

## PROPERTIES OF MIDGAP STATES IN DOPED AMORPHOUS SILICON AND CARBON

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Using Hartree-Fock *ab initio* and the Fragment Self-consistent Field method the energy level positions belonging to dopant pairs was investigated in substitutionally doped four-fold coordinated amorphous carbon and silicon. Our models contain 45-583 carbon or silicon atoms. Hydrogen atoms have been used to model the bulk and surface of clusters. Boron, phosphorus and nitrogen impurities have been incorporated into the amorphous networks. It has been found that the distance between the impurity atoms primarily determines the position of midgap states, and the role of the random network is only subordinate. A general relationship is proposed for the determination of the midgap energy levels as a function of the distance between dopant pairs investigated for the amorphous carbon and silicon.

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### 1. Introduction

In this paper we study the position of the energy levels belonging to dopant pairs of substitutionally p- or n-type doped four-fold coordinated amorphous carbon and silicon by means of *ab initio* and semiempirical molecular orbital calculations. Only four-fold coordinated impurities are considered in amorphous environment, since dopants having three or five neighbors satisfying the 8-N rule are electrically inactive. Doped amorphous semiconductors (like silicon and carbon) have crucial importance in materials science, since their physical properties approach those of crystalline ones, but they have indisputable technological advantage over them.

Doped amorphous silicon (a-Si) has been the subject of intensive experimental and theoretical research since Spear and LeComber reported that they could dope hydrogenated amorphous silicon (a-Si:H) by boron and phosphorous [1]. It is remarkable that Chittik et al. [2] published earlier the same result. At early time 8-N rule was strong enough to ignore the first successful experimental result. Doped amorphous carbon (a-C) has attracted growing interest for a decade because of its possible practical applications. One of the most important parameters of a-C is the  $sp^2/sp^3$  ratio [3]. Recently, a new form of a-C, called tetrahedral amorphous carbon (ta-C), has been grown [4] with a high concentration of tetrahedral bonding. Its applicability to electronic devices, its extreme hardness close to that of diamond and large band gap over 2 eV and its ability to accept dopants make ta-C a promising high-tech material [5]. Earlier we investigated the midgap states in undoped graphitic-type a-C. On the basis of tight binding (Hückel) calculation we concluded that topologically determined states exist at Fermi level [6].

Using Hartree-Fock (HF) *ab initio* calculation we obtained that this topologically determined states are shifted to the  $\sigma$  band. So, this states have lower energies than  $E_F$ , but they still remain the highest occupied states in the electronic density of states and they decrease the gap [7]. The  $\pi$  band can be divided into two parts: a part with topologically determined states having higher energy and the rest of  $\pi$  band (see Fig. 1).

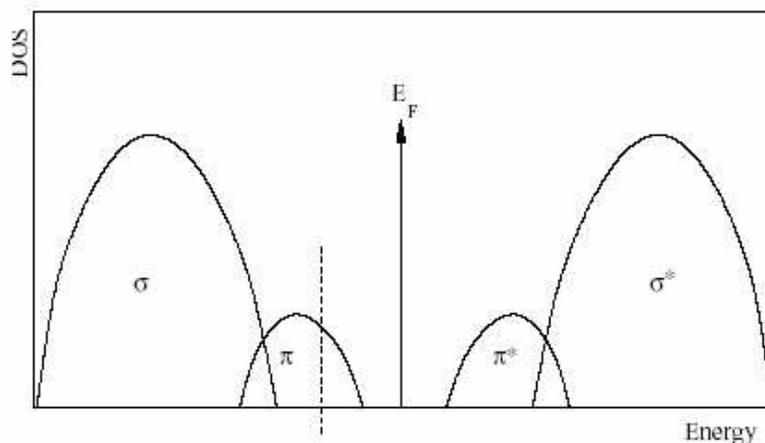


Fig. 1.  $\sigma$  and  $\pi$  bands of amorphous carbon. Topologically determined states can be found at higher energies of the  $\pi$  band (over dashed line).

## 2. Models and methods

### 2.1. Cluster models for calculations

The amorphous carbon and silicon model clusters were constructed on the basis of the continuous random network (CRN) model developed by Wooten et al. [8] (WWW model). There are neither dangling bonds nor coordination defects in the CRN model, and it can be considered as an idealized structure of tetrahedrally coordinated a-Si. This model consists of 216 silicon atoms interacting through the Keating local empirical potential. It seems to be the best CRN model so far since it agrees very well with the experimental on-dimensional radial distribution function of tetrahedrally coordinated amorphous silicon [9]. Recently, some doubts of the validity of WWW model were published [10]. The dangling bonds at the cluster boundaries were saturated by hydrogen atoms. Based on the close physical and chemical analogy between saturated silicon and carbon compounds, our t-C model was built from the a-Si CRN model by rescaling the first neighbor atom-atom distances in a-Si from 2.35 Å to 1.54 Å. This procedure has been proved to yield an adequate model for ta-C, too [11].

In all cases one or two carbon (silicon) atom was substituted by dopants. Nitrogen or boron was incorporated into the ta-C network and phosphorus was used to dope a-Si. The structural change caused by the impurities was investigated. The study was performed by geometry optimization of the dopant and its first neighbors [12], while the amorphous environment was kept fixed. Impurities caused no significant structural rearrangement in the examined amorphous environments.

### 2.2. Calculation methods

Because of the lack of translational periodicity the electronic states of a non-crystalline system cannot be described within the Bloch's theory. Therefore, cluster calculations can be applied to investigate amorphous structures. In our studies HF *ab initio* molecular orbital method with 3-21G-basis set has been applied using the GAMES [13] program package. Our models used for *ab initio* calculations consisted of 45 carbon (silicon) and 52 hydrogen atoms.

In order to eliminate the artifacts caused by the presence of the saturating hydrogen atoms at the cluster boundaries, the Fragment Self-consistent Field (FS) method based on the neglect of diatomic differential overlap (NDDO) approximation has been used [14,15]. According to this method the cluster is divided into two parts: a central part, where the investigated processes take place and an environment (localized region) which perturbs the central part, but does not change significantly

during the processes. The central part is treated by a more accurate quantum chemical method (AM1 in our case) and the localized region is calculated by a less demanding method. Strictly localized molecular orbitals (SLMO) composed from atomic hybrids are built for the atoms of the localized region, and the coefficients of the hybrids are calculated. This is an SCF procedure due to the Coulomb interactions of the SLMOs. Atoms on the boundary between the central and localized regions have hybridized basis functions. Some of them are basis orbitals of the central part, while others are basis orbitals of SLMOs. At the cluster boundaries – instead of saturating hydrogen atoms – pseudo carbon (silicon) atoms with less than four valence orbitals were applied. In our ta-C model the central atoms are within a radius of about 5 Å. The localized region forms a spherical shell with a radius of 4.2 Å and contains 475 atoms. The a-Si model has 110 central atoms forming a sphere with a radius of 7.6 Å and 470 atoms build up the localized region (a spherical shell with a radius of 6.4 Å). The electronic density of states (DOS) curve was obtained from the calculated eigenvalues with a Gaussian line broadening method, using  $\sigma = 0.01$  [7].

### 3. Results and discussion

Model clusters containing two dopants have one of them always at the same position, while the place of the other impurity is changed. Donor impurities are atoms having more valence electrons than the atoms building up the surrounding semiconductor matrix. They supply additional electrons to the density of states. Fig. 2 summarizes the results of three *ab initio* calculations obtained for ta-C. The solid line curve displays the electronic density of states of a ta-C model cluster containing two nitrogen dopants at first neighbor position. As usually, the HF method overestimates the gap. There are two levels in the gap (peak 1 and 4). One of them (1 is a deep level and belongs to the highest occupied molecular orbital (HOMO). It is doubly occupied since the method cluster contains two nitrogen atoms. This state is mainly localized on the dopants. The other midgap state is the lowest unoccupied molecular orbital (LUMO). In our model it can be found just below the conduction band. To keep clear representation, only the HOMO levels of the other two models are displayed on the figure. In both cases the rest of the DOS curves are very similar to the solid line curve. Peak 2 (dashed line) represents the HOMO level of the same ta-C model cluster having two nitrogen atoms at fourth neighbor position. Peak 3 (dashed line) belongs to a ta-C model cluster containing only one N dopant. This case can be considered when the other dopant is in the infinity. The calculations show that the HOMO level changes its position within the gap. One of the possible reasons for this change may be the random structural network, which can cause a small shift of energy levels. Fig. 2 displays, however, a relatively large difference between the numbered HOMO levels (peaks 1, 2 and 3) in the gap, so an additional, more dominant mechanism must exist for this effect. As the distance between dopants increase, the donor level is shifted towards higher energies. Similar results have been obtained also for phosphorus doped a-Si. To examine the effect of doping in our ta-C models on the electronic structure we compare the Mulliken and Löwdin population of the atomic orbitals of the nitrogen atoms to those of the corresponding carbon atoms of the undoped model cluster. Significant increase of the population in the nitrogen valence orbitals was found. The population of the nitrogen 2s orbital increased by 0.39-0.57 electrons as obtained from the Mulliken population analysis and 0.33-0.58 electrons as obtained from the Löwdin analysis, depending on the position of the dopant. The population of the p-orbitals also grew, the increase was 0.08-0.48 (Mulliken) and 0.07-0.46 (Löwdin) electrons.

In the following, the results obtained from FSCF calculations will be presented. As it was written above this method has two advantages: it allow to treat more than 100 carbon or silicon atoms and with pseudo carbon (silicon) atoms at the cluster boundaries we can avoid using saturating hydrogen atoms, which cause spurious charge transfer. We compared the results of the FSCF calculations for several models to those of *ab initio* 3-21G calculations. Considering the relative position of midgap states within a gap, a very good agreement has been found. However, *ab initio* calculations generally give wider gap than the semiempirical FSCF method.

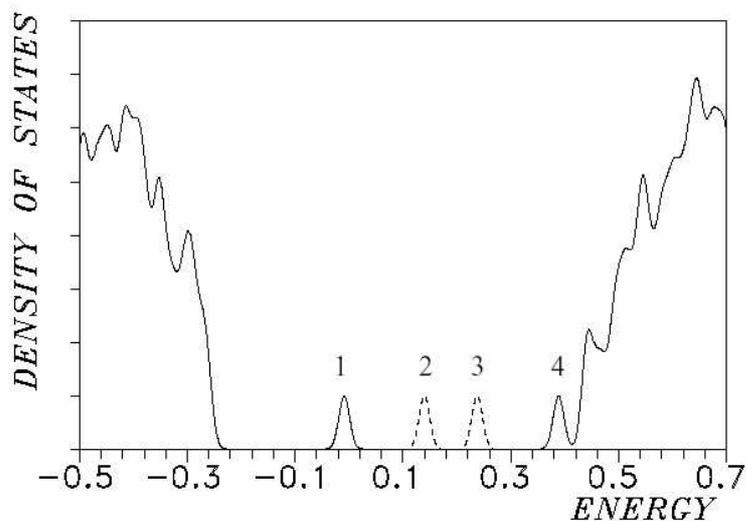


Fig. 2. Electronic DOS (in arbitrary units) of ta-C models as obtained from HF *ab initio* molecular orbital calculations. Solid line: DOS of a model cluster having two N atoms at first neighbor position (Peak 1: HOMO level). Peak 2 and 3 (dashed line) belong to the HOMO levels of clusters with two N at fourth neighbor position and with only one N, respectively. The energy is measured in atomic units.

Similarly to the *ab initio* calculations, in n-doped ta-C there are two levels in the gap. The HOMO level appears as a deep level in the gap, and it is mainly localized on the nitrogen atoms. The other midgap state is the LUMO, which can be found just below the conduction band. In p-doped ta-C the HOMO level shifts into the valence band. The LUMO level, localized on boron dopants, appears as deep level in the gap.

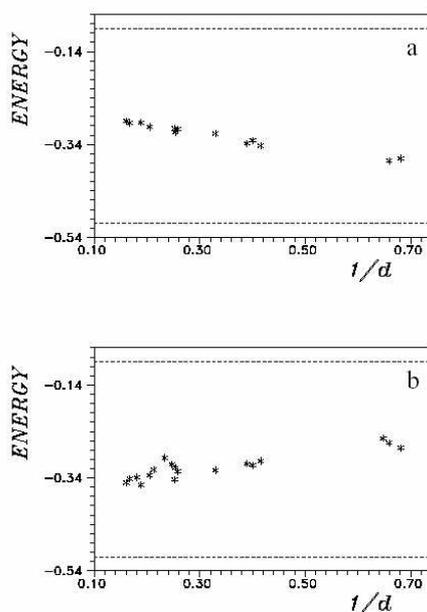


Fig. 3. Energy of the HOMO level in nitrogen doped ta-C models vs. the inverse distance of dopants (panel a) as obtained from FSCF calculations. Panel b: energy of the LUMO level in boron doped ta-C models as a function of the inverse distance of boron impurities. The dashed lines represent the edge of the valence and conduction bands. The energies are given in atomic units, the distances are in Å.

Fig. 3a shows the energy of the HOMO level in nitrogen doped ta-C models. Fig. 3b displays the energy of the LUMO level in the same models doped by boron, as a function of the inverse distance of dopants. A fair linear correlation was obtained in both cases between the energy levels and the inverse distances of the dopant pairs. Beyond this simple relationship we can also draw another conclusion from the result: the shorter N-N distances are energetically favored, so formation of nitrogen clusters is expected in ta-C.

The HOMO level in phosphorus doped a-Si, localized on P impurities is a deep level. The LUMO level shifts into the conduction band. The results for phosphorus doped a-Si as obtained from FSCF calculations are given in Fig. 4. The energies of the HOMO levels are displayed as a function of the inverse distance of dopant pairs. A simple linear relationship has been found between the HOMO energy and the inverse distance of the impurities. Furthermore, the slope of the best-fit line is the same for nitrogen doped ta-C and for phosphorus doped a-Si.

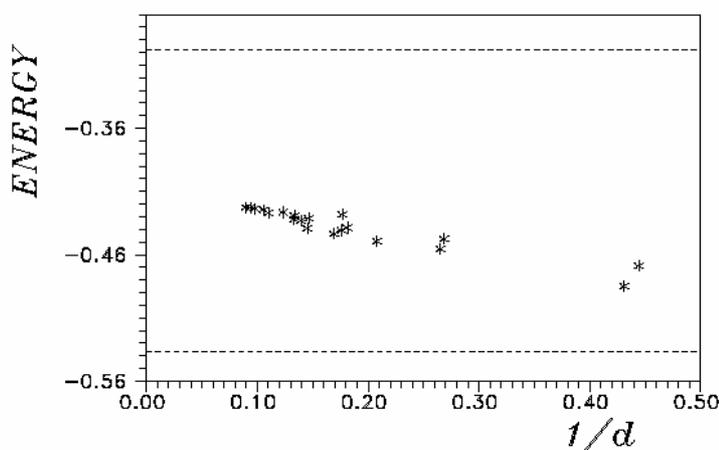


Fig. 4. Energy of the HOMO level calculated by FSCF method in phosphorus doped a-Si models as a function of the inverse distance of impurity atoms. The energies are measured in atomic units, the distances are in angstroms. The dashed lines represent the edges of the valence and conduction bands.

From the results obtained for ta-C and a-Si a general conclusion can be drawn: the relative position of dopant pairs determines the formation of midgap states in tetrahedrally coordinated amorphous semiconductors primarily, and the random network plays only a subordinate role. A simple relationship was found between the HOMO(LUMO) energy ( $E_d$ ) and the inverse distance ( $d$ ) of dopant pairs:  $\Delta E_d \approx k/d$ , where  $\Delta E_d = E_d - E_{d \rightarrow \infty}$ .  $E_{d \rightarrow \infty}$  is the HOMO(LUMO) energy of a model cluster in which the distance between dopants is infinite, and  $k$  is a constant.  $k$  is primarily independent on the dopant and the host matrix. Our calculations give deep donor and acceptor states in all the cases. Increasing the size of the model cluster these states remain at their positions and the gap becomes narrower. Allan et al. [16] have also found a confinement effect for a-Si nanoclusters. Thus, the deep states obtained from our calculations may become shallow in larger models.

#### 4. Conclusions

Investigating different ta-C models doped by nitrogen or boron and a-Si models doped by phosphorus we conclude that in these cases there is no significant structural rearrangement due to substitutional doping. Our results as obtained by both HF *ab initio* 3-21G and FSCF calculations show that it is the relative position of impurity atoms that determines the energy of midgap states in tetrahedrally coordinated amorphous semiconductors and the random network has only subordinate influence on it. A simple linear correlation has been found between the HOMO(LUMO) energy and the inverse distance of dopant pairs. The proportional constant ( $k$ ) is primarily independent on the dopant (N, B in ta-C and P in a-Si) and the amorphous host matrix.

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