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Raman spectra of carbon thin films

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In this paper we report the results of Raman spectroscopy investigation on diamond like carbon (DLC) films obtained by Thermionic Vacuum Arc (TVA) deposition. The TVA technology is suitable for producing nanostructured materials because of the high power density of the vapor plasma generated by accelerated electron flux from the cathode and high energy of the ions incident on the depositing film, both these properties ensuring a high dispersion of the evaporated material. At condensation, the size of the generated structures is in the range of nanometers. From the Raman spectra we can notice that there were two peaks, one at 1379 cm^{-1} and the other at 1558,69 cm^{-1} which brought us to the conclusion that we have obtained DLC films (the spectra are typical for sp^2 structure – D and G bands characteristic for such structure).

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1. Introduction

The Raman spectrum of carbon films offers valuable information about the atomic bonds and level structure of the molecule. Especially in the nanostructured carbon thin films range Raman spectra has a great importance for define the structure of this kind of films. For example, magnetic disks for information storage are protected with a thin layer of semi-ordered (diamond-like) carbon film. The most common method of testing the integrity of these films is to simulate the disk drive's start-up/shut-down procedure many times over the course of 2-4 days and determine the degree of wear. Raman spectroscopy gives much faster, non-destructive analysis.

A great interest of many scientists is focused on a special form of carbon's structure, namely diamond like carbon (DLC), due its widespread applications as protective coatings in areas such optical windows, magnetic storage disks , car parts, biomedical coatings and as microelectromechanical devices (MEMS).

DLC is a metastable form of amorphous carbon containing a signification fraction of sp^3 bonds.[1]. The sp^3 bonding confers on DLC many of the properties on diamond itself, like mechanical hardness, chemichal and electrochemical inertness and wide band gap, but it is much cheaper to produce than diamond itself. For this reason, there are a wide range of deposition methods to obtain DLCs. From 1971, when J. Aisenberg and R. Chabot have been reported the first DLCs film prepared using ion beam deposition [2], more than ten methods have been used to obtain DLCs, both for laboratory studies or industrial production. For example mass selected ion beam , PECVD were used for laboratory work, and on the other side for industrial applications were used sputtering and cathodic vacuum arc. All these methods have some very valuable advantages, but also some limits [3-9].

In this paper, we have reported some aspects regarding the Raman spectroscopy investigations on DLC thin films prepared by other method like the usuals, Thermionic Vacuum Arc [10,11]. Some of the advantages of this method are: deposition of pure metal film in high or ultra - high vacuum conditions (less than 10^{-5} torr); no gas consumption or gas incorporation in the growing film; the growing thin film is bombarded just during deposition with the ions of the depositing material insuring the compactness of the film; the energy of bombarding ions can be controlled and can be even changed during deposition; the deposition rate can be easily controlled and can be greater than in the sputtering case (0.1 – 2 nm/s).

2. Experimental

Thermionic Vacuum Arc (TVA) is a method suitable for deposition of high purity thin films with compact structure and extremely smooth, just convenient for nanostructure film preparation.

TVA is an externally heated cathode arc, which can be established, in high vacuum conditions, in vapors of the anode material [4]. Thermionic Vacuum Arc is ignited between a heated cathode surrounded by an electron-focusing Wehnelt cylinder and an anode (tungsten crucible) containing the material to be deposited. Due to the electron bombardment of the anode by the accelerated thermo-electrons from the grounded cathode towards the anode (which is at high voltage), the anode material first melts and afterwards starts to evaporate. In this way a steady state concentration of the evaporated atoms is ensure in the cathode-anode space. At further increase of the applied high voltage, a bright discharge in the vapors of the anode material is established inside of the vacuumated vessel.

In the case of deposition of carbon thin film the anode is even a rod of carbon (Fig. 1).

For carbon film deposition using TVA technology the main used working parameters are: the applied d.c. high voltage 1300 V in a working pressure of 10^{-6} torr, the intensity of arc current being of 1.25 A. The cathode filament was made by thoriated tungsten wire with 1.5 mm diameter, three times wound and heated by a current of 100 A. During the arc running and C thin film deposition, the anode was continuously rotating with 6 rotation/minute, and also the cathode-anode distance was adjusted each time when the arc current was decreasing more than 10%.

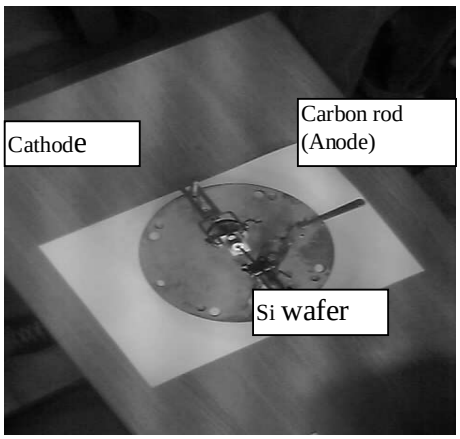

Fig. 1. Foto of the electrodes arrangement before the ignition of arc.

The time of deposition was maintained about 300s, at a distance between electrodes of 164 mm (Fig. 2). The substrate was Si wafer with of 20 mm × 15 mm dimensions and the deposition rate was 2 Å/s.

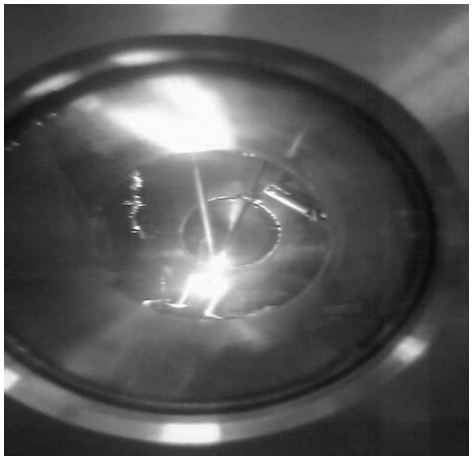

Fig. 2. Image of the discharge inside of the vacuum vessel.

Raman measurements were performed at room temperature with a "JOBIN YVON/SPEC/DILOR" device. Raman spectrometer is supplied by He-Ne laser at 632.817 nm wavelength. Objective 100x was used. We used the LabRam system which is a fully integrated package designed to perform the measurements. The LabRam has a completely stigmatic spectrograph with two interchangeable gratings for variable spectral resolution. The 1800g/mm grating provides a spectral resolution of ~2.5cm^{-1} in 3 pixels using the standard HeNe laser. The second grating (600 g/mm) can be chosen for a wide Raman spectroscopic overview in one scan or for recording fluorescence spectra over a broad wavelength range. Each grating is rotated using the motorized computer controlled drive. The sample was placed on a stage driven with stepper motors capable of 0.5um movement in the X and Y directions. The light beam of HeNe laser for sample excitation can be focused to a diameter of 1 μm spot.

3. Results and discussion

The key property of DLC is its sp^3 bonding. The deposition process which promotes sp^3 bonding is a physical process, namely ion bombardement. In the TVA technology, the energy of ions can be fully controlled during deposition, and if it is considered that the highest sp^3 fractions are formed by C^+ ions with ion energy around 100 eV, in the TVA method the ion energy can reach even higher energy.

Let us consider the intensity/frequency spectra presented in the Fig. 3.

In this figure the frequency is plotted relative to the laser frequency, so the frequency scale represents the Raman shift. The peaks in the intensity occur at the frequencies of the Raman active modes. The DLC films show common features in their Raman spectra in the 800 -2000 cm^{-1} region, the so called G and D peaks, which lie at 1558.69 cm^{-1} and at 1380 cm^{-1} respectively, for visible excitation and the T-peak at approximately 1060 cm^{-1} which is visible only with UV excitation. The G peak is due to the bond stretching of all pears of sp^2 atoms in both rings and chains. The D peak is due to the breathing modes of sp^2 atoms in rings. The T peak is due to the C-C sp^3 vibrations.

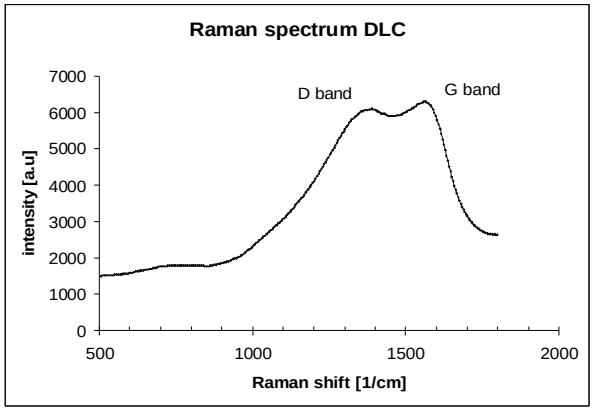

Fig. 3. Raman spectra for DLC on Si wafer with TVA method.

From the Raman spectra we can notice that there were two peaks, one at 1379 cm^{-1} and the other at 1558,69 cm^{-1} which brought us to the conclusion that we have obtained DLC films (the spectra are typical for sp^2 structure – D and G bands characteristic for such structure).

4. Conclusions

We investigated different carbon thin films deposited by Thermionic Vacuum Arc technology, used in different conditions of operation. Raman spectroscopy has been used successfully to monitor the carbon thin film. The obtained two peaks, D peak at 1379 cm^{-1} and G peak at 1558.69 cm^{-1} highlight an important observation that it is possible to obtain DLC film with a very high purity. The next step in our investigation will be to study the mechanical properties of these DLC films.

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