DENSITY OF STATES OF AMORPHOUS HYDROGENATED Si

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Abstract. - In this paper, we analyze the electronic density of state of amorphous semiconductors with a dangling bond, either unsatisfied or satisfied by a monovalent atom (H, Cl, F ...) as it is now currently achieved. The electronic properties are calculated within the tight binding framework. In the simplified case of the Bethe lattice, exact formulas are obtained. We observe an isolated dangling bond state in the gap, with a weight depending on the gap width. The density of states is also obtained when an adatom is covalently attached to the dangling bond. The range of parameters required for emptying the gap is analyzed. Finally more sophisticated numerical calculations are done on a realistic hand built SOD atom model.

1. Introduction

It is well established that amorphous group IV semiconductors have bad electrical properties because their gap has a too large density of states; in particular they cannot be doped. The presence of bonded hydrogen reduces the density of localized states in the mobility gap to values less than $10^{19} \text{ cm}^{-3} \text{ eV}^{-1}$ and is essential for doping as demonstrated by Spear and coworkers /1/.

The aim of this paper is the analysis of the electronic density of states (d.o.s.) of non ideal amorphous semiconductors i.e. with an isolated or a double dangling bond (d.b.). We also consider the case where the d.b. is satisfied by a monovalent atom e.g. H.

A tight binding or LCAO formalism is used: it involves the 3s and 3p valence electrons of Si. Such a simple description is particularly useful in the case of strongly disordered system where more sophisticated band structure calculations cannot be applied. The tight binding interaction parameters are obtained from more sophisticated band structure calculations on crystalline structures [e.g. see the values on Fig. 3]. The valence band is then correctly reproduced but the conduction band - corresponding to extended electronic states - is poorly described.

The paper is divided into two sections: in section 2 exact results are obtained in some schematic situations. In section 3 the local density of states is calculated on various orbitals of a hand built structural model and the results are discussed in term of the experimental data.

2. Exact results for the isolated, double and hydrogenated dangling bond

It is well known that the local density of states in tight binding systems depends primarily on the local environment of the atoms (see also section 3). Consequently a model that describes correctly the local coordination and position of the atoms gives the trends of the electronic properties, at least in the valence band and the gap region.

A Bethe lattice (B.l.) is a structure with a given coordination N everywhere but with no closed rings of atoms /2/. The advantage of the Bethe lattice is that exact formulas can be simply obtained and they allow a rapid analysis when varying the parameters of the problem. It is closer to reality than the molecular model; the valence and conduction band have a finite bandwidth in the B.l. approximation whereas in the molecular model the bands are reduced to energy levels. Thus the B.l. allows a discussion of the absorption of gap states in the bands e.g. as shown on Fig. 1. However the B.l. bandwidth suffers from a narrowing of the band due to the absence of closed rings. As the shortest rings are sixfold in the diamond lattice (fivefold in the amorphous structure), the B.l. approximation is more accurate in open structures than in compact phases (FCC ...) where threefold rings are present.

In a simple tight binding description (usually referred to as the Weaire-Thorpé hamiltonian /3/) with only two resonance (or hopping) integrals: β (interatomic) between two orbitals pointing in the direction of the bond and ϵ ($= (E_p - E_s)/N$, intraatomic) between two equivalent sp^{N-1} orbitals on the same atom of coordination N , the local Green function (resolvent) on the dangling bond takes the simple analytic form

$$G_{db}(z) = \frac{1}{z - \frac{(N-1)\epsilon^2}{z - (N-2)\epsilon - \beta^2 G_{db}(z)}} \quad (1)$$

It is easily demonstrated that a dangling bond peak appears in the gap at the energy $E_0 = (E_s + (N-1)E_p)/N$, independently of the β parameter, with a weight

$$W = 1 - (N-1)\epsilon^2/\beta^2 \quad (2)$$

for $\beta\epsilon \gg N-1$, i.e. in the semiconducting region. Let us notice in addition that as the dangling bond state falls above the Fermi level, charge transfer effects should lower the dangling bond level, except in the case of the linear chain ($N=2$).

Whether or not a double dangling bond exists in a-Si is an open question: at least the existence of SiH_2 has been proved by infrared spectroscopy. The electronic states of a double sp^3 d.b. differ qualitatively from the isolated d.b. A state in the gap moves from ϵ to $-\epsilon$ (Fig. 1) with a weight increasing like (2). A second non resonant localized state appears at E_p with the constant weight 0.5. The Green function writes:

$$G_{2db}(z) = \frac{1}{2} \frac{1}{z-\epsilon} + \frac{1}{2} \frac{1}{z-\epsilon-2\epsilon^2} \frac{1}{z-\beta^2 G_{db}(z)} \quad (3)$$

Fig. 1 - Position of the bands and dangling bond states.

Fig. 2 - Variation of the number of localized states in the gap, /4/

It is well established that the presence of bonded hydrogen (or other elements) in a-Si is essential for the electrical and doping properties. It is easy to write down a general formula relating the Green function on H to the d.b. Green function

$$G_H(z) = \frac{1}{z - \epsilon_H - \beta'^2 G_{db}(z)} \quad (4)$$

where β'^2 is the effective interaction between H 1s and the dangling orbital of Si. When varying ϵ_H and β , one observes the existence of 0, 1 or 2 states in the gap. Fig. 2 shows which values of ϵ_H and β are necessary for emptying the gap. One sees that for physical values of β (3 - 4 eV) the d.b. state enters the conduction band /4/.

3. Density of sp states on a realistic structure

We have built a realistic model of amorphous fourfold coordinated Si containing 500 atoms around an isolated dangling bond. Seven complete shells of nearest neighbours are developed around the central atom. We have checked that the pair correlation function ($r_1 = 2.35 \text{ \AA}$, $\sigma_1 = 0.06 \text{ \AA}$, $r_2 = 3.82 \text{ \AA}$, $\sigma = 0.21 \text{ \AA}$) and the angular distribution ($\theta = 109.11^\circ$, $\sigma = 8.54^\circ$) fit the experimental data on a-Si.

A tight binding hamiltonian is used to determine the electronic properties of the system: nearest neighbour interactions are taken from Chadi et al. /5/; the values are given on Fig. 4. As no relaxation of the model was performed, we ignored the variation of the parameters with interatomic distance. The absence of translational invariance requires the use of special techniques of calculation of the d.o.s., described elsewhere /6/. The first 28 moments of the d.o.s. (twice the number of shells) are computed; this corresponds to an energy resolution of the spectrum of the order of 1 eV. Fig. 4 shows the local d.o.s. on various orbitals of the atom bearing the d.b. as well as the average $n_{sp}(e)$. The d.b. points in the z direction and the backbonds are three coplanar sp^2 hybrids. The local d.o.s. $n_{pz}(E)$ on the p_z (unsatisfied) orbital shows a narrow peak at E_p , i.e. just below the conduction band edge, as expected from the local geometry. As we learned from the B.I. results, a sp^3 type dangling bond had given a peak at the lower energy $(E_s + 3 E_p)/4$.

Fig 3

Fig 4

The $n_x(e)$ and $n_y(e)$ densities of states are very similar to the corresponding p density of states in fourfold coordinated system (crystalline or amorphous). They show that the p character of the states increases with increasing energy in the valence and the conduction bands. By contrast, the bottom of the bonds are s type as shown on $n_s(E)$. The top curve of Fig. 3 is the average of the curves drawn below: it is characterized by a reduction of the peak at the top of the valence band (relatively to the crystal) and the appearance of the d.h. peak below the conduction band edge.

The hydrogenation of the d.h. (or its passivation by any other element) has a definite effect on the gap states. For the values of the H-Si interaction parameters mentioned on Fig. , the p dangling bond states are pushed in the conduction band. In addition, the local d.o.s. on the H atom show a three peak structure, two of them are at -5eV and -2.5eV in the valence band. They can be related to the states observed in photoemission experiments /7/. A smaller value of the interaction parameter (e.g. $ss\sigma = -1.5\text{eV}$, $sp\sigma = 2.5\text{eV}$) produces neither the emptying of the gap nor the splitting of the H peak in the valence band.

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