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Raman Scattering of Amorphous Carbons

Summary of the Ph.D. Thesis

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**Budapest
2005**

1. Introduction

In the last two decades the study of different types of amorphous materials turned into one of the main directions of materials 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. Due to its excellent mechanical properties – hardness and friction, similar to those of diamond – the diamond-like amorphous carbons find wide usage as protective coatings for surfaces of highly employed devices.

Besides the concentration of sp^3 , sp^2 and sp hybridized carbon atoms, the properties of amorphous carbon films strongly depend on their arrangement too. Structural investigations showed that the sp^2 and sp^3 hybridized carbon atoms distributed inhomogeneously in the structure of the films. The clustering is energetically favourable for the sp^2 hybridized carbon atoms by creating bonds between themselves. The optical and electronic properties of the layers are determined by the bonding configuration and the size of the clusters. So the atomic bonding configuration and the intermediate range ordering of the sp^2 hybridized carbon atoms is of great importance from the viewpoint of structural determination of the amorphous carbons.

The Raman spectroscopy proved to be particularly useful for structural investigations of different forms of amorphous carbons, because it allows determining both the bonding configuration and the intermediate range ordering of the layers. Numerous experimental results proved that the structural units in the sp^2 clusters (aromatic condensed rings, other ring-like structures and olefinic chains), as well as the cluster size can be determined from the parameters of the D and G bands of spectrum.

Additional information on the structural ordering can be evaluated from the half-width and intensity ratio of the two bands.

There are several reasons for the wide use of Raman spectroscopy as characterization method for amorphous carbons. This non-destructive tool is of high sensitivity the measurement and the evaluation of the data can be easily automated. Due to this properties the Raman spectroscopy became one of the most important method for quality control of hard disk manufacturing. The quality of the protective diamond-like amorphous carbon layer of the disk surface controlled by a Raman spectrometer installed on the production line.

Considerable results have been achieved in the Raman spectroscopy of amorphous carbons concerning the determination of bonding configuration. However there are still open questions in this field. The Raman scattering of amorphous carbons excited by visible light interpreted exclusively on the decomposition of the spectra to D and G bands. In contrary to this additional bands were observed in the D and G band region of the spectra of several amorphous carbon samples. The investigations aimed to explain the origin of these extra bands gave controversial results. Thus the additional peaks were ignored during the evaluation of the Raman spectra. Only a few experiments were performed to study the dispersion the Raman bands with excitation in the visible and ultraviolet wavelength region. However the analysis of the limited Raman spectroscopic data, obtained by infrared excitation proves the presence of additional composite bands besides the D and G peaks in the Raman spectra. This implies that the infrared excited Raman spectra of amorphous carbons provide more information on the structure compared to visible excited ones.

2. Aims

My work was focused on the systematic study of infrared excited Raman scattering of hydrogenated amorphous carbon (a-C:H) films prepared by different deposition parameters in order to identify new composite bands in the Raman spectra, to assign these peaks to specific structural arrangements and to characterize the variation of this structural arrangement with the sample deposition circumstances. From the comparative study of infrared excited Raman spectra of nano-clusters and thin films prepared simultaneously it was aimed to relate their structure on the atomic bonding scale and to conclude for the film formation process. The objective of the Raman scattering study of diamond-like amorphous carbon thin films and a-C:H layers containing silicon, as well as silicon and oxygen was to determine how these foreign atoms incorporate into the amorphous carbon structure and which type of bonding configurations they prefer.

3. Experimental methods

Hydrogenated amorphous carbon thin films were deposited prepared by radio frequency (2.54 MHz) chemical vapour deposition 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 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, plasma pressure and the type of the source hydrocarbon material which we have used. The a-C:H films were deposited from methane and benzene at different plasma pressures in the range of 8 Pa and 50 Pa. In the case of a given pressure the self-bias voltage of the working electrode was varied between -10 V and -700 V by varying the applied radio frequency power.

The Raman spectra were recorded on a Renishaw 1000 micro-Raman spectrometer at excitations of a 488 nm line of an Ar ion laser or by using a 785 nm diode laser as excitation source. The beam diameter on the sample surface was 1 micron.

The infrared transmittance spectra were measured on a Bruker IFS-28 Fourier-transform infrared spectrometer attached to a microscope. The spectrum of Si substrate was used as background, which was recorded before each of measurement series.

4. New scientific results

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

1. By measuring the Raman scattering excited at 488 nm and 785 nm of the amorphous carbon thin films prepared from benzene at low ($|U_{SB}| < 200$ V) self-bias voltages I have proved experimentally the unusual behaviour of the Raman D band in these samples. This anomaly of D band I have explained with localization of the bonding π electrons of sp^2 hybridized carbon atoms [5].
2. Comparing the 488 nm excited Raman spectra of amorphous carbon layers prepared from benzene and methane I have showed that in the sample series prepared at $|U_{SB}| < 300$ V self-bias voltages the peak called generally as G Raman band behaves differently with decrease of self-bias voltage. The different behaviour was explained by different structural origin of the G band in the two sample series [1,5].
3. Recording the Raman spectra with 488 nm and 785 nm excitation of amorphous carbon thin films prepared from benzene and methane in wide range of self-bias voltages I have showed that the wide band in the $1500-1600\text{ cm}^{-1}$ wavenumber region, which called G band in the literature is composite. One of the two components of the band exhibits dispersion with increase of the excitation wavelength, while the position of the other remains unchanged. The component peak showing no dispersion was assigned to scattering contribution of chains and rings of sp^2 hybridized carbon atoms having small delocalization length of π electronic states [5].

4. From the 785 nm excited Raman spectra of nano-clusters formed in benzene plasma I have proved that these clusters contain intact benzene rings in their structure even at self-bias voltage of -200 V. By measuring the 785 nm excited Raman spectra of the amorphous carbon films prepared simultaneously with nano-cluster formation I have concluded that the structure of the nano-clusters changed significantly when they are incorporated into thin layers, the benzene rings are broken and the structural disordering increases [2,3].
5. Raman scattering spectra of silicon containing diamond-like amorphous carbon thin films measured by 488 nm and 785 nm excitation verify that the silicon substitutes partially the carbon atoms in the sp^2 clusters and promotes also the formation of condensed aromatic rings containing no silicon. Analyzing the Raman spectra of films containing both silicon and oxygen I have proved that the oxygen incorporated into the structure prefers the formation of condensed aromatic rings too [4].

5. Publications related to my Ph.D. Thesis

- [1] M. Veres, M. Koós and I. Pócsik, *IR Study of the Formation Process of Hydrogenated Amorphous Carbon Film*, *Diamond and Related Materials* **11** (2002) 1110.
- [2] I. Pócsik, M. Veres, M. Füle, S. Tóth, M. Koós, J. Kokavecz, Z. Tóth and G. Radnóczy, *Carbon Nano-Particles Prepared by Ion-clustering in Plasma*, *Vacuum* **71** (2003) 171.
- [3] M. Veres, M. Füle, S. Tóth, M. Koós, I. Pócsik, J. Kokavecz, Z. Tóth and G. Radnóczy, *Simultaneous preparation of amorphous solid carbon films, and their cluster building blocks*, *Journal of Non-Crystalline Solids* (accepted for publication, available on-line) (2005).

- [4] M. Veres, M. Koós, S. Tóth, M. Füle, I. Pócsik, A. Tóth, M. Mohai, I. Bertóti, *Characterization of a-C:H and oxygen-containing Si:C:H films by Raman spectroscopy and XPS*, *Diamond and Related Materials* (accepted for publication, available on-line) (2005).
- [5] M. Veres, S. Tóth, M. Füle, M. Koós, *Systematic study of hydrogenated amorphous carbon films by Raman spectroscopy excited in the infrared region*, (in preparation).

6. Additional publications

- [6] M. Koós, M. Füle, M. Veres, S. Tóth and I. Pócsik, *Composite Character of the Photoluminescence in Hydrogenated Amorphous Carbon Films*, *Journal of Non-Crystalline Solids* **299-302** (2002) 852.
- [7] M. Koós, M. Veres, M. Füle and I. Pócsik, *Ultraviolet photoluminescence and its relation to atomic bonding properties of hydrogenated amorphous carbon*, *Diamond and Related Materials* **11** (2002) 53.
- [8] L. Nánai, M. Füle, K. Bali, M. Veres, M. Koós and I. Pócsik, *Optical Strength in UV Region of Amorphous Carbon*, *Diamond and Related Materials* **11** (2002) 1106.
- [9] M. Koós, M. Füle, M. Veres, S. Tóth and I. Pócsik, *Multi – Band Structure of Amorphous Carbon Luminescence*, *Diamond and Related Materials* **11** (2002) 1115.
- [10] S. Tóth, A.P. Caricato, M. Füle, M. Veres, M. Koós and I. Pócsik, *Electronic structure of pulsed laser deposited carbon thin films monitored by photoluminescence*, *Diamond and Related Materials* **12** (2003) 911.
- [11] Pócsik, M. Veres, M. Füle, S. Tóth, M. Koós, *Specific Statistical Features of Surface Enhanced Raman Scattering (SERS) Spectra of Graphite*, *Journal of Non-Crystalline Solids* **338-340** (2004) 496.

- [12] M. Veres, M. Füle, S. Tóth, M. Koós, I. Pócsik, *Surface enhanced Raman scattering (SERS) investigation of amorphous carbon*, *Diamond and Related Materials* **13** (2004) 1412.
- [13] S. Tóth, M. Füle, M. Veres, M. Koós, I. Pócsik, J.R. Selmán and D. Arcon, *Influence of amorphous carbon nano-clusters on the capacity of carbon black electrodes*, *Thin Solid Films* (accepted for publication)
- [14] S. Tóth, M. Füle, M. Veres, M. Koós, I. Pócsik, A. Tóth, T. Ujvári, I. Bertóti, *Photoluminescence of ultra-high molecular weight polyethylene modified by fast atom bombardment*, *Thin Solid Films* (accepted for publication)
- [15] M. Veres, I. Pócsik, M. Koós, M. Füle, S. Tóth, A. Tóth, M. Mohai, I. Bertóti, *Raman scattering of ultra-high molecular weight polyethylene treated by plasma immersion ion implantation*, *Thin Solid Films* (accepted for publication)

