Nitrogen Doping of Amorphous Carbon Surfaces

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The surface properties of amorphous carbon (a-C) are studied using first-principles electronic structure methods. The effect of nitrogen doping near the surface and, in particular, the effect of nitrogen on the work function is studied by doing a series of nitrogen substitutions near the surface. It is found that the work function is reduced by nitrogen doping of the a-C surface at "on top of the surface" sp^1 and sp^2 sites. Nitrogen doping by low energy ion bombardment is suggested as a doping method to minimize work function of the a-C surfaces.

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Amorphous carbon (a-C) is an interesting material with mechanical and electronic properties close to those of diamond. It can be produced under standard laboratory conditions with reasonable growth rates ($\sim$1.0 μm/h) [1–3]. Amorphous carbon films have been proposed as candidates for flat electron emitting devices [4]. Similarly to diamond, there is experimental evidence of low electron affinity in a-C films, especially in nitrogen doped a-C [5].

Since as-grown amorphous carbon and diamond are naturally weakly p type, a controllable doping mechanism is needed to produce n-type material in order to have a significant number of electrons in the conduction band. Nitrogen is the most widely studied candidate for n-type dopant in diamond and a-C. However, in diamond the substitutional nitrogen atom moves spontaneously to a nondoping lone pair configuration [6]. In contrast to diamond, some forms of amorphous carbon can be doped n type using nitrogen [7], but the control over the distribution of the compensating carbon related π^* states may be difficult [8,9]. Satyanarayana and coworkers have studied the effect of nitrogen doping on the field emission from a-C thin films [5]. They found that the electron affinity is at minimum with a low nitrogen content of 0.4 at. % in the a-C:N film. With higher nitrogen concentration electron emission decreases, which they address to the fact that nitrogen tends to decrease the sp^3 content in a-C [5]. The negative electron affinity (i.e., the electrons in conduction band escape spontaneously to vacuum) of a hydrogen terminated diamond 100 surface has been shown to arise from a surface dipole [10], but until now no theoretical explanation has been given for the observed low electron affinity and especially for the role of nitrogen in it for a-C.

In this Letter, the a-C surface and the effect of nitrogen are studied using state-of-the-art electronic structure methods. We investigate both the microscopic, atomic scale phenomena upon the substitution of a single nitrogen dopant at various initial bonding configurations (sp^3, sp^2, and sp^1) near or on the surface, as well as the collective influence of heavy nitrogen doping (12.5 and 25 at. %) to the a-C surface with three different implantation profiles. The structural and electronic properties as well as the changes in the work function are investigated in all cases. Finally, an explanation for the decrease in the work function of the N-doped a-C films is proposed.

We have used a plane-wave pseudopotential method based on density-functional theory (DFT) in the local-density approximation (LDA) [11]. The Vanderbilt ultrasoft pseudopotentials [12] are used for C, N, and H atoms. Brillouin-zone sampling is done by employing a $2 \times 2 \times 1$ Monkhorst-Pack mesh [13]. Well-converged results are achieved with a 25 Ry kinetic energy cutoff for the plane-wave basis set. To our knowledge this is the first study of a-C surfaces using self-consistent DFT-LDA methods. The initial structure of the amorphous carbon structure studied here is obtained from a previous study with bulk a-C of density 3.0 g/cm^3 (Ref. [14]). A two dimensional slab of a-C is obtained by removing the periodicity in the z direction (surface normal direction). This is done by using a supercell of dimensions 14.2 Å $\times$ 14.2 Å $\times$ 45.5 Å^3 instead of 14.2 Å $\times$ 14.2 Å $\times$ 14.2 Å^3 in the bulk a-C. The length of the vacuum region between the periodic slabs is thus twice the thickness of the slab. The periodic images of sixteen atoms at the bottom of the slab in z direction are copied on the top of the surface. The dangling bonds at the bottom of the slab are terminated with seven hydrogen atoms, yielding an initial surface structure with totally 87 atoms (80 C and 7 H). The energy of the a-C structure is minimized using a Broyden-Fletcher-Goldfarb-Shanno

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(BFGS) minimization [15] with slightly randomized initial atomic positions. In all doping studies the positions of all carbon and dopant atoms, except for the 16 C and 7 H atoms at the bottom of the slab, are optimized.

The structural properties of the relaxed *a*-C film are summarized in Table I. Our structure has slightly lower sp^3 content compared to a 213 atom *a*-C slab studied by Dong and Drabold [16] using a more approximate non-self-consistent Harris functional method. The lower sp^3 in our model is likely because we use a random C network as a starting configuration for bulk *a*-C, whereas Dong and Drabold use a fully sp^3 coordinated network. Because of the well-known LDA tendency for overbinding, our 3.0 g/cm^3 density resembles rather to a slightly lower density in experimental structure. Clark *et al.* have shown that the sp^3 fraction increases as the density of *a*-C is increased [17]. The calculated bulk properties agree well with the other DFT-LDA studies [17,18].

The sp^3 concentration remains the same in our undoped *a*-C slab as in the bulk. Some of the former bulk sp^2 atoms change to sp^1 coordination on the surface. The number of three membered carbon rings increases from two to five. The two new 3-rings are formed not on the surface but slightly deeper in the subsurface layers. The 3-rings always consist only of sp^3-bonded atoms. The 3-rings are usually lacking from the *a*-C models based on more approximate methods, whereas they are always present in pseudopotential plane-wave based models. Also the number of 4-rings increases slightly, from two in bulk to three in the surface system (Table II). 4-rings consist only of sp^3-bonded atoms, except in one case, where one atom is sp^2 bonded terminating a four-atom sp^2 chain. Furthermore, there is a 3-4 ring complex on the surface having two atoms in common.

As in earlier DFT-LDA studies [17,18] for bulk *a*-C, the calculated Kohn-Sham one-electron total density of states (TDOS) shows no gap for the *a*-C surface system (see Fig. 1, the solid line). The states in the gap are localized mostly at the surface atoms and at isolated or stretched sp^2 atoms in the subsurface region.

Single nitrogen substitutions are made on five sp^3, five sp^2, and three sp^1 sites. All the N atoms substituted to an sp^2 site remain threefold coordinated, but the final geometries are not planar due to an extra electron compared to an sp^2-site C atom. The nitrogen atoms positioned to an sp^3 site decrease their coordination number in all cases, two of five end up to sp^2, two to a nonplanar threefold coordination. One case, an sp^3 substitution on the surface, results a N atom with three neighbors, but the bonding cannot be classified as sp^2, because the bond angles are 88°, 112°, and 112°. The tendency of N substituting an sp^3-site C to lower its coordination number explains partly the observed decrease of sp^3 content in N-doped *a*-C samples [19]. The sp^1-site substituted N atoms remain sp^1, relaxing less than 0.1 Å.

The total energies of the relaxed structures after a single N substitution are as follows. On the average the sp^1 and sp^3 sites are almost isoenergetic, the sp^3 site being 0.1 eV lower. The sp^2 site substitutions are, on the average, 1 eV higher in energy. This result for the *a*-C surface system is opposite compared to our earlier results in bulk *a*-C, where the formation energy of an sp^2 substitution is lower compared to sp^3 substitution [14]. The highest energy of the single substitutions occurs when a carbon atom to be substituted is at an sp^2 site at the end of a four-membered carbon atom chain of sp^2 atoms. The total energy of this structure is 2.54 eV higher than the lowest energy case. Even when the extreme cases are filtered out the trend is clear: all the final configurations when substituting an sp^3 carbon atom with nitrogen are lower in energy compared to the sp^2 substitutions. However, a nitrogen atom in the sp^3 site does not remain sp^3 coordinated. The highest binding energy in the single atom substitutions is 6.1 eV with respect to a free N atom, but only 0.5 eV with respect to N_2 abstraction.

A single nitrogen substitution at an sp^3 site or at an sp^2 site in the subsurface layers increases the TDOS below the gap. This is mainly due to the lone pair states. Thus the Fermi energy moves down, increasing the work function (i.e., the energy required to extract an electron from the Fermi energy to the vacuum). With the sp^1 or big-ring-sp^2 substitutions on the "top of the surface" the TDOS increases near the conduction band edge. Therefore, the Fermi energy moves up and the work function decreases. The states near the conduction band

TABLE I. The structural properties of *a*-C and N-doped surface systems. Values are in %. For the undoped structure the values in the parentheses are for the sp^2, a nonplanar sp^2 bonding, and for the sp^1, a nonlinear sp^1 bonding. Atoms with only one neighbor or with bond angles <90° are classified as defects. The reference structure is *a*-C surface.

Configuration	*a*-C, bulk	*a*-C, slab	*a*-C, Ref. [16]	N-20-top	N-20-random	N-10-bottom
C sp^3	59	59	64	58	52	49
C sp^2	41(9)	36(9)	33	42(13)	40(8)	34(14)
C sp^1	···	5(1)	3	0	13(5)	6(1)
C defect	···	0	0	0	3	3
N sp^3	···	···	···	0	5	20
N sp^2	···	···	···	17(17)	75(20)	70(10)
N sp^1	···	···	···	83(83)	10(10)	0
N defect	···	···	···	0	10	10

TABLE II. The ring size distribution of the a-C and various doping configurations.

Atoms in ring	3	4	5	6	7	8	9	10–12
a-C, bulk	2	2	22	16	10	4	6	0
a-C, slab	5	3	23	15	13	8	3	0
N-20-top	3	2	18	10	9	7	3	0
N-20-random	3	3	15	10	11	7	6	3
N-10-bottom	3	3	16	12	16	6	5	0

edge may arise, for example, from a N atom in a surface-carbon ring having two double bonds to neighboring C atoms, leaving one weakly N-bonded electron state near the conduction band edge. Additionally, the decrease in the work function is due to the change in the surface dipole. Examples of typical changes in TDOS after single N atom substitutions are shown in Fig. 2.

Heavy nitrogen doping is studied with initial N concentrations of 12.5 and 25 at. %. In the 12.5 at. % doping 10 C atoms at the bottom of the a-C slab are substituted with N atoms (N-10-bottom). The 25 at. % doping is carried out by randomly substituting 20 C atoms with N (N-20-random). A third sample is made by substituting 20 C atoms on the surface with N atoms (N-20-top).

The structural properties of the heavily doped samples after the BFGS energy minimization are summarized in Tables I and II. In accordance with experimental studies heavy nitrogen doping decreases the sp^3 content of the film [19]. The overall tendency for sp^1 chains or big rings consisting of both C and N atoms is visible with the heavy N doping, as already pointed out by Weich *et al.* [20]. Moreover, the number of small (ring size ≤ 6) rings decreases. In the N-10-bottom or N-20-random doping, the structural rearrangements remain local. In the surface substitution (N-20-top) eight of the original 20 nitrogen atoms desorb as N_2. The remaining twelve N atoms on the surface relax on average 0.6 Å compared to 0.3 Å in the two other heavy doping cases.

The Kohn-Sham total electron densities of states near the Fermi energy ε_F after massive N doping are shown in Fig. 1. The carbon σ peak is weakened indicating decreasing carbon sp^3 bonding. All the heavy N dopings bring new states in the gap region. The peak below the Fermi energy in TDOS with a N-10-bottom system originates from two kind of defects. First, there is a 3-ring structure, consisting of one N and two C atoms. The N atom is bonded *only* to the two carbon atoms in the 3-ring. The N atom causes additionally unoccupied states in the gap. Second, a nonplanar threefold coordinated carbon atom with three carbon neighbors causes another state below the ε_F. All the neighbors of this carbon atom have one nitrogen atom as their neighbor. This disables the usual π bonding between the carbon atoms leaving one nonbonding π orbital which can be seen in TDOS below the ε_F.

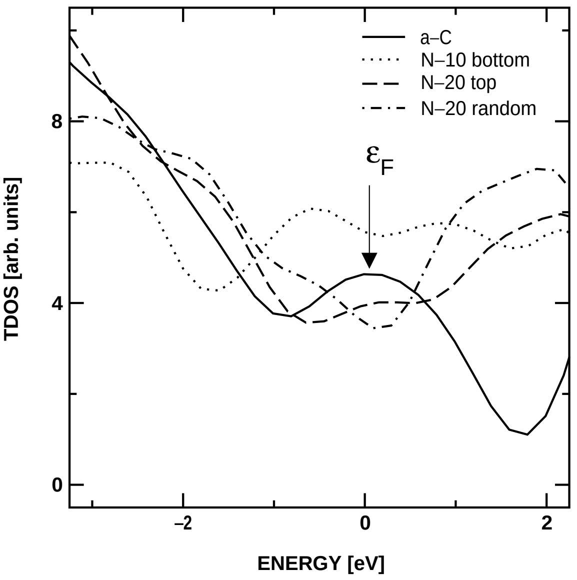

FIG. 1. The Kohn-Sham total electron density of states (TDOS) for the pure and heavily N-doped samples near the Fermi energy. The heavy nitrogen doping increases the number of the gap states. The Fermi energy of each sample is set to zero.

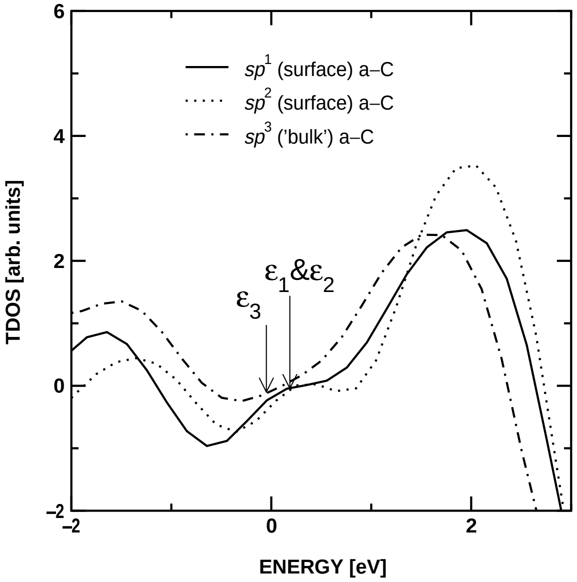

FIG. 2. Typical changes in the Kohn-Sham total density of states (TDOS) after a single N substitution at various bonding environments (sp^1 and sp^2 are located on the surface, sp^3 in the subsurface). The densities are obtained by subtracting the original undoped a-C TDOS. The Fermi energies ε_1, ε_2, and ε_3 after a single N substitution at sp^1, sp^2, and sp^3, respectively, with respect to the Fermi energy of the undoped a-C are indicated in the figure.

On the other hand, N-20-random doping removes some gap states, probably by removing isolated sp^2 carbon atoms. The nonplanar sp^2 N atoms and ill-coordinated N atoms are most responsible for new gap states. There is one sp^3 coordinated N atom, which yields unoccupied states near the conduction band edge.

With the N-20-top system, most of the new gap states are associated with the nitrogen atoms. Some new carbon related defects, for example, elongated sp^2 bonds, are formed.

The work functions of the surface systems are shown in Table III. The electron affinity (the energy required to extract an electron from the bottom of the conduction band to vacuum) is not estimated here because the difficulties in determining the gap size (LDA deficiency) and the difficulties in defining the surface dipole of an amorphous layer. The electron affinities for diamond surfaces have been estimated by Rutter and Robertson [10].

The desired effect, a decrease in the work function, is obtained when the nitrogen is substituted on the top of the surface at an sp^1 site or at an sp^2 site. However, the sp^2-site atom must be a member of a big carbon ring (ring size ≥9). The reason for the decrease in the work function is twofold. First, the new states after N substitution are above the ε_F, so the extra electron from the N atom increases the Fermi energy. Second, there is a change in the charge distribution on the surface, thus the surface dipole changes.

In conclusion, the nitrogen substitutions near the surface of a-C are most preferable at sp^3 sites, at which the N atom changes to sp^2 coordination. This is different from the earlier bulk results. The control over the distribution of the states in the gap is very difficult, and requires knowledge not only of the immediate neighborhood of the substitution site but also information about extended states. However, one can affect the work function (and thus also the electron affinity). The nitrogen substitution on the surface at either sp^1 or sp^2 site in a large (ring size ≥9) carbon ring reduces the work function. Our result also explains the experimental observation that the electron affinity is lowest at 0.4 at. % doping concentration [5]. We believe that at this density most of the surface sites contributing for the lowering of the electron affinity are occupied. The dynamics of the growth process may favor the adsorption on the surface and not into the subsurface layers. This could be the case, for example, with chemical vapor deposition or molecular beam epitaxy with low energies. At higher nitrogen concentrations the surface N atoms tend to pair and leave the surface as N_2 molecule. Low energy N-ion bombardment for undoped a-C thin film should result in effective filling of sp^1 sites with nitrogen. At the same time the undesired effect of nitrogen doping to decrease the sp^3 content of the film should be minimal.

TABLE III. Work functions for a-C surfaces. The averages in the single substitution cases sp^2 and sp^3 are calculated without the substitutions on the very top of the surface. The sp^1 is averaged over three substitutions; sp^2 and sp^3 are averaged over four substitutions. A surface sp^3, yielding work function 5.38 eV, and a big-ring surface sp^2 substitution, with work function 4.60 eV, are left out from the averages. a-C (no H) stands for a test calculation, where the hydrogen atoms are removed and all the atoms in the slab are allowed to relax.

Slab	Work function [eV]
a-C	5.23
a-C (no H)	5.24
N-20-top	6.35
N-20-random	5.11
N-10-bottom	5.20
sp^1 average	4.73
sp^2 average	5.20
sp^3 average	5.24

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