

ON THE PHOTOLUMINESCENCE OF a-C:H FILMS

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a-C:H films deposited from methane and helium mixture in a capacitively coupled rf plasma were found to show photoluminescence (PL) with peak intensities at energies far above the Tauc gap of these films. Apart from the PL the films were investigated with respect to their IR and UV/VIS absorption properties as well as their Raman spectra were examined. The ultraviolet (UV) and blue luminescence from hard a-C:H thin films are explained by incorporation of polycyclic hydrocarbons from gas-phase reactions in the methane helium plasma into the film.

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1. Introduction

There is a great interest in the deposition of carbon films containing a high fraction of sp^3 bonds [1-3]. This so-called diamond-like carbon is amorphous carbon material, either hydrogenated (up to 50 at. % hydrogen, a-C:H) or non-hydrogenated (films contain less than 1 % hydrogen, a-C). Studies on this material have been performed extensively since 1971, due to Aisenberg and Chabot [4] who prepared for the first time such films. This field has reached maturity in understanding the growth mechanisms, material properties and usage in industrial applications. Chemical inertness and mechanical hardness are the most prominent properties of a-C:H thin films. The PL of this material might become interesting as well, because there are films that show a reasonable PL efficiency between 2 eV and 2.6 eV. They provide potential for applications in light emitting devices.

The aim of this contribution is to study the PL of a-C:H in the UV and blue region of the visible spectrum. Peaks in the energy range from 2.8 eV to 4 eV were reported [5, 6]. A PL above the Tauc gap was reported earlier as well [7], but this PL was found to be below E_{04} [8] and was considered in recent models for PL in a-C:H [9,10]. The results presented here give evidence of PL far (about 4 eV) above either the Tauc gap or E_{04} from a-C:H thin films. This, to our knowledge, was not reported before.

2. Sample preparation and measurements set-up

The a-C:H films were deposited from a methane (5 sccm) and helium (75 sccm) gas-mixture in a PECVD process. The rf plasmas were generated from a 13.56 MHz rf power supply being applied between two capacitively coupled parallel plate electrodes. Prior to being placed in the reactor chamber, the substrates were cleaned in an ultrasonic bath with methanol, acetone and isopropyl alcohol after a nitric acid dip. The substrate was further treated with an in-situ Ar sputter clean prior to deposition (for 30 s). During deposition, the substrate temperature was maintained at 20 °C using a feedback controlled cooling system. Depositions were given at a pressure of 100 mTorr or 300 mTorr.

The deposition power values were 30 W, 50 W, 100 W and 200 W, resulting in power densities (σ_p) of 0.07 W/cm², 0.11 W/cm², 0.22 W/cm² and 0.44 W/cm². As substrates we have used silicon with and without oxide, glass and quartz. With these deposition conditions, the growth rate varies between 8 nm/min and 15 nm/min.

Unpolarized Raman spectra were recorded *ex situ* at room temperature, in backscattering geometry, using an I.S.A. Jobin-Yvon T64000 triple grating spectrometer with a liquid nitrogen cooled camera detection system. The spectral resolution was about 3 cm⁻¹. As excitation source was used the 514.5 nm line of an Ar laser. Spectra were recorded both in the macro (minimum spot size 100 μ m) and micro (spot size 1 μ m) configurations with laser powers of 100 mW and 10 mW respectively. Repeatability of the spectra in both configurations assures that no Raman detectable damage was caused during the measurements.

UV-VIS reflection and transmission spectra were measured between 6.2 eV and 1.1 eV, with a UNICAM UV⁷ spectrometer. The Tauc gap of films deposited on quartz and glass substrates were determined. Using a Research Series FTIR spectrometer, the FTIR absorption spectroscopy was performed for films deposited on quartz or silicon without oxide.

Films deposited on silicon with and without oxide were used for PL measurements, using two experiment set-ups. The first apparatus is a Perkin Elmer PE204 fluorescence photospectrometer, with which the photoluminescence from the edge of a film is measured. Excitation in this instrument is done by a 150 W Xe-Lamp which provides a continuous spectrum from VUV to the far infrared. Its range is limited in this experiment to the energy range between 1.6 eV and 5.6 eV by the excitation monochromator. The exponential decay of emission intensity of the Xe-Lamp for photon energies above 4.2 eV causes problems with stray light, which are taken into account and do not appear in the second PL set-up used.

In this experiment the PL is excited with 3 mW HeCd laser, i.e. with photons of 3.8 eV. The beam of this laser is widened with a spherical mirror and incident on the sample surface under an angle of approximately 20° with respect to samples' surface. The PL emitted from the surface is collected by another spherical mirror focused into a LOT-ORIEL 77250 monochromator and detected by a Hamamatsu 943-R photomultiplier tube.

The edge PL of films for each plasma power density was investigated under excitation with 5.6 eV, 5.0 eV and 4.4 eV. The excitation spectra were measured detecting PL intensity at the peak position found measuring the PL spectra.

3. Results and discussion

Transmission and reflection spectra taken in the range from 1.1 eV to 6.2 eV were used to determine the absorption coefficient spectra, $\alpha(E)$. It is well known that for amorphous semiconductors, the optical gap, E_{gT} , is conventionally defined by the Tauc relationship $\alpha E = B_T(E - E_{gT})^2$, where B_T is the Tauc parameter [11]. As can be seen in figure 1, the Tauc gap values for the studied films varied between $E_{gT} = 1.2$ eV for a film deposited at $\sigma_p = 0.44$ Wcm⁻² and $E_{gT} = 1.7$ eV for a film deposited with $\sigma_p = 0.06$ Wcm⁻².

Fig. 2 shows the FTIR spectra of the films which present a broad peak in the C-H stretching region of the spectrum around 3000 cm⁻¹. This peak is resolved in up to three gaussians at roughly 2850 cm⁻¹ attributed to sp³ CH₂ in hard or polymeric a-C:H as the bands at 2920 cm⁻¹ and 3025 cm⁻¹ attributed to olefinic sp² CH [12].

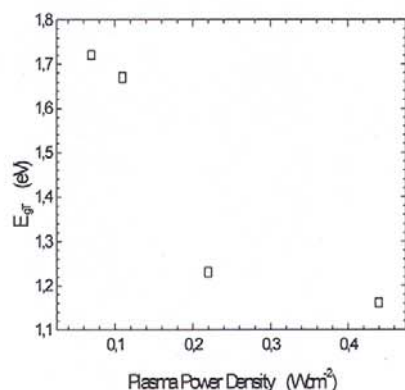


Fig. 1. The Tauc gap of the a-C:H films as a function of plasma power density in a PECVD System.

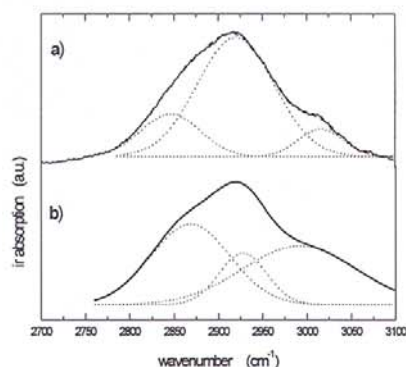


Fig. 2. Resolved FTIR spectra of films deposited with (a) $\sigma_p = 0.22 \text{ W/cm}^2$ and (B) $\sigma_p = 0.44 \text{ W/cm}^2$.

Raman measurements were performed on a-C:H films deposited at $\sigma_p = 0.22 \text{ Wcm}^{-2}$ and $\sigma_p = 0.44 \text{ Wcm}^{-2}$. A fit of the intermediate frequency region of the spectra was performed with two gaussians. The position of the G and D peaks in Figs. 3 is 1544 cm^{-1} and 1365 cm^{-1} respectively, while the intensity ratio, I_D/I_G , is 0.53. A comparison of the two spectra shows an increase in G and D position and of I_D/I_G with the decrease of their FWHM. This is consistent with a slightly more graphite-like character of the film deposited at $\sigma_p = 0.44 \text{ Wcm}^{-2}$ as witnessed by its lower gap.

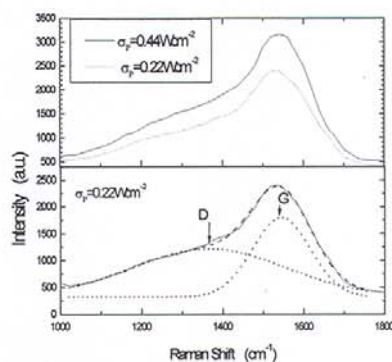


Fig. 3. Raman spectra of films deposited with $\sigma_p = 0.44 \text{ W/cm}^2$ and $\sigma_p = 0.22 \text{ W/cm}^2$. The last spectrum is fitted with two gaussians that correspond to peaks D and G [13].

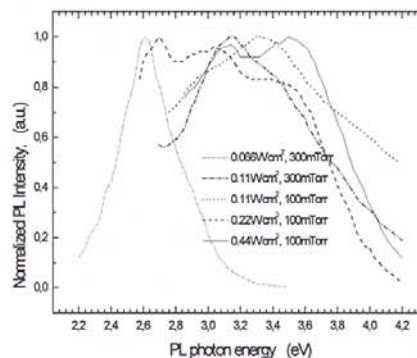


Fig. 4. PL spectra for films deposited under various conditions and excited at $E_{\text{ex}} = 5 \text{ eV}$.

This trend and the absolute values of the peak parameters are fully consistent with those reported by Tamor and Vessel for the a-C:H [13]. Taking into account the general trend of the gap in a-C:H with the sp^3 content comprehensive of both protonated and not protonated carbon [14], a roughly estimation of the sp^3 content gives 40%. The appearance of a D band as a shoulder of G peak is indicative for the presence of aromatic rings, of which the D peak is a breathe mode, but the increase of I_D/I_G with gap and the values of the peak parameters [15, 16], prevent the use of the Tuinstra and Koenig relationship to get the cluster size but poses an upper limit of $\sim 2 \text{ nm}$ to it [16].

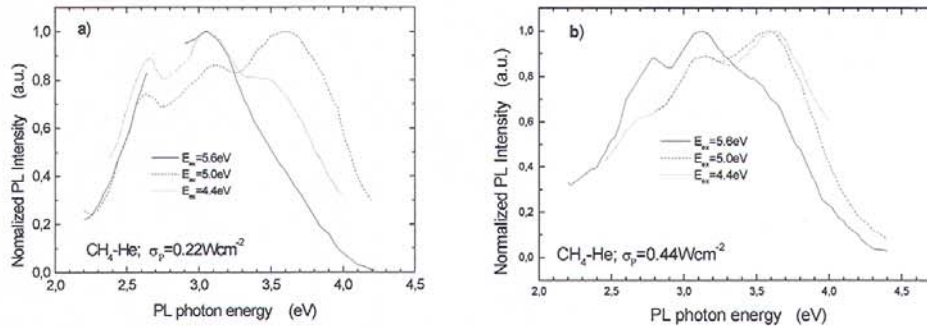


Fig. 5. Excitation energy influence on the PL spectra for samples deposited with (a) $\sigma_p = 0.22 \text{ W/cm}^2$ and (b) $\sigma_p = 0.44 \text{ W/cm}^2$.

The PL emitted from the samples and detected in the PE204 shows mainly three features located at 2.6 eV, 3.2 eV and 3.6 eV (Fig. 4). They appear at 3.2 eV and 3.6 eV in films deposited at any plasma power density except for $\sigma_p = 0.06 \text{ W/cm}^2$. For this power density there is only one peak at 2.6 eV. A feature at this energy is observed in PL spectra for all plasma power densities but is often distorted by the second order of refraction of the excitation light. The PL at 3.6 eV shows its maximum intensity at $E_{ex} = 5.0 \text{ eV}$, while, for excitation at 5.6 eV, a peak at 3.2 eV dominates the spectra. Both these behaviours are observed for $\sigma_p = 0.22 \text{ W/cm}^2$ and $\sigma_p = 0.44 \text{ W/cm}^2$. For the same plasma power densities, the excitation at 5.0 eV gives either the 3.2 eV and 3.6 eV feature rather effectively (Figs. 5a and 5b). Looking at the excitation spectra, various features are observed but all excitation spectra present a more or less pronounced shoulder at approximately 4.6 eV (Fig. 6).

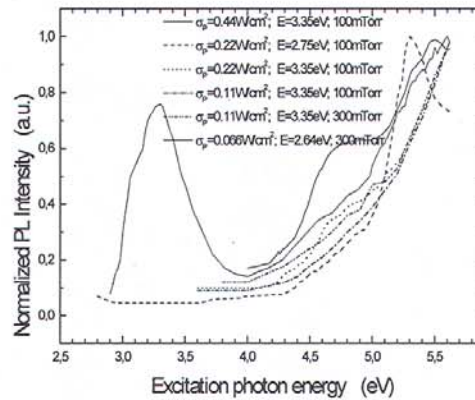


Fig. 6. Excitation spectra corresponding to emitted energies.

When the HeCd laser is used as excitation source, all samples show an edge luminescence. It appears as yellow-green in the case of silicon with oxide as substrate material and as blue-violet for a-C:H deposited on silicon without oxide. This change in colour is due to different wave-guiding properties with respect to these substrates. Surface luminescence from the a-C:H films with smooth surface is difficult to measure, if as it is the case with the films presented here, the refractive index of

the film is high and the concentration of straight centres is low [17]. From rough surfaces in turn, light is emitted and could be measured easily.

Summarising these results, the films could be classified as a hard a-C:H thin. They contain a non-negligible amount of hydrocarbon chains and show a luminescence with energies at least 1 eV above the Tauc gap. The model given by Robertson [9] or in modification by Demicheli et al. [10] generally explains this observation. The distance between gap and PL of more than 1 eV though gives rise to two questions concerning the character of the clusters considered here and the way in which they are isolated from the matrix to keep luminescent transitions up which get so deep into the band.

These luminescent centres should provide a system of three or four levels. The first transition is expected to require energy of about 4.6 eV and the transition between the second and the third states should make up energy of 2.6, 3.2 or 3.6 eV respectively.

Compared to a-Si_{1-x}C_x:H films with an internal efficiency of more than 1%, the PL of the films presented here seems rather weak. The efficiency of these a-Si_{1-x}C_x:H films should therefore been taken as an upper limit for the internal efficiency of our films. Assuming that the lifetime of the excited states is in the order of ps and the laser power of 3 mW is fully absorbed in the film, the photon flux at 3.8 eV is $4.9 \times 10^{15} \text{ s}^{-1}$ and 4.9×10^{13} luminescent centres should be found. For a film of 200 nm thickness and an illuminated area of 158 nm², this results in a concentration of $1.6 \times 10^{18} \text{ cm}^{-3}$. Given that the density of the material is 2.0 g/cm³ and neglecting the hydrogen content there are 10^{23} carbon atoms/cm³. The resulting required sensitivity for detecting luminescent centres made up of 10 atoms is therefore 10^{-4} . Taking into account that this is an estimate for the best case and the PL centre itself is very similar to the matrix it is embedded in, its identification is difficult. This low required concentration is on the other hand a good explanation for the possibility of high energy PL in a low band gap material and the absence of features of the excitation spectra in the UV-VIS absorption spectra.

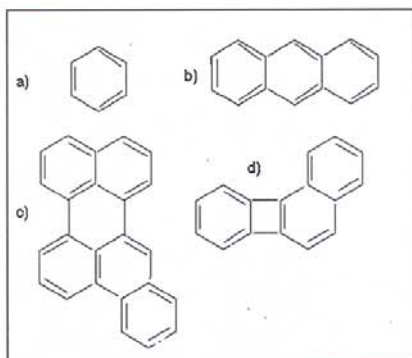


Fig. 7. Structural formula for (a) Benzene, (b) Anthracene, (c) 2,3 Benzoperylene and (d) 1,2 Benzobiphenylene.

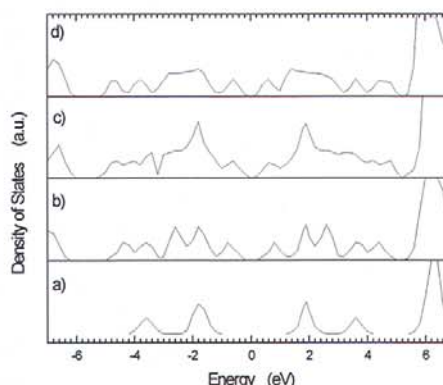


Fig. 8. Calculated density of states for (a) Benzene, (b) Anthracene, (c) 2,3 Benzoperylene and (d) 1,2 Benzobiphenylene.

In the case of films investigated here polycyclic hydrocarbons are promising candidates for being PL centres. Firstly because the formation of such stable molecules is likely in our plasma as they were found forming in the inner part of a laminar methane flame with even more than 20 rings per molecule [18]. Secondly, polycyclic hydrocarbons were found in methane hydrogen plasmas for the low-pressure deposition for diamond as well. Furthermore, some of the polycyclic hydrocarbons show absorption spectra which indicate the possibility for transitions observed in the PL measurements. Examples for such molecules are anthracene, 2,3 benzoperylene and 1,2 benzobiphenylene (Fig. 7). The calculated densities of states (Fig. 8) for these molecules support this assumption as with a larger number of rings the gap between bonding and antibonding states closes as it would with embedding them to a a-C:H matrix and shows structure that is similar to that observed in the PL spectra. Even if one takes into account that the temperature in the plasma used is much lower than it is in a methane flame it has to be considered that the activation energy is provided

by the applied plasma power. The low concentration of PL centres needed answers concerning the significantly lower pressure in the deposition plasma. The different character of these transitions explains the difference in the precise position of the PL and absorption spectra. The red-shift needed to explain the excitation shoulder around 4.6 eV has origins in the link of the respective molecules to the matrix of the a-C:H films. Finally the absence of such structures in macrocells calculated by simulating the cooling down of a "gas" of carbon atoms can – with present models and computer capabilities – take only about 100 atoms in account which combined with the needed concentration of PL centres estimated above results in a very low probability for the observation of the respective molecules in these simulation-wise structured basic cells. Additionally molecules built up in the gas phase are not taken into account using the carbon "gas". Finally the size of all the proposed groups (Fig. 7) does not exceed the restriction given by the results of Raman measurements.

4. Conclusion

In summary, a PL in a-C:H films deposited from methane was found which peaks at energies well above the band gap in all cases. It is proposed to explain this PL by the presence of the polycyclic hydrocarbons weakly bounded into the a-C:H matrix with a concentration of not more than 10^{18} cm^{-3} . Hence the Tauc gap of the film could be determined by the matrix which provides non radiative recombination paths for excited charge carriers, while the PL originates from the integrated polycyclic hydrocarbon groups.

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