

Structural properties and surface morphology of laser-deposited amorphous carbon and carbon nitride films

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Abstract

A study of the relationship between structure and growth parameters for existing and candidate carbon-based protective coatings has been carried out. In particular, diamond-like carbon (DLC) and carbon nitride thin films were deposited on silicon wafers by pulsed Nd:YAG laser (wavelength 532 nm) ablation of graphite in high vacuum ($p = 1.5 \times 10^{-7}$ Pa) and in a nitrogen atmosphere ($p = 13$ Pa). The composition (N/C ratio), the structural and electronic properties and the surface morphology of the deposited films were investigated as a function of laser fluence (1–12 J/cm²). The highest N/C ratio 0.40 was obtained with a laser fluence of 12 J/cm²; for this nitrogen concentration X-ray photoelectron spectroscopy (XPS) reveals an increase of C–N bonds instead of C=N bonds with respect to lower concentrations.

Electron energy loss spectroscopy (EELS) and XPS show an increase of sp² carbon bonded sites in the DLC films deposited with lower laser fluences in agreement with the theory of the so-called sub-implantation model. EELS also reveals a gradient in the chemical nature of the films through the thickness. Atomic force microscopy analysis shows that the root-mean-squared roughness of the DLC samples is about 3 Å over the laser fluence range investigated. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: AFM; CN_x films; Diamond-like carbon films; EELS; Pulsed laser deposition; XPS

1. Introduction

Amorphous carbon films with diamond-like properties are good materials for a wide range of technological applications. In particular, diamond-like carbon (DLC) films are currently used in the production of hard coatings because of their extreme hardness, chemical inertness and excellent tribological, corrosion and adhesive properties. However, a tendency toward CN_x films in carbon coatings is taking place because of improved wear durability, lower coefficient of friction, and compatibility with existing lubricants [1].

DLC and CN_x films have been grown using different methods, mainly sputter deposition, cathodic arc, direct ion beam deposition [2] and pulsed laser deposition (PLD). This last method is particularly interesting because of the high adhesion and low substrate temperature during film growth [3].

There still exist several unanswered questions regarding how the process of growth influences the resulting structure in DLC and CN_x films. All these films usually contain a mixture of carbon sites characterized by ‘diamond’ sp³, ‘graphite’ sp² and, to a lesser extent, sp¹ hybrid configurations. The improvement of the quality of the films such as hardness is strictly correlated with the increase of the sp³ concentration in the films. An important parameter characterizing the films prepared under different depositions conditions is, hence, the sp³/sp² ratio.

Since nitrogen is a weak dopant in carbon, techniques like core-level analysis are required to establish the chemical bond of nitrogen with carbon. In this paper X-ray photoelectron spectroscopy (XPS), electron energy loss spectroscopy (EELS), and atomic force microscopy (AFM) are used to investigate how the laser fluence changes the structural, electronic and morphological properties of DLC and CN_x films grown with PLD.

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2. Experimental

DLC and CN_x films were deposited in the PLD system shown in Fig. 1. This system consists of an ultrahigh vacuum (UHV) chamber with a base pressure of 1.5×10^{-7} Pa, a Q-switched Nd:YAG laser with a wavelength of 532 nm, a pulse duration of 20 ns and a frequency of 10 Hz. The distance between the target and the substrate was 3 cm. The laser beam was moved by an oscillating mirror attached to two loudspeakers in order to provide each pulse with a fresh surface. Much attention was paid to measuring the power of the laser on the target, while the laser spot on the target was determined from a scanning electron microscope image of the hole left on the target by the laser. The laser fluence so measured ranged from 1 to 35 J/cm². During the growth of CN_x films we used a nitrogen pressure of 13 Pa. Silicon wafers, cleaned with acetone, were used as substrates. XPS and EELS were used to characterize the electronic and structural properties of the deposited thin films. Core levels were measured using an Al K α 1486 eV X-ray source. Charging effects were not observed on the samples during measurements. The resulting experimental resolution, including the width of the X-ray line and the energy resolution of the analyzer, is about 1.1 eV. The Si 2p core level of an uncovered part of the silicon substrate was used to calibrate the scale of binding energies (BEs), whereas to calculate the chemical composition at the surface we used standard sensitivity values. EELS measurements were performed using an EG5 VSW Scientific Instruments electron gun. The energy losses were studied in the range from zero loss (at primary electron energy) up to 50 eV loss. The energy resolution as deduced from the width of the primary peak is 2 eV. For both XPS and EELS measurements we utilized a hemispherical analyzer. A Digital Instruments Nanoscope III atomic force microscope operating in the tapping mode was utilized to measure the surface roughness of the deposited films. A DEK TEK profilometer was used to measure the thickness of the samples. The average thickness of the deposited films is 100 nm. The growth rate changes significantly

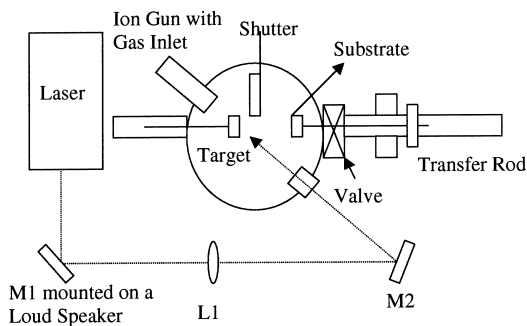


Fig. 1. The experimental set-up for growth of the films. M1 and M2 are mirrors and L1 is a lens.

with the laser fluence, going from 200 Å/min for $I_L = 35$ J/cm² to 6 Å/min for $I_L = 1$ J/cm². All the characterizations were performed ex situ. The O 1s/C 1s intensity ratio, evaluated by taking into account the O 1s and C 1s sensitivity factors, is 0.03 for all the DLC samples and 0.1 for the CN_x samples.

3. Results and discussion

Fig. 2(a) and (b) shows the C 1s core-level XPS spectra of two DLC samples grown with two different laser fluences: 12 J/cm² and 1 J/cm² respectively. The full-width at half-maximum of both our samples is about 1.8 eV. The C 1s core-level shifts by 0.6 eV towards lower energies in the sample grown with lower laser fluence. A quantitative indication of the population ratio between sp^2 and sp^3 hybridization can be evaluated by fitting the C 1s core-level spectra with two components [4]. The first one at lower BE is related to sp^2 hybridization, the second one to sp^3 hybridization. This is in accordance with the shift of 0.9 eV between the C 1s core levels of diamond and graphite [5]. Each component is a convolution of a Gaussian and a Lorentzian

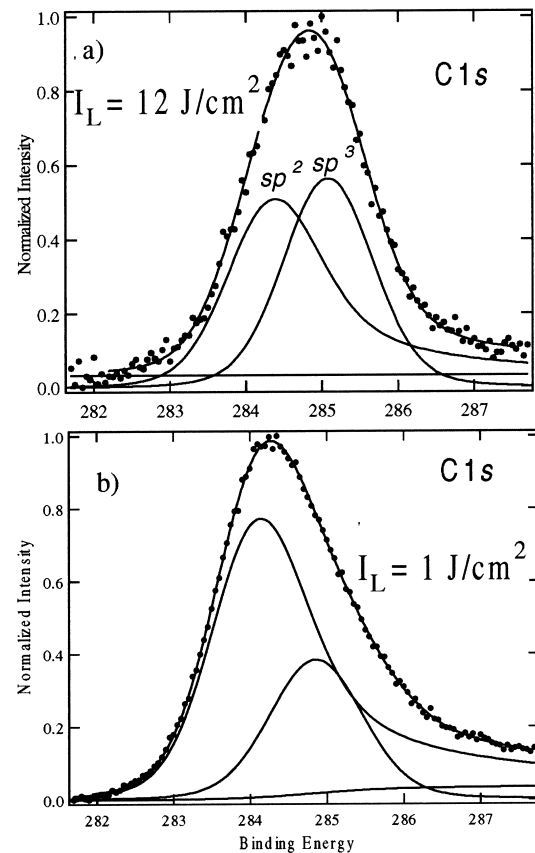


Fig. 2. C 1s XPS spectra of two DLC films grown with fluences of (a) 12 and (b) 1 J/cm². The subtracted Shirley background and the components in which the spectra have been decomposed are shown. The resulting fit is superimposed on the data.

and a Shirley background is subtracted. The Gaussian component accounts for the instrumental broadening and the chemical disorder, and the Lorentzian accounts for the finite core hole lifetime of the photoionization process. The Lorentzian lifetime is fixed in both components as 215 meV [4]. Because of the semi-metallic character of the graphite the sp^2 component is fitted including the Doniac–Sunjic function. The asymmetry parameter for the C 1s of graphite was set at 0.14 in agreement with the literature [4]. The C 1s spectra were fitted with five parameters: the BE and the Gaussian width of each component and the singularity index for the sp^2 component. The Gaussian widths were 1.25 ± 0.05 eV for all the resulting components and the singularity index results were 0.16 ± 0.02 , in agreement with values in literature [4]. This Gaussian width is larger than the width predicted by the instrumental broadening of 1.1 eV. This further broadening is probably due to the chemical disorder and to the phonon broadening. The components related to sp^2 and sp^3 hybridizations result in each sample being shifted by 0.9 ± 0.05 eV, in agreement with previous results [5]. We remark that changes of the free fitting parameters within reasonable ranges do not affect the overall conclusions drawn in this paper. Our analysis shows that the sample grown with higher laser fluence has 53% sp^3 , whereas the other sample has 34% sp^3 .

The decrease of sp^2 hybrid carbon atoms in the sample grown with higher laser fluences is also confirmed by EELS. In Fig. 4 the EELS spectra of the same two samples normalized at the intensity of the elastic peak are shown. The first peak at about 6 eV, called the π -plasmon peak, is related to π electrons; it is not present in a pure sp^3 configuration, whereas it is present at 6.6 eV in the graphite [6]. The second peak at about 28 eV is related to $\sigma + \pi$ electrons [6]. This peak is located at about 27.6 eV in graphite and at 33 eV in diamond [6]. The energy of this plasmon excitation is predicted by the free electron model to be equal to [6]:

$$\omega_p = \left(\frac{4\pi n_e e^2}{m^*} \right)^{1/2}, \quad (1)$$

where n_e is the electron density of the material and m^* and e are the electronic effective mass and charge respectively. From Fig. 3 it is evident that there is a decrease in intensity of the π -plasmon peak in the sample grown with higher laser fluences. These results indicate a decrease of sp^2 sites in this sample with respect to the other one. XPS and EELS experimental results on DLC films are in accord with the sub-implantation model [7] taking into account that the laser fluence growth changes almost linearly with the energy of the carbon ions [8]. This model indicates for carbon ion energies greater than 30 eV a low density sp^2 -rich surface layer below which a dense sp^3 -rich layer develops, whereas for

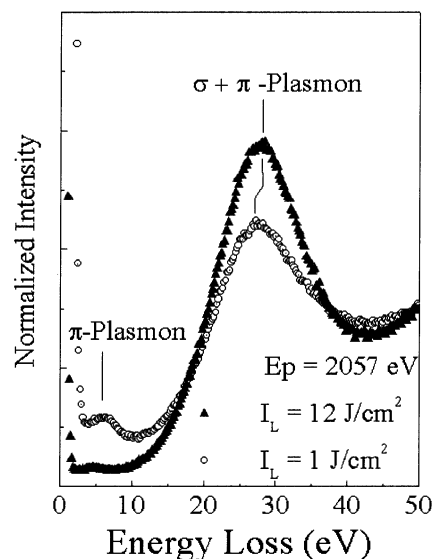


Fig. 3. EELS spectra of two DLC films grown with fluences of 1 and 12 J/cm².

energies lower than 30 eV one obtains just an sp^2 -rich film.

The possibility of an inhomogeneous pattern of properties as a function of depth was explored by exploiting the energy-dependent electron mean free path of the primary electron beam in EELS. In Fig. 4 we report some EELS spectra normalized at the intensity of the elastic peak for three different primary energies: 2057, 993.2, 617.2 eV. From Fig. 4 it is possible to observe the growth of the π -plasmon peak and the shift of almost 2 eV of the $\sigma + \pi$ plasmon peak for the lowest primary

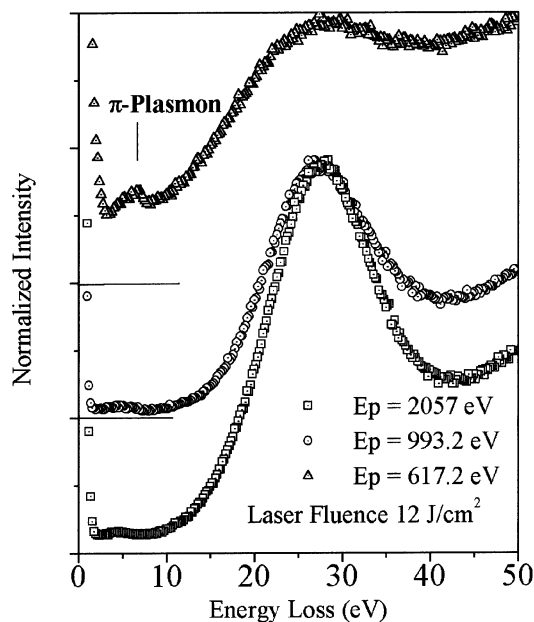


Fig. 4. EELS spectra of a DLC film for different primary energies. The spectra are shifted on the y-axis.

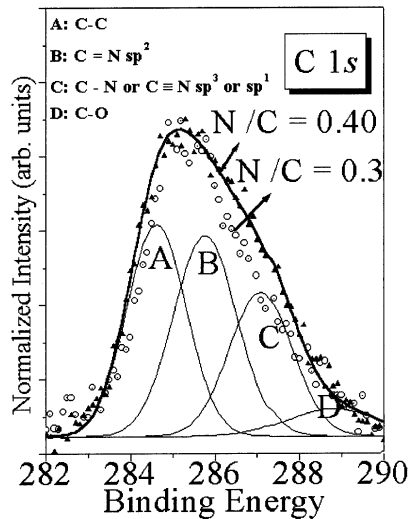


Fig. 5. C 1s core-level spectra of two CN_x films with $\text{C}/\text{N}=0.30\text{--}0.40$.

energy, suggesting the presence of a very thin sp^2 layer at the surface.

The N/C ratio of the deposited thin films was measured by XPS. The N/C ratio is 0.30 for a laser fluence of $5 \text{ J}/\text{cm}^2$ and 0.40 for $12 \text{ J}/\text{cm}^2$. Figs. 5 and 6 show the XPS C 1s and the N 1s spectra of two CN_x films with varying nitrogen content. The C 1s peak broadens and becomes more asymmetric with increasing nitrogen concentration. These effects are a clear indication that nitrogen atoms are involved in chemical bonds with carbon in three possible distinct chemical states: C–N, C=N, C≡N bonds. A clear image of the possible chemical bonds between nitrogen and carbon can be deduced from the deconvolution of the individual C 1s and N 1s lines into Gaussian lineshapes [1]. The best Gaussian fits to the XPS lines resulted in four different peaks for the C 1s line and three peaks for the N 1s line. Fig. 5 shows the deconvolution of peak C 1s of the sample with the ratio $\text{N}/\text{C}=0.4$. The deconvoluted

spectrum exhibits peaks at 284.7 eV (A), 285.9 eV (B), 287.1 eV (C) and 289.17 eV (D) that are attributed to C–C, C=N, C–N or C≡N, and C–O bonds, respectively [1]. Likewise, the deconvolution of the N 1s line for the same sample, shown in Fig. 6, gives three peaks at 399.6 eV (A), 401.3 eV (B), and 402.1 eV (C) which are assigned to C–N or C≡N, C=N and N–O bonds, respectively [9]. These values agree quite well with organic polymers containing nitrogen [1]. Pyridine (C=N, sp^2 hybridization) has a C 1s BE at 285.5 eV and an N 1s BE at 400.6 eV. Urotropine or HMTA (C–N, sp^3 hybridization) exhibits a C 1s BE at 286.9 eV (287.3 eV for HMTA) and an N 1s BE at 399.4 eV. Polyacrylonitrile (C≡N, sp) has a C 1s BE at 286.4 eV and an N 1s BE at 399.6 eV. From Fig. 5 it is evident that the sample with higher nitrogen content ($\text{N}/\text{C}=0.4$) has a greater contribution coming from peak C, which is related to sp or sp^3 hybridization. Also, the N 1s spectra in Fig. 6 show that this film has a large contribution from peak A, which is related to sp or sp^3 hybridization. This contribution clearly decreases in favor of a greater contribution coming from peak B related to C=N bonds in the sample with lower nitrogen content ($\text{N}/\text{C}=0.3$). There still exists debate in the literature on whether the deconvoluted peaks from the C 1s spectra at $\sim 286 \text{ eV}$ and from the N 1s spectra at $\sim 399 \text{ eV}$ are assigned to C–N, C≡N, or $\beta\text{-C}_3\text{N}_4$ bonding. In this study the $\beta\text{-C}_3\text{N}_4$ bonding is not expected because our films contain less than the required $\text{N}/\text{C}=1.33$. We suggest that in the sample with $\text{N}/\text{C}=0.4$ there is a considerable number of N– $\text{sp}^3\text{-C}$ bonded sites (C–N bonds) because the corresponding BE, peak C in Fig. 6, is at 287.1 eV, which is much closer to the values 286.8 and 287.3 eV of materials with sp^3 configuration with respect to the value 286.4 eV of polyacrylonitrile (C≡N bonds).

In Fig. 7 the EELS spectra of the DLC sample grown

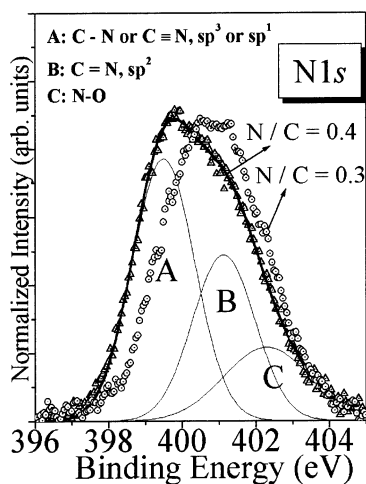


Fig. 6. N 1s core-level spectra of two CN_x films with $\text{C}/\text{N}=0.30\text{--}0.40$.

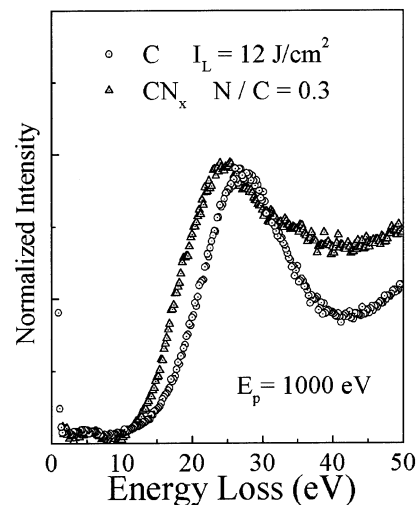


Fig. 7. EELS spectra of a CN_x film and a DLC film.

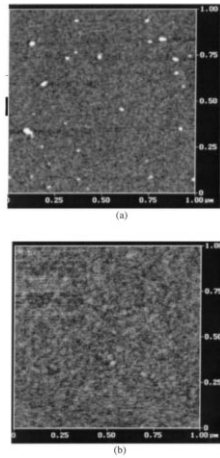


Fig. 8. AFM images of two DLC samples grown with a laser fluence of (a) 1 and (b) 3 J/cm².

with a laser fluence of 12 J/cm² and of the CN_x film with N/C=0.3 normalized at the intensity of the elastic peak are shown. It is possible to observe that the π plasmon peak is depressed in the CN_x sample as in the DLC sample grown with high laser fluences, suggesting that the fraction of sp² C bonds is almost equal in the two samples, whereas the $\sigma + \pi$ plasmon energy is shifted towards lower energies. If we suppose the same density in the two materials and if we consider that nitrogen contributes three electrons instead of the four of carbon, from Eq. (1), with the composition N/C=0.3, we obtain the energy shift of the $\sigma + \pi$ plasmon in Fig. 7.

AFM images of a 1 × 1 μm² DLC surface are shown in Fig. 8(a) and (b) for laser fluences of 32 J/cm² and 1 J/cm² respectively. Even though the root-mean-squared (rms) roughnesses of all the samples grown from laser fluences of 1 to 35 J/cm² are about 3 Å (the same of the silicon substrate), we can observe in Fig. 8(a) and (b) the appearance of small particulates of nanometer size on the surface of the sample grown with a laser fluence of 1 J/cm². The same particulates are observed on the sample grown with a laser fluence of 35 J/cm².

4. Conclusions

In this paper we have presented a study of the structural, electronic and morphological properties of

DLC and CN_x thin films deposited by PLD. In particular, the CN_x films were grown by laser ablation of graphite in a nitrogen atmosphere. The N/C ratio of the films can reach a value of 0.4. XPS analysis shows that in the DLC films the fraction of sp³ C sites doubles when the laser fluence increases from 1 to 12 J/cm². This result is confirmed by EELS measurements and it is in accord with the so called ‘sub-implantation model’ developed to explain the growth of DLC films.

More importantly, the XPS analysis shows that in the CN_x films the carbon and nitrogen atoms form stable bonds instead of simple mixing. There is a considerable amount of N–sp³-C bonded sites in a predominant N–sp²-C bonded matrix in the film with N/C=0.4. Decreasing the nitrogen (N/C=0.3) results in a decrease of N–sp³-C bonded sites. EELS analysis seems to indicate that the DLC film grown with laser fluences of 12 J/cm² and the CN_x film with N/C=0.30 have the same density and the same fraction of sp²-C bonded sites.

AFM shows an rms roughness of 3 Å on a surface of 1 × 1 μm² for all the DLC films grown with laser fluences in the range: 1–35 J/cm². Small particles of nanometer size are visible for the lowest laser fluences.

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