

Random Phononic Structure and Indirect Optical Transitions: An Explanation for the Hydrogen Dependence of the Amorphous Silicon Band Gap?

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The relationship between an indirect semiconductor band gap and a distribution of phonon scatterers is explored. A forbidden phonon gap results from an array of appropriately sized and spaced phonon scatterers in a host matrix. Possible phonon scatterers include impurity atoms, atomic clusters, and other structures such as the dihydrogenated silicon atoms. In indirect band gap semiconductors, the interaction of the electronic bands and the *phonon band* can result in marked changes in the observed optical transitions. A phonon band–indirect optical gap model is suggested for the observed dihydride dependence of the amorphous silicon band gap. [S0031-9007(98)07380-3]

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Recent advances in photonic physics have opened many exciting avenues for further development. Generally, photonic effects have been observed in materials engineered to have one-, two-, or three-dimensional periodic arrangements of regions with varying refractive index. When the size and spacing of these refractive index varied regions are near to that of an electromagnetic radiation wavelength, the systematic photon scattering can prohibit propagation. These prohibited propagation spectral regions result in forbidden gaps, “photonic” bands, and in some cases photon localization [1–3]. Presently, semiconductor thin film deposition techniques can be used to prepare two-dimensional layered materials which exhibit photon bands and/or localization. In an analogous manner a material that has a periodic arrangement of regions of differing phonon velocity and/or atomic vibration spectra may, when the size scales are appropriate, exhibit phonon localization, forbidden gaps, and bands.

Yu and Cardona [4] summarized some of the two-dimensional work on phonon bands and phonon localization in semiconductor-based *superlattice* layered materials. While much progress has been made in preparing two-dimensional photonic materials, the lack of a convenient fabrication method to prepare arrays of the small sized, three-dimensional features has inhibited progress. This work explores the possibility that three-dimensional arrays of phonon scatterers of appropriate size and vibration spectra, when dispersed in an indirect band gap semiconductor, result in observable changes in the optical band gap. The most significant optical absorption changes are expected when the forbidden phonon gap coincides with the phonon wavelength range associated with the indirect optical transition. The concept is further elucidated by applying it to the recently reported dihydride dependence of the amorphous silicon band gap.

For a phonon band to appear in silicon, the phonon scatterers must be spaced roughly one lattice parameter

apart. Since the phonon velocity is smaller than that of light, the spacing and size of phonon scattering features must be smaller and more closely spaced than those required to induce a photonic effect. In analogy with the photonic band case, a phonon band is expected [5] when phonon scatterer spacing d and the phonon wavelength λ satisfy the Bragg condition $\lambda = 2d$, and/or when the analog of Mie resonance occurs within the scatterer. The Mie resonance condition is $\lambda/4n = L$, where L is the diameter of the scatterer.

In crystalline silicon the energy of the phonon involved in the indirect transitions is approximately 0.04 eV (e.g., see Bube [6,7]). Assuming that the phonon speed in crystalline silicon is $\sim 1 \times 10^6$ cm/s based on the elastic constant of crystalline silicon [8] and using the Bragg condition, the spacing at which phonon bands appear is ≤ 10 Å. This spacing implies large densities of scatterers, making it unlikely to experimentally induce phonon–indirect optical band gap effects in crystalline silicon, because the solubility of impurities and/or inhomogeneous structures is too low.

Hydrogenated amorphous silicon, *a*-SiH, is an appealing candidate since experimentally it has been shown that hydrogen content (C_H) can be varied from ~ 1 to 25 at.%. However, the *a*-Si:H optical absorption may or may not be indirect. Both Mott and Davis [9] and Cody [10] point out that many features of *a*-Si:H absorption are not understood. The Cody [10] description is among the more successful and transparent descriptions of the *a*-Si:H band gap. In order to make an easy connection to both earlier *a*-Si:H and the crystalline silicon descriptions, it is convenient to follow Cody’s [10] *a*-Si:H band gap description and then retain the crystalline constraints, as well as adding new constraints as required. The Cody description is cast in terms of crystalline (and/or virtual crystal) silicon matrix elements and lattice disorder induced relaxation of the indirect band gap momentum conservation rules. The one-electron approximation expression is

$$\varepsilon_2 = (2\pi e)^2(2/V)Q^2 \sum_{v,c} |\langle v|T|c \rangle|^2 \times \delta(E_c - E_v - E_{\text{photon}}), \quad (1)$$

where ε_2 is the imaginary part of the dielectric function, e is the electronic charge, V is the illuminated volume, Q and the first term in the summation are related to the optical matrix elements and the momentum conservation (details below), the sum is over occupied and unoccupied single-particle one-electron states (the factor of 2 is for spin conservation), and the last term is for photon energy conservation (E_c and E_v are the energies of an electron in the conduction and valence bands, respectively). An energy independent optical matrix element in which k_v and k'_c represent Bloch wave functions appropriate for the valence and conduction band electrons, respectively, and with a Kronecker delta for momentum conservation can be written as $Q\delta_{k_v,k'_c}$, where Q is a constant and

$$Q\langle v|T|c \rangle = Q \sum_{K_v, K_c} \langle v|\vec{k}_v\rangle \delta_{k_v, K_c} \langle \vec{k}_c|c \rangle, \quad (2)$$

where k_v must equal that of the electron in its conduction band state, k'_c after the photon absorption event occurs. The initial valence band single electron state and the conduction band state are taken to be crystalline Bloch waves (or virtual crystal Bloch waves in the amorphous case). Cody assumed that the amorphous case allowed the value of Eq. (2) to be constant, thus removing the k conservation, specifically,

$$\langle v|T|c \rangle^2 = T_0^2 = 1/N_0, \quad (3)$$

where T_0 and $1/N_0$ are related to the measured disorder and/or the slope of the absorption edge (the Urbach energy). By fitting the absorption profiles and other optical data to various density of states profiles, many optical parameters of a -Si:H could be fit. However, this required that the absorption spectrum (and ε_2) and the local bond distributions be linked. Earlier a -Si:H studies sited by Cody [10] supported this procedure, and it is fair to say that the model is both reasonably concise and has been very useful. Note that in amorphous and crystalline silicon at photon energies near the band gap the refractive index varies slowly; therefore, the behavior of ε_2 and the absorption coefficient as a function of photon energy are similar.

Recently Fukutani *et al.* [11] demonstrated that a -Si:H band gaps are independent of the local silicon bond environments by preparing a series of samples with a remarkable range of band gaps (1.52 to over 2.1 eV Tauc band gaps) all having the same short range order. In particular, Fukutani *et al.* [11] established the bonding distributions from the Urbach energies (Cody [10,12] linked the Urbach energies to the disorder), as well as by using the Raman scattering peak position and the Raman peak width. It should be noted that the Raman peaks used to deduce bonding environments have wave numbers

far from those related to the indirect optical transitions discussed below. No discernible relationship between the measured band gap and silicon bonding environment was obtained; that is, the silicon-silicon bond length and angle distributions were maintained across the entire band gap range. However, a large band gap dependence on the various hydrogen structures and their densities was clearly seen. Figure 1 shows the relationship between band gap and the hydrogen structures reported by Fukutani [11]. The a -Si:H band gap was most strongly correlated to the total Si-H₂ concentration (C_{SiH_2}). Weaker correlation to the total SiH concentration (C_{SiH}), the total hydrogen content (C_{H}), and the SiH₂/SiH ratio can also be seen. The insets of Figs. 1(a)–1(c) indicate that the correlation between a given hydrogen structure and C_{SiH_2} are similar to the corresponding correlation between the band gap and that hydrogen structure. The pseudodielectric function and its peak energy were reported to be most correlated with C_{SiH_2} (therefore, also correlated with the band gap). It is also significant that small angle neutron scattering studies of these materials showed an absence of voids or other inhomogeneous structures with dimensions greater than 10 Å [13].

Because the recent results preclude using disorder to justify and fit the a -Si:H optical absorption to the nondirect description using Eq. (3), we return to Eq. (1) with the assumption that the dominate a -Si:H band to band optical

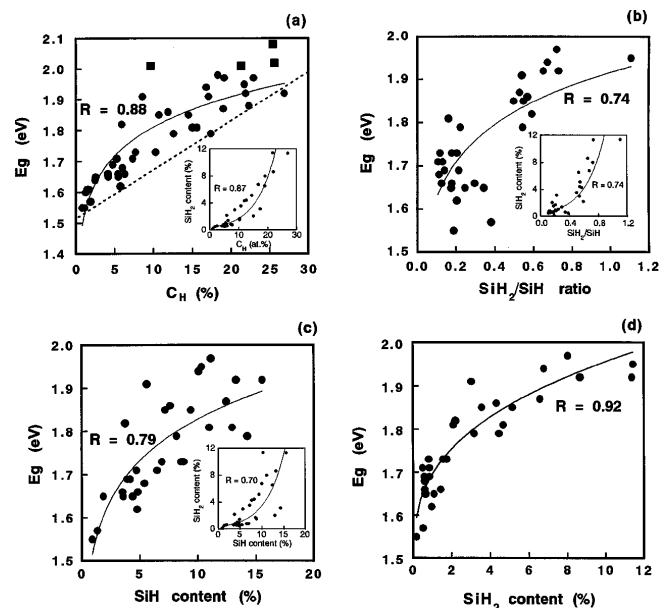


FIG. 1. The optical band gap of CA and ArA a -Si:H films as a function of C_{H} (a), the SiH_2/SiH ratio (b), C_{SiH} (c), and C_{SiH_2} (d). The dotted line of (a) is the linear relationship reported by Cody *et al.* [17]; ($E_g = 1.53 + 0.051C_{\text{H}}$) eV. In (a)–(c) the solid lines are the best fits, with correlation parameter R . In (d) the line corresponds to Eq. (7). The insets show the relationship between the various hydrogen structures and C_{SiH_2} , the corresponding correlation parameters as indicated. For experimental details see Fukutani [11].

transition is indirect and is influenced by the phonon spectrum. While removing the disorder issue from the fundamental description of the strength of the optical transition elements is justified, however, disorder in the a -Si:H network does exist and it affects among other things the electronic transport. Nagels [14] pointed out that the disorder in the local periodic electron potential leads to very short range scattering (~ 2 Å) and the corresponding low electron mobility (~ 2 cm²/V s). Therefore, the accurate treatment of the a -Si:H absorption requires that a hierarchy of disorder effects be considered. At the smallest scale bonding disorder is associated with the electron potential which results in short scattering lengths which are consistent only with short wavelength (large k) electrons. At slightly larger size scales, the spacing of phonon scatterers becomes important. Equation (1) allows both disorder effects to be concisely expressed. The presence of only large k electrons (and the lack of small k electrons) is treated in this work by multiplying the right-hand side of Eq. (1) by a step function which is 0 for $\vec{k} < \vec{k}_e$ and unity otherwise, where \vec{k}_e is the smallest k value (longest wavelength) consistent with disorder lattice (illustrated in Fig. 2).

An indirect band gap is consistent with the temperature dependence of the a -Si:H band gap reported by Cody [10]:

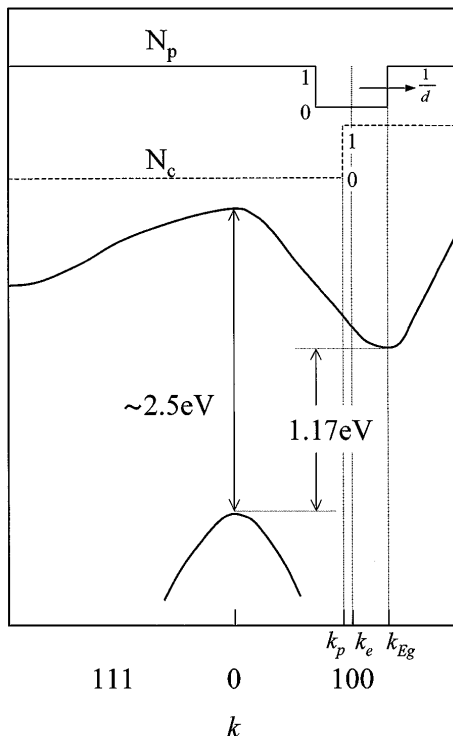


FIG. 2. Illustration of the indirect crystalline silicon band structure (after Bube [8]). Also illustrated are an electronic state density step function caused by atomic disorder in the a -Si:H structure and a phonon band (*well* function) related to phonon Si-H₂ scatterers dispersed in an a -Si:H matrix as described in the text.

$$\Delta E_g = \left(\frac{1}{e^{400/T} - 1} \right), \quad (4)$$

where ΔE_g is $E_g(T=0) - E_g(T)$. In comparison, the indirect crystal silicon band gap is given by

$$\Delta E_g(\text{eV}) = 1.169 - \left(\frac{1}{e^{350/T} - 1} \right). \quad (5)$$

The crystalline silicon band gap is consistent with a phonon energy of ~ 0.031 eV, while that of the assumed amorphous silicon indirect transition would be ~ 0.035 eV. The assumption that a -Si:H band gap is indirect is further supported by a phonon spectrum which is very similar to that of the crystalline phase [15,16]. Note, large ($\alpha \geq 1$ cm⁻¹) defect absorption in amorphous silicon make it impossible to observe processes with much lower absorption.

The C_{SiH_2} band gap dependence reported by Fukutani *et al.* [11] is interesting for three reasons: One is that the silicon atom having two bonded hydrogen atoms (Si-H₂) is only slightly more massive than that of the silicon atom. Two, the spring constant that couples the silicon atom to the lattice has been reduced by almost a factor of 2 relative to the average silicon atom in an a -Si:H matrix. Three, the random spacing of the Si-H₂ sites is of the same scale as the phonon wavelength needed for an optical transition. These observations suggest that the a -Si:H band gap is indirect and that the observed Si-H₂ dependence is the result of a phonon band. The solid curve in Fig. 1(d) is a fit involving the average distance between the Si-H₂ sites:

$$E_g(\text{eV}) = 1.47 + 0.226[C_{\text{SiH}_2}(\text{at. \%})]^{1/3}, \quad (6)$$

where E_g is the Tauc band gap in eV and C_{SiH_2} is the concentration of Si-H₂ sites in the materials in atomic percent. Equation (5) can be recast in terms of the distance between the Si-H₂ sites:

$$d(\text{cm}) = \left[C_{\text{SiH}_2}(\text{at. \%}) \frac{5 \times 10^{22}}{100} \right]^{1/3}, \quad (7)$$

$$\begin{aligned} E_g(\text{eV}) &= 1.47 + 0.226 \times \left(\frac{100}{5 \times 10^{22}} \right)^{1/3} d^{-1} \\ &= 1.47 + 2.85 \times 10^{-8} \left(\frac{1}{d} \right). \end{aligned} \quad (8)$$

Relating the dihydride spacing to an assumed phonon band requires that d (cm) be related to the wavelength at which phonons undergo Bragg reflection, $d = \lambda/2 = \pi/k$. Recasting Eq. (8) in terms of these phonon band k values,

$$E_g(\text{eV}) = 1.47 + 8.95 \times 10^{-8} |\vec{k}|. \quad (9)$$

The phonon band is expected to modify Eq. (1) through a trough in the phonon density of states centered on the k value for which the Bragg condition is met, \vec{k}_p . Therefore, because there are no phonons within the

phonon forbidden gap to satisfy momentum conservation, the minimum photon energy needed for an allowed electron transition (from the top of the valence band to the conduction band minimum) will increase as the phonon band moves to larger \vec{k}_p values. The phonon band (and forbidden gap) move to higher k values with increasing Si-H₂ density, as shown in Fig. 2. The movement of \vec{k}_p to larger values (with increasing Si-H₂ density and therefore decreasing d) forces the optical band gap to larger energies.

Starting from the crystal silicon band structure, applying the step function for large k value electrons and the phonon band “well” function to Eq. (2), and then inserting Eq. (2) into Eq. (1) reproduces the crystalline silicon indirect transition for k values ranging from the conduction band minimum to the zone boundary. Using a phonon velocity of 10⁶ cm/s, a phonon energy of 0.031 eV, and assuming a linear conduction band slope between the conduction band minimum, \vec{k}_m , a conduction band minimum energy of 1.17 eV, E_m , a conduction band maximum of 2.1 eV at the zone boundary, E_B , occurring at the zone boundary wave number, \vec{k}_B , and the crystalline silicon lattice parameter (5.43×10^{-8} cm) yields

$$\begin{aligned} E_g(\text{eV}) &\approx 1.17 + \left(\frac{E_B - E_m}{|\vec{k}_B| - |\vec{k}_m|} \right) (|\vec{k}_B| - |\vec{k}_m|) \\ &= 1.17 + 9.24 \times 10^{-8} (|\vec{k}_B| - |\vec{k}_m|) \\ &\quad \text{for } \vec{k} \geq \vec{k}_m (\text{cm}^{-1}). \quad (10) \end{aligned}$$

The values of Eq. (10) are in remarkable agreement with Eq. (9). The minimum energy (1.17 eV) in the crystal case is related to the detailed band structure; however, the minimum band gap of *a*-SiH (~ 1.47 eV) could result from a short maximum electron coherent length (k_e), pushing the allowed transitions out beyond the 1.17 crystal conduction band minimum. The increase in band gap with increasing C_{SiH_2} is consistent with a phonon band (centered on \vec{k}_p), pushing the allowed electronic transitions farther out to higher energies by reducing the available phonon states in the critical region about the electronic band minimum. The exponential band edge of *a*-Si:H is therefore related to two different gaps, the indirect electronic gap and the phonon gap. The steeper of the two gaps is most responsible for the observed absorption edge. While more detailed calculations are necessary in order to fit the magnitude of the *a*-Si:H

absorption and its measured Urbach energies, the model has many implications related to the use of phonon scattering structures and/or impurities to influence the optical properties of semiconductors.

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