

Substantiation of Subplantation Model for Diamondlike Film Growth by Atomic Force Microscopy

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Atomic force microscopy studies of films deposited from C^+ ions are reported. For C^+ energies $E \geq 30$ eV the films are diamondlike and retain the initial smoothness of the silicon substrate. For $E < 30$ eV graphitic films evolve with the surface roughness increasing with decreasing C^+ energy. It was further found that for 120 eV C^+ deposition, at substrate temperatures $T_s < 150^\circ\text{C}$ diamondlike, smooth films are deposited, while for $T_s > 150^\circ\text{C}$ graphitic, rough films are produced. The results substantiate the subplantation model, manifesting the role of subsurface internal growth in diamondlike film formation.

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Hyperthermal species ($\sim 1\text{--}1000$ eV) are currently extensively used to produce films with beneficial properties including increased density and hardness, and also to form metastable phases [1–8]. Aisenberg and Chabot [9] have initiated many studies where hyperthermal carbon containing species originating from a variety of deposition techniques were applied for carbon film deposition. Films with properties varying between those of graphite (the stable carbon allotrope with sp^2 trigonal bonding) and diamond (the metastable allotrope with sp^3 tetragonal bonding) were reported [2,3,7–22]. Amorphous carbon films, possessing diamond density and other diamondlike properties, have been specifically deposited on substrates bombarded with C^+ ions in an appropriate energy range [21,22]. The recently proposed subplantation model by Lifshitz and co-workers [23,24] suggests that deposition by hyperthermal species is a shallow implantation process. The incorporation of (carbon) species in subsurface layers followed by large internal stresses is claimed to be the dominant mechanism forming a dense diamondlike phase. Surface analysis data obtained *in situ* during C^+ deposition on various targets [10,23–25] and Monte Carlo simulations based on the dynamic TRIM (TRYDIN) code [24,25] were provided to support the subplantation model, and indeed confirm the subsurface nature of the deposition from low energy ions. These data, however, focused on the first stage of the deposition process, i.e., the internal growth of a carbon phase in subsurface layers until the surface target atoms are sputtered and diluted by the incoming C^+ flux. The processes involved in the second stage of the deposition process, i.e., bombardment of a carbon film with C^+ ions and the successive growth of this film are much more difficult to analyze experimentally since the target atoms and the bombarding atoms are identical.

This Letter aims at the second stage of the deposition. It provides the first direct data obtained by atomic force microscopy (AFM) showing that C^+ bombardment of a carbon matrix may involve surface carbon deposition processes that lead to graphitic films or subsurface processes that lead to diamondlike film formation. More specifi-

cally, the present study shows that the ion energy and substrate temperature conditions appropriate for diamondlike film formation are associated with a smooth surface (i.e., internal growth) while graphitic film formation from energetic particles may be associated with a rough surface (i.e., a surface growth process). These new findings confirm previous predictions of molecular dynamic calculations [19,26] that show decreased surface roughness upon increasing carbon energy. The present work also assists in clarifying two key issues relevant to the large community of scientists who employ hyperthermal carbon containing species for carbon film deposition: (i) the role of ion energy and (ii) the role of substrate temperature in diamondlike film formation.

For the present study, carbon films ~ 1000 Å thick were deposited onto silicon (100) substrates using a mass selected ion beam source as previously described elsewhere [21,22]. Two series of film samples were investigated for the present study: (i) samples deposited onto substrates held at room temperature using ion energies in the range 5–1000 eV and (ii) samples deposited with 120 eV C^+ ions bombarding silicon substrates held at temperatures in the range 25–220°C. Extensive analyses of these films using density measurements, Raman, electron energy loss spectroscopy (EELS), and resistivity measurements were reported in previous publications [21,22], will be reported in detail elsewhere [27], and can be summarized as follows: (i) a broad ion energy region of 30–600 eV exists where the film density is ~ 3.5 g/cm³ (diamond density) and other properties are only slightly affected by the ion energy. (ii) A transition from diamondlike properties (i.e., density ~ 3.5 g/cm³) to graphitic properties (i.e., density ~ 2.4 g/cm³) occurs either when the silicon substrate temperature is increased above 150°C, or when the carbon ion energy is less than 30 eV or higher than 600 eV. All these samples were analyzed by AFM using a Digital Instruments Nanoscope II system. The surface morphology and the surface roughness R_q of these films were studied. R_q is defined as $R_q = [\sum(Z_i - Z_{ave})^2/N]^{1/2}$ where Z_{ave} is the average of the Z height values within a given area, Z_i is the current Z

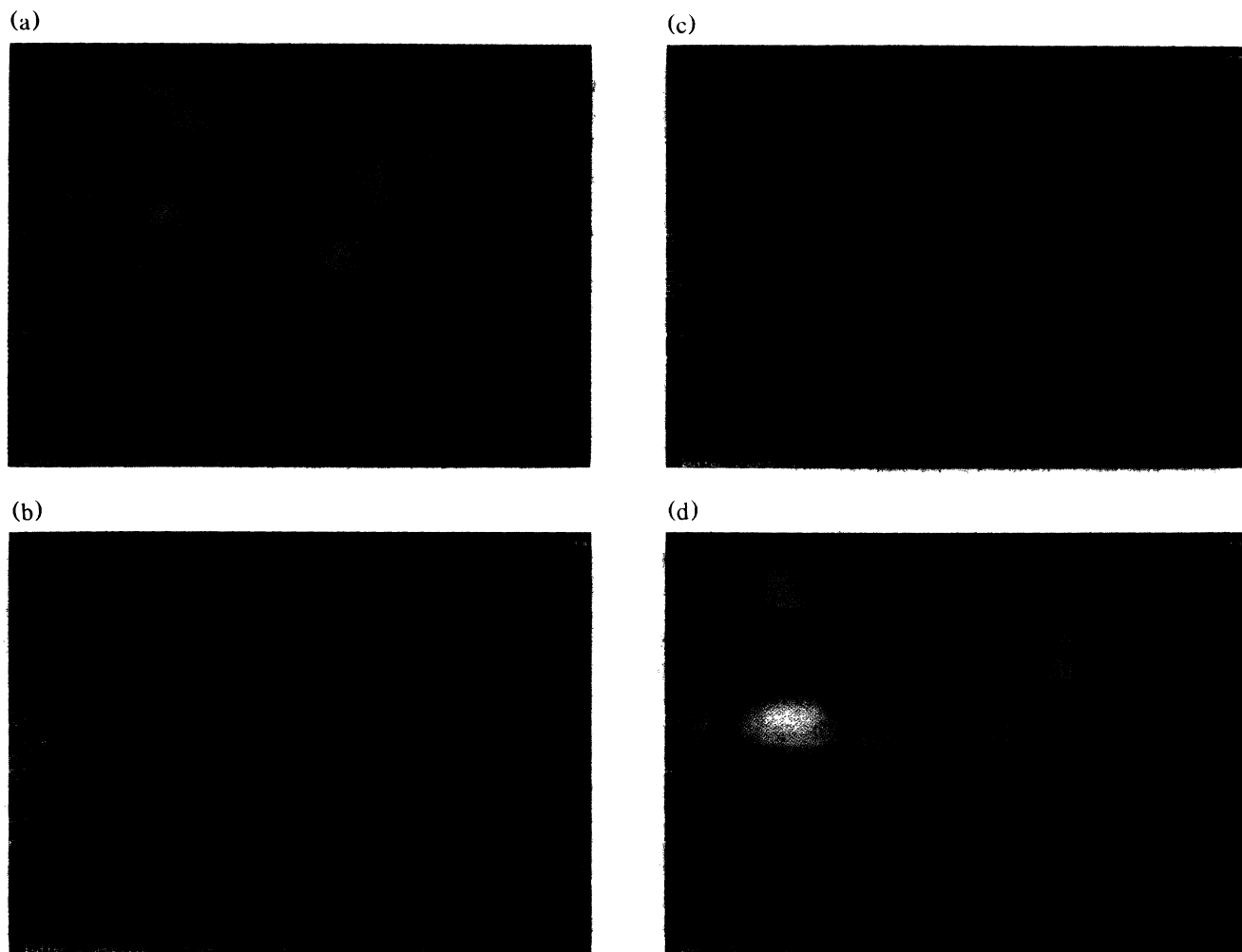


FIG. 1. 1000 nm \times 1000 nm AFM images of 1000 Å carbon films deposited using various carbon ion energies (E) onto silicon held at different temperatures (T_s): (a) $E=5$ eV, $T_s=25^\circ\text{C}$; (b) $E=30$ eV, $T_s=25^\circ\text{C}$; (c) $E=120$ eV, $T_s=25^\circ\text{C}$; (d) $E=120$ eV, $T_s=222^\circ\text{C}$. Vertical scales: 10 nm per bar for (a)–(c); 40 nm per bar for (d).

value, and N is the number of points within the given area. Films deposited by low energy ions [Figs. 1(a) and 1(b)] were found to be very rough. The roughness decreases with increasing ion energy (Fig. 2) and reaches that of the pristine nondeposited silicon substrate for C^+ energies > 30 eV [Fig. 1(c)]. Figure 2 presents the surface roughness dependence on the C^+ energy. Several films deposited with the same energy were studied and for every one of them different locations were analyzed. For each location the roughness was averaged on 1000 nm \times 1000 nm images. The correlation between the onset of the diamondlike properties (e.g., diamond density) and the transition from a rough surface structure to a smooth surface structure is evident. A similar correlation was found for the samples deposited using a constant C^+ energy (120 eV) but at different substrate temperatures [Figs. 1(d) and 3]. The surface topography retained the

initial silicon smoothness up to $\sim 120^\circ\text{C}$ and exhibited a significant increase of the surface roughness for substrate temperatures exceeding 150°C , correlating again with the transition from diamondlike to more graphitic properties.

The present data can be readily explained in terms of the subplantation model. The C^+ ions bombard a very smooth silicon target ($Rq \leq 2$ nm) upon which a carbon layer evolves. For energies higher than 30 eV the carbon atoms occupy subsurface positions, and the silicon surface atoms are being sputtered and diluted as has been previously shown by Lifshitz and co-workers [10,23–25] using both *in situ* surface analysis measurements and Monte Carlo simulations. Successive incorporation of C atoms in subsurface positions of the evolving film leads to a high internal stress and to the formation of a dense diamondlike phase. The initial smoothness of the silicon surface is

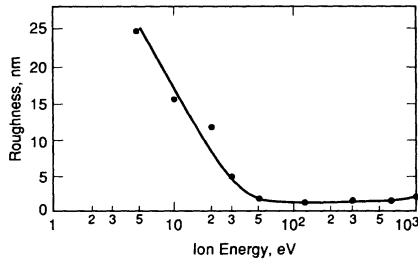


FIG. 2. The surface roughness of films deposited from C^+ ions with different energies onto silicon held at room temperature. The surface roughness was averaged on $1000\text{ nm} \times 1000\text{ nm}$ AFM images. Each data point represents an average of several samples for each of which several images were taken at different locations. Note that for $E > 30\text{ eV}$ the initial low roughness of the silicon surface is retained. For $E \leq 30\text{ eV}$ the surface roughness increases with decreasing energy. For $E = 30\text{ eV}$ smooth surfaces and diamondlike properties are obtainable, but variations in deposition conditions may yield rougher surfaces as well.

retained due to the internal carbon film growth, even for films 1000 \AA thick which contain several hundreds of atomic layers. For energies lower than 30 eV most of the carbon atoms do not occupy subsurface positions. The fraction of carbon atoms trapped on the target surface follows standard surface growth mechanisms leading to a graphitic, rough surface. The lower the energy, the higher is the surface trapped carbon fraction, leading to a rougher surface and more graphitic properties.

For $120\text{ eV } C^+$ deposition onto silicon held at elevated temperatures (T_s) the mobility of the carbon atoms trapped in subsurface positions of the evolving layer increases until for $T_s > 150^\circ\text{C}$ the mobility is high enough for the carbon atoms to migrate to the surface where they follow surface growth processes. Since the stresses associated with the incorporation of carbon in subsurface positions no longer exist, graphitic, rough films are formed. Again, the mobility of the carbon increases with temperature leading to higher surface roughness and more graphitic properties.

Films deposited with $1000\text{ eV } C^+$ ions are still characterized by a very low surface roughness though their density is lower than that of diamond. Several physical quantities [23,24] are required to describe implantation effects: (i) the range and distribution of the ions, (ii) the backscattering coefficient, (iii) the sputtering yield, and (iv) the damage due to atomic displacements. For C^+ ions with sufficiently low energies quantities (ii)–(iv) are very small. The evolution of the carbon layer is affected mainly by the incorporation of carbon in subsurface (i.e., range and distribution) and by thermal diffusion as previously discussed. For C^+ energy $E \geq 1000\text{ eV}$ the other physical quantities may start playing a significant role. $1000\text{ eV } C^+$ ions penetrate deeper into the carbon matrix than C^+ ions with lower energies [23,24]. Radiation

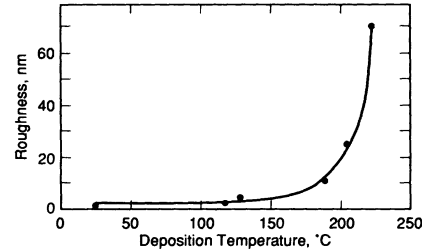


FIG. 3. The surface roughness of films deposited from $120\text{ eV } C^+$ ions onto silicon held at different substrate temperatures (T_s). Each data point represents an average of several $1000\text{ nm} \times 1000\text{ nm}$ images taken at different locations.

enhanced diffusion (e.g., due to atomic displacements) is a reasonable way by which the surface roughness would increase and the diamondlike properties would simultaneously be suppressed. The AFM data, however, show that the initial smoothness of the target is still retained indicating that the carbon growth is still an internal process for $1000\text{ eV } C^+$ ions. The stress relief and the suppression of the diamondlike properties for $1000\text{ eV } C^+$ ions thus occur in a different way than for either very low energy C^+ ions or for deposition on surfaces held at $T_s > 150^\circ\text{C}$. This may be due to the broader distribution of the subplanted carbon (leading to lower stresses) or to radiation damage by ions (via atomic displacements) that graphitizes even real diamond surfaces [28]. The mechanisms associated with the subplantation process that maintain the smooth film surface, lower the film density, and suppress the diamondlike properties at high C^+ energies will be the subject of future studies.

Several studies have investigated the optimal energy needed for diamondlike carbon film formation from hyperthermal carbon species. Contradictory results were reported ranging from $20\text{--}40\text{ eV}$ by McKenzie, Muller, and Pailthroe [18], 140 eV by Fallon *et al.* [20], $100\text{--}200\text{ eV}$ in Ishikawa *et al.* [16], and $\sim 200\text{--}500\text{ eV}$ by Hirvonen *et al.* [15]. In a previous publication we have shown [22] that the optimal energy for dense ($\sim 3.5\text{ g/cm}^3$) diamondlike carbon formation is $E \geq 30\text{ eV}$ up to more than 300 eV (300 eV was the highest energy used in the previous study). Ongoing research [27] indicates that the optimal energy region for dense diamondlike film formation extends beyond 600 eV . The present data further support our findings that the onset of diamondlike film formation relates to the minimal energy needed to penetrate to subsurface layers ($E \geq 30\text{ eV}$). The contradictory data in the other reported works may relate to intrinsic properties of the deposition systems used. Indeed, the use of a well controlled mass selected ion beam facility with a very small ($< 5\text{ eV}$) energy spread is crucial to the present study. The observed sharp dependence of the surface roughness on the ion energy verifies our previous estimates of the energy spread of our beam.

Many systems employing energetic ions for carbon film formation are characterized by a large energy distribution. In such systems one expects a superposition of surface and subsurface processes leading to rough surfaces and a mixture of graphitic (sp^2 -rich) and diamondlike (sp^3 -rich) phases.

The present work focused on carbon film formation from hyperthermal C^+ ions. The visualization of the role of the ion energy and substrate temperature in controlling the nature of the growth process (surface or subsurface) is also relevant to the wide general field of deposition from hyperthermal species and provides direct experimental evidence for processes previously suggested [8, 29, 30] on a theoretical basis only.

To summarize, (i) AFM studies of carbon films deposited from mass selected C^+ ions reveal a clear correlation between surface roughness and the degree of diamondlike (sp^3) properties; i.e., the roughness increases with the amount of graphitic (sp^2) component. (ii) For C^+ energies $E \geq 30$ eV the surface of the evolving film retains the initial roughness of the substrate. For lower energies the surface roughness increases with decreasing ion energy. (iii) 120 eV C^+ deposition onto silicon yields smooth surfaces for deposition temperatures $T_s < 150^\circ\text{C}$ and roughness increasing with temperature for $T_s < 150^\circ\text{C}$. (iv) AFM, using the correlations established in the present work, offers a simple and powerful probe to study the processes involved in carbon deposition from hyperthermal species. The applicability to ion deposition of other materials is inferred. (v) Mass selected ion beam deposition in which all relevant physical parameters can be finely controlled proved itself a viable technique to elucidate the ion beam deposition mechanisms.

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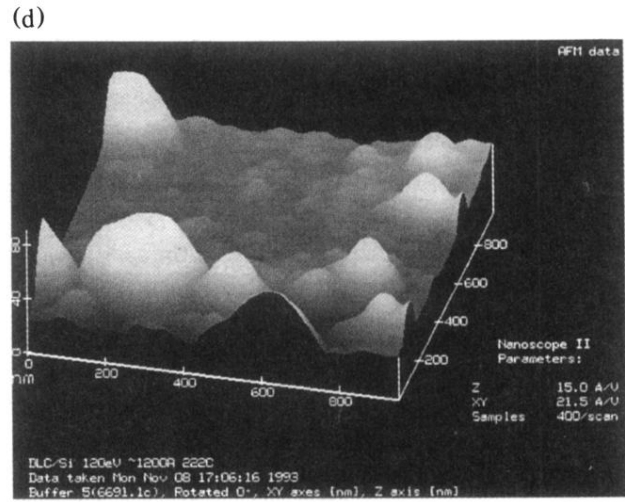
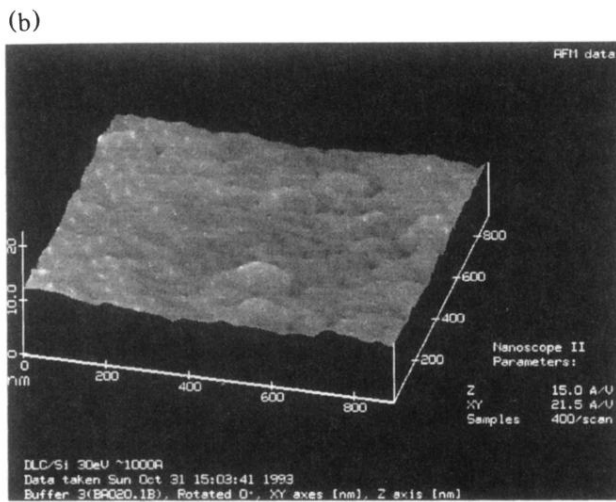
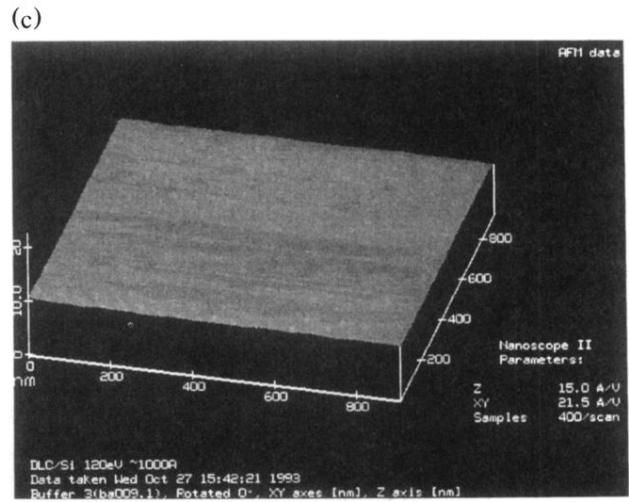
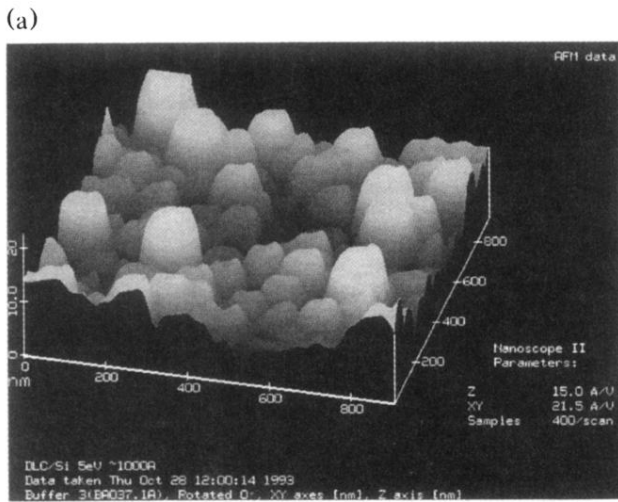


FIG. 1. 1000 nm \times 1000 nm AFM images of 1000 Å carbon films deposited using various carbon ion energies (E) onto silicon held at different temperatures (T_s): (a) $E = 5$ eV, $T_s = 25^\circ\text{C}$; (b) $E = 30$ eV, $T_s = 25^\circ\text{C}$; (c) $E = 120$ eV, $T_s = 25^\circ\text{C}$; (d) $E = 120$ eV, $T_s = 222^\circ\text{C}$. Vertical scales: 10 nm per bar for (a)–(c); 40 nm per bar for (d).