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**Photoluminescence and optical absorption at the band edges in
amorphous carbon**

Ph.D. Theses

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1. Introduction

A new and important field of material researches is the production of such materials that can be easily designed to meet the requirements of the applications. Among these materials the different type of amorphous materials are economically producible due to the lack of the long range order of the crystalline counterpart.

The first aim of the researches focusing on amorphous carbon materials was to produce films with characteristics close to that of diamond. Therefore numerous deposit procedures were developed. It turned out that within a given technology the film characteristics can be tuned in a wide range with the change of the depositing parameters. Nevertheless to produce films with expected characteristics the detailed knowledge of the structural, optical and electronic properties of the hydrogenated amorphous carbon (a-C:H) films is needed.

According to the several optical and electronic applications the researches focusing on the electronic states of the a-C:H films showing semiconducting properties become important. These states that join the delocalized states near the mobility edge are localized in a different extent due to the fluctuations in the bonding angles and lengths. From this point of view the a-C:H films are extremely important since in them the π and π^* states of the sp^2 hybridized atoms constitute the tail states and the boarding of the tail states are determined by the size distribution of the clusters formed due to the sp^2 bonding symmetry.

The band tail states influence the optical absorption near the band edge; the optical properties, the photoluminescence and the electronic transport of semiconducting thin films, therefore the investigation of these macroscopic properties offer the opportunity to deduct the properties of the localized states. The determination of the shape of the absorption edge and the optical band gap enables the determination of the concentration and energy dependence of the tail states. With the help of the luminescence spectroscopy those localized states can be investigated where the radiating recombination takes place. The main goal of the researches described in my dissertation was the determination of the optical properties and luminescence characteristics of a-C:H films prepared in different conditions and to deduct from these measurements the electron states of the band tail.

2. Literature, premises and aims

The optical absorption in a-C:H films was investigated by several research groups. These researches were done on carbon films prepared with different techniques, but the results of measurements performed on systematic film series prepared with a given technique are not or are rarely published. Regarding the fact, that the bonding and electron structure can be varied in a wide range with the change of the preparation parameter, to understand the dependences between the structural and the optical properties of a-C:H films such systematic measurements have significant importance.

The bonding structure of a-C:H films is inhomogeneous due to the sp^3 and sp^2 hybridization of the carbon atoms. For the sp^2 hybridized atoms due to the bonding symmetry the cluster formation is favored energetically which clusters are embedded into the matrix built up by the sp^3 hybridized atoms. This bonding structure results such an electron structure, in which the tail states close to the Fermi level originate from the p bonding of the sp^2 hybridized atoms while the states belonging to the s bond rest faraway from the Fermi level. The concentration, and the space distribution of the sp^2 hybridized atoms and the hydrogen content of the films determine mainly the concentration and energy dependence of the tail states. Therefore at lower photon energies the $\pi-\pi^*$ optical transition can be investigated while at higher photon energies in the UV range we have the opportunity to investigate $\sigma-\sigma^*$ transitions.

Therefore my aims during my research focusing on the optical properties were the followings:

- To determine the absorption spectrum, optical band gap and the dispersion of the refractive index of the a-C:H films with optical measurements in the 1-5 eV photon energy range. To follow the change in these properties when the deposition parameters are varied systematically. To investigate the bonding background of the observed changes with infrared absorbance and Raman spectroscopy.
- To investigate how the post heat-treatment of the samples effects the above described properties.

- To determine the concentration and broadening of the tail states from the optical absorption spectra with model fitting

The intensive room temperature luminescence of the a-C:H films is in connection with the inhomogeneous structure of them, with the clusters formed by the sp^2 hybridized atoms. This property enables the versatile applicability of the films, thus after the observation of the photo luminescence of the films an intensive research started in this field. The spectral distribution of the luminescence, the band gap and excitation photon energy dependence of the position of luminescence peak was investigated. It was established that the luminescence intensity decreases significantly with the decrease of the band gap, and in the case of the low band gap films it is under the detection limit. In order to clear up the luminescence mechanism, the excitation spectra were determined, the polarization properties of the luminescence was investigate and the effect of electric field on the luminescence intensity was studied. Furthermore the luminescence life time was detected with kinetic measurements. On the base of these measurements a luminescence model was developed, which was built on the radiative recombination of the electron-hole pairs localized in the clusters.

Due to the great full width at half maxima of the luminescence spectra emerges the question, whether the band has more components, or an other mechanism causes the broadening. In connection with this the explanations of change of the position of the emission peak with the varying of the excitation photon energy, which can be found in the literature are quite questionable. If the luminescence spectra are complex than the detailed study and understanding of the emission-excitation spectra is also essential. It is an interesting question, what the largest size of clusters can be, into which the localization of the electron-hole pair still results in radiative recombination.

Therefore the aims during my research focusing on the luminescence properties were the followings:

- The detailed study of the shape of the luminescence spectra of a-C:H film series prepared at different deposition parameters, in order to explore the complex structure of the spectra.

- The detailed study of the luminescence emission-excitation spectra and the determination of the excitability of the constituting bands.
- The calculation of localization length of the radiatively recombining electron-hole from the resonant excitation of the emission centers.

3. Sample preparation and investigation methods

The a-C:H films were prepared with the plasma enhanced chemical vapour deposition (PECVD) technique at room temperature onto crystalline silicon or quartz substrates. The substrate surface was cleaned with Ar plasma the films were deposited from plasma created in methane gas. Film series were deposited at a given pressure with the change of the bias voltage of the substrate via the change of the coupled radiofrequency power.

The optical properties were determined with spectral ellipsometry (Woollam M 2000F) and transmittance measurements. The ellipsometer works in the 1-5 eV photon energy range and the angle of incidence can be varied, which enables high precision measurements. The ellipsometric measurements were analyzed with the use of four models. From the transmittance measurements performed on different thickness samples the absorption spectra were also determined. The absorption spectra of both procedures were compared.

The luminescence properties were determined with a fluorimeter that enables the measurement of the luminescence spectra in the 200-900nm (6.19-1.37 eV) range, while the excitation can be varied in the 200-600 nm (6.19-2.06 eV) range. This gave the opportunity to study in detail the emission spectra at a given excitation, while with the change of the excitation wavelength the evolution of the spectra, the appearance of new bands could be followed.

The bonding structure of the films was analyzed with infrared absorption and Raman spectroscopy. The infrared measurements were performed with a Bruker IFS-28 Fourier transformation spectrometer, while the Raman spectra were taken at 488nm and 785nm excitation with a Renishaw 1000 Raman microscope.

4. New scientific results

1. I determined the absorption spectra of the a-C:H films prepared with PECVD from methane in the base absorption range (1-5 eV) and I investigated the influence of the bias voltage and heat treatment on to the spectra. I established that the absorption of the films broadens towards smaller photon energies and the optical band gap decreases as the bias voltage is increased. I showed that the absorption of the films is increased at a given photon energy and the optical band gap is decreased as a consequence of heat treatment. I connected these changes with the bonding structure of the films. [1]
2. I determined the distribution of the electron states near the band edge with the help of the absorption spectra and refractive index dispersions. I established that the full width at half maxima of the $\pi-\pi^*$ band increases with increasing bias voltage. This broadening decreases the energy gap between the $\pi-\pi^*$ bands and thus results in the decrease of the optical band gaps. The structural background of the change is in the change in the size distribution of the clusters containing the sp^2 hybridized atoms.
3. I established with detailed study of the photoluminescence spectra of a-C:H films prepared with PECVD from methane that the luminescence spectra is composite in the 1.5-3.5 eV photon energy range. I decomposed the composite spectra experimentally, and I established that their position and broadening does not change with the deposition parameters. I concluded from this observation that the bands can be correlated to different luminescence centers.[2]
4. With the investigation of the three dimension photoluminescence emission-excitation spectra of the a-C:H films I showed experimentally that the different luminescence emission bands can be excited from different threshold wavelength. I showed that the relative efficiency of the main emission band below 270 nm (~ 4.59 eV) is decreasing.

Furthermore I established that luminescence bands in the UV range are more intense when the films are prepared at higher bias voltage [3].

5. With the use of luminescence excitation spectroscopy I determined the excitation spectra of the component emission bands and I showed that these are characterized with two maxima. With the help of the relative efficiency curves I showed that the peak at lower photon energies has resonant properties, while the peak at higher photon energies is located above the band gap in all cases [3,4].
6. Using the resonant properties of the luminescence excitation I determined the localization length of electron-hole pairs in the clusters formed by the sp^2 hybridized atoms belonging to several emission bands [4].

5. Publications

Main publications

1. M. Koós, M. Veres, S. Tóth, **M. Füle**: Raman spectroscopy of CVD carbon thin films excited by near-infrared light, In: Carbon: the future material for advanced technology applications, Eds. G. Messina and S. Santangelo, Springer' series Topics in Applied Physics, (2005) pp 415-437
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