Chemically Bonded Diamondlike Carbon Films from Ion-Beam Deposition

Srinandan Kasi, Hoen Kang, and J. Wayne Rabalais

Department of Chemistry, University of Houston, Houston, Texas 77004

(Received 27 January 1987)

Carbon films on a Ni(111) surface are deposited from 1–300-eV mass-selected C^+ beams in a UHV chamber and the energy and dose dependence of the C Auger line shape is monitored. Initial deposition forms a carbide structure which is chemically bonded to the surface. The Auger line shape evolves with increasing C^+ dose into that of a "diamondlike" structure for ion energies in the range 10–300 eV. Features of the x-ray- and the ultraviolet-photoemission spectra support this interpretation. The diamondlike films do not chemisorb O_2, have a low sputtering yield with O^+ ions, and exhibit a higher thermal stability than the carbidic films; these results are discussed in terms of a qualitative model.

PACS numbers: 68.55.Gi, 68.55.Rt, 81.15.Jj, 82.80.Pv

Experiments with low-energy reactive ion bombardment of surfaces with ions of carbon, nitrogen, and oxygen have shown[1-5] that both the gaseous reaction products and the surface film growth and properties are very sensitive to the energy and momentum of the impingent beam species. Solid-state phases in the surface region that are far from thermodynamic equilibrium, such as unusual metastable structures, can be formed as a result of the condition of high available activation energy which is rapidly quenched by the solid. An example[6-14] of this is the production of insulating carbon films by a variety of plasma and ion beam techniques. These films have been shown[6-10] to be mechanically hard, chemically resistant, and optically transparent, while having a resistivity, refractive index, lattice constant, dielectric constant, optical absorption edge,[15,16] and valence-band structure[17,18] similar to that of diamond. The appelation "diamondlike" films has developed, even though the properties of these films can vary considerably depending upon the method of production. In this work we will use the term "*i*-C" films, as previously suggested,[19] emphasizing that the films are deposited by ion beams.

The growth mechanism and optimum conditions for obtaining diamondlike properties for such films are of obvious interest. The nature of these carbon films has not been studied *in situ* under carefully controlled conditions of ion type, energy, and dose in an ultraclean environment. Miyazawa *et al.*[7] used mass- and energy-selected carbon ion beams for film production; however, they did not have ultrahigh-vacuum conditions and surface analysis tools in the deposition chamber; these features are necessary in order to characterize fully the film growth. The *i*-C films are in metastable amorphous or quasiamorphous states[19] whose relative stability and physical properties may be strongly dependent on incorporation of constituents, e.g., hydrogen, within the structure.

In this Letter we present the first *in situ* measurements of the Auger line shapes, O_2 chemisorption, and O^+ sputtering of carbon films formed by C^+ deposition on a Ni(111) surface as a function of C^+ dose and energy in a UHV environment. The evolution of the Auger line shapes as a function of C^+ dose at different energies provides the basis for understanding the mechanism by which such films grow during C^+ deposition. It will be shown that (1) the *i*-C films are chemically bonded to the substrate surface, and (2) the Auger spectrum corresponding to the diamondlike structure is obtained only for a certain combination of ion energy and dose and that outside of the range, other carbon forms prevail.

The requirements for this experiment are (i) a low-energy mass-selected active-ion beam, (ii) efficient differential pumping in order to maintain a clean target surface, and (iii) *in situ* techniques for analysis of the reaction products. The setup is a modified version of the low-energy active-ion beam chamber[1-4] which will be described in detail elsewhere.[20] Briefly, C^+ ions generated by electron impact of CO gas are extracted from the ion source region at the potential of interest, accelerated to high energy, mass selected to pass $^{12}C^+$, and transported through a long flight tube designed to eliminate fast neutrals. The ions are decelerated just prior to impact with the target. Efficient differential pumping of the beam line allows maintenance of the system pressure in the low 10^{-10}-Torr range during exposure to the C^+ ions. The C^+ beam currents were in the range of 10–100 nA in a spot size of 0.12 cm^2 with an energy spread of 1 eV. The sample target is a single crystal of Ni with a polished (111) surface which is cleaned by 3-keV Ar^+ sputtering and electron-beam annealing to 900 °C before each experiment. The techniques of Auger-electron spectroscopy (AES), x-ray and uv photoelectron spectroscopy, and direct-recoil spectrometry[21] are available in the UHV chamber for sample analysis. The total impurity level (sum of H, C, and O) on the surface after cleaning was < 1% of a monolayer as determined by direct-recoil spectrometry; AES detected no C or O under these conditions.

In a typical experiment, the ion energy was fixed in the range 1–300 eV and a clean Ni surface was irradiat-

ed with a C^+ flux that was predetermined in a Faraday cup mounted on the sample holder; with ion currents of 25 nA, 4–5-h irradiation time was required for a dose of 2×10^{16} ions/cm². The beam was interrupted at fixed dose intervals by closing a gate valve in the beam line and AES spectra were measured in the derivative mode, i.e., $dn(E)/dE$, by means of double-pass cylindrical mirror analyzer with a low-current (2 μA) electron beam at 1.6 keV. The highly surface-sensitive direct-recoil technique[21] was used to monitor the carbon and the impurity hydrogen and oxygen level; the impurities were found to be negligible. The low C^+ flux from the ion beam precludes the generation of larger, thicker films suitable for other physical measurements at this time.

Figure 1 (upper part) shows the evolution of the carbon AES line shape as a function of dose for an 11-eV C^+ beam and representative spectra for a 50-eV C^+ beam at three specific doses are shown on an expanded scale in Fig. 1 (lower part). The positions of the peak maxima, labeled P_i, along with their spectral assignments are listed in Table I. The assignments are made

TABLE I. Peak energies[a] and assignments for the AES structure of Fig. 1 (lower part).

Peak	Energy (eV)	Assignment
P_1	275.9	$KL_{2,3}L_{2,3}$
P_2	269.7	$KL_{2,3}L_{2,3}$
P_3	261.6	$KL_1L_{2,3}$
P_4	254.3	KL_1L_1
P_5	242.9	Plasmon loss

[a]Energies are listed for the peak positions, i.e., the position where the derivative lines go through zero. The positions of P_n, $n = 1$–4, are chosen for the peaks of the carbide spectrum [Fig. 1 (lower part), curve a] and the position for P_5 is chosen for the low-energy peak of the diamondlike spectrum [Fig. 1 (lower part), curve c].
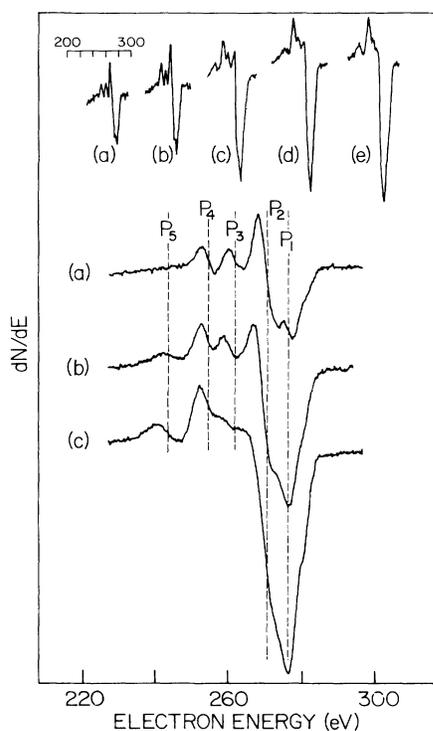

FIG. 1. Upper part: Evolution of the AES line shape from carbidic (a) to diamondlike (e) for 11-eV C^+ deposition on Ni. The doses are as follows: a, 2.0×10^{15}; b, 4×10^{15}; c, 8×10^{16}; d, 1.4×10^{16}; and e, 2×10^{16} ions/cm². Lower part: Details of the AES line shape for 50-eV C^+ deposition on Ni. The doses are as follows: a, 2×10^{15} ions/cm² (carbidic structure); b, 6×10^{15} ions/cm² (intermediate structure); and c 2×10^{16} ions/cm² (diamondlike structure).

by comparison to band-structure calculations[22] for diamond and graphite, both of which exhibit three principal valence-band maxima, and to previous experimental measurements.[23–29] The intensity pattern P_2, P_3, and P_4 is the characteristic signature of a metal carbide.[23–29] Nickel carbide has a very narrow valence band, providing a wide separation between the penultimate carbon L_1 level and the outer $L_{2,3}$ valence bands; the result is an AES spectrum with several sharp structures. As the C^+ dose increases, the line shapes gradually evolve through an increase in P_1, P_4, and P_5 and a decrease in P_2 and P_3, to a final line shape (e) at high dose that is identical to previously reported[26,27] spectra for diamondlike films. The broadening of the P_1 to P_4 structures is in concert with the broadening of the valence bands for diamond or graphitic structures; P_5 has been identified[23] as a plasmon loss structure. The observed diamondlike signature differs from that of either pure graphite of pure single-crystal diamond,[29] a result which may indicate that there are domains of both allotropes as suggested previously.[6] Preliminary x-ray and uv photoelectron spectroscopy measurements are in accord with these findings. Moravec and Orent[26] have shown that the physical properties of these films are similar to those of diamond. The electron-beam damage on pure diamond crystals reported by Pepper[28] was not observed; this may be due to our low electron-beam current and the absence of charging as a result of the thinness of the film and the metallic substrate.

The evolution of the above structures was found to be strongly dose and energy dependent in the 1–300-eV region studies. With reference to the upper part of Fig. 1 for the line shapes, structure a was obtained for initial doses $< 4 \times 10^{15}$ ions/cm² over the entire range. Over the range $10 < E < 175$ eV, the sequence of line shape changes shown in the upper part of Fig. 1 was obtained. For $E < 10$ eV, the line shape evolved only to stage c and never reached the final stage (e) within the limits of our dosing capability. For $E > 175$ eV, significantly higher ion doses than those of the upper part of Fig. 1 are re-

quired to reach each stage, i.e., $a-e$, of the evolution process.

The O_2 chemisorption and O^+ sputtering of the carbon films were tested *in situ* on structures a and e of the upper part of Fig. 1. For chemisorption, the films were exposed to 80 L of O_2 after which the AES spectrum was monitored. Oxygen was found to chemisorb readily on a with a resulting 90% decrease in the carbon AES signal and simultaneous formation of NiO. No chemisorption was detectable on e nor was there any noticeable carbon removal. The results of low-energy O^+ sputtering showed that a has a sputtering yield of $S = 1$ even below 10 eV, while the yield from e is much lower even at E_k as high as 100 eV. Preliminary thermal desorption studies show that the a-type films are completely desorbed at 440 °C while the e-type films are stable up to temperatures at least 150° higher.

These results show that ion-beam deposited carbon films on Ni(111) form an initial reactive carbide layer which evolved continuously with increasing dose of C^+ ions into a film with diamondlike AES line shape which is highly resistant to both O_2 chemisorption and O^+ sputtering. At the initial low doses, AES indicates that the surface is covered with a dispersed carbide layer in which each carbon atom is bonded directly to the Ni. With an increasing dose, the surface C concentration increases and clustering on neighboring C atoms begins to form a continuous film with C—C bonds. These clusters are chemically bound to the surface through several C—Ni bonds. The fact that films with the latter properties have an energy and dose dependence indicates that the energy of the incoming C^+ ions is important to the mechanism of film growth and resulting structure and properties of the film. We consider a mechanism for interpreting this effect below.

It has already been suggested[6] that the kinetic energy carried by reactive ions might be responsible for the formation film structures or high-pressure phases that require a certain activation energy. It has also been demonstrated[19] that the crystalline nature of the deposits exhibits an incident ion-energy dependence. Diamond is a metastable allotrope of carbon which requires such an activation energy. Although these are low-energy ions, the concept of thermal spikes can be applied. Such slow ions will be efficiently neutralized by Auger and resonant electronic transitions with the metallic surface as described elsewhere.[2] The nascent neutrals impacting the surface will intrude only into the topmost atomic layers and cause local temporal agitations near the impact site. Consider the treatment of Seitz and Koehler[30] for describing thermal spikes. When a particle with energy E strikes a surface of thermal conductivity K, heat capacity C, density ρ, the temperature T at a distance r from the site and after a time t is given by

$$T = E(C_\rho)^{1/2}/[8(\pi K t)^{3/2}]\exp[-C\rho r^2)/4K t)]. \qquad (1)$$

Inserting the data for carbon in the diamond phase and 10-eV ions, it is determined that a hemispherical region of radius 7 Å can be elevated to a temperature higher than the melting point of 3823 K and that this condition persists for a time period of 2×10^{-11} s. This is three orders of magnitude longer than the vibrational period of diamond $(2.6 \times 10^{-14}$ s$)$ as estimated from the Debye temperature. Although this is a crude model, it shows that a localized transient high-temperature environment can be produced by such low-energy ions that this condition prevails for a sufficiently long interval to allow for vibration and migration over short distances. The extremely high quenching rates (of the order of 10^{14} K/s) associated with collapse of the spikes provide unique conditions for trapping material in a metastable phase.

The energy dependence of the development of the i-C structures can be considered within this model. If E is too low ($<$ ca 10 eV), spike conditions are not sufficient to allow the migration and rearrangement necessary for obtaining the metastable structure. Also, the growth of several layers necessary for producing the i-C structure may be impeded by the ease with which such low-energy ions are deflected by small surface charges. If the E is too high, severe damage is created over a large region; the migration distances will be long (e.g., for recombination of vacancy-interstitial pairs) and the corresponding recombination time periods may be longer than the quenching time of the thermal spike. Also in this region, self-sputtering by impingent C^+ ions becomes significant and limits the ultimate carbon concentration obtainable.

In conclusion, this work demonstrates the use of ion-beam kinetic energy for producing films in metastable or high-pressure phases. Specifically, pure carbon films deposited on a Ni surface within a specific energy range grow initially as a carbide phase which is chemically bound to the metal, evolving into a diamondlike Auger structure at higher doses. The Auger line shape provides an excellent fingerprint for monitoring these allotropes. Efforts are presently underway to map out a phase diagram of dose versus kinetic energy and to determine sputtering yields as a function of energy.

[1]H. Kang, T. R. Schuler, and J. W. Rabalais, Chem. Phys. Lett. **128**, 348 (1986).
[2]T. Darko, D. A. Baldwin, N. Shamir, J. W. Rabalais, and P. Hochmann, J. Chem. Phys. **76**, 6408 (1982); N. Shamir, D. A. Baldwin, T. Darko, and J. W. Rabalais, J. Chem. Phys. **76**, 6417 (1982).
[3]D. A. Baldwin, N. Shamir, and J. W. Rabalais, Surf. Sci. **141**, 617 (1984).
[4]H. Hu and J. W. Rabalais, J. Phys. Chem. **85**, 2459 (1981).

[5]H. Kang, S. Kasi, and J. W. Rabalais, J. Chem. Phys. **86**, 3753 (1987).

[6]G. Gautherin and C. Weissmantel, Thin Solid Films **50**, 135 (1978); C. Weissmantel, K. Beivilogua, D. Dietrich, H.-J. Erler, H.-J. Hinneberg, S. Klose, W. Nowick, and G. Reisse, Thin Solid Films **72**, 19 (1980); C. Weissmantel, Thin Solid Films **92**, 55 (1982).

[7]T. Miyazawa, S. Misawa, S. Yoshida, and S. Gonda, J. Appl. Phys. **55**, 188 (1984).

[8]S. F. Pellicore, C. M. Peterson, and T. P. Henson, J. Vac. Sci. Technol. A **4**, 2350 (1986).

[9]J. Koskinen, J. P. Hirvonen, and A. Anttila, Appl. Phys. Lett. **47**, 941 (1985).

[10]L. Holland and S. M. Ojha, Thin Solid Films **58**, 107 (1979).

[11]E. G. Spencer, P. H. Schmidt, D. C. Joy, and F. J. Sansalone, Appl. Phys. Lett. **29**, 118 (1976).

[12]J. M. E. Harper, Thin Solid Films **92**, 107 (1982).

[13]J. Amano, Thin Solid Films **92**, 115 (1982).

[14]S. Aisenberg and R. Chabot, J. Appl. Phys. **42**, 2953 (1971).

[15]S. I. Vakula, V. G. Padalka, V. E. Strel'nitskii, and A. O. Vsokin, Pis'ma Zh. Tekh. Fiz. **5**, 1362 (1979) [Sov. Tech. Phys. Lett. **5**, 573 (1979)].

[16]D. F. Edwards and E. Ochoa, J. Opt. Soc. Am. **71**, 607 (1981).

[17]R. G. Cavell, S. P. Kowalezyk, L. Ley, R. A. Pollak, B. Mills, D. A. Shirley, and W. Perry, Phys. Rev. B **7**, 5315 (1973).

[18]J. J. Cuomo, J. L. Freeouf, and P. Oelhafen, Bull. Am. Phys. Soc. **27**, 147 (1982).

[19]C. Weissmantel, in *Thin Films from Free Atoms and Particles,* edited by K. J. Klabunde (Academic, New York, 1985).

[20]H. Kang, S. Kasi, and J. W. Rabalais, to be published.

[21]J. W. Rabalais, J. A. Schultz, and R. Kumar, Nucl. Instrum. Methods **218**, 719 (1983); J. A. Schultz, M. H. Mintz, T. R. Schuler, and J. W. Rabalais, Surf. Sci. **146**, 438 (1984); M. H. Mintz, J. A. Schultz, and J. W. Rabalais, Surf. Sci. **146**, 457 (1984).

[22]G. S. Painter, D. E. Ellis, and A. R. Lubinsky, Phys. Rev. B **4**, 3610 (1971); R. F. Willis, B. Fitton, and G. S. Painter, Phys. Rev. B **9**, 1926 (1974).

[23]J. P. Coad and J. C. Riviere, Surf. Sci. **25**, 609 (1971).

[24]P. G. Lurie and J. M. Wilson, Surf. Sci. **65**, 476 (1977).

[25]J. G. McCarty and R. J. Madix, J. Catal. **48**, 422 (1977).

[26]T. J. Moravec and T. W. Orent, J. Vac. Sci. Technol. **18**, 226 (1981).

[27]A. K. Green and V. Rehn, J. Vac. Sci. Technol. A **1**, 1877 (1983).

[28]M. Dayan and S. V. Pepper, Surf. Sci. **138**, 549 (1984); S. V. Pepper, Appl. Phys. Lett. **38**, 344 (1981).

[29]B. B. Pate, Surf. Sci. **165**, 83 (1986).

[30]F. Seitz and J. S. Koehler, *Progress in Solid State Physics* (Academic, New York, 1957), Vol. 2, p. 30.