Defects, doping, and conduction mechanisms in nitrogen-doped tetrahedral amorphous carbon

P. Stumm[a] and D. A. Drabold
Department of Physics and Astronomy and Condensed Matter and Surface Sciences Program, Ohio University, Athens, Ohio 45701-2979

P. A. Fedders
Department of Physics, Washington University, St. Louis, Missouri 63130

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First principles methods are used to study N doping of diamondlike amorphous carbon. A structural model containing 216 atoms is introduced, whose properties are in agreement with the available experimental data. The topological and electronic properties for different N doping concentrations are investigated. We find that N occurring in tetrahedral sites or chains of an even number of π bonded sites results in an increase of the Fermi energy, while N incorporation in strained network sites induces structural changes that lead to an increase in the sp^2 fraction of the material. The prevalent conduction mechanisms are identified and discussed. While the Fermi energy increases upon N doping, the localization of the conduction-band-tail states limits extended state conduction. These results are compared to the recent experimental reports on N doping of ta-C and we find that the nondoping threefold N incorporation (N_3^0) is energetically most likely, which explains the low doping efficiency seen in experiments.
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I. INTRODUCTION

Tetrahedral amorphous carbon films (ta-C) have recently received widespread interest due to their promising electronic properties.[1,2] Depending on the deposition process the sp^3 content approaches 90% for a virtually hydrogen-free material.[3,4] Undoped ta-C is a wide-band-gap semiconductor ($E_g=2$ eV) that shows intrinsic p-type behavior; the Fermi level is ~0.2 eV above the valence-band edge.

Recently[5] the spin density of ta-C was measured as a function of sp^3 content and was found to be roughly constant at a value of 8×10^{18} cm^{-3} for sp^3 fractions larger than 60%. If all of the 10%–20% sp^2 hybridized C atoms were randomly distributed in the material the spin density would be of the order of 10^{21} cm^{-3}; therefore, a very large percentage of all sp^2 atoms is paired up in order to not give a spin signal, as was already suggested in earlier theoretical work.[6]

Numerous experiments have been performed on doping ta-C with N.[5,7–12] The only major theoretical discussion on doping that has been forthcoming is from Robertson and Davis,[13] who compare N doping of ta-C to the diamond case, where N doping leads to a deep gap state. Robertson argues that since for ta-C the gap is substantially smaller due to the π and π^* band tails, the gap state is now shallow with respect to the conduction-band edge.

In this article we find that the simple view of substitutional doping is essentially true, for those bonding environments where it occurs. That is, we find that if N is incorporated into the network at diamondlike sites (meaning sites with four neighbors and bond angles within 10° of the tetrahedral angle), slightly disordered fourfold sites, or chains of an even number of sp^2 sites (where the topology is locally graphitelike), then the Fermi level moves higher, and the N can be viewed as in effective mass theory. That is, a N atom is substituted for a C atom and the N atom contributes an extra electron. This is exactly what happens in c-diamond if no relaxation of the N is allowed. However, in an isolated threefold coordinated site N acts as a nondoping valence three atom. Thus, the chemistry of a N atom in ta-C depends heavily on its local environment.

Experiments by Veerasamy *et al.* conclude that ta-C can be controllably n-type doped with nitrogen and phosphorus, with doping concentrations varying between 0.15% and 10%.[7,8] An increase in the disorder of the material is observed with increasing N content. 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. Veerasamy *et al.* interpreted the changes in activation energy with increasing N content as an indication that a shift of the Fermi energy was achieved. Further experimental measurements of the conductivity versus temperature and thermopower experiments[7] suggest that beyond a doping concentration of 1% and up to 5% electronic transitions take place through thermally excited electrons in the conduction band.

Ronning *et al.*,[9] on the other hand, draw the conclusion that hopping conduction occurs via localized states at the Fermi level. These workers further report that plots of log σ vs T^{-1} and log σ vs $T^{-1/4}$ give equally good linear dependencies. However, one should be cautious in comparing these results, since the sp^3 content of the Ronning *et al.* films is yet unknown, though it is believed to be close to ta-C values.

Electron-energy-loss spectroscopy (EELS) experiments measuring the C and N K edges have been performed for

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[a] Electronic mail: stumm@helios.phy.ohiou.edu

films containing 0.45%–28% N.[7,11] The C and N *K* edges appear to be identical (within the experimental error) for all doping concentrations. Davis *et al.*[11] conclude that ''the N is substitutional in all networks, ranging from highly tetrahedral as in the film containing the least N to highly sp^2 as in the film containing most nitrogen.'' The presence of the π^* peak indicates that the π^* states are not occupied, which is consistent with a location of the Fermi level below the π^* conduction-band edge as reported by Ref. 7. A further interpretation of the low doping efficiency in ta-C, which is only about 1%, is still required. Also, measurements of the sp^3/sp^2 ratio of the undoped versus the 1% doped material show that the sp^2 ratio increases from about 11% to 25% in the N-doped network.[12] This rather large increase of the sp^2 fraction for even very low dopant concentrations shows that some kind of network rearrangement has to be present due to the incorporation of N atoms. Clearly, more experimental and theoretical work is required to explain these contradicting results.

It must be noted, however, that movement of the Fermi level is difficult to achieve in ta-C. The doping is heavily compensated: A large number of highly localized band-tail states must be filled by an equal number of doping N atoms, and the effect is exacerbated by the fact that the intrinsic material is weakly *p* type. Further, N incorporation in some sites actually causes more dangling bond defect states. In turn these states need to also be compensated by more substitutional N atoms. This mechanism leads to the low doping efficiency seen in experiments. In our models, and accounting for the fact that some N atoms do not contribute due to relaxation effects, effective doping requires such a large concentration of impurities that the material is better thought of as a C–N alloy rather than a simple doped material. Also, at such N concentrations any effective mass picture fails as impurity band effects become important because of the large number of interacting N atoms in the matrix.

Thus, from the perspective of electronic applications, this work stresses the need for experimentalists to fabricate films with the smallest number of defects, or incorporate the N such that no additional defect gap states are created through its presence. It is also suggestive that hydrogenated films, as for the case of Si, may be more effectively *n*-type doped with N incorporation (albeit possibly with undesirable light-induced metastability).

The rest of this article is an atomistic study of how N enters the network, the importance of relaxation effects, and collective effects associated with N incorporation, such as a tendency for N to induce graphitization.

Although the introduction of N into amorphous C might have led to a very diverse and complex chemistry, our simulations show that that is not the case. One might expect a group-V element such as N to be incorporated into a group-IV amorphous network in one of two different ways. If the N atom is incorporated into a fourfold site then one might expect the N atom to act according to effective mass theory. This is what occurs in doping crystalline Si with P or As. The P or As goes into the Si lattice substitutionally and bonds much like the replaced Si atom. However, the extra positive charge forms the nucleus for a donor level near the conduction-band edge and, since an extra electron is supplied, the Fermi level is raised by one-half of an electronic state per dopant atom. On the other hand one might expect N to act as a valence three atom. That is, the two last *s* electrons can form states well into the valence band and then hybridize with the other valence-band electrons. This leaves three *p* electrons for bonding. In this case the N atom (N_3^0) acts similar to a B atom, although the details of sp^3 and p^3 bonding are different. In an isolated dangling bond site this will not dope the material. According to our molecular-dynamics (MD) simulations, the two cases outlined above are exactly what happens. That is, as outlined earlier, N atoms in fourfold coordinated sites on in chains of an even number of π bonded chains act according to effective mass theory. On the other hand, N atoms in isolated threefold coordinated sites act as valence three atoms.

II. ELECTRONIC-STRUCTURE METHOD

An approximate first-principles electronic-structure method, first introduced by Sankey *et al.* in 1989,[14,15] is used for the calculations described in this work. This method is based on density-functional theory within the local-density approximation (LDA) and the nonlocal pseudopotential scheme. Basis functions of four pseudoatomic orbitals per site are used, with a confinement[14] radius of $r_C = 4.1a_B$ and $r_C = 3.75a_B$ for carbon and nitrogen, respectively. The utility of this basis has recently been explored in comparison with plane waves methods by Sanchezportal, Artacho, and Soler.[16] To demonstrate the suitability of this method to describe carbon structures in a very wide range of bonding environments, the phase diagram for several existing and hypothetical carbon structures was computed. Comparison to self-consistent LDA calculations[17] showed excellent agreement, even for the cubic phases. We have also used Car–Parrinello (self-consistent plane-wave methods) with a converged plane-wave cutoff to investigate smaller (64 atom) models of ta-C and find that, despite some rearrangements, our earlier predictions of defects and electronic structure were confirmed in detail.[18]

III. COMPARISON BETWEEN SELF-CONSISTENT AND HARRIS FUNCTIONAL APPROACHES

To further demonstrate the accuracy of our electronic structure method to correctly describe an amorphous material, we compared it to a more sophisticated first principles self-consistent method (FIREBALL96).[19] This was done by using a 63 atom ta-C model already investigated in earlier work[20] and performing single N substitutions in several kinds of bonding environments. These cells were then relaxed for 100 steps for each method and the structural and electronic changes in the two cells were compared. There is very close agreement of the structural relaxation present in both cells with N incorporation. Changes in bond lengths of the N nearest neighbors when incorporated in diamondlike and π bonded sites differ by less than 0.04 Å. For the electronic properties our electronic structure method in general overestimates the highest occupied molecular orbital–lowest unoccupied molecular orbital (HOMO–LUMO) gap, but

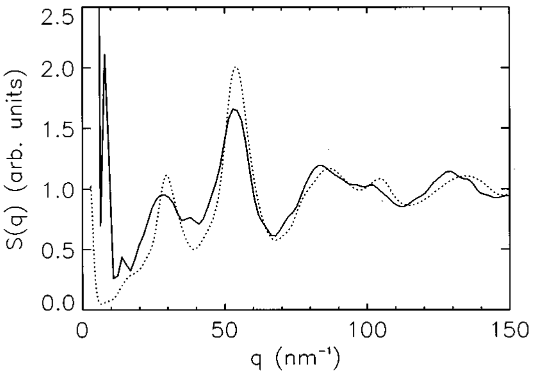

FIG. 1. Structure factor for the 216 atom ta-C cell. The dashed and solid lines show the experimental and theoretical results, respectively. The experimental result is from Ref. 23.

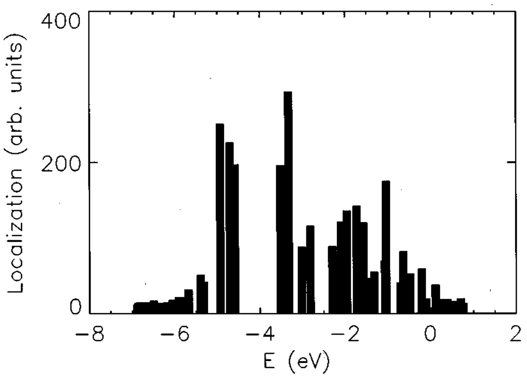

FIG. 2. Electronic density of states and localization (inverse participation ratio) for the undoped 216 atom ta-C cell.

apart from this intrinsic difference both methods agree extremely well on the electronic structure. The position of gap states and the localization of these states are very similar for both methods.

IV. EFFECTS OF INTRODUCING *N* INTO ta-C MODEL

We created a 216 atom ta-C model obtained by rescaling a model of *a*-diamond provided by Djordjevic, Thorpe, and Wooten.[21] This new larger model has the advantage over the previously used 64 atom cell that finite size effects are greatly reduced. The larger supercell also aids in comparing to the experimental through the small concentration of dangling bonds. The initial *a*-diamond cell has a density of 3.5 g/cm^3 compared to the experiment density of ta-C (3.0 g/cm^3) and was entirely four-coordinated, as one might expect at the higher density. By a process of rescaling this cell to the experimental density and heating it briefly to a high temperature (5000 K for 150 fs), annealing at 1500 K for 1 ps, and then quenching to $T=0$, we obtained a network with 12% three coordinated carbon atoms. 90% of these threefold coordinated carbon atoms occur in π pairs, there is one π triplet, and three dangling bonds. π pairs and triplets are characterized by neighboring threefold coordinated carbon atoms, with a graphiticlike geometry. Further defects consist of stretched and strained bonds. The structure factor for this cell is shown in Fig. 1 and is in typical agreement with the experimental data.[22,23] The HOMO–LUMO gap for this cell is 1.08 eV, but the first two unoccupied eigenvalues are substantially localized on dangling bond defects and should therefore be interpreted as gap rather than conduction-band-tail states. The experimental evidence suggests a dangling bond density of about 1 out of 10^4 atoms. A realistic theoretical description of the dangling bond density is therefore prohibited due to the large cell size necessary, but important information on the influence of dangling bonds on the structure can be gathered from higher dangling bond densities nevertheless. Also the number of gap states is substantially more realistic than other proposed models.[24,25] Viewing these eigenvalues as gap states we have a π–π^* gap of 1.26 eV. All band-tail and gap electronic eigenstates are strongly localized. Localization always occurred on more than one atom for a given state in the valence and conduction band. Typically two atoms that share a π bond are localized for a given state, although one of the atoms exhibits more localization. The energy eigenstates around the band gap and their localization are shown in Fig. 2. The density of valence-band-tail states is larger and their localization is significantly less than for conduction-band-tail states. Localization of a particular state is determined by the inverse participation ratio.[26]

To determine whether doping is taking place it is important to analyze the movement of the Fermi level with different amounts of N incorporation. This is a rather difficult task, since upon N substitution the energy of the valence and conduction-band states changes. Further, in some cases new states are created in the valence- or conduction-band tails. In this work we analyze by how many states the Fermi level has moved either upward or downward due to new states in the conduction or valence band, respectively.

Obviously our simulations are not what happens in lab-fabricated material and we have not considered growth kinetics at all although they have an enormous influence in real materials. Any growth simulations are far beyond what can be accomplished by *ab initio* codes today. In spite of this, we believe that our simulations are a valuable aid in understanding the types of bonding that can occur and the energetics of various configurations.

A. N in diamond

Since a large part of the ta-C network locally resembles the diamond topology it is important to understand the relaxation of the crystalline network upon N incorporation. Substituting a single C atom with a N atom and relaxing the structure leads to only minor changes in the network. All atoms, including the N atom, stay fourfold coordinated, the N—C bond lengths increase to 1.57 Å, and all bond angles remain diamondlike. No new states are created around the gap, and the Fermi level moves up by 1/2 state to the first conduction-band state, which is now singly occupied. There are no localized states. That is, N acts just as one would expect from effective mass theory. This is only a metastable configuration for the cell, however. Replacing a N atom for a C atom in the diamond lattice and slightly displacing the atom before the relaxation leads to structural changes that result in the lowest energy configuration, which is 0.97 eV

TABLE I. Average energies and energy range for single N substitution.

Site specification	ΔE (eV) (per cell per N atom)	Energy range (eV)
Dangling bond (C)	0.000	0.821
Stretched bond (D.2)	+0.641	⋯
π bond (B)	+0.857	0.259
Stretched bond (D.3)	+1.094	⋯
Diamondlike (A)	+1.207	0.194
Stretched bond (D.1)	+1.354	0.302

lower than the above case. The N atom and one of its C nearest neighbors become threefold coordinated, as the distance between them increases to 1.988 Å. The remaining three nearest neighbors of the N atom reduce their nearest-neighbor distance by 0.03 Å. Second-nearest neighbors hardly relax at all. In this case the N atom is in the N_3^0 configuration and does not give rise to a localized state. The newly created dangling bond C atom, however, exhibits a strongly localized gap state pinning the Fermi level about 2.5 eV below the conduction-band edge. Our result is nearly identical to that of Kajihara *et al.*[27,28]

B. Nitrogen substitutions

N atoms were substituted in several diamondlike, stretched, strained, π bonded and dangling bond sites, with doping concentrations in the cell varying from 0.46% to 3.2%. The 216 atom cell was then relaxed for 100 steps using Γ point Brillouin zone (BZ) sampling. In most quenches there was no change in coordination for any atoms including the N atom. Further, relaxations at higher dopant concentrations were qualitatively similar to the single N substitutions, except for the largest doping concentration investigated (3.24%). Consistent with the fact that the observed relaxation effects are similar for N atoms within a given kind of bonding environment at all doping concentrations below 3%, the ordering of the energetics at different dopant concentrations is the same for single and multiple N substitutions.

The total energies for N substitutions in similar bonding environments were found to be very dependent on the exact local topology. For example, N incorporation in different strained bond sites showed total energies being less likely or more likely than N incorporation in diamondlike sites, dependent on which strained bond site was chosen. An examination of each relaxation showed that the disorder of the amorphous structure led to differences in the way each N bond and its C nearest neighbors relaxed, which leads to the broad energy distribution. Dangling and strained bond sites have the highest variance for the energies, followed by π bonded sites. Diamondlike sites show only a small energy distribution. This result has to be expected, since for N substitution in dangling and strained bond sites the structural rearrangement is (sometimes) large and different for each site. The average total energies for all single N substitutions are listed in Table I. The energy range is given for those sites, where a locally similar bonding environment showed a wide energy distribution.

It must be emphasized that mere substitution with steepest descent quench tends to ‘‘lock in’’ the local structure, and that structural rearrangements can lead to important energy improvements (we note this particularly below in connection with a tendency to π bonded chain formation). In fact, even for a steepest descent quench, we find several cases where introduction of N into the ta-C network near sp^2 bonded sites nucleates additional π bonding. One could view this as ‘‘impurity-induced graphitization.’’

Single N atoms were substituted in several different diamondlike (A), π bonded (B), and slightly strained (D.1) sites in the 216 atom cell. In all cases the coordination of the N atom remains unchanged after the relaxation, as nearest neighbors of the N atom relax by less than 0.05 Å. Thus, as noted above, the N atom donates an extra electron. That is, it acts like a dopant. The Fermi level moves up by 1/2 state to the lowest midgap state. All other energy eigenstates and the amount of localization on the atoms remain similar to the undoped case. No new valence band or gap states have resulted from the N incorporation.

Replacing the C atom by a N atom in dangling bond sites again results in no changes of coordination, and relaxation is moderate and limited to the N nearest neighbors. However, in this case, the N atom enters the lattice in the N_3^0 configuration and does not act as a dopant, but is inert and does not create a localized state. Initially the C dangling bond was strongly localized on a gap state above E_F. The substitution of a N atom for a C atom removes the localized gap state associated with the dangling bond. A new state is also created below the valence-band edge that arises from the s states on the N atom as discussed earlier. This configuration will not effect the Fermi level of the material since there are two electrons to fill each of these states; however, in our simulations it does remove a dangling bond. In general this can move the Fermi level of the supercell in either direction because the dangling bond level is removed. If it is removed below the Fermi level, the Fermi level moves up and if it is removed above the Fermi level the Fermi level moves down. In our cases the dangling bond state was above the Fermi level, therefore the Fermi level is lowered compared to the undoped cell by 1/2 state (0.4 eV).

For substitution of a N atom in a different stretched bond site, the N—C bond breaks and the N atom becomes threefold coordinated (N_3^0). The new threefold coordinated C atom forms a π quartet (chain) with the neighboring π triplet. There is a new conduction-band-tail state moderately localized on this C atom (D.2). N substitution in another stretched bond site results in a relaxation of the network, such that the N atom (N_3^0) and one of its former nearest neighbors are threefold coordinated. The C dangling bond state is localized in the conduction-band tail (D.3). For N substitution in both of these strained bond sites the Fermi level moves toward the defect gap states by 1/2 state, and is pinned by those states.

To find out if the interaction of N atoms at higher dopant levels leads to changes in the electronic structure, dopant concentrations of 0.9%–3.2% were investigated extensively as well.

When substituting several N atoms in different diamondlike and slightly stretched bond sites, the relaxations are

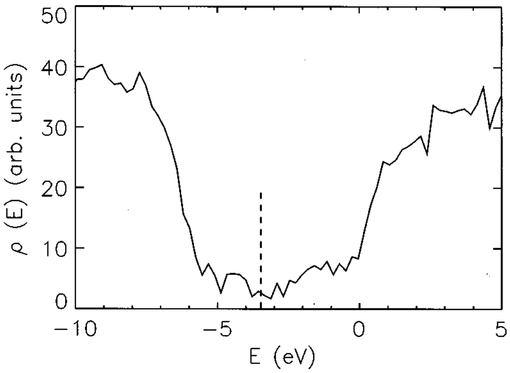

FIG. 3. Electronic density of states for cell with seven N atoms in diamondlike sites. The dashed line shows the position of the Fermi level.

qualitatively similar to the single N substitutions. No changes in coordination occur and relaxation effects are small ($\leqslant$0.09 Å) and limited to the vicinity of the N atoms. For each substitutionally incorporated N atom in these bond sites the Fermi level will move up by 1/2 state. Only for dopant concentrations above 3% do significant changes in the bond lengths occur and the disorder of the network increases, as was observed when seven N atoms were incorporated in diamondlike sites. In this case several C and N atoms change their bond lengths, although no changes in coordination occur. The increase in the disorder is not limited to the vicinity of the N atoms. All gap states are occupied and the Fermi level has moved up by 7/2 states into the localized conduction-band-tail states. The electronic density of states (EDOS) for this ta-C:N structure is given in Fig. 3.

Substitution of two N atoms in two well-separated dangling bond sites again confirms the results from the single N substitution in this type of bonding environment. The energy eigenstate associated with the former unoccupied C dangling bond gap states is shifted to energies below the valence-band edge, which lowers the Fermi level by one state (0.7 eV in our supercell). Also these states are no longer localized.

N substitution in two strained bond sites, where one N atom is a second nearest neighbor to a dangling bond, results in a rearrangement of the network. The N atom becomes threefold coordinated, while the former C nearest neighbor π bonds to the previously dangling bond site. The gap energy eigenstate that had been associated with the dangling bond atom is moved below the valence-band edge, which lowers the Fermi level by one state.

Two N atoms substituted in a shared π bond change the electronic states around the Fermi level. The last (doubly) occupied eigenstate is shifted to lower energies by about 0.8 eV. About 50% of the π pairs exhibit no relaxation of the N—N bond, in which case a new unoccupied state arises right below the conduction-band edge that is substantially localized on the N pair. If there is relaxation of the N–N π pairs, a new state in the valence-band tail is created, that is moderately localized on both N atoms. In both cases the other band-tail and -gap states remain highly localized. The Fermi level moves up when the new energy state is in the conduction band and it moves down when the new energy state is in the valence band. In both cases the absolute position of the Fermi level with respect to the conduction-band edge remains nearly unchanged, because of the closely spaced gap states.

Replacing up to five C atoms with N atoms in different well-separated π pairs does not result in relaxation around the N atoms, consequently, the Fermi level moves up by 5/2 states. Valence-band and gap states show the same localization as in the undoped case. There is a new unoccupied state in the conduction-band tail, which is weakly localized on the carbon atom sharing the N—C π bond.

V. DISCUSSION

The 216 atom ta-C cell used in this work correctly describes the structural and electronic properties of the material.

In particular, we confirm our earlier results[6,29] that sp^2 bonded C atoms pair, as was also seen in subsequent experimental measurements of the spin density.[5] The EDOS also agrees with the experimental results that the gap states are distributed asymmetrically. We find that valence-band-tail states are spaced closely within a small energy range, while π^* states show a wider energy separation between the tail states. At the same time the number of localized states in the conduction-band tail significantly exceeds that of the valence-band tail.

For the crystalline counterparts of ta-C, diamond, and graphite, substitutional N incorporation in computer simulations is possible; the Fermi level is moved across the band gap and the lowest conduction-band state becomes occupied; but, these observations cannot be necessarily transferred to ta-C, first, because of the high defect density in the gap, and second for an amorphous material substitutional N incorporation is less likely, since the topological constraints are less severe than in the crystalline network.[30]

Our results show that N does enter the ta-C lattice approximately substitutionally for diamondlike, dangling, π, and weakly stretched bond sites. Some very stretched, or otherwise strongly disordered, bond sites show a relaxation around the N atom that is comparable to the relaxation associated with a N atom in the diamond lattice (N_3^0). Further, N incorporation in the network can lead to a graphitization around the N atom, such that the N atom becomes threefold coordinated (N_3^0) and one of its carbon nearest neighbors π bonds to neighboring, already π bonded C atoms. The total energies for all structures with equal N concentrations are similar, although dangling bond sites are most energetically favored. Next likely is a local rearrangement of the network around the N atom to form π bonded chains or graphitization around the N atom, followed by N incorporation in π bonded sites, diamondlike, and stretched bond sites.

Considering only the energetics for N substitution in different sites, most N atoms are likely to be incorporated in dangling bond sites. Dangling bond sites are energetically most favored since the former dangling bond midgap state is shifted below the valence-band edge when a N atom is substituted for the C dangling bond atom, correspondingly the Fermi level is lowered. Dangling bond sites are rather rare in the real material and for typical doping concentrations there are many fewer dangling bond sites than N atoms. Therefore, on energetic grounds at least, the remaining majority of N atoms will enter the network in the energetically next favored, also threefold, coordination. These N atoms are likely to either promote the formation of graphitic chains without creating an undercoordinated bonding environment (i.e., no dangling bonds appear), or substitute in π bonded sites. A fourfold bonding environment is energetically least preferred by the N atom.

This is consistent with the experimental results, where N dopant concentrations of up to 1% lead to an increase in the sp^2 ratio of the material from about 11% to 25%.[12] Our results for the energetics of different N substitutions show that this increase in the sp^2 content is in part due to graphitization around the N atom.

The π bonded sites, as well as diamondlike and strained fourfold bonding environments for the N atoms, are potential doping configurations, since N incorporation in these sites is mostly substitutional. For N incorporation in these sites there is little relaxation of the network. No new valence-band or gap states are formed and all gap/band-tail states remain localized on the same atoms, although the energy of a level may change. Up to a dopant concentration of 2% the Fermi level moves upward by no more than 0.2 eV, as the gap states are filled (Fermi level remains pinned). Increasing the N concentration in these sites further will eventually compensate all gap states and the Fermi level will move up into the strongly localized conduction-band-tail states.

Interestingly, the structural and electronic changes for N in slightly disordered diamondlike ta-C sites are different than for N in diamond. In diamond a single N substitution and moving the N atom off center to break the symmetry leads to a relaxation of one of the N—C bonds, such that both the N atom and one of its carbon nearest neighbors are threefold coordinated. A strongly localized deep trap state is associated with the carbon dangling bond. This relaxation is not present for N substitution in diamondlike bonds in the ta-C structure, even though none of the diamondlike sites in ta-C possess perfect diamond symmetry. Only for very disordered ta-C sites does N substitution result in a relaxation and a corresponding new deep trap state in the conduction-band tail. The N atom enters the lattice at its optimal valence, as determined by the 8-N rule,[30] which for N means threefold coordinated (N_3^0). In this case the Fermi level will only move up to the position of the new defect states created below the conduction-band edge.

In order to get conventional effective mass doping in an amorphous material several different criteria have to be met: The N atom would have to be incorporated not only substitutionally, but also give rise to a donor state fairly close to the conduction-band mobility edge. This means that the dopant atom is coordinated such that an electron would occupy the antibonding state if there were no midgap defect states which now take up this electron (compensated doping).

For ta-C most (but not all) of these requirements are fulfilled. Compensated doping is taking place. Each substitutionally incorporated N atom will be in the N_4^+ configuration and donate one electron to occupy gap defect states. Diamondlike relaxations of the network upon N incorporation will initially compensate midgap defect states, until the Fermi level has moved up to the position of the thus newly created defect states in the conduction-band tail.

These observations can be categorized into three different mechanisms, all of which will increase the conductivity. First, we find that N incorporation proceeds smoothly without much relaxation in diamondlike and π bonded sites as well as in some of the strained bond sites investigated. The N atom incorporation in these sites is a dopant configuration (N_4^+). The Fermi level is not moved across the band gap for small doping concentrations, because the doping effect is being compensated by the defect states in the band gap, which will take up the donor electrons. Only for a sufficiently high substitutional N incorporation in the above-mentioned bonding environments will the Fermi level move up into the conduction-band tail. Still, conduction through thermally excited electrons into the extended conduction band states is limited, since the conduction-band-tail states are strongly localized (being largely π states) over a wide energy range; however, this doping will increase the hopping conductivity.

Second, for N atoms substituted in strongly disordered fourfold sites the network will relax such that the bond between the N atom and one of the C nearest neighbors breaks, leading to a new conduction-band-tail defect state associated with the C dangling bond. This (N_3^0) is not a doping configuration for the N atom, because no electron is promoted to the antibonding state. All N atom electrons are in bonding or fully occupied lone pair orbitals. In this case the conductivity can be expected to increase because the Fermi level will move up toward the conduction-band edge where the density of localized states is higher.

Third, for N atoms incorporated in diamondlike sites within a second nearest-neighbor distance of an existing π pair, it is likely that the N atom changes its coordination to threefold, while one of the nearest-neighbor C atoms π bonds to the already existing π configuration. This lattice rearrangement is energetically very likely and will not increase the number of defect states as there are no dangling bonds created. Further, because of the about 11% existing sp^2 bonds distributed evenly throughout the material,[31] there is a high probability to find a N atom in the vicinity of existing π bonds, so the above-described network relaxation is likely to occur. This graphitization around the N atom can lead to graphitic chains throughout the material and therefore an increase in the conductivity. The N atom though, similar to the second case, is threefold coordinated (N_3^0) and no electrons are in antibonding states.

VI. CONCLUSIONS

Our results concerning the structure of N-doped ta-C are consistent with the experimental results. Our calculations indicate that there are three different kinds of N incorporation in the ta-C network, all of them resulting in an increase of the conductivity.

We were able to identify the possible conduction mechanisms, resulting from N incorporation and the corresponding lattice relaxation. Substitutional N incorporation in all except dangling bond sites will compensate gap states and therefore move the Fermi level up toward the conduction-band edge.

On the other hand, relaxation of the lattice due to the N presence will increase the number of conduction-band-tail defect states. In this case there will be initial upward movement of the Fermi level up to the conduction-band tail, where the new defect states were created. Third, N incorporation close to existing π bonded sites will lead to graphitization around the N atom with a corresponding increase in the conductivity because of conduction along π bonded chains.

These results also explain the low doping efficiency observed experimentally for N-doped ta-C films, where only about 1% of all N atoms incorporated in the structure contribute to the conductivity. We have explained that the low doping efficiency is due to only a small fraction of all dopant atoms hybridizing in a dopant configuration.

While the Fermi level can be moved toward the conduction-band tail through N doping, further upward movement is difficult to achieve. This is due to the large number of defect states that were created through N incorporation in disordered fourfold sites leading to the ''diamond relaxation'' with the corresponding new localized carbon dangling bond state in the conduction-band tail. This was also seen in experiments by Veerasamy *et al.*,[10] who report that activation energies below 0.12 eV cannot be achieved through increased doping.

The ratio of substitutional to relaxed N atom incorporation will depend on the actual experimental conditions. An increase in the Fermi energy is seen if most N atoms are incorporated substitutionally. If more defect gap states are created the Fermi level will move up toward the newly created defect states and the conductivity of the sample will increase due to increased hopping at the Fermi level. The conduction-band-tail states though are strongly localized over a wide energy range and far below the conduction-band mobility edge. Therefore, even though the Fermi level in N-doped ta-C has moved up toward the conduction-band tail, extended state conduction through thermally excited electrons from below the mobility edge is limited. Hopping conduction is strongly enhanced through the greatly increased number of available states at the Fermi level. The change in activation energy and the increase in conductivity is probably due to all three effects. The creation of gap states states due to a relaxation of the network with N incorporation, graphitization around the N atom, as well as the filling of gap states with the corresponding increase in the Fermi energy.

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