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CALCULATIONS OF THE ELECTRONIC AND TRANSPORT PROPERTIES IN Si-Ge-H ALLOYS

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In previous work[1,2], we have obtained an understanding of the role of hydrogen in amorphous silicon (a-Si) performing first principles calculations of the electronic and transport properties of a-Si:H using the coherent potential approximation (CPA).

Recently experimentalists[3] have directed their attention to hydrogenated Si-Ge alloys with the thought that this is a way of adjusting the energy gap for specific applications such as solar cells. For a comprehensive review of the photoemission and optical properties of a-Si the reader is refered to the article by Ley[4].

In the present work we have applied our CPA methodology to study the electronic states of Si-Ge and Si-Ge-H alloys to provide further insight to the above experiments. Our calculations utilize the three-center Slater-Koster (SK) parameters of Li and Lin-Chung[5]. These parameters which include second neighbor interactions, give a reasonable tight-binding representation of the energy bands of crystaline Si and Ge with energy gaps of 1.12eV and 0.6leV respectively. However, they produce a shape of the density of states (DOS) on both sides of the gap which is not as good as our previous fit (which includes third neighbors as well)[6] to the pseudopotential results for Si.

In the tight-binding Hamiltonian we treat diagonal disorder within the CPA and make a virtual crystal approximation (VCA) for the SK-parameters that appear in the off-diagonal matrix elements. For the Si-Ge-H alloy we need the SK parameters associated with the site of the 4-hydrogen cluster. We first define the effective pure hydrogen parameters from the expression:

$$\varepsilon^{H} = (\varepsilon^{HSi})^2/\varepsilon^{Si} \qquad (1)$$

where $\varepsilon^{HSi}, \varepsilon^{Si}$ have the values used in our previous work[1].
Then we obtain ε^{HGe} from the relation:

$$(\varepsilon^{HGe})^2 = \varepsilon^{H}\varepsilon^{Ge} \qquad (2)$$

For the nearest neighbor off-diagonal matrix elements we used a geometric average:

$$\varepsilon = (\varepsilon^{H})^{c}(\varepsilon^{Si})^{x}(\varepsilon^{Ge})^{y} \qquad (3)$$

where c is the concentration of vacancies which are replaced by 4-H clusters, x the concentration of Si and y the concentration of Ge. Obviously the following condition is satisfied:

$$x + y + c = 1 \qquad (4)$$

In the present work we have fixed c=0.05 so that the 4-H clusters will give us an amount of hydrogen equal to 4c.

Having determined the off-diagonal matrix elements using the above procedure, Eq.(3), we proceed to solve the following equation which results from the CPA condition of zero scattering on the average:

$$x\tilde{t}^{Si} + y\tilde{t}^{Ge} + c\frac{x}{x+y}\tilde{t}^{HSi} + c\frac{y}{x+y}\tilde{t}^{HGe} = 0 \qquad (5)$$

where $\tilde{t}^A = \tilde{U}^A(\tilde{1}-\tilde{G}\tilde{U}^A)^{-1}$ and A stands for Si, Ge, HSi or HGe. $\tilde{G}$ is a 4x4 matrix representing the effective Green's function and $\tilde{U}^A$ is a diagonal 4x4 matrix with diagonal elements $\varepsilon_s^A - \Sigma_s$ and $\varepsilon_p^A - \Sigma_p$ with the self energies Σ_s and Σ_p determined from Eq.(5).

The values of the on-site SK parameters used in our calculations are:

$$\varepsilon_s^{Si}=-5.176eV, \varepsilon_s^{Ge}=-6.226eV, \varepsilon_s^{HSi}=-8.72eV, \varepsilon_s^{HGe}=-9.56eV$$

$$\varepsilon_p^{Si}=1.33eV, \varepsilon_p^{Ge}=1.33eV, \varepsilon_p^{HSi}=-1.60eV, \varepsilon_p^{HGe}=-1.60eV$$

In Fig.1 we present the densities of states (DOS) of $Si_{.50}Ge_{.50}$. As expected the main features of the pure Si and Ge DOS are preserved. Indeed the three peaks seen in the valence band of both Si and Ge as well as the double peak shape of the conduction band remain in the alloy calculation. So the CPA results are very similar to those given by a VCA calculation. The main difference is that the CPA allows the disorder to introduce small tails in the DOS which make the energy gap smaller than that of the VCA. This is consistent with the findings of Stroud and Ehrenreich[7] who performed a similar calculation using the CPA in conjunction with a local pseudopotential model.

The DOS of $Si_{0.475}Ge_{0.475}H_{0.20}$ is similar to that shown in Fig.1. The main features found due to hydrogenation are the further broadening of the DOS due to the additional disorder and the widening by about 0.25eV of the energy gap.

In Fig.2 we show the DOS gap of both the Si-Ge and the Si-Ge-H calculation as a function of Ge content and for a fixed amount of hydrogen C_H=0.20. We note that in both cases the gap decreases monotonically from Si to Ge and that the hydrogenated alloy has a wider gap for the same Ge concentrations.

We have argued before, and so did Brodsky[8], that the optical gap is wider than the DOS gap in a-Si:H. We have used a Kubo-Greenwood[9] formalism to calculate the electrical conductivity in these alloys and subsequently the absorption coefficient α. The optical gap can be determined[10] by an extrapolation of the $(\alpha E)^{\frac{1}{2}}$ vs E graph or as the value of E at which $\alpha \sim 10^4 cm^{-1}$. Our results for the optical gap vs Ge concentration, as summarized in Fig.3, are consistent with the experimental data especially in view of the uncertainties in the operational definition of the optical gap and in the

experimental determination of the hydrogen content. The results in Fig. 3 were obtained assuming a constant hydrogen concentration of 0.20. Based on recent unpublished work[11] of ours we expect that a more dispersed way of hydrogen incorporation would produce a wider DOS and optical gap, improving thus the agreement with the experimental data.

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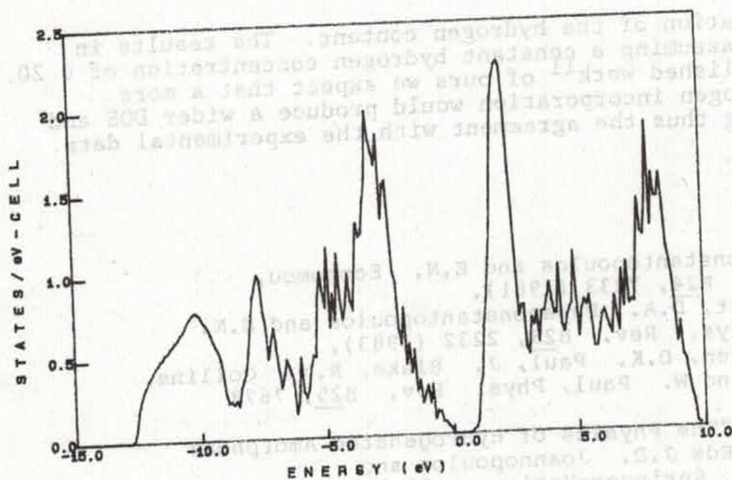

Fig.1 Density of states for $Si_{0.5}Ge_{0.5}$

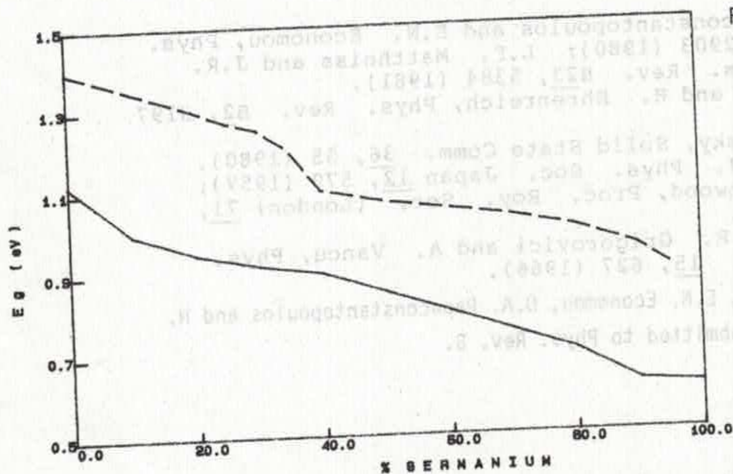

Fig.2 Density of states gap as a function of Ge content. The solid line represents $Si_{1-x}Ge_x$ and the broken line denotes $Si_{1-x}Ge_xH_{0.20}$

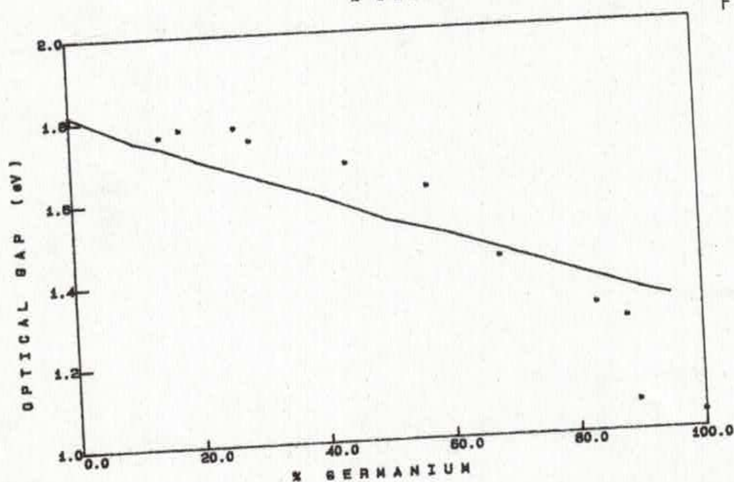

Fig.3 Optical gap as a function of Ge content. The dots correspond to the experiment of Ref.3