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Synchrotron-radiation studies of the transition of hydrogenated amorphous carbon to graphitic carbon

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Using the synchrotron-radiation facility at Brookhaven National Laboratory, we have studied the electronic structure of thin hydrogenated amorphous carbon films produced by dc glow discharges of hydrocarbons. Valence-band photoemission measurements on these films yielded information on the occupied valence-band density of states, while near-edge absorption at the carbon K edge elucidated features of the unoccupied conduction band. The as-deposited, unannealed films are essentially amorphous, showing no extended x-ray absorption fine-structure (EXAFS) features. Valence-band photoemission results show that these films are insulating, suggesting tetrahedral (diamondlike) coordination. The near-edge-absorption results, however, show some unsaturated carbon-carbon bonds as evidenced by a $1s \rightarrow \pi^*$ feature. Upon annealing, the films become more graphitic as evidenced by both the photoemission and near-edge-absorption measurements showing fine structure in agreement with that observed for crystalline or microcrystalline graphite. They also become conductive. Annealing is accompanied by evolution of hydrogen from the films, and this appears correlated with the development of certain features of the band structure as the film orders. The annealed films also show the beginnings of features in the EXAFS region.

I. INTRODUCTION

In this paper we report both valence-band and near-edge structure measurements on glow-discharge-deposited, hydrogenated amorphous carbon films. Such films have been prepared[1,2] with "diamondlike" properties (high hardness, high optical transparency, and low electrical conductivity). As such they have significant potential for use as wear-resistant transparent optical coatings. There remain many outstanding questions concerning both the nature of the short-range order in these amorphous films and also the role of the incorporated hydrogen. We have produced amorphous carbon films and studied the transition into graphitic carbon upon annealing. These experiments show significant changes in both the near-edge structure and extended x-ray absorption fine-structure (EXAFS) structure as the films are annealed and hydrogen evolves from them. Concurrent valence-band photoemission measurements show the addition of states near the gap region and other characteristic graphite features.

II. SAMPLES AND APPARATUS

The films were formed by dc-glow-discharge decomposition of ethylene at a pressure of 100–400 mTorr, a substrate bias of -400 V, and a deposition time of 10–20 min. Films similarly produced with methane gave essentially identical results. In general, we were not concerned with the film thickness which was estimated to be several thousand angstroms thick from work on films made under similar conditions.[1] The vacuum chamber was equipped with stages of cryopumping and turbopumping to achieve the necessary low pressures for operation on the storage ring. In order to allow heating of the sample, the films were deposited on either Nb- or Mo-foil substrates. During deposition the substrates were either at room temperature or mildly heated ($\approx 100\,^\circ\mathrm{C}$). To anneal the films, we heated for 30 sec and monitored the foil resistance and maximum hydrogen partial pressure during this time. The heating time was kept short in order to monitor changes in the films before there was significant diffusion of C into the substrate. In fact, for films deposited on Nb substrates, continued heating over about 800 °C for more extended times (>2 min) produced a carbide layer on the surface, with Nb features present. Hence these results are not meant to provide a quantitative description of hydrogen content as a function of annealing temperature. The ionizing radiation was provided by the uv storage ring of the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory. Efficient use of the limited initial operating time of the ring was a second factor that influenced our choice of a relatively short anneal cycle. We used a plane-grating monochromator designed by Howells; details are described elsewhere.[3] There are

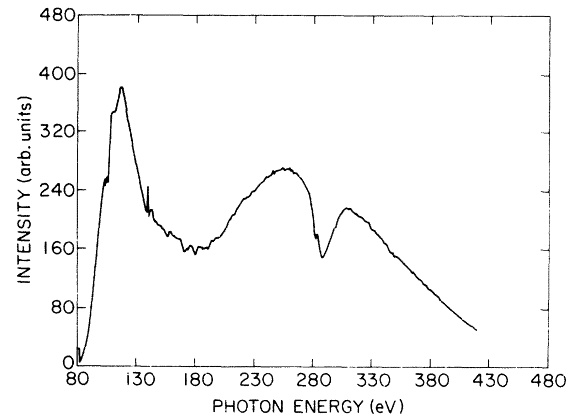

FIG. 1. Monochromator spectral output measured with Xe-gas ionization cell.

four possible photon-energy ranges spanning 20–800 eV. For this work we used the range giving 80–450 eV photon energy. Despite the ultrahigh vacuum maintained in the monochromator ($\approx 6\times10^{-10}$–2×10^{-9} Torr), some carbon contamination of the optical surfaces was visible and was taken account of in the data analysis. This is seen near 280 eV in Fig. 1, which shows the spectral output of the monochromator measured with an ionization cell containing Xe gas. The structure near 120 eV is due to the Xe$4d$ ionization cross section. This cross section is relatively constant through the region of interest around the C *K* edge and above. Angle-integrated photoemission spectra were taken with a cylindrical mirror analyzer. Absorption was monitored by measuring the partial yield with a 2-eV-wide final-state energy window fixed near either the C *KLL* Auger peaks (250–270 eV) or the secondary peak (≈ 1 eV). In the experiments discussed below no significant differences arose between the absorption spectra taken with these two final-state energy windows. Since the photoelectron mean free path in the sample is much larger at the lower energy,[4] this implies that our experiments probed mainly bulk properties of the films. Near the C *K* edge the monochromator resolution was about 1.5 eV. Valence-band features were measured by taking electron-energy distribution curves at a photon energy of 120 eV and a total resolution of 1.2 eV.

III. RESULTS AND DISCUSSION

A. Introduction and discussion of previous work

In Fig. 2, curves *a*–*c*, we show the near-edge-absorption structure of both as-deposited and annealed carbon films corrected for monochromator transmission. Figure 3, curves *a*–*c*, shows the corresponding valence-band spectra. The photon-energy scale of Fig. 2 has been calibrated by measuring the π^* resonance in gaseous benzene and comparing the results with published values.[5] For the valence-band energy-distribution curves in Fig. 3 we have normalized the abscissa to the Fermi level of the underlying metallic substrate.

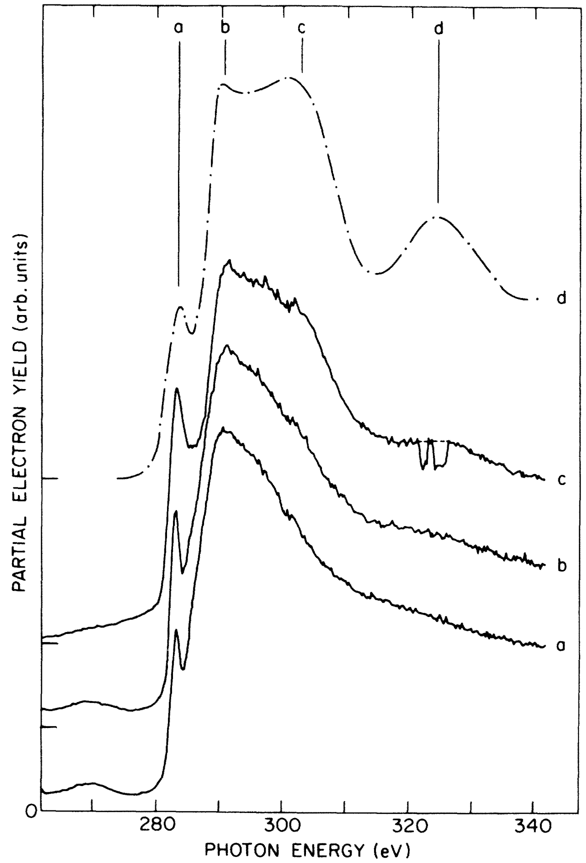

FIG. 2. Near-edge-absorption measurements using partial Auger electron yield at a photoelectron final-state energy of 250 eV. The curves are corrected for monochromator spectral output. Curve *a*, unannealed; curve *b*, after annealing at approximately 500 °C; curve *c*, after annealing at approximately 800 °C. The structure near 320–325 eV in curve *c* is due to an instability in the incident photon flux. Curve *d* is the near-edge-absorption measurement of Denley *et al.* (Ref. 6). The optical density of a thin microcrystalline carbon film was monitored. The short vertical lines at the top give their peak identifications.

Whereas the valence-band spectra in Fig. 3 contain information about the density of occupied states below the Fermi level, the near-edge features in the absorption spectra shown in Fig. 2 reflect the unoccupied region above the Fermi level. The latter has been studied in detail by Denley *et al.*[6] by measuring the optical density of various graphite samples. Figure 2, curve *d*, shows their result for an annealed polycrystalline graphite film with a crystallite size ≈ 2500 Å, along with their peak identifications. Their abscissa had to be shifted downward by about 2 eV in order to align our major features with theirs. Since this discrepancy is of the order of the monochromator resolution, it may not be significant. A microcrystalline sample with crystallite size ≈ 10–15 Å was also studied by Denley *et al.*, but is not shown in Fig. 3. According to Denley *et al.*, feature *a* occurring at 283.5 eV photon energy is due to a transition from the 1*s* core level to empty π bands below the vacuum level. An analogous absorption structure was observed by Eberhardt *et al.*[5] at the C *K* edge of simple gas-phase hydrocarbons. In that case a strong absorption peak just below the edge was ascribed to a transition to the π^* molecular orbital in unsaturated hydrocarbons (C_2H_2, C_2H_4, and C_6H_6). For the saturated hydro-

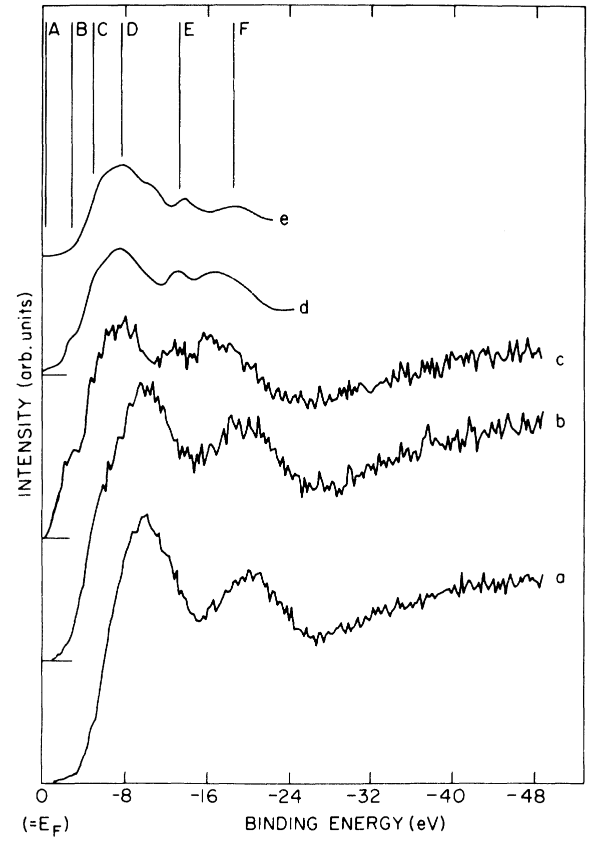

FIG. 3. Valence-band photoemission energy-distribution curves taken at a photon energy of 120 eV. Curve *a*, unannealed; curve *b*, after annealing at approximately 350 °C; and curve *c*, after annealing at approximately 500 °C. Curve *d* shows the results of Bianconi *et al.* (Ref. 7) for crystalline graphite at a photon energy of 120 eV. The vertical lines at the top give the peak identifications of Bianconi *et al.* Curve *e* shows the results of Pate *et al.* (Ref. 10) for a diamond(111) surface at a photon energy of 140 eV.

carbons (CH_4,C_2H_6) a relatively much weaker peak was seen and attributed to Rydberg excitations. Peak *b* at 291.5 eV photon energy is assigned by Denley *et al.* to transitions to σ_1 and σ_2 bands which are $sp^2\sigma$ in character. Peak *c* was correlated with critical points in the σ band at 19.2 eV above the Fermi level. Peak *d* and five additional ones in the extended absorption region correspond to true EXAFS features although Denley *et al.* mention that *d* may still be influenced by band-structure effects.

Bianconi *et al.*[7] studied the valence band of crystalline graphite with angle-integrated photoemission at various photon energies. Reproduced in curve *d* of Fig. 3 is one of their curves taken at 122 eV photon energy. The main features they identified are indicated by short vertical lines at the top of the graph. These were found to correlate well with critical points of the graphite band structure calculated by Willis *et al.*[8] and measured in angle-resolved photoemission by McGovern *et al.*[9] In Fig. 3, curve *e*, a similar scan is shown for the diamond(111) 1×1 surface obtained by Pate *et al.*[10] at 140 eV photon energy. It shows little qualitative difference to a spectrum obtained at 80 eV photon energy; therefore, a comparison with our spectra taken at 120 eV photon energy should be appropriate. One striking difference between the crystalline graphite and diamond spectra is the absence of feature *B* in the latter. This lack of emission near the Fermi level in diamond is explained by the large band gap. With the above summary of the previous diamond and graphite results, the various features that develop at different annealing temperatures can now be discussed.

B. Results on unannealed films

In the as-deposited "amorphous" state the photoemission spectrum shown in curve *a* of Fig. 3 is not characteristic of the spectrum of either crystalline graphite or diamond. The two broad peaks observed are characteristic of emission from the *s*- and *p*-like parts of the valence band with no particular features due to structure. However, these films were insulating when thicker than a few thousand angstroms, and charging became evident in the photoemission spectra. This is seen in Fig. 3 as a uniform shift of about 2.5 eV between parts *b* and *c*. The two broad features near -9 and -20 eV shift toward the Fermi level, as would be expected if the films were originally charging and became conducting after the 500 °C anneal. Care must be exercised in interpreting the photoemission spectrum of an insulating sample. As a further check we made thinner films and found no shift of the broad features toward the Fermi level with annealing. In this case the unannealed spectra resemble curve *c* of Fig. 3 but without the fine structure (features *B* and *E*). The existence of a band gap in the unannealed film and the lack of photoemission intensity just below the Fermi level are suggestive of an insulator, and hence are consistent with a diamondlike electronic structure. The lack of any further detailed diamondlike features in the valence band may be compatible with this. Calculations[11] show the persistence of a band gap for several models of amorphous semiconductors even when the valence- and conduction-band densities of states are quite featureless. Weaire and Thorpe[12] believe that tetrahedral coordination is crucial to gap formation.

The unannealed near-edge structure (Fig. 2, curve *a*) also shows little resemblance to the polycrystalline graphite results of Denley *et al.* The only clear feature is *a* which is at nearly the same energy and looks similar to the feature found by Denley *et al.* We argue that this feature implies unsaturated bonds as in the case of graphite and the gas-phase hydrocarbons. It seems plausible that the unsaturated bonds are localized defects in a tetrahedrally coordinated insulating matrix. This expectation is consistent with the results of Meyerson and Smith[1] who observed a lack of any significant electrical conductivity in other similar unannealed films. Other observations on unannealed hydrogenated amorphous C films have also suggested that they contain a mixture of bonding types. Moravec and Orent[13] concluded that a broad π-plasmon loss feature observed in electron spectroscopy for chemical analysis (ESCA) data indicated the presence of both saturated and unsaturated C bonds. From optical-absorption and electrical conductivity measurements Anderson[14] concluded that films deposited from an acetylene glow discharge probably contained a mixture of threefold and fourfold coordinated C atoms.

With regard to the rest of our unannealed-film near-edge structure, there is no evidence of peak *c*, and extended scans showed no features in the EXAFS region. The absence of EXAFS structure in the unannealed film indicates variation in the nearest-neighbor spacing which would greatly smear the EXAFS peaks. Such variations are to be expected in the unannealed film which contains carbon—carbon bonds, probably in both tetrahedral and trigonal morphologies, in addition to carbon atoms bonded to hydrogen. This leads to a great variation in bond spacings. It is estimated that a variation in bond length of about 0.15 Å would explain the absence of structure.

C. Annealing experiments

Upon heating to 500 °C hydrogen starts slowly coming out of the films. In the absorption spectrum (curves *b* and *c* of Fig. 2) the intensity between features *a* and *b* decreases, *d* grows, and a weak feature can be seen in the EXAFS region near $\hbar\omega = 360$ eV (not shown in Fig. 2.). At higher energies in the EXAFS region little structure is seen, implying that the ordering is still less than what Denley *et al.* observe in their polycrystalline samples. The relatively small photon-energy range scanned and the apparently still disordered nature of the films precluded any reliable EXAFS analysis of neighbor distances. With the annealing feature *a* strengthens relative to the total absorption curve, suggesting that more π-like orbitals are developing as hydrogen evolves from the film. Additionally, there may be a matrix-element effect operating as the orientation of the graphitic regions becomes more uniform. Even though the above indicates only weak structural features, the photoemission results (curves *b* and *c* of Fig. 3) already show unmistakable graphitic features: *B*, *C*, and *E* are clearly evident. The presence of *B* suggests that graphitic rather than diamondlike order is developing in the film, since feature *B* is related to the graphite π bands. Measurements[15] of the optical properties of similarly prepared films have shown increasing optical absorption in the visible region due to shrinking of the optical energy gap as the films are annealed. The graphitic states we observe appearing near the top of the valence band with annealing are consistent with this. This appearance of graphitic features in the valence-band coincided with the disappearance of the charging effects and the increased conductivity is also suggestive of a graphitic film. A possible alternative explanation for the conductivity change involves the loss of hydrogen. This could create dangling-bond states near the Fermi level which would contribute to the conductivity through hopping mechanisms. However, the simultaneous appearance of graphitic features in the valence band argues for the former explanation. We did not observe peak *A* seen by Bianconi *et al.* very near the Fermi level. Feature *E* is characteristic of the σ bonds in the graphite rings (or in the diamond structure).

Feature *c* in the near-edge structure apparently reflects the density of conduction-band states; this feature first develops after further annealing near 800 °C when large amounts of hydrogen come off the film. By this time the graphitic valence-band features have already developed. This seems intuitively correct: Higher-energy electronic states have more extended plane-wave character and would be expected to show more sensitivity to long-range order. Calculations by Kramer on amorphous Si (Ref. 16) using a complex band-structure model have shown this. Kramer's density-of-states results for crystalline and amorhpous Si differ most sharply in the conduction band. In the valence band the density of states in the amorphous material follows the crystalline more closely, except for an overall blurring of the fine structure. It appears that with the evolution of significant amounts of hydrogen from the film at about 800 °C microcrystallites of graphite can finally form, and features *c* and *d* of the near-edge structure, which appear to be sensitive to long-range order, grow significantly. A further point is that feature *a*, which is ascribed to the 1*s* to π^* transition, broadens in the more ordered material, as compared to the amorphous case. This probably indicates a transition to a more delocalized π band whereas in the amorphous material the transition is to localized states which produce a sharper peak.

One further point should be made concerning the origin of peak *a* in the near-edge structure. As mentioned above, the unannealed films, when made thick enough, are insulating. One might expect core-exciton effects[17] in such an insulating material, and this could produce near-edge structure in the region of peak *a*. We do not believe these effects are significant in our case. One argument for this is that peak *a* changes very little in energy or shape as the film is annealed through the insulating to conducting transition which would presumably affect any excitonic states. (The width changes discussed above occur somewhat later.) A further argument is based on the gas-phase spectra[5] mentioned previously which show a strong $1s \rightarrow \pi^*$ transition in unsaturated hydrocarbons. This occurs at ≈ 284.5 eV for ethylene, which is close to the energy of 283.5 eV given by Denley *et al.* for feature *a*. On the other hand, for saturated hydrocarbons such as methane or ethane, no feature is seen until about 286.9 eV and this much weaker feature does not have the origin mentioned above. Hence core-level excitons in the gas phase do not occur near ≈ 284 eV in saturated hydrocarbons, and we argue by analogy that this mechanism will not produce a peak at 284 for saturated bonds in the solid state. On this basis core-level excitons do not explain the peak we see in the unannealed films. Thus we believe the assignment of peak *a* to the $1s \rightarrow \pi^*$ transition is valid and indicates unsaturated bonds.

IV. CONCLUSIONS

To briefly summarize, our picture of the carbon-film structure is as follows. In the as-deposited film there is both structural and compositional disorder which smears both the valence-band and near-edge features. Because of feature *a* in the near-edge structure which indicates unsaturated π-like orbitals, it appears that there are at least some graphitic "defects" in an insulating, tetrahedrally coordinated matrix. Other investigators[13,14] have also observed a mixture of threefold and fourfold bonding in similar films. The tetrahedral structure in our films is probably stabilized by the hydrogen in the film, because as the film is heated and hydrogen evolves, graphitic features become apparent in the valence-band spectrum. Only minor changes are seen in the edge features which implies that only a small degree of order has been achieved. Finally, with the evolution of significant amounts of hydrogen at 800 °C, the near-edge features characteristic of microcrystalline graphite develop.

An interesting point is the absence of any obvious hydrogen-related features in either the valence-band or near-edge regions. This is in sharp contrast with the case of amorphous Si, where several distinct features in the valence band have been ascribed to various Si—H bonds.[18] The hydrogen in our carbon films, while apparently connected with the relative disorder of the structure, does not cause any distinct features in the valence-band density of states.

Although we will not describe the measurements here, we have found that a Nb-C surface compound can be formed at higher annealing temperatures (about 1000 °C), or by longer heating at lower temperatures, and this can be seen by both a change in the valence-band features and the structure in the edge regime. Finally, at even higher temperatures, the carbon features are gone and the photoemission is characteristic of the metallic substrate.

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