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TIME-RESOLVED LUMINESCENCE IN AMORPHOUS SEMICONDUCTORS

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Time-resolved luminescence spectra of some amorphous semiconductors are reported. In a-Si:O:H, the Coulomb interaction of the recombining electron and hole is explicitly observed in the time dependence of the luminescence peak position, at delay times ranging from 200 nsec to 30 μsec. Peak shifts at longer times are analyzed in terms of a distribution of recombination energy due to band tailing. It is deduced that the addition of oxygen to a-Si:H broadens the tails. In As_2S_3 we find no evidence of the Coulomb interaction, and this result supports the charged defect model.

1. Introduction

Photoluminescence has been extensively studied in both chalcogenide and tetrahedral amorphous semiconductors. One characteristic feature of both materials is a distribution of luminescence decay times that extends over a very broad time scale.[1,2] The recombination mechanism is radiative tunnelling[1,2] which results in a lifetime τ given by

$$\tau = \tau_0 \exp(2R/R_0), \qquad (1)$$

where τ_0 is of order 10^{-8} sec., R is the separation of the electron and hole, and R_0 is the effective Bohr radius of the larger particle. The distribution of distances R, and to a lesser extent R_0, are responsible for decay times ranging from 10^{-8} to 10^{-2} sec.

Since Eq. 1 relates τ and R/R_0, one can probe differing values of R/R_0 by measuring the luminesence at various times after an excitation pulse. Previously[1,3] it was shown that there are at least two mechanisms that contribute to the shift of the peak energy E_p of the time-resolved luminescence spectra of hydrogenated amorphous silicon (a-Si:H). At short times (< 1 μsec) there is a rapid decrease of E_p attributed to carrier thermalization. At longer times (> 10 μsec) there is a further decrease of E_p which was explained by the correlation of the Bohr radius R_0, and the binding energy of a band tail state. In this material R_0 is the radius of the electron.

In this paper, time-resolved measurements of other amorphous semiconductors are reported. It is shown that in some circumstances there is a third contribution to the time dependence of E_p from the Coulomb interaction of the electron and hole. The presence or absence of a Coulomb term gives direct information about the nature of the electronic states involved in recombination, and thus provides a means of testing recombination models.

The time resolved measurements are performed by gated photon counting as described elsewhere.[1] An S-1 photomultiplier allowed measurements of the spectra down to ~1.15 eV, and all the spectra were normalized to the detector response. The minimum pulse and gate time used was 50 nsec, and the excitation wavelength was 5309Å.

2. Amorphous-Si:O:H Alloys

Samples of hydrogenated Si:O alloys were prepared by plasma decomposition of $SiH_4/O_2/Ar$ mixtures as described elsewhere,[4] with oxygen contents ranging from zero to about 50 at %. The addition of oxygen to a-Si:H results in a systematic increase in the energy of the optical band gap, the cw luminescence peak, and the luminescence linewidth.[4] From the continuous changes observed in all the luminescence properties, it is evident that oxygen does not change the character of the transition. However, the increase in the linewidth is attributed to a larger electron-phonon interaction as oxygen is added.

Figure 1 shows examples of time resolved spectra of an a-Si:O:H sample. We estimate the oxygen content of this sample to be 20-40 at.%, from the observed shift of the optical gap compared to evaporated Si-O alloys.[5] There is a substantial and nonmonotonic shift of the luminescence peak with time. However, the shape of the spectrum is very similar to that of the cw spectrum, and shows no structure indicative of additional luminescence transitions. In Fig. 2, the peak position, E_p, of the time-resolved spectra is plotted as a function of time, and compared to similar data for an a-Si:O:H alloy of smaller oxygen content, estimated to be 2-

4 at.%. Previous data[1] for a-Si:H are also shown. The total energy shift of the heavily oxygenated sample is observed to be about twice that of a-Si:H. Furthermore, in the time interval from 200 nsec to 100 μsec, E_p actually increases with time. In the lightly oxygenated sample there is also an increase in E_p with time between 10^{-5} sec and 10^{-4} sec, although the effect is much smaller. No increase is detected in a-Si:H. From the data of Fig. 2 we conclude that in addition to the two mechanisms observed in a-Si:H, there is a third contribution to the shift of E_p which is observed in the intermediate time range, and which is strongly material dependent.

We attribute the increase of E_p to the Coulomb interaction. The attraction between the electron and hole will contribute an energy

$$E_c = -e^2/4\pi\varepsilon\varepsilon_0 R \qquad (2)$$

to the luminescence energy. From optical measurements of the refractive index between 0.5 and 1 eV, we find that the dielectric constant ε of the heavily oxygenated sample is 4.4. Using this value, it is shown in Fig. 2 that insofar as one can deconvolve the various contributions to E_p, the data are consistent with Eq. 2 and a Bohr radius R_0 of about 10Å. It is also clear that the same Coulomb component is not explicitly observed in a-Si:H. It seems probable that this is the combined result of three effects. First, the dielectric constant of 11.5 is nearly three times larger, thereby correspondingly reducing E_c. Second, thermalization apparently extends up to 10^{-5} sec and therefore masks the Coulomb term. Third, the measured value[1] of R_0 in a-Si:H is somewhat larger than 10Å which also reduces the expected E_c. In Fig. 2 we plot the predicted Coulomb contribution in a-Si:H. We note that the predicted curve for E_c is fairly sensitive to the value of τ_0 in Eq. 1, which may be in error by as much as a factor of 10.

The existence of the Coulomb term in a-Si:O:H provides explicit information about the states involved in luminescence. In particular, the results show that the centers are neutral in the ground state (i.e., before photoexcitation). The data therefore strongly support the model that recombination in these materials is between conduction and valence band tails.[1] The Coulomb interaction could not be observed if either the electron or hole center were initially charged, and would have the opposite sign if both were oppositely charged, as in donor-acceptor pair recombination.

3. The Long Time-Constant Region

It was proposed previously[3] that the decrease in E_p at long times occurs because the Bohr radius R_0 decreases as the binding energy of the state increases. Thus from Eq. 1 the long time constant components are increasingly dominated by deeper states which results in a shift of E_p to lower

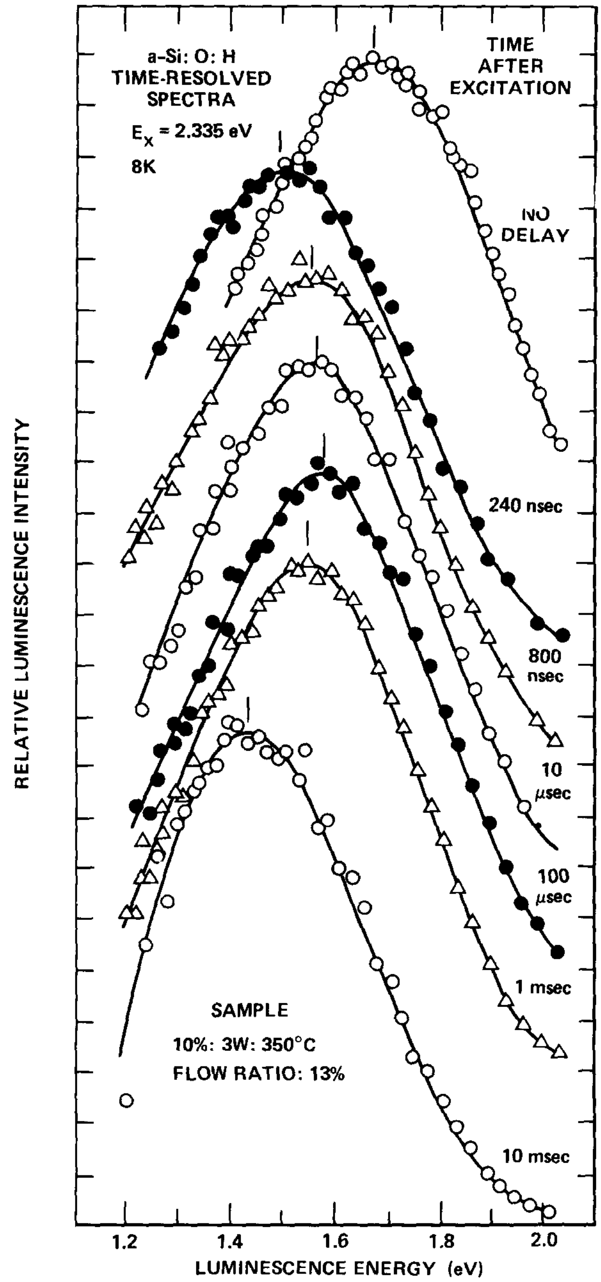

FIG. 1 Time resolved luminescence spectra of a-Si:O:H, at various times after photoexcitation. The deposition parameters of this sample are 3W r.f. power, 350°C substrate temperature and a reactor gas SiH_4:O:Ar in proportion by volume 8.7:1.3:90. The estimated oxygen content of the films is 20-40 at.%.

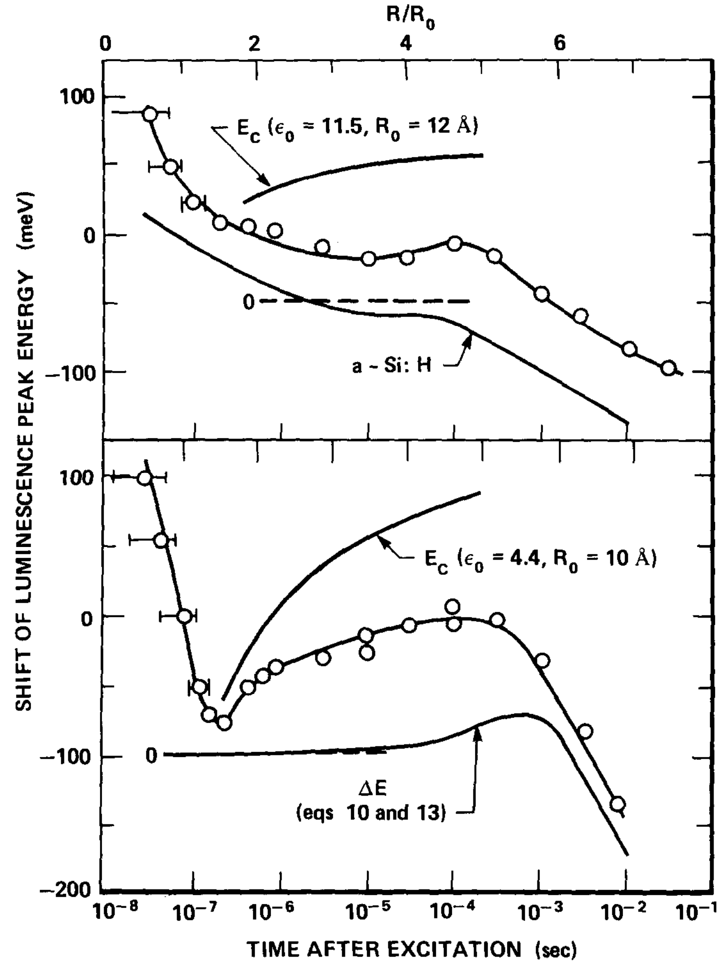

Fig. 2 The shift of the luminescence peak as a function of time after photoexcitation. The zero of energy is the cw luminescence peak. The upper scale shows values of R/R$_0$ from Eq. 1, assuming τ_0 = 10^{-8} sec. **Upper diagram** shows data for a-Si:O:H with 2-4 at.% oxygen, and previous data for a-Si:H (offset zero). The coulomb interaction E$_c$ appropriate for a-Si:H is indicated. **Lower diagram** shows data for the a-Si:O:H sample of Fig. 1, the estimated E$_c$ for this sample, and the value of ΔE from Eqs. 10 and 13, with an arbitrary energy scaling factor. In both diagrams, the zero of E$_c$ is shifted for convenience.

energy. This model is now analyzed in more detail. We ignore the thermalization and Coulomb effects by assuming that the recombining pairs have independent normalized distributions g(E) in energy and f(R) in pair separation, so that the total distribution G(E,R) is given by

$$G(E,R) = g(E)\,f(R) \qquad (3)$$

This distribution clearly has a mean energy which is independent of the value of R. When there is a broad distribution of decay times, as in a-Si:H, the luminescence at time t_0 after excitation is dominated by decay components with τ = t_0. Therefore, from Eq. 1, we describe the time resolved luminescence by a constant value of

R/R_0 (= x, say), where R_0 is now a function of energy. Thus the time resolved spectrum corresponds to a new distribution $G_1(E,R)$ given by

$$G_1(E,R) = g(E)\, f(xR_0(E)) \qquad (4)$$

Since f is now a function of E, the mean energy is different from that of G(E,R), and is time dependent because it is no longer independent of R. We equate the time dependent change in the mean energy of G_1 to the time resolved shift of the luminescence peak energy.

It is expected that R_0 is given approximately by

$$R_0 = \text{const.}\, E_B^{1/2} \qquad (5)$$

where E_B is the binding energy of the electron. Thus

$$R_0 = \bar{R}_0 (E/\bar{E}_B)^{1/2} \qquad (6)$$

where $\bar{R}_0$ and $\bar{E}_B$ are mean values for the distribution. Since we are only interested in calculating relative changes in the luminescence energy, the zero of E can be arbitrarily defined, and is now taken to be the conduction band mobility edge. The actual luminescence energy depends on the band gap energy and the Stokes shift, both of which are assumed to be constant. Expanding Eq.. 6 to first order in $\varepsilon = E - \bar{E}_B$ gives

$$R_0 = \bar{R}_0 (1 + \varepsilon/2\bar{E}_B) \qquad (7)$$

From Eqs. 3 and 4, using a first order expansion of f,

$$\delta G = G_1 - G \qquad (8)$$

$$= g(E)\, \bar{R}\, \varepsilon\, f'(\bar{R})/2\bar{E}_B \qquad (9)$$

where we have defined $\bar{R} = x\bar{R}_0$ and f' is the derivative of f. The (small) change δG in the distribution corresponds to a change ΔE in the mean energy given by

$$\Delta E(R) = \bar{R} f'(\bar{R}) \cdot \int \varepsilon^2 g(E)\, dE/2\bar{E}_B \qquad (10)$$

The integral in Eq. 10 scales the magnitude of ΔE, depending on the energy distribution of the states involved. If g(E) is an exponential with a cutoff energy (perhaps the mobility edge) at E_m,

$$g(E) = E_0^{-1} \exp((E-E_m)/E_0) \qquad (11)$$

then the integral in Eq. 10 reduces to $E_0/2$.

The shape of the time dependence of ΔE is determined by the term $\bar{R} f'(\bar{R})$ in Eq. 10, together with Eq. 1 which relates τ and R. It is clear that if f is a broad distribution then the largest change in ΔE will occur on the high-R side of the distribution, and this result agrees with observation. An approximate expression for $\bar{R} f'(\bar{R})$ can be obtained directly from the luminescence decay data I(t), using the relation[1]

$$f(R) \simeq \text{const.}\, t\, I(t)\, S(t) \qquad (12)$$

where S(t) = d(LnI)/d(Lnt).

We obtain

$$\bar{R} f'(\bar{R}) = \text{const.}\ \text{Ln}t\ I\ t[S(1+S) + dS/d(\text{Ln}t)] \qquad (13)$$

Fig. 2 shows a plot of the expression in Eq. 13 for one oxygenated sample. We use the decay data measured at the peak energy of the cw spectrum, and then corrected for the time resolved shift of the luminescence.

The rapid decrease of E_p above 1 msec is readily accounted for by the model. ΔE has a peak at ~1 msec which corresponds to there being a point of inflexion in f(R). We note that near the peak, ΔE depends strongly on the derivative of S, and this quantity is difficult to obtain accurately from the data. At small t, the I t Lnt factor in Eq. 13 ensures that $\Delta E \rightarrow 0$. Thus in the time region where the Coulomb interaction is most evident, the contribution to ΔE from the energy distribution of states is negligible.

It is evident from Fig. 2 that the magnitude of ΔE increases with the addition of oxygen to a-Si:H.

Since the time dependence of the decay changes very little, we attribute the difference to an increasingly broad distribution of band tail states, possibly the result of increased compositional disorder. Other luminescence data also indicate increased band tailing.[4]

4. Time Resolved Measurements in As_2S_3

Fig. 3 shows the shift of the time-resolved luminescence spectrum in glassy As_2S_3. The experimental uncertainty is somewhat larger than for a-Si, because the luminescence peak is generally at a lower energy, and much of the lower half of the band is out of the detectable energy range. Nevertheless we again observe shifts of E_p that can be separated into different time zones. It is seen that the As_2S_3 results differ significantly from those of a-Si:H. The thermalization component at short times covers a larger energy range (~250 meV), but is complete after 500 nsec. Part of the peak shift may be due to the higher energy luminescence band with a short time constant reported by Bosch and Shah.[6] We do not explicitly resolve this peak in our spectra. However this result is consistent with our use of an excitation pulse length of 50 nsec and above.

Between 500 nsec and 50 μsec there is virtually no shift of E_p, whilst at longer times, E_p again decreases markedly. We attribute this latter region to the energy distribution of the localized states as discussed in §2. The predicted shift of E_p (arbitrarily scaled) is obtained from Eq. 13 using the analytic expression for the known decay data.[2] As shown in Fig. 3, the result is in good agreement with the data which strongly suggests that this mechanism is the only contribution to the shift of E_p above 10^{-6} sec. A comparison with the data of Fig. 2 suggests that the range of localized states in As_2S_3 is comparable to that for the heavily oxygenated a-Si:O:H sample.

The intermediate time region between 3.10^{-7} and 3.10^{-5} sec in which E_p is constant indicates that in As_2S_3 there is no observable Coulomb interaction

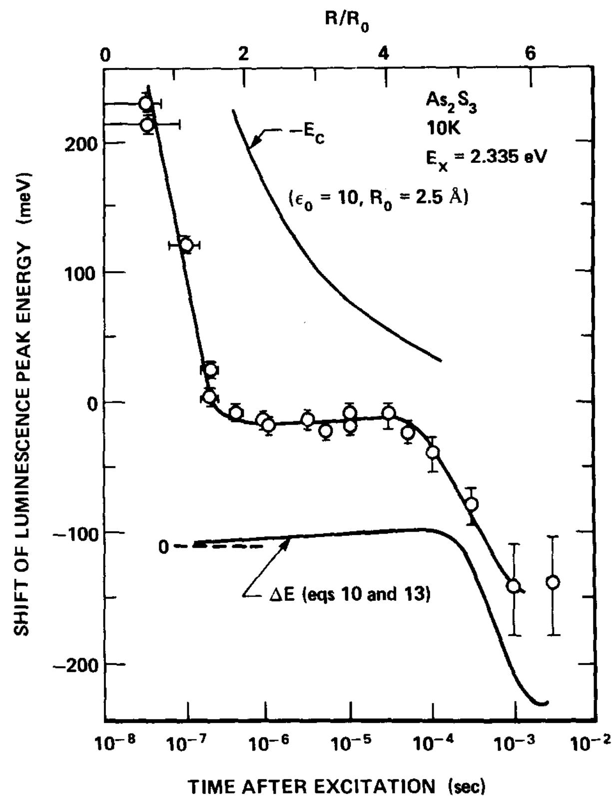

Fig. 3 Time resolved shift of the luminescence peak of glassy As_2S_3. The zero of energy is given by the cw luminescence peak, and values of R/R_0 are from Eq. 1 assuming τ_0 = 10^{-8} sec. The upper curve is the Coulomb interaction E_c assuming the recombination center is a VAP (D^+D^- pair) with R_0 = 2.5Å (Ref. 7). The lower curve is the peak shift predicted by Eqs. 10 and 13 (arbitrarily scaled) using the decay data of Ref. 2.

between the recombining electron and hole. This conclusion is in conflict with other recent studies.[7] However, we emphasize that the magnitude of the Coulomb interaction can only be established after the other contributions to the shift of E_p have been identified. The absence of the Coulomb interaction is consistent with previous luminescence results,[8] and with the model of charged defects,[9] the suggested center being D^-. According to this model, D^- captures a hole after photo-excitation, and the recombination is between a tail state electron and the D°. Thus there is no Coulomb term. We note that the involvement of tail states in this model provides a natural explanation of the similar short time and long time behaviour of E_p shown in Figs. 2 and 3.

The data of Fig. 3 cannot be readily explained by the model which supposes that the recombination center is a D^+D^- pair of varying separation and a Bohr radius of ~2.5Å.[7] This model predicts a large Coulomb term as indicated in Fig. 3. The data are only consistent with the D^+D^- model if R_0 exceeds about 20Å.

It has also been suggested that the luminescence is a transition between band edge polarons.[10] This model predicts a negative Coulomb term as for a-Si:O:H. Whilst the data do not support this model, it is harder to rule out because of the possible overlapping effects of the short time and long time components as in a-Si:H. However we estimate that the negative Coulomb term could only be present if R_0 is greater than about 10Å, and this value seems incompatible with the polaron hypothesis.

5. Conclusions

Time-resolved luminescence spectra can give information about the origin and energy distribution of radiative recombination centers in amorphous semiconductors. In a-Si:O:H we observe the Coulomb interaction of the recombining electron-hole pair, and this result supports our previous model that in this type of material, the dominant radiative recombination is between band tail states. It is also shown that the time resolved measurements give a rough estimate of the band tail widths. In As_2S_3 no Coulomb interaction is detected, which supports a previous model of a single charged defect.

It is evident that both the luminescence decay and time-resolved peak shifts are very similar in As_2S_3 and materials based on a-Si:H. We suggest that the recombination mechanism of radiative tunnelling may be of widespread applicability to amorphous semiconductors, as a consequence of the general presence of localized band tail states. The technique of time-resolved luminescence provides a powerful means of identifying the recombination centers. However, the technique is complicated by the presence of (at least) three different contributions to the peak shift, and therefore must be applied with care.

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