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Optimization of radio frequency inductively coupled plasma enhanced chemical vapour deposition process of diamond-like carbon films

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The diamond-like carbon materials have unique mechanical, optical, electrical and chemical properties. The material is commonly applied in automotive industry, medicine and in other everyday life products. However, the diamond-like carbons are not used in micro- and optoelectronics on a wider scale due to technological problems. The application of the diamond-like carbon films in electronic structure is limited because the standard methods do not ensure that the quality and properties of the deposited film will be satisfactory for a specific application. On the other hand, more sophisticated methods that allow manufacturing the diamond-like carbon film with adequate properties, such as microwave assisted chemical vapour deposition, require heating of the substrate to high temperature (above 1000°C). The solution to the problem is the radio frequency inductively coupled plasma enhanced chemical vapour deposition method that allows deposition of the diamond-like carbon films with satisfactory properties and the process can be carried out at room temperature. In the paper, basic information and issues concerning the diamond-like carbon films manufacturing technology by radio frequency inductively coupled plasma enhanced chemical vapour deposition method will be explained. The diamond-like carbon films were investigated by the Raman scattering spectroscopy and the spectroscopic ellipsometry.

Keywords: diamond-like carbon, radio frequency inductively coupled plasma enhanced chemical vapour deposition (RF ICP PECVD), Raman scattering spectroscopy, spectroscopic ellipsometry.

1. Introduction

The diamond-like carbon (DLC) films are metastable form of amorphous carbon, which contains fractions of sp^3 and sp^2 bonds. The sp^3 bonding configuration is typical for diamond, while the sp^2 bonding configuration occurs in graphite or graphene. In the case of the DLC films, the bonding configuration has a significant influence on the properties of the films and is meant as the relationship between the fractions of sp^3 and sp^2 bonds.

In the literature, the DLC films are generally classified on the basis of the sp^3 fraction content. The sp^3 bonds confer on the DLC many beneficial properties of the diamond and so the higher is the sp^3 fraction content in the DLC film bonding configuration, the properties of the film are more similar to the properties of diamond. The DLC films with low sp^3 fraction content (around 30–50%) are classified as amorphous carbon films (a-C). Films with high sp^3 fraction content (above 70%) are defined as tetrahedral carbon films (ta-C) and the films have properties comparable to diamond [1]. The important influence on the properties of the DLC has also the hydrogen content in the film. The DLC material with hydrogen content exceeding a few percent is described as hydrogenated (*e.g.*, a-C:H).

The diamond-like carbon films have found application in many fields of technique, medicine and even everyday life products. For example, DLC films are applied in automotive industry or in medicine as protection coatings due to their exceptionally good tribological and mechanical properties. Engine parts, prosthesis elements and medical tools covered by DLC coating can work or be used for much longer period of time comparing to uncoated products [2–4].

The quality (the sp^3 fraction content) and properties of the DLC film depend on the deposition method applied for manufacturing of the film. Most commonly, for manufacturing of the DLC on the industrial scale production, are applied the plasma enhanced chemical vapour deposition (PECVD) and magnetron sputtering (MS) methods. The PECVD and MS methods allow deposition of a-C films with satisfactory mechanical properties, but the quality of the film is not good enough to meet the demands of semiconductor industry.

The DLC films for micro- and optoelectronics applications should have high resistivity, heat conductivity and specified values of optical parameters (*e.g.*, refractive index, transmission coefficient). The microwave assisted chemical vapour deposition (MWCVD) method allows fabrication of DLC and diamond films that fulfill the requirements. However, the high temperature of the substrate (exceeding 1000°C) during the growth of the film creates many technological problems. Fabrication of the micro- and optoelectronic structures requires that the following technological steps are carried out in lower temperature than the preceding ones. Therefore, the application of the DLC films grown by the MWCVD method is limited.

The DLC films are not widely applied in micro- and optoelectronics due to the above mentioned technological problems. The problems have been solved by modification and development of the PECVD method. The radio frequency inductively coupled plasma enhanced chemical vapour deposition (RF ICP PECVD) allows deposition of DLC films with high sp^3 content, good electrical and optical properties. Moreover, the method does not have the disadvantages of the MWCVD method. The DLC films deposited by RF ICP PECVD can be grown at the room temperature, providing technological versatility in the design of microelectronic structures.

It is expected that in the near future, the DLC films will be commonly applied in the photovoltaic cells (antireflective coatings, photonic crystals), laser and light emitting diodes (heat dissipation layer) and other electronic structures (passivation layer) [5, 6]. However, the RF ICP PECVD method is more complex than the standard PECVD method. In order to apply the DLC films in micro- and optoelectronics with satisfactory results, it is necessary to investigate and optimize the deposition process of the DLC films by the RF ICP PECVD method.

2. Experimental method

The deposition processes of the DLC films by the RF ICP PECVD method are processes with multiple parameters. Therefore, the deposited DLC films could have different properties depending on the values of process parameters and the properties of the film could be also modified after the deposition process (*e.g.*, heat or plasma treatment). The DLC films applied in a micro- or optoelectronic structure must have specified properties and parameters, for example, the value of the refractive index should be matched to the value of the refractive index of the base material of the optoelectronic structure.

The aim of the research was to investigate the correlation between the deposition process parameters and the properties of the deposited DLC films. The results presented in the paper and during the presentation continue the previous research on DLC films deposition technology [7, 8].

In the current research, an experiment was designed in order to investigate the relationship between the deposition process parameters and the properties of the DLC films. The investigated DLC films were deposited from the methane (CH_4) used as the gaseous precursor. The films were deposited in the Plasmalab System 100 manufactured by Oxford Instruments company. The films were deposited on *p*-type polished silicon substrates (111). The DLC was deposited on a square silicon substrate (10 mm×10 mm) that was inserted on the top of the 2″ silicon “transport plate”.

The programmed experiment was based on the $L_9 3^4$ orthogonal matrix. As the input parameters of the matrix, the following parameters were selected: the RF generator (13.56 MHz) power value P_{RF}, the ICP generator (13.56 MHz) power value P_{ICP}, substrate temperature T and total pressure in the working chamber p. The values of the parameters were selected in the range of values that ensure the stability of the plasma discharge. The flow rate of CH_4 was constant in each deposition process and set on 100 sccm.

According to the plan of the experiment, for each set of process parameters values, four DLC films were manufactured. The deposition processes were sequentially carried out for 3, 5, 7 and 10 minutes, making a group of four samples for an experimental run.

3. Results

The quality of the deposited DLC films was measured by the Raman scattering spectroscopy while the samples were being excited by two different wavelengths of the excitation laser (Fig. 1). In the presented research, the spectra were acquired during excitation of the samples by the Ar^{2+} laser (514.5 nm) and the He-Cd laser (325 nm).

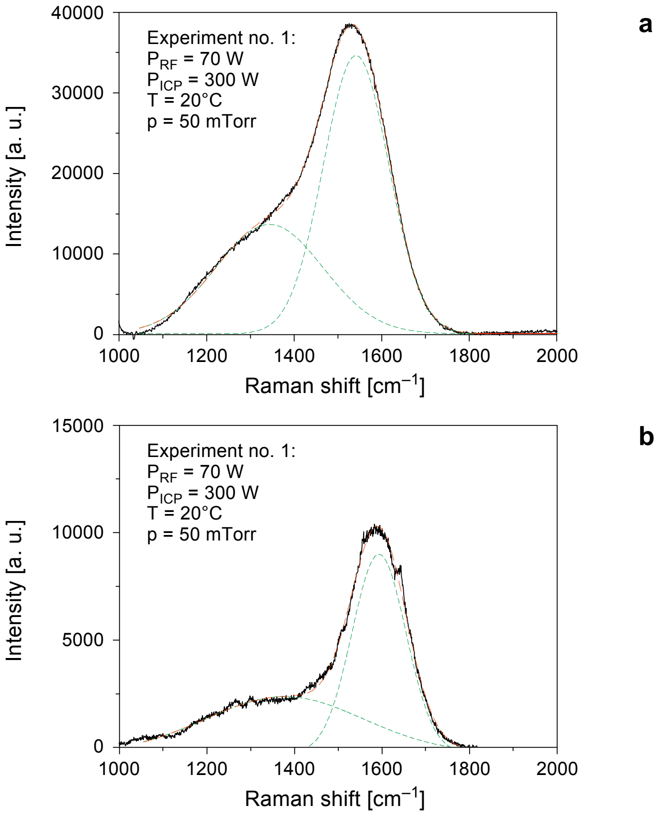

Fig. 1. Raman scattering spectra of the deposited DLC film in the experimental run no. 1 for different wavelengths of the excitation radiation: 514.5 nm (**a**), and 325 nm (**b**).

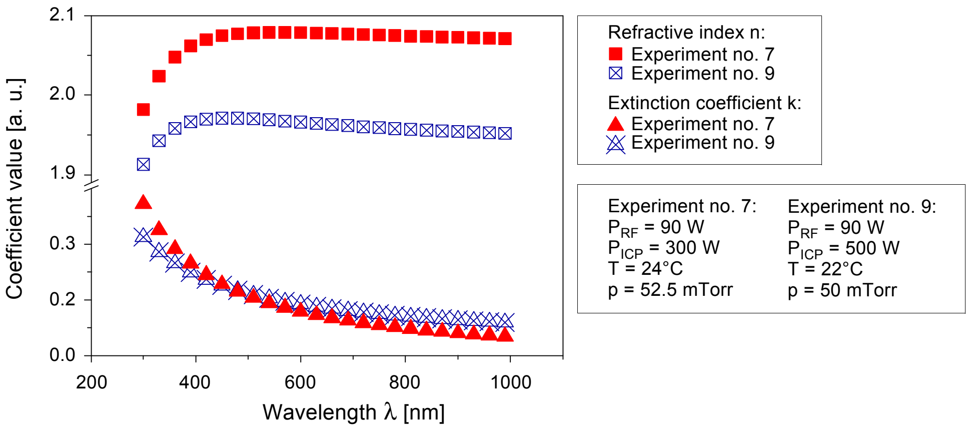

Fig. 2. Comparison of the spectral characteristics of the refractive index and the extinction coefficient values of the DLC films deposited in the experiments nos. 7 and 9.

In the work, the sp^3 fraction content was estimated from the relationship between the intensities of the *D* and *G* peaks (I_D/I_G) and from the dispersion of the *G* peak position. The sp^3 fraction content of the deposited films was ranging from around 60% to 66%. The results acquired from two mentioned methods are similar and convergent.

The ellipsometric spectra were calculated for the wavelengths ranging from 300 to 1000 nm with resolution of 10 nm. The spectroscopic ellipsometry measurements were performed by the V-VASE ellipsometer with a HS-190 scanning monochromator manufactured by J.A. Woollam Company and a rotating analyzer.

From the analysis of the measured data it follows that the refractive index of the DLC films was ranging from 1.968 to 2.053 and the extinction coefficient from 0.18438 to 0.20121, depending on the parameters values of the deposition process. Additionally, the thicknesses of the deposited films were measured. The acquired results showed that the deposition rate of the DLC film was changing from 5.23 to 13.74 nm/min.

The measured spectra of DLC films with the lowest and the highest value of refractive index are presented in Fig. 2.

4. Conclusions

The acquired data from the measurements were analyzed by the elements of the Taguchi method. The results of the research are presented in detail in our previous papers [9, 10] and are comparable with results presented in the literature [11].

The study showed that the properties of the deposited DLC film can be modified and controlled by the deposition process parameters. This possibility is important in order to use the DLC films in specific micro- and optoelectronic applications such as passivation layers or antireflective coating. The highest achieved sp^3 fraction content of the deposited DLC film was around 70% and is adequate for potential applications of DLC such as heat dissipation layer in quantum cascade laser.

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