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It has been extremely difficult to produce n -type conducting diamond, whereas it seems that n -type conducting tetrahedrally bonded amorphous carbon (ta -C) can be obtained using phosphorous or nitrogen as dopant. In this work we have studied substitutional, group V, VI and VII impurities (N, O and Cl) in diamond and in ta -C using first-principles electronic structure methods. Electronic structure calculations reveal the differences between ta -C and diamond in the microscopic level and ease therefore the experimental search for producing n -type conducting diamond-like materials.

Diamond is a promising material for devices operating in extreme environmental conditions. This stems from its outstanding materials properties, such as the extreme hardness and the wide electron band gap. Usually, both n - and p -type conducting materials are needed in manufacturing electronic components. Diamond shows normally intrinsic p -type conductivity due to a small fraction of boron impurities. Also in laboratory environment p -type conducting diamond can be produced by using B-doping methods. In contrast, n -type conducting diamond has been extremely hard to produce and only very little success has been achieved so far. Tetrahedrally bonded amorphous carbon [1], which has many materials properties similar to diamond, can be n -doped using nitrogen or phosphorous. Tetrahedrally bonded amorphous carbon (ta -C) has been studied theoretically by various groups [2–7]. From the studies only those reported in Refs. [6] and [7] are based on fully self-consistent first-principles (SCFP) calculations.

Three-member carbon rings recently found in *ab-initio* calculations for bulk ta -C [6,7] and for graphite surfaces [8] are absent in tight-binding (TB) studies of ta -C [3–5]. Also four-member rings are less probable in non-self-consistent studies than in fully self-consistent *ab-initio* ones. Therefore, the TB-method is not capable to describe ta -C accurately and fully SCFP methods have to be applied. To our knowledge, no fully SCFP studies for doping of ta -C exist. The works by Stumm *et al.* [2] and Stich *et al.* [3] are, the only existing electronic structure calculations for the doping of ta -C.

Nitrogen doping has most often been performed by the Chemical Vapor Deposition (CVD) method. The addition of N_2 molecules in the CVD-reaction gas results in a narrowing of the bandgap as the amount of nitrogen increases. The ensuing bulk resistivity is reported to reduce by two to four orders in magnitude [9].

Oxygen doping improves the film quality and reduces the number of lattice defects in CVD diamond. Oxygen is found to be incorporated into the diamond lattice [10]. It can remove the non-diamond-like hybridised carbon atoms from the film.

To our knowledge, there exists no experimental evidence for chlorine dopant atoms in diamond or in ta -C. Chlorine has been used as a reactant gas in the CVD growth, and therefore it may play a role in surface growth pro-

cesses [11].

We have performed fully self-consistent plane-wave-pseudopotential calculations for carbon networks at the density 3.0 g/cm^3 . Our calculations employ the density-functional theory [12] within the local density approximation (LDA) for electron exchange and correlation effects [13]. We have used a 64-atom simple cubic simulation cell, and the supercell Brillouin-zone sampling consists of the $2 \times 2 \times 2$ Chadi-Cohen \mathbf{k} -point mesh [14]. The use of the Vanderbilt ultrasoft pseudopotentials [15] reduces significantly the number of plane waves needed to treat sharply-peaked electronic states of carbon, nitrogen, oxygen and chlorine accurately. A kinetic energy cut-off of only 20 Ry was needed in calculations for generating ta -C networks. Calculations involving chlorine or oxygen were performed with a kinetic energy cut-off of 27 Ry and for calculations involving nitrogen the cut-off energy of 25 Ry was sufficient.

We have used several methods to generate good non-doped ta -C structures to start with. These methods range from the direct total energy minimization starting from randomized atomic positions with several randomizing amplitudes to the molecular dynamics calculation in which a (liquid) sample at 5000 K was followed for 0.36 ps and thereafter instantly cooled to zero temperature. All these calculations give very similar results. The sp^3 fraction in the simulated carbon networks varies from 55 to 68 percent. Three- and four-membered rings were present in all structures obtained. The radial distribution functions are almost identical and the total energies of these structures at 0 K nearly coincide. From these structures we chose the one with the lowest total energy to serve as our ta -C network in the subsequent doping studies. The final ta -C structure is visualized in Fig. 1 and the structure analysis is given in Table I.

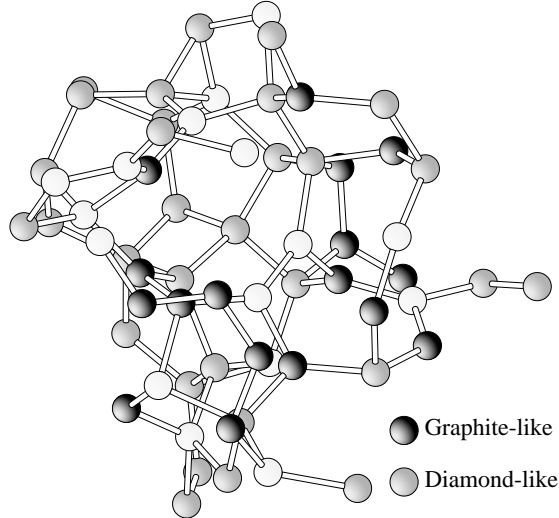


FIG. 1. 64-atom *ta*-C supercell. Carbon atoms in diamond- and graphite-like sites are indicated by gray and black spheres, respectively. We define that a carbon atom is 'diamond-like' if it has four neighbours within the distance of $1.53 \pm 0.1 \text{ \AA}$ and the bond angles are in the range of $109.28 \pm 10 \text{ deg}$. Similarly, an atom is considered to be 'graphite-like', if it has three neighbors, its bond lengths are $1.3 - 1.5 \text{ \AA}$ and the bond angles are $110 - 130 \text{ deg}$. The white spheres correspond to carbon atoms which cannot be considered as 'diamond-like' or 'graphite-like'. Three-membered rings present in structure are visible *eg.* at the top of the figure and four-membered rings at the center.

TABLE I. Details of the simulated *ta*-C structure. The sp^3 fraction and the ring statistics are compared with other published data for densities close to 3.0 g/cm^3 .

Ref.	$\rho(\text{g/cm}^3)$	N_{at}	$sp^3(\%)$	3	4	5
This work	3.0	64	59	2	9	14
Clark <i>et al.</i> ^a	2.905	64	47	6	4	17
	3.147	64	53	4	5	21
Marks <i>et al.</i> ^b	2.9	64	65	3	3	21
Frauenheim <i>et al.</i> ^c	3.0	64	53	0	0	20
	3.0	128	64	0	3	18
Wang and Ho ^d	3.0	216	33	0	0	10

^aref. [7] ^bref. [6] ^cref. [4] ^dref. [5]

When calculating dopants in the diamond structure a 32-atom supercell and the $2 \times 2 \times 2$ Monkhorst-Pack \mathbf{k} -point mesh [16] has been employed. The calculated lattice constant of 3.531 \AA is slightly smaller than the experimental value of 3.567 \AA [17]. This is expected to be due to the well-known LDA tendency for overbinding. In all of our dopant calculations for the diamond as well as for the *ta*-C structure all the atoms in the supercells have been allowed to move to their minimum-energy positions without any symmetry assumptions.

We have studied substitutional nitrogen in diamond

and trigonally symmetric structures. The tetrahedrally and trigonally symmetric structures. The tetrahedral structure is stable for the positive charge state, while the trigonal structure is unstable. For the neutral and negative charge states the trigonal structure, for which one of the C-N bonds is broken (the C-N distance is 2.13 \AA), was found to be the stablest structure. This in good agreement with experiments and other theoretical studies [18]. The tetrahedral configurations are metastable in the neutral and negative charge states. The total energy differences between the metastable tetragonal and the stable trigonal configurations are 0.2 eV and 1.1 eV for the neutral and negative charge states, respectively. The calculated donor level (2.3 eV below the conduction band minimum) is 0.6 eV lower in the band gap than the experimental value (1.7 eV below the conduction band minimum [19]).

In the case of *ta*-C we studied the nitrogen doping by substituting a sp^3 - or a sp^2 -hybridized carbon atom or by substituting a carbon atom in a three- or four-membered ring by a N-atom. The nitrogen atom substituting an sp^2 -bonded carbon atom was found to be the most probable one: the formation energy for the substitution of an sp^3 bonded carbon atom is in all charge states about 3 eV larger than that for the sp^2 -bonded carbon atom. The energetics for the substitutional nitrogen in diamond and in *ta*-C are collected in Table II.

TABLE II. Formation energies for the different nitrogen impurities in diamond and in amorphous carbon. The reference chemical potential used for the nitrogen atom corresponds to the dimer N_2 . For the carbon atom in *ta*-C the chemical potential is chosen as the $1/64$ of the total energy of the undoped supercell, even though the chemical potential of carbon atoms occupying diamond- and graphite-like sites should slightly deviate from each other, introducing a small inaccuracy into the formation energies given. The chemical potential for the carbon atom in diamond is $1/32$ of the bulk diamond supercell total energy.

Defect	Formation energy (eV)
N_C^{1+} (diamond, tetrahedral)	$-0.01 + \mu_e$
N_C^0 (diamond, trigonal)	3.53
N_C^{1-} (diamond, trigonal)	$6.34 - \mu_e$
N_C^{1+} (<i>ta</i> -C sp^3)	$1.45 + \mu_e$
N_C^0 (<i>ta</i> -C sp^3)	1.62
N_C^{1-} (<i>ta</i> -C sp^3)	$1.83 - \mu_e$
N_C^{1+} (<i>ta</i> -C sp^2)	$-1.47 + \mu_e$
N_C^0 (<i>ta</i> -C sp^2)	-1.40
N_C^{1-} (<i>ta</i> -C sp^2)	$-1.21 - \mu_e$
N_C^{1+} (<i>ta</i> -C 3-ring)	$0.08 + \mu_e$
N_C^0 (<i>ta</i> -C 3-ring)	0.02
N_C^{1-} (<i>ta</i> -C 3-ring)	$0.05 - \mu_e$
N_C^{1+} (<i>ta</i> -C 4-ring)	$-0.53 + \mu_e$
N_C^0 (<i>ta</i> -C 4-ring)	-0.48
N_C^{1-} (<i>ta</i> -C 4-ring)	$-0.40 - \mu_e$

Group VI atoms such as oxygen are expected to be

double donors in diamond and in *ta*-C. The induced donor levels are too low in the bandgap (~ 1.8 eV above valence band maximum) in order to contribute enough electrons to the conduction band and make the material *n*-type. In diamond the lattice relaxations lower the symmetry around the oxygen atom in the charge states 1+, 0, and 1-. In the charge states 2+, for which the gap states are empty, the tetrahedral symmetry is preserved. In *ta*-C the oxygen impurity prefers, similar to the nitrogen impurity, to substitute an sp^2 -hybridized carbon atom. For the oxygen impurity this preference is calculated to be even stronger than for the nitrogen impurity. The calculated formation energies for the substitutional oxygen in diamond and in *ta*-C are collected in Table III.

TABLE III. Formation energies for the different oxygen impurities in diamond and in amorphous carbon. The reference chemical potential used for the oxygen atom corresponds to the dimer O_2 .

Defect	Formation energy (eV)
O_C^{2+} (diamond, tetrahedral)	$0.99 + 2\mu_e$
O_C^{1+} (diamond, trigonal)	$2.62 + \mu_e$
O_C^0 (diamond, trigonal)	4.45
O_C^{1-} (diamond, trigonal)	$7.41 - \mu_e$
O_C^{2+} (<i>ta</i> -C sp^3)	$1.50 + 2\mu_e$
O_C^{1+} (<i>ta</i> -C sp^3)	$1.56 + \mu_e$
O_C^0 (<i>ta</i> -C sp^3)	0.38
O_C^{1-} (<i>ta</i> -C sp^3)	$1.59 - \mu_e$
O_C^{2+} (<i>ta</i> -C sp^2)	$-1.85 + 2\mu_e$
O_C^{1+} (<i>ta</i> -C sp^2)	$-3.12 + \mu_e$
O_C^0 (<i>ta</i> -C sp^2)	-3.26
O_C^{1-} (<i>ta</i> -C sp^2)	$-2.62 - \mu_e$

The chlorine atom has seven valence electrons and can thus promote up to three electrons to the conduction band in diamond or in *ta*-C. The chlorine-related electronic states are, however, so low (2.4 eV and 3.2 eV above valence band maximum) in the bandgap that they became occupied immediately in *n*-type materials. In diamond the lattice relaxation lowers the symmetry in the charge states 2+, 1+, 0, 1-. For the 3+ charge state there is no occupancy of the gap states and the symmetry is tetrahedral. In *ta*-C, the chlorine atom prefers also to substitute an sp^2 hybridized carbon atom. The formation energies for the substitutional chlorine in diamond and in *ta*-C are collected in Table IV.

TABLE IV. Formation energies for the different chlorine impurities in diamond and in amorphous carbon. The reference chemical potential used for the chlorine atom corresponds to the dimer Cl_2 .

Defect	Formation energy (eV)
Cl_C^{3+} (diamond, tetrahedral)	$6.41 + 3\mu_e$
Cl_C^{2+} (diamond, trigonal)	$8.91 + 2\mu_e$
Cl_C^{1+} (diamond, trigonal)	$11.33 + \mu_e$
Cl_C^0 (diamond, trigonal)	14.47
Cl_C^{1-} (diamond, trigonal)	$17.70 - \mu_e$
Cl_C^{3+} (<i>ta</i> -C sp^3)	$8.01 + 3\mu_e$
Cl_C^{2+} (<i>ta</i> -C sp^3)	$8.12 + 2\mu_e$
Cl_C^{1+} (<i>ta</i> -C sp^3)	$8.25 + \mu_e$
Cl_C^0 (<i>ta</i> -C sp^3)	8.75
Cl_C^{1-} (<i>ta</i> -C sp^3)	$9.38 - \mu_e$
Cl_C^{3+} (<i>ta</i> -C sp^2)	$1.98 + 3\mu_e$
Cl_C^{2+} (<i>ta</i> -C sp^2)	$1.89 + 2\mu_e$
Cl_C^{1+} (<i>ta</i> -C sp^2)	$1.91 + \mu_e$
Cl_C^0 (<i>ta</i> -C sp^2)	2.17
Cl_C^{1-} (<i>ta</i> -C sp^2)	$2.50 - \mu_e$
Cl_C^{3+} (<i>ta</i> -C 3-ring)	$3.04 + 3\mu_e$
Cl_C^{2+} (<i>ta</i> -C 3-ring)	$2.85 + 2\mu_e$
Cl_C^{1+} (<i>ta</i> -C 3-ring)	$2.29 + \mu_e$
Cl_C^0 (<i>ta</i> -C 3-ring)	2.43
Cl_C^{1-} (<i>ta</i> -C 3-ring)	$2.73 - \mu_e$

In conclusion, all the substitutional impurity atoms in diamond studied in this work induce a symmetry lowering lattice relaxation in the charge states which have occupied levels in the band gap. Nitrogen is expected to be the most effective donor among the atomic species studied. The double (O) and triple (Cl) donors are shown to have too deep donor states in order to promote a useful concentration of electrons into the conduction band.

In *ta*-C the most probable site hosting an impurity atom is shown to be a graphite-like carbon atom site. The preference of the sp^2 site over sp^3 site is shown to increase as the number of the impurity valence electrons increases.

We would like to thank Dr. S. Clark and Dr. T. Mattila for useful discussions. We also acknowledge the generous computing resources of the Center for the Scientific Computing (CSC), Espoo, Finland.

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