained by Mansour and Ugolini from a-C(N):H films deposited by ion beam deposition IBD [17]. The abnormally large width of the N 1s level may be accounted for by assuming the existence of two chemical environments: one with the N atoms surrounded by C atoms (the high-energy side of the spectra) and the other one with the N atoms bound to H (the low binding energy region of the spectrum) [17]. Some authors prefer to attribute these two regions to N atoms bound to sp^3 -hybridized C with isolated lone pair of electrons as in β - C_3N_4 , for the low-energy region, and to substitutional N in a graphitic-like configuration, responsible for the peak at higher binding energy [6].

In Table 1, we present the values of the friction coefficient and the RMS roughness obtained by AFM. A reduction of a factor of two was observed in the friction coefficient while the roughness remained constant. In nanoscale tribology, a direct correlation between surface roughness and friction coefficient does not necessarily occur [18]. In fact, in a-C(N):H films deposited by PECVD the incorporation of nitrogen results in an increase of the roughness while the friction coefficient is constant [19]. On the other hand, in [11] a substantial reduction of the roughness was observed when V_b increases and this was attributed to thermal effects on the substrate caused by ion bombardment. However, for a-C(N):H films treated in an Ar r.f.-plasma the roughness increases [10]. These results clearly indicate that more work is necessary for a better understanding of the tribological properties of a-C(N):H films.

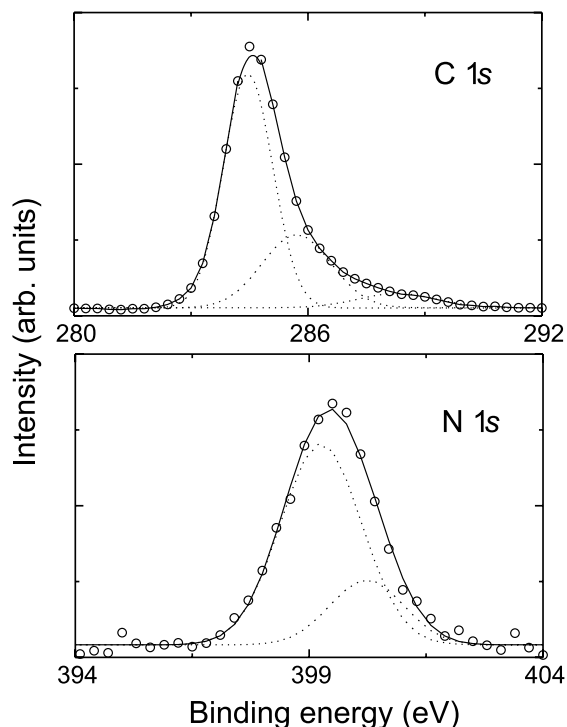


Fig. 4. C 1s and N 1s core-level XPS spectra obtained from a sample treated during 20 min at -250 V and 3 Pa.

4. Summary and conclusions

a-C:H films deposited by PECVD in CH_4 atmosphere were treated in N_2 r.f.-plasma, at

Table 1

Friction coefficient and RMS roughness measured by AFM as functions of the self-bias voltage^a

V_b (V)	Friction coefficient	RMS roughness (nm)
As-deposited film	0.17 ± 0.01	0.13 ± 0.01
–100	0.23 ± 0.03	–
–150	0.20 ± 0.03	0.20 ± 0.03
–250	0.07 ± 0.01	0.13 ± 0.02
–300	0.07 ± 0.01	0.13 ± 0.01
–450	0.07 ± 0.02	0.09 ± 0.03
–500	0.09 ± 0.04	0.16 ± 0.02

^a The films were treated during 1200 s and the chamber pressure was 3 Pa.

different pressures, self-bias voltages and exposure times. A steady-state regime is obtained within few tens of seconds. The erosion rate increases with V_b and tends to saturate for chamber pressures around 10 Pa. The friction coefficient determined by LFM is drastically reduced when V_b increases but the surface roughness remained constant. These behaviors cannot be directly attributed to different chemical states at the treated surfaces since no changes in the chemical environment were observed upon self-bias voltage variation, as shown by XPS.

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