

IN SITU XPS CHARACTERIZATION OF DIAMOND FILMS AFTER Ar⁺ CLUSTER ION BEAM SPUTTERING

ARTEMENKO Anna, BABCHENKO Oleg, KOZAK Halyna, UKRAINTSEV Egor, IZAK Tibor,
ROMANYUK Oleksander, POTOCKY Stepan, KROMKA Alexander

*Institute of Physics, Academy of Sciences of the Czech Republic, Prague, Czech Republic, EU,
artemenko@fzu.cz*

Abstract

Diamond films are attractive materials for electronics, optics and medical applications. For these applications diamond film quality and controllable surface composition are often crucial parameters. In this work, in situ XPS analysis of chemical composition of H- and O-terminated nano- and microcrystalline diamond (NCD and MCD) films before and after their sputtering by the Ar⁺ cluster ion beam was investigated. Scanning electron microscopy confirmed sputtering of all diamond surfaces with a rate about 0.5 ± 0.2 nm / min. Raman spectroscopy and XPS revealed surface graphitization of diamond surface (transformation of sp³ carbon phase to sp²) induced by sputtering. Moreover, XPS data showed the presence of about 0.7 % of Ar atoms on the investigated diamond surface after 66 min of sputtering. Also, oxygen residuals (0.2 at. %) were still presented on the H-NCD surface after 66 min of sputtering. In contrast, no oxygen was found on the H-MCD surface just after 2 min of sputtering (in the depth about 1.5 nm). Surface composition is discussed in respect to the diamond films growth parameters and surface structure.

Keywords: Diamond, depth profiling, XPS, sputtering, Raman

1. INTRODUCTION

Extraordinary properties of diamond films attracted a great attention of the researches due to their possible applications in medicine, optics and microelectronics. For these applications, distribution of dopants in diamond films is crucial for fabrication of functional devices. Despite of a large number of reports [1-3], there is still not enough information about depth profiling of diamond films and their resistance to the irradiation or ion bombardment. There are numerous techniques for diamond depth profiling such as elastic recoil detection analysis (ERDA) [1, 2] or non-Rutherford backscattering spectrometry (NRBS) [2]. The most commonly used depth profiling methods is the secondary ion mass spectrometry (SIMS) which gives information about qualitative elemental composition of diamond films by sputtering of their surfaces [3]. In particular, SIMS is commonly used for obtaining the concentration profiles of dopant layers inside the diamond film. However, SIMS has few disadvantages such as a low accuracy for rough surfaces or low surface sensitivity [3]. On the other hand, XPS provides a better surface sensitivity due to a limited inelastic mean free path of photoelectrons [4]. In particular, for a standard X-ray source AlK α with photon energy of 1486 eV, photoelectrons come from the depth of a few nanometers. If deeper layers have to be investigated, higher photon energy or sputtering of the near surface layers is required.

The Ar⁺ cluster ion beam can be used for a lateral surface sputtering [5, 6]. For low beam energies, the sample surface damage caused by clusters is smaller than in a case of the monoatomic beam sputtering. Moreover, surface structure of the near surface layer is better conserved. The sputtering rate can be varied gently by choosing Ar⁺ cluster size and the ion beam energy. Therefore, in combination with XPS, this method is well-suitable for the depth profiling and chemical composition analysis of the near surface layers and interfaces [7]. In particular to the diamond films, XPS analysis provides information about the atomic composition on a surface. Moreover, components of C 1s peak give information about type of carbon bonds (diamond vs. graphite).

Diamond morphology and surface terminations have to be tailored for specific diamond uses [8]. In addition, appropriate functionalization has to be also applied for electrochemical [9] and biological [10] experiments.

In the present study, in situ XPS analysis of H- and O-terminated NCD and MCD films before and after their sputtering with Ar⁺ cluster ion beam was carried out. Influence of ion beam sputtering on a chemical composition and surface morphology of diamond films is discussed.

2. EXPERIMENTAL

2.1. CVD diamond growth

Prior to the deposition procedure, the Si substrates were seeded by procedure previously published in [9]. Diamond films with nanocrystalline (NCD) and microcrystalline (MCD) morphology were grown. The NCD films were grown in modified linear antenna microwave plasma system (AK 400, Roth&Rau) [11] from a gas mixture of H₂ : CH₄ : CO₂ (100 : 5 : 30 in sccm). The other parameters were as follows: total pressure 10 Pa, substrate temperature 500 °C, microwave power 1700 W, and deposition time 20 hours. Finally, the surface of diamond films was hydrogenated in hydrogen-rich plasma for 30 min. All other process parameters were kept constant.

Oxygen termination of diamond films was done by radio frequency (rf) plasma system (Femto, Diener) in 100 % O₂ atmosphere at pressure 110 Pa, rf power 100 W for 4 min.

The MCD films were grown in focused microwave reactor with an ellipsoidal cavity resonator (AIXTRON P6, Germany) [12] at low methane concentration (1 % CH₄ in H₂), total gas pressure 3000 Pa and microwave power of 1.5 kW for 7.5 hours. The substrate temperature was about 500 °C. Hydrogen termination of the as-grown MCD films was performed at 500° C for 10 min in H₂ plasma. The oxygen termination of the MCD samples was carried out similarly as described above.

2.2. Characterization of diamond films

The grain size and surface morphology of diamond films before and after sputtering were investigated by scanning electron microscopy (SEM, e_LINE writer, Raith GmbH). The thickness of the diamond films was measured from cross-sections SEM images. The surface topography of the diamond films was measured by atomic force microscopy (AFM) in the tapping mode on ICON AFM (Bruker). Medium frequency Multi75Al cantilevers (Budget sensors) with spring constant $k = 3 \text{ N / m}$ treated in CF₄ rf plasma (CF₄ pressure 100 mTorr, rf plasma power 50 W, process duration 30 sec) were used. The surface root mean square (RMS) roughness was calculated from $1 \times 1 \mu\text{m}^2$ scans.

Chemical composition of the diamond surfaces was analyzed by X-ray photoelectron spectroscopy (XPS) using XPS spectrometer (Kratos, AXIS Supra) equipped with a hemispherical analyzer and a monochromatic AlK α X-ray source (1486.6 eV). The XPS spectra were acquired from the area of $700 \times 300 \mu\text{m}^2$ with the take-off angle 90°. The survey XPS spectra were recorded with the pass energy of 80 eV, whereas the high resolution spectrum scans with pass energy of 20 eV. The CasaXPS software with implemented linear baseline and Gaussian line shapes of variable widths for peak fitting was used for spectra processing. XPS peak positions were determined with an accuracy of 0.2 eV. The obtained survey XPS spectra were calibrated on C 1s peak with binding energy of 285.1 eV that corresponds to sp³ phase [13]. The C 1s XPS spectra were deconvoluted into four peaks [9]: sp² carbon phase (284.2 eV), sp³ carbon phase (285.1 eV), C-O bonds (286.1 eV) and C=O bonds (287.6 eV).

The diamond films were additionally studied by Raman spectrometer (Renishaw InVia Reflex) using the excitation wavelength of 442 nm.

2.3. Ar⁺ cluster ion beam sputtering

In situ sputtering of diamond films was carried out by Ar⁺ cluster ion source (GCIS, Kratos) in XPS analytical chamber. Cluster size with 500 Ar atoms and energy of 20 keV was used for sputtering. The incidence angle

of ion beam to the sample surface was set to 40°. The size of sputtered area was 1.8 × 1.8 mm². The sputtering time was varied from 2 to 66 min. XPS measurements were carried out before and after each sputtering cycle without exposing the samples to air.

3. RESULTS AND DISCUSSION

The initial thickness of NCD and MCD films was ~ 370 nm and ~ 250 nm, respectively. They consisted of grains in size up to 50 nm for NCD and 200 nm for MCD films. **Fig. 1** shows surface morphologies of NCD and MCD films before and after Ar⁺ ion beam cluster sputtering. For all samples, the grain size was decreased significantly after ion beam, i.e. initially well faceted crystals changed to feature-less (or polished like) character. Such a polishing effect was confirmed by AFM measurements: the diamond surface roughness decreased by ~ 3 nm after 66 min of sputtering time (i.e. the RMS decreased from 11 to 8 nm for NCD and from 30 to 27 nm for MCD films, respectively). The calculated average sputtering rate was 0.5 ± 0.2 nm / min.

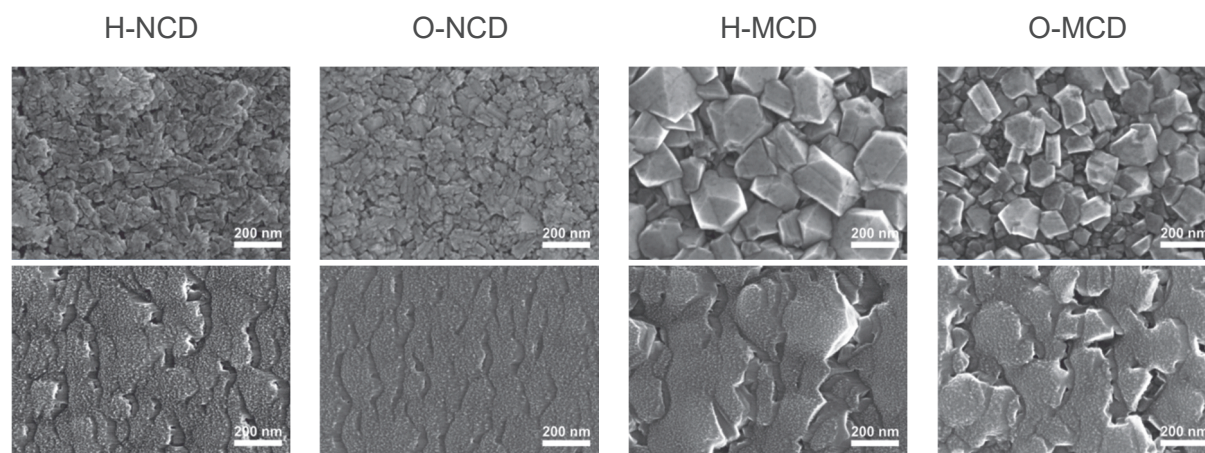


Fig. 1 SEM images of diamond films before (top row) and after (bottom row) Ar⁺ ion beam cluster sputtering for 66 min

Fig. 2 shows the C 1s XPS spectra of diamond films before (i.e. 0 min sputtering time) and after Ar⁺ ion beam cluster sputtering (for 2, 21 and 66 min). XPS spectra confirmed transformation of sp³ into sp² carbon phase after Ar⁺ ion beam cluster sputtering, i.e. the graphitization of diamond. Similar effect has also been observed by other authors [7, 14].

For 2 min Ar⁺ ion beam cluster sputtering of NCD films, the graphitization rate depends on the surface termination (**Figs. 2a and 2b** - blue lines), as evaluated from the ratio of sp³ and sp² carbon peak intensities. For longer sputtering time, a monotonous increase (decrease) of the sp² (sp³) carbon peak intensity was observed for both NCD and MCD films (**Fig. 2**). This trend is independent on the diamond surface termination. Faster graphitization process is observed for NCD films than for MCD films. Moreover, XPS measurements revealed the presence of Ar atoms at sputtered surfaces (0.7 at. %).

Normalized Raman spectra of H-terminated NCD and MCD films before and after sputtering are shown in **Fig. 3**. There are three characteristic peaks (or bands): (i) the sharp diamond-peak at 1332 cm⁻¹ corresponding to sp³ carbon bonds, (ii) the D-band (defect-band) at 1350 cm⁻¹ and (iii) the broad G-band (graphite-band characteristic for sp² carbon bonds) at ~ 1520 ÷ 1640 cm⁻¹ [15]. Comparing the Raman spectra of NCD and MCD films before sputtering, it is evident that for MCD films the D- and G-bands are less detectable. However, after sputtering of MCD, the G-band increased due to graphitization of the larger diamond crystals characteristic for MCD film (i.e. increase of sp² carbon phase). This effect was also confirmed by XPS. For NCD film, the change in the Raman spectra before and after sputtering is negligible due to structure and morphology of the film (i.e. higher content of sp² carbon bonds, smaller grain sizes). The Raman spectra of O-

terminated diamond films showed the same behaviors as for H-terminated diamond due low sensitivity of Raman spectroscopy to surface terminations.

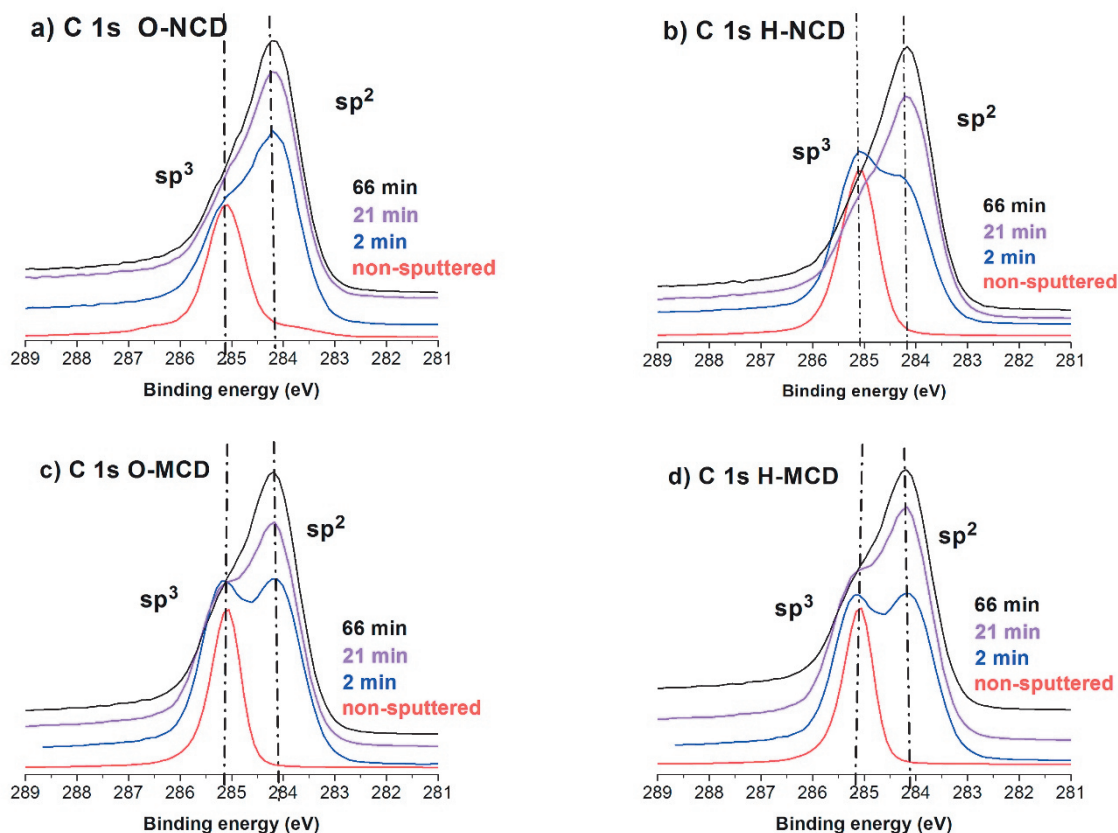


Fig. 2 The C 1s XPS peaks of a) O-NCD, b) H-NCD, c) O-MCD, d) H-MCD films before and after Ar⁺ ion beam cluster sputtering for different times

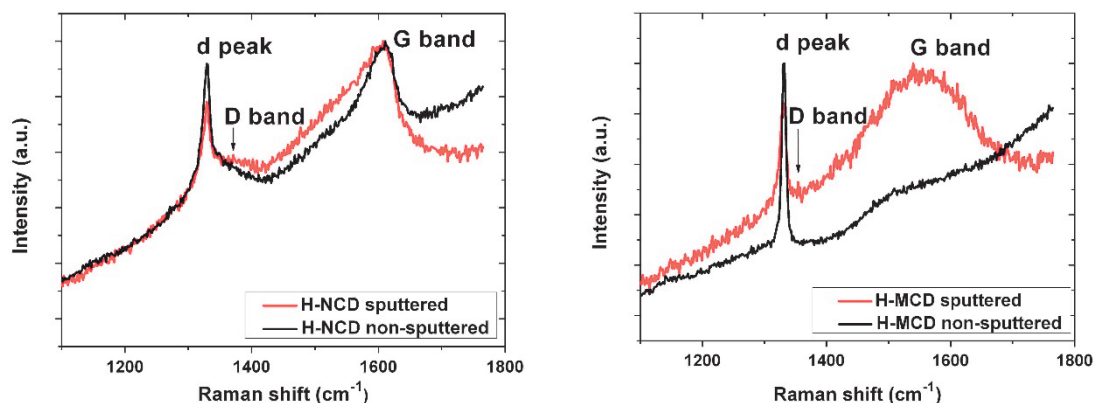


Fig. 3 Normalized Raman spectra of H-terminated NCD and MCD films before and after Ar⁺ ion beam cluster sputtering for 66 min

Table 1 summarizes atomic concentrations of oxygen in diamond films before and after 66 min of Ar⁺ ion beam cluster sputtering, as determined by XPS. Oxygen atoms were completely removed from the H-MCD surface after 2 min of sputtering. On the other hand, 0.2 at. % of oxygen was presented on H-NCD films even after 66 min of sputtering. This effect can be explained by sample preparation conditions: the oxygen containing gas mixture (i.e. CO₂ : CH₄ : H₂) was used in deposition process. We suppose that during the CVD growth some

amount of oxygen might be incorporated into diamond film probably at the grain boundaries. For sputtered O-terminated diamond films, the detected oxygen content should originate from the primary oxidized valleys. In these areas, Ar⁺ sputtering is hindered (shadowed) by surface roughness (i.e. the sputtered depth is comparable with diamond peak-to-valley Z-height).

Table 1 The concentration of oxygen in diamond films before and after sputtering estimated from XPS survey spectra

Sample name	Oxygen [at. %]	
	non-sputtered	sputtered (66 min)
H-NCD	2	0.2
H-MCD	1	0
O-NCD	11	0.5
O-MCD	10	0.3

4. CONCLUSION

H- and O-terminated nano- and micro-crystalline diamond films were investigated by in situ XPS, Raman spectroscopy, AFM and SEM. Depth profiling was carried out by Ar⁺ cluster ion beam with sputtering rate of 0.5 ± 0.2 nm / min. After each sputtering cycle, diamond films were measured by XPS. It was observed that the Ar⁺ cluster ion beam sputtering results in diamond polishing and graphitization. The polishing was independent on the film surface termination or morphology. The graphitization was influenced by the surface termination for NCD films sputtered for 2 min. The MCD films graphitized slower than the NCD films. Ex situ Raman measurements confirmed the diamond surface graphitization and supported XPS results. The depth profiling of diamond films revealed the presence of oxygen traces after 66 min of sputtering. Obtained results demonstrate a great potential of Ar⁺ cluster ion beam sputtering tool in combination with XPS for depth profiling and chemical composition analysis of carbon-based materials.

ACKNOWLEDGEMENTS

We would like to acknowledge Karel Hruska for SEM measurements. This work was supported by the projects 15-01687S (GACR) and SVV-267305-2013.

REFERENCES

- [1] KIMURA K., NAKAJIMA K. Hydrogen depth-profiling in chemical-vapor-deposited diamond films by high-resolution elastic recoil detection. Applied Physics Letters, Vol. 78, No. 12, 2001, pp.1679-1681.
- [2] GARRATT E., ALFAIFY S., CASSIDY D. P., DISSANAYAKE A., MANCINI D. C., GHANTASALA M. K., KAYANI A. Depth profiling of nitrogen within ¹⁵N-incorporated nano-crystalline diamond thin films. Applied Physics Letters, Vol. 103, 2013, pp. 131602-5.
- [3] OTHMAN M. Z., MAY P. W., FOX N. A., HEARD P. J. Incorporation of lithium and nitrogen into CVD diamond thin films. Diamond & Related Materials, Vol. 44, 2014, pp. 1-7.
- [4] ZANGWILL A. Physics at Surfaces, University Press, Cambridge, 1988.
- [5] SEKI T., MATSUO J., TAKAOKA G. H., YAMADA I. Generation of the large current cluster ion beam. Nuclear Instruments and Methods in Physics Research No. B 206, 2003, pp. 902-906.
- [6] YOSHIDA A., DEGUCHI M., KITABATAKE M., HIRAO T., MATSUO J., TOYODA N., YAMADA I. Atomic level smoothing of CVD diamond films by gas cluster ion beam etching. Nuclear Instruments and Methods in physics Research B, Vol. 112, 1996, pp. 248-251.
- [7] WILSON J.I.B., WALTONA J.S., BEAMSON G. Analysis of chemical vapour deposited diamond films by X-ray photoelectron spectroscopy. Journal of Electron Spectroscopy and Related Phenomena, Vol. 121, 2001, pp. 183-201.

- [8] BABCHENKO O., REZEK B., STUHLÍK J., KROMKA A., ARNAULT J. Ch., BERGONZO P. Surface Treatment of Diamond Films Grown on Glass by Different Microwave Plasma Systems . Advanced Science, Engineering and Medicine, Vol. 6, No. 7, 2014, pp. 802-808(7).
- [9] ARTEMENKO A., KOZAK H., BIEDERMAN H., CHOUKOUROV A., KROMKA A. Amination of NCD Films for Possible Application in Biosensing. Plasma Processes and Polymers Vol. 12, Issue 4, 2015, pp. 336-346.
- [10] LISKOVA J., BABCHENKO O., VARGA M., KROMKA A., HADRABA D., SVINDRYCH Z., BURDÍKOVA Z., BACAKOVA L. Osteogenic cell differentiation on H-terminated and O-terminated nanocrystalline diamond films International Journal Nanomedicine, Vol. 10, 2015, pp. 869-884.
- [11] KROMKA A., BABCHENKO O., IZAK T., HRUSKA K., REZEK B. Linear antenna microwave plasma CVD deposition of diamond films over large areas. Vacuum, Vol. 86, 2012, pp. 776-4.
- [12] FUNER M., WILD C., KOIDL P. Novel microwave plasma reactor for diamond synthesis. Applied Physics Letters, No. 72 (10), 1998, pp. 1149-1151.
- [13] ZEMEK J., HOUDKOVA J., LESIAK B., JABLONSKI A., POTMESIL J., VANECEK M. Electron spectroscopy of nanocrystalline diamond surfaces. Journal of Optoelectronics and Advanced materials, Vol. 8, No. 6, 2006, pp. 2133-2138.
- [14] POPOK V.N. Implantation of keV-energy argon clusters and radiation damage in diamond. Physical Review B Vol. 85, 2012, pp. 033405-4.
- [15] FERRARI C., ROBERTSON J. Origin of the 1150-cm-1 Raman mode in nanocrystalline diamond. Physical Review B, Vol. 63, pp. 121405.