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## Role of ion energy in determination of the $sp^3$ fraction of ion beam deposited carbon films

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The role of ion energy over the range 5 eV $\leq E \leq 20$  keV in the production of the dense diamondlike  $sp^3$ -bonded phase of carbon films deposited from ion beams has been investigated. Films with a significant  $sp^3$  component (>40%), as determined by electron energy loss spectroscopy (EELS), can be formed over the wide energy region 30 eV $\leq E \leq 10$  keV at room temperature. The  $sp^3$  fraction is completely suppressed only for  $E \leq 10$  eV or  $E \geq 20$  keV. For both cases, this suppression is associated with a sharp increase of the surface roughness, as determined by atomic force microscopy (AFM). The different nature of the mechanisms responsible for the suppression of  $sp^3$  bonding in both the low and high energy regions is discussed. © 1996 American Institute of Physics. [S0003-6951(96)02804-9]

Energetic ions have been employed in a variety of film deposition technologies.<sup>1–7</sup> The kinetic energy of the impinging species plays an important role in determination of the evolving film characteristics.<sup>1-7</sup> Since the work of Aisenberg and Chabot,<sup>8</sup> carbon-containing energetic species have been used<sup>1-3,7-17</sup> for deposition of diamondlike carbon (DLC) films with properties that vary between those of the  $sp^3$  tetrahedrally bonded diamond allotrope and the  $sp^2$  trigonally bonded graphite allotrope. It has recently been shown that amorphous carbon films with the density of diamond, as well as other diamondlike properties, can be deposited by using  $C^+$  ions of the appropriate energy range<sup>18,19</sup> on room temperature substrates. The deposition using hyperthermal species is best described by the subplantation model<sup>20-22</sup> in terms of a shallow implantation process. Incorporation of carbon species in subsurface layers followed by large internal stresses is believed to be the dominant mechanism contributing to formation of a dense diamondlike phase. Accurate data regarding the variation of film properties with  $C^+$ energy is crucial to the understanding of this deposition mechanism, to the development of more detailed models, such as proposed by Robertson<sup>23</sup> and Davis,<sup>24</sup> and to the design of deposition processes for specific applications.

The data from different laboratories regarding the effect of C<sup>+</sup> ion energy, which has been used for comparison to the proposed models,<sup>23,24</sup> contain some inconsistencies.<sup>13,14,16–19</sup> Two of our recent works<sup>19,22</sup> have established the variation of the carbon film characteristics with C<sup>+</sup> energy (*E*) in the range 5 eV $\leq E \leq 1$  keV. The films were deposited using a controlled mass-selected ion beam deposition system and the main features studied were the  $sp^3$  fraction by electron energy loss spectroscopy (EELS), the surface morphology by atomic force microscopy (AFM), and the density by a combination of Rutherford backscattering spectroscopy (RBS) and profilometry. It was found that (i) a minimal energy of E=30 eV was necessary for formation of films with a significant amount of  $sp^3$  bonding and (ii) films with a high  $sp^3$  fraction could be formed even for E=1 keV, which is a higher energy than previously expected. This letter provides data that allow elucidation of the yet unknown effect of higher energies (1 keV $\leq E \leq 20$  keV) on the evolution of carbon film properties; specifically, it shows for the first time that complete suppression of carbon  $sp^3$  bonding occurs as *E* approaches 20 keV. The new findings are important for resolving the mechanisms that govern stabilization and suppression of  $sp^3$  bonding in the C<sup>+</sup> ion deposition process. The data also indicate that the  $sp^3$  suppression observed in many practical systems at much lower energies<sup>14,16,17</sup> results from intrinsic properties of the deposition systems employed.

Carbon films  $\sim 1000$  Å thick were deposited onto silicon (100) substrates using a mass-selected ion beam instrument.<sup>18,19</sup> Direct C<sup>+</sup> ion deposition on clean silicon was used for the range 5 eV $\leq E \leq 2$  keV. For energies of 10 and 20 keV, the ranges (R) of the  $C^+$  ions in silicon calculated from the TRIM<sup>25</sup> program are 309 and 592 Å, respectively, compared to R=46 Å for E=1 keV. Therefore, pure 1000 Å thick carbon films on Si substrates cannot be deposited directly by  $C^+$  ions with  $E \ge 10$  keV. In order to overcome this problem, we bombarded a set of  $\sim$ 500–1000 Å thick DLC films (previously deposited by  $C^+$  ions with E=10, 120, and 1000 eV, the data of the 120 eV precoated films are presented in the present work but similar data were obtained for the other films) with a dose of  $10^{18}$  C<sup>+</sup>/cm<sup>2</sup> with E=10 and 20 keV, producing pure carbon layers of  $\sim$ 1000–2000 Å. These latter films represent the combined effect of the incorporation and collisional damage of 10 and 20 keV C<sup>+</sup> ions.

Auger electron spectroscopy (AES) depth profiles for 10 keV C<sup>+</sup> ions implanted into both silicon and a 1000 Å thick DLC film at doses of  $10^{18}$  cm<sup>-2</sup> indeed show that implantation into clean silicon yields a carbon layer that contains a

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FIG. 1. Surface roughness [from atomic force microscopy (AFM)] and  $sp^2$  fractions [from electron energy loss spectroscopy (EELS)] of 100 nm films deposited using C<sup>+</sup> energies in the range 5 eV to 20 keV on room temperature silicon substrates. Note that the complete suppression of the  $sp^3$  component is associated with a sudden increase in the surface roughness at both low and high energy.

10%–20% concentration of silicon, while implantation into the DLC film yields a pure carbon layer. All of the films were analyzed by EELS,<sup>26</sup> Raman,<sup>18,27</sup> and AFM;<sup>19,22</sup> in addition, the 5 eV–2 keV films were analyzed by RBS<sup>18,27</sup> and the 10 and 20 keV films were analyzed by AES depth profiling.

The  $sp^3$  fractions of the films were derived from the near K edge EELS spectra as previously described<sup>26</sup> and the surface roughness  $(R_q)$  was derived from the AFM images using  $R_q = [\Sigma (Z_i - Z_{av})^2 / N]^{1/2}$ , where  $Z_{av}$  is the average of the Z height values within a given area,  $Z_i$  is the current Z value, and N is the number of points within the given area. Figure 1 shows plots of the  $sp^2$  fraction and  $R_a$  for 5  $eV \le E \le 20$  keV. The plots show that the optimal ion energy region for a maximal  $sp^3$  fraction (minimal  $sp^2$ ) is 50  $eV \le E \le 600 eV$ . The  $sp^2$  fraction increases sharply with decreasing E for  $E \leq 30$  eV, reaching 90%  $sp^2$  bonding for E=10 eV. In the high energy region, the  $sp^2$  fraction increases with increasing E for  $E \ge 2$  keV, reaching 90%  $sp^2$ bonding for E=20 keV. The figure also shows that for both the low energy and the high energy regions, full suppression of  $sp^3$  bonding is associated with a sharp increase of the surface roughness, while the films retain the initial atomically smooth texture of the silicon substrate over the wide energy region 50 eV  $\leq E \leq 10$  keV.

The effect of ion energy on the properties of carbon films can be addressed in terms of the subplantation model.<sup>20-22</sup> The C<sup>+</sup> ions bombard a smooth silicon target ( $R_q$ <0.2 nm) upon which a carbon layer evolves. For energies greater than 30 eV, the carbon atoms occupy subsurface positions while the silicon atoms on the surface are being sputtered and diluted.<sup>20–22</sup> Successive incorporation of C atoms into subsurface positions of the evolving films leads to a high internal stress that is conducive to formation of a dense diamondlike phase. The initial smoothness of the silicon substrate is retained due to the internal carbon film growth, even for films 1000 Å thick. For energies lower than 30 eV, most of the carbon atoms do not occupy subsurface positions but are trapped on the surface, leading to rougher, graphitic films.

As the  $C^+$  energy is increased further, the deposition becomes a deeper implantation process and the system becomes more complicated due to several physical phenomena that can affect the film growth process: (i) range (R) and distribution ( $\Delta R$ ) of the C<sup>+</sup> ions; (ii) backscattering coefficient; (iii) sputtering yield; and (iv) damage due to atomic displacements. These quantities can be simply calculated for a crude assessment of the deposition process using the TRIM<sup>25</sup> code. TRIM, however, does not treat the incorporation of carbon species for which a dynamic version  $(TRIDYN^{28})$  is needed. A code that treats the complete deposition process including diffusion and density gradients does not exist to the best of our knowledge. Our data indicate that for  $C^+$  ions with E < 1 keV, processes (ii), (iii), and (iv) appear to have a minimal effect and are not deleterious to  $sp^3$  bond formation. The evolution of the carbon layer is affected mainly by the incorporation of carbon into subsurface sites. As long as the substrate temperature is kept low enough to freeze the trapped carbon atoms in their final subsurface positions after being thermalized, they are incorporated and dense,  $sp^3$  rich, smooth films evolve. As the energy increases, the  $C^+$  ions penetrate deeper into the carbon matrix (R=26, 44, 180, 350Å for E=1, 2, 10, 20 keV, respectively) and the damage  $N_{v}$  [number of vacancies per impinging C<sup>+</sup> ion (vac/ion)] increases ( $N_v = 8.3$ , 15, 52, 83 vac/ion for E = 1, 2, 10, 20keV, respectively). The backscattering and sputtering yields for a normal incidence angle of C<sup>+</sup> on carbon remain small.<sup>21</sup>

Our AFM data show that the mechanism that suppresses the formation of  $sp^3$  bonding at low energy, i.e., transition from subsurface to surface deposition, does not occur at high energies. Robertson<sup>23</sup> and Davis<sup>24</sup> suggested that the stress or density relief due to dissipation of the excess energy, i.e., a thermal spike, is the dominant mechanism leading to suppression of the  $sp^3$  configuration in the high energy region. Their calculations, however, indicate a sharp decrease of the  $sp^3$  fraction with energy, in contradiction to our present data. We suggest that the moderate increase of the  $sp^2$  fraction with energy up to E=10 keV is due to the increasingly broader range and distribution of the subplanted carbon ( $\Delta R$ =11, 19, 66, 112 Å for E=1, 2, 10, 20 keV, respectively), and the increasing radiation damage by atomic displacements that is known to graphitize even real diamond surfaces.<sup>29</sup>

For energies  $E \leq 10$  keV, the carbon atoms are incorporated in subsurface positions and the film grown internally. The film can be roughly considered as consisting of three distinguished layers with different properties: (i) a top, defected layer (width  $\sim R - \Delta R/2$ ) in which the carbon species are not trapped and only radiation damage occurs; (ii) an evolving layer (width  $\Delta R$ ) beneath the top layer; and (iii) a deeper layer not affected by the impinging carbon species. As the film incorporates carbon the initial evolving layer (layer ii) is gradually covered and (as a crude approximation) becomes part of the nonaffected layer (layer iii) after the film thickness has increased by  $\Delta R$ . If ion mixing, diffusion, and sputtering are neglected (the sputtering yield of carbon at normal incidence angles is low), the defected layer (layer i) remains constant. This analysis indicates that for films thick enough, the defected layer incorporates very high levels of radiation damage that may lead to graphitization. The damage in the evolving layer (layer ii) which can be estimated as  $(N_n/R)\Delta R$  thus increases with increasing ion energy  $(N_v/R \sim \text{conts.}, \Delta R \text{ increases with energy})$  and so does the total damage in the final film. The defected layer thickness  $(R - \Delta R/2)$  increases with energy but the total damage in this layer for a fixed fluence  $\phi$ ,  $(N_n/R)\phi$ , is constant with energy. The moderate  $sp^2$  increase with energy is thus mainly due to the higher damage in the evolving layer and partially due to the increased thickness of the defected layer, which is predominantly  $sp^2$  bonded. The internal growth nature of the carbon films for high E (large R) maintains the initial smooth nature of the films unless one of the above possible mechanisms occurs: (i) roughening due to sputtering; (ii) enhanced diffusion of C species to the surface due to radiation damage; (iii) deformation of the defected layer due to radiation damage. The smooth nature of the deposited films indicates that none of these mechanisms occurs for  $E \leq 10$  keV. At E = 20 keV, however, a sudden large increase of the surface roughness is observed. Since the sputtering yield for E=10 and 20 keV is similar and so is the damage in the defected layer, it is very likely that a sufficient enhancement of the diffusion due to the increased damage [process (ii)] leads to the observed surface roughening at E=20 keV. Similar films bombarded with same fluence of 20 keV Ne ions did not exhibit a significant roughness increase indicating that the roughening (and probably the complete suppression of the  $sp^3$  fraction) is a complex process that involves diffusion due to both C incorporation and radiation damage.

Contradictory data regarding the  $sp^3$  fraction of carbon films deposited at room temperature as a function of C<sup>+</sup> ion energy have been reported in the literature.<sup>13,14,16,17</sup> Since it is the  $sp^2$  bonded configuration that is the stable allotrope and since system perturbations lead to the suppression of the  $sp^3$  phase, it is evident that a correct "phase diagram" of the  $sp^3$  fraction versus E should be an envelope of the maximal  $sp^3$  fractions (minimal  $sp^2$ ) obtained in different laboratories for specific energy values. Figure 1 indeed appears to form such an envelope. The lower  $sp^3$  fractions obtained by other laboratories at specific energy values reflect intrinsic properties of the deposition systems employed and not necessarily the effect of kinetic energy alone. Indeed, films with diamondlike properties, i.e., relatively high  $sp^3$  fractions for E > 1 keV have been reported by at least two other groups.13,30

The findings can be summarized as follows: (i) carbon films with significant amounts of  $sp^3$  bonding can be deposited at room temperature over a wide range of 30 eV $\leq E \leq 10$ keV C<sup>+</sup> energy; (ii) the complete suppression of the  $sp^3$ bonding at  $E \leq 10$  eV or  $E \geq 20$  keV is associated with an increase in film roughness; (iii) high fractions of  $sp^3$  bonding are associated with the subsurface growth of atomically smooth films; (iv) the suppression of  $sp^3$  bonding by high energy C<sup>+</sup> ions is due to ballistic effects of the higher energy implantation and the resulting enhanced diffusion.

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