Photoluminescence, Disorder and Localization In Amorphous Silicon Carbon Alloys

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Received August 8, 1993; revised manuscript received November 1, 1993

From Photoluminescence (PL) aiid Photothermal Deflection Spectroscopy (PDS) measurements in amorphous silicon carbon alloys, a. linear relationship between the line-width of tlie PL (77K) spectra aiid the Urbach energy was found. This relationship is interpreted considering only disorder with small or none broadening due to electron-phonon interaction. From the PL temperature dependence and sub-gap absorption measurements a localization length of trapped carriers is estimated

I. Introduction

Ill tlic last ten years, a great number of applications have been developed for a-Si:H aiid some of its alloys, such as solar cells, photoreceptors and thin film transistors. We remark tlie particular application of a-SiC:H as window contact ill solar cells[1]. One of the more important aspects of amorphous silicon carbon alloys is the possibility of changing the optical gap by increasing the carbon concentration[2].

In contrast to a-Si:H, tlic hydrogenated a-Si alloys prepared for conventional glow discharge are not photosensitive and show poor optical and electroiiic properties[2]. Recently, however, Matsuda and Tanaka[2] and Baker et al.[3] demonstrated that relative good a-SiCx:H films can be achieved by diluting with H_2 tlie methane-silane gaseous mixture used during the glow discharge deposition.

In this work we have addressed the problem of the cause of tlie PL width, the PL dependence on tlie temperature and the influence of disorder on the localization length of trapped carriers. m(report studies of photoluminescence (PL) and absorption experiments in two groups of a-SiC:H samples grown with different degrees of hydrogen dilution gaseous mixtures. The first group, called "Standard" (ST), was grown by the conventional glow discharge metliod, i.e., without hydrogen dilution of the gaseous mixture. They have optical gaps (E_g) varying between 1.75 aiid 2.76 eV, Urbach tails (E,,) between 70 and 120 meV aiid density of states (DOS) of about 10^{17} cm^{-3}. These films were grown onto a. roughened glass substrate. The second group was grown from a highly hydrogen-diluted (HD) gaseous mixture of silane and methane on smooth quartz plate. These samples have E; varying between 1.90 and 2.15 eV, E, between 58 and 100 meV and DOS of about 10^{16} cm^{-3}. More details about deposition aiid characteristics of these samples were published elsewhere[4].

II. Experimental details

The samples were excited with a chopped (13 - 14 Hz) argon ion laser and the PL emission detected with a silicon diode operating in the photovoltaic mode by a standard phase detection system. The spectra were corrected by the response of the optical system. The PL measurements were obtained at temperatures varying between 77 and 200 K.

For the ST samples grown upon roughened glass, no interference fringes in tlieir PL spectra were found. On the contrary, for the HD samples deposited on smooth quartz, interference patterns were found in their spectra. In order to eliminate the interference patterns, several spectra were taken by varying the incident angle of excitation laser. A resulting spectrum was obtained by averaging them and it was found that three spectra were enough to cancel the interference pattern.

The sub-gap absorption coefficient was obtained by photothermal deflection spectroscopy (PDS)[5]. The

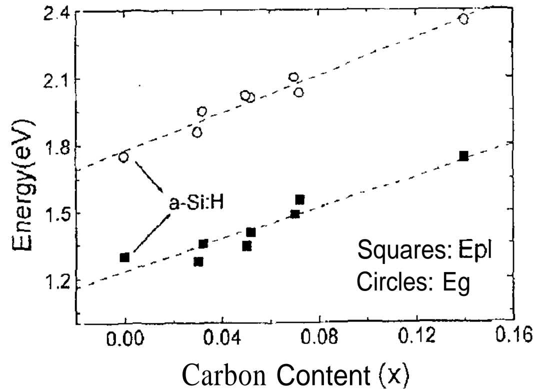

Figure 1: Tl e Photoluminescence (PL) peak positions at 77 K and tlic optical gap (E,) related with the carbon content (x) for tlic Standard (ST) samples.

absolute DOS was determined by scaling the sub-gap absorption coefficient with tlie absorption coefficient from standard absorption experiments[6]. The carbon conteiit of Standard samples was determined by Auger analysis. Tlie carbon content in TID samples was not determined.

III. Results and discussion

The PL spectra are featureless broad bands, with widths varying, between 0.30 - 0.55 eV aiid peaking at about 1.5 eV for both groups of samples. Tlie PL mechanism is assumed to be similar to that commonly accepted for amorphous silicon. After the electron-hole creation, deep iii the bands, the pair is separated by diffusion before being trapped in tail states. This process occurs iii the times of the order of picoseconds. After that, a. much slower thermalization process takes place in which car iers can hop inelastically between localized states or recombine radiatively via. tunneling. Assuming the latter process, the maximum of tl-ie PL spectrum is determined by the convolution of tl-ie tail density of states times the occupation probability distribution of the carriers, i.e., the quasi-equilibrium Fermi distribution of carriers. Therefore, the energy of the maximum can be written as[7]:

$$E_{pl} = (E_c - E_v) - (E_{te} + E_{th}), \qquad (1)$$

where E_{pl} is the position of the PL peak, E, and E,, are the conduction and valence band energies, respectively, and E_{th} and E_{te} are tlie maximum energies of the steady state carrier's distribution in the tail states.

Fig. 1 shows the PL peak positions at 77K and E_g, both a.s a function of tlie carbon content (x) for the ST snmples. As the carbon content increases, E_g and E_{pl} also increase, as expected. In eq. (1), it is not assumed any electron-phonon interaction, but only effects of thermalization that could cause an energy shift between tlie absorption energy and the PL emission maximum. In other words, we have assumed that the shifting in these two curves is mainly due to disorder, rather than due to electron-phonon interaction. Therefore, from figure 1 the energy shift between E_{pl} and E_g caused by thermalization would be approximately constant and is about 0.6 eV. What follows is an attempt to evaluate how large is the electron-phonon interaction and its iiifluence on the PL emission broadening and shifting. We notice that the total PL width can be expressed by[8]:

$$(\Delta E_1)^2 = 4\ln(2)\Delta E\hbar w + (\Delta E_{\text{disorder}})^2 \qquad (2)$$

where ΔE_1 is the full width half maximum (FWHM) PL energy, ΔE is the Stokes shift energy due electron-phonon interaction, $\hbar w$ is the dominant phonon energy for the alloy and $\Delta E_{\text{disorder}}$ is the contribution of the disorder to the emission line-width. Fig. 2 shows the FWHM vs Urbach energy (E,,) at 77K for both sets of samples. The FWHM for a-Si:H (0.25 eV) is also included. Within the experimental error, there is a linear relationship between the FWHM and E,. The extrapolation to zero disorder, i.e., E,, = 0, gives a FWHM $\sim$ 0.08 eV. Assuming this value as the maximum contribution to the electron-phonon interaction, an estimation of the Stoltes shift can be done. We will consider the alloy phonon energy as the average value between the Si (60 meV) and the stoichiometric silicon-carbide (80 meV) phonon energies[9], i.e., 70 meV. Thus, assuming E,, = 0, $\Delta E_{\text{disorder}} = 0$ and $\Delta E \approx 0.08$ eV, from eq. (2) a. Stoltcs shift of about 0.04 eV is obtained. This value is much smaller than the Stokes shift of 0.4-0.5 eV estimated by Street[7] for a-Si:H but almost twice when compared to 0.02 eV obtained by Searle and Jackson for silicon nitride[8]. With this result one can conclude that the PL band width is probably mainly due to disorder. Consequently our assumption about the energy shift between E_g and E_{pl} as due mainly to thermalization effects seems to be correct.

Now we will discuss the teinperature dependence

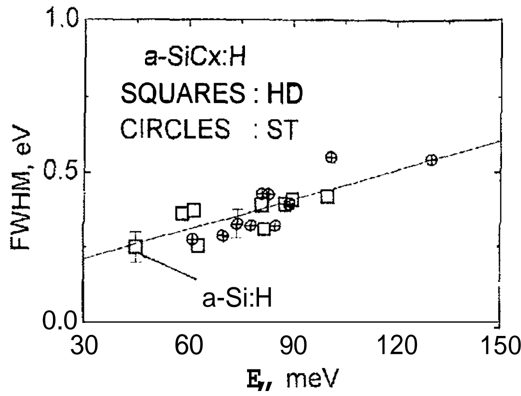

Figure 2: PL full width half maximum (FWHM) vs Urbach energy (E_u) at 77 K for both materials.

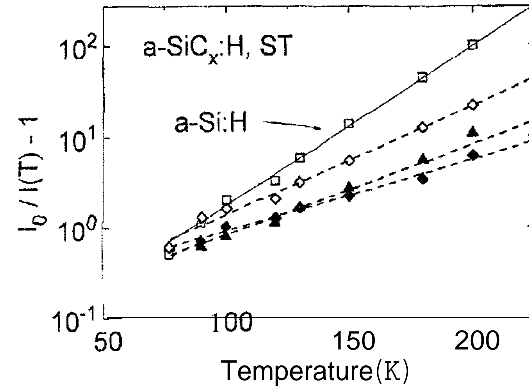

Figure 3: The best fit of expression (5) for a-Si:H and a-SiC:H ST saniples. Tlte curves are normalized to one.

Now we will discuss the temperature dependence of PL. In the luminescence process there is a competition between radiative and non-radiative recombination. The photoluminescence intensity as a function of temperature can be expressed as[10]

$$I(T) = I_0\{p_r(T)/[p_r(T) + p_{nr}(T)]\} \quad (3)$$

where I_0 is the maximum PL intensity extrapolated to 0 K. p_r and p_{nr} are tlie radiative and non-radiative recombination probabilities, respectively. Expression (3) can be written as:

$$(I_0/I(T)) - 1 = (p_{nr}(T)/p_r(T)) \quad (4)$$

In a-Si:H a. good fitting to tlie experimental data is obtained with

$$(p_{nr}/p_r) \sim \exp(T/T_0) \quad (5)$$

where T_0 is a parameter that depends of E_u as[7]:

$$kT_0 = E_u/\ln(\tau/\tau_0) \quad (6)$$

where k is the Boltzman constant, r and τ_0 are the tunnel pre-factor[11] and radiative recombination characteristic time of the material, respectively. Thus we adjusted a value of I_0 that obeys the simple function (5) with $T_0 \approx 23$K for a-Si:H. We found that the a-SiCx:H alloys also follow equation (5) fairly well.

Fig. 3 shows the best fit obtained using expression (5) for tlic ST a-SiC:H samples. For the sake of clarity only selected curves are presented. Similar curves are obtained for HD deposited samples. We emphasize that at low temperatures (77K) the a-Si:H PL intensity is about one order of magnitude greater than the a-SiC:H PL intensities. The parameter To for all samples was obtained from this set of curves.

Now, we return to eq. (6). The recombination time can be expressed, also, by $\tau(r_c) = \tau_0\exp(\alpha r_c)$, where $L_0 = 2/\alpha$ is the effective Bohr radius (localization distance) and r_c is thc electron-hole defect distance[7]. m a-Si:H, L_0 is estimated to be $\sim 10 - 12\AA$, using $\tau_0 \approx 10^{-12}$s [12]. The critical distance hetween tlie electron and defect, r,, is defined in such a way that a. carrier having r < $r_c(r >$ r,) will recombine non-radiatively (radiatively). This critical distance is estimated considering tlie mean value < r > of a distribution of randomly distributed defects $G(r) = 4\pi r^2 N\exp(-4\pi r^3 N/3)$, where N is the DOS. Combining tlie resulting expressions, the localization distances for samples with different carbon contents is estimated by[13]

$$L_0 \simeq 0.5(kT_0/N^{1/3}E_u) \quad (7)$$

Fig. 4 shows the curves obtained substituting the experimental values of To, E, and DOS in eq.(7). The shorter localization lengths obtained for ST samples suggest stronger disorder than in HD samples. We also notice that the deposition parameters used in the deposition of tlie ST samples seem to produce a material with properties converging to those of a-Si:H. Finally tlie larger values of L_0 in HD samples with low E_u suggest the existence of micro-crystals.

IV. Summary and conclusions

This work reports photoluminescence studies in a-SiC:H materials that differ in the glow discharge man-

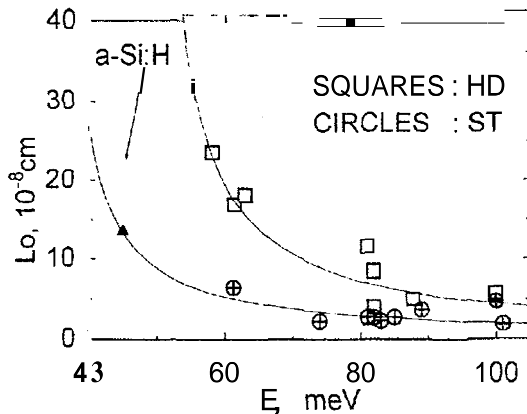

Figure 4: Curves substituting the experimental values of T_0, E_u and DOL in eq. (7).

The shift between tlie PL maximum aiitl tlie optical gap for the non-diluted samples was interpreted as due to carrier thermalization. In both types of samples a Stokes shift of 0.04 eV was estimated in a-SiC:H corresponding to a 0.08 eV contributioii to tlie PL emission broadening.

Foi both types of materials it was found a similar dependence of the PL intensity on temperature. Combined results of PL, Urbach energy and density of states allowed to estimate the localization length of trapped carriers (L_0). L_0 is shorter in non-diluted than in diluted samples, an indicative of a greater localization of carriers. Tlie values of L_0 obtained for the ST samples seem to be s milar to that observed in a-Si:H, suggesting that tlie deposition parameters used in this case produce materials converging to a-Si:H. Furthermore, the higher localization parameters observed for some HD samples, could indicate the existence of micro-crystals.

Acknowledgments

Tlie au hors acknowledge I;. Evangelisti and his group, Dipartimento di Fisica, La Sapienza, Roma., Italy where some of the samples were prepared. This work was partially supported by CNPq, CAPES, FAPESP (contract 92/1603-2), FAEP (contracts 0171/92 and 0144/93), and CEE.

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