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MIDGAP STATES IN NITROGEN DOPED DIAMOND-LIKE AMORPHOUS CARBON

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Ab initio and semiempirical quantum chemical methods have been used to investigate the effect of nitrogen doping in amorphous carbon. We propose a simple relationship for the determination of midgap energy levels in substitutionally doped diamond-like amorphous carbon in function of distances between N atoms. ©1997 Elsevier Science Ltd

1. INTRODUCTION

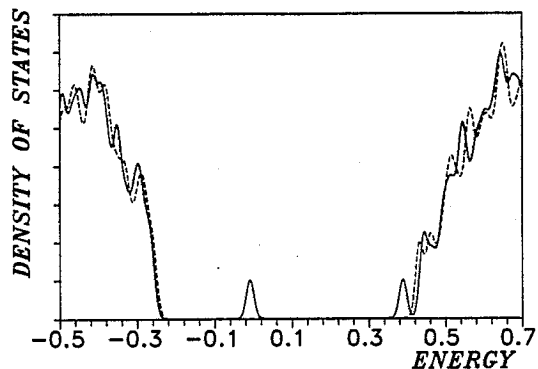
Amorphous carbon (a-C) received considerable interest in the past decade because of technological importance. Various methods have been used to prepare such kind of films. Considering the electronic properties which are in connection with atomic structure having different $sp^2:sp^3$ ratio, these different methods produce a wide range for macroscopic parameters of a-C. Some structural investigations [1,2] indicated the presence of sp^2 sites in a ratio of up to near 100 % in various types of a-C. In the past few years tetrahedrally coordinated a-C (ta-C) with a majority of sp^3 sites [3] attracted much interest because of its extreme hardness, a large band gap over 2 eV, suitability for devices, and ability to accept dopants. It seems to be a realistic goal in the near future to increase the concentration of diamond-like carbon sites in ta-C up to 100 %.

Taking into account the possible applications of diamond-like amorphous carbon as a semiconductor the controlled variations of the electronic structure by doping have a primary importance. It has been shown that successful substitutional doping of ta-C using nitrogen is possible without changing the local geometrical arrangements. In this paper we examine the electronic properties of ta-C with nitrogen incorporation and the influence of the interaction between dopants on the donor levels appearing in the gap. Some calculations were carried out on a-C as well.

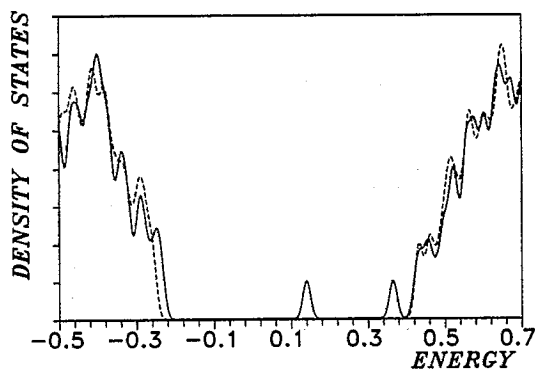
2. METHODS AND MODELS

Hartree-Fock (HF) *ab initio* and AM1 semiempirical calculations were carried out using the GAMESS program package [4]. The standard STO-3G minimal basis set was applied in the *ab initio* calculations. The electronic density of states (DOS) curve was obtained from the calculated one electron energies with a Gaussian line broadening method, using $\sigma = 0.01$ a.u. [5]. The dangling bonds at the cluster boundary were saturated by hydrogen atoms. We have studied several cluster structures of carbon atoms.

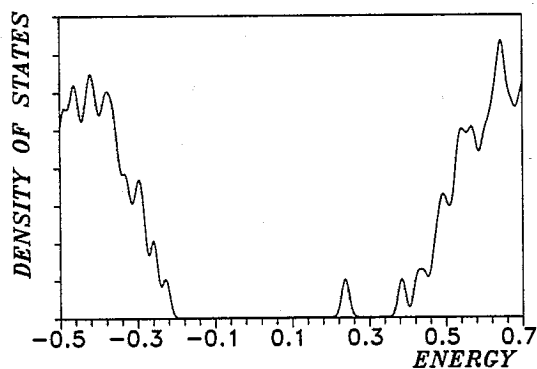
The ta-C model clusters containing only sp^3 sites have been constructed on the basis of a continuous random network model (CRNM) for a-Si and for ta-C by Wooten et. al. [6]. Based on the close analogy between saturated carbon and silicon compounds we may suppose that scaling down the first-neighbour atom-atom distances in a-Si from 2.35 Å to 1.54 Å yields an adequate model for ta-C, too. Each of our model clusters consisted of at least 45 but not more than 82 carbon atoms and 52-78 hydrogen atoms located at the surface of the clusters. Additional calculations were carried out on a model [7] containing a small fraction of sp^2 type carbon atoms and 57 tetrahedrally coordinated C atoms. 66 hydrogen atoms have been used to model the bulk at the boundary of the cluster. In all cases we replaced one or two carbon atoms by nitrogen. There was no significant structural relaxation effect after substitution. Similar conclusion was reported earlier from calculations based on density-functional theory [8].



(a)



(b)



(c)

Fig. 1. The density of states of a model having 3 different N substitutional configurations. Panels (a) and (b) show the DOS when two dopants are in first and fourth neighbour positions, respectively. Panel (c) belongs to a model containing only one nitrogen atom.

3. RESULTS

First, we consider models containing only fourfold coordinated carbon and nitrogen atoms. HF *ab initio* and semiempirical calculations were performed on

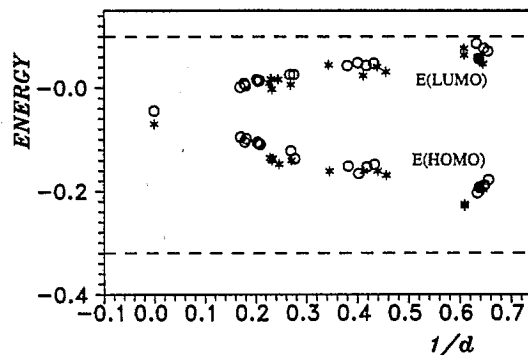


Fig. 2. HOMO and LUMO energies vs the inverse distance of the N pairs. The dashed lines represent the edges of the valence and conduction bands.

several models. Figure 1 compares the density of states of one model having 3 different substitutional configurations. The energies are measured in atomic units, the distances in Å and the density of states is given in arbitrary units. In all cases the gap is greater than expected, according to the well-known property of the HF method. Panel (a) shows the electronic DOS in the case when the two dopants are in first neighbour site (solid line curve). The dashed line curve belongs to the model containing no nitrogen atoms. On panel (b) the two nitrogen atoms are fourth neighbours. The definition of solid and dashed lines is the same as on panel (a). The density of states curve on panel (c) belongs to a model containing only one nitrogen atom. We consider it that the distance between two dopants is infinite. All the three configurations were calculated by HF *ab initio* method and one N atom was always at the same position.

Donor impurities are atoms that have higher chemical valence than the atoms making up the pure host environments. They supply additional electrons to the density of states. In our cases there are two levels in the gap. One of them is doubly occupied because the models contain a N pair, and it belongs to the highest occupied molecular orbital (HOMO). The other level is the lowest unoccupied molecular orbital (LUMO). These levels are moving at the different configurations. Because of the random structural networks these energy levels may vary a little bit from one site to another. Figure 1 illustrates a relatively large difference between energy levels in the gap, so it is likely to be an additional more dominant mechanism for this effect.

From further investigations we concluded that the variation of the midgap states are in connection with the N atomic distances. A serie of AM1 calculations was carried out on two models. The difference between clusters is the position of the fixed N (open circles and asterisks on Fig. 2). A fair linear correlation was ob-

tained between the energy levels and the inverse distance of the N pairs as is shown on Figure 2. Each open circle and asterisk at lower position represent an energy level of highest doubly occupied molecular orbital due to a cluster model while the upper set of symbols belongs to the lowest unoccupied states. At zero inverse distance both open circles and asterisks are at the same position, which represents a single occupied level. The same relationship was obtained by using HF *ab initio* method. The calculations also show that among the different N–N distances the shorter ones are energetically favoured, so formation of nitrogen clusters is expected.

In case of amorphous carbon the gap is narrower because of π electrons [5]. Our calculations provide an evidence for the fact, that substituting sp^3 type carbons by a pair of nitrogen atoms the midgap states move similar way as in ta–C case, but in function of $sp^2:sp^3$ ratio the bandtail can overlap the midgap states.

It has been shown that successful doping of ta–C using phosphorus is also possible without significant changing of of atomic arrangement [9]. We have already made calculation on substitutionally phosphorus doped ta–C and we found the same linear relationship between energy levels and inverse distances [10].

4. CONCLUSION

Investigating different models of ta–C we conclude that substituting carbon atoms by nitrogen there is no significant geometrical rearrangement after the relaxation. Our results show that the relative position of the dopants determines the formation of midgap states in doped amorphous carbon primarily, and the random network has only subordinate influence on it. We have found a simple linear relationship between the HOMO

(LUMO) energy levels and the inverse distance of the dopants in highly sp^3 bonded amorphous carbon. We have obtained that the formation of nitrogen clusters is energetically favoured.

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