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Photoluminescence in *a*-C:H films

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Amorphous hydrogenated carbon films show a characteristic photoluminescence behavior that is of great interest for the study of their electronic structure. In the present paper we develop a model of the photoluminescence process in a polymerlike hydrocarbon on the basis of a mixed sp^2-sp^3 hybridization of the carbon atoms in this material. The sp^2 phase is assumed to be confined in clusters embedded within a sp^3 matrix. We assume excitation and recombination to take place within a single cluster. Thus the overall photoluminescence signal consists of the contribution of all single clusters, having different energy-gap values E_g, due to their various sizes and/or shapes. Applying the model to experimental data, we deduce a material-characteristic function $f(E_g)$ that turns out to be representative of the distribution of the different energy-gap values E_g of the sp^2 clusters in the film. The good agreement with experimental data suggests that the classical Tauc gap E_{Tauc} in *a*-C:H films is a value averaging over all single-cluster gap values E_g. Moreover, our model reproduces all the peculiar features of the photoluminescence behavior of *a*-C:H films, such as the nonactivated dependence upon temperature.

I. INTRODUCTION

In the recent years, *a*-C:H films have become well known in solid-state physics as well as in technology because of their diamondlike characteristics.[1–3] However, in dependence on the deposition process and parameters the material can be tailored in order to obtain very different physical properties.[3,4] Usually, attention is focused on high hardness, opaque material, referred to as DLHC (diamondlike hydrocarbon). This material has a high amount of sp^2 hybridized carbon atoms, where the sp^3/sp^2 ratio is almost equal to unity, and a relatively low hydrogen content (20–30 at. %) has been quoted.[5]

On the other hand, the PLHC (polymerlike hydrocarbon) modification of *a*-C:H, that is characterized by high hydrogen (> 50 at. %) and sp^3 contents (the sp^3/sp^2 ratio amounts to more than 2), shows peculiar characteristics as well.[6] Although it is transparent and soft, so that its use as a mechanically protective coating cannot be foreseen, it has a very peculiar photoluminescence behavior. Light-emitting diodes based upon PLHC active layers have already been realized.[7,8] Actually, the performance of these devices is not enough to allow their commercial use. This can be traced back to two different reasons. On one side, an effective doping procedure has not yet been set up for PLHC. On the other side, despite the fact that many authors have been reporting about photoluminescence measurements,[9–13] the mechanism of the photoluminescence is quite unclear and has still to be explained in a proper way. Although we will deal in the following with PLHC, most of the features can be observed in DLHC films. The most important points that are common to all photoluminescence spectra are as follows.[9–13]

(1) No clear relationship between the peak energy of the photoluminescence spectra and the optical Tauc gap can be quoted (see Fig. 1).

(2) The intensity of the signal has only a weak dependence upon temperature. No activated behavior is observed, at least not for an energy lower than the excitation one.

(3) The peak is a rather broad one, its half width being of the order of 0.5 eV (see Fig. 2).

(4) A tail at energies higher than the absorbed photon energy is observed (see Fig. 2).

(5) The recombination process in *a*-C:H is much faster than in *a*-Si:H[13], where a recombination process through band tail states is dominant.[14]

The aim of this paper is to present and discuss a model describing the mechanisms which cause the photoluminescence of PLHC to have a distinctive behavior. This model is based on the assumption that an energy distribution of photoluminescence centers exists in PLHC films. As a consequence, the main characteristics of the photoluminescence in amorphous hydrogenated carbon

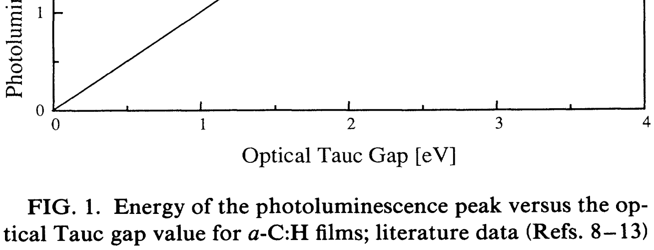

FIG. 1. Energy of the photoluminescence peak versus the optical Tauc gap value for *a*-C:H films; literature data (Refs. 8–13) (triangles) and our own values (squares).

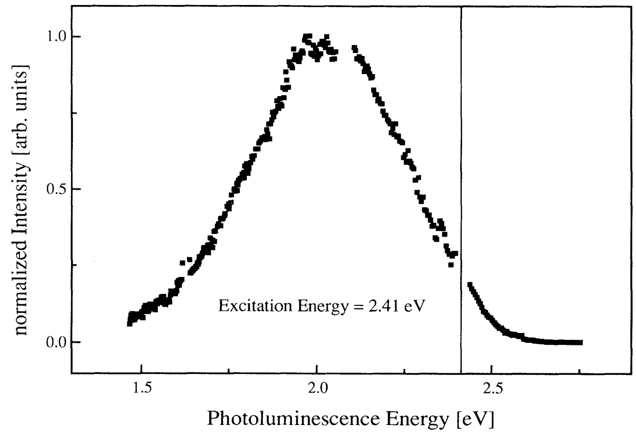

FIG. 2. Typical photoluminescence spectrum of a polymer-like a-C:H film with an optical gap of 2.75 eV. The vertical line indicates the excitation energy.

are explained. In particular, the origin of the almost temperature independent intensity is clarified. The model is applied to experimental data, in order to check its validity.

II. EXPERIMENT

The films were deposited by PECVD, either of methane or acetylene onto quartz substrates. Deposition apparatus and procedure are described in detail elsewhere.[15] The photoluminescence spectra were measured using a grating spectrometer of the type Jobin Yvon Ramanor U 1000 and a water-cooled photomultiplier C 2761 of Hamamatsu Photonics. For excitation, various lines (2.41, 2.60, and 2.71 eV) of an argon-ion-laser were applied. The samples have been held at room temperature during data acquisition. The absorption coefficient α was determined from the transmittance and reflectance measurements at an UV-VIS-NIR Perkin Elmer Lambda 9 spectrophotometer.

III. MATERIAL STRUCTURE OF a-C:H FILMS

Among the different models proposed for the structure of a-C:H films, the more commonly accepted is the one in which sp^2 hybridized carbon atoms are organized in clusters having different size and shape. It has been shown,[16] that the energy gap of the clusters depends both upon their shapes and upon the number of atoms in the cluster. So, a distribution of clusters sizes and shapes implies a distribution of E_g values of the clusters. Thus, the value for the optical gap obtained applying the Tauc procedure represents an average value of this distribution and not a real energy spacing between the conduction and valence band[17] of the film.

Since the sp^3 phase, in which the clusters are embedded, has a much larger optical energy gap (over 6 eV) (Ref. 18) with respect to the clusters $E_g \leq 3$ eV), we can think of carriers free to move inside the clusters, but almost forbidden to move from one cluster to the other. This is confirmed by the high-resistivity ($>10^{14}$ Ω cm) (Ref. 19) of PLHC films.

Indeed, some care has to be taken about this point. It is true that the value of E_g does not represent the distance between extended states of valence and conduction band. Nevertheless, the magnitude of the absorption coefficient for energies over the E_g value of the film is large enough to suggest that an overlapping of the states may occur. In such a case, the carriers are not confined to the cluster in which they are produced and the present model should be modified. In the following paragraphs, $f(E_g)$ will represent the relative abundance of clusters having an energy gap between E_g and E_g+dE_g. Our interest is mainly concentrated on the shape of the photoluminescence signal, so that in the calculation we will disregard all constants that do not affect the shape of the spectra.

IV. PHOTOLUMINESCENCE MODEL

A. Single-cluster process

Irradiating the film surface with a laser beam consisting of photons of an energy E_l, a certain number of photons is reflected just at the surface, according to the reflection coefficient R. From the remaining photons that enter the film, a part is absorbed by clusters having an energy gap between E_g and E_g+dE_g, whereas the others are transmitted throughout the film, without having caused any excitation, with a probability

$$\exp[-\alpha(E_l,E_g)tf(E_g)dE_g]\,, \qquad (1)$$

where t stands for the film thickness, $\alpha(E_l,E_g)$ is the absorption coefficient at excitation energy E_l of a hypothetical material that completely consists of clusters having gap E_g, and $f(E_g)dE_g$ is the probability of the existence of clusters with a gap between E_g and E_g+dE_g in the real material. However, because of the small value of the exponent in (1), the probability of a photon to be absorbed within such a cluster can be approximated by

$$\alpha(E_l,E_g)tf(E_g)dE_g\,. \qquad (2)$$

The absorption of the photon promotes an electron from a valence-band energy state to a conduction-band state of the cluster, increasing its energy from E_i up to $E_f=E_i+E_l$.

At this point, we assume that all promoted electrons thermalize to fill up the states near the edge of the conduction band, that is we can apply a Boltzmann distribution:

$$f_e(E',F_e^{\text{quasi}})=e^{-[(E'-F_e^{\text{quasi}})/k_BT]}\,, \qquad (3)$$

where F_e^{quasi} is the quasi-Fermi level of electrons. In a similar way, the holes thermalize to fill up the states near the edge of the valence band and their distribution is similar to that of the excited electrons in the conduction-band states:

$$f_h(E'',F_h^{\text{quasi}})=e^{[(E''-F_h^{\text{quasi}})/k_BT]}\,, \qquad (4)$$

where F_h^{quasi} is the quasi-Fermi level of holes. The radiative recombination of the carriers gives rise to a photon having energy E close to, and larger than the E_g value of the cluster. To evaluate the number of emitted photons of energy E, we remember that the number of electrons in a state of energy E' is given by the product

$$N_c(E',E_g)f_e(E',F_e^{\text{quasi}}) \ , \tag{5}$$

where $N_c(E',E_g)$ is the number of states of energy E' in the conduction band of the cluster and $f_e(E',F_e^{\text{quasi}})$ its probability of being occupied by electrons. In the same way, we find the term for the holes in the valence band to be

$$N_v(E'',E_g)f_h(E'',F_h^{\text{quasi}}) \ , \tag{6}$$

where $N_v(E'',E_g)$ is the number of states of energy E'' in the valence band of the cluster. Labeling with E the energy of the emitted photon, we can write $E''+E=E'$.

The total contribution of the clusters having gap E_g is then given by

$$\begin{aligned} I(E,E_g)dE_g \propto \alpha(E_l,E_g)tf(E_g)dE_g \\ \times \int_{E_g/2-E}^{-E_g/2} N_v(E',E_g)f_h(E',F_h^{\text{quasi}}) \\ \times N_c(E'+E,E_g) \\ \times f_e(E'+E,F_e^{\text{quasi}})dE' \ , \end{aligned} \tag{7}$$

where the zero of energy was set at midgap. Assuming now, with E_c being the lowest-energy state of the conduction and E_v being the highest-energy state of the valence band,

$$N_c(E'',E_g)=\text{const}\times(E''-E_c)^{m_c} \ , \tag{8}$$

and

$$N_v(E',E_g)=\text{const}\times(E_v-E')^{m_v} \ , \tag{9}$$

for the density-of-states (DOS) distribution in the conduction and in the valence bands, respectively, it can be shown that[20]

$$\begin{aligned} e^{(E''-\text{QF}_h)/k_BT}e^{(\text{QF}_e-E')/k_BT} \\ \propto (k_BT)^{-(2+m_v+m_c)}e^{(E_g-E)/k_BT} \ . \end{aligned} \tag{10}$$

Using the above quoted expressions for the distribution of electrons and holes, the integral in Eq. (7) becomes equal to (apart from some more constants)

$$\begin{aligned} (k_BT)^{-(2+m_v+m_c)}e^{(E_g-E)/k_BT}\int_{E_g/2-E}^{-E_g/2} N_v(E',E_g) \\ \times N_c(E'+E,E_g)dE' \ . \end{aligned} \tag{11}$$

This integral is exactly the same that we obtain if we consider the absorption coefficient of the cluster of gap E_g for photons having energy E, apart from an energy dependence due to the transition matrix element:[20]

$$\alpha(E,E_g) \propto E^s \int_{E_g/2-E}^{-E_g/2} N_v(E',E_g)N_c(E'+E,E_g)dE' \ , \tag{12}$$

where s depends upon the type of transition.[20]

To get the contribution to the measured intensity, one has to observe that the emitted photons have a probability $\exp[-\alpha(E)d_{\text{av}}]$ to exit the film (t_{av} is an average path of photons, which, for sake of simplicity, we assume to be $t/2$).

Finally, we can write the relationship representing the contribution of all clusters with gap E_g to the photoluminescence intensity at energy E, again disregarding nonrelevant constants:

$$\begin{aligned} I(E,E_g)dE_g \propto \eta_r(E_g)t\alpha(E_l,E_g)\frac{\alpha(E,E_g)}{E^s}e^{(E_g-E)/k_BT} \\ \times e^{-\alpha(E)t_{\text{av}}}(k_BT)^{-(2+m_v+m_c)}f(E_g)dE_g \ , \end{aligned} \tag{13}$$

where $\eta_r(E_g)$ is the probability of radiative recombination for carriers inside clusters having energy gap E_g.

B. Total photoluminescence intensity

1. Evaluation

The photoluminescence of the film at energy E is given by the sum of the contributions of the single clusters, which we have grouped together on the basis of their E_g. Assuming a continuous distribution of E_g and equal m_v and m_c for all clusters, we can write for the overall intensity

$$\begin{aligned} I(E) \propto e^{-\alpha(E)t_{\text{av}}}(k_BT)^{-(2+m_v+m_c)} \\ \times \int_{E_{gm}}^{E} \alpha(E_l,E_g)f(E_g)\frac{\alpha(E,E_g)}{E^s}e^{(E_g-E)/k_BT}dE_g \ , \end{aligned} \tag{14}$$

where E_{gm} represents the minimum E_g and, for sake of simplicity, we have set $\eta_r(E_g)$ equal for all clusters.

To evaluate this relationship one has to assume a shape for the conduction and valence bands and a value for E_{gm}, while $\alpha(E)$ can be measured directly.

2. Estimation of the main features

In the following paragraph, we will perform the calculation of relationship (14) in some real cases. Here, we want to analyze from a more general point of view the features of the photoluminescence spectra derived from (7).

Using once again Eqs. (8) and (9) to describe the DOS in the bands of a cluster, we obtain

$$\begin{aligned} \alpha(E,E_g) \propto E^s \int_{E_g/2-E}^{-E_g/2} (E_v-E')^{m_v} \\ \times(E_g'+E-E_c)^{m_c}dE' \ , \end{aligned} \tag{15}$$

from which it can be shown that[17]

$$\alpha(E,E_g) \propto E^s(E-E_g)^{m_v+m_c+1} \ . \tag{16}$$

The overall intensity then reads

$$\begin{aligned} I(E) \propto E_l^s e^{-\alpha(E)t_{\text{av}}}(k_BT)^{-(2+m_v+m_c)} \\ \times \int_{E_{gm}}^{E} f(E_g)[(E_l-E_g)(E-E_g)]^{(m_v+m_c+1)} \\ \times e^{(E_g-E)/k_BT}dE_g \ . \end{aligned} \tag{17}$$

Since we are interested in studying the behavior of this relationship, we are forced to make some additional assumptions. If, as we expect, $f(E_g)$ is a slowly varying function of E_g, over an energy range of a few k_BT, it is possible to show that the maximum contribution to the integral of Eq. (17) comes, at a photon energy E, from the clusters obeying $E_g=E-(m_v+m_c+1)k_BT$ if $E_l-E \gg k_BT$. Assuming the function to be integrated as constant in a range of a few k_BT and setting $m=m_v+m_c+1$, we can write

$$I(E) \propto E_l^s e^{-\alpha(E)t_{\mathrm{av}}}(k_BT)^{-(m+1)} f(E-mk_BT) \times[(E_l-E+mk_BT)mk_BT]^m k_BT \;, \tag{18}$$

which can be rewritten as

$$I(E) \propto E_l^S e^{-\alpha(E)t_{\mathrm{av}}} f(E-mk_BT)(E_l-E+mk_BT)^m \;. \tag{19}$$

It can be observed that no activated temperature dependence occurs: only a power dependence upon the temperature is present. In our approximation ($E_l-E \gg k_BT$), the only temperature dependence occurs in the choice of the E_g of the clusters, which give the main contribution to the intensity at energy E [see text before Eq. (18)]. We then expect a shift of the order of a few k_BT of the photoluminescence peak energy varying the temperature from 0 to T: i.e, about 0.1 eV for $T=300$ K. The peak energy shifts to higher values as temperature increases. A weak dependence of the photoluminescence intensity of the order of a few per cent can be observed, when the calculation is performed in detail.

The physical reason for the lack of temperature dependence can be understood as follows: as temperature is varied, the main contribution to the intensity at energy E comes from clusters having different gaps, keeping the activation factor $\exp[-(E-E_g)/k_BT]$ almost constant and, in our approximation, equal to $\exp[-(m_v+m_c+1)]$.

C. Comparison with experiment

In order to check the validity of the model, two different procedures are applied. In one procedure, the photoluminescence spectra, that are acquired at different excitation energies, are analyzed for one film in order to calculate the $f(E_g)$ function. That is, from each spectrum $f(E_g)$ is derived independently and the different results of $f(E_g)$ are compared. This was done using three different laser energies (2.41, 2.60, 2.71 eV) for a sample having a Tauc gap value of $E_{\mathrm{Tauc}}=2.75$ eV. Equation (17) was evaluated assuming $m_c=m_v=\frac{1}{2}$ and using the measured absorption coefficient. The exponent s was set at $s=-1$ as it is true for constant momentum transition. The results are reported in Fig. 3. It can be observed that the three $f(E_g)$ functions are very close together. This indicates that the method is reliable and, moreover, an insight into the distribution of the clusters with gap value E_g is obtained. Let us point out that only the shape of $f(E_g)$ has a physical meaning, since we have disregarded many constants.

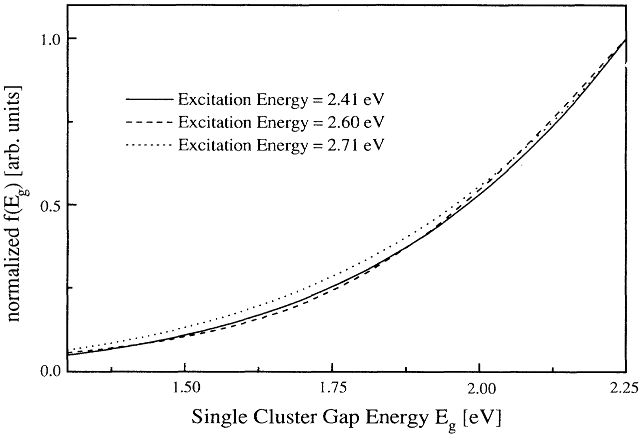

FIG. 3. $f(E_g)$ distribution functions for the sample of Fig. 2. They are calculated from three experimental data sets, obtained for different excitation energies. See text for details.

In the other procedure, the $f(E_g)$ function is determined only from the photoluminescence spectrum that corresponds to the highest laser energy. Then, the computed $f(E_g)$ together with the value of the relevant excitation energy is used in Eq. (17) in order to evaluate the other spectra mathematically. These calculated spectra are compared with the experimentally acquired data. The results of this procedure are reported in Fig. 4. The agreement between model and experimental data is good. It has to be noted that, in this case, the difference in the intensity of the laser energies can be taken into account, by multiplying Eq. (17) for the photon flux I_l/E_l where I_l is the laser light intensity that arrives at the film surface.

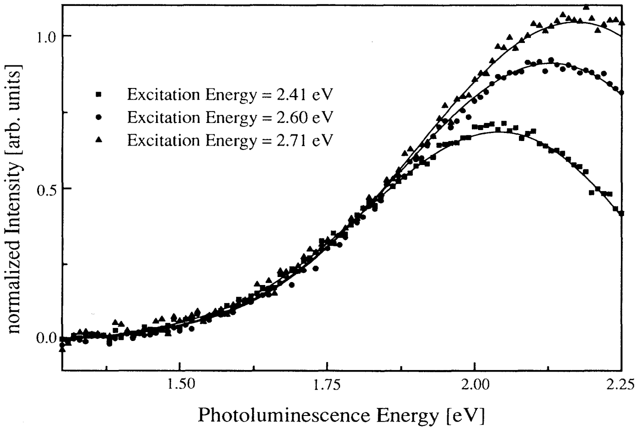

FIG. 4. Normalized photoluminescence intensity versus the photoluminescence energy for different excitation energies (same sample as in Fig. 3). The symbols indicate experimental data. The lines represent the results of the model [Eq. (17) in the text], where the $f(E_g)$ function is calculated only from the data at highest excitation energy.

V. CONCLUSION

Following the lines of the model presented in the previous paragraphs, a reason for the various features of photoluminescence spectra of *a*-C:H films can be identified.

(1) No clear relationship between the peak energy of the photoluminescence spectra and the optical Tauc gap can be quoted: the peak energy is due to the balance between the increasing $f(E_g)$ (see Fig. 3) and the decreasing $(E_l - E)^{m_v + m_c + 1}$ factors and nothing has to bear with the E_{Tauc} value of the film.

(2) The intensity of the signal has only a weak dependence upon temperature as it was shown in approximation (19) and afterwards. No activated behavior is observed.

(3) The peak is a rather broad one, its half width being of the order of 0.5 eV (see Fig. 2): the width of the peak is determined by $f(E_g)$, that is by the distribution of the cluster gap values and not by thermal effects.

(4) A tail at energies higher than the absorbed photon energy is observed (see Fig. 2): it is the thermal effect of the excitation of carriers generated in clusters having E_g close (a few $k_B T$) to the laser energy. More detail about this effect will be given in a following paper.

(5) The recombination process in *a*-C:H is much faster than in *a*-Si:H, where a recombination process through band tail states is dominant. In the cluster, we have a band to band process, which is much faster than a tail to band or tail to tail transition.[13,14] For the region of $\alpha > 10^4$ cm^{-1} the present model should be modified: because of the overlapping of states, the assumption of independent sp^2 clusters is no longer valid.

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