

Impurity levels in phosphorus- and boron-doped amorphous silicon

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ABSTRACT

The AM1 semiempirical quantum-chemical method has been used to investigate phosphorus and boron-doped amorphous silicon. A simple relationship for the determination of midgap energy levels is proposed for substitutionally doped amorphous silicon as a function of distances between dopants.

§1. INTRODUCTION

More than 20 years ago Spear and LeComber (1975) reported that they could dope hydrogenated amorphous silicon (a-Si:H) by boron and phosphorus. Since that time the electronic structure of doped amorphous silicon (a-Si) has been investigated by means of an enormous number of experimental and theoretical methods (Street 1991). The reason for the intense interest is the possibility of controlling the electronic properties of these materials. Impurities such as boron and phosphorus remained the most important dopants until now because they are used for the n- and p-type layers in different devices.

In this brief paper, only the fourfold-coordinated phosphorus and boron are studied in the a-Si environment since the impurities having three or five neighbours satisfying the 8-*N* rule are electrically inactive. We investigate the influence of dopant pairs on the electronic density of states (DOS).

§2. METHODS

Amorphous structures cause more difficult problems for theoretical investigations than crystalline systems do. Because of the absence of translational periodicity the electronic states cannot be described within Bloch's theory. Quantum-chemical cluster calculations are more useful tools for investigating such systems. For studying doped a-Si, Hartree-Fock (HF) AM1 semiempirical calculations were carried out using the MOPAC program package (Stewart 1989). The electronic DOS curve was obtained from the calculated one-electron energies with a Gaussian line-broadening method, using $\sigma = 0.003$ au. The dangling bonds at the cluster boundaries were saturated by hydrogen atoms. Earlier a group in Mexico made a similar investigation on a-Si doped with various group-III and group-V elements using the pseudopotential self-consistent field (SCF) HF methods (Sansores *et al.* 1992, Cogordan *et al.* 1995).

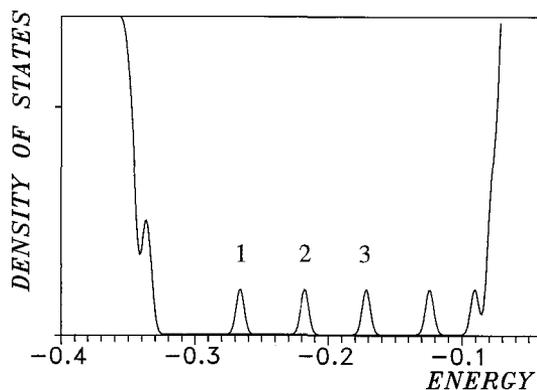
§3. MODEL

In our calculations we have used the continuous-random-network (CRN) model for the structure of pure a-Si. Neither coordination defects nor dangling bonds exist inside the model. The CRN model can be considered as an idealized structure of tetrahedrally coordinated a-Si. The finite clusters have been constructed on the basis of a CRN model for a-Si by Wooten *et al* (1985). This model consists of 216 silicon atoms interacting through the Keating (1966) local potential. It seems to be the best CRN model at present since it reproduces the experimental one-dimensional radial distribution function of fourfold-coordinated a-Si excellently within the interval of 0–8 Å (Kugler *et al.* 1989). Our model contains 82 silicon and 78 hydrogen atoms located at the surface of the clusters. In all cases we replaced one or two silicon atoms by phosphorus (boron). There was no significant structural relaxation effect after substitution in the n-doped case. Boron substitution led to noticeable geometrical changes; the bond distances changed by maximum 10%. During geometry optimization the coordinates of the dopant and its first neighbours were relaxed and the environment was kept fixed.

§4. RESULTS

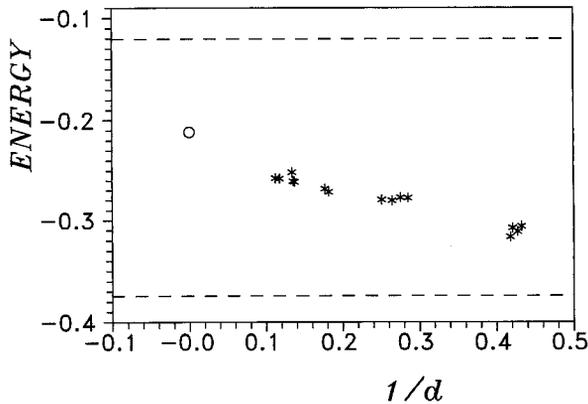
Semiempirical AM1 calculations were performed on a-Si models doped with phosphorus and boron. Figure 1 compares the midgap states of an a-Si model doped with two (one) phosphorus atoms, having three different substitutional configurations. One of the dopants was always at the same position. The energies are measured in atomic units and the DOS is given in arbitrary units. To keep a clear representation, only the DOS of the model having two dopants at the first-neighbour position and the midgap states of the other two models are shown in fig. 1. The peaks labelled with numbers represent how the donor level shifts according to the relative position of dopants. Peak 1 belongs to the a-Si model in which the two dopants are first neighbours. Peak 2 displays the donor level of a model with dopants at fourth-neighbour positions. In the case of peak 3 the model contains only one phosphorus atom. The second dopant is considered to be at infinity.

Fig. 1



The gap region of the DOS of a-Si models. Peaks 1 and 2 represent the donor levels of models in which the two dopants are first and fourth neighbours respectively. Peak 3 displays the donor level of an a-Si model substituted by only one phosphorus atom.

Fig. 2



HOMO energies of n-doped a-Si against the inverse distance of phosphorus pairs: (---), edges of the valence and conduction bands.

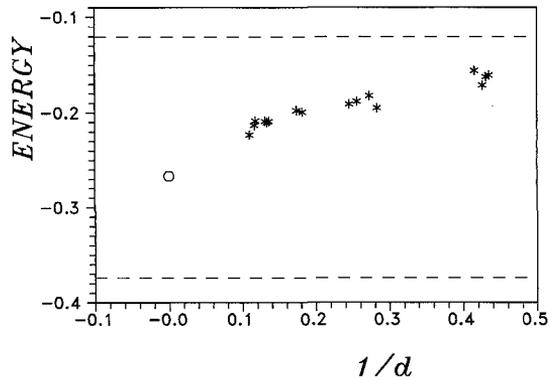
Donor impurities supply additional electrons to the DOS. In our n-doped models there are two levels in the gap. One of them belongs to the highest, doubly occupied molecular orbital (HOMO), while the other level is the lowest unoccupied molecular orbital (LUMO). These levels are moving at the different configurations. Because of the random structural network these energy levels may change their place slightly within the gap; so for this a more dominant mechanism must exist.

Our further calculations prove that the position of the midgap states are determined by the phosphorus atomic distances; a fair linear correlation was obtained between the energy levels and the inverse distance of the phosphorus pairs as is shown in fig. 2. Each asterisk displays the result of a closed-shell HF calculation carried out on a given configuration. The distances are measured in ångströms. The open circle at zero inverse distance represents a single occupied level derived by an open-shell calculation because this model contains only one phosphorus atom. The result from an open-shell calculation is generally not comparable with those from closed-shell calculations.

Models of a-Si substitutionally doped with boron have also been investigated. Boron is an acceptor impurity having a lower chemical valence than the surrounding silicon matrix. Similarly to the previous series a set of different doped configurations have been calculated. Two boron atoms have been incorporated into the model clusters so that one of the dopants was always at the same position. Before the SCF calculations, geometry optimization was performed on all models and the atomic positions have changed slightly.

Figure 3 shows a simple linear relationship between the acceptor level (LUMO) energies and the inverse distance of boron impurity atoms, similarly to the n-doped case. At zero inverse distance the open circle shows a single occupied level having the same difficulty as in the phosphorus-doped case. If we turn fig. 3 upside down it is very close to fig. 2. This indicates that, in phosphorus- and boron-doped a-Si electron-hole symmetry exists.

Fig. 3

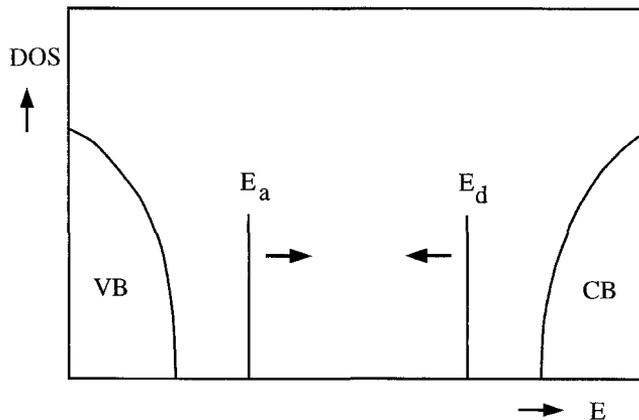


Acceptor levels of p-doped a-Si against the inverse distances of boron dopants. The definition of the broken lines is the same as in fig. 2.

§5. CONCLUSIONS

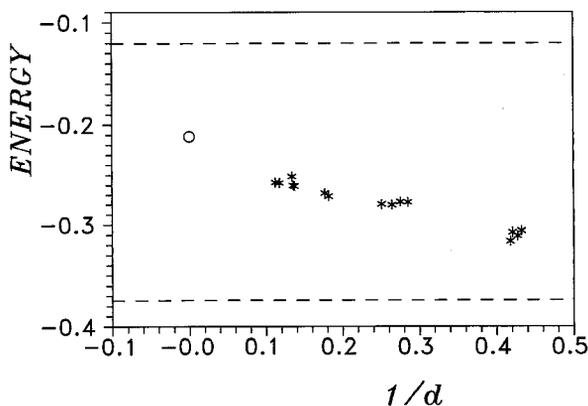
Studying phosphorus- and boron-doped a-Si models, we conclude that substitution of silicon atoms by phosphorus impurities results in no significant geometrical rearrangement after relaxation; however, boron dopants cause marked changes in the local geometry. The midgap states are primarily determined by the relative position of dopants, and the role of the random network is only subordinate. A simple linear relationship was obtained between the HOMO (LUMO) energy levels and the inverse distance of dopants in n- and p-doped a-Si. As the distance between the dopants decreases, the donor (acceptor) levels shift towards the valence (conduction) band as illustrated in fig. 4.

Fig. 4



Schematic representation of the electronic DOS of doped a-Si. E_a denotes an acceptor level, and E_d a donor level. VB stands for the valence band, and CB for the conduction band. The arrows indicate the direction of donor (acceptor) level shifting as the distance of the dopants decreases.

Fig. 2



HOMO energies of n-doped a-Si against the inverse distance of phosphorus pairs: (---), edges of the valence and conduction bands.

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