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Characterization of sp^3 bond content of carbon films deposited by high power gas injection magnetron sputtering method by UV and VIS Raman spectroscopy

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ABSTRACT

This paper presents the results of investigations of carbon films deposited by a modified version of the magnetron sputtering method – HiPGIMS (High Power Gas Injection Magnetron Sputtering). In this experiment, the magnetron system with inversely polarized electrodes (sputtered cathode at ground potential and positively biased, spatially separated anode) was used. This arrangement allowed us to conduct the experiment using voltages ranging from 1 to 2 kV and a power supply system equipped with 25/50 μF capacitor battery. Carbon films were investigated by VIS/UV Raman spectroscopy. Sp^3/sp^2 bonding ratio was evaluated basing the elementary components of registered spectra. Our investigation showed that sp^3 bond content increases with discharge power but up to specific value only. In extreme conditions of generating plasma impulses, we detected a reversed relation of the sp^3/sp^2 ratio. In our opinion, a energy of plasma pulse favors nucleation of a sp^3 phase because of a relatively higher ionization state but in extreme cases the influence of energy is reversed.

1. Introduction

Diamond – like carbon (DLC) coatings exhibit some of typical properties of diamond, i.e. high hardness, wear and corrosion resistance, low friction, wide bandgap, etc. [1–3] so the coatings are considered in a wide range of applications: biomedical [4,5], optical [6,7], anti-wear [8, 9], anticorrosive [10,11], etc. They are a metastable form of amorphous carbon with a significant content of sp^3. bonding. DLC films are synthesized by Chemical Vapor Deposition (CVD) as well as Physical Vapor Deposition (PVD) methods, for example: Ion Deposition [12,13], Sputtering [14,15], Cathodic Arc [16,17], Pulsed Laser Deposition [18, 19], radio frequency Plasma Enhanced CVD [20,21], Impulse Plasma Deposition [22]. All these methods have their own limitations and reach different values of sp^3./sp^2. ratio. Since this ratio is crucial in the properties of films [23], there is still a strong interest from the research community to develop novel modifications of commonly used methods. Recently, the High Power Magnetron Sputtering (HiPIMS) method was reported as an alternative for DLC synthesis [24–28]. These papers report that an sp^3 bond content up to 80% may be reached by the HiPIMS method. Encouraged by the literature, we tested the efficiency of our own modification of the Magnetron Sputtering (MS) method in the synthesis of DLC coatings. This modification was established by us as Gas Injection Magnetron Sputtering (GIMS) [29,30]. The idea was to use a pulse action of a gas valve to reduce the process pressure, therefore increasing the energy of plasma particles by preserving their energy from dissipation by inelastic collisions with molecules of inert gas during the process of synthesis. In our recently reported experiment, which concerned deposition of TiO_2 coatings by GIMS and Pulsed MS (PMS) methods, we proved that the GIMS method favors nucleation of the metastable phase of rutile, while PMS favors – anatase [31]. We considered this result as significant, because the rutile phase, so far, was observed after the processes utilizing an additional source of energy i.e. biasing [32] or using a high power supply [33]. At the stage of planning the current experiment we expected that using the pulse manner of valve operation might be as beneficial as in the case of TiO_2 coatings. Additionally, we decided to use a high power source of plasma excitation based on a capacitor battery, charged by an HV power supply. Our purpose was to combine the advantages of generating high power plasma impulses and preserving plasma particle momentum. In our opinion, these conditions were favorable to obtain an amorphous film with significant content of sp^3. The other scientific goal of this experiment was to determine the changes in the sp^3 phase content with the power of plasma impulses. Since Raman spectroscopy is known as a powerful tool for the investigation of carbon – based materials [23] we considered it useful here. Single crystal graphite shows a Raman active band E_{2g}, labeled as G (Graphite), at ~1580 cm^{-1}. G mode is assigned to stretching vibration of sp^2 sites. With the graphite amorphization, an extra mode

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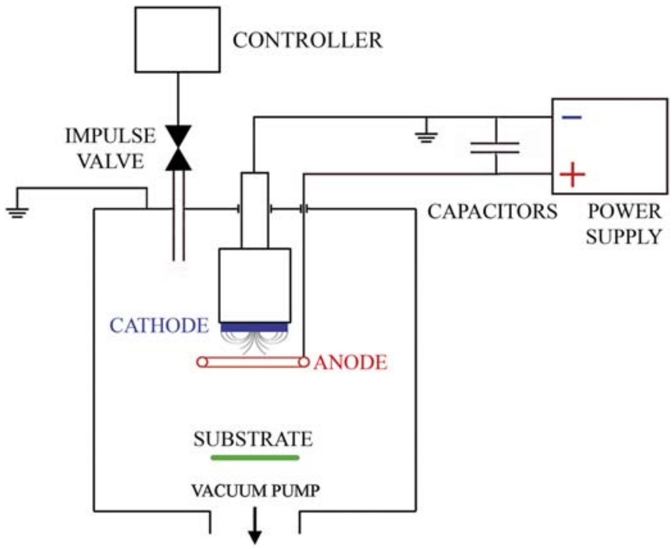

Fig. 1. Diagram of apparatus used in the experiment.

A_{1g} appears at ~1350 cm^{-1}, known as D peak (Disorder). D peak is attributed to breathing modes of sp^2 sites in rings. According to the Ferrari diagram of 3 – stage carbon amorphization [34], the sp^3 bonding is expected, when in – plane correlation length L_s is below 2 nm [35]. A proper determination of the characteristics of G and D peaks (positions, intensity and FWHM) from the DLC Raman spectra is reported as the method of evaluation the sp^3 bond content.

2. Experiment

2.1. Apparatus

In the Fig. 1 the diagram of the experimental setup is presented. The deposition chamber consisted of a 40 cm diameter quartz tube, connected at the bottom to vacuum pump system and closed by a stainless - steel lid at the top. The circular magnetron was mounted through the lid and oriented downward. $B_{Z0,}$ the point of the magnetic system, was located at 27 mm under the target, so, according to the Gencoa criterion [36], the magnetron was very unbalanced (target diameter – 50 mm). The whole construction of the magnetron (including its target) was electrically connected with the grounded lid. The sputtering of an electrically grounded surface is possible because of plasma localization at the locally applied magnetic field [37,38]. An anode made from a copper tube in the form of a 7 cm ring, was installed through the lid by an insulating feedthrough and distanced at 3 cm from the magnetron target. Also the working gas supply was installed through the lid. This unusual electrode arrangement (grounded cathode and positively biased anode) was proposed by us in our latest work. It presents the advantages of using this arrangement for TiO_2 coating deposition by the MS method. We observed the tendency of nucleation of a rutile phase in the structure of coatings [39]. This is why we decided to use a reversely biased magnetron system in the current experiment. We expected a higher efficiency in the formation of a metastable form of carbon film. As a source of carbon species a 50 mm diameter target made of pure graphite was used. As a source of electric energy an HV DC power supply

Table 1
Process parameters of coating deposition.

Voltage [kV]	1	1.2	1.4	2	
Capacitance [μF]	25			25	50
Frequency [Hz]	0.5				
Deposition time [s]	1000				

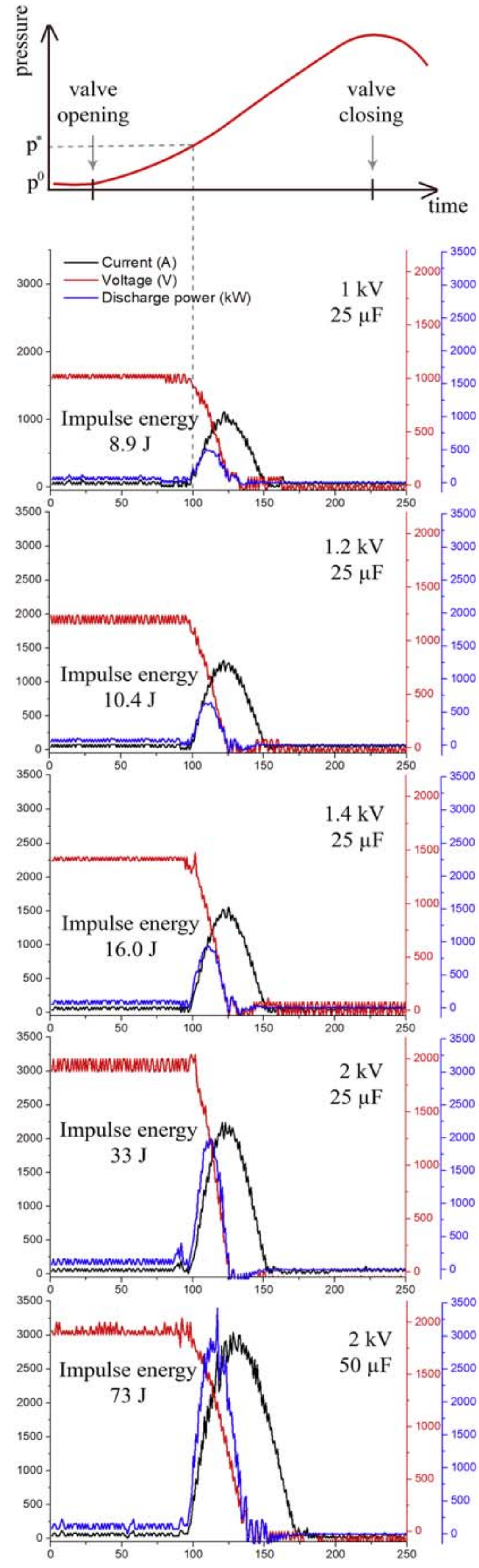

Fig. 2. Current, voltage and power waveforms registered for various parameters of discharges.