Diamond-Like Coatings: Microstructural Evolution under Ion Beam Assistance

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Abstract : Non-hydrogenated diamond-like carbon films have been prepared by Dual Ion Beam Sputtering and Ion Beam Assisted Magnetron. The assistance parameters –ion energy, ion mass, ion flux/atom flux– have been systematically varied and their effect on the microstructure of the films studied. The films have been characterised by Rutherford Backscattering Spectroscopy (RBS), High Resolution Transmission Electron Microscopy (HRTEM), Electron Energy Loss Spectroscopy (EELS), Positron Annihilation Spectroscopy (PAS), and Raman Spectroscopy (RS). RBS and PAS results showed that the density and the degree of disorder of the films go through a maximum with ion energy, and that the void concentration goes through a minimum. EELS and RS show that the films are mostly sp^2 bonded, with a maximum concentration of sp^3 bonding of about 16% for the largest values of density. The evolution of density with ion flux and energy is consistent with a combined effect of atomic displacements in the film leading to densification, and with damage build-up leading to progressive graphitisation as the energy is increased.

1. INTRODUCTION

During the past years, a strong interest in the field of diamond-like carbon (DLC) film deposition and characterisation has been demonstrated. This is due to the interesting properties of DLC such as high hardness, wear resistance, friction coefficient, chemical inertness, optical transparency, and high electrical resistance [1]. The DLC films can be produced by Plasma Assisted Chemical Vapour Deposition [2] or various forms of Physical Vapour Deposition [3] such as Ion Beam Sputtering [4], Magnetron Sputtering [5] and Arc deposition [6]. The latter techniques allow production of non-hydrogenated diamond-like carbon (a-C) which has been relatively little studied compared with hydrogenated diamond-like carbon. A common characteristic of these techniques is the use of energetic ions to bombard the coating during its growth. This leads to the formation of metastable microstructures showing interesting properties which are related to the different bonding configurations of the carbon atoms. The characterisation of these films is complex, and a large number of investigations have been performed to characterise the microstructure, for instance Raman spectroscopy [7,8,9], Electron Energy Loss Spectroscopy (EELS) [10,11], Transmission Electron Microscopy, X-ray Photoelectron Spectroscopy (XPS) [12] and Neutron Diffraction [13,14]. It

was found that both sp^2 and sp^3 bonded atomic sites are present in the films. The sp^2/sp^3 ratio changes strongly with the deposition technique and film growth conditions. The films obtained by these non equilibrium techniques are strongly disordered, and a large fraction of voids can also be present. The changes in sp^2/sp^3 ratio as well as the void concentration have a strong influence on the film properties such as density, mechanical or optical properties.

Not only the concentration, but also the organisation of the sp^2 and sp^3 bonds is important. Structural models of a-C films have been proposed in the literature, in relation with the sp^3/sp^2 ratio. For instance, Robertson and O'Reilly [15] and Tamor and Wu [16] proposed a model of a disordered graphitic phase imbedded in an sp^3 bonded matrix. The mechanical properties of the solid were determined by the matrix, and their optical properties by the size of the sp^2 aggregates. Beeman et al. [17] proposed a microstructural model based on a random covalent network of sp^2 - sp^3 atoms with distorted bond angles and lengths. It was also proposed that the formation of sp^2 bonded microcrystals relieves the compressive stress caused by a constrained random distribution of covalent sp^2 and sp^3 bonds [18] and thus decreases the system energy. A different configuration was proposed by Collins et al. [19] to explain the high density of their samples prepared by laser ablation. Their model proposed a distribution of sp^3 bonded microcrystals linked by sp^2 and sp^3 bonded atoms.

These results show that many unresolved questions remain concerning the microstructure of a-C in relation to its physical properties and the deposition conditions. In the present paper, we present Physical Vapour Deposition experiments of a-C under different ion bombardment conditions, and study the relationship between the microstructure and physical properties of the a-C samples as a function of the deposition parameters, in particular the ion mass, the ion energy, and the ratio between ion flux and atom flux (I/A).

2. EXPERIMENTAL

2.1. Film deposition

The effect of ion beam assistance on the properties of thin carbon layers was studied using two different techniques: Dual Ion Beam Sputtering (DIBS) and Ion Beam Assisted Magnetron (IBAM). In DIBS experiments, sputtering of a graphite target is performed with a Kaufman source. In the case of IBAM, sputtering of the graphite target is performed by a magnetron discharge. In both experiments, bombardment of the growing carbon film is performed by the same Kaufman source. For ion beam assistance, the source was fed with different inert gases, and the discharge potential was chosen in order to create the ion beam and avoid double ionisation of the gas. The Ion/Atom flux ratios (I/A) were calculated using the deposition rate of non-assisted films, taking into account the bombardment by neutrals [20].

The use of DIBS and IBAM allowed us to study the effect of ion bombardment in a large domain of parameters. We could vary the ion mass, ion energy and I/A ratio independently and study the effect of ion beam assistance on film density, sp^3 content, void concentration and microstructure.

2.2. Film characterisation

Because properties such as density are sensitive to the bonding characteristics of the film and void concentration, a combination of techniques is necessary to characterise the microstructure. These techniques are Rutherford Backscattering Spectrometry (RBS) for the density, Elastic Recoil Detection Analysis (ERDA) and Auger Electron Spectroscopy (AES) for chemical analysis, Raman spectroscopy for the short

range structure, Electron Energy Loss Spectroscopy (EELS) for sp^3 content, and the positron-annihilation S- parameter method (PAS) for the void concentration [21].

Observations made by High Resolution Transmission Electron Microscopy showed characteristic features of oriented turbostratic graphite microcrystallites in the a-C films. No pattern corresponding to diamond diffraction could be observed in the diffraction diagram, and no difference between different preparation conditions could be found.

3. RESULTS

3.1. Composition

The composition of the samples has been measured by RBS and ERDA. It was found that the main contamination of the films was coming from the ion assistance. The Ar incorporation was limited to 2% and that of Xe to 4%. An average H concentration of 3 at% for DIBS samples and 10at% for IBAM samples was measured by ERDA. No systematic variation of the contamination with bombardment parameters could be found[22].

3.2 Density measurements:

In order to study the effect of ion mass on the densification process, deposition experiments were performed with DIBS using different ions at a constant energy (200 eV) and a beam current corresponding to an I/A ratio of 0.24. The maximum density (2.3 g/cm^3) was observed for Ne^+ ions assisting the growth. The density decreased very rapidly for both lighter and heavier ions.

Figure 1: Variation of the density of the films obtained with the DIBS process as a function of energy transfer coefficient, with an ion energy of 200eV and an I/A ratio of 0.24.

Changes in the film density are presented in Fig. 1 as a function of the energy transfer factor, defined as $\gamma = 4m_i m_c / (m_i + m_c)^2$, where m_i is the mass of the ion, m_c the mass of carbon. It can be seen that the density increases with γ , illustrating the fact that the densification mechanism is assisted by ballistic effects.

Fig.2. Variation of the density of the carbon films with the ratio of the ion flux to atom flux I/A , in the case of IBAM and DIBS deposition for 200eV Ar^+ ions.

The influence of Ion flux/Atom flux (I/A) on the densification process was studied with both DIBS and IBAM devices for 200 eV Ar^+ ions. The linear increase of the density with I/A can be clearly seen in Fig. 2. The two curves do not coincide, but have the same slope. The higher density of IBAM coatings can be attributed to the background bombardment from the magnetron discharge [23]. The highest values of the density (i.e., larger than 3.0) were measured for high fluxes, but these results include a constant amount of about 2.5 to 4 at% argon incorporated into the carbon. The contribution of Ar to the film density was approximately 10% to 15%. Film cracking caused by high stress values [24] was observed for the higher fluxes.

The effect of ion energy on the density of the film was studied for Ar and Xe ions at constant I/A values. Figure 3 shows the changes in the density of the films with the Ar^+ and Xe^+ ion energy at a fixed value of I/A for DIBS and IBAM (0.24 and 0.1 respectively): A maximum density is obtained around an ion energy of 100 eV to 150eV for Ar and 250eV to 300eV for Xe. The Ar and Xe content of the films was constant at around 2 at.% and was not responsible for this trend. We could not produce films with energies higher than 300eV in the case of Xe, because of spallation due to the high stress level in the film.

Fig. 3: Variation of density of the carbon films with energy in the case of Ar^+ and Xe^+ . The two sets of experiments with Ar^+ were performed with DIBS (curve labelled $I/A=0.1$) and IBAM (curve labelled $I/A=0.24$). Xe^+ experiments were performed with IBAM and a value of $I/A=0.1$.

3.3 Positron Annihilation Spectroscopy

PAS is based on the measurement of the shape of the 511 keV annihilation line from thermalized positrons annihilating in the sample. The 511 keV line is Doppler broadened as a result of the motion of electrons in the sample, and hence its shape is a measure for the momentum distribution of the electrons. The line shape is characterised by a parameter S , defined as the ratio between the area under a suitably defined central part of the spectrum peak and the total area under the spectrum line. The S parameter is particularly sensitive to the presence of open-volume defects in the sample such as vacancies or voids, which constitute a negative potential and thus can trap positrons: In a vacancy, the density of high momentum core electrons is lower than in the bulk, while the density of low momentum valence electrons is comparable to the bulk value. As a result, the S parameter increases when open-volume defects are present.

Fig. 4 shows S parameter curves obtained for different DIBS and IBAM samples. The low energy part of the curve corresponds to the a-C layer, the high energy part to the Si substrate. The S -values of the films averaged over the energy interval between 1 and 4 keV have been normalised relative to Si. This “relative S parameter” is plotted against the ion assistance energy in Fig. 5 in the case of DIBS and Ar^+ ion assistance. It can be seen that the S -parameter, i.e. the concentration of voids, changes with the ion energy with a minimum value around 150 eV. For comparison, the value of the relative S parameter for pyrolytic graphite is 0.925.

In most cases, the a-C layers have a higher concentration of voids than graphite, but also a higher density. It can then be concluded that in the present case, there is no direct proportionality between the concentration of voids as measured by PAS and the density. This could be explained by changes in the H concentration

between DIBS and IBAM since hydrogen reduces the void concentration and has a strong influence on density at the same time. Another possible explanation could be that the changes in density are provoked by a damage induced graphitisation as will be explained in section 4.

Fig. 4 : S parameter curve as a function of positron energy for 3 different samples prepared by DIBS and IBAM.

Fig. 5 : S parameter and density curves as a function of ion assistance energy. The samples were prepared with DIBS and Ar⁺ ions with an I/A ratio of 0.24.

3.4 Electron Energy Loss Spectroscopy

EELS spectra for DIBS samples are shown in Fig.6, as well as spectra for Highly Oriented Pyrolytic Graphite (HOPG) and diamond. For HOPG, the two peaks at eV and 26 eV can be attributed to the π and ($\pi + \sigma$) electron plasma resonances respectively [25]. In the case of diamond, two plasmon peaks can be observed around 24 eV and 32 eV. In the case of a-C samples, the π peak can hardly be detected in the direct signal and its position was found using the derivative of the spectrum. The position of the $\pi + \sigma$ plasmon peak changes between 26 and 28.8 eV, indicating a low concentration of sp^3 sites present. By using the calculations proposed by Wang et al.[25], sp^3/sp^2 ratios can be calculated following the formula :

$$\frac{C_{sp^3}}{C_{sp^2}} = \frac{0.23}{4 \omega_p^2(\pi)} \left\{ \omega_p^2(\pi + \sigma) - \frac{4 \pi e^2}{m} \cdot C_H \right\} - 1$$

where $\omega(\pi)$ and $\omega(\pi + \sigma)$ are the π and $\pi + \sigma$ plasmon energies, C_H the hydrogen concentration, m and e the mass and charge of an electron. The hydrogen concentration could not be measured for all samples and was neglected in the evaluation of sp^2/sp^3 ratios. This leads to average values of sp^3 concentrations between 0 and 16% which are plotted against density in Fig. 7. Since we did not take into account the contribution of H, these values are slightly overestimated. An interesting point is that large changes in density are induced by a relatively small amount of sp^3 bonding, much smaller than a simple proportionality rule between graphite (density 2.26g/cm³ and 0% sp^3) and diamond (3.54 g/cm³ and 100% sp^3) would lead us to expect.

Fig. 6 : EELS spectra of a-C films prepared by DIBS under different Ar⁺ assistance energies. The π peak clearly apparent in the HOPG films indicates the dominant sp^2 character of the bonding. The position of the π and $\pi + \sigma$ peaks is used to calculate the sp^3 concentration in the films.

Fig. 7 : Values of sp^3 concentrations plotted against density as measured by RBS, for DIBS and IBAM samples.

3.5 Raman Spectroscopy

Raman spectroscopy was performed on three samples prepared by IBAM with Ar^+ ion assistance and labeled A, B and C. The Raman spectrum of crystalline diamond consists of a single sharp peak at 1332 cm^{-1} . The Raman spectrum of crystalline graphite consists of two peaks: the G peak centred on 1550 cm^{-1} is the zone centre E_{2g} mode of the perfect graphite crystal and the D peak centred on 1350 cm^{-1} is a zone edge A_{1g} mode activated by disorder in the graphite crystal [26,27]. The D mode is a common feature of disordered graphitic carbon. Its intensity relative to the G mode (as measured by the ratio I_D/I_G) changes with the disorder [28]. Tuinstra and Koenig [29] have shown that the ratio I_D/I_G is inversely proportional to the graphitic crystallite size L_a as measured by XRD. In mixed sp^2 - sp^3 bonded carbon layers, the overall Raman spectrum is dominated by the G component, because the cross section of the graphite stretching mode is much higher than that of the 1332 diamond mode. Details of the analysis are reported elsewhere [8]. The ion energies used for the preparation of samples A, B, and C were 50, 100 and 300 eV respectively. The value of I/A was constant and equal to 0.1. The corresponding densities obtained were 2.16, 2.23 and 1.68. The Raman spectra of the 1st order are similar to other results in the literature [27,30,31]. The experimental results are best fit by 3 gaussians and a constant background. Two D and G peaks can be observed around 1350 cm^{-1} and 1580 cm^{-1} and their positions vary with the ion bombardment conditions. Abello et al. [8] showed that the G and D bands in our samples cannot be attributed to independent species (for instance well isolated sp^2 and sp^3 domains), owing to the existence of the G+D band that can be seen in the second order spectra. Taking the relationship proposed by Tuinstra and Koenig [29] between L_a and I_D/I_G leads to small values of L_a equal to 45, 25 and 50 Å for samples A, B and C respectively. The highest density corresponds to the lowest crystallite size. Moreover, the ratios Γ of the half widths of the G

and D peaks are indicative of strong disorder within graphitic bonding and a large variation in bond angle [30]. The highest degree of disorder is found for sample B with a value of Γ equal to 0.35, to be compared with 0.65 and 0.73 for sample A and C respectively. We find that the decrease of density at high ion energies is accompanied by a decrease of the degree of disorder.

4. DISCUSSION

4.1 Microstructure

Raman spectroscopy indicates that our films are characterised by a strongly disordered graphitic phase and small graphitic clusters. The high density samples are characterised by the greatest degree of disorder and the smallest graphitic crystallite size. These graphitic domains represent a very low volume concentration, as confirmed by EELS spectra and HRTEM, but the total sp^3 concentration, as calculated from the EELS spectra, is of the order of 0% to 15%. This means that the phase embedding the clusters is mostly graphitic, with a low concentration of sp^3 bonds. Our results need to be compared with the models of a-C proposed by Robertson and O'Reilly [15] and Tamor and Wu [16]. In these models, a-C is described as a disordered graphitic phase imbedded in an sp^3 bonded matrix. Our experiments thus lead to a completely different picture. In particular, the EELS and Raman results completely exclude the possibility of presence of sp^3 clusters but, on the contrary, indicate that sp^3 bonds are distributed homogeneously in the disordered graphitic phase. In that sense, the formation of sp^3 bonds results from the destruction of sp^2 bonding, followed by internal reorganisation of the lattice.

4.2 Effect of ion bombardment

The results of characterisation of the films lead to a clear picture of the effect of ion bombardment. The influence of ion beam assistance on the microstructure of a-C can be described by two types of actions depending on the ion energy. The transition between the two regimes depends on the ion mass, or in other words, on the energy transfer between the ion and the target.

4.2.1 Low ion energy regime

At low energies, ion bombardment produces an "ion pinning effect" as described by Müller [32]. The ion bombardment leads to a reduction of the voids in the film by compacting of the atoms deposited on the surface. In the absence of bombardment, the mobility of the condensing atoms is low and results in a large void concentration and a low density. The ion bombardment leads to increased atom mobility, which results in filling of the voids, and thus reduction of the void volume and increase of disorder. The increase of disorder produces cross linking between graphitic planes by sp^3 bonds which can explain the observed increase in density and the corresponding sp^3 concentration. Raman results show that this disordered phase grows at the expense of the sp^2 bonded domains and reduces their size. Kaukonen and Nieminen have shown that the increase of disorder leads to strong changes in the coordination of the atoms in the films, i.e. changes in the average atom ring numbers [33]. The PAS results give very precious and unique information on this phenomenon, although the distinction between voids and structure "openness" related to the formation of different four-, five- and six-fold rings is difficult to make.

4.2.2 High ion energy regime

Beyond an energy threshold which depends on the ion mass, the film density and the sp^3 concentration decrease. The decrease of density is related to two mechanisms: an increase of the void concentration which can clearly be seen in the PAS spectra, and an increase in size of the graphitic clusters, which can be observed in the Raman spectra. The decrease in the densification efficiency at higher energies could thus be explained by a damage-induced graphitisation of the films under ion bombardment. Such a mechanism has also been invoked to explain conductivity changes in ion irradiated a-C:H [34]. This explanation is also consistent with the cumulative effect of ion bombardment illustrated by the density evolution with I/A shown in Fig. 2.

4.2.3 Energy transfer in ion beam assistance

In the experiments described above, we have seen that three parameters have a strong influence on the densification mechanism : ion mass, ion energy, and I/A ratio. Generally, the fact has been recognized that ion energy and the ion-to-atom ratio should not be looked at separately, and attempts have been made to identify one significant and universal parameter combining these two values, which would describe these different preparation conditions. For instance, Targove and McLeod [35] have proposed to use the average momentum transfer between the ions and the target atoms, defined as :

$$P_{av} = P_{max} \frac{I}{A}$$

with

$$P_{max} = \sqrt{2 m_i \gamma E_i}$$

where γ is the ballistic factor already defined above. This parameter was again used for instance by Kester and Messier [36] to analyse their results on cubic boron nitride (c-BN) formation. Using this parameter allowed a direct comparison of the different experiments performed under different energies and I/A values. This was illustrated by a strong reduction of the scattering of experimental results (such as density [35] or cubic phase content [36]) as compared to an analysis of the results against ion energy or I/A alone. In fact, the use of momentum transfer as defined above is not consistent with the common understanding of ion beam irradiation of materials. It is well known that the energy of the incoming ion is released in the solid in the form of electronic excitation, phonon excitation and nuclear collision losses. The above definition of momentum transfer using the total initial energy implies that the entire energy of the ion is consumed in "hard sphere" nuclear collisions, which is simply not true.

In order to evaluate the energy release in the solid, we have run TRIM92 Monte Carlo simulations [37], using a density of 2 g/cm³, a displacement energy E_d of 35 eV and a surface binding energy of 7.4 eV, the values generally accepted now for this type of calculation [38].

We define an average deposited energy density by :

$$\langle E_{dep} \rangle = \frac{E_{dep}}{V} \cdot \frac{I}{A} = \frac{E_{dam} + E_{ph.}}{V} \cdot \frac{I}{A}$$

where E_{dep} is the deposited energy defined as the sum of the damage energy E_{dam} (point defect production) and phonon excitation energy E_{ph} . The cascade volume is defined as:

$$V = \pi R \cdot \Delta y^2$$

where R is the ion mean projected range and Δy the lateral projected range. $\langle E_{\text{dep}} \rangle$ thus represents the energy released per unit volume of the film and per deposited atom in the form of atomic collision processes. Fig. 8 shows the evolution of density as a function of $\langle E_{\text{dep}} \rangle$ for all the different DIBS and IBAM experiments presented in Fig. 1 to 3. Results from other experiments using N_2^+ for ion assistance [39] have also been plotted in the same graph. We can see that although the scattering of the results is important, the evolution of density of a-C films under the different ion bombardment conditions is represented by a single curve, going through a maximum at about $0.2 \text{ eV/\AA}^3$. This limit indicates the transition for which ion induced graphitisation occurs.

in agreement with the different models of a-C proposed in the literature. Our results are consistent with a microstructural model where a-C is composed of sp^2 bonded clusters embedded in an amorphous phase containing an intricate mixture of sp^3 and sp^2 bonded atoms. The density evolution of the layers observed in these experiments is consistent with an "ion pinning" effect at low energies which increases damage and sp^3 bonding in the films up to a disorder threshold. Beyond this threshold, damage induced graphitisation leads to an increase in the void concentration and a decrease in the film density. The effect of the ion bombardment under different ion mass, energy and I/A ratios can be evaluated by a single parameter which is the average deposited energy in nuclear processes.

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