Hard graphitic-like amorphous carbon films with high stress and local microscopic density

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Citation: Journal of Vacuum Science & Technology A 19, 971 (2001); doi: 10.1116/1.1365130

View online: http://dx.doi.org/10.1116/1.1365130

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I. INTRODUCTION

For two decades, there has been a continuous effort to characterize and understand the structure of amorphous carbon films produced by various methods. However, a full understanding of the microstructure of $a$-C films is still a challenge mainly due to the ability of carbon to bond with different hybridization. For example, depending on the mixing of the $sp^2$ and $sp^3$ bonds, it is possible to prepare materials with completely different structures and properties. Furthermore, it is well known in the literature that the type of carbon hybridization alone does not completely determine the properties of $a$-C films: they are also critically dependent on the deposition conditions and applied technique. Due to the strong in-plane bonds of graphite, a question was raised recently about the possibility of preparing graphitic-like amorphous carbon films with high hardness.1 Recently, $a$-C films with a graphitic-like structure and relatively high hardness (20–40 GPa) have actually been developed and treated as a new form of hard $a$-C films.2–4 However, the microstructure of hard graphitic-like $a$-C film and its influence on other properties are still unclear and a subject of intense investigation. The understanding of this hard $sp^2$ microstructure is of fundamental importance for the optimization of the material for possible technological application. In this work, we report on the preparation of hard predominantly $sp^2$-bonded amorphous carbon films deposited by ion beam-assisted deposition (IBAD) technique using neon, argon, and krypton ions.

II. EXPERIMENT

The $a$-C films were deposited by the IBAD technique using two Kaufman ion sources. A detailed description of the deposition system can be found elsewhere.5 Three sets of films were prepared using separately Ar$^+$, Kr$^+$, and Ne$^+$ as bombarding ions. Each noble gas was introduced in both Kaufman sources, one for the sputtering of a graphite target and the other for the simultaneous assisting of the growing film. The graphite target was sputtered using ion beam energy of 1500 eV. Films of about 100 nm thick were prepared at 150 °C with ion beam-assisting energies in the range of 0 to about 800 eV. The ion per C atom flux ratio ($I/A$) increases, for the three series of films (Ne, Ar, and Kr), from 0.2 to 1.8 with the assisting energy. For each assisting energy, the flux ratio is about the same (within 10%) for the three series. The ion flux ($I$) was obtained by measuring the assisting ion beam current density, and C atom flux ($A$) was determined from the deposition rate without using the assisting gun. After the deposition, the samples were transferred within the vacuum system to the ultrahigh vacuum chamber (pressure $<10^{-7}$ Pa) for in situ photoelectron spectroscopy measurements (XPS, UPS). No oxygen was detected. In addition, no contaminants (such as hydrogen, water, etc.) were detected by Fourier transform infrared spectroscopy within the spectrometer resolution. After the XPS/UPS analysis, the

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(Received 25 August 2000; accepted 19 February 2001)

In this work, we report unusual properties of amorphous carbon films prepared by ion beam-assisted deposition using different noble gases (neon, argon, and krypton). Independent of the noble gas ions used, the intrinsic compressive stress and plasmon energy increase sharply with the assisting ion beam energies up to 100 eV. Above this energy, the material properties depend on the mass of the ion. The highest values of stress (~12 GPa) and plasmon energy associated with the C $1s$ core electron (29.5 eV) are of the same order of magnitude as those reported for highly tetrahedral amorphous carbon films. Structural results, however, indicate that the material is composed of a hard, highly stressed, and locally dense graphitic-like network, i.e., a predominantly $sp^2$-bonded material. It is suggested that the ion bombardment compacts the film structure by reducing the interplanar cluster distances, generating high compressive stress and high local density. The differences in the properties of the films introduced by Ne, Ar, and Kr bombarding ions are also discussed. © 2001 American Vacuum Society. [DOI: 10.1116/1.1365130]
III. RESULTS AND DISCUSSION

Figure 1(a) shows the dependence of the plasmon energy associated to the C 1s core electron (from now on “plasmon energy”) as a function of the assisting energy. The plasmon energy increases significantly upon increasing assisting energy. Provided that the assisting energy is below 100 eV, similar plasmon energies are obtained independently of the bombarding ion (Ar\(^+\), Ne\(^+\), or Kr\(^+\)). By using Ne\(^+\), a maximum plasmon energy value of about 28.7 eV is reached at an assisting energy of 100 eV. On the other hand, when Ar\(^+\) (Kr\(^+\)) is used, maximum plasmon energy of 29.5 eV (29.1 eV) is obtained at assisting energies of about 400 eV. The plasmon energy peak, measured by XPS, is produced by the inelastic scattering of C 1s electrons before leaving the sample.\(^7\) In the free-electron model, the plasmon energy represents the collective excitations of valence electrons. For various materials, such as a-C, the maximum of the electron energy-loss function corresponds to the classical plasmon energy.\(^8,9\) As is well known, the square of the plasmon energy \(E_p^2\) is proportional to the local electronic (atomic) density of the material.\(^10,11\) Therefore, in amorphous materials the plasmon energy can be used as a probe of the local microscopic density rather than to the global macroscopic density of the film.\(^5,7\)\(^-\)\(^11\) So, the variation of the plasmon energies displayed in Fig. 1(a) indicates a local density modification of the films.

The compressive stress reaches a maximum of \(~10\) GPa for Ne\(^+\) assisting energies of \(~100\) eV. Most probably due to the experimental uncertainties, no differences in the stress were obtained with Ar\(^+\) and Kr\(^+\) ions. It is noteworthy that both stress and plasmon energy have a similar dependence on the assisting energy. The highest (smallest) plasmon energy and stress is obtained for Ar\(^+\) (Ne\(^+\)) by assisting the growth with \(~400\) eV [Fig. 1(a)]. Moreover, the highest stress values (\(~12\) GPa) and plasmon energy (\(~29.5\) eV) obtained for Ar\(^+\) assisted films are comparable to those reported for highly tetrahedral amorphous carbon films.\(^12,13\) Also, the maximum of the plasmon energy depends on the bombarding ion species. Since the deposition conditions of the three series of films (Ne, Ar, and Kr) are similar, including the same energy dependency of the flux ratio, an explanation of these findings is attempted.

For assisting energies under 100 eV, the mechanism of material densification and stressing is independent of the ion atomic mass [Figs. 1(a) and 1(b)]. This behavior can be understood by the classical scattering theory. The energy transferred \((\Delta E)\) by the ions to the growing film is given by \(\Delta E = \gamma (I/A) E_a\) where \(\gamma = 4m_1 M_{\text{ion}}/(M_{\text{ion}} + m_c)^2\), \(m_1\) is the carbon mass, \(M_{\text{ion}}\) is the ion mass, \(I/A\) is the ion to atom flux ratio (\(I = \text{Ne}^+\), \(\text{Ar}^+\), or \(\text{Kr}^+\) and \(A = C\) in our case), and \(E_a\) is the ion assisting energy. As indicated in Fig. 1(c), the energies transferred by Ne\(^+\), Ar\(^+\), and Kr\(^+\) are about the same for energies below 100 eV. This may explain why the ion mass starts to exert more influence on the properties of the films at bombardment energies above 100 eV. Another important point is that the plasmon energy [Fig. 1(a)] is larger (smaller) for materials assisted with Ar\(^+\) (Ne\(^+\)), indicating a more efficient densification when Ar\(^+\) ions are used. It is well known from classical scattering theory that the energy transfer is more effective between atoms of equivalent mass (see above the expression of \(\Delta E\)). Among the noble gases, Ne\(^+\) is the one with a mass closest to C atoms and hence has the most effective energy transference on ion bombardment, see Fig. 1(c). This probably means that the large energy transferred by Ne\(^+\) would sputter and damage the material rather than efficiently increase its local density. On the other hand, the massive Kr\(^+\) ions would weakly interact with the C atoms and a less effective material compaction would be achieved. Results of Marton et al. reporting TRIM simulations of total displacements and defects created in graphite by noble gas bombardment at various energies seems to support...
this interpretation.\textsuperscript{14} These researchers show that Ne\textsuperscript{+} is the one which produces the largest total atom displacements and vacancies in graphite. Conversely, the Kr\textsuperscript{+} ion is less effective in generating displacements (i.e., compression) in graphite, indicating the poor interaction between Kr\textsuperscript{+} and carbon atoms. In short, we suggest that there is an optimum ion assisting energy window for maximum material densification. This is probably the reason why Ar\textsuperscript{+}, an ion having an intermediate atomic mass, compacts the material more efficiently.

The plasmon energy has been widely used to estimate the degree of $sp^3$ bonding in pure amorphous carbon films.\textsuperscript{12,13,15} Values of about 30 eV have been reported for films with high concentration of $sp^3$ sites ($ta$-C).\textsuperscript{12,13,15} In addition, these films also show very high stress (>7 GPa).\textsuperscript{13,16} It is to be noted that similar values of plasmon energy and stress of those of $ta$-C were also found in our films (see Fig. 1). As will be seen, however, a careful analysis of the film structure shows no evidence of a highly tetrahedral carbon phase. Figure 2 shows a Raman spectrum of the film with the highest plasmon energy. The disorder ($D$) band ($\sim$1340 cm$^{-1}$) and graphitic ($G$) band ($\sim$1540 cm$^{-1}$) are clearly observed. The ratio between these two bands is commonly used to obtain structural information of a-C films.\textsuperscript{17} All films reported here have a high $I_D/I_G$ ratio of about 2. This high $I_D/I_G$ ratio indicates a strong presence of $sp^2$ clusters in the film structure, in contrast with the low $I_D/I_G$ ratio ($\sim$0.1) found in $ta$-C films.\textsuperscript{17} This result is also supported by UPS measurements. Figure 3 depicts the UPS spectra of films prepared with the three noble gases used. A shoulder at the top of the valence band (0–4 eV) is characteristic for C–C $\pi$ bonds, indicating the predominant presence of $sp^2$ sites in the material. No significant variation of these states was observed as a function of the assisting energy and the noble gas used. For comparison purposes, the top of the valence band of a $ta$-C film was also included in Fig. 3.\textsuperscript{15} In addition, the analysis of the C 1$s$ core level spectrum of our films (Fig. 4) also indicates the predominance of $sp^2$ sites. It is known that the C 1$s$ peak is located at around 284.3 eV for graphitic structures, while the respective position for diamond is around 285.0 eV.\textsuperscript{15,18} The C 1$s$ spectrum, shown in Fig. 4, was deconvoluted using three Gaussians components representing the $sp^2$ (284.3 eV), $sp^3$ (285.0 eV) bonding structures, and a small background component. This procedure has already been used to estimate the relative concentration of $sp^3$ and $sp^2$ sites.\textsuperscript{15,18} By using the relative ratio of the areas [$A_1(sp^2)/A_2(sp^3)$], we estimate a concentration of about 80% of $sp^2$ sites in our films, which is in agreement with the UPS results. Moreover, the low optical band gap (0–0.5 eV) obtained for all samples is consistent with a material with a high number of $sp^2$ sites. Using an empirical relation between band gap and $sp^2$ concentration reported by Ferrari, Chowalla and co-workers,\textsuperscript{17,19} a content higher than 80% of $sp^2$ sites is expected.

Figure 5 shows the nanohardness measurement for the hardest a-C film prepared under Ar\textsuperscript{+} bombardment as a function of the indentation depth. As expected, the hardness
The energetic noble gases ions striking the film surface can assist the growth of the film. The energetic ions can be related to the difference in the deposition process, and the low density contrasts to the low density obtained by RBS, Fig. 6. The values of macroscopic density dependence on the noble gas assistance energy.

The high microscopic (local) density contrasts to the low macroscopic density obtained by RBS, Fig. 6. The values of about 2.3 g/cm$^3$ are similar to the density of graphite but are relatively small compared to $\sim 3$ g/cm$^3$ reported for ta-C films. This result indicates that our films have indeed a graphitic-like structure, as also supported by the results of UPS, XPS, and Raman. The difference between the high microscopic density and the low macroscopic density can be explained in terms of the presence of voids in the material structure, which reduces the average macroscopic density.

On the other hand, as already mentioned, the plasmon energy is sensitive to the local carbon environment and is not affected by the presence of voids. Another important point is that the macroscopic density dependence on the noble gas assistance energy (Fig. 6) is different from those IBAD samples obtained by Andre et al., which found decreasing density values at energies as low as 200 eV. This can be understood due to the low values of ion/C flux ratio (I/IA) used in their work (<0.2) compared to the higher I/IA (~1.8) values used in our work.

The analysis presented above strongly suggests the existence of a hard graphitic-like structure with high stress and high local density. In short, these films are composed of a matrix of strained and locally dense $sp^3$ clusters, probably cross linked by a small fraction of $sp^2$ sites. Usually, hard a-C films with a high concentration of $sp^3$ sites (ta-C) are prepared by the direct bombardment of carbon species ($C^+$). The relatively high stress (>7 GPa) and plasmon energy (~30 eV) observed for these films are generally interpreted by the subimplantation model. In this model, the carbon ions arriving within an optimum energy range (50–600 eV), are implanted beneath the film surface increasing the local density and generating high compressive stress by the preferential formation of $sp^3$ C–C bonds. Thus, the high stress and local density are directly related to the formation of the $sp^3$ C–C bonds in the film during growth. In this work, however, we report the formation of a mainly graphitic-like a-C structure with both high stress and local density comparable to those obtained for ta-C films. Therefore, it is evident that the (standard) subimplantation model cannot be applied to these experimental findings. The reason can be related to the difference in the deposition process, since we used noble gases to assist the film during growth, instead of an ion beam of carbon atoms.

In an attempt to understand how such a structure could be formed, it is interesting to analyze the effects of high pressure on the lattice parameters of polycrystalline graphite. By applying different hydrostatic pressures on powdered graphite, Lynch and Drickamer reported a decreasing interplanar distance with increasing pressure, see Fig. 7. On the other hand, these authors also reported a nonsignificant variation in the in-plane distance of the graphite powder. As indicated in Fig. 1, there is a correlation between the plasmon energy and the compressive stress. To compare these results with those of Lynch and Drickamer, we have plotted the relative plasmon energy, i.e., the relative local density as a function of compressive stress of our films (Fig. 7). It is worth noting that the range of hydrostatic pressure used by Lynch and Drickamer is equivalent to the compressive stress of our films. As observed in the plot, the behavior of the local relative density on increasing stress has a very similar dependence to that of the graphite interplanar distance reduction as a function of the applied pressure. Therefore, it is probable that a similar reduction of the distance between planes of the graphitic-like clusters would be the cause of the increasing local density in our samples.

The suggested reduction of the interplanar distance of graphitic-like domains, generating high stress and high local density, is probably related to an implantation process induced by the intense noble gas bombardment during growth. The energetic noble gases ions striking the film surface can
generate a "knock-on" process, forcing the implantation of carbon atoms without necessarily creating \( sp^3 \) bonds. Therefore, the implanted carbon atoms compress the film structure, increasing the local density and maintaining the \( sp^2 \) bonding structural character. The reduction of the interplanar distance and the random distribution of the \( sp^2 \) clusters, crosslinked by a small concentration of \( sp^3 \) sites, can be responsible for the relatively high hardness of the films. These results are also in agreement with the recent finding obtained by Monte Carlo simulations, showing that it is possible to form highly compressed threefold coordinated sites.23 Also, the implanted noble gases incorporated into the film structure (~3 at. %) may be partially responsible for the observed stress. Indeed, stress of the order of 1 GPa has been reported for implanted noble gas into amorphous semiconductors and metallic films.24

IV. CONCLUSIONS

In summary, we presented novel results in graphitic-like \( \alpha-C \) films with high stress, local density, and hardness by intense noble gases bombardment of the film during growth. It is suggested that the strong ion bombardment knock-on carbon atoms beneath the surface. The implanted carbons compact the film structure by the reduction of the distance between the \( sp^2 \) clusters, inducing both high compressive stress and local (microscopic) density. The achievement of highly stressed and locally dense films with low concentration of \( sp^3 \) sites can also be understood with the ideas of the subimplantation process. Finally, it is shown that the plasmon energy alone cannot be used as a measure of the degree of \( sp^3 \) bonding in pure \( \alpha-C \) films.

ACKNOWLEDGMENTS

This work was partially sponsored by FAPESP, CNPq, and PADCT. The authors are in debt to Dr. F. L. Freire, Jr. for the RBS measurements.

Fig. 7. Normalized interplanar distance (CICO) of graphite (*) as a function of the applied pressure from Ref. 22 and relative local density increase \( (P_o, P) \) of \( \alpha-C \) films as a function of the compressive stress using neon (\( \Delta \)), argon (○), and Kr (■) as working gases. \( C_o \) represents the graphite interplanar distance under a pressure of about 1 GPa, and \( P_o \) represents the plasmon energy squared for the three sets of films with a compressive stress value of about 1 GPa.