

Electronic and transport properties of hydrogenated amorphous silicon

A. D. Zdetsis, E. N. Economou, D. A. Papaconstantopoulos,* and N. Flytzanis

Research Center of Crete and Department of Physics, University of Crete, Heraklio, Crete, Greece

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We have extended previous coherent-potential-approximation calculations of the electronic and transport properties of hydrogenated amorphous silicon (*a*-Si), in order to examine the effects of fully dispersed hydrogen in *a*-Si. The present calculation replaces random vacancies in the Si matrix by single H atoms instead of the four-H-atom clusters previously considered. In addition, to eliminate dangling-bond states in the gap we have introduced an *ad hoc* reconstruction of the lattice around the vacancy by effectively saturating the dangling orbitals with other Si atoms. Our results reinforce previous claims that an understanding of various experiments in *a*-Si:H can be obtained from first-principles calculations which neglect topological disorder and the precise configuration of the hydrogen atoms. The present calculations lead to an improved agreement with the photoemission and optical absorption data.

I. INTRODUCTION

Recent calculations¹ of the electronic states of hydrogenated *a*-Si using the tight-binding coherent-potential-approximation (CPA) method² have reproduced several of the features shown in the experiments on this material. Specifically, these calculations have demonstrated the existence of dangling-bond states in the gap; they have shown the restoration of the band gap E_g upon hydrogenation and the widening of E_g due mainly to a recession of the valence band; they have identified hydrogen-induced peaks in the density of states (DOS) both in the valence and conduction bands. These calculations were also extended³ to calculate the electrical conductivity of *a*-Si:H and have shown by an evaluation of the absorption coefficient α that the optical gap is larger than the DOS gap as previously suggested by Brodsky.⁴ The ability of these calculations to provide good agreement with various experiments in *a*-Si:H leads us to the conclusion that many properties of this system can be understood without knowledge of the precise atomic positions.

The model upon which the above calculations were based describes *a*-Si:H by constructing an effective lattice whose sites may have probability c of being vacant, and probability $1-c$ of having a Si atom. In addition it has been assumed that H atoms may be located along the lines connecting a vacant site with its nearest neighbors. Thus this model includes, at random, Si sites, vacancy sites, and sites surrounded by one, two, three, or four H atoms which saturate the Si dangling bonds. This model neglects topological and reconstruction disorder. Given the good agreement obtained with the optical-absorption measurements,⁵ we believe that, at least, near the band gap the effect of topological disorder is small, and that reconstruction is minimal when a substantial amount of hydrogen is introduced.

The calculation³ of α was based on the special case of the model where the vacancy is surrounded by four H atoms, thus fully saturating the Si dangling bonds. It was

argued^{1,3} that the qualitative features of the results do not depend on the particular configuration, but simply on the presence of H-induced disorder. However, there may be quantitative differences due to different configurations of the H atoms.

In the present work we consider the other extreme case of completely dispersed H, assuming that the lattice reconstructs itself around each isolated H atom so that no dangling bonds survive. It is obvious, and it is also exhibited in particular models,⁶ that such a reconstruction must be quite extensive in order to avoid dangling bonds. When H is incorporated in a completely dispersed way, it induces more disorder than when it goes in clusters of four H atoms. The main reason is that the number of scattering centers increases by a factor of 4. Furthermore, although near the H site the cluster of four H atoms probably creates a stronger scattering potential than that of the single H atom, the extent of the latter is considerably larger; thus the scattering strength of one hydrogen atom (1H) may be even stronger than that of the four-hydrogen-atom cluster (4H). In this paper we have made the additional simplifying assumption that the lattice heals immediately around the 1H atom. This assumption definitely underestimates the 1H-induced disorder and hence our results for the dc conductivity must be considered as upper limits.

In Sec. II we describe the new features of the model introduced by the 1H configuration, and we give details on the mathematical and computational aspects of the calculations. In Sec. III we discuss the results of the calculations with particular emphasis on the quantitative differences from the 4H-cluster case. Finally in Sec. IV we present the conclusions of this work.

II. THE MODEL

The theoretical framework for the present model is similar to the one presented earlier¹ but with some rather significant modifications concerning the configurational

disorder (related to the distribution of hydrogen), the reconstruction of the effective lattice around hydrogenated sites and the treatment of the dangling bonds.

In the previous model reconstruction was not allowed to occur and therefore when one, two, or three H atoms surrounded the vacancy there were still dangling bonds which created states in the gap. Hence, only the case of the 4H clusters which saturates completely the dangling bonds was emphasized and used to study transport properties and to compare with experiment.

In the present model we have introduced two types of hydrogenated vacancy sites, one type associated with a cluster of four hydrogen as before and one type associated with only one hydrogen. To avoid the three dangling bonds in the last case, we have effectively introduced reconstruction by appropriately modifying the corresponding Si-Si and Si-H matrix elements. The physical picture behind this choice is that the dangling bonds are saturated by the reorganization of the Si-Si bonding configuration around the single hydrogen atom. As before, no topological disorder (TD) is included in the calculation.

The disorder is dealt through a tight-binding (TB) form of the coherent-potential-approximation method.² To determine the Green's function \tilde{G}_e of the effective medium we use a Slater-Koster⁷ (SK) Hamiltonian H which includes up to third-neighbor interactions.⁸ The basis used includes the four outer orbitals of Si one s and three p states, but in considering Si-H matrix elements it is more convenient to use the equivalent four sp^3 hybridized orbitals. The parameters for the starting SK Hamiltonian (to be used in a CPA iteration scheme) are chosen by fitting accurately the pseudopotential band structure of Si.⁸ The result of replacing a silicon atom by a hydrogen atom is to replace the Si-Si matrix element by H-H or Si-H matrix elements. The H-H and Si-H matrix elements are evaluated from small-molecule matrix elements¹ in the sp^3 basis and are then transformed to fictitious s - and p -orbital matrix elements. Since we use a unit cell with two atoms (or vacancies) in the CPA with only diagonal disorder, we take an average of the first-neighbor matrix elements for Si-Si and Si-H and the result is the corresponding SK parameters $F_{ij}(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ with $i, j = s, x, y, z$ for the s and p orbitals. Thus the nearest-neighbor off-diagonal disorder is treated within the virtual-crystal approximation while the second- and third-neighbor interaction matrix elements are assumed unaffected by the disorder. Reconstruction is not included near the 4H vacancies while the reconstruction in the 1H vacancies is introduced by effectively saturating the remaining Si dangling orbitals with other Si atoms forming weak bonds [see the scattering matrix in Eq. (4)]. The corresponding matrix element can essentially be taken equal to the normal Si-Si bond matrix element. This choice is justified since the results for the DOS turn out to be rather insensitive to these "weak" bonds for reasonable deviations (less than 40%) from the normal Si-Si bond matrix elements.

To obtain the DOS for the a -Si:H we must evaluate the effective-medium Green's function \tilde{G}_e (a 4×4 matrix), self-consistently to obtain the complex self-energies Σ_s

and Σ_p that will replace the ϵ_s and ϵ_p , the on-site parameters for the crystalline silicon in the starting SK Hamiltonian. The self-consistency condition is that in the effective medium there is, on the average, zero scattering when one replaces an effective atom by a silicon atom or by a hydrogenated vacancy. The quantities calculated from the Green's function \tilde{G}_e such as the DOS, and transport properties are a good approximation to those that would be obtained using the actual nonperiodic Hamiltonian. The single-site CPA condition for the present model can be written as

$$(1-c)\tilde{U}_{\text{Si}}(1-\tilde{G}_e\tilde{U}_{\text{Si}})^{-1} + \frac{x_1}{4} \sum_{i=1}^4 \tilde{U}_{1i}(1-\tilde{G}_e U_{1i})^{-1} + x_4 \tilde{U}_4(1-\tilde{G}_e \tilde{U}_4)^{-1} = 0. \quad (1)$$

\tilde{U}_{Si} is the Si scattering matrix in the (SK) basis of s and p orbitals,

$$\tilde{U}_{\text{Si}} = \begin{pmatrix} \epsilon_s - \Sigma_s & 0 & 0 & 0 \\ 0 & \epsilon_p - \Sigma_p & 0 & 0 \\ 0 & 0 & \epsilon_p - \Sigma_p & 0 \\ 0 & 0 & 0 & \epsilon_p - \Sigma_p \end{pmatrix}, \quad (2)$$

with $\epsilon_s = -3.953$ eV and $\epsilon_p = 1.512$ eV as determined from the initial fit to the crystalline Si band structure.⁸ \tilde{U}_4 and \tilde{U}_{1i} are the scattering matrices for 4H sites and 1H sites, respectively, and can be written as

$$\tilde{U}_4 = \begin{pmatrix} \epsilon'_s - \Sigma_s & 0 & 0 & 0 \\ 0 & \epsilon'_p - \Sigma_p & 0 & 0 \\ 0 & 0 & \epsilon'_p - \Sigma_p & 0 \\ 0 & 0 & 0 & \epsilon'_p - \Sigma_p \end{pmatrix}, \quad (3)$$

where $\epsilon'_s = -7.88$ eV and $\epsilon'_p = -1.88$ eV are the hydrogen on-site effective matrix elements in the fictitious s' and p' basis. U_{1i} corresponds to four equivalent configurations where $i = 1, 2, 3, 4$. The general form of U_{11} is

$$\tilde{U}_{11} = \tilde{S} \begin{pmatrix} \gamma'_1 & \gamma & \gamma & \gamma \\ \gamma & \Gamma & \Gamma_2 & \Gamma_2 \\ \gamma & \Gamma_2 & \Gamma & \Gamma_2 \\ \gamma & \Gamma_2 & \Gamma_2 & \Gamma \end{pmatrix} \tilde{S}^{-1} - \tilde{\Sigma}, \quad (4)$$

and, similarly, for \tilde{U}_{12} , \tilde{U}_{13} , and \tilde{U}_{14} . Γ and Γ_2 are the weak-bond Si-Si matrix elements in the sp^3 basis (where one can estimate their values) and they have been chosen so that Γ_2 is zero and Γ is essentially equal to the on-site Si matrix element $\gamma_1 = 0.146$ eV; the corresponding on-site H matrix element is $\gamma'_1 = -3.38$ eV. The parameter γ is the matrix element between the H and the nearest reconstructed Si atom. \tilde{S} is the 4×4 transformation matrix between the SK and the sp^3 basis. $\tilde{\Sigma}$ is a 4×4 diagonal matrix with elements $\Sigma_{11} = \Sigma_s$ and $\Sigma_{22} = \Sigma_{33} = \Sigma_{44} = \Sigma_p$. The variables x_1 and x_4 are equal to the probabilities for the corresponding configurations and are related by

$$c = x_1 + x_4, \quad (5)$$

where c is the concentration of vacancy sites, while the hydrogen atomic concentration x is

$$x = x_1 + 4x_4. \quad (6)$$

One could, in principle, estimate the values of the parameters Γ , Γ_2 , and γ from first principles using, for instance, cluster-calculation techniques. However, since for any value of Γ between the values of the corresponding matrix elements for Si-Si ($\gamma_1 = 0.146$ eV) and Si-H ($\gamma_1 = -3.380$ eV), our results did not show substantial changes we have chosen $\Gamma = \gamma_1 = 0.146$ eV. The position and the size of the gap are insensitive to changes up to 40% from this value. Similarly, no substantial changes were observed by varying Γ_2 and γ between zero and the corresponding Si-Si and Si-H matrix elements $\gamma_2 = -1.366$ eV and $\gamma_2 = -1.780$ eV; therefore, we have chosen $\Gamma_2 = \gamma = 0$.

The CPA conditions that determine Σ_s and Σ_p must be solved numerically since the effective-medium Green's function \tilde{G}_e implicitly depends on the self-energies Σ_s and Σ_p . One can decrease significantly the amount of computer time by reducing the CPA conditions analytically as far as possible. Here we present their final form after some simple but tedious manipulations. The CPA condition has only diagonal elements due to the symmetric form of Eq. (1) and from those only two are independent leading to Eqs. (A1a) and (A1b) (see Appendix).

Once the self-energies Σ_s and Σ_p are determined by solving Eqs. (A1a) and (A1b) numerically, \tilde{G}_e is known and the total DOS can be obtained from the expression

$$N(E) = \frac{-1}{\pi} \text{Im}(\text{Tr} \tilde{G}_e). \quad (7)$$

One can also separate the DOS to that of Si sites and that due to hydrogenated sites as follows:

$$N_{\text{Si}}(E) = \frac{1-c}{\pi} \{ -\text{Im} \text{Tr}[(1 - \tilde{G}_e \tilde{U}_{\text{Si}})^{-1} \tilde{G}_e] \}, \quad (8a)$$

$$N_{\text{H}}(E) = \frac{x_1}{4\pi} \sum_{i=1}^4 \{ -\text{Im} \text{Tr}[(1 - \tilde{G}_e \tilde{U}_{1i})^{-1} \tilde{G}_e] \} \\ + \frac{x_4}{\pi} \{ -\text{Im} \text{Tr}[(1 - \tilde{G}_e \tilde{U}_4)^{-1} \tilde{G}_e] \}. \quad (8b)$$

Furthermore, by separating the s -like matrix element in the trace in Eqs. (8a) and (8b) from the other three p -like diagonal elements we can obtain s - and p -like DOS for each site.

Once the Green's function is obtained we can evaluate the ac and dc conductivity as well as the absorption coefficient using the standard Kubo-Greenwood-type formulas. The energy-dependent dc conductivity is given³ by

$$\sigma(E) = \frac{2e^2 \hbar}{\pi \Omega m^2} \sum_k \sum_{i,j,m,n} p_{x,ij} \langle \text{Im} \tilde{G}_{jm} \rangle p_{x,mn} \langle \text{Im} \tilde{G}_{ni} \rangle, \quad (9)$$

where $\langle \rangle$ denotes a configurational average and we have ignored the vertex corrections arising from correlations in intermediate scatterings, i.e., we have set $\langle GpG \rangle \approx \langle G \rangle p \langle G \rangle$ and $\langle G \rangle$ is the Green's function \tilde{G}_e previously calculated. In Eq. (9), (p_x) is the momentum p_x matrix element in a basis which is a Bloch sum of s and p orbitals of Si. We mention here the the finite-temperature

conductivity $\sigma(T)$ is related to $\sigma(E)$ by

$$\sigma(T) = - \int dE \frac{\partial f}{\partial E} \sigma(E), \quad (10)$$

where f is the Fermi function.

The optical-absorption coefficient is given in terms of the evaluated ac conductivity $\sigma(\omega)$ and the experimentally determined index of refraction $n(\omega)$:

$$\alpha(\omega) = \frac{4\pi \text{Re}\sigma(\omega)}{cn(\omega)}, \quad (11)$$

where c is the speed of light. Ignoring vertex corrections we obtain for $\sigma(\omega)$ the expression

$$\text{Re}\sigma(\omega) \approx \frac{2e^2}{\pi \Omega m^2 \omega} \\ \times \sum_k \int_{E_F - \hbar\omega}^{E_F} dE \text{Tr}[\tilde{p}_x \langle \text{Im} \tilde{G}(\vec{k}, E + i0) \rangle \\ \times \tilde{p}_x \langle \text{Im} \tilde{G}(\vec{k}, E + \hbar\omega + i0) \rangle], \quad (12)$$

where Ω is the normalization volume, \tilde{p} is the 4×4 matrix with elements $p_{x,ij}$, and $\langle \tilde{G} \rangle = \tilde{G}_e$ is the CPA Green's function. Expression (12) reduces to (9) in the limit $\omega \rightarrow 0$.

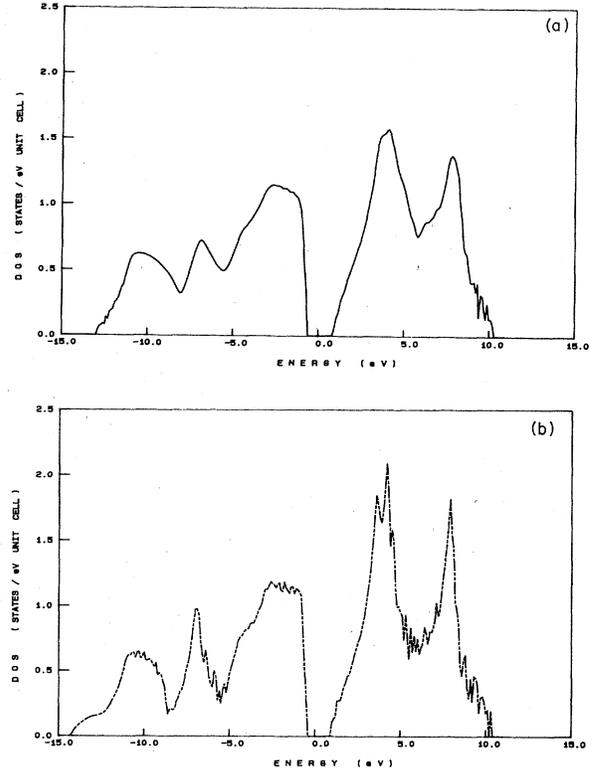


FIG. 1. Total density of states for the 1H (a) and the 4H (b) models of α -Si:H $_x$ with $x = 0.20$.

III. RESULTS AND DISCUSSION

In Fig. 1(a) we show the results for the DOS of the present 1H model. In Fig. 1(b) the corresponding results for the four-hydrogen-atom-cluster model are shown. The 1H model produces a larger gap ($E_g = 1.55$ eV) than the 4H model ($E_g = 1.36$ eV). The difference is due to the larger recession of the top of the valence band in the present model. The 1H model produces also a smoother DOS. Both differences can be attributed to the higher concentration of scattering centers and hence to the stronger disorder incorporated in the 1H model. We have attempted to evaluate the effects of the reconstruction disorder by modeling the latter through a continuous distribution of the diagonal matrix elements. For widths up to $W=0.15$ the effects were negligible in comparison with the hydrogen-induced disorder.

In Fig. 2 we plot the H site DOS for the present 1H model (solid line) together with the corresponding results for the 4H model. We also indicate by arrows the positions of the experimentally observed peaks from photoemission measurements. Although the present model produces peaks which are at slightly higher energies than the photoemission data, nevertheless there is a clear improvement near the bottom of the valence band. Indeed the 4H model produces a peak around -13 eV where no similar structure is observed, while it fails to reproduce the third observed peak near -10 eV. On the other hand, the present 1H model produces a broad peak near -9 eV and no structure at -13 eV, in fair agreement with the experimental data. It is not unreasonable to expect that a proper combination of clustered and dispersed hydrogen would provide results in even better agreement with the photoemission measurements.

In Fig. 3 we show results for the dc conductivity $\sigma(E)$ according to the present 1H model (solid line) and the 4H model. The exhibited fine structure for the 4H model is probably due to slow convergence of the k space integrations and it does not seem to represent physical effects. This structure is eliminated from the 1H model results due to the stronger disorder introduced in this case. It is worthwhile to point out that the 1H conductivity is lower

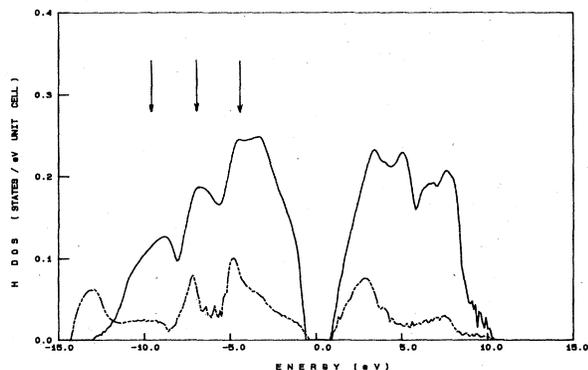


FIG. 2. H-site density of states for the 1H (solid line) and 4H (dashed line) models of $a\text{-Si:H}_x$ with $x=0.20$. The arrows indicate the peak positions from the photoemission measurements (Ref. 9).

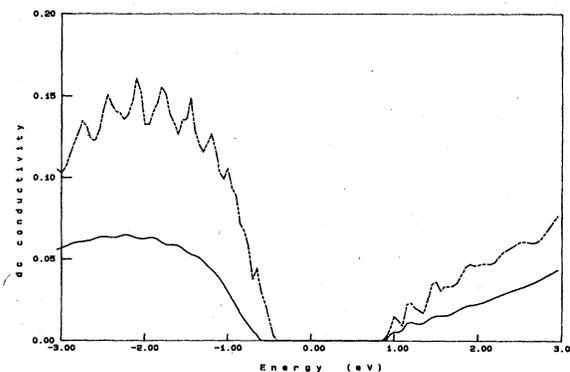


FIG. 3. The zero-temperature dc conductivity in $(\mu\Omega \text{ cm})^{-1}$ for $a\text{-Si:H}_x$ with $x=0.20$. Solid line corresponds to the 1H model and dashed line to the 4H model.

than the 4H result roughly by a factor of 3. This was to be expected, since the difference between the two models in the concentration of scattering centers justifies a factor of 4, which is reduced somehow due to the fact that the 1H scattering potential was assumed weaker than the 4H scattering potential.

In Fig. 4 we plot the absorption coefficient α versus $\hbar\omega$. Crosses are experimental points. The solid line in Fig. 4(a) is our theoretical result based on the 1H model while the dashed line in Fig. 4(b) is based on the 4H model. The theoretical results were normalized at $\hbar\omega=3$ eV to the experimental values by multiplying the calculated values by

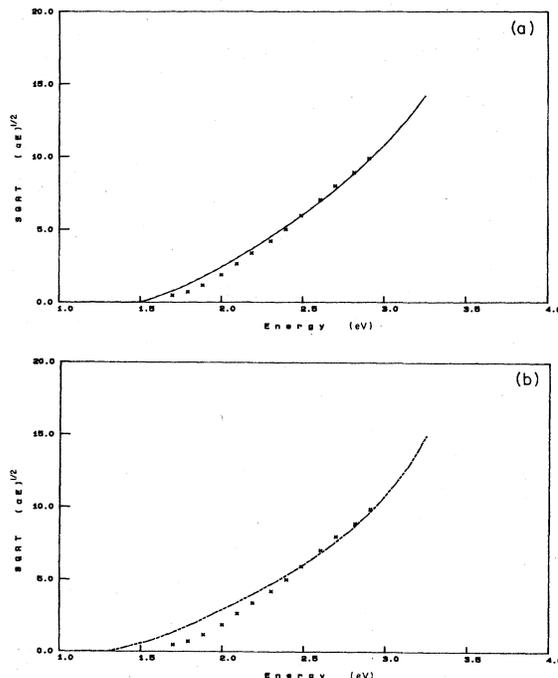


FIG. 4. Absorption coefficient α for $a\text{-Si:H}_x$ with $x=0.20$. The quantity $(\alpha E)^{1/2}$ for the 1H model (a) and the 4H model (b) is compared with experimental data (crosses) of Ref. 5. Units are $(\text{eV}/\mu\text{m})^{1/2}$.

1.66 and 1.48 for the 1H and 4H cases, respectively. It is clear that the 1H result is in rather good agreement with the experimental data, and it represents a definite improvement over the 4H result. This improvement is mainly due to the wider gap produced by the 1H model. It must be pointed out that the slight discrepancy shown in Fig. 4(a) for $\hbar\omega$ equal to 2 eV is to a large extent due to spurious tails of the DOS in the gap. These spurious tails are due to the numerical uncertainty of determining the small value of the DOS at the edges of the gap. Thus the agreement between the results of our present model and the experiment is impressive and it strongly suggests that (a) the electronic features near the gap are dominated by hydrogen-induced disorder and (b) that the CPA is an adequate method for obtaining the optical absorption.

The optical-absorption coefficient is a convolution of the DOS in the valence band times the DOS in the conduction band times the square of the dipole matrix element $M_p = \langle i | \vec{p} | f \rangle$, where \vec{p} is the momentum operator. The matrix element M_p can be expressed as $M_p = i\omega m M_x$, where $M_x = \langle i | \vec{r} | f \rangle$. It is not unusual to assume that $\langle |M_p|^2 \rangle_{av}$ is a constant to be taken out of the convolution integral. This assumption is very convenient because it allows one to obtain $\hbar\alpha\omega$ as being proportional to the convolution of the DOS in the valence and the conduction bands. The present explicit results for $\hbar\alpha\omega$ allows us to check the assumption of the constancy of $\langle |M_p|^2 \rangle_{av}$ and to actually determine the frequency dependence of $\langle |M_p|^2 \rangle_{av}$. In this connection we must mention that Cody¹⁰ and others have proposed that it is $\langle |M_x|^2 \rangle_{av}$ rather than $\langle |M_p|^2 \rangle_{av}$ which is a constant. Recently Cohen¹¹ has advanced a line of reasoning providing strong theoretical support to the proposition that

$$\langle |M_x|^2 \rangle_{av} = \text{const.} \quad (13)$$

We have checked these suggestions against our explicit theoretical results for the 1H and the 4H models. In both cases we found that Eq. (13) is obeyed very well. Actually the simple calculation based on Eq. (13) produces results for α which are identical to the ones shown in Fig. 4(a).

As a matter of fact, Eq. (13) combined with the 1H DOS with no tails in the gap produces results in complete agreement with the experimental data down to $\hbar\omega \approx 1.7$ eV.

IV. CONCLUSIONS

The first conclusion to be drawn from the present work is that the particular way of hydrogen incorporation does not seem to affect certain qualitative features such as the recession of the top of the valence band, the almost constancy of the bottom of the conduction band, and the apparently dominant role (at least in the vicinity of the gap) of the hydrogen-induced disorder. The details of the hydrogen incorporation produce quantitative changes. Thus a fully dispersed hydrogen atom produces the maximum concentration of H-induced scattering centers and as a result it increases the disorder, it reduces further the conductivity, and it lowers the top of the valence band. The position of the lowest in energy peak in the H-site DOS of the valence band seems to depend very sensitively on the details of the hydrogen incorporation. The DOS gap for a typical *a*-Si:H ($x=0.20$) is about 1.5 eV. Our results suggest that H is incorporated in *a*-Si partly dispersed and isolated and partly in clusters. The details will vary with preparation conditions.

The present model produces results for the optical-absorption coefficient which are in very good agreement with the experimental data. Furthermore, our results allow us to confirm the suggestion of Cody¹⁰ and others and the first-principles argument of Cohen¹¹ that in a strongly disordered semiconductor the dipole-moment matrix element $M_x = \langle i | \vec{r} | f \rangle$, (where $|i\rangle$, $|f\rangle$ are one in the valence and the other in the conduction band) can be taken as constant.

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APPENDIX

The single-site CPA condition [Eq. (1)] leads, in the present case, to the following equations:

$$(1-c) \frac{\epsilon_s - \Sigma_s}{1 - (\epsilon_s - \Sigma_s)G_{e11}} + x_4 \frac{\epsilon'_s - \Sigma_s}{1 - (\epsilon'_s - \Sigma_s)G_{e11}} + x_1 \frac{CV_{11} - 3M_{21}M_{12}}{D} = 0, \quad (A1a)$$

$$(1-c) \frac{\epsilon_p - \Sigma_p}{1 - G_{e22}(\epsilon_p - \Sigma_p)} + x_4 \frac{\epsilon'_p - \Sigma_p}{1 - G_{e22}(\epsilon'_p - \Sigma_p)} + x_1 \left[-M_{12}M_{12} + V_{22} \frac{D}{A} + \frac{F}{A}(V_{22} + 2V_{23}) \right] / D = 0, \quad (A1b)$$

where

$$V_{11} = \frac{1}{4}[\gamma'_1 + 3(\Gamma + 2\Gamma_2 + 2\gamma)] - \Sigma_s, \quad (A2a)$$

$$V_{12} = \frac{1}{4}[\gamma'_1 - (\Gamma + 2\Gamma_2) + 2\gamma], \quad (A2b)$$

$$V_{22} = \frac{1}{4}[\gamma'_1 + (3\Gamma - 2\Gamma_2) - 2\gamma] - \Sigma_p, \quad (A2c)$$

$$V_{23} = \frac{1}{4}[\gamma'_1 - (\Gamma - 2\Gamma_2) - 2\gamma] \quad (A2d)$$

are the independent elements of the scattering matrix for

the 1H vacancy in the *s* and *p* orbitals. The independent elements of the matrix $\tilde{M} = 1 - \tilde{G}_e \tilde{U}_{li}$ are

$$M_{11} = 1 - G_{e11}V_{11}, \quad (A3a)$$

$$M_{12} = -G_{e11}V_{12}, \quad (A3b)$$

$$M_{21} = -G_{e22}V_{12}, \quad (A3c)$$

$$M_{22} = 1 - G_{e22}V_{22}, \quad (A3d)$$

$$M_{23} = -G_{e22}V_{23} . \quad (\text{A3e})$$

G_{eij} are the matrix elements of \tilde{G}_e in the s and p basis. The other quantities in Eqs. (A1) are given in terms of the elements of the matrix \tilde{M} :

$$A = M_{22} - M_{23} , \quad (\text{A4a})$$

$$C = M_{22} + 2M_{23} = A + 3M_{23} , \quad (\text{A4b})$$

$$F = M_{12}M_{21} - M_{11}M_{23} , \quad (\text{A4c})$$

$$D = M_{11}C - 3M_{12}M_{21} . \quad (\text{A4d})$$

*Permanent address: Metal Physics Branch, Naval Research Laboratory, Washington D.C. 20375.

¹D. A. Papaconstantopoulos and E. N. Economou, Phys. Rev. B **24**, 7233 (1981).

²P. Soven, Phys. Rev. B **2**, 4715 (1970); J. S. Faulkner, *ibid.* **13**, 2391 (1976).

³W. Pickett, D. A. Papaconstantopoulos, and E. N. Economou, Phys. Rev. B **28**, 2232 (1983).

⁴M. H. Brodsky, Solid State Commun. **36**, 55 (1980); in *Fundamental Physics of Amorphous Semiconductors*, Vol. 25 of *Solid State Sciences*, edited by F. Yonezawa (Springer, Berlin, 1981).

⁵G. D. Cody, C. R. Wronski, B. Abeles, R. B. Stephens, and B.

Brooks, Sol. Cells **2**, 227 (1980).

⁶G. A. N. Connell and J. R. Pawlik, Phys. Rev. B **13**, 787 (1976).

⁷J. C. Slater and G. F. Koster, Phys. Rev. **94**, 1498 (1954).

⁸D. A. Papaconstantopoulos and E. N. Economou, Phys. Rev. B **22**, 2903 (1980).

⁹B. von Roedern, L. Ley, and M. Cardona, Phys. Rev. Lett. **39**, 1576 (1977); B. von Roedern, L. Ley, M. Cardona, and F. W. Smith, Philos. Mag. B **40**, 433 (1970).

¹⁰G. D. Cody, in *Hydrogenated Amorphous Silicon*, edited by J. Pankove (Academic, New York, 1984).

¹¹M. H. Cohen (private communications).