UNIVERSITY OF NIŠ
The scientific journal **FACTA UNIVERSITATIS**
Series: **Physics, Chemistry and Technology** Vol. 2, No 1, 1999 pp. 21 - 26
Editor of series: Momčilo Pejović, e-mail: pejovic@elfak.ni.ac.yu
Address: Univerzitetski trg 2, 18000 Niš, YU
Tel: +381 18 547-095, Fax: +381 18 547-950

DIAMOND DEPOSITION ON WIDIA METAL SUBSTRATE

UDC 549.21+537.533.35+548.73

Gordana S. Ristić[1], Žarko D. Bogdanov[1], Slavica Zec[1], Zoran Laušević[1], Šćepan S. Miljanić[1,2]

[1]Vinča Institute of Nuclear Sciences, P.O.B. 522, 11001 Belgrade, Yugoslavia
[2]Faculty of Physical Chemistry, University of Belgrade, P.O.B. 137, 11001 Belgrade, Yugoslavia

Abstract: *Diamond coating was deposited by hot filament Chemical Vapour Deposition (hfCVD) method on a Widia metal platelet. Deposition conditions and process characteristics were recorded. Several methods (scanning electron microscopy, X-ray diffraction analysis, Raman spectroscopy) were used to examine the deposited film.*

Keywords: *diamond film, hot filament, CVD, Co cemented tungsten carbide*

Chemical Vapour Deposition (CVD) of diamond films on cemented tungsten carbide has aroused great interest in recent years [1]. It is due to the possibility to combine the toughness of cemented carbide with the hardness of diamond resulting in an outstanding wear resistance. Co cemented tungsten carbide is commonly used for cutting and drilling tools, mining machinery, structural components and wear resistance parts of all kinds [2]. Increased lifetime and better technical performance are expected for the components made of diamond-coated carbide.

Our observations on a growth of the diamond film on the cemented carbide substrate using the hot filament CVD method are presented in this paper.

EXPERIMENTAL

A tungsten carbide platelet, a tip for scrapers, VK 6-OM (Stankoimport, USSR) was used as the substrate in this study. The substrate surface was subjected to a few pretreatments in order to enhance nucleation and growth of the diamond film. The

Received March 27, 1999

deposition surface was firstly ground by a whetstone, in order to obtain favourable surface roughness. Then, a content of the Co binder at the surface of WC-Co was reduced by etching in a hot acid solution (HNO_3:HCl:H_2O = 1:1:1). After that, the scratching/seeding procedure with a diamond powder (grain size 0.3 μm) suspended in ethanol was carried out in an ultrasonic bath. Finally, the substrate was mounted in a holder at a distance 1 mm from the filament.

Diamond deposition was performed in a four-arm reaction chamber specially designed for different methods of a CVD technique [3]. It was connected to a vacuum apparatus for gas handling, equipped for process monitoring. The gas mixture of methane (2%) and hydrogen was activated by a tantalum filament (0.5 mm in diameter). Before the actual deposition process the filament was conditioned [4] in order to be stable in the course of the deposition. The filament temperature was estimated to be around 2300 ^oC, using an optical pyrometer with the disappearing filament. The substrate temperature, measured by a chromel-alumel thermocouple, was kept at 900±10 ^oC during the whole deposition time. The total gas pressure in the reaction chamber was 50 mbar, and the flow rate 13 cm^3min^{-1}. Well developed film was obtained during the full deposition time of 24 hours.

Morphology and growth stages of the film were investigated by scanning electron microscopy (SEM). Microphotographs were taken by JSM-35 (JEOL), accelerating voltage 25 kV.

X-ray diffraction (XRD) analysis was done using the powder diffractometer Siemens D500 with Cu Kα, Ni filtered radiation. A continuous scan over 2θ range from 20-90^o was performed at a rate 0.02 $^o2\theta\ s^{-1}$. Identification of crystal phases was carried out using JCP data basis.

Laser Raman spectroscopy, commonly used for recognition and distinguishing of diamond and diamondlike structures, was used to confirm evidences found by other methods. Room temperature Raman spectrum was taken in backscattering geometry with unfocused Ar^+ laser beam (λ = 514.5 nm) having a diameter of about 2.5 mm. The applied laser was a Spectra Physics unit (Model 2020). Its power was approximately 0.7 W. The spectrum was recorded by a Spex 1401 spectrometer (at a slit width of 300 μm) interfaced to a computer. The scans were acquired in steps of 1 cm^{-1} with a 3 s counting time, accumulating over 10 scans per spectrum.

RESULTS

As mentioned above, for experimental conditions quoted (gas composition, total pressure, flow rate, filament and substrate temperatures), the growth of the diamond thin film is accomplished. There is an agreement on the mechanism of the diamond thin film formation [5], which proceeds in several steps. After an initial nucleation period, which depends essentially on substrate surface conditions (pretreatment, temperature) and a filament-substrate distance, the formation of tiny crystals - nuclei of the film, is completed. With prolonged deposition time, an agglomeration of crystalline stacks leads to the formation of the continuous film. Further crystal growth is accompanied by the formation of faceted crystals with a defined habit.

The effect of the filament-to-substrate distance which, in our case, settles to the effect

of an atomic hydrogen concentration is shown in Fig. 1, (a)-(d). As it comes out of the SEM study, the homogeneity of the film and its morphology are strongly affected by the filament-to-substrate distance: In a periphery region (farthest from the filament) the film is non-uniform, crystal shapes are not apparent (a). With approaching the filament, the continuous film is developed (b), morphology can be recognized (c). Faceting of the crystals and the film homogeneity are the best directly under the filament (d). So, the fact the atomic hydrogen is indispensable for diamond film formation is clearly seen. At the same time, octahedral facets observed in the deposited film reflect deposition conditions. In agreement with other authors [6], the octahedron habit prevails at lower temperatures (900^{o}C).

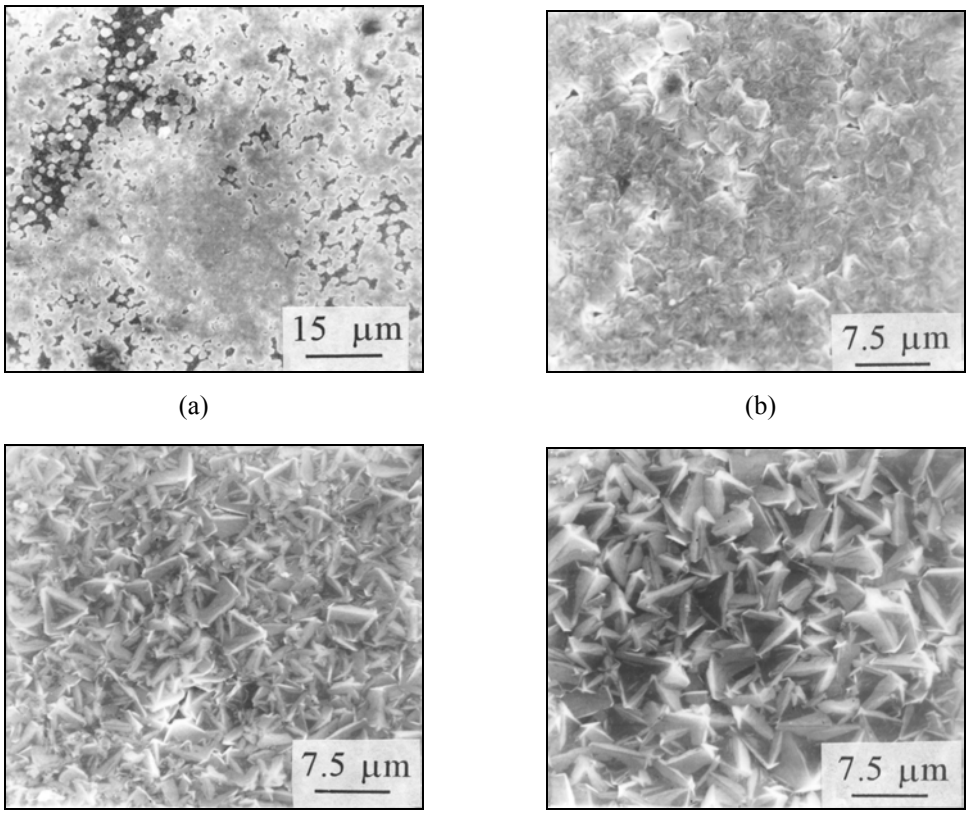

Fig. 1. SEM photographs of the diamond film grown at different distance from the filament: (a) 5.0 mm, (b) 2.5 mm, (c) 1.5 mm, (d) 1.0 mm.

The X-ray diffraction analysis was used to assess the quality of the diamond film. As is thoroughly discussed elsewhere [7], the full width at half maximum of the (111) $K\alpha_1$ diamond peak ($FWHM_x$) is very sensitive to changes in crystalline order, and is a suitable parameter to estimate diamond quality. In Fig. 2 is given the X-ray diffraction pattern of the deposited film. In addition to the diamond reflection (111) and reflections that are

due to the substrate material, there are some reflections which originate from the filament material. Evaporation of the filament is greatly reduced by means of the carburization pretreatment [4], [8], but definitely, the contamination of the diamond film with the evaporated filament material is unavoidable. Therefore, reflections of the filament material make common "satellites" in X-ray diffractograms.

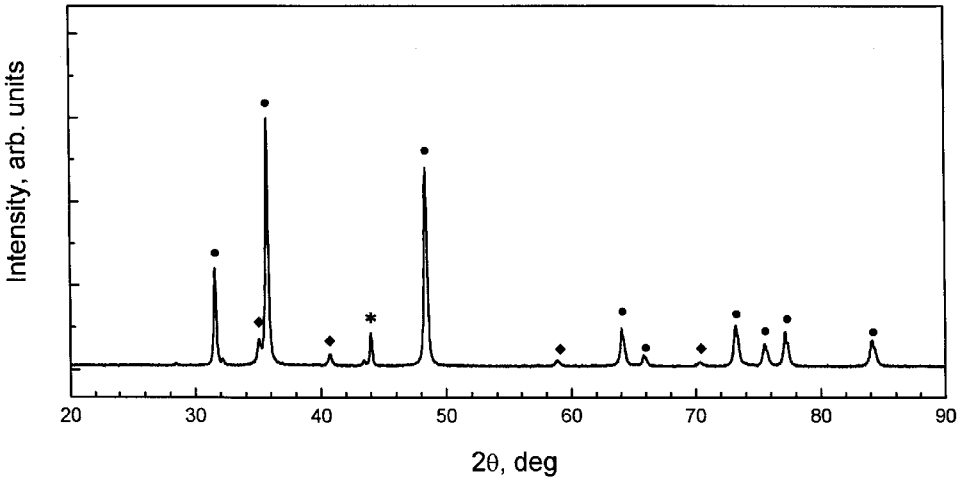

Fig. 2. X-ray diffraction pattern of the diamond film deposited on the Widia metal platelet. Reflections stemming from different materials are denoted as follows: WC (•), TaC (♦), diamond (∗)

However, the corrected $FWHM_x$ value of the (111) $K\alpha_1$ diamond peak of 0.120 $^o2\theta$ indicates good quality of the deposited film. Corresponding data for coatings obtained by the same hfCVD method range from 0.24 to 1.2 $^o2\theta$, or by the combustion flame method, from 0.05 to 0.87 $^o2\theta$ [7]. For all these, the smaller $FWHM_x$ value means the higher crystal order. The 0.120 value results obviously from a fairly good order. The pertaining apparent crystallite size value, calculated from the Sherrer formula is 71 nm. The lattice constant yields 0.3561 nm.

Raman scattering from the deposit unambiguously certified the diamond identity of the film. In the Raman shift range of 1300-1600 cm^{-1}, given in Fig. 3, the spectrum shows a characteristic diamond feature and complete absence of non-diamond carbon. The only one Raman active vibrational mode of diamond gives line positioned at 1332.5 cm^{-1} [9], and the one of graphite at 1575 cm^{-1} [6]. Disordered carbons usually show two, more or less, broad maxima at 1355 and 1590 cm^{-1} [6]. The Raman spectrum, at the same time, revealed existence of high residual stresses within the film. Splitting of the diamond line, which amounts 3 cm^{-1}, indicates the compressive stress perpendicular to a growth direction (in-plane stress) [10], [11]. Hypsochromic shift of the Raman peak and its broadening are also due to the compressive stress [12], [13].

Residual stresses in diamond CVD coatings can be of different origin (thermal, intrinsic, epitaxial, phase transformation) and can act in different directions facing the substrate surface (compressive stress, tensile stress) [11], [14]. Therefore, the Raman line

is an important indicator of the residual stress field in the diamond coating and can help in optimizing the deposition.

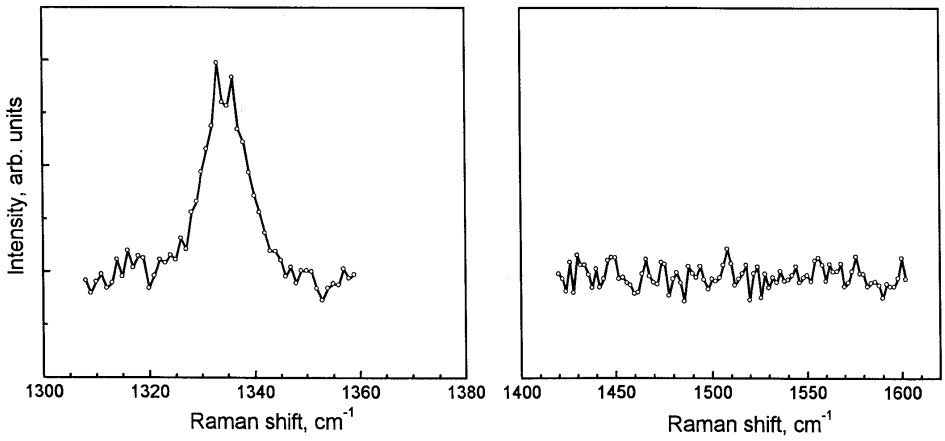

Fig. 3. Raman line of diamond split into two components set at 1333 and 1336 cm^{-1}, and shifted to greater wave numbers. Over 10 scans on a single sample acquired; S/N ratio is over 6:1

In concluding, we repeatedly emphasize the crucial role of atomic hydrogen for the growth of the diamond film. All other parameters could and should be met, but are useless in deficiency of an activating/etching agent.

Acknowledgement: *Mr S. Šašić, Faculty of Physical Chemistry, University of Belgrade, is gratefully acknowledged for taking the Raman spectrum.*

REFERENCES

1. B. Lux and R. Haubner, Diamond as wear-resistant coating, *Phil. Trans. R. Soc. Lond. A* **342**, 297-311 (1993).
2. H. Tulhoff, Carbides, in *Ullmanns Encyclopedia of Industrial Chemistry, A* **5**, W. Gerhartz (Ed.), 5th Ed, VCH Weinheim, 65-68, 1986.
3. G.S. Ristić, Lj.T. Petkovska, Ž.D. Bogdanov and Š.S. Miljanić, Four-arm reaction chamber for synthesis of special, new materials, 18th SPIG, Contributed papers & Abstracts, Kotor, Yugoslavia, 1996, pp 217-220.
4. G.S. Ristić, Lj.T. Petkovska, Ž.D. Bogdanov, S. Zec and Š.S. Miljanić, Conditioning of the filament for diamond deposition by hot-filament chemical vapour deposition method, *J. Serb. Chem. Soc.* **63** (3), 231-235 (1998).
5. B. Bliznakovska and C. Meixner, *Progress in diamond and diamondlike coatings processing,* Sci. Ser. Int. Bureau, Forschungszentrum Jülich, GmbH, 1994.
6. A.R. Badzian, T. Badzian, R. Roy, R. Messier and K.E. Spear, Crystallization of diamond crystals and films by microwave assisted CVD (Part II), *Mat. Res. Bull.* **23**, 531-548 (1988).
7. S. Marinković and S. Zec, Characterization of diamond coatings by X-ray diffraction, Raman spectroscopy and scanning electron microscopy, *J. Serb. Chem. Soc.* **58**, 679-689 (1993).
8. T. Tsutsumoto, Improvement of Ta filament for diamond CVD, *Thin Solid Films* **317**, 371-375 (1998).
9. J.E. Field (Ed.), The Properties of the Diamond, Academic Press, London, 1979.

10. S.K. Baldwin Jr, T.G. Owano, M. Zhao, and C.H. Krugger, Enhanced deposition rate of diamond in atmospheric pressure plasma CVD: effects of a second discharge, *Diamond &Relat. Mater.* **6**, 202-206 (1997).
11. H. Mohrbacher, K. Van Acker, B. Blanpain, P. Van Houtte, and J-P. Celis, Comparative measurement of residual stress in diamond coatings by low-incident-beam-angle-diffraction and micro-Raman spectroscopy, *J. Mater. Res.* **11**, 1776-1782 (1996).
12. A. Fernandes, A. Neves, R.F. Silva and M.H. Nazaré, Evaluation of MPCVD diamond film adhesion on hard metal substrates by micro Raman spectroscopy, *Diamond & Relat. Mater.* **6**, 769-773 (1997).
13. P. Scardi, S. Veneri, M. Leoni, R. Polini and E. Traversa, Lattice disorder and texture in diamond coatings deposited by HFCVD on Co-cemented tungsten carbide, *Thin Solid Films* **290-291**, 136-142 (1996).
14. C.T. Kuo, C.R. Lin and H.M. Lien, Origins of the residual stress in CVD diamond films, *Thin Solid Films* **290-291**, 254-259 (1996).

DEPOZICIJA DIJAMANTA NA PODLOZI OD VIDIJA METALA

G.S. Ristić, Ž.D. Bogdanov, S. Zec, Z. Laušević, Š.S. Miljanić

Dijamantska prevlaka deponovana je na pločici od volfram karbida cementiranog kobaltom metodom hemijskog deponovanja iz pare pomoću usijanog vlakna. Zabeleženi su uslovi deponovanja i karakteristike procesa. Skanirajuća elektronska mikroskopija, rentgenska difrakcija i Ramanska spektroskopija upotrebljene su za evaluaciju dijamantskog filma.

Ključne reči: *dijamantska prevlaka, usijano vlakno, HDP, Co-cementirani wolfram karbid*