

Disorder and the Optical-Absorption Edge of Hydrogenated Amorphous Silicon

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The effect of thermal and structural disorder on the electronic structure of hydrogenated amorphous silicon is investigated by measurement of the shape of the optical absorption edge as a function of temperature and thermal evolution of hydrogen. The data are consistent with the idea that the thermal and structural disorder are additive, and suggest that the disorder, rather than the hydrogen content, is the fundamental determining factor in the optical band gap.

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Exponential optical absorption edges (or Urbach edges) are a well known feature in the optical properties of crystalline and amorphous semiconductors and insulators.¹ Although there are unresolved details to the theory, there is general agreement, for crystalline semiconductors, that the width of the exponential tail is a direct measure of temperature-induced disorder and reflects the thermal occupancy of phonon states in the crystal.^{1,2} This interpretation suggests that amorphous semiconductors, in which there is an additional nonthermal component to the disorder, should exhibit a temperature-independent component to the Urbach edge.³ To determine the relative sizes of the two components and to compare the effects of structural and thermal disorder, we have measured the optical absorption edge as a function of temperature on high-density⁴ α -SiH_x films. We find that our data are consistent with the interpretation that both the width of the exponential edge and the optical band gap are controlled by the amount of disorder, structural and thermal, in the network, and that hydrogen affects the band gap *indirectly*, through its effect on disorder. This relationship between the optical gap and the sharpness of the absorption edge suggests that there is a fundamental tradeoff in α -SiH_x solar cells between optical absorption and electron-hole pair extraction efficiency.

Details of film preparation and the optical measurements have been given previously.⁵ In order to compare the effects of structural and thermal disorder on the absorption edge we induced structural disorder intentionally in the films by introducing dangling bonds through thermal evolution of hydrogen. In Fig. 1 are shown optical measurements as a function of photon energy, E , at $T = 12.7, 151,$ and 293 K on an as-prepared film of composition SiH_{0.13}. We also show data obtained at $T = 293$ K on a similar film, from which hydro-

gen was evolved in a stepwise manner through isochronal heating in a vacuum at 25-C intervals from 400 to 600 C for 30 min at a time. We note that the absorption edge broadens and shifts to lower energy either with increasing thermal disorder or with structural disorder due to the isochronal heating. The exponential dependence of α on E , for $2 \times 10^2 \text{ cm}^{-1} < \alpha < 5 \times 10^3 \text{ cm}^{-1}$, has been shown in a previous paper to extend for

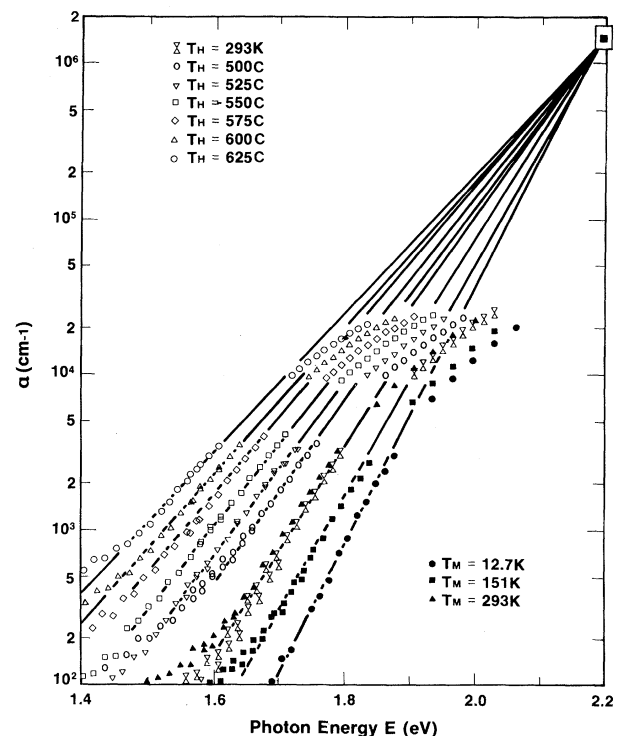


FIG. 1. Optical absorption coefficient, α , as a function of photon energy. The solid symbols refer to data obtained at different measurement temperatures, T_M . The open symbols refer to a film that has been isochronally heated at temperature T_H , as described in the text.

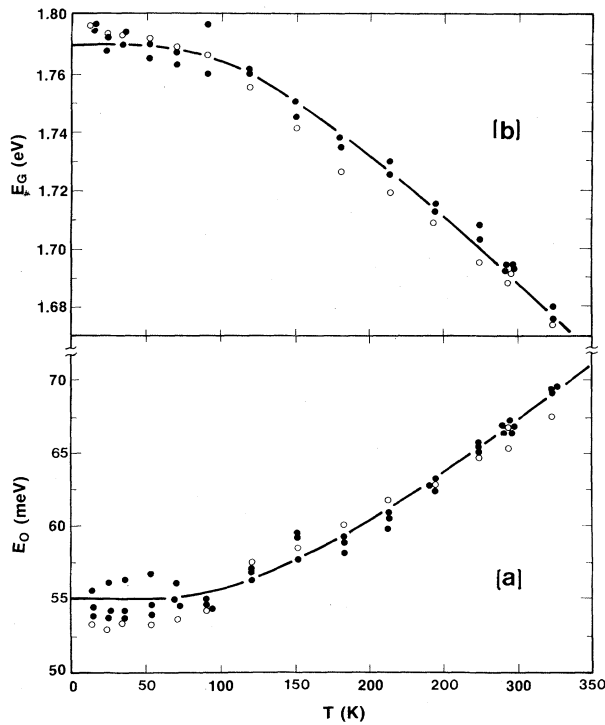


FIG. 2. (a) Width of Urbach tail [Eq. (1)], E_0 , as a function of temperature. The solid points correspond to isoabsorption; the open circles are from a least-squares fit to Fig. 1. The curve is theoretical and is defined in the text [Eq. (4)]. (b) Optical band gap E_G defined by Eq. (2) as a function of temperature. The solid points represent isoabsorption data; the open circles represent extrapolations of Eq. (2). The solid curve is defined in the text [Eq. (7)].

about three and a half orders of magnitude in α .⁶ From Fig. 1 we draw the more general conclusion that $\alpha(E, T)$ can be expressed by the Urbach form⁷

$$\alpha(E, T) = \alpha_0 \exp[(E - E_1)/E_0(T, X)], \quad (1)$$

where $E_0(T, X)$ is the width of the exponential tail, X is an as yet to be defined parameter describing structural disorder, and $\alpha_0 = 1.5 \times 10^6 \text{ cm}^{-1}$ and $E_1 = 2.2 \text{ eV}$, as determined by a least-squares fit of Eq. (1) to the data for $2 \times 10^2 \text{ cm}^{-1} < \alpha < 5 \times 10^3 \text{ cm}^{-1}$.

To deduce the temperature dependence of the optical energy gap E_G , we fitted $\alpha(E, T)$ outside the exponential region ($\alpha > 10^4 \text{ cm}^{-1}$) by the expression

$$[\alpha(E, T)E]^{1/2} = C[E - E_G(T)], \quad (2)$$

where the constant $C = 6.9 \pm 0.2 (\text{eV } \mu\text{m})^{-1/2}$ was found to be independent of temperature. Equation (2) is widely used to define the band gap in amor-

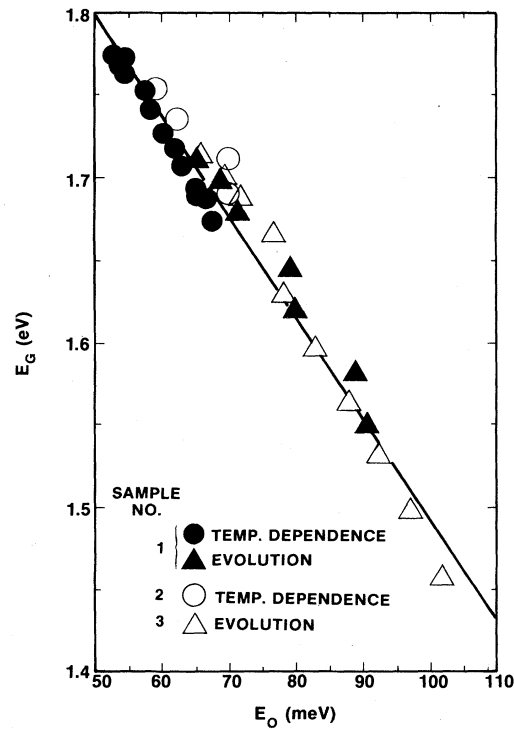


FIG. 3. Optical gap $E_G(T, X)$ as a function of $E_0(T, X)$ for three samples of $a\text{-SiH}_{0.13}$. The solid and open circles are for measurements at constant X and variable T_M . The solid and open triangles are for measurements at constant T_M (300 K) and variable X ($425 < T_H < 624 \text{ C}$).

phous semiconductors from optical absorption data.⁸ With this definition of E_G , the temperature dependences of E_G and E_0 are shown in Fig. 2. The striking similarity between the temperature dependences of the two quantities is illustrated in Fig. 3 where $E_G(T)$ is plotted against $E_0(T)$, with temperature as a parameter. The linear relationship between E_G and E_0 confirms that their temperature dependences have the same functional form. In addition in Fig. 3, we show that the same relationship between E_G and E_0 continues to hold when the plot is extended to include the (E_G, E_0) values for a film measured at room temperature after a progressive series of heat treatments in which H is evolved, disordering the lattice. This relationship between E_G and E_0 can be explained in terms of a simple model which embodies the idea of the equivalence of structural and thermal disorder.

Standard treatments of the Urbach edge in crystalline semiconductors^{1,2} conclude that the width of the adsorption edge E_0 is proportional to $\langle U^2 \rangle_T$, a thermal average, like the Debye-Waller factor,

of the square of the displacement U of the atoms from their equilibrium positions. To include the effect of structural disorder on E_0 , we make the plausible generalization that

$$E_0(T, X) = K[\langle U^2 \rangle_T + \langle U^2 \rangle_x], \quad (3)$$

where $\langle U^2 \rangle_x$ is the contribution of structural (topological) disorder to the mean-square deviation of the atomic positions from a perfectly ordered configuration. As a justification of this central hypothesis the dynamic phonon disorder and static structural disorder, in the adiabatic approximation, should have similar effects on the electronic energy levels. In order to estimate the temperature dependence of E_0 we approximate the phonon spectrum of the material by an Einstein oscillator with characteristic temperature Θ . For the purposes of this Letter, the Einstein model is a good approximation to a Debye phonon spectrum with a Debye temperature Θ_D equal to $4\Theta/3$. In this model, Eq. (3) can be expressed as

$$E_0(T, X) = \frac{\Theta}{\sigma_0} \left[\frac{1+X}{2} + \frac{1}{\exp(\Theta/T) - 1} \right], \quad (4)$$

where we have eliminated K in Eq. (3) by imposing the condition that $E_0(T, X) \rightarrow kT/\sigma_0$ as $T \rightarrow \infty$, with σ_0 an Urbach edge parameter of order unity. In Eq. (4), $X = \langle U^2 \rangle_x / \langle U^2 \rangle_0$ is a measure of the structural disorder normalized to $\langle U^2 \rangle_0$, the zero-point uncertainty in the atomic positions.

To relate the temperature dependence of $E_0(T, X)$ to $E_G(T)$, we first separate the temperature dependence of E_G into two different components as follows⁹:

$$\left(\frac{\partial E_G}{\partial T} \right)_P = \left(\frac{\partial E_G}{\partial T} \right)_V + \left(\frac{\partial E_G}{\partial \ln V} \right)_T \left(\frac{\partial \ln V}{\partial T} \right)_P. \quad (5)$$

The first term on the right-hand side of Eq. (5) is the explicit temperature dependence and the second term is the implicit dependence due to thermal expansion. The relative contribution of the second term can be estimated from the thermal expansion of crystalline Si, $(\partial \ln V / \partial T)_P = 7 \times 10^{-6} \text{ K}^{-1}$,¹⁰ the measured room-temperature value of $(\partial E_G / \partial T)_P = (-4.7 \pm 0.2) \times 10^{-4} \text{ eV/K}$ from Fig. 2, and the value of $(\partial E_G / \partial \ln V)_T = 1.0 \pm 0.5 \text{ eV}$ inferred from pressure measurements¹¹ on α -SiH_x and the compressibility of crystalline Si ($9.8 \times 10^{11} \text{ dyn/cm}^2$).¹⁰ From these values we conclude that the explicit temperature dependence in Eq. (5) is the dominant one and we neglect the implicit thermal-expansion term [$(7 \pm 4) \times 10^{-6} \text{ eV/K}$].

The explicit temperature dependence of the gap

in crystalline semiconductors can be written⁹

$$E_G(T) = E_G(0) - D(\langle U^2 \rangle_T - \langle U^2 \rangle_0), \quad (6)$$

where $E_G(0)$ is the zero-temperature optical gap and D is a second-order deformation potential. If Eq. (6) is generalized analogously to Eq. (3) to include the effects of structural disorder, then the mean-square lattice displacements in Eq. (6) can be expressed in terms of the experimentally measured quantity $E_0(T, X)$, and Eq. (6) can be rewritten as follows:

$$E_G(T, X) = E_G(0, 0) - \langle U^2 \rangle_0 D \left(\frac{E_0(T, X)}{E_0(0, 0)} - 1 \right). \quad (7)$$

This relationship between the band gap and the width of the absorption tail is in good agreement with the experimental data, insofar as the experimentally determined model parameters are physically reasonable, as we discuss below.

For example, the solid curve in Fig. 2(a) is a fit to $E_0(T, X)$ with $X=2.2$, σ_0 set equal¹ to 1, and $\Theta=400 \text{ K}$, corresponding to a Debye temperature of 536 K, in reasonable agreement with the Debye temperature of crystalline Si (625 K).¹⁰ The structural disorder $X=2.2$ is somewhat larger than the room-temperature thermal disorder $\{2[\exp(\Theta/T) - 1]^{-1} = 0.7\}$, as might be expected. The deformation potential D which determines the temperature dependence of the band gap in Eq. (6) is 30 eV/\AA^2 based on $E_0(0, 0) = \Theta/2$, the linear fit to the E_G vs E_0 plot shown as a solid line in Fig. 3, and $\langle U^2 \rangle_0^{1/2} = 0.08 \text{ \AA}$ appropriate to an oscillator with frequency $k\Theta/h$. This value for D is of the same order as similar deformation potentials in crystalline germanium.⁹ The remaining undetermined parameter in the model, namely $E_G(0, 0)$, is obtained from a fit of Eq. (7) to the temperature dependence of E_G in Fig. 2(b) with the other parameters as discussed above. The result, $E_G(0, 0) = 2.0 \text{ eV}$, represents an upper limit for the band gap of the α -SiH_x family of materials at zero degrees.

The data in this Letter suggest that the optical band gap $E_G(T, X)$ is determined by the degree of disorder in the lattice, rather than by the H content, as is commonly assumed in the literature.¹² In our model, the H affects the band gap only indirectly through its ability to relieve strain in the network. This conclusion is further borne out by the fact that measurements on films with different as-prepared H contents show practically the same E_G and E_0 . We have accumulated data on a large number of 2- μm films whose as-prepared H content was near 9%, for which the aver-

age value of E_G is 1.70 ± 0.01 eV and E_0 is 70 ± 3 meV; films made with H content near 13% exhibited $E_G = 1.70 \pm 0.03$ and $E_0 = 66 \pm 2$ meV. The data for all these samples fall on the line in Fig. 3 within the experimental error.

These results are important for optimization of solar cells. The coupling of E_G to E_0 suggests an unanticipated trade-off between the electrical "quality" of α -Si:H and its optical absorption. Sharpening of the band tails is desirable from the viewpoint of transport since it lowers trap densities as well as deep recombination centers. However, such electrical improvement in the material results in an increase in E_G and significantly poorer optical absorption! If lower band gaps are unattainable in the α -Si:H system, substantial improvements in efficiency can only come from substantial increases in open-circuit voltage and fill factor since the short-circuit currents are already within 15% of the maximum expected for materials with $E_G = 1.72$ eV.^{5,13}

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Stress-Wave Probing of Electric Field Distributions in Dielectrics

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The spatial distribution of the electric field within a dielectric sample is shown to be obtainable unambiguously from the time dependence of the open-circuit voltage or short-circuit current during the propagation of a stress wave across the sample. Experiments in which the pressure wave is generated by the impact of a pulsed laser beam on a metal target bonded to the dielectric plate under investigation have led to the first straightforward visualization of electric field distributions in solid dielectrics.

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For many years, dielectric materials have been studied mainly by such macroscopic methods as the measurement of the complex dielectric constant or the analysis of the thermally stimulated currents. A large amount of information is now available and has led to phenomenological models describing the charge transport and

storage properties of dielectrics. However, it has become increasingly clear that, in order to understand the microscopic processes and analyze the evolution of various phenomena such as charge storage in electrets or breakdown effects in insulators, new approaches are necessary. In this respect, the determination of the charge