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Theoretical study of optical absorption in hydrogenated amorphous silicon

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We present the first application of the coherent-potential approximation in the evaluation of optical absorption $\alpha(E)$ of a-SiH$_x$ with the use of a realistic multiband model. The optical gap is larger than the calculated density-of-states gap and the theoretical $\alpha(E)$ agrees well with experimental data. These results suggest that $\alpha(E)$ is determined primarily by the local H-Si configuration and short-range order, but that it is insensitive to the particular long-range order, which is not included in our model.

In spite of several recent developments in the theoretical understanding of the electronic spectrum of a-SiH$_x$, a gap remains in the interpretation of measured quantities[1-3] such as the optical-absorption coefficient α, photoconductivity, photoluminescence, etc. These properties depend not only on the electronic density of states (DOS), $N(E)$, but also upon transition matrix elements involving the eigenfunctions of the system. Since *realistic* matrix elements are much more difficult to obtain theoretically than is $N(E)$, the usual approach is to assume that the matrix elements are constant, i.e., energy independent. With this assumption $\alpha(\omega)$ is proportional to the convoluted DOS (CDOS),

$$\alpha(\omega) \sim \omega^{-1} \int_{E_F-\hbar\omega}^{E_F} N_v(E) N_c(E+\hbar\omega)\, dE \tag{1}$$

(v and c denote valence and conduction band), and the resulting optical gap $E_g^{\rm opt}$ coincides with the DOS gap $E_g^{\rm DOS}$. In this paper we show that both the magnitude of α and the measured[1,2] $E_g^{\rm opt}$ of fully hydrogenated a-SiH$_x$ are reproduced by our calculations if we remove the assumption of constant matrix elements, and a better understanding of the optical process is thereby obtained.

In the present work we calculate $\alpha(\omega)$ within a recently developed multiband model[4,5] of a-SiH$_x$. These calculations are the first application of the coherent-potential approximation (CPA) in the evaluation of optical properties of a real material using a realistic multiband system; previous calculations[6] of the optical conductivity have been limited to simple single- or double-band models. The significant aspects of our work include the following: (i) Without adjustable parameters we obtain good agreement with experiment[1] for $\alpha(\omega)$, both in energy dependence and absolute magnitude, and (ii) we find that $E_g^{\rm opt} > E_g^{\rm DOS}$ is due primarily to remanent conservation of the magnitude of the wave vector resulting from short-range order.

The optical-absorption coefficient is given in terms of the optical conductivity $\sigma(\omega)$ and index of refraction $n(\omega)$ by

$$\alpha(\omega) = 4\pi\, \mathrm{Re}\sigma(\omega)/cn(\omega) \ , \tag{2}$$

where c is the speed of light. The weak ω dependence of n has been measured[1] and is included in the calculations below. For $\sigma(\omega)$ we use the general expression[7]

$$\begin{aligned}\mathrm{Re}\sigma(\omega) &= \frac{2e^2}{\pi\Omega m^2\omega} \sum_{\vec{k}} \int_{E_F-\hbar\omega}^{E_F} dE\, \mathrm{Tr}\langle \tilde{p}_x \mathrm{Im}[\tilde{G}(\vec{k},E+i0)]\tilde{p}_x \mathrm{Im}[\tilde{G}(\vec{k},E+\hbar\omega+i0)]\rangle \\ &\approx \frac{2e^2}{\pi\Omega m^2\omega} \sum_{\vec{k}} \int_{E_F-\hbar\omega}^{E_F} dE\, \mathrm{Tr}\{\tilde{p}_x \langle \mathrm{Im}[\tilde{G}(\vec{k},E+i0)]\rangle \tilde{p}_x \langle \mathrm{Im}[\tilde{G}(\vec{k},E+\hbar\omega+i0)]\rangle\} \ ,\end{aligned} \tag{3}$$

where Ω is the normalization volume, p_x is the x component of the momentum operator, and G is the Green's function of the system. The angular brackets indicate an ensemble average over the disorder and $\tilde{A}$ denotes that A is an 8×8 matrix. For G we use CPA results for a highly successful model a-SiH$_x$ system discussed elsewhere.[4] The model consists of a tight-binding description of 20 at.% H bonded to 5% Si vacancies in random positions on a Si lattice. The second approximate relation (3) results from ignoring vertex corrections[8] to the exact expression, and allows the evaluation of Reσ directly from the CPA Green's function $\langle G\rangle$. The momentum matrix is given by

$$\tilde{p}_x = \frac{d\tilde{H}(\vec{k})}{dk_x} \ , \tag{4}$$

where $\tilde{H}$ is the virtual-crystal tight-binding Hamiltonian.[4]

The results for Re$\sigma(\omega=0,E_F)$ have been presented previously[5] as a function of E_F. There it was found that contributions from off-diagonal matrix elements of $\tilde{p}_x$ and $\langle\tilde{G}\rangle$ were negligible (typically $\sim 2\%$), consistent with an "intraband" picture of the dc conductivity. In crystals, absorption at finite frequency occurs due only to interband transitions, but disorder admits the possibility of "intraband" transitions. Whereas it will be seen that the $\vec{k}$ dependence of the matrix elements is necessary to an understanding of the energy gaps, the full matrix summations in the trace in Eq. (3) are necessary in order to obtain the correct magnitude of α.

Our result for $\alpha(\omega)$, calculated from Eqs. (2)–(4) at $T=0$ (no thermal disorder) with no adjustable parameters is compared in Fig. 1 (as the dashed line) in the form $(\alpha E)^{1/2}$

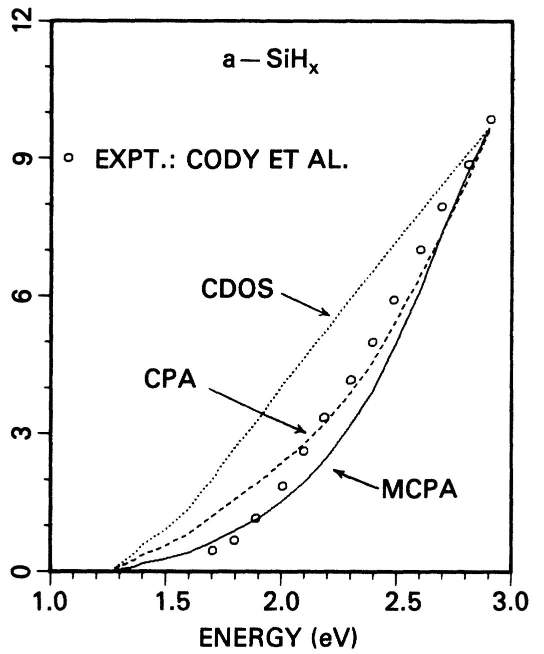

FIG. 1. Comparison of calculated absorption coefficient α with measured value (data points) of Cody *et al.*, Ref. 1, plotted as $(\alpha E)^{1/2}$ vs E. The CPA and MCPA results were multiplied by 1.5 and 2.4, respectively, to normalize to the experimental data at 2.9 eV.

vs E ($E=\hbar\omega$) with the experimental data of Cody *et al.*[1] (symbols) and with the CDOS expression of Eq. (1) (dotted line) corresponding to energy-independent, momentum-nonconserving matrix elements of $\tilde{p}_x$. In the range $2.1 \lesssim E \lesssim 3.0$ eV, $(\alpha E)^{1/2}$ is an excellent agreement with the data apart from an overall factor of 1.5. In the region $1.6 \lesssim E \lesssim 2.1$ eV the calculation leads to higher absorption (relative to the higher-energy region) than is found for the sample shown in Fig. 1. This could be due to the lack of full atomic disorder or to the absence of off-diagonal disorder, either of which would require a more sophisticated CPA model.

Another possibility, which we now address, is that the approximation of Eq. (3) of neglecting vertex corrections is breaking down in this region. Examination of contributions to $\alpha(\omega)$ for $\hbar\omega < 2$ eV from various regions of $\vec{k}$ space shows that this absorption is due entirely to transitions for which either $(\vec{k},E)$ or $(\vec{k},E+\hbar\omega)$ is rather far from a broadened "band" of a-SiH$_x$. In terms of the spectra density S given by

$$S(\vec{k},E) = -\pi^{-1}\mathrm{Tr}\tilde{G}(\vec{k},E+i0) \ , \tag{5}$$

either the initial or the final state of the transition lies where S is small. The CPA, however, is designed primarily to provide average, macroscopic properties of the system, and it may be overestimating $S(\vec{k},E)$ in regions far away from bands which, for example, contribute little to $N(E)$. In a region where the influence of a single band m with energy $E_{\vec{k}m}$ is dominant, $S(\vec{k},E)$ assumes the form

$$S(\vec{k},E) \approx \frac{1}{\pi}\frac{|\mathrm{Im}\Sigma_m(E)|}{(E-E_{\vec{k}m})^2+[\mathrm{Im}\Sigma_m(E)]^2} \ , \tag{6}$$

since for the tight-binding CPA we find that the self-energy $\Sigma_m(\vec{k},E)$ in the band representation is nearly $\vec{k}$ independent. Therefore, $S(\vec{k},E)$ is Lorentzian in $E_{\vec{k}m}$ at fixed E. Observation of first-principles muffin-tin CPA spectra functions,[9] however, suggests a much faster than Lorentzian fall-off of $S(\vec{k},E)$; i.e., $|\mathrm{Im}\Sigma_m(\vec{k},E)|$ should *decrease* as $\vec{k}$ leaves the vicinity of band m.

Following this line of reasoning we modified the CPA self-energy to conform to this more physical behavior by defining a k-dependent on-site self-energy $\hat{\Sigma}$ by[10]

$$\mathrm{Im}\hat{\Sigma}_{s,p}(\vec{k},E) = c_{s,p}\frac{\Gamma^2}{(E-E_{\vec{k}n})^2+\Gamma^2}\mathrm{Im}\Sigma_{s,p}(E) \ , \tag{7}$$

$$\Gamma = c\,|\mathrm{Im}\Sigma_s(E)+3\,\mathrm{Im}\Sigma_p(E)|/4 \ , \tag{8}$$

where $E_{\vec{k}n}$ is the eigenvalue at $\vec{k}$ nearest to E. The real part of Σ is relatively less important in the calculation and was left unchanged. The constants c_s and c_p were determined iteratively by the requirement that the derived "modified CPA" (MCPA) DOS N_s, N_p differ by less than 10% from the CPA values. The value $c=0.2$ was used, but with this self-consistency constraint on N_s and N_p the results are weakly dependent on the choice of c.

The effect upon $S(\vec{k},E)$ of this modification is shown in Fig. 2 for $\vec{k}$ along the Δ direction and for two energies, -0.8 and 1.1 eV, which contribute to absorption at $\hbar\omega=1.9$ eV. S peaks near the eigenvalues of the underlying crystalline Hamiltonian. Far from a peak, S in the MCPA is typically reduced by an order of magnitude, which in turn reduces the low-frequency absorption. By constructing this more physical form for $\langle\mathrm{Im}\tilde{G}\rangle$ by our MCPA procedure, we obtain corrections to α which must be included in the vertex corrections neglected in Eq. (3). The result is shown in Fig. 1 as the full line. The energy dependence of $(\alpha E)^{1/2}$ calculated from the MCPA is slightly steeper at higher energy than the experimental values of Cody *et al.*, but the behavior below 2 eV is much improved over the CPA results.

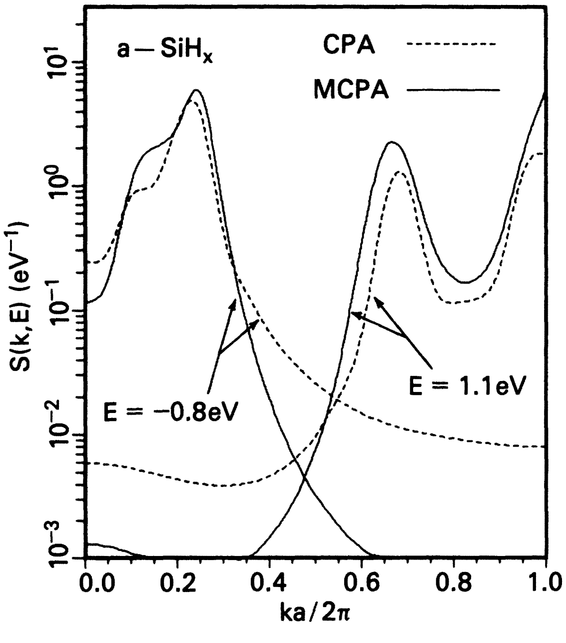

FIG. 2. Semilog plot of CPA and MCPA spectral densities $S(\vec{k},E)$ at $E=-0.8$ eV and $E=1.1$ eV for $\vec{k}\parallel[100]$. The MCPA value is roughly one order of magnitude smaller than the CPA value far from the peaks.

Comparison of the calculated value of $(\alpha E)^{1/2}$ to that arising from a simple CDOS (Ref. 4) demonstrates that $E_g^{\rm opt} > E_g^{\rm DOS}$ (Fig. 1). Linear extrapolation of $(\alpha E)^{1/2}$ to zero from the linear high-frequency region leads to a value $E_g^{\rm opt} \approx 1.8$ eV (CPA) or 2.1 eV (MCPA), whereas $E_g^{\rm DOS} = 1.4$ eV from the CDOS. Cody *et al.*[1] have shown that $E_g^{\rm opt}$ varies from 1.5 to 2.0 eV with increasing hydrogen content. It is encouraging that our model, which contains 20% H, gives an optical gap of the order of 2 eV, in excellent agreement with data[1] on samples with similar H content. By making the replacement $\tilde{p}_x \rightarrow$ diagonal constant in Eq. (3) we obtain a similar frequency dependence, indicating the widening of the optical gap is due primarily to $\vec{k}$-space correlations of the electron and hole in the excitation process rather than an explicit energy dependence of $\tilde{p}_x$. Physically this remanent $\vec{k}$ conservation is due to the short-range order in a-SiH$_x$. Note that our value $E_g^{\rm opt} \approx 2$ eV is much smaller than that for crystalline Si (~ 3 eV) in spite of the widening of the gap[4] due to lowering of the valence bands upon incorporation of H. All of the absorption below 3 eV arises from the disorder in the model, and the close agreement with experiment indicates both that the underlying "crystallinity" of our model is not a serious defect and that knowledge of the long-range disorder in a-SiH$_x$ is not essential for describing α.

We performed two additional calculations which illustrated other features of our model. First, we reduced the density of fully hydrogenated vacancies from 5% to 2.5%. This introduced two competing effects; the decrease of the [H]/[Si] ratio reduced $E_g^{\rm DOS}$, but since the disorder was also severely reduced, $E_g^{\rm opt}$ actually widened somewhat, demonstrating the approach to the crystalline Si limit $E_g^{\rm opt} \approx 3$ eV. The net effect was to reduce $(\alpha E)^{1/2}$ by a factor of 2 below $E = 2.6$ eV. Secondly, we replaced $\frac{1}{4}$ of the H atoms in the original calculation by dangling bonds. This caused a dramatic increase of $(\alpha E)^{1/2}$ below 2 eV due to both the increased disorder and dangling-bond gap states, and resulted in a much smaller $E_g^{\rm opt}$. Although this result follows the trend in the data when the H content is reduced, it should not be expected to agree numerically with the experimental $E_g^{\rm opt}$-vs-H-content line[1] because the dangling bonds have not been allowed to reconstruct. "Fully hydrogenated" a-SiH$_x$ does not reconstruct significantly because all potential dangling bonds have bonded with hydrogen. Therefore, our model, when fully hydrogenated, corresponds semiquantitatively to fully hydrogenated samples (as long as localized band-tail and -gap states are not crucial), but it does not have the flexibility to model situations with reduced H content to the same accuracy.

To summarize, we have presented here realistic microscopic calculations of the absorption coefficient of a model for a-SiH$_x$. The calculated absorption coefficient, obtained without adjustable parameters, is within a factor of 2 of the experimental value, which is itself sample dependent. Considered alongside the other successes[4] of the model, this agreement indicates that knowledge of the precise atomic positions are not necessary for the understanding of many properties of a-SiH$_x$ for which band-tail or -gap states are not intimately involved.

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[10] In the region $|E_{\vec{k}n} - E| < \Gamma$ the use of Eq. (7) occasionally resulted in a lower spectral density. In those cases we set $\mathrm{Im}\hat{\Sigma} = \mathrm{Im}\Sigma$.