

Luminescence and π electronic states in
amorphous carbon thin films

Summary of the Ph.D. Thesis

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1. Introduction

In the last two decades the study of different types of amorphous materials turned into one of the main directions of material science. Amorphous carbon has great scientific interest among the non-crystalline materials both from the viewpoint of fundamental and applied research. The main reason for this is the large diversity of the structure and properties of amorphous carbons, which gives the possibility to study a lot of scientific problems related to amorphous materials. The presence of different bonding structures (sp^3 , sp^2 and sp hybridized carbon atoms) and hydrogen in a-C:H enables to vary of properties of thin films over a wide range including polymer-like, diamond-like and graphite-like thin films as well. The quantity and the spatial ordering of the different bonding constituents have significant influence on the properties of a-C:H.

The most popular deposition method of a-C:H involves the radio frequency (rf) plasma decomposition of a hydrocarbon source gas onto negatively self biased substrate. The bias voltage (U_{sb}) - developed on the powered electrode - varies with rf power and operating pressure and depends on factors such as the electrode areas. The ion energy (characteristic parameter of films forming species) depends on the bias voltage and the ion mean free path in the sheath. At a typical operating pressures there is a spectrum of ion energies with a mean value about $E_i=0,6 U_{sb}$ for a typical pressure of 3 Pa. Low ion energy favour formation of soft, highly hydrogenated film with relatively high band gap (3-4 eV). By increasing the ion energy the quantity of the sp^3 hybridized carbon atoms start to grow, in contrast to the hydrogen-content.

In most cases the research on amorphous carbon films has practical motivation, namely tuning the properties of layers to meet special requirements. In this case it is very important to know the relation between the structure and different macroscopic properties of a-C:H films. The majority of these films behaves as semiconductor, so the mapping of electronic states near band edges

and in the band gap is indispensable. Photoluminescence method is suitable to explore these electronic states.

A-C:H films deposited at low self bias are high band gap materials with intensive, broadband photoluminescence spectra at room temperature. My Ph.D thesis examines the characteristic features of intensive room temperature luminescence observed in a-C:H films and relates them to the bonding structure of thin layers.

2. Aims

The presence of different hybridized states of carbon atom and the hydrogen in a-C:H films makes the structure of the layer very complicated, so its examination too. Photoluminescence is an appropriate technique to find how the deposition parameters influence the electronic structure, and this method could help us to find what the connection is between electronic states near band edges (π - π^* states) and the microstructure of a-C:H layers. Generally accepted model of photoluminescence is that clusters contained sp^2 hybridized carbon atoms are the luminescence centres, if they cause strong spatial localisation of electron-hole pairs which than recombine radiatively. This was confirmed by several experiments. There are a few examinations about the spatial arrangement of clusters, namely aromatic rings or olefin chains, etc. Our work with the use of the appropriate source gas was focused to prepare a-C:H thin layers from structural units which luminescent in molecular states.

Preparation of thin films from source gas such as benzene, depending on the deposition parameters, the presence of undamaged, substituted and condensed benzene rings, as well as conjugated double bonds in chain structure can be expected in the deposited films. In addition damaged molecular structural units could also form. Since these units contain sp^2 bonds, they contribute to the π - π^* electronic states near band edges, so to the photoluminescence. *Based on*

this idea I have studied the dependence of luminescence properties on deposition parameters such as self bias and have tried to correlate the characteristic features with the bonding peculiarities of sp^2 sites.

The hybridized state of carbon atom is one of the most important feature of the bonding structure of a-C:H films. The sp^3 hybridization favour the formation of three dimensional structures, which the sp^2 and sp hybridization prefer planar and linear structural arrangement respectively. It is presumable that the internal stress inside the sp^2 hybridized carbon clusters increases with increasing layer thickness and it results in some structural rearrangements. This modification of the structure influences the electronic states near band edges and the properties of the layers. Results just for very thin (<100 nm) films are known in the literature, but significant changes are not probably at this layer thickness. In my work I have addressed this problem. *Samples in wide layer thickness range I have prepared and the alteration of the photoluminescence and optical features with layer thickness I have studied experimentally.*

Due to different bonding configuration of carbon films compared to that of crystalline silicon substrate it is expected that the internal stress of the self supporting samples relaxes. The internal stress increases the probability of the non-radiative recombination; *it is interesting to compare the luminescence feature of the samples on silicon wafer with the self-supporting samples prepared in the same deposition circumstances.* Self-supporting samples because of the relation of the refractive indexes provides a possibility to examine resonance enhancement of luminescence.

3. Experimental methods

Hydrogenated amorphous carbon thin films have been prepared by radio frequency (RF) plasma enhanced (PE) chemical vapour deposition (CVD) method in the plasma reactor built by our group at the Research Institute for Solid State

Physics and Optics. The structure and properties of the a-C:H films can be varied in a wide range by changing the deposition conditions. The main parameters affecting the properties of the forming layer are the self-bias voltage and the gas pressure. In my work the a-C:H films were deposited from pure benzene at different plasma pressures (18,5 and 26,5 Pa). For the preparation a sample series at the given pressure the self-bias voltage of the working electrode was varied between -10 V and -700 V by applying different rf power.

Steady state photoluminescence was measured at room temperature and in some cases at 10 K in reflection geometry ($\sim 45^\circ$) with Hitachi model F4500 fluorescence spectrophotometer. The excitation and emission photon energy was varied in the 1,55 – 6,2 eV region.

The Raman spectra were recorded on a Renishaw 1000 B micro-Raman spectrometer by using a 785 nm diode laser as excitation source. The measurements were performed in the 1100-1750 cm^{-1} wavenumber region.

Spectral ellipsometric data obtained by a Woollam M2000F rotating compensator spectroscopic ellipsometer were analyzed in the 1-5 eV photon energy region on samples deposited onto crystalline silicon wafer.

To determine optical properties of the layers the reflection and the transmission of samples was also measured in ultraviolet, visible and near infrared regions. The transmission data were recorded by JASCO V-550 UV/VIS spectrophotometer equipment. The reflection measurements were performed by Shimadzu UV-2100 spectrophotometer with 8° angle of incidence.

4. New scientific results

The new scientific results achieved in my research work are summarized in the following Thesis:

- 1) I determined the spectral distribution of the photoluminescence on a-C:H thin films prepared from benzene in the (-20)-(-200) V self bias range. The emission band has been decomposed into component bands and by using excitation spectroscopy I have verified their presence in photoluminescence spectra. I have showed that neither the photon energy belonging to the PL centre of gravity nor the maximum position of the excitation spectrum do not scale with the band gap. On these basis I have arrived the conclusion that the PL of a-C:H films prepared from benzene shows molecule-like behaviour. Taking into account the results of Raman scattering study the possible structural origin of the PL spectral distribution is suggested [1].

- 2) I have pointed that the integral PL intensity decreases exponentially with increasing the self bias. This exponential dependence still exists if an inner parameter of the film, the absorption coefficient value taken at photon energy between the excitation and emission energy in place of the self bias. Analysing some different nonradiative recombination channels I have proved that the most probable nonradiative transition is the dissociation of an excitonic electron-hole pair mediated by the tunnelling of the electron in site (1) to an acceptor site (2) at the same energy [2].

- 3) Thickness series of a-C:H films deposited at -20, -30 and -50 V self biases I have prepared and by examination of their PL spectra I have pointed that the positions of the emission centre of gravity shifts into the lower photon energy range with increasing the film thickness. From the thickness dependence of the band gap and of the maximum of the excitation spectra I have concluded

that the maximum position of the excitation spectra did not follow the change of the band gap with increasing the layer thickness, but the energetic position of the luminescence maximum. I have affirmed experimentally that the optical transitions effective in the excitation of the luminescence radiative recombination takes place in the same sp^2 bounded cluster in a-C:H films prepared from benzene plasma [3].

- 4) I have affirmed experimentally the strong decrease of the integral luminescence intensity with the increase of film thickness. By the determination of refractive index in the 1,5-5 eV photon energy range on samples with different thicknesses, I have pointed that the optical density of the samples increases with the film thickness. Deformation of the aromatic structure followed by the development of conjugated double bounded chains with increase of film thickness I have proved by Raman scattering measurements. These structural changes could explain the increase of the optical density and of the probability of nonradiative transitions with layer thickness.

- 5) Strong modulation of luminescence intensity on the low energy side of the photoluminescence spectra of self supporting films I have observed. This modulation I have attributed to the resonance enhancement and inhibition of the photoluminescence light which reflected totally in the self supporting samples. Justification of this idea has been done with independent optical (transmission-reflection spectroscopy and spectral ellipsometry) measurements. Hence the observed modulation in the photoluminescence spectrum is the result of Fabry-Perot resonance with quality factor of $Q=35$ and line width of $\Delta\lambda=15$ nm for our best resonator [4].

5. Publications related to my Ph.D. Thesis:

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- [13] M. Veres, I. Pócsik, M. Koós, M. Füle, **S. Tóth**, A. Tóth, M. Mohai, I. Bertóti,
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