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Section 7. Density of states: deep defects and band tails

WEAK BONDS AND ATOMIC CHARGE DISTRIBUTION IN HYDROGENATED AMORPHOUS SILICON

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Semiempirical molecular orbital calculations were carried out in order to estimate static charge fluctuation in a-Si:H. We derived an empirical formula determining Si-Si bond lengths as a function of atomic net charges. It was found that Si-Si bonds adjacent to Si-H bonds are longer, i.e. weaker, than others.

1. INTRODUCTION

Charge fluctuations[1,2] and light-induced phenomena[3–5] in hydrogenated amorphous silicon (a-Si:H) received much attention in the literature. It has been suggested that the Si-Si bond adjacent to the Si-H bond becomes weaker than others and thus may be broken by prolonged illumination to create dangling bonds[4]. This may be the basis of the Staebler-Wronski effect[6], a reversible increase in the density of paramagnetic defects in a-Si:H caused by exposure to light.

This paper addresses the problem of static charge fluctuation and ground-state Si-Si bond strength on the basis of semiempirical molecular orbital calculations. Bond strength is characterized by the Si-Si distance since, as it is known[7], an inverse relation exists between these two quantities.

2. METHODS

Atomic net charges for large clusters were calculated by a semiempirical method developed recently[8,9]. A cluster of bulk atoms is described by a wave function expanded in terms of strictly localized molecular orbitals (SLMO). These are linear combinations of sp^3 atomic hybrids directed along the corresponding bond axis and subsequently orthogonalized. Hybrid coefficients are derived through solution of a coupled 2x2 secular equation which is based on the diagonalization of a valence electron effective Hamiltonian. The method is based on the CNDO approximation and parametrization[10]. In order to determine equilibrium geometries and to find empirical bond length-atomic net charge relations we applied the MNDO method[11] with the PM3 parametrization[12,13].

Though atomic net charges are not physically observable quantities therefore it has no sense to speak about their "accuracy", it is

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not without interest to compare charges obtained by various methods. In a recent publication[14] we have shown that silicon and hydrogen net charges, as obtained by the SLMO and *ab initio* 4-31G methods, show a fair correlation. An excellent correlation exists also between CNDO and SLMO, furthermore, between MNDO/PM3 and SLMO charges as shown by the following linear regression equations

$$q_{CNDO} = 1.07\, q_{SLMO} \quad (n = 33,\ s = 0.021)$$

$$q_{MNDO} = 0.98\, q_{SLMO} \quad (n = 56,\ s = 0.034)$$

The MNDO/PM3 method fairly reproduces experimental bond lengths. We obtained 240 (235) pm for Si-Si and 149 (148) pm for Si-H distances in Si_2H_6 (experimental values in parentheses). In the light of the fair agreement with experiment we may state that our conclusions drawn from theory are reliable.

3. CHARGE FLUCTUATION

In order to determine charge fluctuation in a-Si:H we used Wooten's Continuous Random Network (CRN) model as a basis[15]. We performed SLMO calculations on some clusters cut out from the 216 atom CRN model and modelled the bulk by pseudosilicon atoms as in our previous work[9], then replaced one or more of these pseudoatoms by hydrogen. We have found that our quantum chemically determined net charges can be approximated by the following empirical formula[9]

$$q_M = A.S + B \qquad (1)$$

A is a constant (-0.69 millielectrons/degrees), S is the combination of bond-angle distortions

$$S = (2\sum_{i=1}^{6} d\theta_i - \sum_{j=1}^{12} d\theta_j)$$

where $\theta_i = XMY <$ and $\theta_j = MXZ <$ if the angle exists, elsewhere it is equal to zero (X and Y are bonded to M, Z to X or Y).

The term B represents the inductive effect of hydrogen. SLMO calculations on crystal-like models show that this does not extend beyond the second neighbour of the hydrogen atom, i.e. putting q_H = -91, q_{Si_1} = 94, q_{Si_2} = -1 millielectrons we obtain a neutral cluster which is transferable from one model to the other. Thus, B is equal to q_{Si_1} if M is adjacent to hydrogen, to q_{Si_2} if it is the second neighbour and zero otherwise. Comparing Eq. (1) to SLMO calculations on some model clusters we obtain a fair agreement. Now applying eq. (1) to the 216 atom cluster of Wooten put by a varying number of hydrogen atoms upto 20 atomic percent we obtain the charge fluctuation as a function of hydrogen content (cf. Fig. 1).

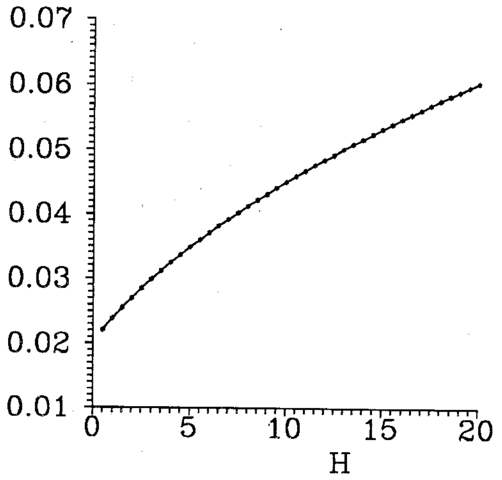

FIGURE 1

Charge fluctuation [in electrons] *vs.* H content [in %].

Our values are compared to experiment investigation[2]. The measured charge transfer $dq_H = 0.15$ electrons from silicon atoms to H, which is larger than expected from Pauling's electronegativy (0.02 electrons) but the measurement overestimates the charge transfer[9]. We feel that our calculated value $dq_H = 0.091$ electron is more realistic.

4. BOND LENGTHS

We made an attempt to check the statement on the weakening of Si-Si bonds adjacent to the Si-H bond[4] by MNDO/PM3 molecular orbital calculations on small silanes (Si_2H_6, Si_3H_8, Si_7H_{16} and Si_8H_{18}). Considering geometry optimized structures of the above molecules we have found that the equilibrium bond length in the ground state depends on the number of hydrogen atoms attached to one or the other silicon forming the Si-Si bond. This is due to the accumulation of positive charges on silicon caused by the inductive effect of hydrogen. We found the following linear relationship between Si_a–Si_b bond lengths and the sum of silicon net charges:

$$d_{Si_aSi_b} = 0.038\ \text{Å}/e\ (q_{Si_a} + q_{Si_b}) + 2.37\text{Å}$$

$$(n = 16, s = 0.002)$$

The relationship is graphically displayed in Fig. 2.

An indirect indication for (H)Si-Si bond weakening is given in Fig. 3 where we displayed the Si-Si radial distribution function as obtained from the geometric model for a-Si:H (12 % H) by Mousseau and Lewis[16]. Compared to pure a-Si a slight shift toward larger Si-Si distances is observed. The average length for Si-Si bonds adjacent to hydrogen is 239 pm which is larger than the average for the whole model (235 pm).

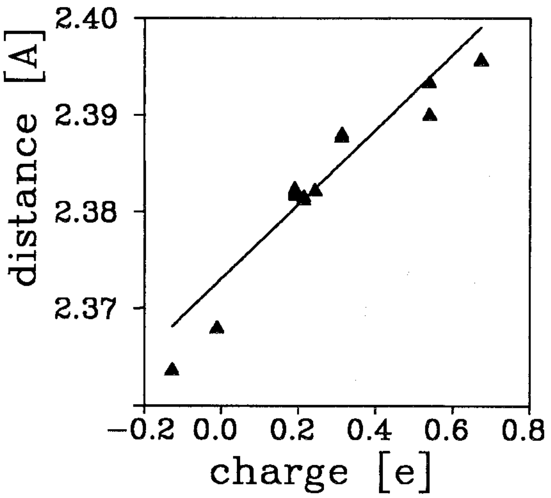

FIGURE 2

Bond distances [in Angstrom] *vs.* charges [in electrons].

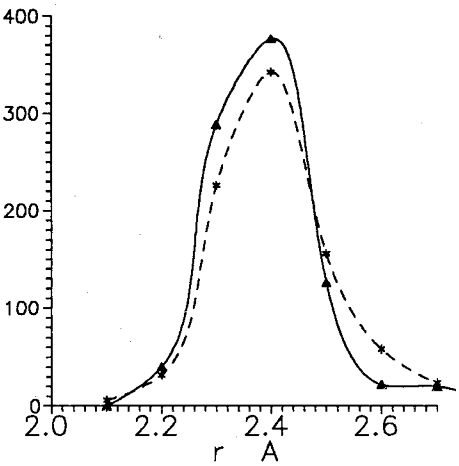

FIGURE 3

The first neighbour peak of radial correlation functions of pure a-Si (dashed line) and a-Si:H [12% H] (solid line).

Though the above statements hold for the ground state there is some evidence that they can be generalized for the first excited state. This is supported by the self-consistent local density functional calculations of Jones and Lister[5] who compared Si-Si bond lengths in Si_8H_{18} and Si_7H_{16} clusters derived from Si_2H_6 by replacing all and all, but one, hydrogen atoms by SiH_3 groups, respectively. In the first excited state the Si-Si bond lengthens from 327 to 332 pm. Our MNDO/PM3 calculations gave for the same bond lengths in the ground state 236.4 and 236.8 pm, respectively. Thus, lengthening is much more moderate but shows the same tendency both in the ground and first excited states.

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