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Structural properties of sp^3-bonded hydrogenated amorphous carbon

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Hydrogenated amorphous carbon (*a*-C:H) is important as a material for hard coatings. Here, we describe the structural properties of computer-generated models of *a*-C and *a*-C:H with nearly ideal sp^3 bonding. Without H, the material is very hard, but it is highly strained compared with ordinary sp^2-bonded *a*-C. Increasing the hydrogen content reduces the internal strain, facilitating sp^3 bonding, but also softens the material. In addition, the number of primitive rings in the structure decreases, and the size of the rings increases, indicating a transition to a polymeric form at high hydrogen content. Implications for very hard ion-beam-deposited *a*-C are discussed.

Carbon, in the form of diamond, has always held a unique fascination, in part because of its unequalled hardness. Synthetic diamond is being actively pursued as a possible material for extremely hard protective coatings. However, amorphous carbon (*a*-C) and hydrogenated amorphous carbon (*a*-C:H) offer important practical advantages. Thus there is tremendous interest in the growth and properties of *a*-C and *a*-C:H, especially hardness.[1]

Here, we generate models for *a*-C and *a*-C:H with nearly ideal sp^3 bonding (i.e., fourfold coordination), and examine their structural properties. The results show how H relieves local strain in *a*-C, facilitating sp^3 bonding, but at the same time limits the achievable hardness. The transition from an extremely hard solid to a soft polymer with increasing H content is reflected in the elastic properties, the internal strains, and the ring statistics. Results for pure *a*-C are relevant for understanding the properties of very hard ion-beam-deposited *a*-C.

We cannot at present hope to realistically simulate the actual growth process. The question of how the growth conditions influence the hydrogen content and the bonding therefore lies outside the scope of this study. Instead, since the goal is to grow material of maximum hardness, and, hence, maximum sp^3 bonding, we restrict consideration here to such material, and study its structure and elastic properties (which correlate closely with hardness) as a function of hydrogen content.

In the present study, a molten C-H mixture is equilibrated and then cooled in a Monte Carlo simulation, with periodic boundary conditions. The goal is to cool the sample slowly; but in practice, any cooling involving feasible amounts of computer time should be considered an ultrafast quench.

The random Monte Carlo moves include both small movements of the atoms and changes in the lengths of the three supercell lattice vectors. Thus the final sample is not under any longitudinal stress, although there could be some residual small shear stress.

The energy at each step is calculated using an empirical classical interatomic potential, of the form introduced in Ref. 2. The parameters used for carbon are those of Ref. 3, which were introduced to simulate carbon atoms with no π bonding. In this way we effectively enforce sp^3 bonding. The parametrization for H was obtained by fitting to the properties of the H_2 and CH_4 molecules.[4] This parametrization was found to be quite satisfactory for describing H atoms that terminate dangling bonds. Whether the resulting potential can satisfactorily describe H in a wider variety of geometries is by no means guaranteed, but is not necessary for the present investigation.

After each sample is cooled to room temperature, its properties are determined. As an example, Fig. 1 shows the (partial) radial distribution function for a sample of 216 atoms, with 25 at.% H. The C-C pair distribution shows a sharp peak around 1.56 Å, which contains 3.62 atoms. The distribution of H about a C atom (not shown) gives 0.33 H neighbors, at an average distance of 1.11 Å from a C. Thus the total number of neighbors is 3.95 per C atom, reflecting the nearly ideal fourfold coordination, with a small number of threefold atoms (and occasional fivefold atoms) present as defects from the rapid quench. In other samples, although the respective number of C and H neighbors varied according to the H content, the total coordination of carbon atoms was consistently very close to 4 per atom.

The property of *a*-C:H which is of greatest interest here is its hardness. However, the direct theoretical calculation of hardness is not feasible, since hardness is defined in

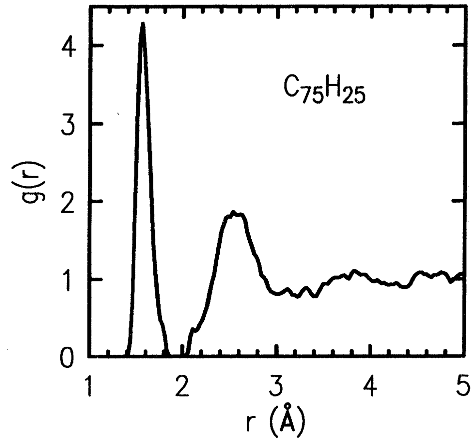

FIG. 1. Radial distribution function, for C atoms only, in an *a*-C:H sample with 25 at.% H.

terms of a macroscopic mechanical failure involving plastic flow. Fortunately, it is observed empirically that hardness is proportional to elastic moduli such as Young's modulus.[5]

We have therefore calculated Young's modulus for each sample. In each case, the modulus was averaged over the three coordinate directions. The results are shown in Fig. 2, normalized to the diamond value. Given the approximate proportionality to hardness, the results can also be interpreted roughly as the calculated hardness, as a fraction of the hardness of diamond. The density for each sample is also shown.

For pure *a*-C, the modulus is already somewhat smaller than for diamond. This is essentially an anharmonic effect. The large local strains (discussed below) weaken the bonds, giving longer bond lengths and smaller elastic moduli. While this effect is physically reasonable, there is no guarantee that the empirical potential used here is quantitatively reliable in this detail. For a harmonic model, such as a Keating model, the pure *a*-C would have a modulus closer to that of diamond.

The density decreases with increasing hydrogen content, as expected. The elastic stiffness (and presumably the hardness) also decreases, tending to zero somewhere around 60 at.% H. According to the Phillips-Thorpe mean-field theory of elastic networks,[6] the stiffness should go to zero when the average C-C coordination (i.e., the average number of C neighbors for a C atom) drops to a critical value of 2.4, i.e., at 62 at.% H for pure sp^3 bonding. The results here agree rather well with this prediction. In fact, in view of the uncertainties in the calculation of moduli for very soft samples, and of the small sample sizes, any deviations from the mean-field theory here are too small to be significant.

These results might be interpreted to imply that hydrogen plays a strictly negative role here, reducing the hardness of the material. However, we find that without any H, sp^3-bonded *a*-C is highly strained, and so energetically unfavorable relative to ordinary sp^2-bonded *a*-C. Hydrogen plays a crucial role in permitting sp^3 bonding without excessive strain.

A previous study[7] found that ordinary sp^2-bonded *a*-C had an energy about 0.4 eV/atom higher than diamond. However, the fully sp^3-bonded *a*-C sample formed here has an energy about 0.8 eV/atom higher than diamond. Even after correcting for the presence of coordination defects, the energy expected here for a defect-free sample is at least 0.7 eV/atom, nearly twice as high as for the sp^2-bonded form. Thus pure sp^3 bonding in *a*-C is energetically unfavorable relative to sp^2. (A material widely believed to represent sp^3-bonded *a*-C is discussed below.)

The presence of H makes the sp^3-bonded material less rigid, and reduces the number of steric constraints, lowering the strain energy and, hence, making sp^3 bonding easier to achieve. We can get a semiquantitative picture of the degree to which H relieves strain in *a*-C:H, by comparing the radial and angular distribution functions of samples with differing H content. For simplicity, in Fig. 3 we show only the two extremes in H content from our set of samples. Figure 3(a) shows the radial distribution functions for these samples, while Fig. 3(b) shows the distribution of bond angles.

Figure 3(a) focuses on the first peak in the distribution, which corresponds to bond lengths. The solid line shows this peak for the sample with no H, while the dotted line

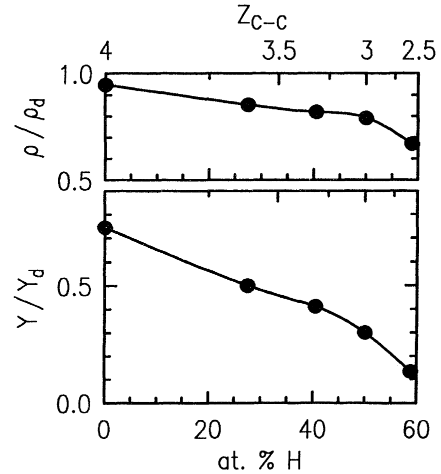

FIG. 2. Density and Young's modulus of *a*-C:H samples, as a fraction of corresponding diamond values, vs H content. Young's modulus is believed to reflect the hardness of the sample (see text). Circles correspond to samples; lines are spline fits to guide the eye. The average number $z_{\text{C-C}}$ of C neighbors for a C atom is given at the top.

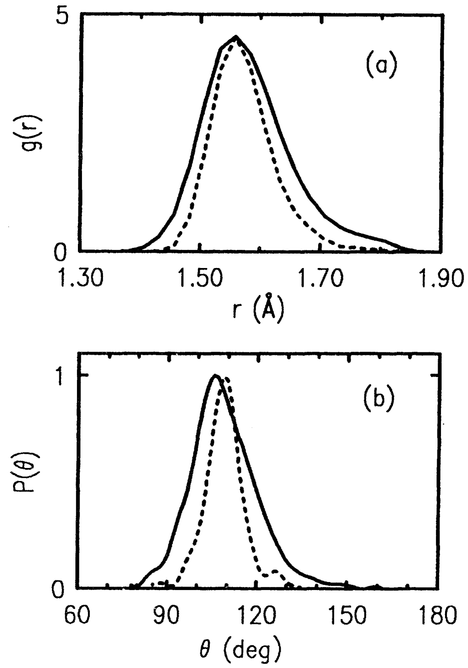

FIG. 3. Distribution functions, for C atoms only, in two samples: Solid lines are for pure *a*-C; dotted lines are for *a*-C:H with 59 at.% H, the highest H content of the samples studied. (a) Radial distribution function; (b) distribution of bond angles, for bond pairs on fourfold coordinated C atoms only. Distributions are normalized to equal heights to emphasize difference in widths.

shows the sample with 59 at.% H. The mean bond length in the two samples is nearly identical, but the rms width of the distribution is 0.08 Å for the pure *a*-C, reflecting a distribution of large compressive and tensile bond strains. The bond strains are considerably reduced in the hydrogenated sample, to only 0.05 Å rms. Since the strain energy is expected to be roughly proportional to the mean-square deviation, the difference corresponds to a factor of more than 2 in strain energy associated with bond-length variations.

Figure 3(b) shows the distribution of bond angles. All vertices are C atoms, since H are singly coordinated. Bonds to both C and H neighbors are included. However, only vertices on fourfold coordinated C atoms are included, to avoid artifacts from the small number of "defects" with three (or five) neighbors. Both samples have mean bond angles within 0.3° of the tetrahedral bond angle, the difference in peak position being due to slightly different shapes of the distributions. As with the bond lengths, the bond angle distribution is considerably wider for the pure *a*-C sample (rms width 11°) than for the *a*-C:H sample (rms width 7°), with the mean-square width again suggesting a difference in strain energy of more than a factor of 2.

Thus in *a*-C:H, H relieves strain and, hence, reduces the energetic cost of sp^3 bonding. However, the desired property, hardness, depends primarily on the number of C-C bonds. If each H promotes more (or less) than one C atom from sp^2 to sp^3, but ties off one C bond, then H increases (or reduces) the total number of C-C bonds. Quantifying this tradeoff, and its dependence on H fraction, is an important but difficult task. Obtaining a high rate of sp^3 promotion per H atom incorporated is essential for the production of very hard *a*-C:H.

In addition to the radial and angular distribution functions, the structures of amorphous networks are traditionally characterized by their ring statistics. However, simply counting all rings in a network is relatively uninformative, since the number of rings typically increases monotonically with ring size. The interesting property is the number of *primitive* rings,[8] i.e., rings which have no "shortcuts" across them.

While criteria for primitive rings have in the past been *ad hoc* in nature, recently a mathematically sound "shortest path" criterion was formulated, leading to an unambiguous way of counting primitive rings.[9] Figure 4 shows the ring statistics determined in this way for our samples.

Diamond has only rings of size 6, with two rings per atom. The *a*-C sample with no H [Fig. 4(a)] similarly has about two rings per atom. But while the distribution is sharply peaked at size 6, there are substantial numbers of rings of size 5 and 7 in addition, with a few rings of other sizes.

With increasing H content, the distribution of ring sizes becomes broader, and the average ring size grows larger. More dramatically, the total number of rings per C atom drops sharply, apparently tending towards zero. Thus with increasing H content, *a*-C:H transforms continuously from an ultrahard solid to a polymer.

Finally, we consider the implications of these results for hard *a*-C. There has been great excitement over the recent development of "diamondlike" *a*-C formed by deposition of a C^+ ion beam from a C arc.[1] For convenience, we call this material *i*-C here, although that term has also been used for softer ion-beam material.

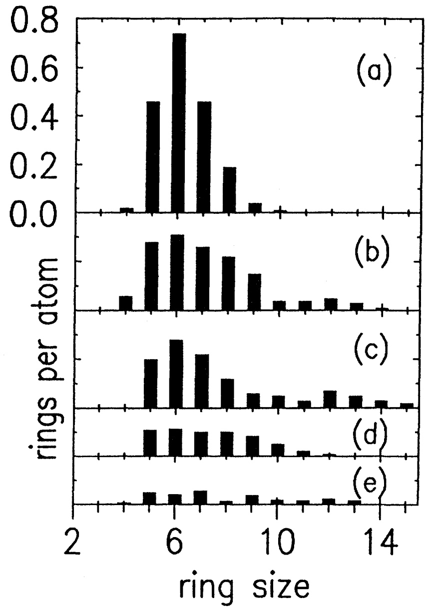

FIG. 4. Distribution of ring sizes for the five samples studied. Only primitive rings, as defined in Ref. 9, are counted. The H content of samples are (a) 0, (b) 28, (c) 40, (d) 50, and (e) 59 at.%. The scale is the same in all panels.

Such *i*-C is generally believed to be almost fully sp^3 bonded and truly amorphous,[1] in which case it should be similar to the pure *a*-C studied here, and closely analogous to *a*-Si and *a*-Ge in structure. Indeed, the radial distribution function for *i*-C recently reported by McKenzie, Muller, and Pailthorpe[10] appears quite consistent with that calculated here.[11]

However, there remain two possible problems with this interpretation. First, as already discussed, we find that pure sp^3 *a*-C is highly strained, and so it is energetically unfavorable relative to sp^2-bonded *a*-C. Second, the calculated density of sp^3 *a*-C is nearly that of diamond, as seen in Fig. 2. This is also consistent with the observed properties of *a*-Si and *a*-Ge. However, the measured density of *i*-C is considerably lower, 15% to 20% lower than diamond.[1,10]

Neither of these problems is decisive. A higher energy phase could still be robustly metastable; and the energy difference might be exaggerated by the fast quench here. Density is difficult to measure accurately, since samples could, in principle, contain small voids. Still, it is worth considering an alternative possible interpretation of *i*-C.

It is quite conceivable that *i*-C might in fact be similar to a new phase of carbon recently predicted in computer simulations similar to those reported here.[7] That phase, originally formed by simulated quenching of liquid carbon under high pressure, contained a roughly equal mixture of sp^2 sites and sp^3 sites, although the proportion could presumably vary somewhat.

Such a phase is a plausible model for *i*-C for several reasons. First, its calculated energy was no higher than that of sp^2-bonded *a*-C, so that, unlike a pure sp^3 phase, there is no energetic barrier to forming it. Second, its density is 14% lower than that of diamond, in rather good agreement with that measured for *i*-C. As a further test, we have calculated the hardness of this material (estimated from Young's modulus as above) to be 60% of diamond's hardness, again consistent with properties of *i*-C.

In this predicted phase, the sp^2 sites play a role analogous to the H in *a*-C:H, relieving strain energy. This mixed phase provides an attractive way of reconciling the measured density and hardness and the calculated energetics. The main theoretical uncertainty is how accurately the empirical potential of Ref. 7 can describe a phase containing a mixture of sp^2 and sp^3 sites.

This interpretation has its own problems. The radial distribution function of the proposed phase clearly reflects the mixture of bond angles,[7] and could be reconciled with the measured distribution[10] only if the latter turned out to be distorted, e.g., by the finite wave-vector cutoff in the data, or by the use of electron diffraction. (This is, however, a very real possibility.[12]) Also, the absence of a π^* peak in the measured excitation spectra[1] argues against sp^2 bonding; but assumptions about how sp^2 bonding is reflected in the excitation spectra may not be valid for such a mixed phase. Thus further study is needed to resolve these issues.

In conclusion, *a*-C has a considerably higher energy in an sp^3-bonded form than in the usual sp^2-bonded form, because the sp^3 form is much more highly strained. In *a*-C:H, H relieves strain and, hence, reduces the energetic cost of sp^3 bonding. This promotion of sp^3 bonding increases hardness, while the tying off of C bonds by H decreases the hardness. Understanding and controlling this tradeoff remains a central issue in *a*-C:H technology.

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[1] For a recent review, see J. Robertson, in *Diamond and Diamond-like Films and Coatings*, edited by R. Clausing *et al.*, NATO Advanced Study Institutes Ser. B (Plenum, New York, in press).

[2] J. Tersoff, Phys. Rev. B **39**, 5566 (1989); for further background on this approach, see J. Tersoff, *ibid.* **37**, 6991 (1988); also Phys. Rev. Lett. **56**, 632 (1986).

[3] J. Tersoff, Phys. Rev. Lett. **64**, 1757 (1990).

[4] The parameters introduced here were determined as follows. (The notation follows Ref. 2.) The parameters R and S for carbon, which were not needed in Ref. 3 (and which are in all cases somewhat arbitrary), are taken here to be 1.8 Å and 2.1 Å. To reduce the number of independent parameters needed to include H, we take $\omega = 1$ and $\lambda = 2\mu$. Since H ends up singly coordinated, we omit bond-angle forces on the H, taking $c = 0$; d and h are then irrelevant. Similarly, for singly coordinated atoms n and β play no role; we somewhat arbitrarily take $n = 1$ and $\beta = 4$ so that H form bonds to no more than one atom at once, and $R = 0.85$ Å, $S = 1.0$ Å. The fitted values of the remaining parameters are $A = 87.193$ eV, $B = 39.520$ eV, $\lambda = 4.0042$ Å^{-1}, $\mu = 2.0021$ Å^{-1}, and $\chi = 0.889$.

[5] This correlation is discussed for the specific case of *a*-C in Ref. 1. For further discussion of this correlation, see, e.g., J. J. Gilman, J. Appl. Phys. **46**, 5110 (1975); A. P. Gerk, J. Mater. Sci. **12**, 735 (1977).

[6] M. F. Thorpe, J. Non-Cryst. Solids **57**, 355 (1983); see also J. C. Phillips, Phys. Today **35** (2), 27 (1982).

[7] J. Tersoff, Phys. Rev. Lett. **61**, 2879 (1988).

[8] S. V. King, Nature (London) **213**, 1112 (1967).

[9] D. S. Franzblau, Phys. Rev. B **44**, 4925 (1991), and references therein.

[10] D. R. McKenzie, D. Muller, and B. A. Pailthorpe, Phys. Rev. Lett. **67**, 773 (1991).

[11] The radial distribution function for *a*-C calculated here is rather similar to that shown in Fig. 1, except for a somewhat more pronounced peak at 3.8 Å. However, a more quantitative comparison would require incorporating the effects of instrumental resolution in the calculation.

[12] As noted by Giulia Galli *et al.* [Phys. Rev. Lett. **62**, 555 (1989)], even with a wave vector cutoff *twice as high* as that used in Ref. 10, the first peak in the radial distribution function can be shifted from its true value by 4%. Since the difference between pure sp^2 and pure sp^3 bonding corresponds to a difference of only 6% in the position of the second peak, the interpretation of data requires considerable caution. Also, electron scattering is a nonlinear process, so future studies with x-ray or neutron diffraction could help clarify the analysis.