

Low-temperature photoluminescence spectrum of amorphous semiconductors

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The low-temperature kinetics of photoexcited carriers in amorphous semiconductors are considered on the basis of a simple theory, and the shape of the steady-state photoluminescence emission spectrum is calculated. This allows an explanation of the relationship between spectral width and Urbach energy that has been found recently in the hydrogenated amorphous silicon-silicon nitride group of materials. *Ad hoc* disorder mechanisms previously invoked to account for the large spectral width are shown to be unnecessary, though they may be additionally present in real cases.

Photoluminescence in amorphous semiconductors has been studied for many years. Early work on the chalcogenides¹ was followed by extensive experimental studies on hydrogenated amorphous silicon (*a*-Si:H); these have been comprehensively reviewed.^{2,3} There is now a growing interest in the luminescence of amorphous silicon nitrides and carbides.⁴⁻⁶

Low-temperature luminescence in *a*-Si:H occurs mostly in a broad featureless band of roughly Gaussian shape peaked at 1.2-1.4 eV, with a full width at half maximum (FWHM) of 0.2-0.3 eV. The intensity in good samples is high; it is much reduced in samples where the defect density, as measured by ESR, exceeds 10^{17} cm^{-3} . It falls sharply for temperatures greater than about 50 K. There is a small blue shift with increasing excitation intensity. The behavior of the nitrides and carbides is generally similar, once allowance is made for the larger gaps in these materials. They also show subgap absorption of the Urbach form $\exp(h\nu/U)$ where $h\nu$ is the photon energy. Searle and Jackson⁵ report a striking correlation in *a*-Si_{1-y}N_y between the FWHM, W , of the main luminescence peak and the Urbach energy U ; they find $W = CU$ with $C = 4.4 \pm 0.2$ over a wide compositional range extending from 0 to 0.5 in the nitrogen fraction y .

There is general agreement that the main emission peak in *a*-Si:H arises from transitions between states in the conduction- and valence-band tails, but none on the details of the analysis. The root of the problem is the large spectral width, which has been difficult to explain without the *ad hoc* introduction of disorder effects. One school^{2,7} holds that the luminescence involves a strong electron-phonon interaction, which causes not only broadening of the spectrum but also a Stokes shift. The broadening is also held to be related to the distribution of tunneling times between pairs of states with varying spatial separations. Other models ignore such effects. Dunstan and

Boulitrop⁸ have presented a picture in which the carriers thermalize in exponential band tails, radiative transitions occurring from tail states that are the deepest within a defined volume; the probability distribution that a given state is the deepest within that volume induces the spectral width. Their result is, however, only about half the experimental width. Earlier thermalization models⁹ have also failed to account for the broadness of the spectrum. Numerical methods have recently been applied^{10,11} but only to the small-signal (linear) transient case, and the spectral width was not a principal interest.

This paper gives a simple analysis of thermalization and recombination in band tails, accounting for the luminescence widths without reliance on *ad hoc* models of disorder. C is calculated as 3.9 for *a*-Si:H, and as close to this value for the nitrides.

We consider an arbitrary gap density-of-states distribution $g(E)$ with tails extending from the band edges E_c and E_v . Band-to-band excitation is considered, with carriers excited from below E_v to above E_c at a rate G per unit volume and time. The model takes explicit account of thermalization down the band tails followed by tail-to-tail recombination (direct or via dangling bonds). Direct band-to-band recombination is not considered; neither is subgap excitation. Transitions from the conduction band to the gap states are described by a rate coefficient b_n , and from the gap states to the valence band by a rate coefficient b_p . Transitions from gap states of energy E to gap states of energy E' ($E' < E$) are described by a rate coefficient $r(E, E')$; the gap states are tail states or deeper (e.g., dangling bond) states. For the low temperatures considered we neglect upward transitions. Then the rate equations for the electron-occupation probability $f(E)$ in the gap, and the free-electron and hole concentrations n and p , are

$$-f(E) \int_{E_v}^E r(E, E') [1 - f(E')] g(E') dE' + [1 - f(E)] \int_E^{E_c} r(E', E) f(E') g(E') dE' + nb_n [1 - f(E)] - pb_p f(E) = 0, \quad (1)$$

$$\int_{E_v}^{E_c} nb_n [1 - f(E)] g(E) dE = \int_{E_v}^{E_c} pb_p f(E) g(E) dE = G. \quad (2)$$

Together with the conservation (neutrality) condition

$$\int_{E_v}^{E_c} f(E)g(E)dE + n - p = \int_{E_v}^{E_F} g(E)dE \quad (3)$$

(where E_F is the equilibrium, i.e., dark, Fermi level) the above equations define the occupation probability $f(E)$. Once $f(E)$ is known, the luminescence rate S at an emission energy E_e is given by

$$S(E_e) = \int_{E_v+E_e}^{E_c} f(E)g(E)r'(E, E-E_e) \times [1 - f(E-E_e)]g(E-E_e)dE, \quad (4)$$

where r' is the radiative contribution to r .

To begin with, we consider the simplest possible model, in which r is a constant independent of E and E' . It can be confirmed that an exact solution of the rate equations is

$$\frac{1}{[1 - 2f(E)]^2} - 1 = \frac{4nb_n \left[pb_p + r \int_{E_F}^{E_c} g(E')dE' \right]}{\left[pb_p - nb_n + r \int_{E_F}^{E_c} g(E')dE' \right]^2} \approx \frac{4G/r}{\left[\int_{E_F}^{E_c} g(E')dE' \right]^2}. \quad (5)$$

The latter is an approximate form for the case when n and p are small compared to the trapped-carrier concentrations (usually so at low temperatures) and $g(E)$ falls sharply away from the band edges. The main expression, used in the numerical work, is for arbitrary $g(E)$, and does not depend on an assumption of exponential band tails. To test the model for a -Si:H, $g(E)$ was taken as a pair of exponential band tails, of characteristic energies $E_1=27$ and $E_2=48$ meV, enclosing a broad (0.4 eV wide) Gaussian distribution of deep (nontail) states centered 0.75 eV above the valence-band edge; r' was taken to be nonzero only for tail-tail transitions. Given the above analytical form for $f(E)$, the integral in Eq. (4) was evaluated numerically. The resulting spectrum, shown as a dashed line in Fig. 1(a), is surprisingly broad and symmetrical. It comes from a convolution of a peak in $f(E)g(E)$ in the conduction-band (CB) tail and a peak in $[1 - f(E)]g(E)$ in the valence-band (VB) tail, which are shown as solid lines in Fig. 1, and between which the luminescence transitions occur. Around midgap f has a fairly constant value, so that $fg \propto g$. As E increases there comes a point at which f begins to fall rapidly, as a result of the downward transitions within the tail. It can be deduced from Eq. (5) that f falls finally as g^{-2} , so that $fg \propto g^{-1}$; this rise as g^{+1} and fall as g^{-1} describes the symmetry of fg . Having an explicit form for $f(E)$, we can study the peak in fg in detail. With no Gaussian states its FWHM turns out to be $2.8E_1$, and the luminescence width is then roughly $2.8(E_1^2 + E_2^2)^{1/2} = 0.16$ eV; this is a minimum value that can be increased by the introduction of the Gaussian states.

Figure 1(b) shows a set of calculations in which the height of the Gaussian-state density was varied so as to simulate a variation of dangling-bond density N_{DB} , N_{DB} being defined here as the integral over the Gaussian-state distribution. For small N_{DB} the luminescence is hardly affected; as N_{DB} increases the recombination path

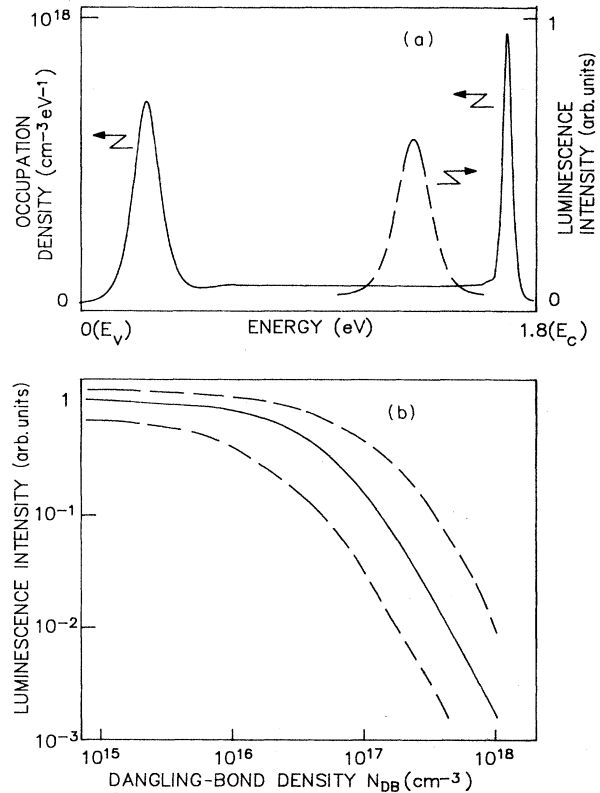


FIG. 1. (a) Calculations for single rate coefficient model with $r = 10^{-14}$ cm³s⁻¹ and $N_{DB} = 1.1 \times 10^{16}$ cm⁻³. Dashed line: Luminescence spectrum. Solid line: Electron density fg and hole density $(1-f)g$ responsible for the spectrum. Generation rate 10^{20} cm⁻³s⁻¹. (b) Fall of luminescence intensity with N_{DB} (as defined in the text) on the same model. The dashed lines enclose experimental results of Ref. 12 on a series of 31 samples, N_{DB} being in this case identified with spin density.

switches rapidly from tail-tail to tail-dangling-bond and the luminescence disappears. Experimental results of Street, Knights, and Biegelsen¹² on a series of 31 a -Si:H samples of differing spin density lie between the dashed lines in Fig. 1(b), showing a similar shape for the decay of emission intensity with N_{DB} (on the assumption that spin density would be proportional to N_{DB}). Street *et al.* attributed this shape to a distribution of pair separations; in the present theory it is a simple consequence of the recombination statistics.

The simplest (constant- r) model thus accounts quite well for some aspects of luminescence in a -Si:H. However, there is no reason to suppose that the rate coefficients are really the same for transitions within a tail as for transitions from one tail to another or for transitions between tail and deeper states. A more versatile model has therefore been developed in which these rate coefficients (denominated v , u , and w , respectively) are distinguished, u being taken as radiative; the gap is correspondingly divided, at energies E_n and E_p , into three regions: VB tail (E_v to E_p), deeper states such as dangling bonds (E_p to E_n), and CB tail (E_n to E_c). b_n is also distinguished for deep-state (B_n) and CB-tail (b_n) transitions, and similarly for

b_p ; CB to VB-tail and CB-tail to VB transitions are neglected. Let P and P' be the concentrations of holes trapped in the first and second regions, respectively, and N that of electrons trapped in the third region. Exact solution of the nonlinear rate equations now gives for $f(E)$ in the CB tail

$$\frac{1}{[1-2f(E)]^2} - 1 = \frac{4nb \left(uP + wP' - vN + v \int_{E_n}^{E_c} g(E') dE' \right)}{\left(uP + wP' - vN + v \int_{E_n}^{E_c} g(E') dE' - nb_n \right)^2}, \quad (6)$$

with a similar expression for $1-f(E)$ in the VB tail. N , P , P' , n , and p are related by the following five algebraic equations:

$$N + n = P + p + P' - \int_{E_f}^{E_n} g dE, \quad (7)$$

$$(nB_n + wN)P' = (pB_p + wP)(N_{DB} - P'), \quad (8)$$

$$(uP + wP')N = nb_n \left(\int_{E_n}^{E_c} g dE - N \right), \quad (9)$$

$$G = nB_n P' + nb_n \left(\int_{E_n}^{E_c} g dE - N \right), \quad (10)$$

$$G = pB_p (N_{DB} - P') + pb_p \left(\int_{E_v}^{E_p} g dE - P \right). \quad (11)$$

Here N_{DB} is the total state concentration between E_p and E_n . Equation (7) is the neutrality condition; Eqs. (8)–(11) are integrals of the rate equations over the defined regions. Equations (7)–(11) can be solved numerically for the total concentrations, and the distribution of electrons in the CB tail is then given by Eq. (6).

Let us now consider the shape of the peak in $f(E)g(E)$ in the CB tail as a function of the intratril rate coefficient v . For $v=0$, of course, f would be independent of energy. However, the integral of g near E_c is so large that when multiplied by even a small value of v it dominates the numerator of Eq. (6). Then using Eq. (10) we obtain

$$\frac{1}{[1-2f(E)]^2} - 1 = \frac{4G/v}{\left(\int_{E_n}^{E_c} g(E') dE' + Z \right)^2}, \quad (12)$$

where $Z \equiv (uP + wP' - nb_n)/v - N$. Maximizing fg for an exponential $g(E)$ is then equivalent to maximizing a function $F(x) \equiv (x - \beta)[1 - x/(1+x^2)]^{1/2}$ with respect to $x \equiv (E_1 g + Z)/(4G/v)^{1/2}$, where $\beta \equiv Z/(4G/v)^{1/2}$. The FWHM of the peak can be found in terms of g and then converted to width in energy. The resulting width, in units of the characteristic energy E_1 , is shown inset in Fig. 2 as a function of β . It begins at $2.8E_1$ at $\beta=0$ and tends to $3.5E_1$ at large β ; at $\beta=1.4$ it has already reached $3.4E_1$. There is thus a large range of values of the parameter β , and thus equivalently of v , in which the width is roughly $3.5E_1$. As the luminescence spectrum is obtained by convoluting the peaks in the CB and VB tails, the FWHM is $3.5(E_1^2 + E_2^2)^{1/2}$. For a -Si:H, where $E_1 \approx E_2/2$, this gives $3.9E_2$. For the nitrides little information is available on E_1 , but if it scales with E_2 we shall again obtain $3.9E_2$ for the luminescence width; in general we ob-

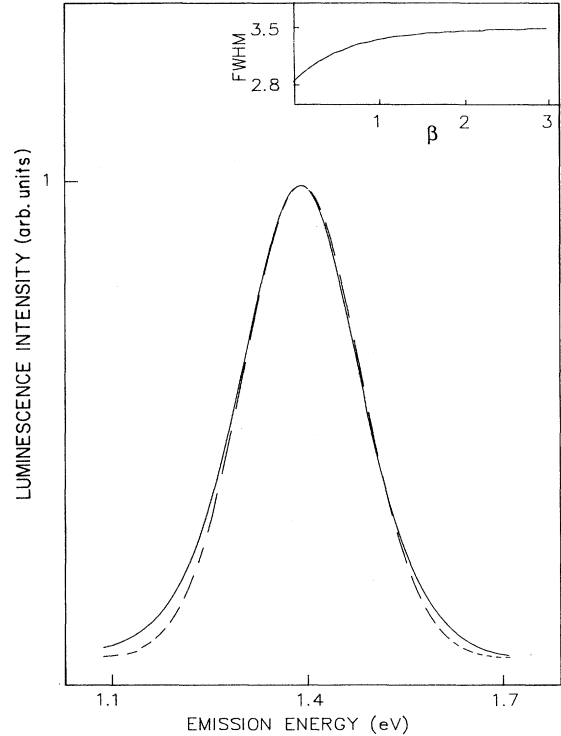


FIG. 2. Calculated luminescence spectrum for multiple rate coefficient model with $u, v, w = 10^{-13}, 10^{-14}, 10^{-12} \text{ cm}^3 \text{ s}^{-1}$, respectively. $N_{DB} = 1.3 \times 10^{16} \text{ cm}^{-3}$; generation rate $= 10^{20} \text{ cm}^{-3} \text{ s}^{-1}$. The dashed line shows a Gaussian fit. The peak is at 1.39 eV; FWHM = 0.20 eV. Inset: Luminescence width, based on exponential density of states, in units of characteristic energy E_1 , against parameter β defined in text.

tain $3.5E_2(1 + E_1^2/E_2^2)^{1/2}$. The exponential subgap absorption in a -Si:H and related materials is usually considered to reflect the exponential distribution of states in the VB tail,⁵ so that $U \approx E_2$. The present theory thus accounts very well for Searle and Jackson's experimental result.

The precise value of the parameter β depends on the solution of Eqs. (7)–(11) in a given case. These simplify drastically if N_{DB} is small, since the neutrality condition is then simply $P \approx N$. If w is small, then from Eq. (9) $N \approx (G/u)^{1/2}$, and thus $2\beta = (u/v)^{1/2} - (v/u)^{1/2}$; thus $\beta > 1.4$ if $u > 9.8v$. However, such simplification of Eqs. (7)–(11) is too drastic, as it exaggerates the blue shift with excitation intensity, giving shifts as high as 0.08 eV for a tenfold increase in intensity. It is likely that in real cases N_{DB} and w are not negligible quantities, and the recombination statistics represented by Eqs. (7)–(11) may be complex. This does not detract from the relative success of Eq. (6) in explaining the luminescence width; any nonexponential contribution to the density of states will in effect increase Z and β [see Eq. (12)], giving again the value $3.5E_2$ for the width.

Figure 2 shows an example of a spectrum calculated numerically from Eqs. (6)–(11) without any of the approximations mentioned in the last paragraph; the density of states is taken largely from an analysis of photoemission

data by Jackson, Tsai, and Kelso.¹³ The dashed line in Fig. 2 shows a Gaussian fit. It is well known that the experimental low-temperature spectrum in *a*-Si:H is essentially Gaussian in shape, with a slightly greater distortion on the low-energy side.⁷ The calculated curve is clearly very close to Gaussian; greater distortion on the low-energy side would result from a higher value of N_{DB} , but there are too many unknown parameters for a fitting procedure to be meaningful at this stage.

The physical assumptions of this theory are contained in the rate coefficients. The tunneling transition probabilities involved in these have a spatial dependence, which has been eliminated (conceptually) by performing configurational averages. Disorder, as such, is only present in this theory in the existence of gap states, and in the small values adopted for the rate coefficients; these are reduced from typical values for crystalline semiconductors by a factor representing the low average probability of finding a neighboring state within tunneling distance.

The basis of the present theory has been very simple: one-electron theory, rate equations, constant or piecewise-constant rate coefficients, and disorder manifested only by the presence of states in the gap, in contrast to the conceptually more complex theories referred to in the introduction. The theory is no more than an exact treat-

ment of the consequences of these simple assumptions. In real *a*-Si:H the more complex effects may also be expected to occur. But it is remarkable that the present theory gives a good account of much of the phenomenology: the decrease of intensity with increasing dangling-bond concentration, the generally Gaussian shape for the spectrum, with a width that is both adequate in size and somewhat insensitive to the values of the rate coefficients, the relationship $W \approx 4U$, and (following from that insensitivity) why it can hold in a series of nitride samples in which one would expect the rate coefficients to be quite different. The model thus shows considerable promise, at least for the VB tail, which accounts for most of the spectral width and shape; conditions in the CB tail may be more complex.

The kinetic theory developed here is of wider application in the field of amorphous semiconductors, and is not restricted to luminescence. The special case represented by Eq. (5) may also be useful as an exact check of numerical algorithms.

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