Superhard and Elastic Carbon Nitride Thin Films Having Fullerenelike Microstructure

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CN_x films were found to have a distorted graphitelike microstructure consisting of buckled and curved basal planes using high-resolution electron microscopy. Nanoindentation showed an elastic recovery of 85%, and a hardness of ~60 GPa. Based on detailed quantum chemical calculations and photoelectron spectroscopy, the observed structure is proposed to consist of a network of buckled sp^2-hybridized CN_x planes, cross-linked by sp^3-hybridized bonds. The buckling is shown to be due to the incorporation of pentagons in the basal planes, giving rise to a fullerenelike microstructure.

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The research in the carbon nitride (CN_x) area is today mainly focused on realizing the superhard β-C_3N_4 compound predicted by Liu and Cohen [1]. Most of the techniques that have been used to synthesize this material are based on vapor phase methods where a thin film is condensed onto a substrate. Structural results in the form of plane distances obtained from diffraction indicate the existence of the β-C_3N_4 phase, in small crystallites immersed in an amorphous matrix [2,3]. Thus far, however, no one has been able to produce large enough quantities of this phase to perform mechanical measurements on it. The type of CN_x films most frequently reported on have N/C ratios between 0.3 and 0.5, and are amorphous. However, the mechanical properties of some of these CN_x films have proven to be very interesting, especially with respect to their elastic deformation behavior [4,5]. Even though the mechanical properties of CN_x films have been investigated, neither the local atomic bonding structure nor the microstructure corresponding to the observed mechanical properties of such carbon nitride films have been reported. In this work we report on CN_x film having a fullerenelike microstructure and extreme mechanical properties, with hardnesses of ~60 GPa and an elastic recovery as high as 85% as determined by nanoindentation. We propose a model where curved graphitelike basal planes containing carbon and nitrogen form a cross-linked structure with covalent bonds in three dimensions, resulting in a strong and elastic structure. The curvature is proposed to be due to formation of pentagons in the basal planes, which otherwise are built up of hexagons only. This suggestion is supported by detailed quantum chemical calculations and x-ray photoelectron spectroscopy (XPS) measurements.

Carbon nitride films having a thickness of 300 nm were deposited onto Si(001) substrates at temperatures between 200 and 600 °C using reactive dc magnetron sputtering of a graphite target in pure nitrogen discharges [5]. Nitrogen content and core electron binding energies in the films were analyzed using Rutherford backscattering (RBS) and XPS, respectively. In the RBS, analysis of the composition of the samples was obtained by comparing the yield from the unknown with that of a pure C sample. Using this procedure for N concentrations below 30 at. %, the accuracy was estimated to be approximately 2%. The specific energy loss values for N used were obtained from Ziegler, Biersack, and Littmark [6]. The XPS measurements were carried out on a V.G. Scientific ESCALAB spectrometer using Mg $K\alpha_{1,2}$ (1253.6 eV) radiation in a vacuum chamber operating at a pressure lower than 7×10^{-10} Torr. High-resolution transmission electron microscopy (HREM) was performed in a Philips CM 20 UT transmission electron microscope having a point resolution of 1.9 Å. The samples for the latter studies were prepared by mechanical cleaving [7]. Load-displacement curves were recorded in nanoindentation experiments using a trigonal Berkowich diamond tip. Because of the low film thickness, the indentation experiments were performed at low (≤5 mN) loads. In order to understand the structure of the films, quantum chemical calculations of total energies and core electron binding energies have been carried out for some selected model systems.

Figure 1 shows the load-displacement curves, obtained from the nanoindentation measurements, for a $CN_{0.2}$ film, and, for comparison, an epitaxial single-crystal TiN film. Both films were deposited onto a Si(001) substrate to the same thickness. An elastic recovery as high as 85% was obtained for the $CN_{0.2}$ film which can be compared to the value for TiN which was 60%. The elastic recovery is most likely even higher since no indents could be detected during high-resolution (4 nm) scanning electron microscopy. Because of the totally nonlinear unloading curve, the exact hardness and elastic modulus cannot be determined accurately using existing models for evaluation of nanoindentation data [8,9]. These models assume a constant contact area during the initial part of unloading, i.e., flat punch approximation. This is not the case for hard and elastic materials like CN_x where the contact area varies through the whole unloading cycle. Thus the contact area for this type of material will be overestimated and thereby the hardness underestimated. However, using the method of Doerner and Nix [9] and

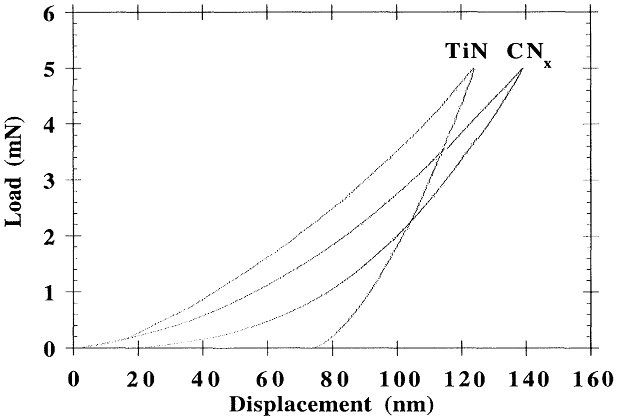

FIG. 1. Load-displacement curves for a pure Si(001) substrate, a Si(001) substrate coated with a 0.3 μm $CN_{0.2}$ film, and one Si(001) substrate coated with a 0.3 μm TiN film.

compensating for overestimation of the contact area using a slightly lower tangent point, an approximation of the contact area and thus the hardness can be obtained.

The estimated values of hardness (H) and elastic modulus (E) for the CN_x films are ~60 and ~900 GPa, respectively, which are close to those for diamond, ~100 and ~1050 GPa [10], respectively, and higher than those for TiN, ~20 and ~600 GPa [10], respectively. The H and E values were also evaluated, utilizing the model for loading curves of elastoplastic materials by Loubet *et al.* [11], as described in Ref. [12]. The H and E values obtained were in good agreement with those obtained using the tangent method described above.

Films exhibiting the extreme elastic properties described above all had the same microstructure, which previously has been assigned by HREM as turbostratic [5]. However, this microstructural analysis was performed on ion-beam thinned samples, and we have found that these differ somewhat in structure from those obtained by mechanical cleaving. The high energetic ions used for ion-beam thinning cause the formation of a thin amorphous layer on the sample surface which distorts the HREM analysis. This effect was seen even when using a low incident angle of the ions of <5°. Using the mechanical cleaving technique, these problems are avoided. Figure 2 is a HREM micrograph displaying the microstructure as seen when analyzing such a cleaved sample. The structure can be described as graphitelike with interplanar distances of 0.347, 0.209, and 0.120 nm as obtained from selected area electron diffraction patterns. However, this structure exhibits features different from both graphite and turbostratic carbon. The basal planes are curved, indicating buckling, in graphite, of the normally flat sp^2-hybridized planes. This buckling of the basal planes leads to intersecting planes. Thus, there is a possibility that the basal planes in this structure are interlocked with covalent bonds of a much shorter bond length than that of the van der Waal bonds between the basal planes in graphite. Furthermore, planes with ring and fingerprint shapes can also be seen in Fig. 2. The ring-shaped features are built up of successive shells and have outer diameters as large as ~35 Å. These microstructural features were seen independently of the sample tilt in the microscope, demonstrating that these basal planes curve into a three-dimensional structure, similar to that of fullerenes like buckyonions [13,14].

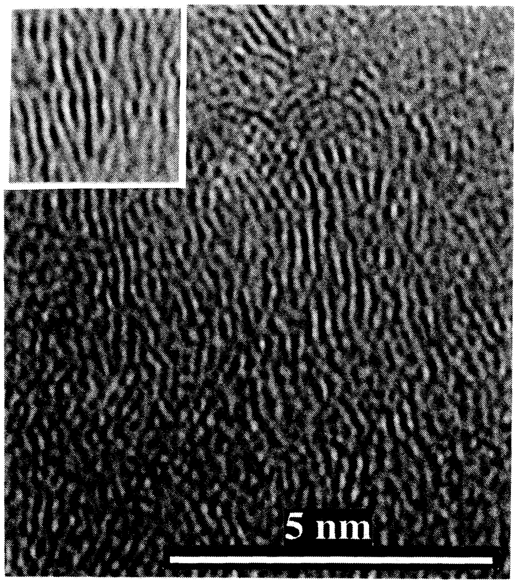

FIG. 2. A HREM micrograph obtained with a point resolution of 1.9 Å, showing the microstructure of a $CN_{0.2}$ film. The basal planes are resolved and short-range buckling as well as 180° bending of them can be seen. The inset shows an area where frequent cross-linking between planes occur. The HREM sample was obtained by mechanical cleaving using the technique described in Ref. [4].

The observation of curved graphite layers similar to those of buckyonions indicates that pentagons are present in the structure. To study this possibility in more detail we have performed total energy calculations using the semiempirical Hartree-Fock-based AM1 method [15] on two different types of structures. One is a planar graphitelike cluster (system A) shown in Fig. 3, the other is curved and includes one pentagon (system B). Both clusters contain 24 heavy atoms (carbon and nitrogen), are hydrogen terminated, and have the same number of identical atoms making a comparison of total energies possible.

Calculations involving full geometry optimizations for the following four configurations were performed: (i) The aromatic rings in both systems A and B contain carbon only. The energy difference between systems A and B, $\Delta E_{A,B}$, is in this case 73.8 kcal/mole, in favor of A. Thus, the carbon system favors strongly the planar graphite structure compared to the pentagon-containing system which has a curved equilibrium geometry. It

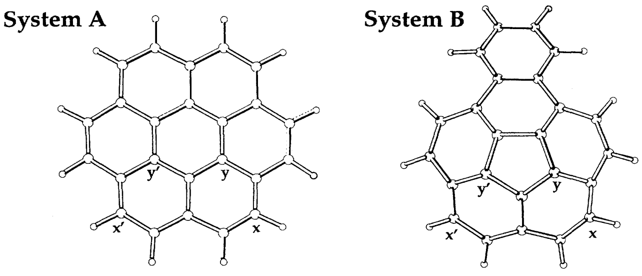

FIG. 3. Schematic presentation of the two model systems used for calculation of total energies of pentagon-containing systems versus nonpentagon-containing systems.

should be noted, however, that systems A and B are terminated in different ways. This difference also contributes to $\Delta E_{\mathrm{A,B}}$, but to the same amount in all configurations. When comparing different configurations, (i) to (iv), this end effect therefore cancels. (ii) Two C atoms are replaced by N atoms in approximately equivalent positions in both systems, positions x and x' in Fig. 3. The pentagon in system B is therefore unchanged as compared to case (i) and contains carbon atoms only. In this case $\Delta E_{\mathrm{A,B}} = 70.7$ kcal/mole. The small difference in $\Delta E_{\mathrm{A,B}}$ values in these two cases shows that incorporation of N in sites away from the pentagon does not have any significant effects on the formation energy of the pentagon. (iii) The N atom in position x in configuration (ii) is exchanged with the C atom in position y, in both systems A and B. In this case $\Delta E_{\mathrm{A,B}} = 53.7$ kcal/mole. Thus, by incorporating one N atom in a pentagon instead of in a hexagon, the total energy decreases by as much as 17.0 kcal/mole. Evidently, the N atoms prefer a nonplanar surrounding as in the curved structure around a pentagon. (iv) Finally, we also considered the case when both the N atoms appear in positions y and y'. In this case $\Delta E_{\mathrm{A,B}} = 47.6$ kcal/mole; i.e., a further energy reduction of 6.1 kcal/mole occurs. We conclude from these results that by incorporating N atoms during growth of carbon films, pentagons become more stable than in the absence of N. This result is fully consistent with the microstructure shown in Fig. 2. Thus we argue that this structure is caused by incorporated pentagons in the basal planes, as in the case of fullerenes.

XPS measurements of the N 1s core level reported earlier [12] demonstrated two types of nitrogen positions in the films, corresponding to binding the energies 398.7 and 400.6 eV, which gives a chemical shift between these two positions of 1.9 eV. In order to deduce the origin of these two N-binding sites, theoretical calculations of chemical shifts in the N 1s core level using the delta-self-consistent-field method [16,17] was performed on two model systems α and β. System $\alpha(\mathrm{C_{15}NH_{10}})$ represents N atoms surrounded by sp^2-coordinated C atoms, whereas system $\beta(\mathrm{C_6NH_{15}})$ represents N atoms surrounded by sp^3-coordinated C atoms. These calculations resulted in a chemical shift between the systems α and β of ~1.8 eV, in very good agreement with the experimentally measured shift of 1.9 eV.

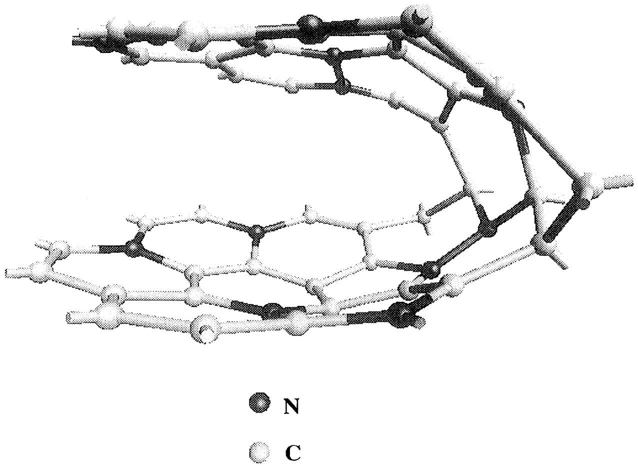

FIG. 4. Schematic picture of cross-linking between two sp^2-hybridized CN_x layers caused by buckling around the pentagons.

Both theoretical and analytical results of the electron binding energies, as well as the microstructure of these films, indicate that N addition induces buckling of the basal planes and thereby facilitates cross-linking between the planes by sp^3-hybridized carbon. A schematic representation of such a structure is shown in Fig. 4. This cross-linking strengthens the weak bonds between the basal planes and results in a structure having the rigidity of a three-dimensional covalently bonded system. Such a stiffening and densifying effect of a graphite structure induced by cross-linking has earlier been proposed by Tamor and Wu [18]. The key to formation of this structure is the incorporation of pentagons in a hexagonal structure to achieve curved basal planes. In our case this occurs due to the presence of nitrogen. It should be noted that this relatively high degree of interplanar cross-linking is induced by a relatively small degree of N incorporation (~20 at. %) as compared to the β-$\mathrm{C_3N_4}$ phase, but nevertheless leads to extreme mechanical properties.

Using a precursor built up of both hexagonal and pentagonal rings, like fullerenes, it should be possible to create a similar structure consisting of carbon only. It has indeed also recently been shown that when sintering $\mathrm{C_{60}}$ at a pressure of ~3 GPa and at a temperature of 700 °C, it will transform into a new carbon phase [19]. This new phase shows many similarities to the phase described in this work, with a hardness of more than 40 GPa and x-ray diffraction peaks corresponding to the interplanar distances 3.47, 2.09, and 1.19 Å. These are identical to the interplanar distances obtained for the films in this work, which indicates similar crystalline structure in these two cases.

For a material to be hard and at the same time elastic, as demonstrated in the present case, it needs to have strong and stable bonds with a high amount of directional flexibility. A structure with strong covalent bonds in all three dimensions having segments of buckled and curved planes similar to those in a fullerene structure would exhibit exactly these properties. In the case of C_{60}, it has also been shown by molecular dynamics that this initially spherical molecule can be substantially deformed and thereafter resume its initial shape [20]. Furthermore, it has been theoretically predicted that the bulk modulus of one single C_{60} molecule should be as large as 843 GPa, which is significantly greater than that of diamond (441 GPa) [21]. In the same work it is suggested that the bulk modulus of a single crystal built up of C_{60} molecules bonded to each other at a pressure of $\sim$20 GPa would be 642 GPa. Further indications of the strength of sp^2-hybridized networks with bonds in three dimensions can be found in the theoretically proposed C structures bct-4 [22] and H-6 [23]. These structures of sp^2-hybridized C with bonds in three dimensions have predicted bulk moduli of 362 and 390 GPa for the bct-4 and H-6 phases, respectively. Both values are close to that of c-BN, 369 GPa [24].

In summary, the results presented in this paper demonstrate experimentally for the first time that structures consisting of a three-dimensional network of covalently bonded C and N atoms can exhibit extreme hardness values. We also propose that the incorporation of N leads to a structure of buckled planes with fullerenelike features that give rise to very high film elasticities. The combination of hardness and elasticity is indeed unusual and of much interest.

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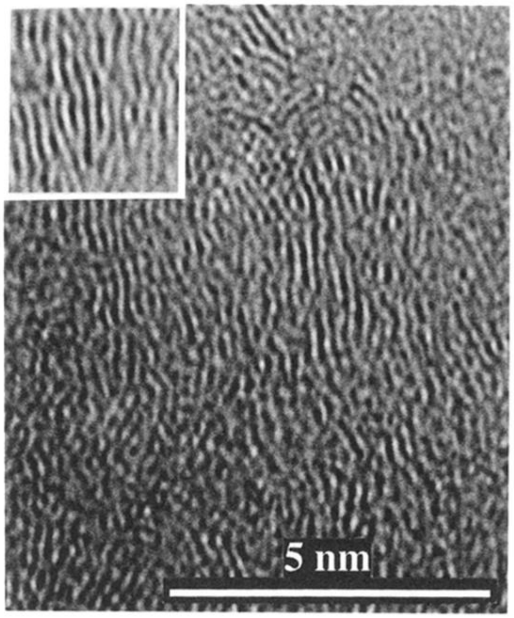

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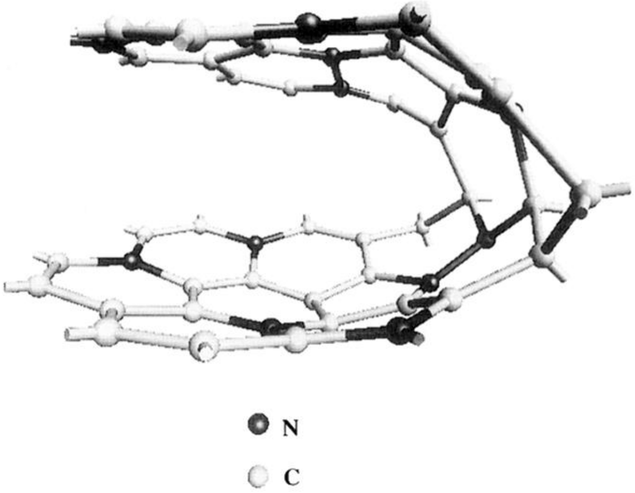

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