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Temperature dependence of photoluminescence in amorphous $Si_{1-x}C_x$:H films

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Abstract. We have investigated the temperature dependence of photoluminescence in hydrogenated amorphous silicon-carbon alloys a-$Si_{1-x}C_x$:H prepared by glow discharge in the low-power regime. The radiative recombination process, due to photocarriers trapped on band-edge states, is in competition with the thermal escape of the photocarriers into the mobility bands. The model gives a quantitative fit with experiment, without any adjustable parameter, provided the width of the band-edge distribution of states is taken as the width of the conduction band only (measured by "photo-induced infra-red spectroscopy") and not as the Urbach energy, as it is usually assumed.

PACS. 72.20.Jv Charge carriers: generation, recombination, lifetime, and trapping – 78.55.Qr Amorphous materials; glasses and other disordered solids – 81.05.Gc Amorphous semiconductors

1 Introduction

Amorphous hydrogenated silicon-carbon alloys have been extensively studied in the past few years [1,2]. Glow-discharge a-$Si_{1-x}C_x$:H, deposited in the "low power regime" [3,4], is an exemplary system of a variable-gap amorphous semiconductor. The photoluminescence (PL) of this material has been studied by Tessler et al. [2] at two temperatures, 77 K and 300 K. At low temperature, the PL is similar to that of pure amorphous silicon [5–7], but its intensity decreases with carbon alloying [2]. We have measured the variation of the PL intensity for a series of silicon-carbon alloys, a-$Si_{1-x}C_x$:H, with a carbon concentration x between 0 and 15%, in a range of temperature between 80 and 300 K. Following the work of Street [6] on the PL thermal quenching in amorphous silicon we discuss the temperature dependence of PL in this series of materials and propose a model which fits experiment quantitatively, in contradistinction with previously published models [2,7,8].

2 Experimental

The amorphous undoped material was deposited by plasma enhanced chemical vapour deposition in the "low-power" regime, where carbon is incorporated in the form of methyl groups ($-CH_3$) [3,4]. The density of states at mid-gap, which act as non-radiative recombination centres, increases abruptly when carbon concentration is greater than 20%. Therefore, the carbon concentration in our films has been varied from 0% to 15% only. For the PL measurements (see Fig. 1), the sample is mounted on a copper plate in a vacuum chamber (pressure 10^{-2} Torr) with a glass window. The temperature of the copper plate is varied by changing the dynamic equilibrium between low temperature cooling by a liquid nitrogen flow and ohmic heating by a resistor. The excitation is provided by a 470 nm blue LED. The luminescence signal is filtered, dispersed by a monochromator and detected by a cooled charge-coupled device detector. The determination of the absolute value of the quantum efficiency requires difficult optical metrology and we did not attempt to do it. However, the relative measurement of the PL intensity for different samples, from one run to another, is estimated to be accurate within better than a factor of 2.

3 Results and discussion

3.1 Experimental results

Figure 2 shows the temperature dependence of the natural logarithm of the PL intensity ($\ln(I_{PL})$). As it has been empirically observed previously [5], the variation of $\ln(I_{PL})$ exhibits a range of linear variation as a function of temperature, indicating a non Arrhenius activated process. For different carbon contents, we observe 3 regions of the variation of $\ln(I_{PL})$ with temperature:

a- between 100 and 250 K, a variation of the PL intensity proportional to $\exp(-T/T_0)$, T_0 being a parameter to

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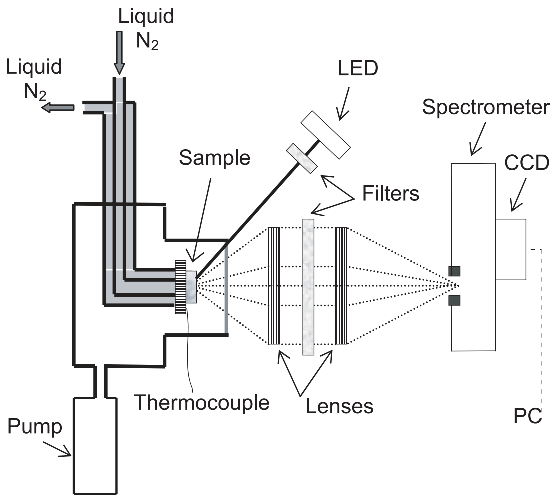

Fig. 1. Photoluminescence set-up. The temperature of the sample can be varied from 77 K to 350 K.

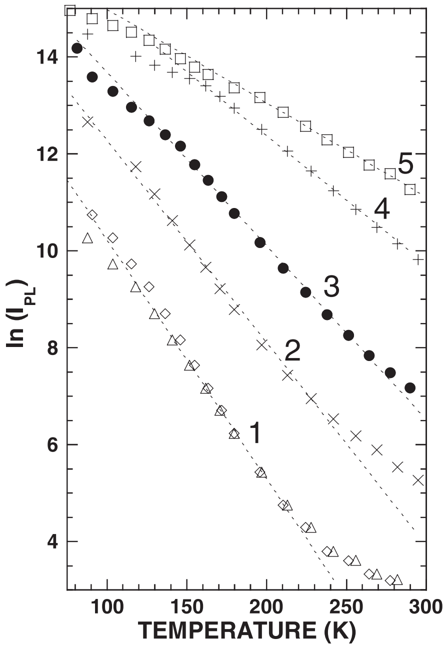

Fig. 2. Plot of the variation of the natural logarithm of the intensity of the photoluminescence I_{PL} (given in a.u.) as a function of temperature. Curve 1: two sets of measurements for pure a-Si:H; curves 2, 3, 4 and 5 correspond to carbon concentrations of 3%, 5%, 10% and 15% and have been shifted vertically by +1, +2, +3, +4 respectively for the sake of visibility. The dotted lines illustrate the linear variation (Eq. (1), see text) in the range 100 K to 250 K.

be discussed below

$$I_{\mathrm{PL}} \propto \exp(-T/T_0); \tag{1}$$

b- at low temperature we observe a levelling of $\ln(I_{\mathrm{PL}})$ with temperature which will be also explained below;
c- at high temperature, we observe a stabilisation of the PL that we do not explain in the present article.

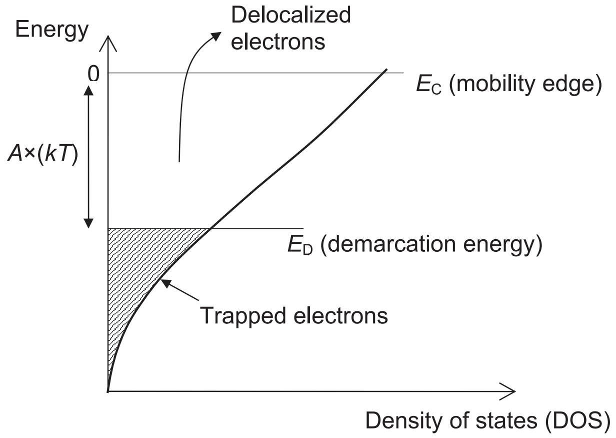

Fig. 3. Recombination path of photocarriers according to their energy. The fraction of carriers with an energy below the demarcation energy E_{D} recombines radiatively and contributes to the PL. Carriers at energies larger than E_{D} are thermally excited into the mobility band: they recombine on a mid-gap center and are lost for photoluminescence. The distance between E_{D} and E_{C} is proportional to kT. The proportionality constant A is calculated in the text.

This "thermal quenching" of PL has been qualitatively explained in a-Si:H [6–8] and more recently in silicon carbon alloys, a-Si$_{1-x}$C$_x$:H [2] by counting, at a given temperature T, the carriers that are trapped on band-edge states and not thermally excited from these states to the mobility bands within the radiative lifetime. For mobile carriers, the recombination is dominated by non-radiative recombination associated with defects lying near mid-gap. These defects (such as dangling bonds, for example) are very efficient recombination centres by a Shockley-Reed process [9] with a *non-radiative* lifetime τ_{nr} typically on the order of 10^{-12} s, much shorter than the *radiative* lifetime $\tau_r = 10^{-3}$ s [10,11].

The very simple model used to explain the temperature dependence of the PL intensity and the value of T_0 in equation (1) is based on the following assumptions (Fig. 3):

1) the photocreated carriers produced across the gap by the exciting light thermalise very rapidly in the band-edge states of the material;
2) at a given temperature, only electron-hole pairs trapped in band-tail states (zero mobility) can recombine radiatively;
3) the carriers thermally excited from band-tail states into the mobility bands will wander around by diffusion. They will eventually reach a non-radiative recombination centre and thus will be lost for the PL signal.

3.2 The demarcation energy

In the following discussion, we consider only electrons near the conduction band, but the same would apply to the photo-created holes near the valence band. We take the energy origin at the mobility edge. We can then define a "demarcation energy" E_D (Fig. 3) which abruptly separates two types of tail states. Electrons with an energy lower than E_D are irreversibly trapped and recombine radiatively. Electrons with an energy higher than E_D are thermally excited into the conduction band faster than τ_r and recombine non radiatively. The rate of emission of a carrier from an energy E below the mobility edge E_C is given, at a given temperature T, by the Boltzmann factor

$$\omega = \omega_0 \exp(E/kT) \tag{2}$$

where ω_0 is a characteristic attempt-to-escape frequency, typically on the order of that of an optical phonon ($\omega_0 \approx 10^{12}$ s^{-1}) [6]. The demarcation level is given by equating $1/\omega$ with the radiative recombination time τ_r. Energies are counted as negative when below the mobility edge E_C. We thus obtain the value of E_D:

$$E_\mathrm{D} = -kT \ln(\omega_0 \tau_r). \tag{3}$$

With typical values of $\omega_0 \approx 10^{12}$ s^{-1} and $\tau_r \approx 10^{-3}$ s [10, 11], we have ln $(\omega_0 \tau_r) \approx 20.7$.

3.3 Temperature dependence of the PL

As discussed in the previous paragraph, the carriers with an energy above E_D are thermally excited into the extended states, they recombine rapidly on non-radiative recombination centres and do not participate to the PL signal. The PL signal is coming from the photo-carriers trapped below the demarcation level E_D. To count the number of states below E_D, we assume a density of states (DOS) with an exponential form:

$$\rho = \rho_0 \exp(E/W_\mathrm{C}). \tag{4}$$

The pre-exponential factor ρ_0 (of the order of 10^{21}–10^{22} eV^{-1} cm^{-3}) is not accurately known, but fortunately it disappears in the actual calculation of T_0. The width W_C of this DOS has been likened to the "Urbach energy" [2,7,8] as measured by optical spectroscopy near the energy of the gap of the material. As we shall see below, this is incorrect and does not give a quantitative fit with experiment.

The signal, with the DOS given by equation (4), is then proportional to the total number of states below E_D:

$$I_\mathrm{PL} \propto \int_{-\infty}^{E_\mathrm{D}} \exp(E/W_\mathrm{C}) \tag{5}$$

$$I_\mathrm{PL} \propto \exp(E_\mathrm{D}/W_\mathrm{C}). \tag{6}$$

By substitution of E_D given by equation (3), we obtain equation (1), $I_\mathrm{PL} \propto \exp(-T/T_0)$, with:

$$kT_0 = W_\mathrm{C}/\ln(\omega_0 \tau_r). \tag{7}$$

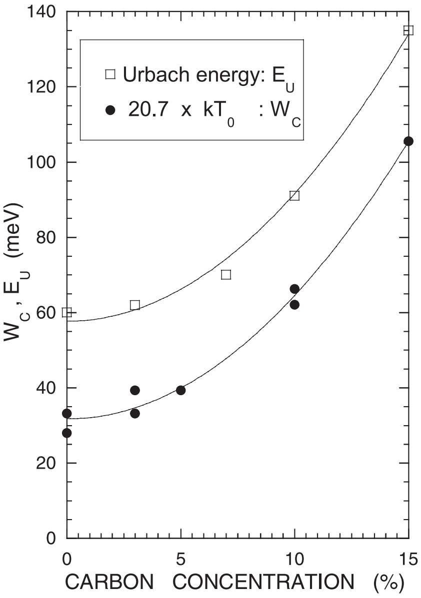

Fig. 4. Variation of $W_\mathrm{C} = \ln(\omega_0 \tau_r) \times kT_0$ and of the Urbach energy E_U as a function of the carbon concentration in the solid. The solid lines are simply a guide to the eye.

3.4 Comparison with experiment

As shown in Figure 2, above about 80 K, $\ln(I_\mathrm{PL})$ exhibits a linear variation with temperature, for a variation of the PL intensity I_PL by several orders of magnitude. From this linear variation, we measure the characteristic temperature T_0, and we determine the value of the width of the density of states W_C from equation (7), where we take the quantity $\ln(\omega_0 \tau_r)$ to be equal to 20.7. In Figure 4, we plot the variation of W_C as a function of the carbon concentration x in a series of a-$\mathrm{Si}_{1-x}\mathrm{C}_x$:H samples.

In the same graph, we plot the variation of the Urbach energy E_U, as obtained from optical absorption [2]. The variations of W_C and E_U are quite similar, but we observe that the two quantities are not equal. Even taking into account the uncertainty on the values of ω_0 and τ_r, (the coefficient $\ln(\omega_0 \tau_r)$ varies at most from 20 to 22 because of its weakly varying logarithmic form), there is no way one can reconcile the discrepancy between W_C and the Urbach energy E_U, in contradiction with what has been published before [2,6,12]. This is not too surprising, since the Urbach energy results from a convolution of the density of states around the conduction band and the valence band. It is in fact dominated by the larger width of the valence band edge and is found experimentally to be close to 55–60 meV for the material with a low carbon content. This is almost twice as much as the value found for W_C, as shown in Figure 4.

Actually, it is not necessary that *both* carriers, electrons and holes, be delocalised in the mobility bands to quench the PL signal. It is sufficient that *one* of the carriers, thermally excited into its mobility band, be mobile and thus can reach a non-radiative recombination centre. So W_C should plausibly be assimilated to the width of one band edge only, the narrowest of the two band edges, namely the one adjacent to the conduction band. Recently, we have been able to measure separately the width of the conduction band-edge for a-Si:H [13]. The measurement, performed by "Photo-induced Infrared Spectroscopy" (PIS) [13], has given a value of 28 ± 5 meV, which indeed is in agreement with the measured value of $W_\mathrm{C} = 30 \pm 6$ meV as shown in Figure 4. It is interesting to note that, if the present model is valid, the values of W_C, as reported in Figure 4, give an experimental method to measure the width of the conduction-band edge for amorphous silicon-carbon alloys, independently of the Urbach energy measured differently. To our knowledge, this is the only experimental method to study separately the edge of the *conduction* band for this type of material: the PIS method mentioned above is limited to materials with a very low carbon concentration ($x < 3\%$) [13].

3.5 Low-temperature photoluminescence

It is found in the literature [14] that, at low temperature (below 50 K for pure silicon and below 100 K for 23% carbon), the variation of the logarithm of the PL intensity deviates from linearity, a phenomenon unaccounted for in the previous model. At low temperature, the basic assumption of this model, namely that the steady-state distribution of the carriers in the conduction-band tail results from the competition between radiative recombination and thermal re-emission above the mobility edge, leads to shallow values of the demarcation energy E_D. For those values, the model is no more realistic, because for energies in this range, the band-tail density of states $\rho_0 \exp(E/W_\mathrm{C})$ becomes large and tunnelling in the band tails may supersede the thermal emission process.

At low temperatures, the population of the band-tail states is then governed by the competition between radiative recombination and tunnelling of electrons trapped in shallow states to deeper states in the band tail. This results in a uniform energy distribution up to a temperature-independent upper bound [15]

$$E_\mathrm{t} = 3W_\mathrm{C} \ln \frac{2\alpha}{\rho_0^{1/3} W_\mathrm{C}^{1/3} \ln(\omega_0 \tau_r)} \quad (8)$$

i.e., $E_\mathrm{t} \approx -0.1$ eV for $\rho_0 = 10^{21}$ eV^{-1} cm^{-3}, a localisation radius $1/\alpha = 10^{-7}$ cm, and W_C, ω_0, τ_r as taken above. In this regime, all carriers trapped far enough from non-radiative recombination centres will undergo radiative recombination (in contrast to the high-temperature regime where thermal re-emission allows for non-radiative recombination due to high carrier mobility in the extended states), and the luminescence intensity is temperature independent.

Equating the above value of E_t with that of E_D, the crossover between the low-temperature and high-temperature regimes is predicted to occur for $T_\mathrm{t} = -E_\mathrm{t}/[k \ln(\omega_0 \tau_r)] \approx 50$ K [16]. This value is compatible with the experimental results, as given in reference [14], and confirms the overall consistency of the model.

4 Conclusion

We have measured the temperature dependence of photoluminescence in a series of amorphous silicon-carbon alloys a-Si$_{1-x}$C$_x$:H prepared by glow discharge in the low-power regime [3,4].

We find a linear decrease of the logarithm of the photoluminescence intensity with increasing temperature:

$$\ln(I_\mathrm{PL}) \approx cst - T/T_0 \quad (9)$$

where the quenching temperature T_0 depends upon the carbon content of the alloy. A very simple model, where photoluminescence is limited by the thermal escape of the photocarriers into the mobility bands, gives a quantitative fit with experiment provided the proper band-edge width is taken into account. To obtain such a quantitative fit, *without any adjustable parameter*, we show that the relevant width of the distribution of states is that of the *conduction band-edge only*, and not the Urbach energy (dominated by the valence band distributions) unlike previously assumed. Conversely, this result provides a very simple way for experimentally measuring the conduction band tail width in this class of amorphous semiconductors. This determination is in perfect agreement with that measured in an independent experiment [13] for a-Si:H and found to be about half the value of the Urbach energy.

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16. The corresponding transition temperature for holes is expected to be nearly twice as large, but is unimportant for the luminescence intensity which is limited by electron detrapping as explained in the previous section