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2002 J. Phys.: Condens. Matter 14 5083

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Effect of simultaneous Ne⁺ ion bombardments on bonding structure of carbon films deposited from thermally evaporated C₆₀ fullerene

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Received 29 October 2001, in final form 24 April 2002

Published 9 May 2002

Online at stacks.iop.org/JPhysCM/14/5083

Abstract

Carbon thin films have been deposited on Si(111) wafers through thermally evaporated C₆₀ with simultaneous bombardments of Ne⁺ ions. C₆₀ film can be prepared for Ne⁺ ion energy up to 500 eV, indicating the high stability of the cage-like structure of the C₆₀ molecule. The conversion from C₆₀ structure into amorphous carbon takes place on increasing Ne⁺ ion energies to 700 eV, in which a morphological change from a nodule-like surface to featureless structure is observed. With further increase of Ne⁺ ion energies from 1 to 5 keV, the surface roughness of the amorphous carbon films is enhanced, while a higher fraction of sp³ bonding and a larger optical bandgap are obtained at relatively low Ne⁺ ion energies. These suggest that the ion sputtering is not only responsible for the surface roughening but also has significant influence on the bonding structure in ion-assisted amorphous carbon films.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Various bonding states of carbon allow it to form a wide variety of phases involving crystalline and noncrystalline forms, such as diamond, graphite, fullerene and amorphous carbon. The interconversions of pure carbon phases have been the subject of intensive research due to fundamental scientific and technological interest [1–3]. It has been reported that C₆₀ fullerene has been squeezed into diamond under high pressure [1]. C₆₀⁺ ion impact is an important approach to transfer C₆₀ to other forms of carbon. Under ion bombardments, C₆₀ or its impact products are deposited onto or into the surface, which leads to formation of other forms of carbon. Gaber *et al* [4] have obtained amorphous carbon from a pulsed fullerene ion beam with energies ranging from 1 to 10 keV; they do not find any evidence for an influence of the ion acceleration voltage on film properties. Zhu *et al* [5] reported the interaction of C₆₀

fullerene and Ar ions by post-irradiation of C₆₀ film. It is still of interest to investigate the evolution of bonding structures of the carbon films deposited from thermally evaporated C₆₀ with simultaneous ion bombardment. Most of these investigations have only been focused on the fragmentation patterns or fullerene stability in impact-induced fragmentation processes based on the mass spectroscopy measurements [6–9].

On the other hand, it is recognized that energetic ions are suitable for the control of microstructure and properties for amorphous carbon films [10, 11]. The optimal ion energy region for the maximal sp³ fraction is 50–600 eV in the direct C⁺ ion deposition of diamond-like carbon (DLC) films [10]. The deposition mechanism is described by a subplantation model [12]. According to this model, the preferential promotion of sp³ bonding over trigonal planar sp² structure occurs due to a quenched-in increase in density during the slowing-down process of the incoming ion. In ion-beam-assisted deposition (IBAD), momentum is transferred to the condensing atoms via the indirect knock-on bombardment of assisting ions. Besides, a series of chemical reactions in IBAD can be generated due to the collisions between incident ions and source species, which induce many atoms, clusters and radicals. These activated precursor species have wide energy ranges. IBAD therefore involves not only the vapour process resulting from collisions between incident ions and molecules/atoms but also ion implantation. The growth mechanism becomes more complex.

In the present study, the carbon thin films were synthesized through C₆₀ vapour assisted with simultaneous bombardments of Ne⁺ ions. We have systematically investigated the effect of ion energy on the bonding structures of carbon films. The conversion from C₆₀ to amorphous carbon film is observed under appropriate ion energy. The further property evolution of amorphous carbon films demonstrates that ion subplantation is an important process but the ion sputtering effect cannot be neglected.

2. Experimental details

Carbon films were prepared by an IBAD technique. This machine is equipped with an ion gun and a sublimator. C₆₀ powder with the purity of 99.99% was placed in a pyrolytic BN crucible of the sublimator. The background pressure in the chamber was less than 2×10^{-6} Pa. The Si(111) wafers used as substrates were rinsed ultrasonically with de-ionized water, acetone and ethanol respectively, before they were placed on the substrate holder.

C₆₀ vapour was produced by heating electrically the sublimator up to 370 °C, and the growing film was bombarded simultaneously by Ne⁺ ions. The incident angle of the Ne⁺ ion is 60° from the substrate normal. The substrate temperature was controlled at 60 °C, while the working pressure was maintained around 6×10^{-4} Pa in the chamber. After the deposition, the carbon films were analysed by micro-Raman spectroscopy, atomic force microscopy (AFM) and optical absorption spectroscopy. Micro-Raman spectra were recorded at room temperature using the 514 nm line of an Ar ion laser. The morphologies of the prepared samples were examined by AFM (JSPM-4200). The root-mean-square (rms) surface roughness was also evaluated through AFM observation. Optical absorption spectroscopy in the visible and ultraviolet region was employed to assess the optical bandgap of the deposited carbon films.

3. Results

Raman spectroscopy is effective for identifying bonding structures of carbon-based materials. For C₆₀ material, ten Raman-allowed (2A_g + 8H_g) modes have been experimentally observed and theoretically calculated [13, 14]. Figure 1(a) displays the Raman spectrum of the carbon film prepared without Ne⁺ ion bombardment. A sharp peak at 1469 cm⁻¹ and two weak peaks

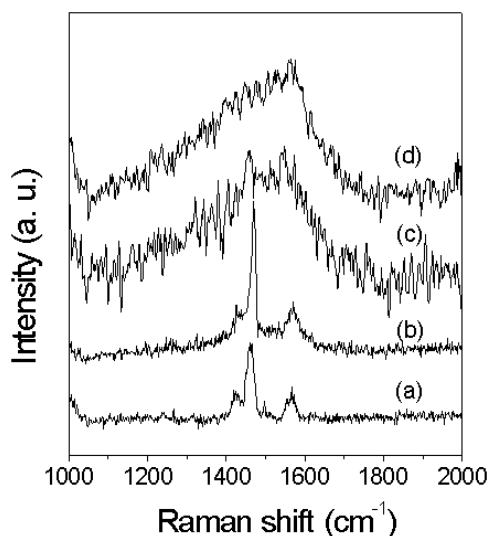


Figure 1. Raman spectra of the films grown without and with Ne⁺ ion bombardments: (a) no bombardment; (b) 500 eV; (c) 600 eV; (d) 700 eV.

at 1426 and 1573 cm⁻¹ appear in this spectrum, which correspond to the Raman-active modes, A_g and H_g, respectively, for C₆₀. Figures 1(b)–(d) give the Raman spectra of the carbon films prepared at three different energies of 500, 600 and 700 eV, respectively. From the spectrum of the carbon film at 500 eV, one can find the same three Raman lines as shown in figure 1(a), and no background band appears. It is evident that the carbon films deposited at 500 eV still retain C₆₀ molecule structures. With increasing Ne⁺ ion energy, C₆₀ molecules begin to decompose, and at 600 eV a strong broad band ranging from 1050 to 1700 cm⁻¹ is induced in the Raman spectrum. This broad band is accompanied by the weak Raman lines at 1469 and 1573 cm⁻¹. However, as the Ne⁺ ion energy is increased further up to 700 eV, these two weak Raman lines disappear, leaving only the broad band. This result indicates that the deposited films become amorphous. Associated with the phase change by Ne⁺ ion bombardment, a dramatic change in the surface morphologies of the deposited carbon films takes place. Figure 2 depicts the AFM top-view images of the carbon films with ion bombardment of 500 and 700 eV. The nodule-like structure appears at 500 eV Ne⁺ ion bombardment, while the carbon film presents the featureless surface at 700 eV.

The bonding structures and the optical properties of amorphous carbon films in the higher-energy region were further investigated by employing Raman spectroscopy and optical absorption spectroscopy. Optical absorption spectroscopy in the visible and ultra-violet region was used to characterize the optical properties of the amorphous carbon films. The optical bandgaps of the films can be determined from the spectra using the Tauc relationship: $\alpha E = B(E - E_g)^2$, where α is the absorption coefficient, E is the photon energy, B is an empirical constant and E_g is the optical bandgap [15].

Figure 3 shows the Raman spectra of the deposited films for Ne⁺ ion energies ranging from 1 to 5 keV. The Raman spectra consist of a broad band centred at 1530 cm⁻¹, similar to the results observed by Siegal *et al* [16], which are typical for amorphous carbon films with high sp³ bonding fraction. These Raman spectra were fitted to two components, the D peak (~1350 cm⁻¹) and G peak (~1570 cm⁻¹). The effects of ion energies on the integrated intensity ratio of the D peak to G peak (I_D/I_G) and G peak position, along with the optical bandgaps, are illustrated in figure 4.

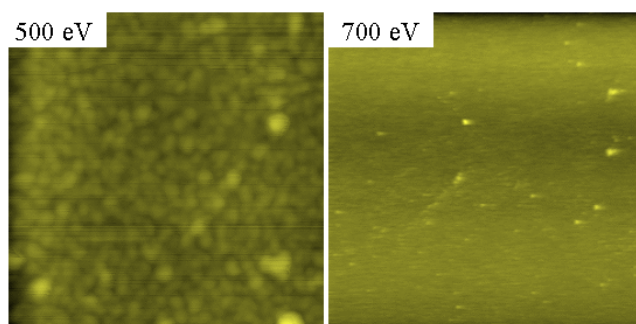


Figure 2. AFM top-view images of the carbon films at 500 and 700 eV. The scanning size is 6700 nm \times 6700 nm. The grey scales are 128 nm for 500 and 21 nm for 700 eV. The film morphology shows the dramatic change from a nodule-like surface to featureless structure.

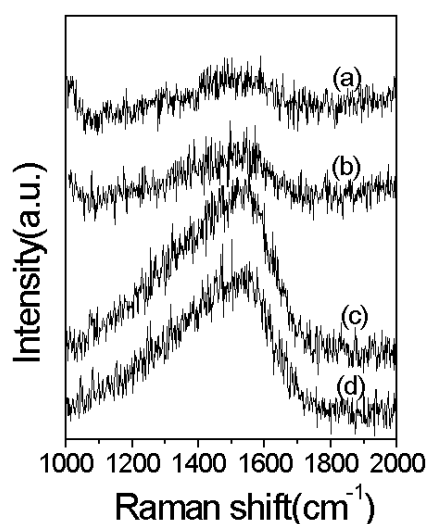


Figure 3. Raman spectra of the amorphous carbon films at different Ne^+ ion energies: (a) 1 keV; (b) 1.5 keV; (c) 2 keV; (d) 5 keV.

Although there is no direct theory that can explain the spectra of amorphous carbon films, there are experimental results that support a good correlation between Raman peaks and film properties. The decrease in I_D/I_G and the simultaneous downshift in the G peak position indicate an increase of sp^3 -bonded atomic sites [17–20]. It can be seen from figure 4 that the intensity ratios (I_D/I_G) at relatively low energies from 1 to 1.5 keV are smaller than those in the films deposited at higher energy from 2 to 5 keV, while the G peak shifts towards higher frequencies in the higher-ion-energy region. Moreover, it is known that the optical bandgap is another indirect probe of sp^3/sp^2 ratio [3, 21], and a larger optical bandgap corresponds to a higher fraction of sp^3 bonding. In figure 4, one can find that the optical bandgaps of the a-C film present inverse change trends with Ne^+ ion energy as compared with I_D/I_G ratio and G peak shift, so the amorphous carbon films deposited at relatively low Ne^+ ion energies must have higher sp^3 bonding fraction.

Figure 5 shows three-dimensional AFM images of the amorphous carbon films prepared at four different Ne^+ ion energies, 1, 1.5, 2 and 5 keV. The rms surface roughness is given

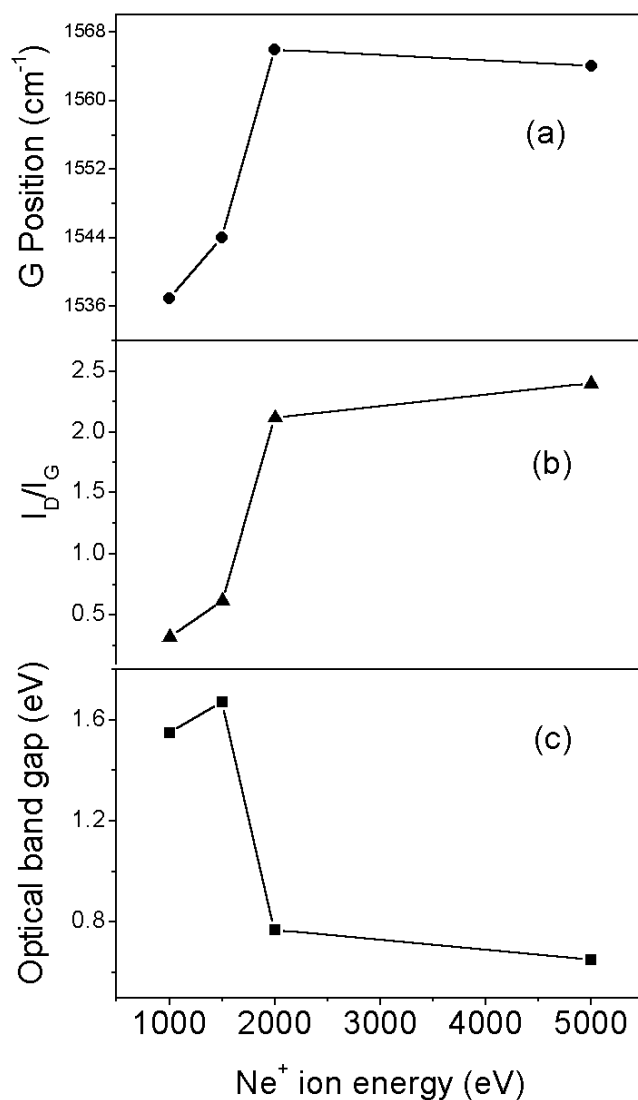


Figure 4. (a) The position of the Raman G peak, (b) the ratio of the integrated intensity of the D to G peak and (c) the optical band gap as a function of the Ne⁺ ion energy.

by the standard deviation over all height-values within the size of 1000 nm × 1000 nm. The rms surface roughness varies from 0.74 to 1.19, which is larger than that of the films with the most diamond-like properties obtained by IBD [10]. This may be attributed to the Ne⁺ ion bombardment effect as discussed later.

4. Discussion

The collision reaction between C₆₀ molecules and ions has been investigated in the recent impact experiments [6, 7, 22]. In C₆₀ + Ne⁺ collisions for ion energy up to 100 eV, the charge transfer occurs in nearly all of the collisions as the only significant process. The dissociative charge transfer may occur at high energies; however, the dissociation efficiency is

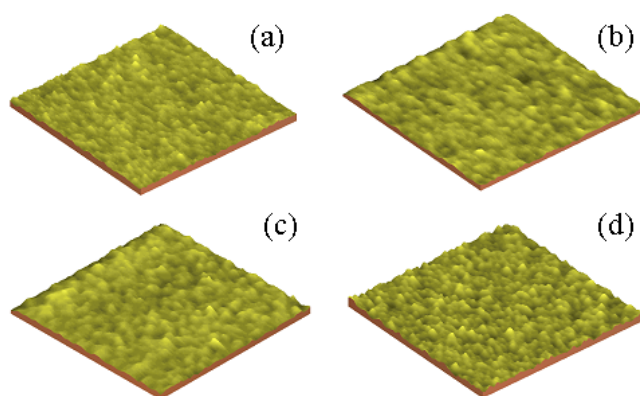


Figure 5. Three-dimensional AFM images (1000 nm \times 1000 nm) of the amorphous carbon films prepared at different energies: (a) 1 keV; (b) 1.5 keV; (c) 2 keV and (d) 5 keV. The values of the surface roughness of the amorphous carbon films are 0.74, 0.92, 1.11 and 1.19, respectively.

only 0.5% at 100 eV [6]. As shown in figure 1, the carbon films deposited at 500 eV Ne^+ ion bombardment still retain the typical characteristic Raman lines of C_{60} . This indicates the high stability of the closed-cage structure of C_{60} . Although charge transfer may occur in the collisions, C_{60}^+ still displays exceptionally high stability. It has been reported that in the impact-induced process of C_{60} ions with graphite and silicon, no impact-induced fragments are observed even for C_{60} ion energy exceeding 200 eV [22]. It has also been predicted in the simulation of C_{60} ion collisions with the H-terminated diamond {111} surface that 150 eV C_{60} ions do not fragment after collision [23]. Therefore, due to the high stability of C_{60}^+ , there is a strong possibility for the neutralization of these cluster ions on the surface, which is attributed to the survival of C_{60} molecules in the IBAD process.

Besides the charge transfer, another important effect is associated with the energy transfer. A significant amount of impact energy may be transferred to the internal energy of the clusters during the collision. With increasing Ne^+ ion energy, the internal energy of the C_{60} clusters after the collision is also raised. If the internal energy becomes large enough, the dissociation of these clusters may be induced. To date, the actual mechanism of fragmentation is not yet completely understood. A sequential C_2 loss mechanism has been proposed by a number of authors [6, 8, 9]. Furthermore, in the $\text{C}_{60} + \text{Ar}$ plasma for the nanocrystalline diamond deposition, *in situ* optical emission measurement reveals a strong green emission (Swan band) at 516.5 nm from the C_2 radicals. The C_2 dimer is proposed to be an important growth species responsible for the film growth [2, 24]. In the present case, it is reasonable to assume that the following processes take place with increasing Ne^+ ion energy: $\text{Ne}^+ + \text{C}_{60} \rightarrow \text{Ne} + \text{C}_{60}^+$; $\text{C}_{60}^+ \rightarrow \text{C}_{60-2n}^+ + n\text{C}_2$. When Ne^+ ion energy is increased to beyond 500 eV, C_{60} molecules begin to decompose and form small carbon species. The further increase of Ne^+ ion energy makes the deposited films more amorphous. As a result, the transition from C_{60} to amorphous carbon occurs with the change of surface morphologies.

The formation of amorphous carbon films with $\text{sp}^2 + \text{sp}^3$ bonding can be understood based on the sub-plantation model [12]. Energetic carbon species produced in $\text{Ne}^+ + \text{C}_{60}$ collisions will penetrate into subsurface layers of the substrate, which may give rise to a local high-density region, and local compressive stress. These environments could induce the formation of sp^3 -bonded atoms. At the higher carbon ion energy, however, the dissipation of excess energy generated by the impinging ions could relax the high compressive stress or excess

density phase, leading to suppression of the sp³ configuration [10, 12]. In the direct ion beam deposition, the amorphous carbons with highest-sp³-bonding sites correspond to the optimal energy range of 50–600 eV [10]. For IBAD, much higher Ne⁺ ion energy is indispensable to dissociate C₆₀ molecules into energetic carbon species having an ability to penetrate into the subsurface. In contrast to the direct ion beam deposition, the sputtering effect cannot be neglected in the present study. Figure 5 clearly shows the change of the surface features, where the rms roughness of the amorphous carbon films increases with increasing ion energy. This, however, does not appear in the direct ion beam deposition [10]. In that case, the deposited films remain smooth in nature even at 10 keV C⁺ ion energy. Only when C⁺ energy is as high as 20 keV does the surface roughness increase sharply. The sputtering yield and the damage caused by C⁺ ion bombardments have been considered to have a minimal effect on the IBD process. The energy transfer depends on the incident ion energy, ion to atom ratio, ion mass, target atom mass and scattering angle. Since the maximum energy of Ne⁺ ions in the present work is only 5 keV, the energies shared by carbon species should be rather less than 10 keV. Therefore, the increase of the surface roughness in amorphous carbon films treated with Ne⁺ ion energies from 1 to 5 keV should be induced by Ne⁺ ion off-normal sputtering on the growing films. At the same time, the Ne⁺ ion sputtering process may promote the diffusion of carbon species and/or local surface heating due to the ion impact in the evolving films, which should also contribute to the decrease in the sp³ fraction at relatively high Ne⁺ ion energies.

5. Conclusion

We have investigated the role of Ne⁺ ion bombardment in the transition from C₆₀ to amorphous carbon and the evolution of materials properties. Micro-Raman spectroscopy, optical absorption spectroscopy and AFM have been employed to assess the samples prepared in this study. It is found that the C₆₀ structures can be maintained for Ne⁺ ion energies up to 500 eV, indicating the high stability of the C₆₀ cage-like molecular structure. Further increase of Ne⁺ ion energy leads to the decomposition of C₆₀ molecules. At 700 eV, the carbon films become amorphous, and also a dramatic change is observed on the film surface from nodule-like to featureless. As Ne⁺ ion energies are increased from 1 to 5 keV, the rms surface roughness of the amorphized carbon films increases, while both sp³ bonding fraction and the optical bandgap for the deposited films show the optimal values at the relatively low Ne⁺ ion energies. These suggest that Ne⁺ ion sputtering must be influential in surface roughening and the bonding configuration in amorphous carbon films.

Acknowledgment

XDZ appreciates support by the STA exchange scientist programme in Japan.

References

- [1] Regueiro M N, Monceau P and Hodeau J L 1992 *Nature* **355** 237
- [2] Gruen D M, Liu S, Krauss A R, Luo J and Pan X 1994 *Appl. Phys. Lett.* **64** 1502
- [3] Hirai H, Terauchi M, Tanaka M and Kondo K 1999 *Phys. Rev. B* **60** 6357
- [4] Gaber H, Busmann H G, Hiss R, Hertel I V, Romberg H, Fink J, Bruder F and Brenn R 1993 *J. Phys. Chem.* **97** 8244
- [5] Zhu Y, Yi T, Zheng B and Cao L 1999 *Appl. Surf. Sci.* **137** 83
- [6] Christian J F, Wan Z and Anderson S L 1993 *J. Chem. Phys.* **99** 3468
- [7] Wan Z, Christian J F and Anderson S L 1992 *J. Chem. Phys.* **96** 3344
- [8] Beck R D, Rockenberger J, Weis P and Kappes M M 1996 *J. Chem. Phys.* **104** 3638

- [9] Hvelpund P, Andersen L H, Haugen H K, Lindhard J, Lorents D C, Malhotra R and Ruoff R 1992 *Phys. Rev. Lett.* **69** 1915
- Foltin M, Lezius M, Scheier P and Mark T D 1993 *J. Chem. Phys.* **98** 9624
- [10] Grossman E, Lempert G D, Kulik J, Marton D, Rabalais J W and Lifshitz Y 1996 *Appl. Phys. Lett.* **68** 1214
- [11] Merkulov V I, Lowndes D H, Jellison G E Jr, Puzos A A and Geohegan D B 1998 *Appl. Phys. Lett.* **73** 2591
- [12] Lifshitz Y, Kasi S R and Rabalais J W 1989 *Phys. Rev. Lett.* **62** 1290
- [13] Bethune D S, Meijer G, Tang W C, Rosen H J, Golden W G, Seki H, Brown C A and de Vries M S 1991 *Chem. Phys. Lett.* **179** 181
- [14] Negri F, Orlandi G and Zerbetto F 1988 *Chem. Phys. Lett.* **144** 31
- [15] Tauc J C, 1972 *Optical Properties of Solids* (Amsterdam: North-Holland) p 372
- [16] Siegal M P, Tallant D R, Martinez-Miranda L J, Barbour J C, Simpson R L and Overmyer D L 2000 *Phys. Rev. B* **61** 10451
- [17] Lim P K, Gaspari F and Zukotynski S 1995 *J. Appl. Phys.* **78** 5307
- [18] Yoshikawa M, Katagiri G, Ishida H, Ishitani A and Akamatsu T 1988 *J. Appl. Phys.* **64** 6464
- [19] Sun Z, Lin C H, Lee Y L, Shi J R, Tay B K and Shi X 2000 *J. Appl. Phys.* **87** 8122
- [20] Dillon R O, Woollam A and Katkanant V 1984 *Phys. Rev. B* **29** 3482
- [21] Lee J, Collins R W, Veerasamy V S and Robertson J 1998 *Diamond Relat. Mater.* **7** 999
- [22] Beck R D, John P S, Alvarez M M, Diederich F and Whetten R L 1991 *J. Phys. Chem.* **95** 8402
- [23] Mowrey R C, Brenner D W, Dunlap B I, Mintmire J W and White C T 1991 *J. Phys. Chem.* **95** 7138
- [24] Zhou D, McCauley T G, Qin L C, Krauss A R and Gruen D M 1998 *J. Appl. Phys.* **83** 540