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LUMINESCENCE IN PLASMA DEPOSITED AMORPHOUS Si_xC_{1-x} ALLOYS

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Abstract - Results are presented on the composition and temperature dependence of the luminescence in plasma deposited amorphous Si_xC_{1-x} alloys using films of composition ranging from pure Si to 90% C in the 77 K to 450 K temperature range. There is evidence to suggest that the radiative recombination rate increases by over a factor of $10^3$ from pure Si to C rich films. This increase is shown to be also consistent with the composition dependence of the quantum efficiency. These results are discussed in terms of a radiative tunnelling model.

Introduction - A previous study on the optical and luminescence properties of plasma deposited amorphous Si_xC_{1-x} (1) showed two distinct features. One was the increase by a factor of about $10^3$ in the ratio of the luminescence at 300 K to that at 77 K with carbon content. This was interpreted in terms of enhancement in the Coulombic electron-hole binding energy due to the decrease in the dielectric constant with C concentration (1). There was however no direct experimental evidence for this change in binding energy and other mechanism, such as an increase in radiative rate, could not be ruled out. The second feature was a relatively high quantum efficiency for C rich films. The composition dependence of the quantum efficiency was discussed in terms of a model based on the tunnelling of electrons to defect centres (2). The experimental results were consistent with an increase in the defect density to about $10^{17}$ to $10^{18}$ cm$^{-3}$ as the carbon concentration was increased and with a reduction in the critical tunnelling distance by a factor between 2 and 3. In this work we present further results on the temperature and composition dependence of the luminescence in a-SixC_{1-x} which allows a better understanding of the different mechanisms which control the luminescence in these alloys.

Experiment - The experimental details regarding sample preparation and measuring techniques have been reported previously (1). All the results in this work refer to films grown at a substrate deposition temperature of 300°C. These films are hydrogenated as determined by infra-red absorption. The Si/C composition, determined by electron microprobe analysis, is described by the parameter x which stands for the number of Si in respect to the total number of Si plus C atoms. The temperature dependence of the luminescence was measured using a "DN 704 Oxford Instrument cyostat and a DTC2 temperature controller operating in the 77 to 450 K temperature range.

Results - The spectral dependence of the luminescence emission for samples of different compositions is shown in Fig. 1. For most compositions the emission is in the form of a single band which broadens and shifts towards higher photon energies as the carbon content of the films is increased. The composition dependence of the peak emission energy and bandwidth have been discussed in some detail elsewhere (1). The emission efficiency as a function of composition is shown in Fig. 2. It should be recalled that the uncertainty in determining the relative value of the quantum efficiency is large (1). The expected corrections, however, would in principle accentuate the features shown in Fig. 2 and it can be concluded that for C rich specimens the emission efficiency is of the same order or larger than in either a-Si:H or Si rich samples.
The temperature dependence of the luminescence is shown in Fig. 3a for samples of three different compositions. The intensity in this plot has been normalized with respect to the intensity at low temperatures (3). In agreement with previous publications (4,5) pure Si samples show a decrease of over a factor of $10^3$ from 77 to 300 K. This can be taken as an indication that our a-Si specimens have a low density of defect centres (6,7). On the other hand in 90% C films the corresponding decrease is less than a factor of four. It can be argued that this weaker temperature dependence is similar in origin to that observed in high defect density a-Si:H (6,7). However these a-Si:H films also show a much lower low temperature quantum efficiency and as discussed with reference to Fig. 2 this is not the case in C rich samples which show the weakest temperature dependence. Furthermore, if an estimate is made using the model proposed by Street (7) of the density of defect centres needed to account for the observed weaker temperature dependence of samples in the mid composition range, an order of magnitude higher reduction in the low temperature quantum efficiency is predicted than that actually observed.

We have suggested that the difference in temperature dependence for different compositions could originate from an increase in the electron-hole binding energy as the carbon concentration is increased (1). If there is a single activation energy the quantum efficiency $Q_L$ is expected to vary as $Q_L = P_R/(P_R + \omega_0 \exp(-E_\text{a}/kT))$ where $P_R$ is the radiative recombination rate, $\omega_0$ an appropriate phonon frequency and $E_\text{a}$ a binding energy which controls the thermal dissociation rate. If the parameter $\omega_0/P_R$ is independent of temperature and composition a change in binding energy will result in a proportional change in the temperature $T_1$ at which a value $Q_{L1}$ is attained. An inspection of Fig. 3a shows that, depending on the value of $Q_{L1}$, the value $E_\text{a}$ can vary by a factor of 1.5 to 3 going from pure Si to 90% C films. This is well within the factor of four change expected from an increase in Coulombic energy owing to the decrease in dielectric constant with carbon content (1). However this explanation is likely to be an over-simplification. Changes in quenching temperature can also originate from variations in the radiative recombination rate which is unlikely to remain constant along the composition range. Also the temperature dependence of the quantum efficiency will not necessarily follow a single activated regime. As shown in Fig. 3b, there is (in similarity with a-Si:H) (4,5) evidence for a double exponential regime of the form

$$Q_L^{-1} = 1 + A \exp(-E_\text{a}/kT) + B \exp(-E_\text{b}/kT)$$

The high temperature activation energy $E_\text{a}$ is thought to represent the thermal dissociation of electron-hole pairs and the pre-exponential factor $A$ is associated with $\omega_0/P_R$.

The composition dependence of the parameters $A$, $B$, $E_\text{a}$ and $E_\text{b}$ as obtained from plots like that in Fig. 3b is shown in Figs. 4 and 5. It would appear that against the expectations of the simplified model considered above, the activation energy $E_\text{a}$ is only a weak function of composition and in fact seems to decrease with increasing
carbon content. The higher threshold quenching temperatures in high carbon content samples seem to originate mostly from a pronounced decrease in the parameter A. If \( A = \omega_0/P_R \) this means an increase in the radiative recombination rate of a factor of \( 10^3 \) to \( 10^4 \) (\( \omega_0 \) is only expected to vary by less than a factor of two).

Further support for the interpretation of the data of Fig. 4 in terms of an increase in the radiative recombination rate comes from the composition dependence of the quantum efficiency shown in Fig. 2. This pattern was interpreted in (1) in terms of the model proposed by Tsang and Street (2) based on a non-radiative process in which the electron tunnels to a nearby defect centre. For a random distribution of centres this model predicts a low temperature quantum efficiency given by

\[
Q_L = \exp \left( -\frac{4}{3} \pi R_C^3 N_S \right)
\]

where \( R_C \) is defined such that the probability of tunnelling to a site a distance \( R_C \) equals the radiative recombination probability and is given by

\[
R_C = \frac{1}{2} R_0 \ln \left( \frac{\omega_0}{P_R} \right)
\]

where \( R_0 \) is the Bohr radius and \( N_S \) the density of non-radiative defect centres. It was argued (1) that as the carbon concentration is increased the defect density also increases to levels of the order of \( 10^{17} \) to \( 10^{18} \) cm\(^{-3} \) so that at compositions

Fig. 3a Photoluminescence intensity \( I_L \) normalized to the low temperature value \( I_0 \) vs \( T^{-1} \) for three \( Si_xC_{1-x} \) films

Fig. 3b (\( I_0/I_L - 1 \)) vs \( T^{-1} \) for the same films as Fig. 3a.

Fig. 4 Composition dependence of the pre-exponential factors A and B

Fig. 5 Composition dependence of the activation energies \( E_a \) and \( E_b \)
of about 40 to 60% Si the efficiency, as predicted by equation 2 is reduced by about an order of magnitude. It was further suggested that for higher C concentrations the defect density did not increase appreciably but there was a reduction in the critical distance $R_C$ by a factor between 2 and 3. An inspection of equation (3) shows that such a reduction in $R_C$ is indeed obtained if the parameter $\omega_0/PR$ is reduced by a factor $10^3$ to $10^4$ from the value of $10^6$ found in pure Si films. This reduction in $\omega_0/PR$ is in good agreement with the change in the pre-exponential parameter $A$ as shown in Fig. 4.

In a model in which the band-gap luminescence is interpreted in terms of radiative tunnelling the radiative rate will be given by (4)

$$P_R = \omega_0 \exp (-2R/R_0)$$

(4)

where $R$ is the electron-hole separation. For a-Si:H a most probable value of $R/R_0 = 5$ has been estimated from time resolved luminescence measurements (4). In order to account for an increase in $P_R$ of a factor of $10^3$ it is necessary according to equation (4) to assume values of $R/R_0$ between 1 and 2. Such a small separation is possible if the electron-hole pair is excited either near the bottom of the band or into localized states so that the carriers are not able to diffuse apart before recombining. A further consequence of this small separation will be a larger binding energy and this appears in principle to contradict our experimental results which show a small decrease in the high temperature activation energy for C rich films. It should be pointed out however that our measurements are limited to a maximum temperature of 450 K. It can be easily appreciated from Fig. 3b that for similar values of $A$ as those found in C rich specimens (about $10^2$) an activation energy factor of three or four times larger than that actually measured could not be observed unless temperatures in excess of 1000 K are used. This is clearly impractical in these hydrogenated amorphous alloys. It could then be argued that the activation energy estimated from the high temperature regime in C rich specimens is still strongly influenced by the low temperature regime and is not a good representation of the true binding energy.

Conclusions - Our measurements of the temperature and composition dependence of the luminescence in amorphous Si$_x$C$_{1-x}$ films suggests that the radiative recombination rate increases by over a factor of $10^3$ from pure Si to 90% C specimens. This increase is tentatively explained as a consequence of a smaller electron-hole separation in C rich sample carriers being excited near or into localized states. A most probable value of the electron-hole separation $R$ is estimated at between 1 and 2 times the Bohr radius.

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