



Photoluminescence of polymer-like amorphous carbon films grown in different plasma reactors

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Abstract

The visible photoluminescence (PL) properties (emission and excitation spectra) of hydrogenated amorphous carbon (a-C:H) have been investigated for polymer-like thin films grown at low substrate temperature and small ion energies. For a large number of a-C:H films grown in three reactors (dual-mode plasma, radio frequency plasma and electron cyclotron resonance plasma) the emission spectra appear as a sum of three peaks with energies (a) 2.28 eV, (b) 2.65 eV and (c) 2.95 eV, being independent of the excitation energy (3.54 eV or 4.13 eV). Their relative intensities depend on the growth parameters while their positions are almost independent. Preliminary picosecond time-resolved PL data indicate a decrease of the decay time for increasing emission energies. A two-phase model of a-C:H is proposed to explain the PL excitation spectra. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

Optical absorption and radiative recombination processes in hydrogenated amorphous carbon (a-C:H) films have attracted attention to understand the electronic structure of a-C:H [1–3]. It is complex due to the coexistence of C atoms mainly in sp² and sp³ electronic configurations and also possibly to the heterogeneity of the material at the nanometer scale [2,4]. The sp³ and sp² sites give σ bonds which form the network skeleton. The sp² sites also form

small binding energy π states which are energetically separated from σ states and which can be treated independently [5,6]. The large difference between π and σ binding energies causes potential fluctuations, which in turn may result in some confinement of photo-excited electrons at π -bonded sites and lead to a luminescence in the visible range [2].

We report some photoluminescence (PL) properties of polymer-like hydrogenated amorphous carbon (a-C:H) films grown at low temperature and low (< 100 eV) ion energies, under well-controlled conditions, using three complementary deposition techniques. In contrast to previous reports showing a single broad emission band, three continuous-wave

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PL emission bands are evidenced. Their origin is investigated using excitation spectroscopy and picosecond time-resolved PL.

2. Experimental

To eliminate effects related only to particular growth techniques, three plasma reactors have been used, including (i) a dual-mode plasma (surface wave-coupled microwave (MW) and capacitively-coupled radiofrequency (RF)) plasma enhanced chemical vapor deposition (PECVD) reactor using (H_2 -Ar) mixtures in the MW plasma and fed with butane in the MW post-discharge [7], (ii) a pure RF plasma fed with ethylene, and (iii) an electron cyclotron resonance (ECR) plasma fed with ethylene or methane, either in the post-discharge region or directly through the cavity source [8,9]. Mean ion energies remain lower than 100 eV in all cases, and may be monitored in reactors (i) and (ii) through the RF power applied to the substrate holder. A post-deposition treatment by a pure Ar plasma (RF + MW) has also been performed (Table 1).

The films were grown on the polished surface of single crystal silicon (c-Si) substrates for PL and ultra violet-visible (1.5–4.5 eV) ellipsometry measurements, along with Rutherford backscattering (RBS) and elastic recoil detection (ERD) stoichiometry measurements. Polymer-like carbon films with low densities (1.2 to 1.7 g cm⁻³), high H content (40 to 50 at.%), wide E_{04} bandgaps (2.5 to 4.0 eV) and low refractive indices (1.2 to 1.7) have been obtained. Ex situ measurements show an O content ≤ 5 at.%, which may originate either from the quartz

chamber walls of the reactor (i) or from atmosphere exposure.

PL measurements were performed with a spectrometer (SPEX Fluorolog) system. UV light from a Xe arc lamp was focused onto the sample through a 0.22 m monochromator with a 1.25 mm slit (excitation bandwidth of 4.5 nm). The excitation light incidence angle was ≈ 50 – 75° . The resulting photoluminescence was collected by a 0.22 m monochromator with a 1.25 mm slit (emission bandwidth of 2.25 nm) coupled with a photomultiplier tube. The system optical response has been calibrated using a solution of rhodamine. No correction has been made for interferences inside the a-C:H films.

Picosecond time-resolved luminescence intensity decays were obtained by the single-photon timing method with excitation from a dye laser (Coherent 701-2), delivering ~ 4 picosecond pulses (≈ 40 nJ/pulse) at a frequency of 3.4 MHz. Detection by a microchannel plate photomultiplier was done by passing the emission through a depolarizer and then through a monochromator (Jobin-Yvon HR320). The instrument response function had an effective full width at half maximum of ~ 35 ps [10].

3. Results

Continuous-wave photoluminescence emission and excitation spectra were measured at room temperature. It appears that all three PECVD processes are suitable for the growth of polymeric a-C:H films with visible PL properties. When the excitation energy is set at 2.30 eV, the PL emission spectra is one band ($E_{em} \approx 2.0$ eV), whose intensity decreases as a function of ion bombardment energy [11,12].

Table 1
Growth conditions, optical gap (E_{04}) and thickness (d) for a-C:H films of Fig. 1

Sample	Reactor	Pressure (Pa)	MW power (W)	RF power (mW cm ⁻²)	Comments	T_s (K)	E_{04} (eV)	d (nm)
(1)	RF + MW	40	400	170	H_2 -Ar carrier	343	3.45	250
(2)	RF + MW	40	400	225	H_2 -Ar carrier	343	2.85	300
(3)	RF + MW	40	400	280	H_2 -Ar carrier	343	2.60	270
(4)	RF + MW	40	400	280	(3) + Ar (RF + MW) plasma treatment	343	–	–
(5)	RF	13	–	100	H_2 -diluted C_2H_4	473	3.21	50
(6)	ECR	1.3	150	–	CH_4 /source	473	3.00	610
(7)	ECR	1.3	150	–	C_2H_4 /post-discharge	473	3.10	500

In contrast, a new result appears for larger excitation energies (Fig. 1). A peak at 2.65 eV is observed from film (2) while from film (4) the emission spectrum is two bands at 2.65 eV and 2.95 eV. The non-luminescent film (3) shows that no PL emission band arises from the optical setup.

More generally, the a-C:H emission spectra appear as a sum of three peaks with energies (a) 2.28 ± 0.10 eV, (b) 2.65 eV and (c) 2.95 eV, being independent of the excitation energy (3.54 eV or 4.13 eV). Their relative intensities depend on the growth parameters while the position of peak (a) may be weakly dependent on the growth parameters or possibly on interference effects for the thicker films. The existence of three emission peaks in a-C:H is not reactor-dependent.

A series of a-C:H films with different optical gaps has been grown in the dual plasma reactor (i) using increasing RF power densities (up to 280 mW cm^{-2} or 100 W nominal power). Fig. 2 shows that this

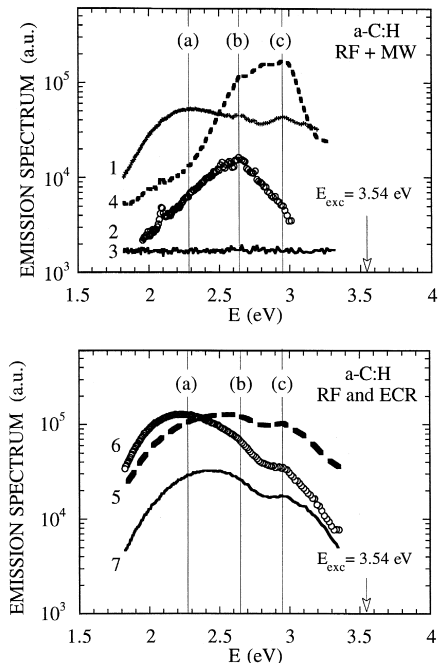


Fig. 1. PL emission intensities (in log scale) from a-C:H films prepared by different techniques: (a) dual-plasma (1–2–3–4); (b) RF (5) and ECR (6–7).

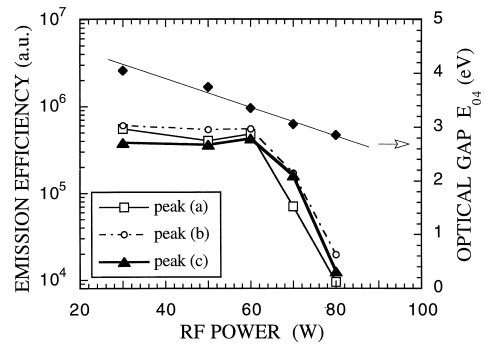


Fig. 2. Optical gap E_{04} (± 0.05 eV) and normalized PL emission intensities (reproducibility $\pm 30\%$) for films grown in the dual-mode plasma reactor. The lines are guides to the eye.

results in a decrease of the optical gap E_{04} (energy at $\alpha = 1.10^4 \text{ cm}^{-1}$) deduced from the Forouhi–Bloomer modelling of ellipsometry data. Changes in the shape of the PL emission and excitation spectra are observed as a function of RF power. However, it is difficult to decompose the respective contributions to peaks (a), (b) and (c) so that only total intensities measured at the peak position were considered and normalized to the film absorbance spectrum.

For emission peaks (a) and (c), the normalized excitation spectrum is constant ($\pm 30\%$) between the energy E_{04} and about 4.5 eV. This result may be interpreted as a constant PL efficiency for all excitation energies in this range. The normalized intensities measured at each peak energy (using 3.54 eV excitation in Fig. 2) show that the PL efficiencies for the different peaks are of the same order of magnitude. PL efficiencies are nearly independent on RF power up to 60 W corresponding to $E_{04} \approx 3.0$ eV. Above 60 W, the decrease of PL efficiency is larger for peak (a) than for peak (c), leading to a relative enhancement of the blue part of the PL spectrum at the higher RF power.

For the same films as in Fig. 2, peak (c) excitation spectra are reported in Fig. 3 after normalization to the maximum intensity (obtained at 5.4 eV excitation) but without normalization to the film absorbance spectrum. For the larger bandgap films, a single quasi-exponential spectrum is observed with an inverse slope ($E_1 \approx 1.5$ eV) while for the denser films with a smaller gap two quasi-exponential regimes are evident with respective inverse slopes,

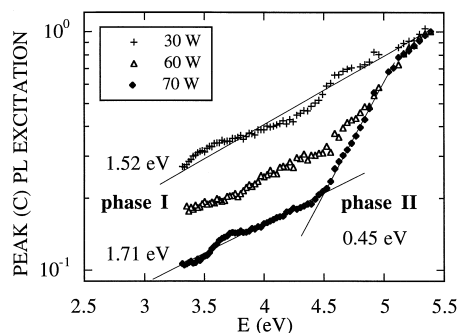


Fig. 3. Relative excitation spectra of emission peak (c) from the same films as in Fig. 2. The inverse slopes of exponential fits are indicated for phase I and phase II.

$E_I \approx 1.7$ eV and $E_{II} \approx 0.45$ eV (the latter regime dominating above 4.5 eV).

4. Discussion

A two-phase *heterogeneous* model for the a-C:H films is thus proposed to account for the PL properties. The description of a-C:H as a denser mixed sp^2 – sp^3 phase II embedded in a hydrogenated (short CH_2 chains) polymer-like phase I has been previously suggested [4]. It is likely that the polymer-like phase contains residual isolated C=C bonds while phase II is expected to contain mostly clustered C=C. Since the excitation spectrum of peak (c) in polymeric a-C:H with wider bandgap is typical of phase I, this indicates that the photo-excited carriers are probably trapped at isolated C=C sites in phase I, after thermalization.

Picosecond time-resolved PL (in the range 5 ps–1 ns) on each emission band has been performed on different films (corresponding to Fig. 1a samples) to minimize the interplay between the three bands and using different experimental bandwidths, ΔE : sample 1 ($E_{em} = 2.34$ eV, $\Delta E = 0.23$ eV); sample 2 ($E_{em} = 2.64$ eV, $\Delta E = 0.52$ eV) and sample 4 ($E_{em} = 2.95$ eV, $\Delta E = 0.65$ eV). Fig. 4 shows the deconvoluted experimental decays approximated by analytic functions. Non-exponential decays have been observed, with an increase of the typical initial decay time by nearly 2 decades from peak (c) in sample (4)

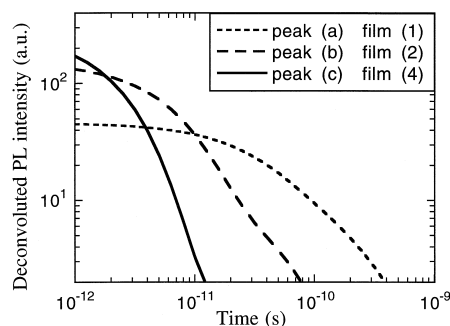


Fig. 4. Analytic approximation of the time-resolved PL excited at 4.0 eV for peaks (a), (b) and (c) corresponding respectively to samples 1, 2 and 4 from Fig. 1.

($\tau_c \approx 5$ ps) to peak (a) in sample (1) ($\tau_a \approx 200$ ps) consistent with exciton radiative recombination. This conclusion needs to be confirmed by decay time spectroscopy studies on the same a-C:H film. More detailed analysis of the time-resolved PL will be reported elsewhere.

5. Conclusion

Novel PL emission characteristics have been evidenced for polymeric a-C:H films grown using complementary PECVD techniques. They indicate that a-C:H is heterogeneous and may be described by a two phase model involving a denser mixed sp^2 – sp^3 phase in a highly hydrogenated polymeric tissue.

Acknowledgements

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