PHYSICAL REVIEW B VOLUME 53, NUMBER 24 15 JUNE 1996-II

Polarization memory of photoluminescence in amorphous carbon

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(Received 16 October 1995)

The polarization memory of the photoluminescence in amorphous hydrogenated carbon (*a*-C:H) has been investigated as a function of its band gap and the excitation energy. The observation of a polarization memory suggests that the excited states are well localized, with a low point symmetry. The decay of polarization memory is found to depend primarily on the energy difference between the excitation and emission energies, that is, the thermalization energy down the tail states. [S0163-1829(96)01724-9]

INTRODUCTION

Amorphous hydrogenated carbon (*a*-C:H) has attracted much interest recently due to a number of useful properties such as chemical inertness and mechanical hardness.[1,2] The wider-band-gap types of *a*-C:H exhibit a photoluminescence (PL) whose quantum efficiency can exceed 10% at room temperature.[3–8] Understanding the luminescence properties of *a*-C:H films is of practical interest because of their possible application in thin-film electroluminescence devices,[5] and of fundamental interest because their luminescence properties provide valuable information for the study of the recombination of carriers in amorphous materials with more than one type of bonding configuration, with atoms in sp^3, sp^2, and sometimes sp^1 hybridization.

The PL properties of *a*-C:H are generally different from those of more extensively studied amorphous materials such as *a*-Si:H.[9,10] For example, in contrast to *a*-Si:H, the PL of *a*-C:H films depends only weakly on temperature and is still strong at room temperature.[3,11] The PL lifetime is much shorter in *a*-C:H than in *a*-Si:H, 10^{-8} s compared to 10^{-3} s. Furthermore, no photoconductivity has been observed in our samples and the PL is not quenched on the application of electric field up to 10^6 V/cm. In the case of *a*-Si:H, the PL is quenched by electric field of about 10^5 V/cm.[9] In addition, in some *a*-C:H the PL peak energy is found to be higher than the optical gap.[6] The PL spectrum also possesses a high-energy tail, with a PL energy above the excitation energy.[3] It has been noted that carbon-rich *a*-$\mathrm{Si}_{1-x}\mathrm{C}_x$:H ($x>0.5$) films also exhibit very similar PL properties to *a*-C:H.[3,11]

The mechanism of PL in *a*-C:H is still under discussion. The short radiative lifetime and the lack of electric field quenching indicate that PL occurs by the geminate recombination of closely bound electron-hole pairs. *a*-C:H contains both sp^2 and sp^3 sites.[12–14] The sp^2 sites possess π states so their local band gap is much smaller than that of sp^3 sites. This gives rise to very strong fluctuations of the band edges. The strong fluctuations inhibit the mobility of carriers and provide a natural means to localize the electron-hole pair, consistent with the PL properties.

A reasonable framework to describe PL in *a*-C:H is provided by the cluster model, in which electron-hole pairs are excited and recombine within clusters of sp^2 sites embedded in an sp^3-bonded matrix.[3,13–15] The cluster model was originally developed from structural calculations of *a*-C:H which suggest that the sp^2 sites tend to form clusters to maximize their π bonding energy.[16] The size of such clusters is still debated but is probably of the order of 2–10 sp^2 sites in the *a*-C:H of interest here.[17] The clusters create symmetric band-edge fluctuations so that the valence-band maximum and conduction-band minimum occur at the same place. This therefore leads to a model in which electron-hole pairs excited and recombining within the sp^2 clusters are responsible for the observed PL.[14]

The PL properties of *a*-C:H can be examined in more detail by studying the correlation between the polarization of the luminescence and that of the excitation light. This so-called ''polarization memory'' of PL is a useful tool because it is closely related to the degree of localization of the recombining carriers.[18] For the PL to retain the polarization of the excitation light, it is necessary that the electron-hole pairs are closely bound to each other and do not diffuse apart. That is, the absorption and emission of radiation must be associated with the same dipole.[18] Otherwise, the polarization memory of the PL is lost. Polarization memory has been observed in other amorphous semiconductors, such as C-rich *a*-$\mathrm{Si}_{1-x}\mathrm{C}_x$:H,[19] and *a*-$\mathrm{As}_2\mathrm{S}_3$.[20] Its origin was attributed to the recombination of a localized exciton in a fluctuating potential as a result of the random structure. Recently, Koos, Pocsik, and Toth[21] have observed polarization memory of PL in *a*-C:H. This paper reports a study of the PL memory of *a*-C:H as a function of the optical gap and excitation energy.

EXPERIMENTS

The *a*-C:H films of thickness 2000–3000 Å were grown on glass substrates using a 13.56 MHz rf plasma-enhanced chemical-vapor deposition (PECVD) system with CH_4 at an operating pressure of 1 Torr. This pressure is higher than is often used for PECVD of *a*-C:H and tends to give a wider optical gap. The substrate temperature was maintained at 20 °C by a feedback-controlled cooling system. Other details of the deposition system are given elsewhere.[22] The E_{04} gap is used as a measure of the optical gap and is derived from the absorption spectra. As in other studies of *a*-C and *a*-Si-based alloys, the E_{04} gap is used in preference to the Tauc gap because of nonlinearities in the Tauc plot. The E_{04} gap is found to range from 2.7 to 4.3 eV. For the 4.3 eV gap film, the absorption of the glass substrate is not negligible and the absorption of this film at higher energies was extrapolated by

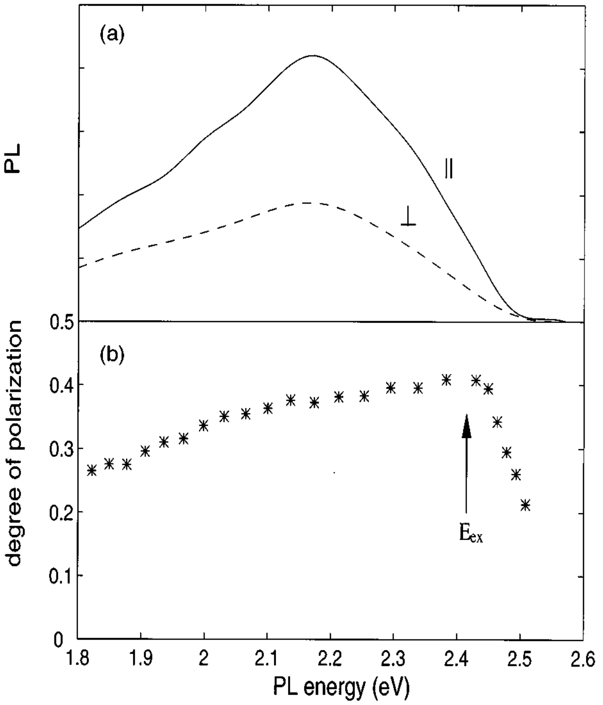

FIG. 1. (a) The PL spectra excited at 2.41 eV for the film with 4.33 eV band gap. The solid line and broken line correspond to polarization parallel and perpendicular to that of the excitation, respectively. (b) The degree of polarization of the PL spectra seen in (a).

using the dispersion relation of Forouhi and Bloomer[23] as used successfully by other workers[24] and as described elsewhere.[25] No photoconductivity and no electric field quenching of PL up to a field of 10^6 V/cm has been observed in these films.

The PL spectra were excited using 2.41, 2.71, and 3.41 eV linearly polarized radiation from an Ar ion laser, dispersed by a scanning double monochromator and detected by a photomultiplier tube using the standard lock-in technique. Light emission within an 8° cone is collected. The PL peak energy of the films can vary from around 2 to 2.6 eV depending on the band gap and on the excitation energy used. Here we are mainly concerned with the study of the polarization memory in such films. The polarization of the PL was determined by using a 300–650 nm range Spindler & Hoyer polarizer. The monochromator response for the two different polarizations of light (parallel and perpendicular to that of the laser source) was checked by using an unpolarized light source such as a tungsten lamp, and corrections have been made for all the spectra obtained. All these measurements were carried out at room temperature.

RESULTS

Figure 1(a) shows two typical PL spectra excited at 2.41 eV and obtained from the film grown at the highest band gap of 4.33 eV, with polarization parallel (solid line) and perpendicular (broken line) to that of the excitation. The overall PL spectrum, which is the sum of the two polarizations, is structureless and broad with a bandwidth of 0.45 eV and is similar to those previously reported for a-C:H.[3,5,6,8,11] Figure 1(b) shows the corresponding degree of polarization (DP) of the film defined by[18]

$$\mathrm{DP}=\frac{I_s-I_p}{I_s+I_p}, \tag{1}$$

where I_s and I_p are the intensity of the PL with polarization parallel and perpendicular to that of the excitation source, respectively.

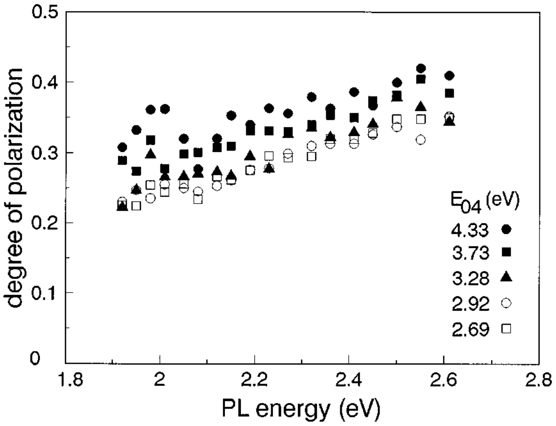

FIG. 2. Degree of polarization for the series of films grown with different optical gap and excited at 2.71 eV. Legend shows the optical gap of the films.

Figure 2 shows the variation of the DP with the PL energy E_{PL} for films of each band gap, for an excitation energy E_{ex} of 2.71 eV. The DP, reaching 0.4 for the 2.71 eV excitation, is seen to be quite high for the immediate radiative recombination of the photoexcited electron-hole pair, given that the theoretical limiting value is 0.5 for a random distribution of dipoles in space.[18] The DP for the 3.41 eV excitation (Fig. 3) also increases as the emission energy approaches the excitation energy, and would extrapolate to about 0.4 for $E_{\mathrm{PL}}-E_{\mathrm{ex}}\rightarrow 0$ V. Figure 2 shows that the DP decreases with decreasing emission energy. This was also observed in a-$\mathrm{Si}_{1-x}\mathrm{C}_x$:H,[19] and in a-$\mathrm{As}_2\mathrm{S}_3$,[20] and was attributed to the interaction of the carriers with phonons during thermalization, which reduces the DP. The results in Fig. 2 also show that the DP is slightly higher for films of wider optical gap.

Figure 3 shows the DP plotted against the energy difference $E_{\mathrm{PL}}-E_{\mathrm{ex}}$ in order to analyze the relation between the DP and the energy loss in the process of thermalization. It is clear from Fig. 3 that the DP varies strongly with the PL energy, and has a weaker dependence on the optical gap and on the excitation energy. For a given film, it is found that the DP for different excitation energies depends primarily on the difference in the excitation energy and PL energy, $E_{\mathrm{PL}}-E_{\mathrm{ex}}$. Thus the DP for three excitation energies is seen to fall almost on a common curve in Fig. 3. There is little explicit dependence on E_{ex} itself. This is an important observation.

It is generally believed that the polarization memory is lost as the carriers hop apart and thermalize down the band tails. Each hop is accompanied by a phonon emission,[10] a loss of energy equal to the phonon energy, and a small loss of DP. Thus the loss of DP is given by the number of phonons emitted times the loss of polarization per phonon, q. This relates the DP to the PL energy as

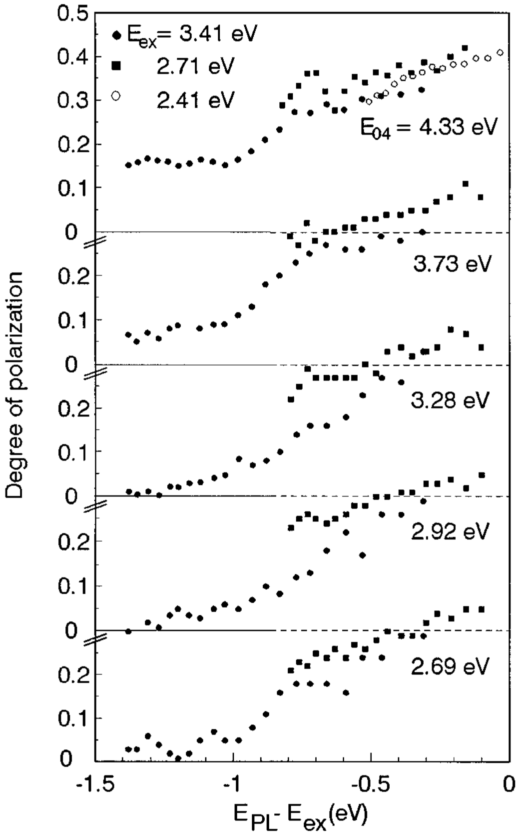

FIG. 3. Degree of polarization of the PL as a function of $E_{\mathrm{PL}}-E_{\mathrm{ex}}$ for the series of films grown with different band gaps and excited at different energies.

$$P=P_0\left[1-\frac{(E_{\mathrm{ex}}-E_{\mathrm{PL}})q}{\hbar\Omega}\right], \qquad (2)$$

where P_0 is the initial DP and $\hbar\Omega$ is the phonon energy. This formula was originally derived to describe the DP observed in As_2S_3,[20] and it is seen to describe the broad features of the DP for 2.71 eV excitation fairly well (see Fig. 4). However, for 3.41 eV excitation, and in closer detail for the 2.71 eV excitation, a simple linear relationship is not seen and the dependence shows some structure, as discussed shortly.

To analyze the data further, we replot the DP in Fig. 4 as a function of $E_{04}-E_{\mathrm{PL}}$, which is a measure of the depth into the gap at which radiative recombination occurs. As expected, excitation of a given energy occurs deeper into the tail for films with a larger optical gap. An interesting feature of Fig. 4 is that the rate of decrease of the DP varies with the PL energy. We have approximated each set of data points by a straight line in Fig. 4. The slope of these fits, $\alpha=q/\hbar\Omega$, the decline of polarization per unit thermalization energy or "depolarization rate," is plotted against the optical gap in Fig. 5, together with the slope of the Urbach tail of the optical absorption edge, $1/E_0$. The depolarization rate α is lowest for wide gaps for both the excitation energies used. We see that α varies roughly in a similar fashion to $1/E_0$. The inverse of E_0 is a measure of the density of tail states. This suggests that the depolarization rate and the coupling factor q in (2) are proportional to the density of tail states available for thermalization transitions. This is confirmed by the observation that α is higher for an E_{ex} of 3.41 eV than 2.71 eV, for excitation higher up the tail.

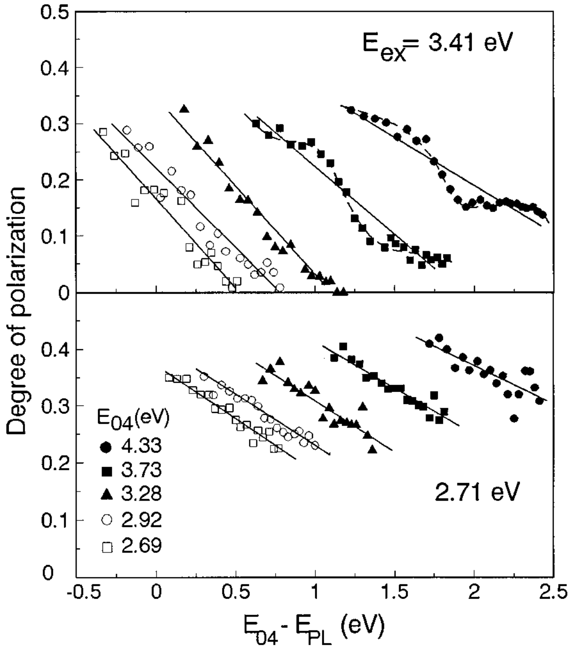

FIG. 4. Degree of polarization of the PL for the series of films grown with different band gaps plotted against $E_{04}-E_{\mathrm{PL}}$ for excitation at 3.41 and 2.71 eV.

Chernyshov *et al.*[3,4] have observed a PL above the excitation energy, the anti-Stokes PL. We have measured the DP for the anti-Stokes PL by exciting the sample with the highest optical gap (4.33 eV) using the 2.41 eV line of the Ar ion laser. This combination is chosen to accentuate the anti-Stokes PL and corresponds to an excitation deeper in the absorption tail. The results are shown in Fig. 1 with the PL spectra in the two different polarizations and also the corresponding degree of polarization obtained. It is seen that the anti-Stokes PL has polarization memory, but the DP decreases more sharply with increasing emission energy. The

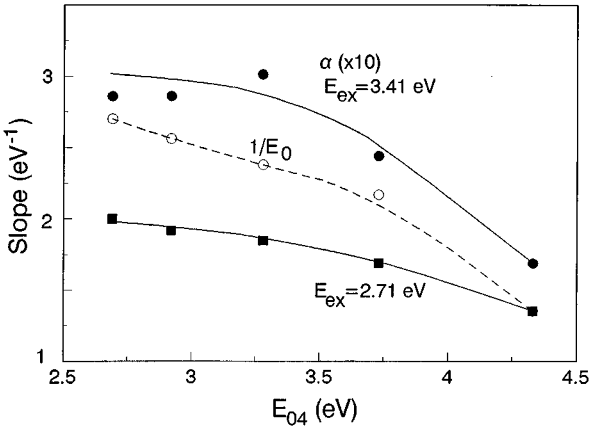

FIG. 5. The slopes of the straight-line fits in Fig. 4, α (solid line), at two different excitation energies are plotted against the optical gap, together with the inverse of the Urbach tail width $1/E_0$ (broken line) obtained from the optical absorption edge. The lines are guides to the eye.

anti-Stokes PL is attributed to the thermal excitation of photoexcited carriers to states of higher energy.[3,4] We attribute the much faster decrease of the DP for anti-Stokes PL to the lower energy of the thermal phonons available for excitation. A carrier loses a typical phonon energy in carbon of, say, 1500 cm^{-1} or 0.18 eV during downward thermalization, but gains energy of the typical thermal phonon energy of 0.025 eV per interaction during upward thermalization. The ratio of the slopes of the DP for the upward and downward scattering is approximately 9, which is close to the ratio of the corresponding phonon energies, 0.18/0.025=7.2, and thus supports this interpretation.

Examination of Fig. 4 for the excitation energy of 3.41 eV shows that the data are not very linear. This is shown by the broken-line curves which follow the data points. For the highest band gap, 4.33 eV, there is a distinct dip between $E_{04}-E_{\mathrm{PL}}$ values of 1.8 and 2 eV. This dip is not due to interference fringes; the film thickness is 2500 Å. The dip could be associated with a nonuniform decrease in the local density of tail states available for thermalization at that energy, arising from localization of states within a cluster. Further work is required to understand this feature in the DP curves.

DISCUSSION

The polarization memory and the value of q in Eq. (2) are related to the degree of localization of the carriers. The localization radius of tail states in a-C:H is likely to decrease with increasing optical gap because the sp^3 content increases with optical gap[14] and because the sp^3 sites act as tunnel barriers between the sp^2 sites which form the tail states. An increase of DP with optical gap is indeed found in Fig. 2. Secondly, Fig. 5 shows that the rate of decrease of the DP is smaller for a 2.71 eV excitation than for a 3.41 eV excitation. This may arise because the lower excitation energy generates carriers deeper into the tails. There are fewer states available for downward thermalization of carriers, so the DP will decrease less rapidly for the smaller excitation energy.

CONCLUSIONS

We have measured the polarization memory of PL in a-C:H with different optical gaps and excitation energies. On the basis of our results, the polarization memory is attributed to the presence of fluctuating potentials which cause a strong localization of the carriers, as first proposed for a-$\mathrm{Si}_{1-x}\mathrm{C}_x$:H,[19] and a-$\mathrm{As}_2\mathrm{S}_3$.[20] The large polarization memory and its variation with optical gap are consistent with the PL arising from the geminate recombination of electron-hole pairs within sp^2 bonded clusters. The variation of DP with PL energy for both the Stokes and anti-Stokes PL is broadly consistent with a loss of polarization by phonon emission, according to Eq. (2), but further work is needed to understand the oscillations in the polarization.

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