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PHOTOLUMINESCENCE IN SPUTTERED AMORPHOUS Si:H ALLOYS

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We present excitation spectra and photoluminescence (PL) spectra as a function of temperature for films of hydrogenated amorphous silicon (a-Si:H) prepared by sputtering in argon with a partial pressure of hydrogen. For samples prepared at 10^{-4}-10^{-3}Torr of H, a single PL peak near 1.3eV is observed. At higher partial pressures of H an additional peak near 0.95eV appears. Using PL spectra, photoconductivity-derived absorption and detailed balance arguments, we present a model for radiative recombination at 1.3eV, not strongly Stokes shifted, based on a proposed model of the gap density of states (GDOS). For PL(1.3) and PL(0.95) excitation spectra are presented and compared with absorption spectra. Our model of the GDOS is then expanded to include samples exhibiting PL(0.95). PL(1.3) and PL(0.95) are presented as a function of temperature and examined in terms of present models of non-radiative recombination.

INTRODUCTION

Hydrogenated amorphous silicon (a-Si:H) prepared by sputtering in an Ar-H plasma exhibits low temperature geminate photoluminescence (PL) near 1.3eV, of 0.3eV FWHM.[1] As the partial pressure of H in the plasma is increased from 0 to 1.5 mTorr, the H content increases monotonically to 20 at. % and the PL quantum efficiency (Y) at 77K increases from 0 to 5%. Further increase of the H partial pressure results in a slight decrease in H-content, a decline in Y to 0.5%, and the appearance of a second PL peak near 0.95eV, of 0.2eV FWHM.[2] See Figure 1.

The 1.3eV peak has been widely studied[3-8] for both glow discharge (gd) prepared and sputtered a-Si:H. Engemann and Fischer[3] (gd) attributed the difference between the band gap energy and the PL peak energy to a mechanism of recombination of an exciton formed from states in the band tails. Lower energy PL peaks were associated with gap states. The Xerox group[6-8] has proposed that a strong electron-lattice interaction leads to a Stokes shift, the magnitude of the most recent estimate[8] being 0.2 eV. In this paper, we shall present a summary of data on the 1.3 and 0.95eV PL as a function of temperature and excitation energy. We shall discuss the mechanism of radiative recombination and present evidence against a large Stokes shift.

EXPERIMENTAL

Excitation spectra and absorption edges were measured on the same samples held at 77K using a monochromated Xe arc source.[5] Each point on the excitation spectra is obtained by integrating a complete PL spectrum. PL peak energy and FWHM were independent of excitation energy. Details of the PL measurement technique are available.[1]

RESULTS AND DISCUSSION

1. Absorption and PL Spectra and the Existence of Stokes Shifts. The absorption spectrum $\alpha(h\nu)$ at the $h\nu$ of PL emission may be derived from photoconductivity (PC) spectra if the mobility-lifetime product ($\mu\tau$) is known versus $h\nu$. Measurements of $\alpha(h\nu)$ and PC($h\nu$) for $1.6 < h\nu < 1.9$eV show $\mu\tau(h\nu)$ to be constant. Further, as T

is reduced, the entire PC edge between 0.9 and 2.0eV shifts essentially rigidly[10] by -6×10^{-4}eV/K. We infer that PC occurs in the same electronic states for this expanded range of $h\nu$ so that $\mu\tau(h\nu)$ may be assumed to be constant. Thus $\alpha(h\nu)$ is calculated from $PC(h\nu)$. See data for sample A in Figure 2. The 1.2eV shoulder in PC is attributed to transport at some level in the conduction band[11] by electrons excited from a feature in the gap density of states (GDOS), 1.2eV lower in energy. See Figure 3. Thus, the corresponding feature in $\alpha(h\nu)$ may be modelled by transitions between localized states in a Gaussian distribution (width σ centered at E=0) and a conduction band DOS proportional to $\sqrt{E-E_c}$:

$$\alpha(h\nu) \propto \int_{E_c-h\nu}^{\infty} (E-E_c+h\nu)^{\frac{1}{2}} \exp(-E^2/2\sigma^2)\,dE \qquad (1)$$

The best fit to our data at 300K corresponds to E_c=1.1eV and 2σ=0.3eV, which may be compared with a PL peak at 1.2eV of FWHM 0.35eV. The close match in position, width and shift with T (see Fig. 2) of $PC(h\nu)$ (or $\alpha(h\nu)$) and $PL(h\nu)$[13] lead us to conclude that the same electronic states are involved and that any Stokes shift is small. We note in passing that a much stronger feature in PC-derived $\alpha(h\nu)$ near 1.2eV is observed for gd material; this may explain the higher Y in gd material and suggests that the higher α and Y are caused by a larger GDOS in gd a-Si:H.[15]

We examine next the extent to which absorption may be quantitatively related to PL by detailed balance arguments. The absorption and radiative recombination between the same two sets of states may be most simply modeled by a discrete two level system:

$$\tau_r^{-1} = (8\pi n^2/h\nu^2)(g/N) \int \alpha(h\nu)\,dh\nu \qquad (2)$$

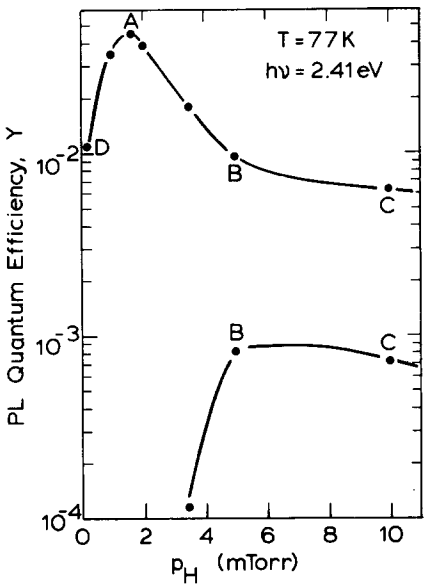

Figure 1. Y(1.3) (top) and Y(0.95) vs. H-partial pressure for samples A-D.

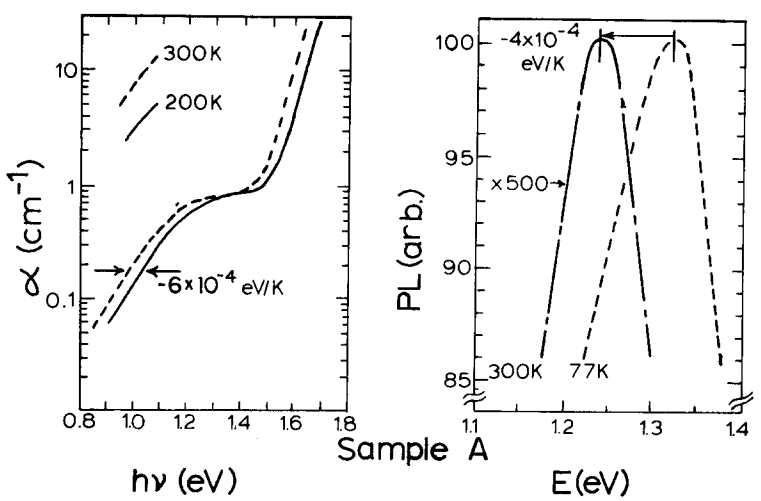

Figure 2. PC-derived absorption edges and PL spectra for sample A at various temperatures.

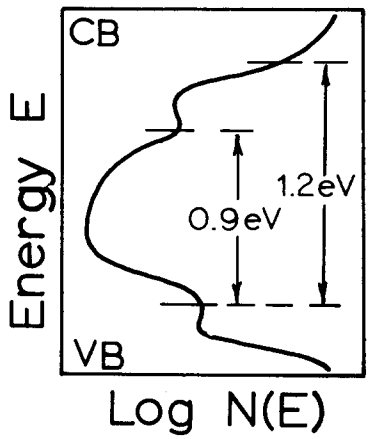

Figure 3. T = 300K EDOS for sample exhibiting both PL peaks.

Here n is the refractive index, g the ratio of degeneracies of the ground and excited states, N the integrated DOS in the presumed Gaussian feature of the GDOS discussed above, and τ_r the radiative lifetime. We assume g = 1. Strictly, N is the number of paired (ground and excited) levels. Using $\alpha(h\nu)=\alpha_o \exp(-(h\nu)^2/2\sigma^2)$ with σ = 0.15eV and α_o(Fig. 2) = 0.8cm^{-1}, we find $N/\tau_r = 1.8 \times 10^{24}$ cm^{-3}s^{-1}. Taking literature values[16], for N = 7.5 x 10^{18}cm^{-3} and τ_r = 10^{-5}s, we obtain $N/\tau_r = 0.8 \times 10^{24}$cm^{-3}s^{-1}. Despite the uncertainty in N, τ_r and α, and the problems of cross-sample correlations, we conclude that detailed balance arguments based on the PC spectrum are consistent with the proposition that PL(1.3) in a-Si:H need not be Stokes shifted. Indeed, we note that the original suggestion for large Stokes shifts was based on the suggestion that the PL spectra (un-Stokes shifted) would demand far higher $\alpha(h\nu = 1.3)$ than was extrapolated from the then-existing data on α. Our $\alpha(h\nu)$ from PC data, which fit the PL spectrum tolerably well, is in fact a lower limit on α since the assumption of constant $\mu\tau$ as $h\nu$ is decreased gives almost certainly an upper limit on $\mu\tau$. Other arguments against strongly Stokes shifted PL in a-Si:H are available.[1,4]

2. Excitation Spectra for the 1.3eV and 0.95eV Peaks. Figures 4a and 4b show PL(1.3) and Y(1.3) as a function of incident $h\nu$ for samples A and B, while Fig. 4c exhibits similar data for the 0.95eV PL peak observed in sample B. High energy PL quantum efficiency Y(1.3) is fairly constant with an increase at lower $h\nu$ indicating a lower probability of exciton dissociation during thermalization for excitation energies nearer the bandgap energy. Figure 4c, in contrast, shows Y(0.95) increasing sharply with decreasing $h\nu$ for $2.0 < h\nu < 2.6$eV. The samples which exhibit PL(0.95) possess transport characteristics interpreted as being the result of a peak in the GDOS 0.3 to 0.4eV from E_c[18]. Thus PL(0.95) may tentatively be assigned to the transition indicated in Fig. 3. The absorption process resulting in PL(0.95) is identified from the following considerations. (i) If the life cycle of electrons eventually recombining to give PL(0.95) involves band to band absorption for $2.0 < h\nu < 2.6$eV followed by relaxation of electrons through conduction band tails, then the $h\nu$- dependences of Y(0.95) and Y(1.3) for sample B should be comparable. They are not. (ii) Longer decay times have been reported for lower PL energies in the 1.3eV band.[8] Thus, if PL(0.95) occurred after electron excitation into the conduction band and subsequent relaxation into the GDOS peak below it, a much longer decay time would be expected for PL(0.95) than for PL(1.3). In fact, we estimate (see below) that τ_r(0.95) is within an order of magnitude of the reported value of τ_r(1.3). (iii) The dependence of Y(0.95) on $h\nu$ can be explained semi-quantitatively by calculations based on a simplified version of the GDOS of Fig. 3, shown in the inset of Fig. 5. Assuming that PL(0.95) occurs after excitation of a valence band electron directly into the GDOS peak below the conduction band, and that the matrix elements involving transitions including at least one extended state are equal, we can calculate the Y(0.95) versus $h\nu$ of Fig. 5, in acceptable agreement with experiment. Thus the present data can be explained with a model of sub-bandgap absorption followed by luminescence.

Observation of PL at 0.95eV is always accompanied in our experience by a relatively strong PC response for $1.2 < h\nu < 1.8$eV. The increased PC is believed to be the result of absorption involving the GDOS feature in the lower half of the gap and states in the conduction band tail.[18] This suggests that the two peaks in the GDOS may be different states of the same defect, although strictly, only their simultan-

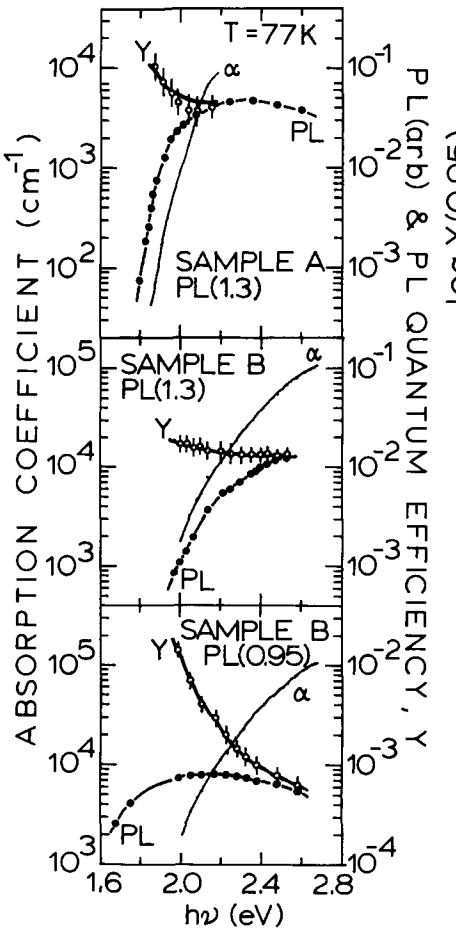

Figure 4. (a) & (b) (top & center) α(hν), PL(1.3,hν) and Y(1.3,hν) for samples A & B (c) (bottom) α(hν), PL(0.95,hν) and Y(0.95, hν) for sample B.

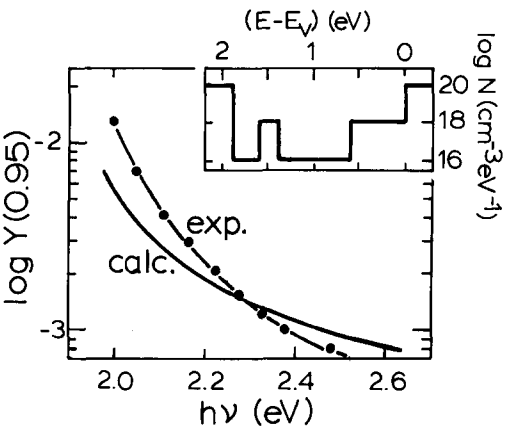

Figure 5. Y(0.95,hν) for sample B from Figure 4 (full circles) and calculated (solid) from EDOS in inset.

eous occurrence is established. The possible origin and nature of the GDOS peaks is discussed elsewhere in this volume.[18]

3. Temperature Dependence of PL(1.3) and PL(0.95). In Figures 6 and 7 we present PL data versus T, although only an inadequately brief discussion is possible here. We assume

$$PL(E,T) = p_r/(p_r + p_{nr}) \qquad (3)$$

where p_r and p_{nr} are the radiative and non-radiative recombination probabilities. We shall assume p_r independent of T. Above 70K, PL(1.3) decreases monotonically with increasing T. We can test the validity of Eq. (3) for our data with two different expressions for $p_{nr}(T)$. In the first $p_{nr}(T) = A \exp(-E_1/kT) + B \exp(-E_2/kT)$ where E_1 and E_2 are activation energies for the thermal dissociation of excitons whose elements then non-radiatively recombine. This expression has been used for both gd[4] and sputtered[1] material. In the second $p_{nr}(T) = C \exp(T/T_o)$, a dependence suggested by a model of phonon-assisted tunneling of carriers to non-radiative centers.[19] From Fig. 6a, the first expression applies better to PL(1.3) for 75 < T < 130K with a single activation energy of 30 meV for sample B (high H-partial pressure) and 65 meV for sample D (low H-partial pressure). The second expression appears to be more suitable for PL(1.3) above 130K, and for PL(0.95) for 50 < T < 200K, with $T_o \approx 20$K. Thus we tentatively conclude[9] that, for these samples, the decrease in PL(1.3) above 130K is dominated by tunneling of electrons to non-radiative centers whereas the decrease for 75 < T < 130K is dominated by exciton dissociation.

The decrease in PL(0.95,T) cannot be attributed to an activated p_{nr}; i.e. phonon-

assisted tunneling to non-radiative centers appears to dominate exciton dissociation. This, along with the finding that PL(0.95) at 77K varies with the excitation intensity I as $I^{0.6}$ for I ~ 10^{19} photons/cm^{2}s suggests non-geminate recombination. A rough estimate of $\tau_r(0.95)$, the radiative decay time for PL(0.95), can be obtained from Fig. 6b. Using

$$PL/PL_o = \tau_r^{-1}/(\tau_r^{-1} + p_o \exp(T/T_o)) \quad (4)$$

we find for the T = 0 extrapolations of samples B and C of Fig. 6b, that $p_o\tau_r(1.3) = 3 \times 10^{-3}$ and $p_o\tau_r(0.95) = 2 \times 10^{-2}$. In the model of phonon-assisted tunneling[19] $p_o = \nu_{ph} \exp(-2\alpha R_o)$ where α is the localization parameter for the electronic state, R_o is the distance between the charge carrier and the non-radiative center and $\nu_{ph} = 10^{14}$ s^{-1} is a typical phonon frequency. Using[8] $\tau_r = 10^{-5}$s to obtain p_o, we obtain $\alpha R_o = 13$ for non-radiative tunneling that quenches PL(1.3). Applying this value of αR_o to the non-radiative tunneling in sample C, we obtain $\tau_r(0.95) = 6 \times 10^{-5}$ s.

In Figure 7 we plot PL(1.3,T) between 20 and 150K for samples prepared at 0.2 and 3 mTorr (samples F and E respectively). Sample F shows a near two-fold increase in PL(1.3,T) between 20 and 60K, whereas sample E exhibits a 5% increase. A smooth trend with H-partial pressure in the fractional increase in Y(1.3) is shown in the inset for an hν of 2.41eV where PL_{23}/PL_{max} is the ratio of the PL intensity at 23K to the PL intensity at its maximum near 60K. Several properties of sputtered a-Si: prepared in this laboratory tend to exhibit similar trends with H-partial pressure between 0.2 and 3 mTorr. Among these are the optical gap[14] the peak energy[1] and quantum efficiency of the PL(1.3) band (see Fig. 1), and the hydrogen incorporation[14]. Thus we indicate here that the relative increase in PL at low temperatures can be explained in terms of more general properties of a-Si:H prepared by sputtering and leave a more detailed discussion to forthcoming work.[9]

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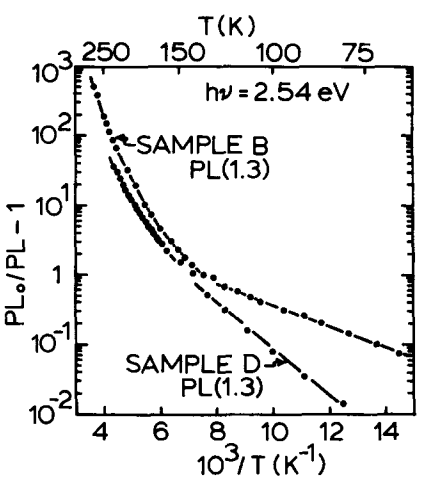

Figure 6a. $(PL_o/PL - 1)$ vs. $10^3/T$ for PL(1.3) of samples B and D.

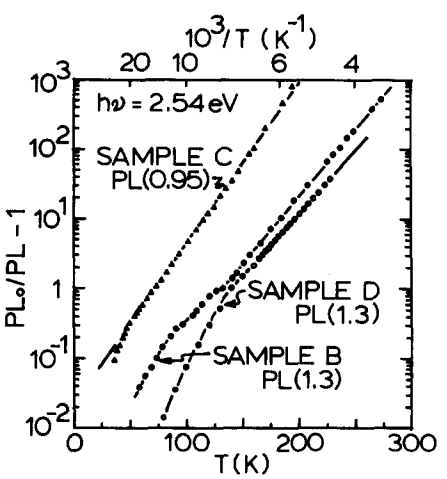

Figure 6b. $(PL_o/PL - 1)$ vs. T for PL(1.3) of samples B and D, and for PL(0.95) of sample C.

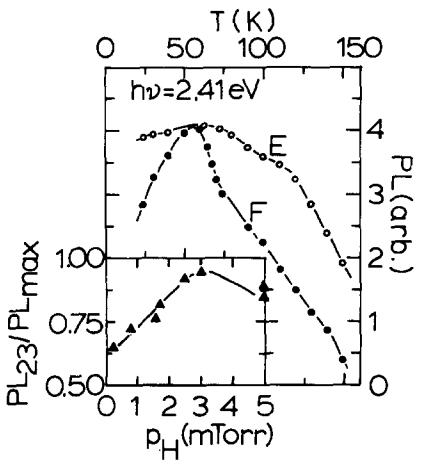

Figure 7. PL(1.3) vs. T for 0.2 mTorr sample (F) and 3.0 mTorr sample (E). Inset: The ratio of PL(1.3) at 23K to the maximum PL(1.3,T) for several samples plotted vs. H-partial pressure in the sputtering gas. The relative increase in PL at low T can be explained in terms of more general properties of a-Si:H

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(10) Shifts of featureless edges can be difficult to interpret since changes in the abscissa and ordinate may be undifferentiable. For Figure 2 this is not a problem. The edge has a distinct feature and the horizontal and vertical shifts are distinguishable. The $\alpha(h\nu)$ curves can be made to superpose identically with a shift of the abscissa of -6×10^{-4}eV/K.
(11) Schottky barrier work[12] implies PC is due to electrons in the conduction band.
(12) Carlson, D.C. and Wronski, C.R., Appl. Phys. Lett. 28 (1976) 671.
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