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Time-resolved photoluminescence spectra in sputtered *a*-Si:H

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We report measurements of the time-resolved photoluminescence spectra of sputtered *a*-Si:H. The dependence of E_p, the peak energy of the luminescence spectrum, on time for 10 ns $<t<0.1$ ms, is discussed for samples produced under different conditions and characterized by other property measurements. A feature in $E_p(t)$ for 10 ns $<t<0.5$ μs is observed and attributed to an electron-hole Coulomb contribution. The excitation energy dependence of $E_p(t)$ is also measured and discussed.

I. INTRODUCTION

Time-resolved photoluminescence measurements have been used to study thermalization, relaxation, and recombination processes in *a*-Si:H.[1,2] It has been suggested that since the recombination mechanism is radiative tunneling, at a time, *t*, maximum emission is observed from electron-hole pairs with a fixed value of R/R_0 given by

$$t=\tau_0\exp(2R/R_0)\ , \tag{1}$$

where R is the separation of the electron and hole, R_0 is the effective Bohr radius of the electron, and $\tau_0\sim 10$ ns.[1] Experimental results on glow-discharge (GD) prepared *a*-Si:H have suggested two specific processes that contribute to the shift in the peak energy of the luminescence spectrum with time, $E_p(t)$.[1] The observed decrease in $E_p(t)$ for $t<1$ μs was attributed to the motion of carriers through localized band-tail states to lower energy. At times longer than 10 μs, the decrease in $E_p(t)$ was found to be consistent with a correlation between the luminescence energy and the decay time, after completion of the band-tail relaxation process. An increase in $E_p(t)$ for 200 ns $<t<100$ μs observed in GD *a*-Si:O:H was attributed to the reduction, with increasing R, in the Coulomb energy between recombining electrons and holes, observable due to the lower dielectric constant of the heavily oxygenated material.[3]

We report the results of similar measurements on sputtered *a*-Si:H and concentrate on $E_p(t)$ as a function of excitation energy, $h\nu$, and sample preparation.

II. EXPERIMENTAL

The samples were prepared[5] by sputtering in Ar and H using different H partial pressures and/or substrate temperatures to obtain a variation in H content from 15–30 at. %. The change in the size of the band gap with H content for these samples is consistent with the results of Freeman and Paul.[6] A comparison sample of *a*-Si:H:F was prepared by dc GD decomposition of a 2:1 ratio of SiH_4 and SiF_4. Approximately 5 at. % F and 25 at. % H was incorporated.[7]

The time-resolved photoluminescence measurements were carried out at 77 K using 5-ns rise time, 25-μJ pulses from a dye laser pumped by an N_2 laser. An S1 photomultiplier tube and boxcar integrator with a minimum gate width of 2 ns were used for detection and signal processing. For measurements as a function of $h\nu$, the excitation intensity was varied such that a constant luminescence output was maintained independent of $h\nu$. The density of absorbed photons was kept roughly constant with $h\nu$ at about 1×10^{17} cm^{-3}.

III. RESULTS AND DISCUSSION

A. Sample dependence

Figure 1 exhibits the photoluminescence spectra measured at 8 ns after the onset of the excitation pulse for three samples of sputtered *a*-Si:H and a fourth sample of GD *a*-Si:H:F. Figure 2 shows $E_p(t)$ for the four samples. The widest gap sample

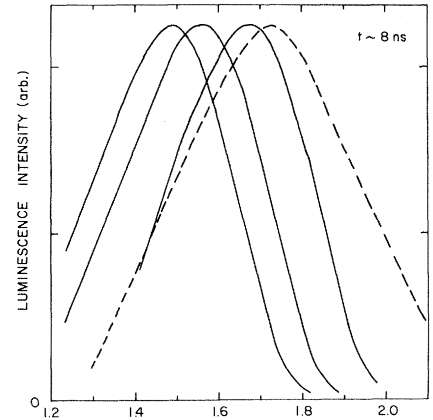

FIG. 1. Normalized photoluminescence spectra for glow discharge *a*-Si:H:F (broken line) and three sputtered *a*-Si:H samples measured at $t=8$ ns. Optical constants for the sputtered samples are (from right to left) E_{04} (300 K) = 2.16, 2.07, 1.97 eV; $n(2.2\ \mu\text{m})$ = 3.11, 3.36, 3.57. For the glow discharge sample $E_{04} \gtrsim 2.25$ eV. E_{04} is the photon energy for which the absorption coefficient is $10^4\ \text{cm}^{-1}$.

exhibits a feature in $E_p(t)$ characterized by a fast decrease in E_p with time for $t<50$ ns, followed by an increase for 50 ns $<t<500$ ns. We observe a progressive weakening of the feature with decreasing band-gap size. We associate the *increase* in E_p with a changing Coulomb interaction between recombining electron-hole pairs as R increases with time for 50 ns $<t<500$ ns. The sample dependence suggests that as the gap size increases and the index of refraction, n, of the sample decreases, the Coulomb interaction is less effectively screened.

Next we shall consider the sample dependence of the $t<50$ ns decrease in $E_p(t)$. We might suggest that for our samples the increase in the size of the band gap is also accompanied by a decrease in the slope of the density of tail states below the conduction-band edge. A broadened band tail may result in a steeper $E_p(t)$, since electrons relaxing through the tail states lose energy at a faster rate.[3] However, since steady-state measurements of the spectral width and the distribution of activation energies for nonradiative recombination[8] indicate that the three sputtered samples have comparable tail-state distributions, we propose that the decrease in $E_p(t)$ also can be attributed to the Coulomb interaction which is less effectively screened in the case of low n material.

In order to extract the Coulomb contribution from Fig. 2, we assume that, in the absence of this contribution, E_p would be given at all times by extrapolation of the linear behavior with log$t$ at long times ($t>1\mu$s) seen in the figure. This general behavior might be expected if the distribution of recombining carriers at low temperature follows the multiple-trapping model in the presence of an exponential tail state density, as described independently by Tiedje and Rose[9] and Orenstein and Kastner.[10] Subtracting the extrapolated linear variation from the data at all t gives the Coulomb contribution. For the three sputtered samples, the contributions are roughly symmetric about $t \sim 25$ ns with maxima of approximately 100, 75, and 25 meV. Figure 3 shows representative data.

Using $\epsilon = n^2$ for the dielectric constant, Fig. 3 predicts $R=50$ Å at both the onset of measurement (6 ns) and at 150 ns. These results suggest that for the lowest n samples the separation of electron-hole pair after thermalization, R_{th}, is smaller than the Onsager escape radius,[11] R_e, given by $R_e = e^2/\epsilon kT$ (200 Å for the sample of Fig. 3,

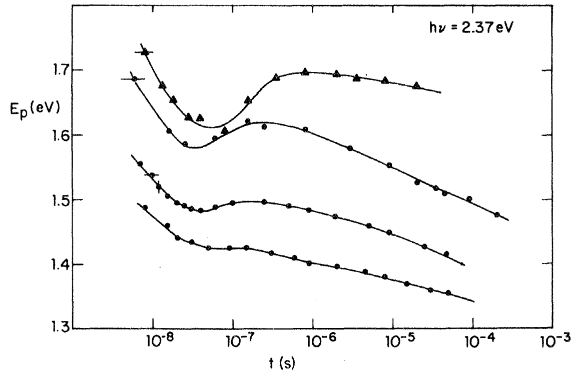

FIG. 2. $E_p(t)$ for the four samples whose photoluminescence spectra are shown in Fig. 1.

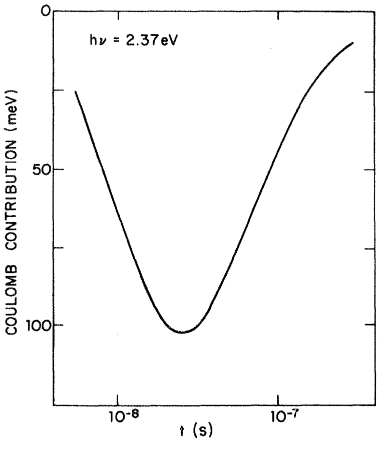

FIG. 3. Estimated Coulomb contribution to $E_p(t)$ for the sputtered sample with $E_{04}=2.16$ eV.

with $T=77$ K). Thus, for pairs radiatively recombining at times shorter than 25 ns, the average electron-hole pair separation R decreases with time and tightly bound pairs are formed. We do not envision a hydrogenic picture but rather one in which electrons and holes occupy localized band-tail states separated by a few interatomic distances. Any further relaxation of the carriers must proceed via tunneling to deeper localized states which are a greater distance apart on the average. Figure 4 shows that the short-time behavior ($t<25$ ns) may be dominated by recombining electrons undergoing type-A relaxation events, whereas the longer-time behavior ($t>25$ ns) may be dominated by electrons undergoing type-B events.

We suggest that in certain cases, Eq. (1) should be more appropriately written

$$t=\tau_0\exp(2R/R_0)+t_0\ , \tag{2}$$

where t_0 is the time required for an electron to relax into a state a distance R from the hole from which it recombines by tunneling after an additional time $t-t_0$. In the absence of a strong Coulomb interaction where R increases monotonically with time, we suggest that $t_0<<\tau_0\exp(2R/R_0)$ and Eq. (1) is applicable. In cases where a strong Coulomb interaction exists and R decreases with time, we suggest that intermediate relaxation events, rather than the final tunneling event that results in radiative recombination, actually determines the recombination time. Thus Eq. (2) would be applicable in such a case.

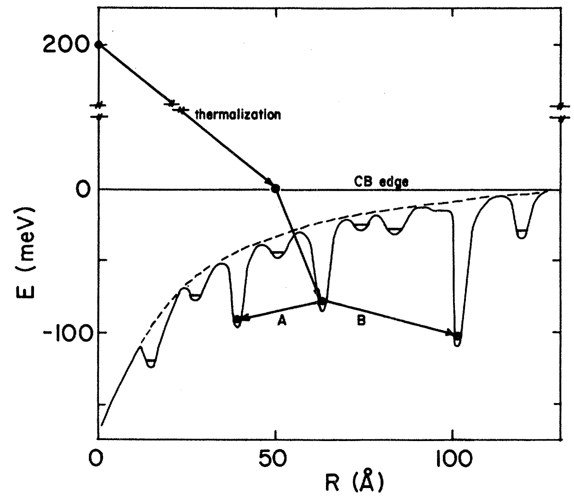

FIG. 4. Schematic diagram of the electron energy E as a function of its distance R from the hole. We show the Coulomb contribution to the energy of localized levels available to the electron. Two types of relaxation events are depicted: those for which R either decreases (A) or increases (B).

Additional information may be obtained from the widths of the time-resolved photoluminescence spectra. Figure 5 shows the width as a function of time for the sample of Fig. 1 with $E_{04}=2.07$ eV. We note that the width is a maximum near the time of maximum Coulomb energy. This may be indicative of the fact that at this time there is the largest spread in the distribution of electron-hole separations.

B. Excitation energy dependence

Next we shall discuss the effects of changing the excitation energy $h\nu$ in the time-resolved luminescence spectra. Figure 6 exhibits $E_p(t)$ for one of the sputtered samples of Fig. 1 ($E_{04}=2.16$ eV) using four different excitation energies. For $h\nu \geq 2.14$ eV, no variation in $E_p(t)$ with $h\nu$ is observed. If the average electron-hole separation after thermalization is completed, R_{th} increases in accordance with the relation[12]

$$R_{\text{th}}=\left[\frac{\mu kT}{e}\frac{h\nu-E_G}{h\nu_{\text{ph}}^2}\right]^{1/2}\ , \tag{3}$$

where μ is the electron mobility in the conduction band, $h\nu-E_G$ is the excess energy lost by the electron via phonon emission during thermalization, and $h\nu_{\text{ph}}$ is the energy per emitted photon. Then, using $E_G=2.07$ eV (see discussion of Fig. 7), Eq. (3) predicts that $R_{\text{th}}(h\nu=2.37\text{ eV})\sim 2R_{\text{th}}(h\nu=2.14\text{ eV})$. Such a large difference between the average electron-hole separations after thermalization for the two different excitation energies would surely be observed in different $E_p(t)$, at least in the

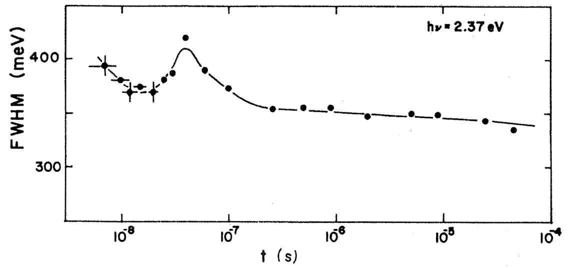

FIG. 5. The full width at half maximum (FWHM) as a function of time for the sputtered sample with $E_{04}=2.07$ eV.

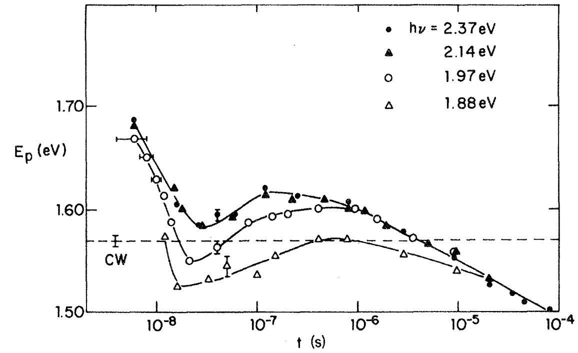

FIG. 6. $E_p(t)$ for different $h\nu$ for the sample of Fig. 3.

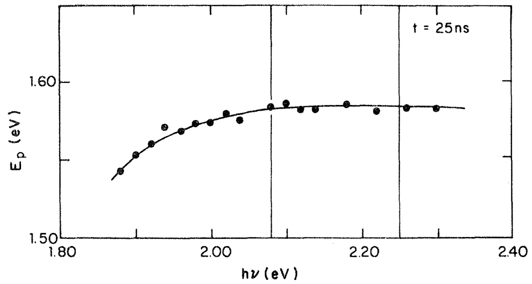

FIG. 7. $E_p(t=25\text{ ns})$ vs $h\nu$ for the sample of Fig. 3. Vertical lines indicate estimated E_{03} (left) and E_{04} at 77 K. E_{03} and E_{04} are the photon energies for which the absorption coefficient is $10^3$and 10^4 cm^{-1}, respectively.

regime of strong Coulombic effects ($t < 500$ ns). The absence of any change indicates that R_{th} is nearly independent of $h\nu - E_G$. This in turn suggests that the time required for complete thermalization is dominated by the final thermalization events when the thermalizing electron approaches the localized states at the conduction-band edge.

Between $h\nu = 2.14$ eV and 1.97 eV, changes in $E_p(t)$ begin to occur in the Coulombic regime. It seems likely that in this range of excitation energy we begin to excite electrons into localized states and the function $R(t)$ is altered measurably, since relaxation begins from a distribution of electron-hole separations that is peaked at a smaller value of R. This may, for example, insure that, for a higher fraction of the electron-hole population, R decreases with time in the $t < 25$-ns regime. This effect would be most important if $R_e \sim R_{\text{th}}$. We also note that in Fig. 6, electrons recombining at longer times have lost memory of the initial distribution of electron-hole separations. The lower the excitation energy, the longer the time required to erase the memory of the initial distribution.

Figure 7 explores the excitation energy dependence of E_p at the time of maximum Coulomb contribution ($t = 25$ ns). There appears to be a steady decrease in E_p with decreasing $h\nu$ beginning at a well-defined value of $h\nu = 2.07 \pm 0.01$ eV. Qualitatively similar results have been observed in E_p vs $h\nu$ data measured from the luminescence spectra of a-As_2Se_3. Murayama *et al.*[13] report that E_p begins shifting to lower energy below a critical $h\nu$ given by $h\nu_c$ such that $E_p = h\nu - E_0$, where E_0 provides a measure of the Stokes shift. Above $h\nu_c$, E_p remains fixed at $E_p = h\nu_c - E_0$. The authors have proposed that as luminescence is excited with photon energies lower than $h\nu_c$, localized electron-hole pairs are created progressively deeper in the gap, the higher-energy luminescence transitions are no longer excited, and the peak shifts to lower energy with $h\nu$. The fact that our data do not fit $E_p = h\nu - E_0$ below $h\nu_c = 2.07$ eV supports our contention that our E_p vs $h\nu$ data in a-Si:H cannot be explained with this model. Additional evidence indicating that our results should not be interpreted using the model of Murayama *et al.* comes from similar work on a-As_2Se_3 by Higashi and Kastner.[14] They find that as the excitation energy is decreased through $h\nu_c$, the spectral width changes dramatically. We find that at 25 ns the spectral width of the luminescence of the sample of Fig. 7 does not change within experimental error as $h\nu$ is decreased below 2.07 eV.

Murayama *et al.*[13] also observe a polarization dependence in the luminescence intensity that sets in as the excitation energy is decreased below $h\nu_c$, suggesting the localized luminescence centers are excited directly. We do not observe such effects at values of $h\nu$ below 2.07 eV for the sample of Fig. 7, suggesting that at excitation energies below $h\nu_c$ (corresponding to absorption coefficients as low as 10^2) relaxation of carriers occurs between excitation and emission. This relaxation destroys the polarization memory of the excited electron-hole pairs.

IV. CONCLUSIONS

We list the following conclusions of this work.

(1) A feature in E_p, the peak energy of the luminescence spectrum versus time is observed in a-Si:H, characterized by a fast decrease in $E_p(t)$ for $t < 50$ ns and an increase in $E_p(t)$ for 50 ns $< t < 500$ ns. The feature becomes weaker for samples of progressively larger dielectric constant and is thus associated with an electron-hole–pair

Coulomb interaction contribution to $E_p(t)$.

(2) For a typical sample of low dielectric constant using super-band-gap excitation, the average electron-hole—pair separation R at the onset of measurement (6 ns) is estimated to be 50 Å. When the Coulomb contribution is at its maximum ($t = 25$ ns), $R = 15$ Å.

(3) In situations where the Coulomb contribution to E_p is large, we question the applicability of Eq. (1) describing radiative tunneling, namely,

$$t = \tau_0 \exp(2R/R_0), \quad \tau_0 \sim 10^{-8}\ \text{s}$$

where R is the average electron-hole separation at time t and R_0^{-1} is the localization parameter.

(4) The absence of changes in $E_p(t)$ with excitation energy $h\nu$ well above the band gap suggests that the electron-hole—pair separation after thermalization is nearly independent of $h\nu$.

(5) We observe changes in $E_p(t)$ in the Coulombic regime as $h\nu$ is decreased below a well-defined (within 0.02 eV) value. We suggest that this represents the onset of the excitation of localized carriers, and this influences the initial distribution of electron-hole separations.

(6) No polarization dependence in the luminescence intensity is observed at values of $h\nu$ corresponding to $\alpha = 10^2$ cm^{-1}. This result suggests that direct excitation of localized luminescence centers does not occur for $h\nu$ above this energy.

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