PHYSICAL REVIEW B

CONDENSED MATTER AND MATERIALS PHYSICS

THIRD SERIES, VOLUME 57, NUMBER 2

1 JANUARY 1998-II

RAPID COMMUNICATIONS

Rapid Communications are intended for the accelerated publication of important new results and are therefore given priority treatment both in the editorial office and in production. A Rapid Communication in Physical Review B may be no longer than four printed pages and must be accompanied by an abstract. Page proofs are sent to authors.

Nitrogen doping in purely sp^2 bonded forms of carbon

G. Jungnickel, P. K. Sitch, and Th. Frauenheim

Institut für Physik, Theoretische Physik III, Technische Universität, D-09107 Chemnitz, Germany

B. R. Eggen and M. I. Heggie

School of Chemistry, Physics and Environmental Sciences, University of Sussex, Falmer, Brighton BN1 9QJ, United Kingdom

C. D. Latham and C. S. G. Cousins

Department of Physics, University of Exeter, Stocker Road, Exeter EX4 4QL, United Kingdom

(Received 29 October 1997)

We postulate wide-band-gap forms of carbon that locally have a planar bonding configuration as in graphite and, in contrast to diamond, are promising candidates for n -type doping by nitrogen. The presence of localized π bonds makes them as stable as fullerene C_{60} and causes large band gaps of ≈ 3 eV to appear. The allotropes accept both nitrogen and boron as substitutional dopants, making them potentially extremely useful for high-power, high-temperature, and high-speed device applications. [S0163-1829(98)51002-8]

Potentially, carbon based semiconductor devices are very exciting. They should naturally lend themselves to effective heat management. Short and stiff carbon-carbon bonds combined with the lightness of the carbon atoms make diamond the best thermal conductor known. The strength of the C-C bonds and the size of the electronic band gap (5.5 eV) make it very stable against degradation by temperature. Electronic transport is uniquely good for diamond: not only has it a large band gap but also the saturation velocity for electrons is very high.^{1,2} Diamond has been at the center of an intense and highly successful research effort to grow it by chemical vapor deposition (CVD) in a region of the carbon phase diagram where it is technically unstable with respect to graphite.

The conjunction of these factors might have been expected to lead to a generation of exceptional high power devices based on diamond. The reality at this time is somewhat different. Diamond can be doped by boron (as a substitutional impurity) to give p -type material but cannot be doped by nitrogen to give n -type material. Nitrogen moves off the normal diamond lattice site, becoming threefold coordinated and leaving a level deep in the gap coming from the bond left dangling on the neighboring carbon atom.⁴⁻⁷ Nitrogen has been found to preferably aggregate and to trap

vacancies⁸ in this way being a source of charge which, however, is captured at the vacancy.

The difference in size between the carbon atoms and almost all other elements reduces their solubility in diamond to near zero. Phosphorus has been used to create n -type material using the cold implantation rapid annealing method⁹ and by adding it to the CVD plasma.¹⁰ The observed electrical activity is much less than would be expected from the P concentration, the doping efficiency is low, and films are reported to be highly resistive.¹⁰ This may be due to a phosphorus-vacancy complex¹¹ that was found to be more stable than substitutional P. The n -type interstitial lithium can be ion-implanted¹² but is easily deactivated during annealing due to diffusion and subsequent trapping at implantation-induced lattice defects. High concentrations of nitrogen have been incorporated into CVD diamond films using urea as a source. The films showed an unusual low-threshold electron emission¹³ promising for cold-cathode technology but the reason for the effect has not been discovered yet. All attempts to achieve efficient n -type doping of diamond have met with limited success and a convincing proof of true n -type conductivity does not yet exist.¹⁴ The electrical properties of CVD diamond films depend largely on grain boundaries and the mobility of carriers can be significantly reduced when the films are not highly oriented.¹⁵

The superficial excellence of diamond is also somewhat lost even in the case of boron doping. It is a shallow diamond acceptor with a level 0.37 eV above the valence band²⁻⁴ but ionization of this level requires a temperature at which the electron mobility is greatly reduced.¹

The doping problem in amorphous carbon *a*-C is exacerbated by the fact that, not only can impurities like N relax off a substitutional site by breaking the bond to one of the carbon neighbors, but also it is possible that they induce significant rearrangements in the carbon network. An injected hole or electron can be trapped at defects or migrates in *a*-C to occupied high energy π or unoccupied low energy π^* states, respectively. The associated carbon π cluster undergoes substantial relaxation to screen the additional charge.^{7,16} Conductivity then occurs through variable range hopping between such clusters. *I*-*V* curve measurements of diode devices¹⁵ made with B, N, and P doped *a*-C confirm this view and do not show any characteristics indicative of a true *p*-*n* junction. Both B and N doping was found to only increase the density of states near the midgap Fermi level and in the band tails.

At higher nitrogen content amorphous carbon nitride films can be synthesized. However, this material becomes increasingly paracyanogenlike with the doping concentration. N catalyzes low carbon coordination numbers and the network loses much of its connectivity. Though large gaps exist in these structures there is no sign of distinct levels close to the band tails which can be identified as donor states.¹⁷

It is the aim of this paper to develop principles that make *n*-type doping in a carbon based material most likely. Therefore, we approach the doping problem from a different point of view. Instead of searching for a possible element or atom complex that acts as a dopant in known carbon allotropes we have been looking for a suitable crystalline host for the nitrogen donor.

We show that *n*-type doping by substitutional nitrogen is possible in hypothetical, purely sp^2 bonded, carbon materials. We report on the local geometries in such carbon phases and obtain conditions that stabilize N in the C network and result in a shallow donor level. The carbon structures contain 8-membered rings, joined to form three-dimensionally connected networks. The topology of such networks has been discussed by Wells.¹⁸ We show that carbon decoration results in metastable allotropes comparable in energy with the previously predicted phase BCT4 (Ref. 19) and fullerene C₆₀. We expect the proposed structures to be thermodynamically very stable, since a transition to diamond or graphite requires a large number of bonds to break and rearrange. The allotropes do not permit a reorganization of the carbon neighborhood after boron or nitrogen are substituted on lattice sites. Relaxation effects are extremely small and injected holes or electrons are localized near these substitutional sites and associated with half-filled electronic levels close to either the valence or conduction bands.

The two hypothetical carbon phases are presented in two viewing directions in Fig. 1. The space group of the network shown in Figs. 1(a) and 1(b) has been identified by Wells¹⁸ to be rhombohedral [$R\bar{3}m$ (No. 166)]. The idealized structure has equal bond lengths and angles as in graphite. Atoms are located in 6*f* positions of the rhombohedral cell with the internal variable $x = \frac{2}{3}$. Under relaxation the lattice is slightly

FIG. 1. Perspective views of the relaxed purely sp^2 bonded structures R6 (a,b) and BCT8 (c,d) showing the 8-membered rings (a,c), the channels (b,d), and the three-dimensional network character.

distorted and becomes monoclinic [$P112/m$ (No. 10)]. We will nevertheless call this carbon allotrope R6. It consists of 8-membered rings in the chair conformation connected to form the faces of adjacent channels bounded by 12-membered rings, as shown in Fig. 1(b).

The structure of Figs. 1(c) and 1(d), which we name BCT8 has a body-centered tetragonal symmetry [$I41md$ (No. 109)]. The atoms are arranged in 16*c* positions of the conventional unit cell with the parameters $x = \frac{1}{4}, y = \frac{3}{8}, z = 0$. In the tetragonal body centered unit cell the number of inequivalent atoms reduces to 8. For the idealized topology the lattice vectors are related to the common bond length by $a = b = 4d$ and $c = \sqrt{8}d$. The structure results from connecting boat-shaped 8-membered rings by creating 10-membered rings, see Fig. 1(d), and avoiding the formation of smaller ones. Allowing 6-membered rings to occur gives rise to a simple cubic lattice known as polybenzene,²⁰ denoted in the following by SC24 [$Pn\bar{3}m$ (No. 224), 24*i* atoms with $x = \frac{1}{3}$]. The latter two models retained their symmetries during relaxation.

SC24 belongs to a class of hypothetical three-coordinated structures known as negatively curved periodic surfaces.²⁰⁻²³ They contain bent graphitic sheets and are not expected to have properties as exceptional as those of diamond. The electron system is delocalized giving only rise to small band gaps. The structures are found to be either metallic or with the exception of SC24 have a gap width well below that of silicon.²⁴ These structures would not compete with existing silicon technology with respect to device applications.

To check the stability of the corresponding carbon models, we explored the potential energy surface with respect to variations of the lattice shape. We started from the idealized structures with equal bond lengths and angles and allowed them to relax in order to find the ground state predicted by the density-functional based nonorthogonal tight-binding (DF-TB) energy functional.^{25,26} In this technique the total energy of a crystal is approximated by a usual tight-binding

TABLE I. DF-TB ground-state properties of hypothetical model structures compared with the results for natural carbon allotropes.

Structure	Density (g/cm ³)	Atomic Volume (Å ³ /atom)	Bulk Modulus (GPa)	Total Energy E-E _{Graphite} (eV/atom)
Diamond	3.51	5.68	491	0.01
Graphite	2.27	8.77	6	0.00
C ₆₀				0.42
BCT8	2.35	8.49	333	0.53
R6	2.26	8.82	276	0.55
SC24	2.14	9.32	325	0.23

expression. The Hamiltonian and overlap matrix elements are explicitly calculated employing the two-center approximation within a minimal basis of localized contracted orbitals. The many-body Schrödinger equation is solved by diagonalization and the Brillouin zone is integrated employing Γ -point sampling through the conventional large unit cell approach. The DF-TB method has been shown to agree with more sophisticated self-consistent field methods considering the energetics and ground-state geometries of small carbon clusters,²⁵ fullerenes,²⁷ diamond surfaces,^{28,29} impurities in carbon materials,⁷ and amorphous carbon phases.³⁰

Structural relaxation was undertaken using a conjugate gradient algorithm, taking care to vary lattice vectors independently in order to avoid artificial symmetry constraints. Finally, the vibrational densities of states have been calculated for the ground-state models to guarantee that negative or zero phonon modes indicative of a saddle-point structure are absent. The carbon allotropes were then substitutionally doped with one boron or one nitrogen atom and were relaxed again leaving the lattice vectors fixed at the carbon bulk values. The resultant dopant concentration was 0.3 at. %.

The static properties of the relaxed ground state models are summarized in Table I, together with structural details of polybenzene and the natural carbon allotropes. Our results for polybenzene agree very well with those previously reported.²⁰ The total energies of diamond and C₆₀ with respect to graphite are well described by the DF-TB method, the experimental values being 0.025 eV/atom for diamond³¹ and 0.441 eV/atom in the case of fullerene.³²

To further test the accuracy of the DF-TB scheme for the application to crystal structures, we examined the predicted metallic BCT4 (Ref. 19) and H6 (Ref. 33) phases. We find them to be 0.50 and 0.76 eV/atom less stable than graphite, respectively. This compares to 0.52 and 0.82 eV/atom obtained recently with an accurate *ab initio* plane wave local-density approximation self-consistent field calculation.³⁴ The densities and atomic volumes of these hypothetical structures are found to be 2.90 g/cm³ and 6.81 Å³ for BCT4 and 3.18 g/cm³ and 6.27 Å³ for H6. This coincides very well with the appropriate SCF results of 2.94 g/cm³ and 6.79 Å³ for BCT4 and 3.18 g/cm³ and 6.26 Å³ for H6. The lattice parameters, bond lengths, and bond angles are equally well described as will be reported elsewhere.³⁵

R6 and BCT8 both contain screw axes. The projection of the screw axis channel onto a perpendicular plane is a square for BCT8 whereas it is a triangle for R6 [see Figs. 1(b) and 1(c)]. These channels are interconnected by bonds between

sp^2 atoms along which there is optimal overlap of π orbitals. Such bonds are strengthened and shortened. Double bonds with the typical length of about 1.34 Å are established. The bonds within the helices have a pronounced single-bond character, since the dihedral angles between them prevent strong π -orbital overlap. These bonds are therefore longer and have typical σ -bond lengths of 1.50 Å. For comparison, the ideal bond length for the diamond lattice is calculated to be 1.55 Å within the DF-TB method. The two distinct bond lengths introduce significant stresses into the crystals. Accompanying bond angles can no longer be equal and differ markedly from the graphite value. One-third of the angles are lower than 120° (117.2° in R6 and 115.6° in BCT8) and two-thirds are larger (121.4° in R6 and 122.2° in BCT8). The strain energy is balanced by the energy gain due to the π -bonded atom pairs. As a result, R6 and BCT8 are about 0.5 eV/atom less stable than graphite.

SC24 is more stable than the models proposed here, since the bond angles in this structure can stay at their ideal values during the relaxation of π bonds in the 6-membered rings. However, the total energy per atom of the predicted allotropes is comparable to fullerene C₆₀ and well below that of the lowest energy forms of amorphous carbon, which have been determined by the DF-TB method to be about 0.7–0.8 eV/atom above graphite.³⁰ We therefore believe that R6 and BCT8 may be synthesized.

A chemical way of producing the proposed allotropes may be by polymerization of isonitriles which spontaneously form helical isomers. Starting from such isomers with an appropriate C:N ratio for doping, motifs such as the helical units observed in the allotropes might be nucleated and subsequently cross linked by annealing or suitable catalysts.

The bulk moduli of SC24, BCT8, and R6 are determined to be about 65% that of diamond. Hence, the structures are quite hard and promising for mechanical applications. The bulk modulus was estimated via calculation of elastic constants by applying suitable strains (see Ref. 36).

The structures contain isolated, well relaxed, π bonds within a σ -bonded frame. Hence, the structures develop pronounced gaps due to the π - π^* splitting of states, a phenomenon which also occurs in ethylene. The gap values are summarized in Table II for the minimal basis sets used to relax the structures as well as extended basis sets which include d -type orbitals and are optimized to reproduce the diamond and graphite conduction band structures up to 15 eV above the Fermi level. Note, that the band gaps found are twice as large as is typical for either silicon, germanium, or gallium arsenide.

Most remarkably, R6 and BCT8 can take up boron and nitrogen at substitutional lattice sites without the strong relaxation typical for diamond and amorphous carbon. Boron and nitrogen atoms are naturally incorporated in their preferred three-fold coordination. The local geometry forces N to take part in two single and one isolated double bond associated with each site. Hence, relaxation is weak and both B and N stay at the lattice site. The highest molecular orbital (HOMO) is occupied by just one electron and acts as a donor and acceptor, respectively. The ionization energies determined within DF-TB are given in Table II. Though there are small contributions to the HOMO from almost all atomic orbitals (AO's) the strongest are detected near the substitu-

TABLE II. Electronic properties of the hypothetical structures compared with diamond. *sp* indicates minimal, *spd* extended basis set, see text. B-C and N-C marks the HOMO participation of the atomic orbitals at the impurity and the nearest carbon neighbors.

Structure	Gap width (eV)		B acceptor level (eV)		N donor level (eV)		AO contribution to HOMO	
	<i>sp</i>	<i>spd</i>	<i>sp</i>	<i>spd</i>	<i>sp</i>	<i>spd</i>	B-C	N-C
Diamond	7.75	6.49	0.09	0.09	4.61	3.28	0.03	0.50
BCT8	2.99	2.72	0.17	0.20	0.32	0.09	0.07	0.25
R6	3.37	2.79	0.37	0.24	0.19	0.03	0.48	0.17
SC24	3.65	3.45	0.03	0.01	0.04	0.02	0.01	0.04

tional atom and its nearest neighbors within a Mulliken participation analysis (see Table II).

Amorphous carbon consists of a mixture of sp^3 - and sp^2 -bonded carbon atoms and can also develop pronounced band gaps up to 3 eV. However, the size distribution of π -bonded clusters frequently formed in *a*-C (Ref. 30) and the associated strain in the systems yield broad bond length distributions.³⁷ The π and π^* bands are broadened and the tails of the bands overlap with the acceptor and donor levels. Electrons are then trapped from the highest-energy carbon π levels or injected into defect states or lowest-energy π^* bands, respectively. This is accompanied by relaxation processes in the carbon network in order to saturate carbon defect states which are always present in amorphous carbon. Doping is very inefficient and cannot be controlled, in stark contrast to the situation in the proposed network models, where the injected hole or electron cannot spontaneously migrate to another π bond in the neighborhood.

We checked the DF-TB doping results using a reliable self-consistent-field cluster method.³⁸ This calculation supports our basic findings that levels occupied by the injected hole or electron are indeed shallow and close to the respec-

tive valence or conduction band edges. The dopants do not relax off the substitutional lattice site.

We have demonstrated shallow level *n*-type doping by nitrogen in carbon based materials. The structures where this works, however, are purely sp^2 bonded carbon allotropes characterized by screw axes of single bonded atoms, held together by isolated double bonds. This particular geometry gives rise to wide band gaps and provides an ideal host for both nitrogen and boron. The metastable carbon systems are predicted to have a density close to graphite and a bulk modulus of about 65% that of diamond. This makes them attractive for electronic, mechanical, and optical applications. The multichannel architecture of the new phases probably causes anisotropic transport effects on a microscopic level. The recent success in producing forms of carbon by fragmentation from organic compounds³⁹ and catalytic acetylene pyrolysis⁴⁰ makes us confident that structures as discussed here may be synthesized.

We gratefully acknowledge support from the Deutsche Forschungsgemeinschaft and the Engineering and Physical Science Research Council of the United Kingdom.

¹A. T. Collins, Mater. Sci. Eng. B **11**, 257 (1992).

²*Semiconductors: Group IV Elements and III-V Compounds*, edited by O. Madelung (Springer, Berlin, 1991).

³S. J. Breuer and P. R. Briddon, Phys. Rev. B **49**, 10 332 (1994).

⁴S. A. Kajihara, A. Antonelli, J. Bernholc, and R. Car, Phys. Rev. Lett. **66**, 2010 (1991).

⁵C. Cunha, S. Canuto, and A. Fazzio, Phys. Rev. B **48**, 17 806 (1993).

⁶S. J. Breuer and P. R. Briddon, Phys. Rev. B **53**, 7819 (1996); P. R. Briddon and R. Jones, Physica B **185**, 179 (1993).

⁷P. K. Sitch, Th. Köhler, G. Jungnickel, D. Porezag, and Th. Frauenheim, Solid State Commun. **100**, 549 (1996).

⁸A. Mainwood, Phys. Rev. B **49**, 7934 (1994).

⁹J. F. Prins, Diamond Relat. Mater. **4**, 580 (1995).

¹⁰H. Spicka, M. Griesser, H. Hutter, M. Grasserbauer, S. Bohr, R. Haubner, and B. Lux, Diamond Relat. Mater. **5**, 383 (1996).

¹¹R. Jones, J. E. Lowther, and J. Goss, Appl. Phys. Lett. **69**, 2489 (1996).

¹²S. Prawer, Diamond Relat. Mater. **4**, 684 (1995).

¹³K. Okano, S. Koizumi, S. R. P. Silva, and G. A. J. Amaratunga, Nature (London) **381**, 140 (1996).

¹⁴H. Hofsäss, M. Dalmer, M. Restle, and C. Ronning, J. Appl. Phys. **81**, 2566 (1997).

¹⁵C. Ronning, U. Griesmeier, M. Gross, H. Hofsäss, R. G. Downing, and G. P. Lamaze, Diamond Relat. Mater. **4**, 666 (1995).

¹⁶P. Stumm and D. A. Drabold, Solid State Commun. **93**, 617 (1995).

¹⁷F. Weich, J. Widany, and Th. Frauenheim, Phys. Rev. Lett. **78**, 3326 (1997).

¹⁸A. F. Wells, *Three-dimensional Nets and Polyhedra* (Wiley & Sons, New York, 1977).

¹⁹R. Hoffman, T. Hughbanks, M. Kertesz, and P. H. Bird, J. Am. Chem. Soc. **105**, 4831 (1983).

²⁰M. O'Keeffe, G. B. Adams, and O. F. Sankey, Phys. Rev. Lett. **68**, 2325 (1992).

²¹D. Vanderbilt and J. Tersoff, Phys. Rev. Lett. **68**, 511 (1992).

²²J. Townsend, T. J. Lenosky, D. A. Muller, C. S. Nichols, and V. Elser, Phys. Rev. Lett. **69**, 921 (1992).

²³H. Terrones, J. Fayos, and J. L. Aragon, Acta Metall. Mater. **42**, 2687 (1994).

²⁴M.-Z. Huang, W. Y. Ching, and T. J. Lenosky, Phys. Rev. B **47**, 1593 (1993).

²⁵D. Porezag, Th. Frauenheim, Th. Köhler, G. Seifert, and R. Kaschner, Phys. Rev. B **51**, 12 947 (1995).

²⁶G. Seifert, D. Porezag, and Th. Frauenheim, Int. J. Quantum Chem. **98**, 185 (1996).

- ²⁷G. Jungnickel, D. Porezag, Th. Köhler, Th. Frauenheim, and M. R. Pederson, in *Fullerenes and Fullerene Nanostructures*, edited by H. Kuzmany, J. Fink, M. Mehring, and S. Roth (World Scientific, Singapore, 1996).
- ²⁸Th. Köhler, M. Sternberg, D. Porezag, and Th. Frauenheim, *Phys. Status Solidi A* **154**, 69 (1996).
- ²⁹G. Jungnickel, D. Porezag, Th. Frauenheim, M. I. Heggie, W. R. L. Lambrecht, B. Segall, and J. C. Angus, *Phys. Status Solidi A* **154**, 109 (1996).
- ³⁰Th. Frauenheim, C. Jungnickel, Th. Köhler, and U. Stephan, *J. Non-Cryst. Solids* **182**, 186 (1995), and references therein.
- ³¹M. T. Yin and M. L. Cohen, *Phys. Rev. B* **29**, 6996 (1984).
- ³²H.-D. Beckhaus, S. Verevkin, C. Ruchardt, F. Diederich, C. Thilgen, H.-U. ter Meer, H. Mohn, and W. Müller, *Angew. Chem. Int. Ed. Engl.* **33**, 996 (1994).
- ³³M. A. Tamor and K. C. Hass, *J. Mater. Res.* **5**, 2273 (1990).
- ³⁴A. Y. Liu (private communication).
- ³⁵G. Jungnickel, P. K. Sitch, Th. Frauenheim, B. R. Eggen, M. I. Heggie, C. D. Latham, and C. S. G. Cousins (unpublished).
- ³⁶J. F. Nye, *Physical Properties of Crystals* (Clarendon, Oxford, 1985).
- ³⁷G. Jungnickel, Th. Köhler, M. Haase, S. Deutschmann, U. Stephan, P. Blaudeck, and Th. Frauenheim, *J. Non-Cryst. Solids* **183**, 161 (1995).
- ³⁸R. Jones, *J. Phys. C* **21**, 5735 (1988).
- ³⁹S. Hill, *New Sci.* **153**, 14 (1997).
- ⁴⁰M. Terrones, W. K. Hsu, J. P. Hare, H. W. Kroto, H. Terrones, and D. R. M. Walton, *Philos. Trans. R. Soc. London, Ser. A* **354**, 2025 (1996).