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Theory of dopant pairs in four-fold coordinated amorphous semiconductors

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Abstract

The position of energy levels belonging to dopant pairs was investigated in substitutionally p- or n-type doped four-fold coordinated amorphous carbon and silicon by means of Hartree–Fock ab initio and the Fragment Self-Consistent Field method. Our models contain 45 to 583 carbon or silicon atoms. Boron, phosphorus and nitrogen impurities have been incorporated into the amorphous networks. It has been found that the position of midgap states are primarily determined by the separation of the impurity atoms, and the role of the random network is only subordinate. A general relationship is proposed for the determination of midgap energy levels as a function of the distance between dopant pairs investigated for amorphous carbon and silicon. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

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. Recently, a new form of a-C, called tetrahedral amorphous carbon (ta-C), has been grown [1,2] with a major fraction 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.

Doped amorphous silicon (a-Si) has been a subject to intensive experimental and theoretical research since Spear and LeComber [3] reported that they could produce hydrogenated amorphous silicon (a-Si:H) doped with boron and phosphorus. These impurity elements are the most important dopants till now, since they are applied in semiconductor devices. The theoretical studies on this field are motivated by the need for controlling the electronic properties of amorphous semiconductors by doping.

In this paper we study the position of 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

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or five neighbours satisfying the 8-N rule are electrically inactive.

2. Models and methods

Both the amorphous carbon and silicon model clusters were constructed on the basis of the continuous random network (CRN) model developed by Wooten et al. [4]. There are neither dangling bonds nor coordination defects in the CRN model, and it can be considered as an idealised structure of tetrahedrally coordinated a-Si. This model consists of 216 silicon atoms interacting through the Keating local potential [5]. It seems to be the best CRN model so far, since it agrees very well with the experimental one-dimensional radial distribution function of tetrahedrally coordinated amorphous silicon [6]. Based on the close physical and chemical analogy between saturated silicon and carbon compounds, our ta-C model was built from the a-Si CRN model by scaling down the first neighbour atom–atom distances in a-Si (2.35 Å) to 1.54 Å. This procedure has been proven to yield an adequate model for ta-C too [7].

In all cases, one or two carbon (silicon) atoms were substituted by dopants. Nitrogen or boron was incorporated into the ta-C network and phosphorus into a-Si. The structural change caused by the impurities was investigated. It was achieved by geometry optimisation of the dopant and its first neighbours [8], while the amorphous environment was kept fixed. Impurities caused no significant structural rearrangement in the examined amorphous environments.

The electronic states of a non-crystalline system cannot be described within Bloch's theory because of the absence of translational periodicity. Therefore cluster calculations can be applied to investigate amorphous structures. In our studies Hartree–Fock (HF) ab initio molecular orbital method with 3-21G basis set was applied using the GAMESS [9] program package. The dangling bonds at the cluster boundaries were saturated by hydrogen atoms. Our models for ab initio calculations consisted of 45 carbon (silicon) and 52 hydrogen atoms.

To eliminate the artifacts caused by the presence of the saturating hydrogen atoms at the cluster boundaries, the Fragment Self-Consistent Field (FSCF) method based on the neglect of diatomic differential overlap (NDDO) approximation has been used [10,11]. According to this method the cluster is divided into two parts: a central part, where the investigated processes take place and an environment (localised region), which perturbs the central part, but does not change during the processes. The central part is treated by a more accurate quantum chemical method (NDDO/AM1 in our case) and the localised region is calculated by a less demanding method. Strictly localised molecular orbitals (SLMO) composed from atomic hybrids are built for the atoms of the localised 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 the 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 0.5 nm. The localised region forms a spherical shell with a radius of 0.42 nm and contains 475 atoms. The a-Si model has 110 central atoms forming a sphere with a radius of 0.76 nm and 470 atoms build up the localised region (a spherical shell with a radius of 0.64 nm). The electronic density of states (DOS) curve was obtained from the calculated eigenvalues with a Gaussian line broadening method, using $\sigma = 0.01$ [12,13].

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. 1 summarises 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 neighbour position. As usually, the HF method

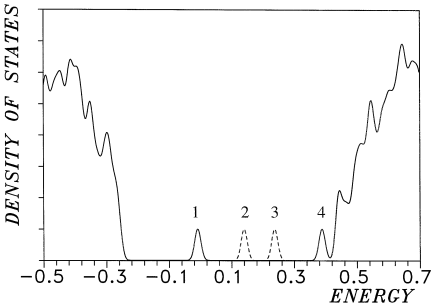

Fig. 1. Electronic DOS (in arbitrary units) of ta-C models as obtained from HF ab initio molecular orbital calculations. Solid line: DOS of a model cluster having two N atoms at first neighbour position (Peak 1: HOMO level). Peaks 2 and 3 (dashed line) belong to the HOMO levels of clusters with two N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

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 model cluster contains two nitrogen atoms. This state is mainly localised 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 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 neighbour 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 placed at an infinite distance. 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. 1 displays, however, a relatively large difference between the numbered HOMO levels (Peak 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 compared 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 0.48 ± 0.09 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 noted above, this method has two advantages: it allows 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 the gap, a very good agreement has been found. However, ab initio calculations generally give a larger gap than the semiempirical FSCF method.

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 localised 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, localised on boron dopants, appears as a deep level in the gap.

Fig. 2a shows the energy of the HOMO level in nitrogen doped ta-C models, Fig. 2b displays the energy of the LUMO level in the same models doped by boron, as a function of the inverse distance of dopants. 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 results: the shorter N–N distances are energetically favoured, so formation of nitrogen clusters is expected in ta-C.

In phosphorus doped a-Si the HOMO level, localised on P impurities, is a deep level. The LUMO

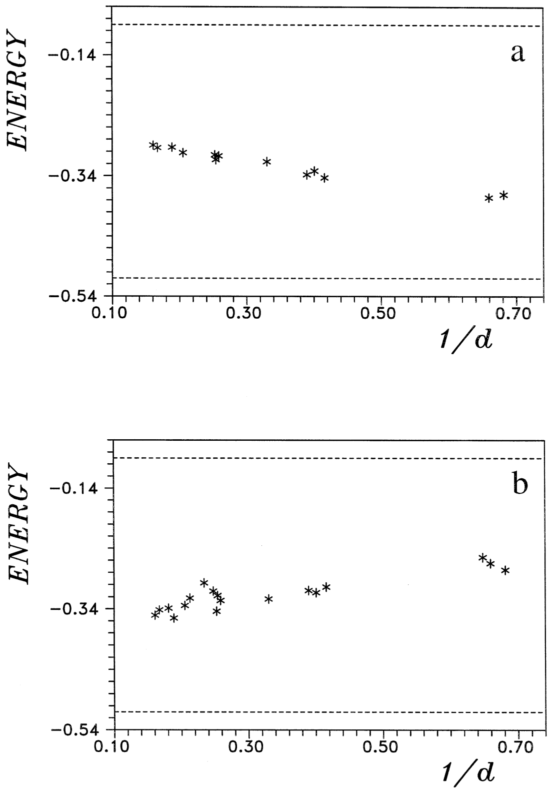

Fig. 2. Energy of the HOMO level in nitrogen doped ta-C models vs. the inverse distance of dopants (panel a) as obtained from FSCF calculations. Panel b: energy of the LUMO level in boron doped ta-C models as a function of the inverse distance of boron impurities. The dashed lines represent the edges of the valence and conduction bands. The energies are given in atomic units, the distances are in Å.

level shifts into the conduction band. The results for phosphorus doped a-Si as obtained from FSCF calculations are given in Fig. 3. The energy 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.

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 pri and the random network plays only a subordinate role. A simple relationship

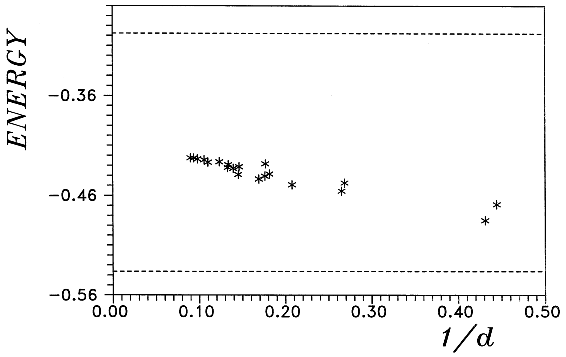

Fig. 3. Energy of the HOMO level calculated by FSCF method in phosphorus doped a-Si models as a function of the inverse distance of impurity atoms. The energies are measured in atomic units, the distances are in Å. The dashed lines represent the edges of the valence and conduction bands.

was found between the HOMO (LUMO) energy (E_d) and the inverse distance (d) of dopant pairs:

$$\Delta E_d \cong K\frac{1}{d},$$

where $\Delta E_d = E_d - E_{d=\infty}$, $E_{d=\infty}$ 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 of the dopant and the host matrix. Nitrogen and boron dopants, which are deep impurities in diamond, are thought to be shallow in ta-C due to the presence of the π states [14]. Our calculations give deep donor and acceptor states in all cases. Increasing the size of the model cluster these states remain at their positions and the gap becomes narrower. Allan et al. [15] have also found a confinement effect for a-Si nanoclusters. Thus, the deep states obtained from our calculations may become shallow in bigger, more realistic 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 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 effect 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. Deep levels appear in the gap in all cases. Increasing the model size these states preserve their positions and the gap becomes smaller. It means that the deep levels may become shallow.

Acknowledgements

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References

[1] P.H. Gaskell, A. Saeed, P. Chieux, D.R. McKenzie, Phys. Rev. Lett. 67 (1991) 1286.
[2] W.I. Milne, J. Non-Cryst. Solids 198–200 (1996) 605.
[3] W.E. Spear, P.G. LeComber, Solid State Commun. 17 (1975) 1193 and private communication.
[4] F. Wooten, K. Winter, D. Weaire, Phys. Rev. Lett. 54 (1985) 1392.
[5] P.N. Keating, Phys. Rev. 145 (1966) 637.
[6] S. Kugler, G. Molnár, G. Pethő, E. Zsoldos, L. Rosta, R. Bellissent, Phys. Rev. B 40 (1989) 8030.
[7] K. Kádas, S. Kugler, Solid State Commun. 102 (1997) 721.
[8] K. Kádas, S. Kugler, Phil. Mag. B 76 281 (1997)
[9] M.W. Schmidt, K.K. Baldridge, J.A. Boatz, S.T. Elbert, M.S. Gordon, J.H. Jensen, S. Koseki, N. Matsunaga, K.A. Nguyen, S.J. Su, T.L. Windus, M. Dupuis, J.A. Montgomery, J. Comput. Chem. 14 (1993) 1347.
[10] G.G. Ferenczy, G.I. Csonka, Fragment SCF program – a semiempirical quantum chemical program for very large electronic systems. The program is available from the authors upon request.
[11] G.G. Ferenczy, J.L. Rivail, P.R. Surján, G. Náray-Szabó, J. Comp. Chem. 13 (1992) 830.
[12] K. Kádas, I. László, S. Kugler, Solid State Commun. 97 (1996) 631.
[13] K. Kádas, I. László, S. Kugler, J. Non-Cryst. Solids 198–200 (1996) 91.
[14] G.A.J. Amaratunga, V.S. Veerasamy, C.A. Davis, W.I. Milne, D.R. McKenzie, J. Yuan, M. Weiler, J. Non-Cryst. Solids 164–166 (1993) 1119.
[15] G. Allan, C. Delerue, M. Lannoo, Phys. Rev. Lett. 78 (1997) 3161.