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Theory of hydrogenated silicon

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Using a coherent-potential approximation, we calculate the effects of hydrogenation on the density of states of silicon containing a finite concentration of ideal vacancies. The results reproduce the main features seen in the measurements including the restoration and the widening of the gap with increasing hydrogen content.

Hydrogenated α-Si has recently received a lot of attention partly because of the possibilities it offers as a device material.[1-4] In particular, emphasis has been given to the determination of the density of electronic states (DOS) by various experimental techniques[5-7] and to a lesser degree by theoretical calculations.[8-10] As a result of these efforts it is generally believed that the gap states in α-Si are associated with dangling bonds; hydrogen is attached to these dangling bonds thus pushing these states out of the gap. The model we consider in this work demonstrates, for the first time in a quantitative way, the appearance of dangling bond states and their passivation by hydrogen, and also shows the role of hydrogen in widening the gap. An alternate computational technique[9] using small Si-H molecules (terminated by Si Bethe lattices) has produced qualitatively similar conclusions to those presented here.

The starting point in our calculation is a Slater-Koster Hamiltonian H_0 including up to the third-nearest-neighbor interactions; the basis is orthonormal with four orbitals (one s-like and three p-like) per atom.[11] This Hamiltonian accurately reproduces[11] both the valence and the conduction bands of crystalline Si; we found that this level of accuracy is essential for our calculation. Randomness is introduced by assuming that there is a finite concentration c of ideal vacancies which means that the diagonal matrix elements of the Hamiltonian, $\langle ni|H|in\rangle$, at a given site n have a probability c to be infinite and a probability $1-c$ to have the perfect-crystal values. This type of disorder produces the essential feature of dangling bonds at the atoms surrounding a vacancy. Topological disorder is simulated by changing the tight-binding parameters $E_{xy}(\frac{1}{2}\frac{1}{2}\frac{1}{2})$ and $E_{xx}(\frac{1}{2}\frac{1}{2}\frac{1}{2})$ from their crystalline Si values[11] to the values 1.39 and 0.31 eV, respectively, as a result of varying the dihedral angle in a range which spans the eclipsed and staggered configurations. We have omitted the reconstruction and relaxation of the Si lattice which tends to push the dangling bond states back into the bands as shown by explicit calculations in the one vacancy case.[12,13] Thus our model would overestimate the number of dangling bond states and consequently the hydrogen required for their passivation. The size of this overestimation depends on how much reconstruction has taken place, which in turn is affected by the method of preparation of the Si-H film.[3] For example reconstruction may be prohibited when the film is grown in the presence of a substantial amount of hydrogen.[2] Finally we point out that no correlation among the positions of the vacancies has been included in the present calculation. It has been shown elsewhere[14] that the main effect of the tendency to cluster the vacancies together to form divacancies, trivacancies, and internal voids, etc., is to replace c by a smaller effective c^*.

Hydrogens are assumed to be located along the lines connecting a vacant site with its nearest neighbors. Thus up to four hydrogens can be accomodated

around a Si vacancy. The H-Si distance is taken as in the SiH_4 molecule. Charge-density contours of a H saturated Si-vacancy calculation[15] suggest the existence of higher than s components of the hydrogen wave function; and show that this multiple l wave function can be approximated by a single s-wave function, $|S_H\rangle$, which is displaced towards Si by about 20%. Using this wave function $|S_H\rangle$, the matrix elements of SiH_4,[16] the results of Chadi[17] that Si wave functions decay as $\exp(-1.04r)$, and Mattheiss's values for hydrogenic matrix elements,[18] we have estimated matrix elements $\gamma_i (i=1,\ldots,6)$ analogous to those defined by Hirabayashi[19] with one or both of the Si sp^3 hybrids replaced by $|S_H\rangle$. When a hydrogen is missing the corresponding γ_1 is taken as infinite. Knowing the matrix elements γ_i for each configuration, we can transform[19] to the original basis $|in\rangle$ and obtain $\langle ni|H|jn\rangle$. For the H-saturated Si vacancy the matrix elements in eV are $E_{ss}(000)=-8.72$, $E_{xx}(000)=-1.60$, $E_{ss}(\frac{1}{2}\frac{1}{2}\frac{1}{2})=-3.05$, $E_{sx}(\frac{1}{2}\frac{1}{2}\frac{1}{2})=1.96$, $E_{xx}(\frac{1}{2}\frac{1}{2}\frac{1}{2})=0.64$, $E_{xy}(\frac{1}{2}\frac{1}{2}\frac{1}{2})=0.98$. The off-diagonal disorder in our model Hamiltonian was treated in the virtual-crystal approximation by averaging the above Si-H matrix elements with those of Si.[11] We then employ the coherent-potential approximation (CPA) to obtain the DOS. The CPA calculates the DOS from a periodic effective Hamiltonian H_e which is obtained by replacing $\langle ns|H|sn\rangle$ by $\Sigma_s(E)$ and $\langle np|H|pn\rangle$ by $\Sigma_p(E)$ where p stands for any of the three p orbitals. The unknown quantities (self-energies) Σ_s,Σ_p are determined from the self-consistency condition

$$\langle U(1-G_eU)^{-1}\rangle = 0 \ , \tag{1}$$

where the parentheses denote average over the following 17 configurations at a given lattice site: the site occupied by Si (one configuration with probability $1-c$), the site being vacant with no H (one configuration with probability x_0), the site being vacant with one dangling bond occupied by H (four configurations each of probability $x_1/4$), the site being vacant with two dangling bonds occupied by H (six configurations each of probability $x_2/6$), the site being vacant with three dangling bonds occupied by H (four configurations each of probability $x_3/4$), and the site being vacant with all four dangling bonds occupied by H (one configuration of probability x_4); G_e is the diagonal 4×4 matrix $\langle ni|(E-H_e)^{-1}|in\rangle$ and U is the configuration-dependent 4×4 matrix $\langle nj|(H-H_e)|in\rangle$. As expected from symmetry considerations, the matrix $\langle U(1-G_eU)^{-1}\rangle$ was found to be diagonal with the three p matrix elements equal to each other. Thus Eq. (1) is actually reduced to two equations which determine the unknown quantities Σ_s,Σ_p.

Explicit results were obtained by assuming that hydrogen occupies dangling bonds in an uncorrelated way. In this case the probabilities x_l, $(l=0,\ldots,4)$ are given by

$$x_l = \frac{4!}{(4-l)!l!}\frac{cx^l(4c-x)^{4-l}}{(4c)^4} \ , \tag{2}$$

where x is the ratio of hydrogen atoms to lattice sites. We found that the numerical work is significantly reduced if the following additional approximation is employed: Eq. (1) is solved for the limiting cases $x=0$, $x=4c$ obtaining thus $\Sigma_s(E;0)$, $\Sigma_p(E;0)$, $\Sigma_s(E;4c)$, and $\Sigma_p(E;4c)$. For intermediate values of x an average t-matrix approximation is used with

$$\Sigma_i(E;x) = \left(1-\frac{x}{4c}\right)\Sigma_i(E;0) + \frac{x}{4c}\Sigma_i(E;4c); \quad i=s,p \ . \tag{3}$$

Using these Σ's we obtain the 4×4 matrix G_e and the configuration-dependent 4×4 matrices U. The Si and the H partial DOS are given explicitly by the equations

$$\rho_{Si}(E) = (1-c)\left(-\frac{\text{Im}}{\pi}\right)\text{Tr}[(1-G_eU_{Si})^{-1}G_e] \ , \tag{4}$$

$$\rho_H(E) = -c\frac{\text{Im}}{\pi}\text{Tr}\langle(1-G_eU)^{-1}G_e\rangle_v \ , \tag{5}$$

where the symbol $\langle\ \rangle_v$ indicates average over only those configurations associated with no Si at the site n. The total DOS is of course:

$$\rho(E) = \rho_{Si}(E) + \rho_H(E) \ . \tag{6}$$

In Fig. 1 we plot the DOS in the gap where one sees that by increasing the hydrogen content x the states in the gap are reduced drastically in agreement with the experimental findings. It is our impression

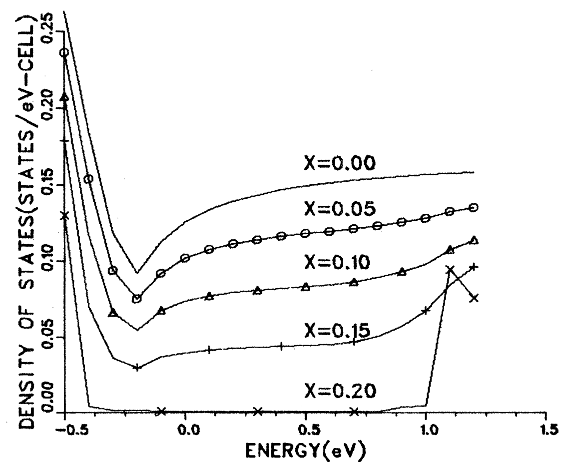

FIG. 1. Density of states in the gap for different hydrogen concentrations x. The Fermi level was found to be at $E=0.4$ eV and was almost invariant with x.

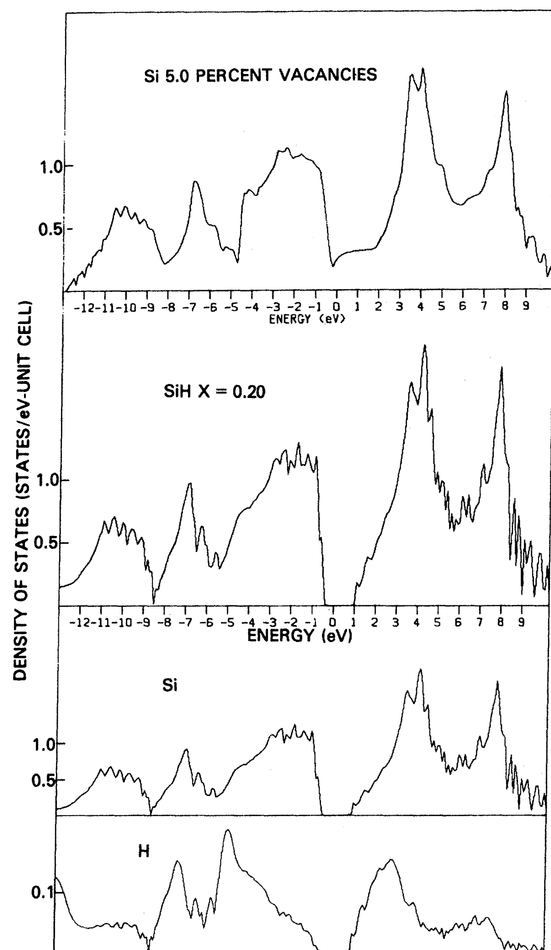

FIG. 2. Total and site decomposed densities of states. Top panel refers to 5% vacancies and no hydrogen, and the bottom panel shows the case with all dangling bonds terminated by hydrogen.

that the present calculation is the first one to show in a convincing quantitative manner, this restoration of the band gap upon hydrogenation.

In Fig. 2 we show the DOS for the whole spectrum including both the valence and conduction bands. Figure 2(a) shows the total DOS for the case of 5% vacancies, i.e., $c=0.05$ and $x=0.0$. This is compared to Fig. 2(b), where all ($x=0.20$) of the dangling bonds are terminated by hydrogen. The H site DOS [in Fig. 2(b)] shows two peaks at approximately 5.2 and 7.6 eV below the Fermi level in good agreement with the photoemission data of von Roedern *et al.*[5] Furthermore our results show a recession of the valence band by about 0.4 eV in agreement with the above experiment.[5] By examining the site decomposition of the DOS and the limiting case of an isolated hydrogen impurity we have determined that

TABLE I. Band gap E_g (in eV) as a function of hydrogen content for cases where all dangling bonds are saturated (i.e., $x=4c$). The estimated uncertainty is ±5%.

$x=4c$	E_g
0.00	1.05
0.05	1.20
0.10	1.25
0.15	1.35
0.20	1.40
0.25	1.45
0.30	1.50

the eigenstates at the bottom of the conduction band of Si-H are resonance states exhibiting an enhanced probability to find the electron around the hydrogen atom. These states can be thought of as antibonding H-Si states mixed with regular conduction-band Si states. We would like to point out that the existence of this type of states has been suggested in order to interpret transport and photoluminescence[4] results in highly hydrogenated samples.

Finally, we wish to emphasize that the present work shows a substantial increase of the gap upon hydrogenation in agreement with experiment.[1,2] This is demonstrated in Table I which gives the size of the gap as a function of hydrogen content for cases where no dangling bonds are present. According to the present theory the widening of the gap is due to the following two effects: (a) The Si—H bond being stronger than the Si—Si bond tends to push the bottom of the conduction band towards higher energies, thus cancelling the opposite effect produced by the diagonal hydrogen matrix elements. (b) The difference $E_{xy}(\frac{1}{2}\frac{1}{2}\frac{1}{2})-E_{xx}(\frac{1}{2}\frac{1}{2}\frac{1}{2})$, which is a measure of the $pp\pi$ interaction, effectively decreases upon hydrogenation; this causes a narrowing[20] of the third peak of the valence band (VB) which results in the recession of the top VB states.

In conclusion our calculations for Si-H reproduce with no adjustable parameters, the main features of the measurements of the DOS, including the widening of the gap.

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