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Observation of graphitic and amorphous structures on the surface of hard carbon films by scanning tunneling microscopy

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The atomic structure of the surface of amorphous hard carbon films, prepared by dc magnetron sputtering, has been studied by scanning tunneling microscopy. Small graphitic domains of ~ 15 Å have been observed. In many disordered areas, five-membered carbon rings were often detected. Other ordered domains are observed which could be interpreted as due to small diamondlike clusters.

Carbon exists in a variety of forms, both crystalline and amorphous. The two ordered forms, graphite and diamond, are characterized by the exclusive presence of a single type of bonding: delocalized sp^2 and sp^3, respectively. The graphitic bond lies between the double and single bonds, with a bond order value of 1.67.[1] More disordered materials such as pyrolytic and glassy carbons are generally characterized by a single sp^2-to-sp^3 ratio, although it would be more accurate to describe them as a continuous distribution of bonds, with orders between 1 and 2.

Over the last decade, interest in the properties of thin, hard carbon films has increased considerably. Their extreme hardness, chemical inertness, and good optical properties make them important technological materials for applications such as optical coatings and protective layers against corrosion and wear. They can be grown by a variety of methods such as plasma decomposition of hydrocarbons, ion beam deposition and plating, and dc or rf sputtering from solid graphite targets.[2] In the so-called hydrogenated amorphous carbons (*a*-C:H), hydrogen termination of dangling bonds favors sp^3 bonding, allowing the growth of more transparent films and also helping the formation of diamond crystallites. On the other hand, carbon films prepared by dc sputtering (*a*-C) do not contain hydrogen, and they are more disordered. They do not show long-range order, and the question of whether or not graphitic and/or diamondlike microdomains are present remains open.[3-7] A fundamental understanding of the structure of these materials has, in fact, been hampered by the lack of techniques that can reveal the local atomic configuration and electronic properties of the carbon atoms.

In this paper, we present the first observations by scanning tunneling microscopy[8] (STM) of the atomic arrangement of carbon atoms on the surface of *a*-C. We will show that small, graphitic-type domains are present. We will show evidence for the existence of irregular arrangements of carbon atoms including five-membered carbon rings and others. Finally, structures that suggest the possible presence of 1×1 and 1×2 reconstructed diamond (111) surface domains will be shown.

Our STM operates in air and has been described earlier.[9] Images composed of 256×256 pixels taken in the current (constant-height) mode[10] were recorded with tip velocities between 3600 and 4820 Å/s. With such scan rates, thermal drift was found to be insignificant. Although piezo calibration was checked on a graphite crystal, absolute distances are reliable only within ±10%, due to the hysteresis of the piezoelectric ceramics. Typical tunneling conditions were 10 nA and ±20 mV for tunneling current and sample bias, respectively. These values were found to give optimum results. The corresponding gap resistance for these conditions, 2×10^6 Ω, is low compared to the 10^8 Ω value typically used. Also, due to the high resistivity of these materials,[2] a significant fraction of the measured gap resistance may correspond to the spreading resistance of the film. In these conditions, therefore, the tip could be close to atomic contact. No evidence of surface damage has been observed, however.

Local barrier-height (LBH) measurements[8,11] were obtained by modulating the tip-surface distance at a frequency of 30 kHz with a peak-to-peak amplitude of 1.6 Å. Tip velocities of 490 Å/s were typically employed. The barrier-height values obtained in this manner were of approximately 1.6 eV and below. According to Lang,[12] such small values indicate close proximity of the tip to the surface that leads to the collapse of the tunneling barrier. In the jellium model, distances below 3.5 Å lead to barrier-height values of less than 1 eV.[12] These observations, therefore, are consistent with the small value of the gap resistance discussed above.

The samples utilized in these studies were carbon films of 100–300 Å thickness deposited at a temperature of ~100 °C on a metallic substrate by dc magnetron Ar^+ sputtering.[13] No significant variations in our results were noticed for different samples.

Some STM images did not show any resolvable features. This might reflect contaminated areas or domains of poor conductivity. Others, although showing neither medium- nor long-range order, displayed disordered bright spots and filamentary structures reminiscent of zig-zag chains.[14] In other cases better recognizable patterns could be observed. Such an area is shown in the image of Fig. 1(a), taken in the current mode. On this 28×12-Å^2 area, two well-resolved structures can be seen. On the right-hand side of the image, a pattern consisting of interconnected six- and five-membered rings is observed. This area is magnified in Fig. 1(c). Measured bond distances are in the range 1.3–1.6 Å, i.e., they are consistent with carbon-carbon distances from single to double bonds. The limited accuracy in the position of the carbon atoms on a given STM spot (±0.15 Å), prevents us from giving a more precise description of the structure's bond order. Several five-membered rings can be observed with bond lengths around 1.4 Å. Other nonhexagonal rings are also observed. C_5 rings have been observed in other images as well and seem to be an intrinsic feature of this type of material. Carbon clusters containing five-membered rings have been proposed in the literature to account for the existence of specific lines (magic numbers) in the mass spectrum obtained after laser-pulse ablation of a graphite target.[15] Extended Hückel calculations have shown that these species are quite stable,[15] and they may form during argon sputtering as well. Such species could condense on the surface of the film to form the observed patterns. It is worth noticing also that pentagonal rings in sputtered carbon films have been predicted in 1973 by Nelson,[16] based on the fact that eclipsed sp^3 bonds are energetically favored compared to staggered ones on the film surface during growth, as they involve fewer dangling bonds. Planar pentagonal rings can then be formed whose 108° angles are close to the tetrahedral 109.47°. Also, Weissmantel *et al.* have suggested the presence of C_5 and C_7 on sputtered films based on electron diffraction.[17]

The left-hand side of Fig. 1(a) is magnified and shown in Fig. 1(b). It shows a distorted honeycomb pattern, indicating the presence of a graphitic domain of approximately 15 Å. Such domains have been predicted in the literature.[7] In contrast to the case of the infinite crystal of graphite in an *AB*-layer stacking, where only every other atom of the basal plane is imaged by STM,[18,19] our observation is consistent with a structure with localized π bonds in a Kékulé arrangement. Such a localization of π bonds has been documented for small polycyclic aromatic hydrocarbons,[1,20] and is basically due to edge effects. The possibility of Moiré-type patterns arising from multiple tip imaging, as invoked by some authors to account for the various images observed in graphite[21,22] is very unlikely in our case, because of the lack of long-range order. Also, the possibility of multiple tip imaging is enhanced in graphite, due to its ease of deformation (in contrast to the extreme hardness of these films) which helps bring secondary tips in tunnel range with the surface. Although we have observed such a phenomenon occasionally on metal surfaces, no evidence for such artifact has been observed here. The bright STM spots will therefore be assigned to the π-electron cloud involved in a

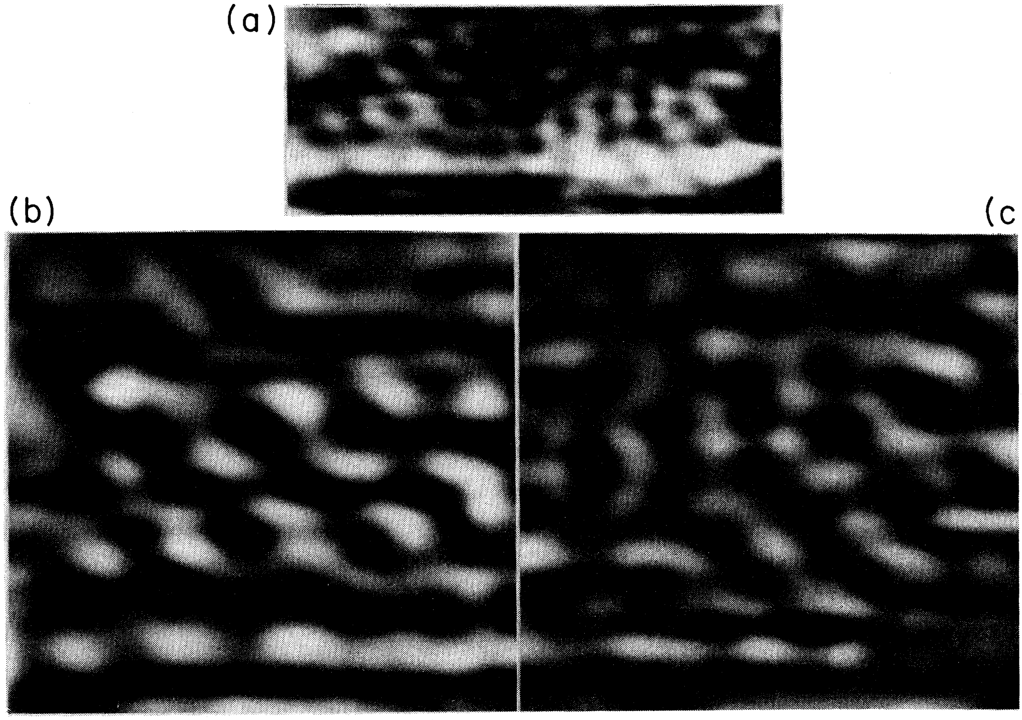

FIG. 1. (a) 28×12 Å^2 STM image of *a*-C film taken in the current mode showing graphitic and pentagonal arrangements of C atoms (crystal bias +20 mV). (b) Magnified left-hand and (c) right-hand parts of the image.

FIG. 2. 40×40 Å^2 STM image of *a*-C film taken in the barrier-height mode (crystal bias +20 mV).

double bond, since the corresponding energy levels in the local density of states (LDOS) are closest to the Fermi level.[7]

Another way of imaging is to perform LBH experiments by modulating the tip-to-surface distance, with lock-in detection of the tunneling current.[8] Such a technique has been proven to yield atomic resolution as well, and with a better signal to noise ratio than in the topographic mode.[11] Figure 2 shows a 40×40-Å^2 STM image recorded in this mode. As in Fig. 1, regions showing a honeycomb-type lattice can be observed. Their size does not exceed 15 Å. Another interesting feature is the presence of two bright domains showing hexagonal symmetry (middle-right and top). The interatomic distance in these domains is approximately 2.5 Å, which corresponds to the (111) surface of diamond (2.52 Å), but which may also originate from the atoms of type *A* observed on the graphite (0001) basal plane (2.46 Å).[18,19] As discussed above, small graphitic domains show mostly quasilocalized π bonding with most of the honeycomb hexagon visible. Therefore, we will prefer the former interpretation of these features as diamondlike carbon clusters. The fact that they appear stable in an atmospheric environment can be explained through termination of the dangling p_z orbitals by hydrogen, which is a major contaminant in the sputtering system.

Another type of structure that is observed in this *a*-C film is shown in the current image of Fig. 3(a), obtained at a negative sample bias of 20 mV. On this image, a short-range translational symmetry can be visualized, and it is best shown by looking at its two-dimensional Fourier transform [Fig. 3(b)]. In the spatial frequency space, the bright spots correspond to the spatial periodicity. The size of the unit cell formed in this manner is approximately 2.7×4.5 Å^2. The diamond (111) surface that is not terminated by hydrogen atoms is known to reconstruct in a 1×2 pattern with lattice constants of 2.5 and 4.4 Å.[23] Within the precision of our piezo calibration, this is consistent with the measured distances. The reconstruction lowers the surface energy by saturating the dangling bonds. Among the existing models, the π-chain model proposed by Pandey[24] seems to be the most probable.[25,26] The bright and oblong maxima in the tunneling probability could then be due to localized π bonds alternating in the chains along the short axis of the unit cell. On the basis of this sole experimental evidence, however, we cannot make a definite identification of this structure.

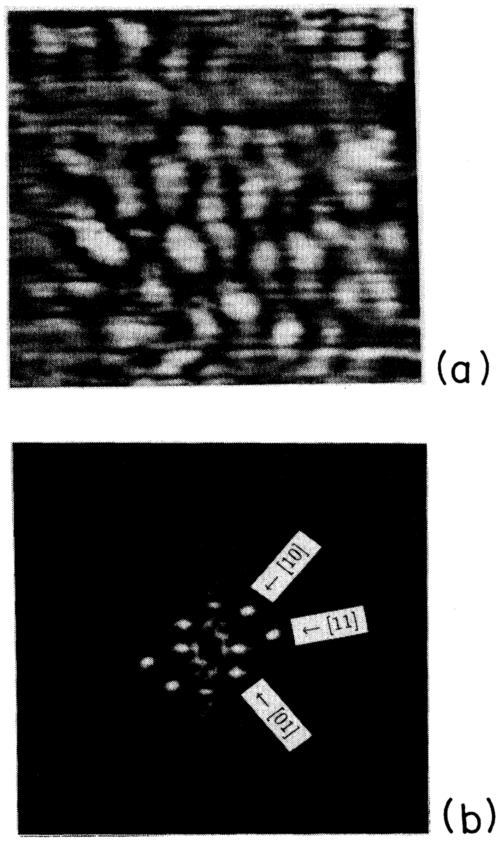

FIG. 3. (a) 24×28 Å^2 STM image of *a*-C film taken in the current mode (crystal bias −20 mV). (b) Corresponding two-dimensional Fourier-transform pattern indicating translational symmetry.

In conclusion, we have used the STM to unravel the structure of amorphous *a*-C surfaces with atomic resolution. To our knowledge, this is the first time that an amorphous structure is resolved at the atomic level with such detail. We were able to prove the existence of small (~15 Å) graphitic domains with localized π bonding. We have also shown the presence of areas with five-membered C rings and other aperiodic structures that have been hypothesized in many previous studies. Our results suggest the possible presence of small, nonreconstructed, as well as 1×2 reconstructed, diamond (111) clusters. None of the ordered structures show a correlation length greater than 20 Å. This study should provide impetus for further investigations of such amorphous materials by STM. For example, the effect of annealing and growth conditions on the surface structure should be studied to establish correlations with the mechanical and electronic properties of these films. This is particularly relevant in view of the growing interest in these technologically important materials.

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[1] E. Clar, *Polycyclic Hydrocarbons* (Academic, New York, 1964), Vol. 1.

[2] H. Tsai and D. B. Bogy, J. Vac. Sci. Technol. A **5**, 3287 (1987), and references therein.

[3] J. J. Hauser, J. Non-Cryst. Solids **23**, 21 (1977).

[4] P. E. Batson and A. J. Craven, Phys. Rev. Lett. **42**, 893 (1979).

[5] N. Wada, P. J. Gaczi, and S. A. Solin, J. Non-Cryst. Solids **35-36**, 549 (1980).

[6] D. Beeman, J. Silverman, R. Lynds, and M. R. Anderson, Phys. Rev. B **30**, 870 (1984).

[7] J. Robertson and E. P. O'Reilly, Phys. Rev. B **35**, 2946 (1987).

[8] G. Binnig and H. Rohrer, IBM J. Res. Dev. **30**, 353 (1986).

[9] M. Salmeron, B. Marchon, S. Ferrer, and D. S. Kaufman, Appl. Surf. Sci. **28**, 279 (1987).

[10] P. K. Hansma and J. Tersoff, J. Appl. Phys. **61**, R1 (1987).

[11] B. Marchon, P. Bernhardt, M. E. Bussell, G. A. Somorjai, M. Salmeron, and W. Siekhaus, Phys. Rev. Lett. **60**, 1166 (1988).

[12] N. D. Lang (unpublished).

[13] Samples have been prepared by Seagate Magnetics, Fremont, CA 94538.

[14] V. Elings and F. Wudl, J. Vac. Sci. Technol. A **6**, 412 (1988).

[15] J. A. Van Vechten and D. A. Keszler, Phys. Rev. B **36**, 4570 (1987).

[16] C. W. Nelson, Data General Inc., internal report, 1973 (unpublished).

[17] C. Weissmantel, E. Ackermanm, K. Bewilogua, G. Hecht, H. Kupfer, and B. Rau, J. Vac. Sci. Technol. A **4**, 2892 (1989).

[18] A. Selloni, P. Carnevali, E. Tosatti, and C. D. Chen, Phys. Rev. B **31**, 2602 (1985).

[19] D. Tomanek, S. G. Louie, H. J. Mamin, D. W. Abraham, R. E. Thomson, E. Ganz, and J. Clarke, Phys. Rev. B **35**, 7790 (1987).

[20] G. M. Badger, *The Structures and Reactions of the Aromatic Compounds* (Cambridge University Press, London, 1964).

[21] H. A. Mizes, Sang-il Park, and W. A. Harrison, Phys. Rev. B **36**, 4491 (1987).

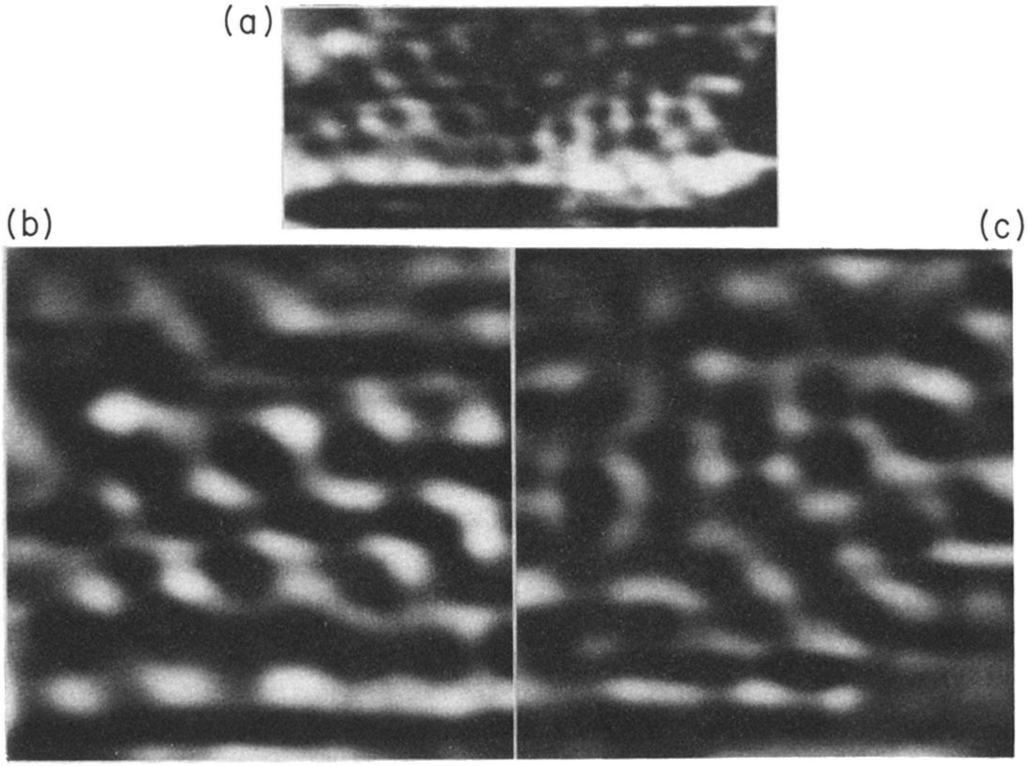
[22] T. Tiedje, J. Varon, H. Deckman, and J. Stokes, J. Vac. Sci. Technol. A **6**, 372 (1988).

[23] B. B. Pate, Surf. Sci. **165**, 83 (1986), and references therein.

[24] K. C. Pandey, Phys. Rev. Lett. **25**, 4338 (1982).

[25] D. Vanderbilt and S. G. Louie, Phys. Rev. B **30**, 6118 (1984).

[26] T. E. Derry, L. Smit, and J. F. Van der Veen, Surf. Sci. **167**, 502 (1986).



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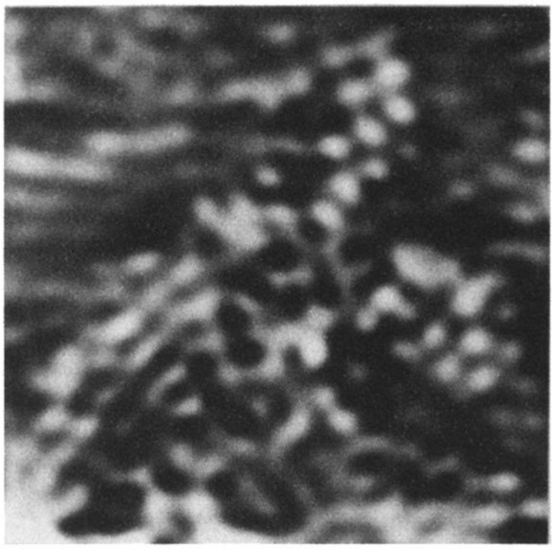
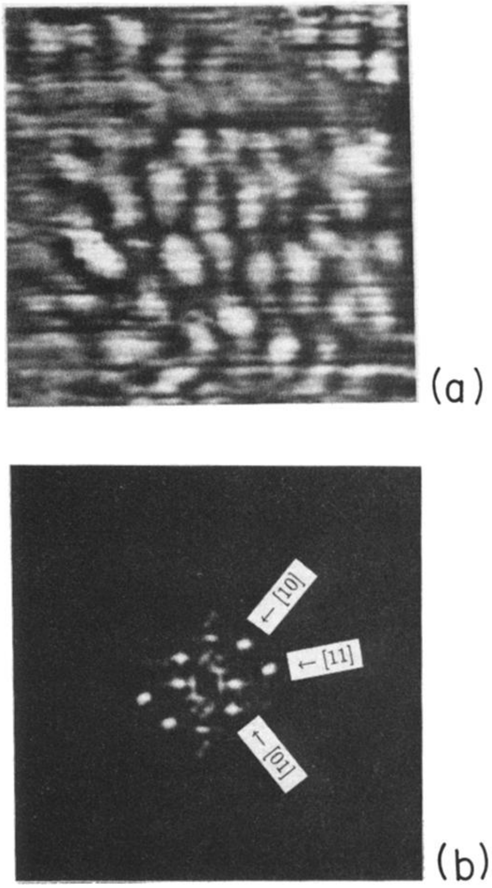


FIG. 2. 40×40 Å^2 STM image of *a*-C film taken in the barrier-height mode (crystal bias +20 mV).



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