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STRUCTURAL AND ELECTRONIC PROPERTIES OF NITROGEN DOPED FOURFOLD AMORPHOUS CARBON

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We use first principles methods to investigate the effects of nitrogen incorporation in fourfold amorphous carbon. Nitrogen concentrations between 1.5% and 10% are examined and the dopant effects on coordination, band structure and vibrational modes are discussed. We find that nitrogen substitution leads to small relaxations, and that nitrogen atoms cluster in order to preserve a state free gap as seen in experiments.

Keywords: A. disordered systems, C. Impurities in semiconductors, D. electronic states (localized).

1. INTRODUCTION

QUATERNARY coordinated amorphous carbon (ta-C) thin films were first grown by McKenzie and coworkers in 1991 [1]. Density, hardness and electrical resistivity are comparable to that of natural diamond. Analysis of the radial distribution function obtained from neutron-scattering experiments results in an estimated bond length of 1.53 Å and a bond angle of 110° [2]. Bond length, bond angle and the coordination number of 3.7 are consistent with the estimated value of about 86% sp^3 hybridization in ta-C. Intrinsic ta-C is a semiconductor with a band gap of about 2 eV. Undoped ta-C films show *p*-type behavior, the Fermi level lies about 0.2 eV above the valence band. The potential usefulness of ta-C for electronic applications has already been demonstrated by using it to build some simple devices including a heterojunction diode and a transistor [3].

Recent experiments by Veerasamy *et al.* show that ta-C can be controllably *n*-type doped with nitrogen and phosphorus, with doping concentrations varying between 0.15% and 10% [4, 5]. An increase in the disorder of the material is observed with increasing N content. The transition to a predominantly trigonal C-N alloy is reported for dopant levels between 5% and 10%. A doping concentration of up to 10% reduces the bandgap from 2.1 to 1.5 eV. For low

doping levels (up to 1%) the dominantly tetrahedral structure of ta-C is not substantially altered and the band gap remains nearly constant. Although a controllable change in conductivity was achieved, the exact doping and conduction mechanisms are still obscure.

In this paper we will focus on examining the structural and electronic properties of ta-C with nitrogen incorporation. Structural relaxation effects and electronic properties will be reported at different dopant concentrations.

2. ELECTRONIC-STRUCTURE METHOD

The calculations described here use an approximate first-principles electronic-structure method which was introduced by Sankey and coworkers in 1989 [6, 7]. It is based on density-functional theory within the local-density approximation and the nonlocal pseudopotential scheme. The basis functions are four pseudoatomic orbitals per site with a confinement [6] range of $r_C = 4.1a_B$ and $r_C = 3.75a_B$ for carbon and nitrogen, respectively. This method was first applied to crystalline phases of silicon and was later extended to describe alloys and covalent carbon structures [7] in a very wide range of bonding environments. The phase diagram for several existing and hypothetical carbon structures was computed and compared to self-consistent LDA calculations

[8]. Excellent transferability was found, even for the cubic phases.

To test the method's suitability for the C–N system, a 64-atom diamond supercell was analysed for structural changes and creation of defect states. Exchanging one C atom by a N atom and relaxing the network results in an asymmetric relaxation of the network. The N atom is three-fold coordinated, a former nearest neighbor atom relaxes to a distance of 1.98 Å. A deep state is created with an energy pinning the Fermi level, which is 2.54 eV below the conduction band edge. These results are in excellent agreement with those of references [9], who used a self-consistent plane wave (Carr–Parrinello) method. They also find isolated N to be a deep trap (with a similar location relative to the band edges) and report the same structural rearrangement. Like other LDA-based methods, the present scheme has difficulty in predicting optical gaps. Typically, LDA calculations underestimate the gap. In the present scheme, the gap tends to be somewhat too *large*, because of the sp^3 basis set employed. Trends in the gap can be taken as reasonable, but as usual, care should be used in the interpretation. See also [6].

3. EFFECTS OF INTRODUCING N INTO ta-C MODEL

A theoretical study of nitrogen doping of ta-C for dopant levels of 1.56 to 9.38% has been performed. The goal of this study is to identify the structural, electronic and vibrational consequences of N incorporation in a variety of possible locations in the ta-C:N network. The 64 atom ta-C cell as described by Drabold *et al.* in 1994 [10] was used.

This cell contains six three-fold coordinated atoms which occur in π -bonded nearest neighbor pairs. The bandgap is about 2.3 eV, in good agreement with experiment. The electronic density of states (DOS) for this structure is given in [10]. To measure the degree of localization on individual eigenstates a Mulliken charge $q(n, E)$ is computed from the one electron orbitals, and is associated with an energy eigenvalue E and an atomic site n [11]. Several different electronic states are found to be localized near the bandgap. The defects responsible for the localization are strained bonds in the valence band, π -bonded atoms and strained bonds in the conduction band.

The vibrational density of states for this cell is given in [10]. It does not show the two distinct peaks that are present in amorphous silicon [11], probably because there are more sp^2 bonded atoms in ta-C and in general the disorder is greater. Modes with a

frequency higher than 1270 cm^{-1} are localized on atom sites with strained bonds or on π -bonded atom pairs.

Because of the small size of the supercell, only dopant concentrations that are multiples of 1/64 are possible, which means that the lowest dopant concentration achievable is 1.56%. In this paper dopant levels of 1.56, 3.13, 4.69 and 9.38% were investigated. Nitrogen was substituted into diamond-like sites, stretched or strained bond sites and π -bonded pair sites. Then a steepest descent quench was performed to relax the network. These quenches used four special k -points in the Brillouin zone to calculate energies and forces [12]. The resulting structures were analyzed for changes in the distribution of bond lengths and angles, increasing disorder, creation of new defects, and localized states and changes in the band gap.

3.1. Single nitrogen substitution

3.1.1. Steepest descent quenches. Substitution of a N atom in a diamondlike site yields two dangling bond defects which are created from a stretched bond defect, neighboring the N atom. Otherwise, no significant structural rearrangement takes place. A midgap state is created which pins the Fermi level. This eigenvalue is most prominently localized on the dangling bond site neighboring the nitrogen atom, but above average localization is also present on another π -bonded site.

Substituting the N atom in a stretched or strained bond site [10] leads to very similar results, though these defects are located at different places in the network. The structural changes in the network are also quite similar. The initially four-fold coordinated N becomes three-fold coordinated, and the average nearest neighbor distance between the N and C atoms is slightly reduced. In both cases the same three-fold defects are created. One is a dangling bond, one combines with an already existing π -bonded pair to form a triplet, and four atoms build new π -bonded pairs. These defects occur along a chain of atoms that is located in the same part of the network as the N. The clean gap of the undoped material is now disturbed by a highly localized spectral defect state associated with the dangling bond site, which pins the Fermi energy. The only difference between the stretched and strained bond N site is that for the strained site, the bandtail states, which are made up of the paired π -defects, are pushed further into the gap, while the gap edges remain constant for the stretched defect site.

Replacing the carbon by a N atom in a three-fold coordinated paired defect site creates the same

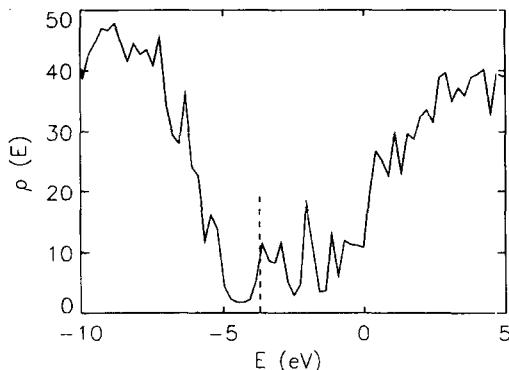


Fig. 1. Electronic DOS for the annealed cell with a dopant concentration of 1.5% for states near the gap. The Fermi level is indicated by the dashed line.

structural defects as when the N is incorporated in the above mentioned stretched and strained bond sites, even though the N is now placed in a different part of the supercell. Again a midgap state is created pinning the Fermi level, which is highly localized only for the dangling bond site.

3.1.2. Simulated annealing study. In order to let the nitrogen explore a wider variety of configurations and to confirm the above results of the steepest descent quenches, a simulated annealing study was performed. For this molecular dynamics simulation the carbon network was heated to 6000 K for 300 time steps, using Γ point sampling, then cooled to a target temperature of 600 K [13]. Finally, a steepest descent quench was done, using now four k -points. The total annealing time is 3.5 ps. This anneal results in the lowest-energy structure found for a doping level of 1.5%. The structure contains twelve three-fold coordinated atoms, of which 50% occur as π pair defects, the others are isolated dangling bonds. The final N site is three-fold coordinated and is not paired to another three-fold coordinated atom. The number of slightly stretched bonds increases, while the number of strained bonds is reduced, as compared to the undoped structure. The electronic DOS for the annealed network is shown in Fig. 1. Three eigenvalues are located in the upper part of the bandgap, which show an above average localization, and are clearly associated with the dangling bond defects. Also, the lowest eigenstate in the conduction band is now pinning the Fermi level, leaving a state-free bandgap of 1.4 eV.

3.1.3. Vibrational spectrum. The vibrational spectrum for this structure is reproduced in Fig. 2. All modes above a frequency of 1280 cm^{-1} are

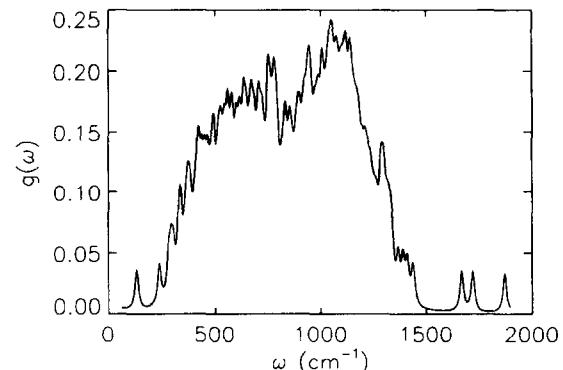


Fig. 2. Vibrational power spectrum for the annealed cell with a dopant concentration of 1.5%. Modes with frequencies higher than about 1280 cm^{-1} show strong localization.

localized on geometrical irregularities in the network. At the lower frequencies these are atom sites with strained or dangling bonds, these modes are located at the higher frequency end of the spectrum. The π -bonded atom pairs exhibit localization in the high frequency tail. No vibrational localization is associated with the nitrogen site. There are no very distinctive features in the spectrum due to nitrogen in these studies which would allow the vibrational spectra to characterize nitrogen content.

3.2. 3.1% N doping

Incorporating two N atoms into the ta-C network corresponds to a doping concentration of 3.1%. Two special cases of N coordination were investigated. First the N atoms were placed in two well separated diamondlike sites. The same defects are created as for the 1.5% doping of the diamondlike site, even though the doping concentration and location of the N atoms in the network are different. The DOS for this structure has bandtail states that extend further into the gap than those of undoped ta-C and are substantially localized on a number of π -bonded pair defects and dangling bond defects. This leaves a clean state-free gap of 1.56 eV, which contains the Fermi level.

The second quench was performed with two N atoms placed in a neighbouring π pair bonded defect. This N configuration is more stable than inclusion in diamondlike sites. The binding energy is increased by $0.023\text{ eV atom}^{-1}$, which suggests that the clustering of N atoms is weakly energetically favorable. *No three-fold coordinated atoms and no states in the bandgap are created.* This π -pair and nearest neighbors are shown in Fig. 3 before and after relaxation. Initially the π -pair and its nearest

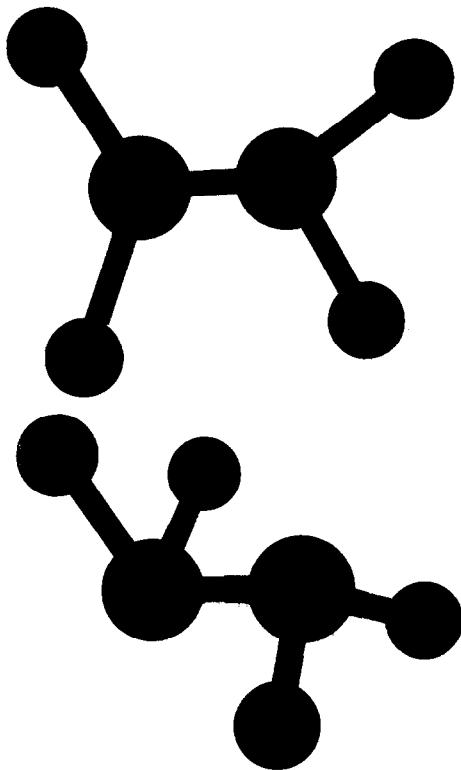


Fig. 3. Sketches of the π -bond defect described in the text. (a) the C π -pair has a planar graphitic like structure, (b) the bond length of the relaxed N π -pair (1.54 \AA) is consistent with a single bond, the planarity of the structure is destroyed.

neighbors form a planar graphitic like structure, while the relaxed configuration is similar to a hydrazine molecule. The N-N bond length increases by 0.2 \AA (15%) and the nearest neighbor distance to carbon atoms increases by 6%.

The DOS for this structure is shown in Fig. 4. Both the DOS and the amount of localization on different sites are very similar to those of the undoped ta-C network. The bandgap is slightly reduced to 2.0 eV as states at the gap edges are moved slightly into the gap. The Fermi level is located 0.8 eV above the valence band. This is the only structure containing nitrogen for which the density of states remains similar to that of the undoped network, again confirming that *N clustering is likely in the real material*.

3.2.1. Vibrational spectrum. The vibrational spectrum for this structure is shown in Fig. 5. The spectrum is very similar to the one of the undoped network, except for one difference. The mode with the highest frequency (1970 cm^{-1}) that exhibits vibrational localization on a π -bonded pair for the

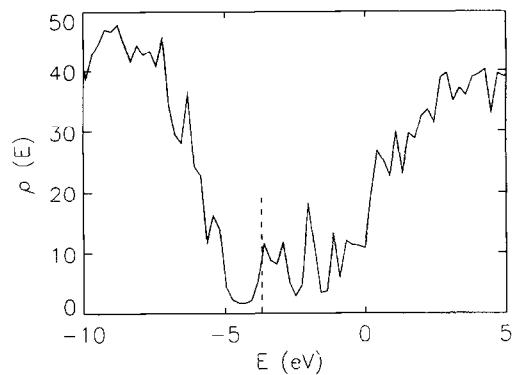


Fig. 4. Electronic DOS for the cell with N substituted in π -bonded pair for states near the gap. The Fermi level is indicated by the dashed line.

undoped network, is no longer present after this π -bonded carbon pair is replaced by N.

3.3. Higher concentrations

Substituting three four-fold coordinated carbon atoms with nitrogen again creates the same defects as in the case of the doping of diamond-like sites at lower doping concentrations. There are minor rearrangements around the nitrogen atoms, and none of them are close to the dangling bond defects. Several states are created in the bandgap, which are highly localized.

A dopant concentration of 9.5% results in a structure that contains about 22% three-fold coordinated atoms. About 75% of these newly created defects occur in π -bonded pairs or form triplets with already existing π -pairs, two are dangling bond defects. All are located in a part of the supercell that initially contains many stretched and strained bonds. Rearrangement of the atoms takes place in such a way, that there are less strained and stretched bond defects in the final network. Several localized states are created in the bandgap that are located

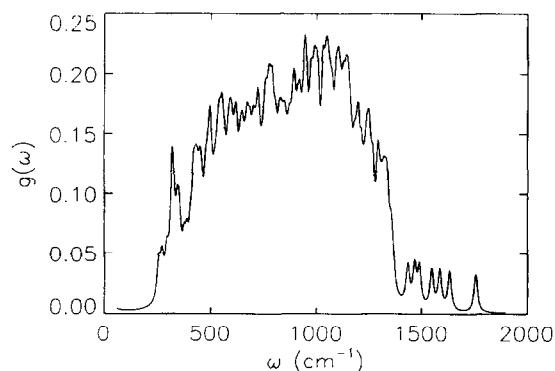


Fig. 5. Vibrational power spectrum for cell with N substituted in π -paired defect.

close to the valence band. The energy gap for this structure is about 1.9 eV.

4. DISCUSSION

(1) No significant relaxation of the network takes place around substitutional nitrogen atoms. There is no localization on eigenstates around the gap associated with the nitrogen site, unless it is three-fold coordinated. In this case the amount of localization is comparable to that of other three-fold coordinated (carbon) sites.

(2) For the quenches, either two or six threefold coordinated states are created. These are located in parts of the network that were initially characterized by a high degree of strain, independent of where the nitrogen is incorporated. They occur in nearest neighbor pairs or triplets and the average bond length between these pairs of defects is notably lower than the average bond length in the network, 1.35 Å as compared to 1.53 Å. This suggests that the nitrogen induces disorder in the network, but locally adapts to the bonding environment of the carbon atom it is substituting. To some extent these results also reflect the metastability of the a-C network.

(3) For all calculations introducing nitrogen there is a reduction in the bandgap. This reduction ranges from small additional bandtailing into the gap, to the creation of several midgap states spread throughout the gap. The valence and conduction bandtail states as well as midgap states arise from three-fold coordinated atoms, which can be paired defects or dangling bonds. The amount of localization of dangling bonds is usually higher than that of paired defects. Above average localization of strained and stretched bonds usually occurs for eigenvalues between the bandtail states created by three-fold coordinated atoms and the valence/conduction band. All different kinds of defects are localized on states in the valence and/or conduction band, but three-fold coordinated defects tend to be more often localized as midgap states or in the conduction band. Stretched or strained bond defects occur hardly at all as localized midgap states.

(4) The clustering of nitrogen atoms in π -bonded atom sites is energetically favored over substitution into a diamond-like environment. Furthermore, clustering is the only incorporation of nitrogen that does not result in additional gap states.

(5) The vibrational spectra of the ta-C:N structures do not seem useful to indicate the presence of N itself. Rather, defects created by nitrogen incorporation will lead to well localized modes. States that are localized on specific atoms in the undoped structure will no longer be localized if these atoms are substituted by nitrogen, even if no structural rearrangement takes place. Observations (1)-(3) are quite consistent with the experimental work of Veerasamy *et al.* [4, 5]. Point (4) provides strong evidence that nitrogen clusters exist in the doped material.

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REFERENCES

1. D.R. McKenzie, D.A. Muller & B.A. Pailthorpe, *Phys. Rev. Lett.* **67**, 773 (1991).
2. P.A. Gaskell, A. Saeed, P. Chieux & D.R. McKenzie, *Phys. Rev. Lett.* **67**, 1286 (1991).
3. D.R. McKenzie *et al.*, *Diamond and Related Materials* **51** (1991).
4. V.S. Veerasamy *et al.*, *Phys. Rev.* **B48**, 17954 (1994).
5. V.S. Veerasamy, G.A.J. Amaralunga, C.A. Davis, A.E. Timbs, W.I. Milne & D.R. McKenzie, *J. Phys. Condens. Matter* **5**, L169 (1993).
6. O.F. Sankey & D.J. Niklewski, *Phys. Rev.* **B40**, 3979 (1989).
7. O.F. Sankey, D.A. Drabold & G.B. Adams, *Bull. Am. Phys. Soc.* **36**, 924 (1991).
8. S. Fahy & S.G. Louie, *Phys. Rev.* **B36**, 3373 (1987).
9. S.A. Kajihara, A. Antonelli, J. Bernholc & R. Car, *Phys. Rev. Lett.* **66**, 2010 (1991).
10. D.A. Drabold, P.A. Fedders & P. Stumm, *Phys. Rev.* **B49**, 16415 (1994); D.A. Drabold, P. Stumm & P.A. Fedders, *Phys. Rev. Lett.* **72**, 2666 (1994).
11. P.A. Fedders, D.A. Drabold & S. Klemm, *Phys. Rev.* **B45**, 4048 (1991).
12. H.J. Monkhorst & J.D. Pack, *Phys. Rev.* **B13**, 5188 (1976).
13. H.J.C. Berendsen, *J. Chem. Phys.* **81**, 3684 (1984).