

Influence of one-fold-coordinated atoms on mechanical properties of covalent networks

P. Boolchand and M. Zhang

Department of Electrical, Computer Engineering and Computer Science, University of Cincinnati, Cincinnati, Ohio 45221-0030

B. Goodman

Department of Physics, University of Cincinnati, Cincinnati, Ohio 45221-0011

(Received 8 September 1995)

One-fold-coordinated atoms in a covalent network mechanically soften a network if it is overcoordinated, and conversely, mechanically stiffen the network if it is undercoordinated. They play no part in network rigidity if the network is optimally coordinated. These features follow directly from constraint theory and provide a quantitative basis to understand the observed nanoindentation hardness of diamond and silicon carbide networks upon progressive hydrogenation when the contribution of one-fold-coordinated atoms is taken into account explicitly.

I. INTRODUCTION

An important beginning towards understanding glasses at a basic level emerged in 1979 when Phillips laid the foundations of constraint theory.¹ He asserted that for covalently bonded networks constrained by bond-stretching (α) and bond-bending (β) forces, a mechanical critical point occurs when the number of constraints per atom n_c equals the degree of freedom n_d of the network, i.e.,

$$n_c = n_d. \quad (1)$$

These ideas were cast in the language of percolation theory by Thorpe² who recognized that the glass condition (1) represents a stiffness threshold. By enumerating the number of constraints per atom (n_c) for a covalent network of N atoms in which atoms bond with a coordination number $r \geq 2$, he showed that

$$n_c = (5/2)\langle r \rangle - 3, \quad (2)$$

where $\langle r \rangle$ represents the average coordination of the network. Within the simple constraint-counting method, the average number F of zero-frequency modes for a statistical ensemble of N atoms in a network is the difference between the number of degrees of freedom, $N_d = Nn_d$, and the number of constraints, $N_c = Nn_c$, i.e.,

$$F/N \equiv n_d - n_c. \quad (3)$$

Detailed calculations^{2,3} of vibrational behavior of simulated random networks have shown that Eq. (3) is a good representation of the number of zero-frequency modes in the region, $n_d > n_c$ [except for a very small region around $n_d = n_c$ where the linear behavior of Eq. (3) does not hold]. The stiffness threshold, which represents a condition where the tendency for glass formation is optimal, occurs at the compositions where F vanishes. Thus, at the glass condition, from Eqs. (2) and (3), the average coordination number of a network acquires the special value:

$$\langle r \rangle = \langle r \rangle^* = 2.4. \quad (4)$$

[Equation (4) and others in this paper are written for three-dimensional geometry, $n_d = 3$.] In this work we retain the notation of Eq. (3) even for overconstrained networks (where $n_c > n_d$). In the latter regime the negative value of F is interpreted as a measure of the network stiffness.

Boolchand and Thorpe⁴ have recently extended the constraint-counting method to networks possessing one-fold-coordinated (OFC) atoms. OFC atoms are considered not to contribute to network connectivity and so are percolatively ineffective. Since such atoms do not contribute β constraints directly, they have to be treated differently from the other atoms of the network for which $r \geq 2$. Starting from first principles and enumerating constraints for a network with a fraction, $x_1 = n_1/N$, of OFC atoms, they found⁴ a modified expression for the number of constraints/atom:

$$n_c = (5/2)\langle r \rangle + x_1 - 3. \quad (5)$$

The glass condition (3) for the total number F , or the number per atom f , is

$$f \equiv F/N = 6 - (5/2)\langle r \rangle - x_1 = 0 \quad (6)$$

or

$$\langle r \rangle = \langle r \rangle^* = 2.4 - 0.4x_1, \quad (7)$$

which brings in a correction term due to OFC atoms explicitly. Equation (7) with the explicit term in x_1 has been shown⁴ to provide a convenient physical basis to account for the observed tendency to form glasses in the Ge-S-I ternary system. In the present work we examine the influence of OFC atoms on the mechanical properties of *overconstrained* covalent networks.

To describe mechanical properties of networks containing OFC atoms, some workers⁵⁻⁷ have employed the expedient of analyzing the ‘‘backbone’’ or ‘‘plucked’’ network constructed by removing all OFC atoms from the original (complete) network, leaving $r \geq 2$ atoms only. The use of the plucked network has intrinsic appeal. (Henceforth primed quantities will refer to the plucked network and unprimed ones to the complete network). The absence of OFC atoms allows one to directly apply the results of Eqs. (2) and (4) to

obtain for the mean number of constraints/atom and the rigidity percolation threshold, respectively,

$$n'_c = (5/2)\langle r' \rangle - 3, \quad (8a)$$

$$\langle r' \rangle^* = 2.4. \quad (8b)$$

As shown in the Appendix, the average coordination number of a plucked network $\langle r' \rangle$ and the complete network $\langle r \rangle$ are related as follows:

$$\langle r' \rangle = (\langle r \rangle - 2x_1)/(1 - x_1). \quad (8c)$$

It is easy to show that Eqs. (8b) and (8c) are consistent with Eq. (7) for the rigidity percolation threshold.

The equivalence of the rigidity-percolation threshold condition using either the plucked or the complete network raises the question, which is the subject of the present work, of whether the enumeration of constraints in one or the other network always has equivalent physical consequences. We first show that taking explicit account of all the atoms in the complete network in counting the constraints *per atom* n_c differs *quantitatively* from using the plucked network value n'_c ; and that this difference has important consequences for the predicted mechanical properties of networks. Only near the stiffness threshold do OFC atoms not contribute to the constraint-count difference $n_c - n'_c$. Although the average coordination number $\langle r' \rangle$ of the plucked network is larger than or equal to $\langle r \rangle$ of the complete network when OFC atoms are present, we will see that, away from the stiffness threshold, the constraint-count difference $n_c - n'_c$ can be of *either sign*, with important physical consequences.

Specifically, in this work we will show that these constraint counting algorithms, when applied to the complete network, provide a quantitative basis to understand results of nanoindentation hardness measurements on diamondlike carbon (DLC) films. On the other hand, when such counting algorithms are implemented on the plucked network, a systematic overestimate of the calculated hardness from the measured value results which can be traced directly to the absence of one-fold-coordinated hydrogen atoms. Thus, while one-fold-coordinated atoms are percolatively ineffective,^{2,3} these play a distinct role in determining the hardness of an overconstrained network, an idea that is recognized here.

II. MECHANICAL PROPERTIES OF NETWORKS WITH OFC ATOMS

To examine the effect of OFC atoms, it is convenient to define the *excess-coordination* parameter s ,

$$s \equiv \langle r' \rangle - \langle r' \rangle^* = \langle r' \rangle - 2.4. \quad (9)$$

[The use of the plucked-network quantities in (9) is done for mathematical convenience only in that $\langle r' \rangle^*$ is a fixed number independent of concentration x_1 .] The parameter s is negative for undercoordinated ($\langle r' \rangle < 2.4$) and zero for the optimally coordinated ($\langle r' \rangle = 2.4$) networks. We present evidence below that, for the overcoordinated regime ($\langle r' \rangle > 2.4$) at least, the number of constraints *per atom* of the complete network n_c correlates *better* with mechanical properties than does n'_c of the plucked network. The differ-

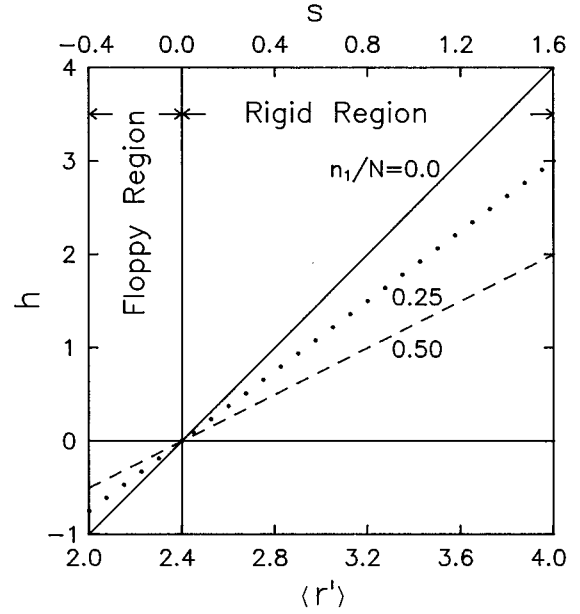


FIG. 1. Graphical representation of Eq. (12) for h vs $\langle r' \rangle$ (or s) showing the straight-line loci for different values of OFC-atom concentration x_1 . The hardness index h' for the plucked lattice is independent of x_1 .

ence between these two *intensive* quantities depends on the concentration x_1 of OFC atoms.

The *total* numbers F and F' of zero-frequency modes are extensive quantities and are the same in the two networks (see Sec. III), while the corresponding intensive quantities are not, namely,

$$f \equiv F/N = n_d - n_c \neq f' \equiv F'/N' = n_d - n'_c. \quad (10)$$

Equation (10) shows again that, only at the rigidity-percolation threshold where F (and F') vanishes, are the n_c - and n'_c -based predictions equivalent. Mechanical properties at other values of n_c and n'_c are *not* equally well represented.

Inserting the relations (8c) and (9) into Eq. (5) gives a convenient form for the constraints/atom in the complete network:

$$n_c = n_d + (5/2)(1 - x_1)s = 3 + (5/2)s - (5/2)x_1s. \quad (11)$$

A closely related quantity, the *hardness index* per atom, is defined by

$$h \equiv n_c - n_d = (5/2)(1 - x_1)s. \quad (12)$$

The *hardness index* per atom is the counterpart in the overconstrained regime of the *floppy-mode* number per atom, $f = F/N = n_d - n_c$, in the underconstrained regime: $h = |f| = -f$. Both h and f vanish at the stiffness threshold, $s = 0$, independently of the concentration of OFC atoms. Figure 1 shows a plot of Eq. (12) for three specific values of x_1 , namely, $x_1 = 0, 0.25$, and 0.5 . It is natural to think of the term $(5/2)s$ on the right in Eq. (12) as the contribution to network constraints due to those atoms which possess a coordination number of 2 or greater and the second term $-(5/2)x_1s$ as the OFC-atom contribution to the constraints.

Note that the first and second terms have opposite signs. Furthermore, since the sign of the parameter s changes from negative to positive in going from undercoordinated networks to overcoordinated ones, the effect of the OFC atoms on mechanical properties also undergoes a sign reversal. Specifically, Eq. (12) and Fig. 1 show that, in an undercoordinated network, the presence of OFC atoms stiffens the network, i.e., $n_c - 3$ increases as x_1 increases. For an overcoordinated network the reverse is the case, viz., OFC atoms soften the network, i.e., $n_c - 3$ decreases as x_1 increases.

III. COMPARISON OF THE MECHANICAL PROPERTIES OF THE COMPLETE AND PLUCKED NETWORKS

The floppy, nominally “zero-frequency,” modes in an undercoordinated covalent network are associated with atomic motions of extended correlation range such as in a group of atoms forming an isolated chain. In the absence of long-range van der Waals forces, the different modes of this kind are the independent zero-frequency solutions of the dynamical matrix.² The mean constraint-counting method gives the *same total number* of these modes for the complete and plucked networks as asserted earlier, i.e.,

$$F = F'. \quad (13)$$

This is because an OFC atom contributes the same number of added degrees of freedom, $\Delta n_d = 3$, as constraints, namely, one radial (α) constraint and two angular (β) constraints to the atom with $r > 2$ to which it is bound.

From Eq. (13) follows directly relations between the intensive (per atom) properties of both networks. Using

$$F \equiv N(3 - n_c) = F' \equiv N'(3 - n'_c) \quad (14a)$$

and

$$N = N' + n_1 = N'/(1 - x_1) \quad (14b)$$

yields

$$n_c - n'_c = (3 - n'_c)x_1 = -(5/2)x_1s. \quad (15)$$

Equations (14a) and (15) lead to the equivalent forms

$$h = h'(1 - x_1), \quad (16a)$$

$$h = h' - (5/2)x_1s, \quad (16b)$$

the first of which is the most transparent statement that OFC atoms reduce the hardness of the complete network relative to that of the plucked network. The ratio h/h' depends on x_1 only.

To test these simple predictions of constraint counting on network rigidity, we need to identify a specific measurable property (or properties) of rigidity. In the following sections, we consider nanoindentation hardness (NIH) as one such property. Substantial NIH results are now available from the literature,⁸⁻¹⁰ so we will explore the correlation between this observable and the theoretical hardness index h .

IV. MECHANICAL RIGIDITY OF HYDROGENATED NETWORKS OF GROUP IV ELEMENTS

Crystalline Si, SiC, C (diamond) consists of ordered networks of tetrahedral building blocks and possess NIH values of ~ 10 GPa,¹¹ 30 GPa,¹² and 100 GPa,¹³ respectively. For a pure tetrahedrally coordinated network, $r = 4(n_c = 7)$ and $h = 4$. The increasing hardnesses measured in the Si \rightarrow SiC \rightarrow C (diamond) sequence reflect the increasing bond strength of the sp^3 covalent bonds as the nearest-neighbor distances decrease. To correlate the hardness of the corresponding hydrogenated alloys with h , it is reasonable to postulate the form

$$\text{NIH} = \alpha \eta(h), \quad (17)$$

where α is the chemical-bond scale factor and $\eta(h)$ represents the dependence of NIH on the network topology within the constraint-counting description.

Thin films of diamondlike carbon (DLC) and silicon carbide have attracted interest as chemically inert hard coatings. These films can be prepared⁸⁻¹⁰ by plasma-enhanced chemical vapor deposition of methane and silane precursors. Their physical properties, including hardness, are found to depend on the microstructure and on the amount of chemically bonded hydrogen in the network. The latter aspects of the structure can be controlled by the processing conditions used to deposit the films. Clearly, starting from the pure materials, the incorporation of hydrogen progressively interrupts network connectivity and can be expected to soften the network mechanically, which is consistent with the constraint/atom-counting prediction for the overconstrained regime.

Hardness provides a measure of the average pressure under an indenter. Conventionally, hardness is determined from the ratio of the load to the projected area of contact between the indenter and the sample. With the introduction of computer-controlled depth-sensitive nanoindentors, hardness is more reliably ascertained¹⁴ by measuring the normal displacement rather than the indentation image. In general, the displacement under a given load has both elastic and plastic components, and in NIH measurements one can separate the elastic from the plastic contributions, as discussed by several workers.⁸ Without subtraction of the elastic recovery, an overestimate of the hardness will result.⁸

A. Diamond

The physical properties of DLC films prepared by RF plasma decomposition of methane have been studied by Jiang, Reichelt, and Stritzker⁸ and Tamor *et al.*⁹ under very similar processing conditions. For example, both groups observed the internal compressive stress of their films to decrease systematically from ~ 3 GPa at -100 V substrate bias voltage to ~ 1 GPa at -1000 V bias voltage. It thus seems reasonable to combine their experimental results. From their ¹³C and ¹H NMR data Tamor *et al.*⁹ inferred the statistics of the different carbon bond configurations (sp^3, sp^2 , etc.), from which the average coordination number $\langle r' \rangle$ of the carbon atom (plucked) network can be extracted as well as the amount x_1 of bonded hydrogen. On the other hand, Jiang, Reichelt, and Stritzker give nanoindentation hardness values.⁸

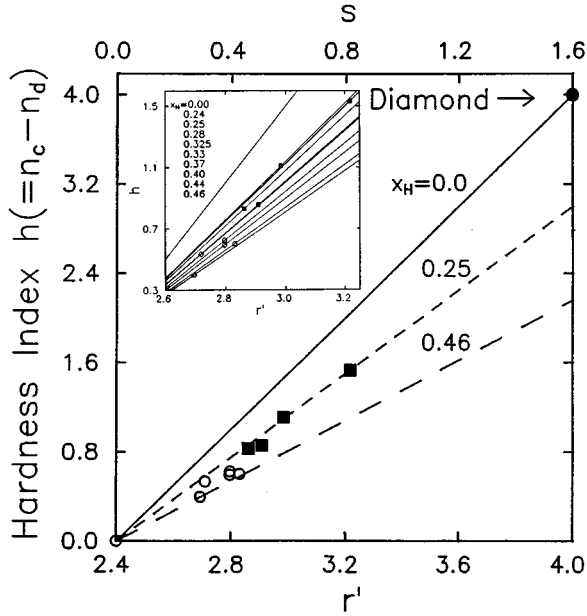


FIG. 2. Application of Fig. 1 to determining the complete-network hardness index h of hydrogenated DLC films and crystalline diamond. The continuous lines are taken from Fig. 1 for the three values of bonded hydrogen, $x_1=0, 0.25$, and 0.46 . The inset shows in more detail how data points from Weiler *et al.* (Ref. 10) and Tamor *et al.* (Ref. 9) lie on different h vs $\langle r' \rangle$ lines corresponding to values of x_1 inferred from NMR data.

Weiler *et al.*¹⁰ also reported on preparation and physical properties (including hardness and internal stress measurements) of DLC films prepared by chemical vapor deposition and plasma beam sources. For each of these samples, we note that the ratio of the Knoop hardness to internal stress is found to be $\sim 7.2(5)$, somewhat larger than the ratio of about $6.0(2)$ found by Jiang, Reichelt, and Stritzker⁸ for their DLC films. We believe this difference probably reflects a slight overestimate in the hardness measurement using Knoop's method.¹⁰ The hydrogen content of the DLC films studied by Weiler *et al.* were established by ¹⁵N forward recoil spectroscopy. For the kinetic energy of ions used, the hydrogen content of their films (24–32.5 %) are significantly lower than those found by Jiang, Reichelt, and Stritzker⁸ and Tamor *et al.*,⁹ probably related to the use of C_2H_2 rather than CH_4 as a working gas. It is for this reason their DLC films possess a larger value of h in relation to those of Tamor *et al.*⁹

The reduction of these data to the hardness index h is illustrated in Figs. 1 and 2. Figure 1 displays Eq. (12) graphically, with each h vs $\langle r' \rangle$ straight line corresponding to a fixed concentration x_1 . In Fig. 2 the points of h vs $\langle r' \rangle$ so obtained are plotted for the hydrogenated DLC film data; and the measured hardnesses NIH are plotted versus the calculated values of h in Fig. 3.

The solid lines in Fig. 3 correspond to a linear relationship

$$NIH = \alpha h, \quad (18)$$

where α is calibrated by the values of NIH for the pure systems at which $h=4$. For diamond, SiC and Si networks,

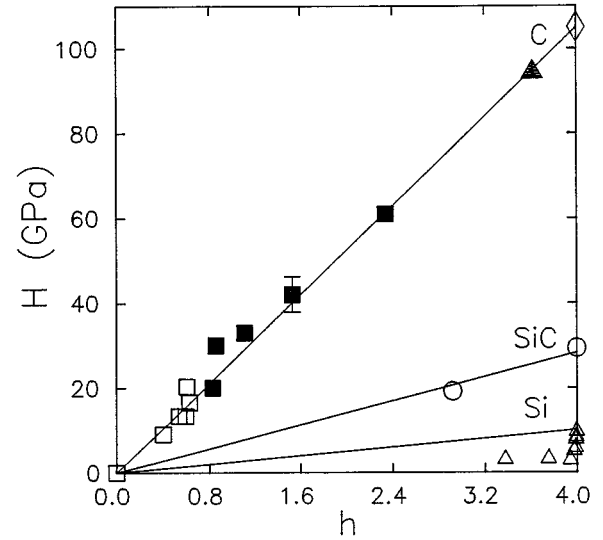


FIG. 3. Nanoindentation hardness (NIH) in GPa of hydrogenated DLC films (\square Ref. 9, Tamor *et al.*, and \blacksquare from Ref. 10, Weiler *et al.*, \blacktriangle from Ref. 24, Lossy *et al.*) plotted as a function of hardness index h . The latter was obtained from Fig. 2. The straight line corresponds to a linear relationship $H = \alpha h$ where $\alpha = 26.5$ GPa is obtained by calibrating against pure diamond (\diamond). The open circles (\circ) represent data on c -SiC and hydrogenated SiC taken from the work of El Khakani *et al.*, Ref. 12. The hardness of hydrogenated silicon samples (\triangle) taken from the work of Jiang *et al.*, Ref. 10 are shown by open triangles.

the α values are 25 GPa/constraint, 7.5 GPa/constraint and 2.5 GPa/constraint, respectively.

An alternative scheme for systematizing the NIH results on DLC films as a function of average coordination number has been advanced by Thorpe.¹⁵ It is based on the hardness index of the plucked network, $h' = n'_c - 3$. He obtains an approximate correlation of h' with the measured hardness of the form.

$$NIH \approx \alpha' h'^{\nu} \quad \text{with } \nu \cong 1.4-1.5. \quad (19)$$

Figure 4 shows the same measured hardnesses for DLC films as those plotted in Fig. 3, but this time plotted vs h' . Also shown are the curves given by Eq. (19) for several values of the power ν . From the available results it appears that the linear correlation shown in Fig. 3 has significantly less scatter than the power-law correlation in Fig. 4.

B. Silicon carbide

The microstructure and hardness of stoichiometric SiC films and hydrogenated-SiC films have been examined by El Khakani *et al.*¹² and Bayne *et al.*¹⁶ The NIH of hydrogen-free amorphous SiC films deposited by either laser ablation or by triode sputtering has been established^{12,16} to be ~ 30 GPa. On the other hand, films prepared by plasma enhanced chemical vapor deposition of $SiH_4:CH_4$ mixtures with argon carrier gas can be compositionally tuned to yield hydrogenated stoichiometric a -SiC:H films containing 27 at. % of hydrogen. The hardness of these films established in nanoindentation experiments was found¹² to be $19.5(2.0)$ GPa. Fourier transformed infrared (FTIR) measurements reveal that

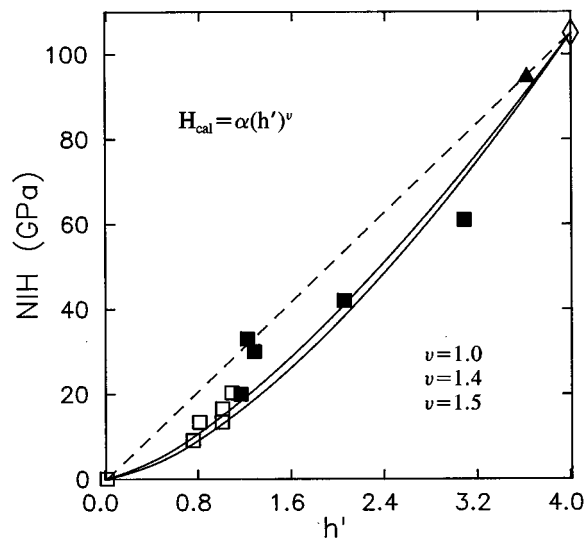


FIG. 4. Nanoindentation hardness (NIH in GPa) of hydrogenated DLC films (\square from Ref. 9, Tamor *et al.*, \blacksquare from Ref. 10, Weiler *et al.*, \blacktriangle from Lossy *et al.*, Ref. 24) plotted as a function of hardness index h' in the plucked network. See Eq. (9) for details. The continuous lines are power-law predictions for nanoindentation hardness with the power coefficient ν' taking on values of 1.4 and 1.5.

inclusion of hydrogen in the films terminates the tetrahedral network both at Si and also at C to form Si-H and C-H signatures. The hydrogen content of the films was established by forward recoil spectrometry and FTIR. Using the microstructure of the films, we have calculated the average coordination number $\langle r' \rangle$ of the plucked network. Further, from the hydrogen content of the films, we next proceeded to calculate the hardness index h for the hydrogenated stoichiometric film. The observed and calculated hardness of SiC are plotted in Fig. 3 using a value of $\alpha = 7.5$ GPa/constraint. The reduction of hardness upon hydrogenation of SiC films is largely a mechanical effect as we will see later.

C. Silicon

The hardness of crystalline silicon films in nanoindentation experiments has been established^{11,12} to be 10.4(5) GPa. Jiang, Reichelt, and Stritzker⁸ have examined hardness of hydrogenated amorphous Si films in nanoindentation experiments. Their films were prepared by reactive sputtering of silicon in a hydrogen-argon ambient at a total pressure ($P_{H_2} + P_{Ar}$) of 26 mbar. The hardness results on those films are plotted in Fig. 3. They saw a surprisingly sharp reduction of hardness by almost a factor of 2 with only 1 at. % hydrogen.

The single-bond dissociation energies¹⁷ of Si-H, Si-Si, and H-H are 373, 310, and 432 kcal/mole, respectively. These data suggest that the preference to form heteropolar (Si-H) over homopolar (Si-Si, H-H) bonds is weak and this may represent a chemical factor responsible for intrinsic heterogeneity of the hydrogenated amorphous Si films of Jiang, Reichelt, and Stritzker.⁸

Unlike the chemistry of carbon, silicon does not form three-fold-coordinated graphitelike configuration to provide

a strain relief of the overcoordinated tetrahedral Si network. At these very low hydrogen concentrations, growth of small Si clusters with internal surfaces terminated by H may provide an intrinsic strain-relief mechanism. The drastic reduction in hardness with only 1 at. % hydrogen in the experiments of Jiang, Reichelt, and Stritzker may be the consequence of such a cluster bearing morphological growth.

Glow discharge decomposition of silane under rather low pressures gives rise to photovoltaic device quality material that also contains 10–20 at. % hydrogen. Although a vast literature¹⁸ exists on the optical, structural, and device properties of these Si-H alloys, we are not aware of systematic studies on mechanical properties of these materials. Investigations of correlation of microstructure and hardness of these films would be of much interest as a test of the ideas developed here in connection with constraint theory of glasses.

V. DISCUSSION

Hardness is an intrinsically plastic property of a material. On a macroscopic level, one physically relates it to plastic flow or flow stress Y when work-hardening of a material occurs.¹⁹ On a microscopic level, one relates plastic flow usually to movement of dislocations in a crystalline material.¹⁹ This phenomenon is to be contrasted to elastic deformation of a solid which is an intrinsically reversible process.

Indentation hardness measurements in elastoplastic materials have in general both a plastic and an elastic contribution.¹⁹ Historically, as modeled by Marsh²¹ for a Vicker's indenter, the indentation pressure P (where the cavity expands) normalized to flow stress Y (i.e., P/Y is found to vary linearly with $\ln E/Y$ as follows

$$P/Y = 0.40 + (2/3)\ln E/Y, \quad (20)$$

where E designates the Young's modulus of the material. The plasticity of a variety of materials including polymers, glasses, semiconductors, and metals has been characterized by Eq. (20). In this equation the ratio P/Y provides a measure of plasticity. Materials with low P/Y (≤ 1.5) are generally considered elastic while those with high P/Y ($= 3.0$) values are considered plastic. Diamond and DLC films, in which atoms display covalent bonding, fall in the middle category²² having $P/Y \sim 2.0$. When an indenter is pressed against a material, in the vicinity of the indentation, a mechanical equilibrium develops between three concentric zones. The first zone consists of a hydrostatic core which plays no part in hardness of the material. This zone is surrounded by a plastic zone where a flow of the material occurs and determines the true hardness of the material. The plastic zone is surrounded by an elastic hinterland. Low values of the indentation pressure P derive from the give of the elastic hinterland, and this is a feature of a highly elastic material like polymers or rubbers. On the other hand, large values of P are characteristic of an intrinsically plastic material.¹⁹ In the NIH measurements on diamond and DLC films reported by Jiang, Reichelt, and Stritzker,⁸ care was taken to separate off the elastic response. The elasticity of the material therefore plays no role for the hardness results plotted in Figs. 3 and 4.

Within the constraint theory of glasses, interatomic forces provide a measure of local softness or stiffness of a network,

as the case may be. For undercoordinated networks the local softness manifests itself in floppy modes, which have been observed²³ in inelastic neutron-scattering or Lamb-Mössbauer factor measurements. For overcoordinated networks such as diamond or silicon or SiC, the local stiffness is connected with the plasticity of the material. Since the average number of constraints/atom increases with average coordination number, one can understand the observed linear correlation in Fig. 2 between NIH (plasticity) and the average coordination number for each of the tetrahedral solids.

Figures 3 and 4 show a considerably better correlation of NIH with the hardness index h derived from counting of constraints in the complete network than with the corresponding index h' from the plucked network constraints. Referring to Eq. (1.6), it is seen that h' always exceeds h and $\langle r' \rangle$ always exceeds $\langle r \rangle$ in the plots of Figs. 3 and 4. It is for this reason that in Fig. 4 the abscissa h' corresponding to a given data point is displaced to higher values as compared with Fig. 3 in proportion to hydrogen content of the film. The effect of not counting H atoms in the DLC films is to increase the average constraints per atom n'_c and therefore to increase h' in relation to h so as to produce the suggestion of a curvature in Fig. 4.

It has been suggested¹⁵ that there is some support from the perspective of theory for the nonlinear power-law relation given by Eq. (19) from numerical calculations^{2,3} of the elastic moduli of simulated random networks with short-range bond forces only (and no OFC atoms) which fit this power-law form well. However, elastic behavior is probably uniquely insensitive (among mechanical properties of networks with short-range bond forces only), to nanoindentation hardness measurements.^{8,14} In these measurements, as discussed above, elastic effects are specifically excluded. The suggestion of a curvature in Fig. 4 is probably the consequence of a difference in the count of constraints in the overconstrained regime between the plucked and complete network, when the latter includes OFC atoms. These results suggest that side groups including OFC atoms play a role in determining hardness of an overcoordinated covalent network. There is evidence from recent inelastic neutron-scattering experiments²⁰ that side groups in polymer glasses contribute to the density of vibrational states at low energies (< 2 meV) and also at energies in the bond-stretching regime (~ 20 meV). The low-energy modes are associated with distortions of relatively long wavelength, but not so long as macroscopic elastic waves. In the neutron-scattering experiments the softening of these distortions due to the side groups manifests itself as free vibrations of low frequency. The connection between side groups and vibrational density of states in a network glass is a subject of continued interest and controversy and will undoubtedly be the focus of future work in the field.

It is important to recognize that there is no *unique functional* relationship between h and h' which might make possible a coordinate transformation taking the functional relation, $H \propto h$, into one of the form, $H \propto h'^\nu$. Thus Fig. 3 *cannot be inferred* from Fig. 4, and vice versa. The empirical correlations shown in the two figures, with Eq. (18) based on constraint counting in complete networks, and with Eq. (19), based on their plucked networks, are mathematically in-

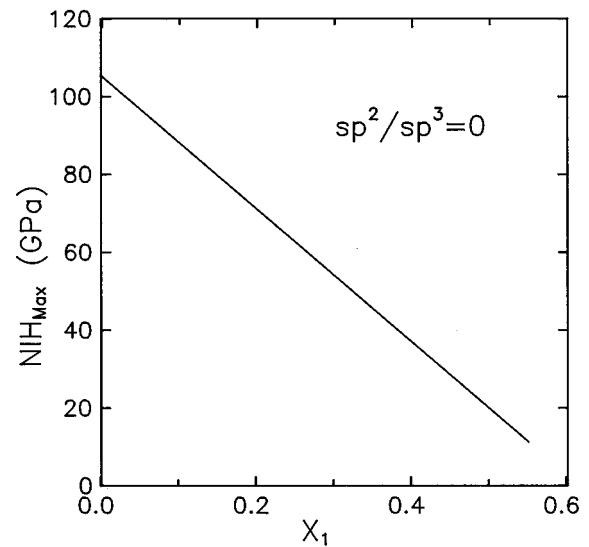


FIG. 5. Predicted maximum hardness of DLC films as a function of hydrogen content based on constraint theory. In the prediction, all C atoms were assumed to be fourfold coordinated.

equivalent; and physically inequivalent also if the OFC atoms influence hardness, since these atoms are missing from h' .

In an overcoordinated glassy network, such as a tetrahedral network ($r=4$), OFC atoms depolymerize the network and eventually fragment it. In this case a loss of hardness is due to facile displacement of atoms or group of atoms due to a loss of connectivity. On the other hand, in undercoordinated glassy networks such as a copolymeric $\text{Se}_{1-x}\text{Te}_x$ chain ($r=2$), OFC halogen atoms (Cl,Br) bond at Te sites and increase the Te coordination number from 2 to 4 as known²⁵ in $\text{Te}_{3-z}\text{Se}_z\text{Cl}_3$ glasses. The increased hardness of the halogenated network results from a stiffening of the chains even though the average coordination number $\langle r \rangle = 2$ remains unchanged upon halogen alloying.

The possible predictive power of constraint theory in the design of solids can be illustrated with Fig. 5 where we plot the maximum NIH value of DLC films as a function of hydrogen concentration x_1 of the films. The maximum hardness of these films corresponds to the case where no graphitic carbon is present. Clearly, if some graphitic carbon is present in the DLC films, then a linear correlation with a higher slope can be expected.

VI. CONCLUSIONS

We have shown that OFC atoms in a covalent network serve to stiffen it mechanically if it is undercoordinated and to soften it mechanically if it is overcoordinated; and that these atoms play no part in determining the mechanical rigidity of an optimally coordinated network. These ideas follow directly from constraint theory, and quantitatively describe nanoindentation hardness results of DLC films and hydrogenated SiC films, when constraint contributions of OFC hydrogen atoms is explicitly taken into account.

ACKNOWLEDGMENTS

We acknowledge useful discussions with Jim Phillips, Mike Thorpe, M. Tabor, and Stan Ovshinsky during the

course of this work. This work was supported by NSF Grants No. DMR-92-07166 and No. DMR-93-09061.

APPENDIX

The average coordination number $\langle r \rangle$ is defined by

$$\langle r \rangle = \frac{1}{N} \sum_{r \geq 1} r N_r, \quad N = \sum_{r \geq 1} N_r, \quad (\text{A1})$$

where N_r is the total number of atoms with r bonds. To get the corresponding average for the plucked lattice which has only $r \geq 2$ type atoms, we first must assume that these atoms themselves are not part of side groups and will remain at least two-fold coordinated upon removal of a OFC-bonded atom. This requires an $r \geq 3$ atom to start with, which will be changed to $r' = r - 1$. This applies to N_1 such atoms. For all the other $r \geq 2$ atoms $r' = r$:

$$\begin{aligned} \langle r' \rangle &= \frac{1}{N'} \sum_{r \geq 2} r' N_r = \frac{1}{N'} \left\{ -N_1 + \sum_{r \geq 2} r N_r \right\} \\ &= \frac{1}{N'} \left\{ -2N_1 + \sum_{r \geq 1} r N_r \right\} = \frac{N}{N'} \{ \langle r \rangle - 2x_1 \} \quad (\text{A2}) \end{aligned}$$

and

$$N' = \sum_{r \geq 2} N_r = N - N_1 = N(1 - x_1) \quad (\text{A3})$$

yielding

$$\langle r' \rangle = \frac{\langle r \rangle - 2x_1}{1 - x_1}, \quad \text{or} \quad \langle r \rangle = \langle r' \rangle + (2 - \langle r' \rangle)x_1. \quad (\text{A4})$$

-
- ¹J. C. Phillips, *J. Non-Cryst. Solids* **34**, 153 (1979); **43**, 37 (1981).
²M. F. Thorpe, *J. Non-Cryst. Solids* **57**, 355 (1983); H. He and M. F. Thorpe, *Phys. Rev. Lett.* **54**, 2107 (1985).
³D. S. Franzblau and J. Tersoff, *Phys. Rev. Lett.* **68**, 2172 (1992); also see D. J. Jacobs and M. F. Thorpe, *ibid.* **75**, 4051 (1995).
⁴P. Boolchand and M. F. Thorpe, *Phys. Rev. B* **50**, 10 366 (1994).
⁵G. H. Dohler, R. Dandolo, and H. Bilz, *J. Non-Cryst. Solids* **42**, 87 (1980).
⁶J. C. Angus and F. Jansen, *J. Vac. Sci. Technol. A* **6**, 1778 (1988); M. A. Tamor, W. C. Vassell, and K. R. Kertner, *Appl. Phys. Lett.* **58**, 592 (1991).
⁷N. Mousseau and M. F. Thorpe, *Phys. Rev. B* **48**, 5172 (1993).
⁸X. Jiang, K. Reichelt, and B. Stritzker, *J. Appl. Phys.* **66**, 5805 (1989); J. W. Zou, K. Reichelt, S. Schmidt, and B. Dischler, *ibid.* **65**, 3914 (1989).
⁹M. A. Tamor, W. C. Vassell, and K. R. Carduner, *Appl. Phys. Lett.* **58**, 592 (1991); and also see M. A. Tamor, J. A. Haire, C. H. Wu, and K. C. Hass, *ibid.* **54**, 123 (1989).
¹⁰M. Weiler, R. Kleber, S. Sattel, K. Jung, H. Ehrhardt, G. Jungnickel, S. Deutschmann, U. Stephan, P. Blaudeck, and Th. Frauenheim, *Diamond Relat. Mater.* **3**, 245 (1994); M. Weiler *et al.*, *Appl. Phys. Lett.* **64**, 2797 (1994).
¹¹A. Kelly and N. H. McMillan, *Strong Solids* (Oxford University Press, Oxford, 1986).
¹²M. A. El Khakani, M. Chaker, A. Jean, S. Boily, J. C. Kieffer, M. E. O'Hern, M. F. Ravet, and F. Rousseaux, *J. Mater. Res.* **9**, 96 (1994).
¹³J. E. Field, *Properties of Diamond* (Academic, New York, 1979).
¹⁴M. F. Doerner and W. D. Nix, *J. Mater. Res.* **1**, 601 (1986).
¹⁵M. F. Thorpe, *J. Non-Cryst. Solids* **182**, 135 (1995).
¹⁶M. A. Bayne, Z. Kurokawa, N. U. Okorie, B. D. Roe, L. Johnson, and R. W. Moss, *Thin Solid Films* **107**, 201 (1983).
¹⁷B. E. Douglas, D. H. McDaniel, and J. J. Alexander, *Concepts and Models of Inorganic Chemistry* (Wiley, New York, 1994), p. 89.
¹⁸S. R. Ovshinsky (private communication).
¹⁹D. Tabor, *Rev. Phys. Technol.* **1**, 145 (1970).
²⁰B. Frick and D. Richter, *Science* **267**, 1939 (1995).
²¹D. M. Marsh, *Proc. R. Soc. London Ser. A* **279**, 420 (1964).
²²J. Robertson, *Prog. Solid State Chem.* **21**, 199 (1991).
²³P. Boolchand, W. J. Bresser, M. Zhang, Y. Wu, J. Wells, and R. N. Enzweiler, *J. Non-Cryst. Solids* **182**, 143 (1995).
²⁴R. Lossy, D. L. Pappas, R. A. Roy, J. J. Cuomo, and V. M. Sura, *Appl. Phys. Lett.* **61**, 171 (1992).
²⁵J. Wells, W. J. Bresser, P. Boolchand, and J. Lucas, *J. Non-Cryst. Solids* **195**, 170 (1996).