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HYDROGEN CONTENT DEPENDENCE OF THE OPTICAL ENERGY GAP IN a-Si:H

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A theoretical attempt has been made on the hydrogen content dependence of the optical energy gap in a-Si:H using a simple tight-binding model. The interband optical absorption coefficient is calculated by CPA. It has been shown that energy spectra of the joint density of states shift to the higher energy side in parallel with increasing hydrogen content. For the comparison with the realistic line shape of experimentally observed absorption spectra, the effect of the Lorentzian distribution of the Si-H bond states is examined.

1. INTRODUCTION

It has been shown by the experimental approach that the optical energy gap E_g^{opt} in a-Si:H and hydrogen content have a correlation shown in figure 1. Moreover, the value of E_g^{opt} in zero hydrogen limit is much larger than that of band gap of crystalline silicon. There have been more than several theoretical studies on energy spectra of the electronic density of states (DOS) of a-Si:H[1]. Papaconstantopoulos and Economou demonstrated the widening of the band gap with increasing hydrogen content for a model of a-Si:H using the tight-binding method[1]. This result is in agreement with the recession of the top of the valence band observed in photoemission experiments[2] and suggests that E_g^{opt} depends on the hydrogen content. However, no clear explanation of the above mentioned correlation between E_g^{opt} and hydrogen content in a-Si:H has been made so far. The aim of this article is to study this hydrogen content dependence of E_g^{opt} in a-Si:H. We take a simple tight-binding model consisting of bonding and antibonding states, while the effects of the hydrogen termination is taken into account by a deep(high) bonding(antibonding) states of Si-H bonds effectively. The effect of the hydrogen content on the electronic states is treated

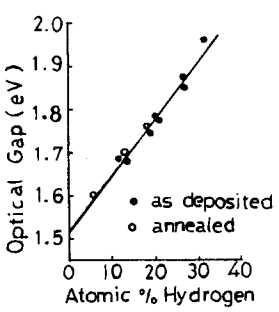

FIGURE 1
Relationship between hydrogen content and the optical energy gap

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with a concept of site-perturbed randomness using the Coherent Potential Approximation(CPA). The interband optical absorption coefficient is calculated in two ways: the calculation of the joint density of states for the non-direct transition and the first principle calculation with the two-particle Green's function method[3].

2. MODEL

We consider a simple model for the amorphous silicon that the valence(conduction) band is produced by the bonding(antibonding) states of Si-Si bonds. The effect of topological disorder of the system is not discussed directly here. Hydrogen incorporated in a-Si:H acts as a terminator of the Si dangling bonds. New states appear in the lower part of the valence band in photoemission spectra due to the bonding of silicon and hydrogen[2]. In the conduction band, Si-H antibonding states are predicted from photoconductivity measurements[4]. Thus the effects of hydrogen on the electronic states of a-Si:H can be taken into account by a deep(high) Si-H bonding(antibonding) states. For simplicity, the fictitious bonding and antibonding states are introduced into the original covalent bond network at the places where hydrogen termination occurs, analogus to the hydrogen saturated vacancy model of Papaconstantopoulos and Economou[1]. Si-H bonds have the larger bonding-antibonding gap than Si-Si bonds in this model, similar to the quantum well model[5]. There are potential fluctuations in bonding (antibonding) states according to whether the bond is the Si-Si bond or the Si-H bond. The CPA is a useful method to treat such a site-perturbed disordered system.

3. FORMULATION

We adopted the following two-band tight-binding Hamiltonian:

$$H = H_v + H_c ,$$

$$H_\mu = \sum_n |n\mu\rangle \varepsilon_n^\mu \langle n\mu| + \sum\sum_{nm} |n\mu\rangle t_{nm}^\mu \langle m\mu| \quad , \quad (\mu = v, c)$$

where $|n\mu\rangle$ denotes a state at the n-th bond in the band , ε_n^μ the randon site energy and t_{nm}^μ the transfer integral. The coupling between the band v and c is not considered. The dipole operator $\Pi^\dagger = \sum_n |nc\rangle p \langle nv|$ describing the electronic excitation connects the two bands. The DOS of the band is given by

$$D_\mu(E) = \langle\langle \mathrm{Tr}_\mu \delta(E - H_\mu) \rangle\rangle ,$$

where $\langle\langle \cdots \rangle\rangle$ denotes the ensemble average and $\mathrm{Tr}_\mu(\cdots) = \sum_n \langle n\mu| \cdots |n\mu\rangle$.

The optical absorption spectra for the case of non-direct transition in which the complete relaxation of the k-selection rule is assumed are calculated by the joint density of states as

$$\alpha(E) \cdot E \propto \iint dE_1 dE_2 \delta(E_1 - E_2 - E) D_c(E_1) D_v(E_2) .$$

In the operator formalism the interband absorption spectrum is represented as

$$\alpha(E)\cdot E \propto \iint dE_1 dE_2 \delta(E_1-E_2-E)\langle\langle Tr_v[\Pi\delta(E_1-H_c)\Pi^{\dagger}\delta(E_2-H_v)]\rangle\rangle$$

and this expression is rewritten in terms of the two-particle Green's function $K(z_1,z_2) = \langle nc|\langle\langle(z_1-H_c)^{-1}\sum_m|mc\rangle\langle mv|(z_2-H_v)^{-1}\rangle\rangle|nv\rangle$ as

$$\alpha(E)\cdot E \propto \iint dE_1 dE_2 \delta(E_1-E_2-E)\frac{1}{(2\pi i)^2}[K(E_1^+,E_2^+)-K(E_1^+,E_2^-)-K(E_1^-,E_2^+)+K(E_1^-,E_2^-)] ,$$

where $E^{\pm} = E\pm i0$. For the detailed procedure of this method, see the reference 3. In this model ε_n^{μ} takes two values ε_S^{μ} and ε_H^{μ} according to whether the bond is Si-Si bond or Si-H bond. The hydrogen content is represented by the Si-H bond concentration cx. A semielliptic DOS with band width B_{μ} was assumed to describe the energy dispersion of the band μ.

4. RESULTS AND DISCUSSION

Values of the band parameters were chosen to reproduce the main features in the DOS of a-Si:H near the gap: ε_S^V=-2.5, ε_S^C=2.5, ε_H^V=-5.0, ε_H^C=3.0, and B_V=B_C=2.0 in eV. The calculated DOS in the case of pure system (cx=0.0) is shown in figure 2(a) and that of cx=0.3 in figure 2(b). The change of the band edge with increasing hydrogen content is shown in figure 3(a). The band gap increases almost linearly as illustrated in figure 3(b). These results are in agreement with the previous one[1]. The calculated absorption spectra $(\alpha\cdot E)^{1/2}$ are shown in figure 4. The results for the non-direct transition case in figure 4(a) are almost straight lines, for the semielliptic DOS was assumed for the energy dispersion. The results for the CPA calculation in figure 4(b) are different from the above. This discrepancy is ascribed to that the relaxation of the k-selection rule is not sufficient in this binary alloy-like treatment. However, it is noted that absorption spectra shift to the higher energy side in parallel with increasing hydrogen content for both

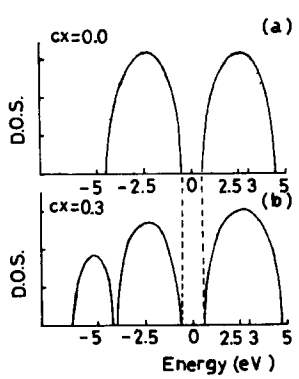

FIGURE 2
Calculated DOSs: (a) cx=0.0 (the pure case) (b) cx=0.3

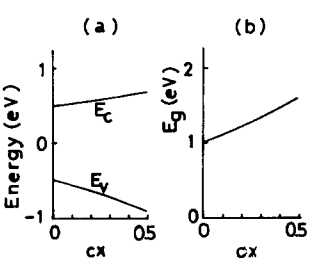

FIGURE 3
Hydrogen content dependence of (a) the valence band edge E_v and the conduction band edge E_c and (b) the band gap

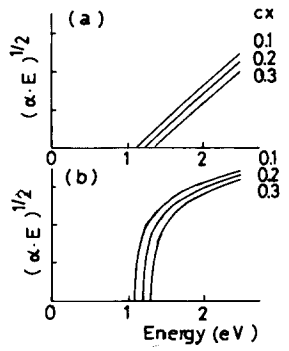

FIGURE 4
$(\alpha \cdot E)^{1/2}$ plots obtained from (a) the non-direct transition case and (b) the CPA calculation for cx=0.1,0.2 and 0.3

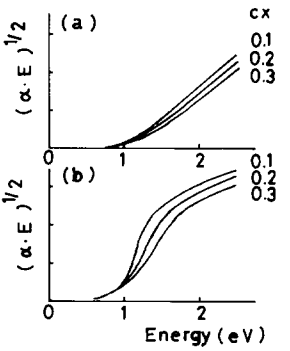

FIGURE 5
The same plots as in figure 4. The Lorentzian distribution is assumed on the energy levels of Si-H bonds

cases. Next we considered the effect of the fluctuation of the energy levels of Si-H bonds, such as due to the bond distortion. A Lorentzian distribution was assumed to describe the above-mentioned fluctuation. The results are shown in figure 5. The width of the distribution was taken to be 0.8 eV in the band v and 0.4 eV in the band c. There occurs the band edge tailing and the results of CPA are improved. Though the absorption spectra are smeared out near the band gap, E_g^{opt} obtained from figure 5(a) has the same value as that obtained from the corresponding spectrum in figure 4(a) and it increases almost linearly with hydrogen content. Thus the one of the features of E_g^{opt} in a-Si:H can be described with this simple model calculation. The other problem that E_g^{opt} in the case of cx=0 is much larger than that of band gap of c-Si seems to be the one in which topological disorder inherent to amorphous systems plays an important role. It was reported that the dihedral angle disorder cause a substantial change in the states near the gap from the analysis of the ideal amorphous semiconductor[6].

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