Journal
of Achievements in Materials
and Manufacturing Engineering

VOLUME 37
ISSUE 2
December
2009

DLC layers prepared by the PVD magnetron sputtering technique

K.T. Wojciechowski [a,*], R. Zybala [a], R. Mania [a], J. Morgiel [b]
[a] AGH University of Science and Technology, Faculty of Materials Science
and Ceramics, Department of Inorganic Chemistry,
Al. Mickiewicza 30, 30-059 Kraków, Poland
[b] Institute of Metallurgy and Materials Science of Polish Academy of Sciences,
ul. Reymonta 25, 30-059 Kraków, Poland
* Corresponding author: E-mail address: wojciech@uci.agh.edu.pl

Received 14.09.2009; published in revised form 01.12.2009

Manufacturing and processing

ABSTRACT

Purpose: The aim of the present paper was to elaborate deposition conditions of the DLC films prepared by magnetron sputtering technique.

Design/methodology/approach: DLC layers were fabricated by the reactive pulsed magnetron sputtering method in the mixture of Ar and methane (CH_4). The gas pressure during sputtering process ranged from 0.3 to 0.7 Pa. The DLC layers were deposited on selected thermoelectric, ceramic and metallic substrates. Microstructure of obtained DLC layers were characterised by TEM and SEM microscopy. Raman spectroscopy was also used to characterise the different forms of carbon in the films.

Findings: Structural investigations showed amorphous character of the produced layers and the lack of presence of nano-crystalline diamond phase both in layers obtained at 35 °C and in higher temperatures. Raman spectroscopy studies confirmed the dominant share of sp2 hybridization in the C - C and the presence of C – H bonds. Obtained layers are characterized by high electrical resistivity.

Practical implications: Microstructure and high resistivity of DLC layers, prepared by magnetron technique, give prospective of their applications e.g. in microelectronics.

Originality/value: Microstructure and high resistivity of DLC layers, prepared by magnetron technique, give perspectives for their applications e.g. in microelectronics.

Keywords: DLC; Raman spectroscopy; Magnetron sputtering

Reference to this paper should be given in the following way:
K.T. Wojciechowski, R. Zybala, R. Mania, J. Morgiel, DLC layers prepared by the PVD magnetron sputtering technique, Journal of Achievements in Materials and Manufacturing Engineering 37/2 (2009) 726-729.

1. Introduction

The plasma assisted deposition of different carbon layers such as the diamond-like-carbon (DLC) [1, 2] polycrystalline diamond [3] or nano-crystalline [4, 5] diamond arouse a lot of interest since the end of the last century. The DLC layers interest in electronic industry guaranteed continuous dielectric hard coating of good thermal conductivity. On the other hand, the high bio-compatibility of carbon resulted in attempts to apply the DLC coatings on the parts of artificial heart [6, 7]. These two examples of faraway applications confirm the important place of these types of coatings.

Most of the past research effort in this area was centered on elaboration of the best deposition conditions for a range of deposition techniques and specific deposition systems, from the point of view of process efficiency represented by the deposition rate. Presently, the interest is shifted toward better control of the structure of the deposited material, what is especially problematic in case of DLC layers. The high hardness of such layers complicates preparation of specimens for the transmission electron microscopy limiting direct observations of their microstructure, while establishing of the nature of the bonding requires as sophisticated techniques as the Raman spectroscopy. Therefore, the correlation between deposition conditions and coating microstructure and functional properties is far from being fully understood.

The aim of the present paper was to elaborate deposition condition of the DLC films using magnetron sputtering technique which allows to prepare layers of good mechanical properties [8-11]. The film microstructure and its character were controlled by transmission electron microscopy observations and Raman spectroscopy, respectively.

2. Experiments

The deposition of the DLC films was performed using magnetron system including TEPRO NP-501A vacuum chamber, SP 2000 vacuum pump and the WMK 50 magnetron gun supplied from DORA Power Supply (DPS) unit. The DPS generates pulses of constant amplitude and negative polarization of 160 kHz modulated with 2.5 kHz frequency. The power transmitted into the plasma is controlled by number of current pulses per time unit. Such arrangement called Pulsed Magnetron Sputtering (PMS) allows maximizing the effective power transmitted directly to the target, what has influence on the efficiency of the sputtering process. The experiments were performed at one of two power supply regimes, i.e. low and high effective power of 70 W /0.15 A and 140 W/0.2 A respectively.

The magnetron target of 5 cm diameter was made of graphite foil. The deposition process was conducted under the flow of a mixture of Ar and methane (CH_4) gases controlled by MKS mass flow meters. The best deposition conditions were elaborated for 1:4 parts of argon to methane respectively, maintaining resulting total pressure between 0.5 to 0.7 Pa. The special ceramic hot plate was used to keep the samples temperature at 35, 200, 300, 400 and 500 ^{o}C at consecutive deposition runs. The temperature was measured by thermocouple attached directly to the sample holder. The average deposition rate, obtained in the above system and under specified conditions was ~3nm/min. The thickness of mostly deposited coatings was about 300 nm. The DLC layers were deposited on various types of substrates such as glass, alumina, Si single-crystals, ZrO_2, molybdenum, $CoSb_3$ thermoelectric material and other materials. The other deposition conditions were described in more details elsewhere [6, 7].

The morphology and microstructure of the deposited layers were characterized using scanning JEOL 5400 (SEM) and transmission TECNAI Super Twin FEG (TEM) electron microscopes. The thin foils were cut from the DLC film (in cross-section) using Focused Ion Beam (FIB) Quanta 3D apparatus.

The electrical impedance characteristic of the DLC film was measured with ZEHNER IM 5d system in 0.1-2.0 MHz frequency range.

3. Results

The SEM observations of the DLC layers deposited on glass substrates show that they have flat smooth surface and uniform microstructure (Fig. 1.). The TEM investigations confirmed that the DLC film local roughness remain below one nanometre.

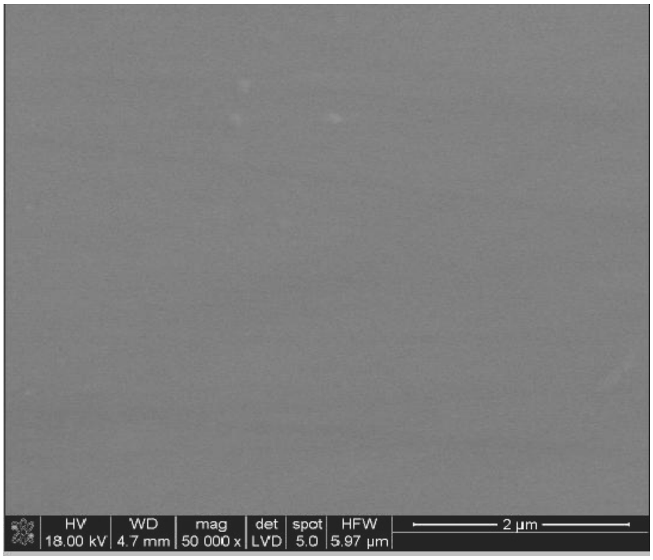

Fig. 1. SEM image of DLC coating deposited at 200 ºC on glass substrate

The observations performed using bright field (BF) technique and electron diffraction in selected area (SA) mode (Fig. 2, 3.) indicated that the layers exhibit amorphous microstructure.

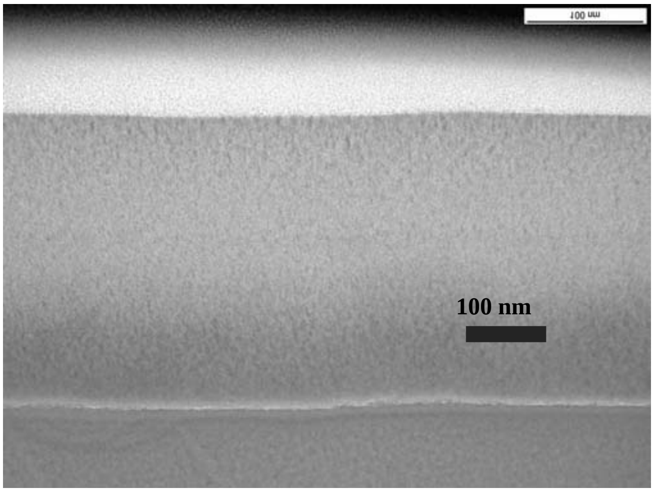

Fig. 2. TEM BF image of DLC coating deposited at 35 ºC on glass substrate

The high resolution electron microscopy (HREM) observations confirmed the random arrangements of atoms in these coatings (Fig.4).

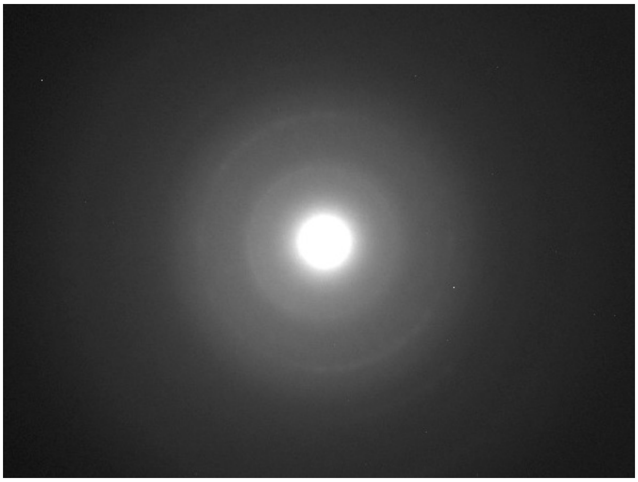

Fig. 3. Electron diffraction of thin DLC film

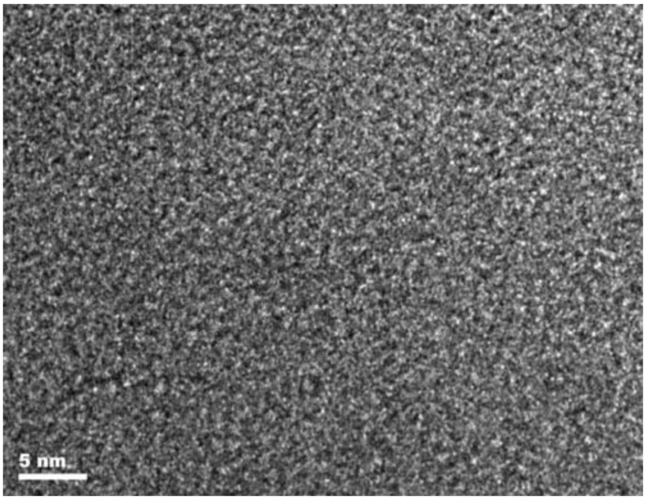

Fig. 4. HREM image of DLC coating deposited at 35 ºC on glass substrate

The Fast Fourier Transformation (FFT) obtained for the whole area reveals only two diffused rings of higher intensity (Fig.5) corresponding to that obtained in electron diffraction pattern. These results exclude presence of any crystallites in DLC films (Fig. 3.).

Raman spectra were obtained with Nicolet Almega high resolution Raman micro-spectrometer at 532 nm wavelength of the laser beam. At this wavelength the scattering cross-section for sp^2 bonds is much stronger (twice the order) than for sp^3 bonds. The diffraction grating was used for the scattered beam energy analysis and the intensity was registered with sensitive CCD detector. The magnification of the lens was 100 times. The spatial resolution was 1µm, the spectral resolution was about 5 cm^{-1}.

Raman spectroscopy measurements of the DLC coatings obtained at 400 and 500 ^{o}C show similar in character, a group of bands grouped in two zones (Fig. 6.). The first zone located between 1200 and 1700 cm^{-1} contains a peak with median value close to 1330 cm^{-1}, and the next located at ~1600 cm^{-1}. According to [12-15] in this area typical bands for C - C bonds can be expected denoted as a G – Graphite in the range of 1500 to 1580 cm^{-1} and the D (Disordered Graphite in the range of 1345 to 1360cm^{-1} . The bands in the second zone, especially those located from 2000 do 3600cm^{-1} should be ascribed to presence of C – H bonds. A sharp peak at 520 cm-1 arose from silica bed at which the coatings were placed.

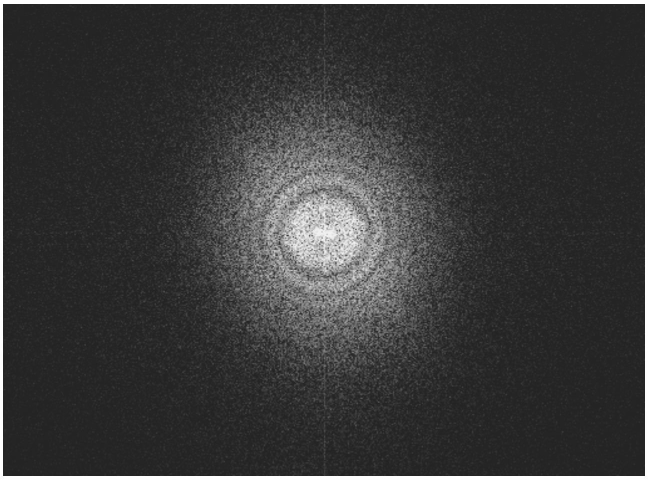

Fig. 5. FFT of HREM image presented in fig.4

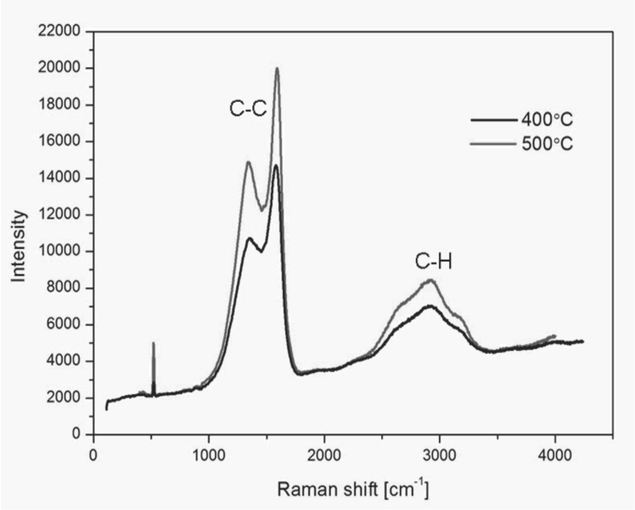

Fig. 6. Raman spectra for DLC coatings deposited at 400 and 500 ºC

The lower intensity of the bands located at 1330 cm^{-1} and 1600 cm^{-1} recorded at 400 ^{o}C, as compared with those recorded at 500 ^{o}C means that the rise in temperature increases. The lack of bands usually connected with carboxyl type bonds indicates either very low level of oxygen contaminants during the deposition or reducing processes at the surface caused by hydrogen form cracked methane particles. The impedance spectroscopy measurements of the investigated DLC films showed the resistivity about 5 GΩm what indicated on their dielectric nature.

The presented results have to be considered as preliminary and cannot be the basis for the final conclusions regarding sputtering process and DLC coatings structure.

4. Conclusions

The conditions for DLC layer were developed for reactive magnetron sputtering technique. Raman spectroscopy studies confirmed the dominant share of sp^2 hybridization in the C - C and the presence of C – H bonds. Obtained layers are characterised by high electrical resistivity. Research by the HR TEM electron microscopy showed amorphous character of the produced layers and the lack of presence of nano-crystalline diamond phase both in layers obtained at 35 °C and in higher temperatures. The TEM investigations confirmed that the DLC film roughness remained below one nanometre. The SEM research on the obtained DLC surface layers shows a homogeneous surface.

Microstructure and high resistivity of DLC layers, prepared by magnetron technique, give perspectives for their applications e.g. in microelectronics.

Acknowledgements

The study was financed as a research project (project No PL0089-SGE-00104-E-V2-EEA, 2007-2010).

References

[1] M. Sokołowski, A. Sokołowska, B. Gokieli, A. Michalski, A. Rusek, Z. Romanowski, Reactive pulse plasma crystallization of diamond like carbon, Journal of Crystal Growth 47 (1979) 421-427.

[2] J. Marciniak, Z. Paszenda, W. Walke, M. Basiaga, J. Smolik, DLC coatings on martensitic steel used for surgical instruments, Archives in Materials and Manufacturing Engineering 28 (2007) 285-288.

[3] R. Mania, L. Stobierski, R. Pampuch, Diamond Synthesis in Cool Plasma, Crystal Research and Technology 16 (1981) 785-788.

[4] S. Mitura, Nanodiam, PWN Warsaw, 2006

[5] S. Mitura, K. Mitura, P. Niedzielski, P. Louda, V. Danilenko, Nanocrystalline diamond, its synthesis, properties and applications, Journal of Achievements in Materials and Manufacturing Engineering 26 (2006) 9-16.

[6] R. Mania, D. Obłąkowska, S. Błażewicz, Carbon coatings for Cardio surgery-preliminary results, Engineering of Biomaterials 4 (2001) 42-44.

[7] J. Grabarczyk, D. Batory, P. Louda, P. Couvrat, I. Kotela, K. Bakowicz-Mitura, Carbon coatings for medical implants, Journal of Achievements in Materials and Manufacturing Engineering 20 (2007) 106-110.

[8] A.A. Ogwu, T.H. Darma, E. Bouquerel, Electrical resistivity of copper oxide thin films prepared by reactive magnetron sputtering, Journal of Achievements in Materials and Manufacturing Engineering 24 (2007) 172-177.

[9] A. Śliwa, L.A. Dobrzański, W. Kwaśny, W. Sitek, The computer simulation of internal stresses on the PVD coatings, Archives of Computational Materials Science and Surface Engineering 1 (2009) 183-188.

[10] W. Ziaja, Finite element modelling of the fracture behaviour of surface treated Ti-6Al-4V alloy, Archives of Computational Materials Science and Surface Engineering 1 (2009) 53-60.

[11] M. Polok-Rubiniec, L.A. Dobrzański, M. Adamiak Comparison of the PVD coatings Archives of Materials Science and Engineering (38) 2009 118-125.

[12] S.M. Huang, Z. Sun, Y.F. Lu, M.H. Hong, Ultraviolet and visible Raman spectroscopy characterization of diamond-like carbon growth by pulsed laser deposition, Applied Physics A 74 (2002) 519-523.

[13] A.C. Ferrari, J. Robertson, Raman mode in nanocrystalline diamond, Physical Review B 63 (2001) 121405-1-4.

[14] Y.M. Yanez-Limon, F. Ruiz, J. Gonzalez-Hernandez, C. Vazquez-Lopez, E. Lopez-Cruz, Characterization of carbon films microstructure by atomic force microscopy and Raman spectroscopy, Journal of Applied Physics 76 (1994) 3443-3447.

[15] B. Marcus, L. Eayette, M. Mermoux, L. Abello, G. Lucazeau, Analysis of the structure of multi-component carbon films by resonant Raman scattering, Journal of Applied Physics 76 (1994) 3463-3470.