Electron confinement in *a*-Si:H and an effective-mass theorem for amorphous semiconductors

G. J. Morgan and J. Okumu*
Department of Physics and Astronomy, The E. C. Stoner Building, Leeds University, Leeds LS2 9JT, United Kingdom
(Received 18 March 1996)

In previous work we have shown that the spectral function, $\rho(kE)$, must become strongly peaked at the band edges in amorphous semiconductors such as *a*-Si:H. This fact can be used to construct an effective-mass theorem and the simplest use of the theorem is made to study the effect of confinement in *a*-Si:H/*a*-SiN_x:H multilayers. We find that the effect of confinement on the density of states is negligible, in apparent disagreement with optical absorption studies of Abeles and Tiedje. However, reanalyzing the absorption coefficient recognizing that only the *a*-Si:H layers will absorb at the band edges we obtain excellent agreement with experiment and extract parameters describing the electronic structure at the band edge. [S0163-1829(96)52120-X]

The spectral function for electrons in an amorphous isotropic solid, $\rho(kE)$, is the probability of finding an electron with energy E if the modulus of the wave vector is k. It is analogous to the complex dielectric function in optics, namely, the imaginary part Γ_I, describes the decay of a coherent wave and the real part Γ_R gives the modification of the dispersion relation when one solves $E=k^2+\Gamma_R(kE)$ (using atomic units). The relationship is

$$\rho(kE)=\frac{1}{\pi}\frac{\Gamma_I(kE)}{[E-k^2-\Gamma_R(kE)]^2+\Gamma_I^2(kE)} \tag{1}$$

and the electronic density of states is given by

$$g(E)=\frac{1}{2\pi^2}\int_0^\infty k^2 dk\rho(kE). \tag{2}$$

If Γ_I is finite then the density of states is finite. If Γ_I is equal to an infinitesimal ξ then $\rho(kE)=\delta[E-k^2-\Gamma_R(kE)]$, and to obtain a zero density of states as in the gap then there must be no roots to $E=k^2+\Gamma_R(kE)$. The numerical calculations of Hickey *et al.*[1] on a small model of *a*-Si show how this occurs and are illustrated in Figs. 1(a) and 1(b). Setting the average potential to be zero, k^2 and $k^2+\Gamma_R(kE)$ are plotted for an energy (a) just below the band gap and (b) in the band gap. The energy is shown as a horizontal line. Below the band gap the intersection is on a steep part of $k^2+\Gamma_R$ and leads to a low density of states. Within the band gap a solution to $E=k^2+\Gamma_R$ is avoided by a singularity. When the spectral function is plotted[2] near the band edges a sharply peaked spectral function is found with the peaks lying close to the modulus of the free-electron Fermi vector k_F corresponding to an $E(k)$ relationship with a vertical slope but where the area under the spectral function goes to zero at the band edges. If

$$E=E_c+\beta_c(k_c-k)^n, \quad \beta_c>0, \quad (k<k_c) \tag{3}$$

and

$$E=E_v-\beta_v(k_v-k)^m, \quad \beta_v>0, \quad (k<k_v) \tag{4}$$

with $1>n>0$ and $1>m>0$ and where E_c and E_v denote the conduction- and valence-band edges, then these lead to an infinite slope when $k=k_v$ and a vanishing density of states. In fact, we will take $n=\frac{1}{2}$ and $m=\frac{1}{2}$ in this paper, which leads to a density of states proportional to $(E-E_c)$, for example. Choosing $n=m=\frac{2}{3}$ would yield a density of states proportional to $(E-E_c)^{1/2}$ as in crystalline semiconductors. We cannot distinguish from computer simulations between these two solutions but the main thrust of this paper would not be altered. Let us now consider forms for $\Gamma_R(kE)$, which would be consistent with that ''observed'' from the computer simulations.[2] Taking the valence band first, then the form

$$\Gamma_R(kE)=A_v\frac{(k-k_v)}{(E_v-E)}, \quad (A_v>0), \tag{5}$$

where $E_v=k_v^2$, has the property required, namely, the slope as a function of k approaches infinity. The value of k_v is approximately k_F, the modulus of the free-electron wave vector. If one solves $E=k^2+\Gamma_R$ then the form (4) is obtained. If we choose the form

$$\Gamma_R(kE)=A_c\frac{[k-k_c(E)]}{(E-E_c)}=A_c\frac{\{k-[k_c-\alpha(E-E_c)^2]\}}{(E-E_c)}, \tag{6}$$

where $E_c=k_c^2$, then one obtains (3) if $\alpha A_c<1$. If $\alpha A_c<1$ then the order of k and k_c is reversed. The precise behavior is not known but future refinements will not change the general arguments, which are based on a mixture of theoretical facts and evidence from numerical calculations.

Within the gap we require a self-energy that is singular. The simplest form to take is

$$\Gamma_R=\frac{E_g^2}{16}\frac{1}{k^2-k_0^2}, \tag{7}$$

where E_g is the energy gap. If one now solves $E=k^2+\Gamma_R(kR)$ for the real value of E then there are two roots for k^2 corresponding to

$$k^2=\frac{E+k_0^2}{2}\pm\frac{iE_g}{4}\left(1-\frac{4(E-k_0^2)^2}{E_g^2}\right)^{1/2}, \tag{8}$$

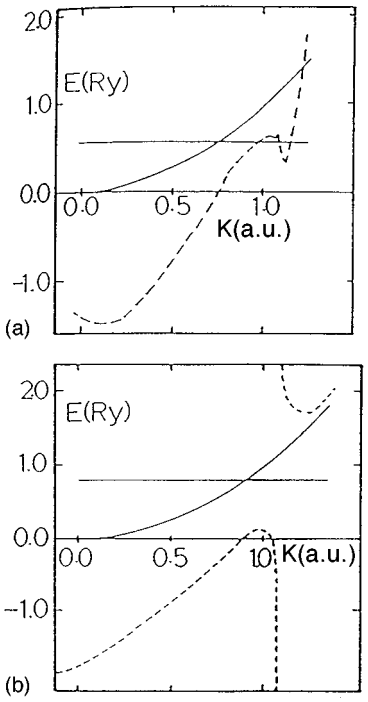

FIG. 1. The behavior of $k^2+\Gamma_R(kE)$ as a function of k (a) for an energy (E) just outside the gap, and (b) for an energy within the gap. The horizontal line denotes the energy and the solid curve is the free-electron form (k^2).

namely, that k^2 has imaginary parts within the gap just as in a crystalline semiconductor even though Γ_I is vanishingly small. k_0^2 is the energy at the center of the gap and again is approximately k_F^2. If we set $E=k_0^2\pm(E_g/2)$ then this establishes k_v and k_c to be

$$k_v=\left(k_0^2-\frac{E_g}{4}\right)^{1/2} \tag{9}$$

and

$$k_c=\left(k_0^2+\frac{E_g}{4}\right)^{1/2}, \tag{10}$$

because k^2 must be real at the band edges. This then links (8) smoothly to (3) and (4). This is not quite consistant with $E_v=k_v^2$ and $E_c=k_c^2$ but this is easily taken care of by making k_0 to be slightly energy dependent, tending to k_c and k_v at the band edges.

The next step in our argument is to recognize that if we have a slowly varying potential $V(r)$ and replace k^2 by $-\nabla^2$ we can construct the following Schrödinger-type differential equations by replacing E by $[E-V(r)]$ for values of k close to k_0, k_v, and k_c. When $[E-V(r)]$ lies within the gap (8) becomes (using atomic units)

$$-\nabla^2\Psi=\left(\frac{E-V(r)+k_0^2}{2}\right)\Psi \pm\frac{iE_g}{4}\left(1-\frac{4[E-V(r)-k_0^2]^2}{E_g^2}\right)\Psi. \tag{11}$$

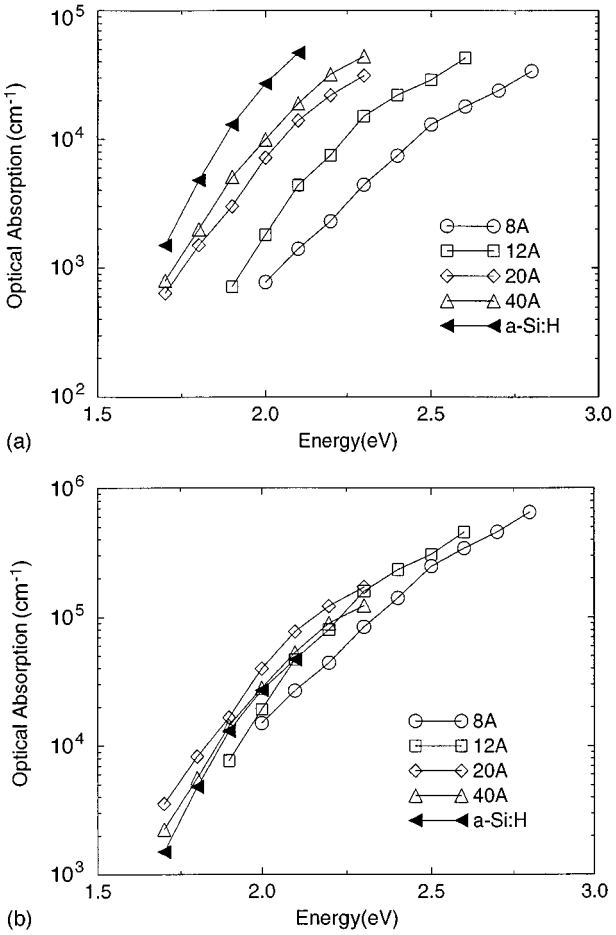

FIG. 2. The optical absorption as a function of energy on a linear-log plot: (a) unscaled data and (b) scaled data for thin layers and bulk *a*-Si:H. The symbols denote points read from the original data for the purpose of rescaling.

When $[E-V(r)]$ lies just in the conduction band (3) becomes

$$\frac{\beta_c^2}{2k_c}(k_c^2+\nabla^2)\Psi=[E-E_c-V(r)]^2\Psi, \tag{12}$$

and when $[E-V(r)]$ lies in the valence band (4) becomes

$$+\frac{\beta_v^2}{2k_v}(k_v^2+\nabla^2)\Psi=[E-E_v-V(r)]^2\Psi. \tag{13}$$

Setting $V=0$ yields (3), (4), and (8) for $k\approx k_0\approx k_c\approx k_v$. Choosing the appropriate sign when taking square roots it should be noted that it is important to retain the plus and minus signs in (11) so that decaying exponential solutions can be obtained using spherical coordinates. We would wish to emphasize at this stage that the only uncertainty concerns the precise values of m and n in (3) and (4) not the general physical argument.

We now turn to the measured optical absorption[3] in *a*-Si:H/*a*-SiN_x:H multilayers where, as usual, we will assume that the band offset is sufficient so that the states in a single *a*-Si:H layer can be regarded as completely confined. Abeles and Tiedje[3] showed that the optical absorption varied with varying thickness of the *a*-Si:H layers from (8–40) Å,

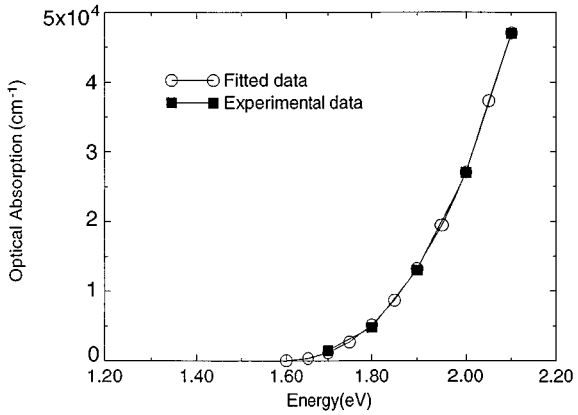

FIG. 3. The optical absorption as a function of energy on a linear-linear plot for the experimental and fitted data on *a*-Si:H.

which could be construed as stemming from variation in the gap due to confinement as in crystalline multilayers. Indeed, Abeles and Tiedje were able to fit their data using effective masses for the valence and conduction bands but the values used correspond to free-electron-like values. This has been a long-standing problem but we will argue that at the band edge of *a*-Si:H it is only the states of *a*-Si:H that are absorbing the radiation because *a*-SiN:H has a much larger band gap. Accordingly, the measured absorption coefficient should be scaled by a factor of $[(L_1+L_2)/L_1]^2$, where L_1 and L_2 are the thickness of Si:H and SiN:H layers, respectively. The reason for the square of $(L_1+L_2)/L_1$ is that the absorption will be proportional to the volume fraction of states in the conduction and valence band. In Fig. 2 we show the scaled and unscaled data plotted on a log-linear scale, and it can be seen that within the scatter resulting from transference of the original data there is no change in the gap with thickness. If we return to Eqs. (3) and (4) then the effect of confinement on, say, the conduction band would be to generate bands in a layer of thickness a in the z direction, such that

$$E_c^n = E_c + \left[\frac{\beta_c^2}{2k_c} \left\{ (k_c^2 - k_\uparrow^2) - \left(\frac{n\pi}{a} \right)^2 \right\} \right]^{1/2}, \qquad (14)$$

where n is an integer and $k_\uparrow^2 = k_x^2 + k_y^2$. Choosing a reasonable value of β_c, as will be discussed shortly, we find a negligible effect on the band density of states even for the smallest values of $a \approx 8$ Å, as the rescaled absorption coefficient would suggest.

We now turn to the problem of analyzing the optical absorption at the band edge in *a*-Si:H. We achieve this by assuming that the absorption is proportional to the joint density of states but we need an estimate of the matrix elements for optical transitions from the valence to the conduction band, which are treated as a constant termed $a^3 P_{\rm av}^2$ by Connell,[4] where a^3 is the volume per atom. We estimate this at about 3 eV from the absorption edge simply by comparing the experimental value[5] with that obtained from the joint density of states as calculated by Holender and Morgan.[6] We obtain the value of $a^3 P_{\rm av}^2 = 20.6$ a.u. We then take $\beta_v = \beta_c$ and fit the absorption at the band edge using E_g as the other fitting parameter. The results are shown in Fig. 3 on a linear-linear plot. The agreement is clearly excellent with $\beta_c = \beta_v = 0.23$ a.u. and $E_g = 1.55$ eV. This value of E_g should be compared with a value of 1.77 eV, which is usually quoted, but of course the precise value depends on how it is extracted from the experimental data and the precise form for the density of states at the band edge. The cubic form for the absorption coefficient at the edge results from the linear densities of states in the conduction and valence bands.

One of us (J.O.) wishes to acknowledge the support of Kenyatta University, the ODA, and the British Council.

*Permanent Address: Dept. of Physics, Kenyatta University, Box 43844, Nairobi, Kenya.

[1] B. J. Hickey, J. N. Burr, and G. J. Morgan, J. Non-Cryst. Solids **262-264**, 114 (1989).

[2] B. J. Hickey and G. J. Morgan, J. Phys. C **19**, 6195 (1986).

[3] B. Abeles and T. Tiedje, Phys. Rev. Lett. **51**, 2003 (1983).

[4] G. A. N. Connell, *Amorphous Semiconductors: Topics in Applied Physics Vol. 26*, edited by M. H. Brodsy (Springer, Berlin, 1976).

[5] D. T. Pierce and W. E. Spicer, Phys. Rev. B **5**, 3017 (1972).

[6] J. M. Holender and G. J. Morgan, Phys. Rev. B **47**, 3991 (1993).