

Double bias HF CVD multilayer diamond films on WC–Co cutting tools

M. Vojs^{a,*}, M. Veselý^a, R. Redhammer^a, J. Janík^a, M. Kadlečiková^a, T. Daniš^a,
M. Marton^a, M. Michalka^b, P. Šutta^c

^aFaculty of Electrical Engineering and Information Technology, Slovak University of Technology, Ilkovičova 3, 812 19 Bratislava, Slovak Republic

^bInternational Laser Center, Ilkovičova 3, 812 19 Bratislava, Slovak Republic

^cUniversity of West Bohemia, Univerzitní 8, 306 14 Plzeň, Czech Republic

Available online 9 February 2005

Abstract

Diamond layers are nowadays of increasing importance for mechanical applications. In our laboratory we grow diamond and DLC layers on WC–Co cutting tools using HF CVD method improved by double biasing. Optimization of growth parameters facilitates to control grain size of polycrystalline diamond layers from microcrystalline to nanocrystalline. Five steps of this process are described and demonstrated. SEM, AFM, Raman spectroscopy, and XRD were used to analyze grown diamond films. The decrease of the RMS surface roughness from 650 nm down to 50 nm was measured. Bias voltage was demonstrated to be the tool for changing the grown layer grain size. Deposition rates were increased to optimal values.

© 2005 Elsevier B.V. All rights reserved.

Keywords: Diamond film; Hot filament CVD; Morphology; Cutting tools

1. Introduction

There is an increasing interest in CVD thin film applications to cutting inserts. Recent advances in chemical vapor deposition (CVD) diamond technology permit diamond coatings to be applied to already available tool inserts such as cemented carbides and silicon nitrides.

CVD polycrystalline diamond coatings have the advantage of being applied to complex geometries in a relatively cost-effective manner. Surface coatings for machining tools must have a good adhesion to the substrate, a high wear resistance and a low roughness to achieve functional properties like high performance in tooling operations and long lifetime [1]. Along with the improvement of adhesion, the diamond film rough surface is still a problem when machining metals, which results in rough surface of work-piece and formation of built-up edge [2]. This represents a critical problem in precision and dry machining processes, where diamond tools are required [3].

The above described problem can be solved by using a multi-step HF CVD process in which a multilayer combination of microcrystalline and nanocrystalline structures is produced. This multilayer structure can be created by regulating the negative bias of substrate with respect to filaments during thin film deposition. The structure of diamond layers can range from high phase purity microcrystalline to nanocrystalline diamond and one layer can be successfully grown over the next. Therefore, the nano-structured smooth diamond films exhibit a better wear resistance than the micro-structured, rough coatings. The extraordinary good wear resistance for thin, nanocrystalline diamond films with optimized adhesion and layer strength could be further enhanced by producing thicker films [4].

2. Experimental

Diamond depositions were carried out in the double bias enhanced HF CVD reactor described previously [5,6]. The gas phase was a mixture of 1% or 2% CH₄ in H₂, the total pressure in the reactor was 3000 Pa and flow rates were

* Corresponding author. Tel.: +42 1 2 602 91 366; fax: +42 1 2 654 23 480.

E-mail address: marian.vojs@stuba.sk (M. Vojs).

Table 1
Deposition process

Step	Process	Time (hour)	CH ₄ /H ₂ [%]	Substrate bias
1	nucleation	2	2	on
2	growth	2	2	off
3	re-nucleation	2	2	on
4	growth	2	2	off
5	re-nucleation	5	1	on

3:300 and 6:300 sccm. Gases were activated by 5 tungsten filaments 0.7 mm thick, 120 mm long, heated to 2100 °C ± 50 °C. The substrate temperature was maintained at 750 °C (measured by a K-type thermocouple mounted in 80 mm molybdenum substrate holder with filament-substrate distance of 10 mm).

Standard cemented carbide cutting inserts (Kennametal-XPHT_160408-Al WC-6% Co) have been used as substrates. Inserts were rinsed in acetone in ultrasonic bath and then underwent two steps of chemical pretreatment, 10 min etching in Murakami's reagent (10 g K₃[Fe(CN)₆]+10 g KOH+100 ml of water) and 10 s etching in solution of 30 vol.% H₂SO₄ and 70 vol.% H₂O₂. The removal of Co from the surface with acids is important to prevent the detrimental effect of Co on diamond deposition and film adhesion [7,8].

The deposition process consisted of five steps given in Table 1. Nucleation took place at negative substrate bias of 220 V with respect to filaments. Both, nucleation and growth, were enhanced by dc plasma formed in the region between heated filaments and above them located grid (positive grid bias of 100 V with respect to filaments).

This process of multilayer diamond film deposition in HF CVD was used to produce our hard coatings. The prepared samples were analyzed as follows.

Raman measurements were conducted in a Raman spectrometer DILOR-JOBIN YVON-SPEX type LabRam. The excitation source was a He-Ne laser with 632.8 nm wavelength operated at 15 mW. The spectrometer was calibrated to the 520.7 cm⁻¹ band of single crystalline Si and to the 1332 cm⁻¹ band of natural diamond. Scanning electron microscope (SEM) LEO 1550 operating in the secondary electron mode was used to study the microtopography of diamond layers. Further studies were done by Atomic Force Microscopy (AFM) NT-MDT Solver P7LS. XRD analysis was carried out with an X-ray diffractometer Bruker D8 with an area detector using CoK-alpha radiation (wavelength CoK-alpha=0.179021 nm). The XRD patterns were collected by setting the detector position at 50° and 90° of 2θ, with counting time of 20 s at each position. The sample-detector distance was set up to 15 cm.

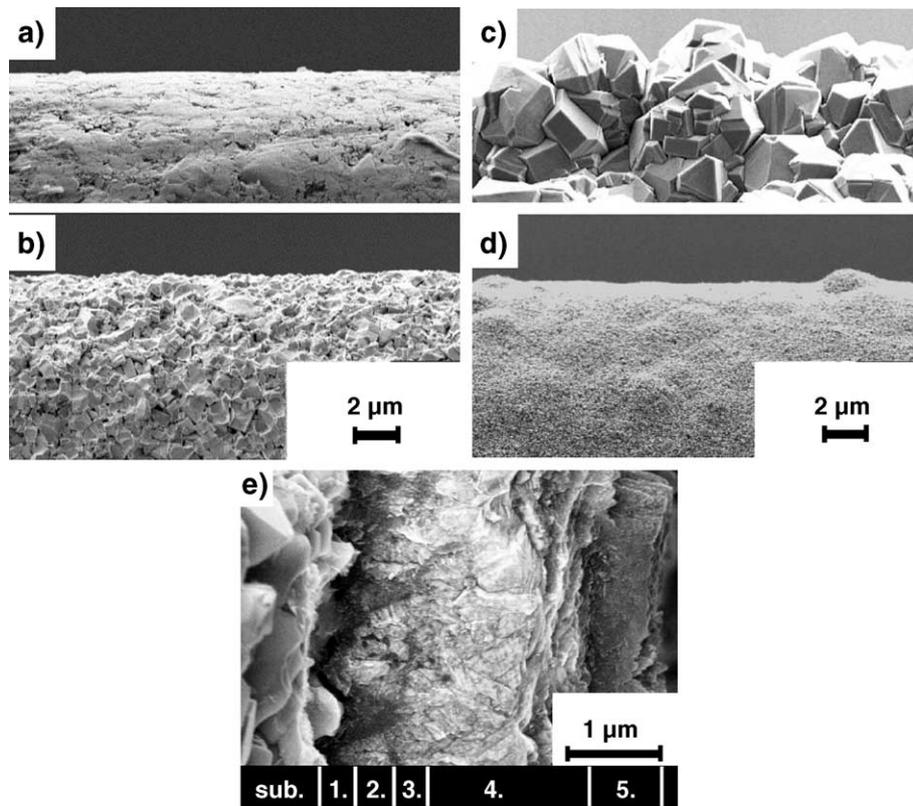


Fig. 1. a) SEM images of cutting edge non-etched and b) chemically etched. c) SEM images of cutting edge microcrystalline diamond after 4th step and d) nanocrystalline diamond after 5th step of growth. e) SEM images cross-section of cutting edge with deposition steps 1–5.

3. Results and discussion

We can see in Fig. 1 SEM images of surface morphology of diamond layers at different stages of diamond deposition on WC–Co cutting tools from uncoated substrate (Fig. 1a)) to smooth nanocrystalline diamond layers (Fig. 1d)). In Fig. 1b) the etched surface can be seen. The RMS roughness of such prepared surface is increased from the original value of 110 nm (Fig. 1a)) to 225 nm (Fig. 1b)). The chemical treatment is followed by a growth of $\sim 3 \mu\text{m}$ thick layer by combination of nucleation and growth. When the negative bias is applied to the insert (substrate) during deposition, the surface morphology and average roughness are influenced by this bias. By changing the bias voltage the roughness of polycrystalline layers can be changed in such a way that by bias increase the roughness is decreasing. Etched surface was covered by nucleation. About 200 nm thick films with growth rate of $0.1 \mu\text{m/h}$ were produced, 1st step. On top about 200 nm thick films of polycrystalline diamond were grown at a rate of $0.1 \mu\text{m/h}$, 2nd step. Afterwards nucleation, 3rd step, again took place. This nucleation is necessary to speed up further growth process. The 4th step is rapid growth of polycrystalline film ($0.7 \mu\text{m/h}$, $1.5 \mu\text{m}$). In (Fig. 1c)) this surface can be seen with RMS roughness of 650 nm.

Fig. 1d) shows SEM micrograph of the surface morphology of diamond films after growth of nanodiamond, 5th step of deposition process. During all steps the grid bias is on (plasma formed in the region between filaments and grid). During nucleation processes, steps 1, 3 and 5, the sample bias with respect to substrate is on. Surface morphology and film character changes drastically. The last layer was formed slowly and is smoother consisting of nanocrystalline diamond grains. The roughness has dropped down drastically from 650 nm to lower than 50 nm. The substrate surface bombardment by energetic ions creates new surface defects, which serve as nucleation sites. If a negative bias is applied to substrate during deposition, nucleation sites will be

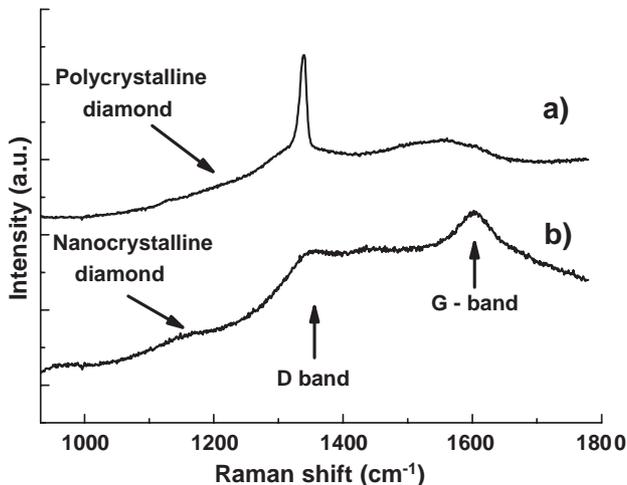


Fig. 2. Raman spectra of diamond layer after a) 4th step and b) 5th step.

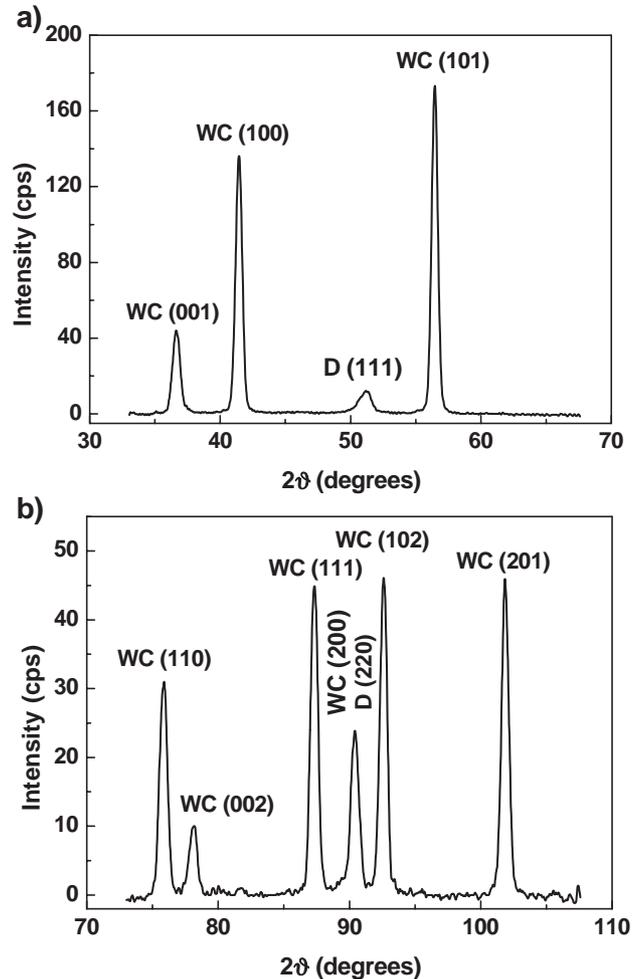


Fig. 3. a) X-ray analysis with (111) line of diamond. b) X ray analysis with (220) line of diamond.

continuously supplied. The ion bombardment energy increases with negative substrate bias voltage increase, which i) enhances the number of re-nucleation sites and ii) destroys already formed polycrystalline diamond grains [9,10].

In Fig. 1e) a SEM micrograph of deposited film cross section is given. Steps 1–5 are clearly identified.

Fig. 2 shows a comparison of the Raman spectra for microcrystalline and nanocrystalline diamond films. The microcrystalline film in Fig. 2a) shows intense sharp peak at approximately 1338 cm^{-1} which is characteristic of high phase-purity polycrystalline diamond. The Raman spectrum of the 4th diamond film layer shown in Fig. 2a) also shows broad band component at approximately 1555 cm^{-1} which is attributed to amorphous carbon with high concentration of sp^3 bonds [11].

Fig. 2b) shows two intense broad peaks around 1350 cm^{-1} and 1590 cm^{-1} ; they appear in the Raman spectrum of the last layer. They are the so called D and G bands, respectively. Next two significant broad bands around 1140 cm^{-1} and 1470 cm^{-1} correspond to diamond of nanocrystalline grain size [12,13] which is in correlation with XRD measurements

revealing the presence of nanodiamond in orientations (111) and (220) with grain size of 10 nm—Fig. 3a, b). One can see from Fig. 3b) that diamond (220) line and WC (200) line appear together, therefore the inter-planar distances for both materials are nearly the same. Line positions were compared with PDF 2 ICDD standards. Apparently this is responsible for the good adhesion of diamond on WC. The line intensity ratio for (220) and (111) is 1.01 at the cutting edge, 1.26 at cutting groove. This means that the texture is in the (110) direction. The reference value for randomly oriented grains is 0.44.

4. Conclusions

We have used HF CVD technology with Double Bias Enhanced Nucleation for multilayer diamond film deposition with surface roughness properties that can be tailored by appropriate use of ion bombardment during growth process. The structure of diamond layers was in the range from high phase purity microcrystalline diamond to nanocrystalline diamond containing an amorphous carbon component and one layer can be successfully grown over the next. The growth rate (Step 4) did increase, thanks to renucleation process (step 3) supplying increased number of nucleation sites.

With the substrate bias increase both roughness and grain size of the deposited films decreased. The deposition of diamond film on WC–Co inserts with negative bias was found to be a very effective way to reduce the surface roughness of final multi-composite diamond layers. This was concluded from SEM Figures and AFM measurements.

X-ray measurements revealed the nanocrystalline form of deposited diamond.

We were able to demonstrate a simple way for grain size regulation during deposition-bias voltage. This enables to grow diamond layers from polycrystalline diamond to nanodiamond. Only two gases are needed for diamond film

production—CH₄ and H₂. Thanks to simple scale up in HF CVD relatively large areas with diamond films can be deposited. The area of filaments roughly dictates the deposition area. The homogeneity of films was measured and will be published elsewhere.

Acknowledgement

This work supported by grant from VEGA No. 1/0275/03, VEGA No. 1/9044/02 and VTP-4-RED-SK1.

References

- [1] Friederike Deuerler, Michael Pohl, Christian Heßing, *Surf. Coat. Technol.* 174–175 (2003) 732.
- [2] Jong-Kuek Park, Wook-Seong Lee, Young-Joon Baik, Ki-Woong Chae, *Diamond Relat. Mater.* 12 (2003) 1657.
- [3] Taijin Lu, James E. Shigley, John I. Koivula, Ilene M. Reinitz, *Diamond Relat. Mater.* 10 (2001) 68.
- [4] A.R. Krauss, O. Auciello, D.M. Gruen, A. Jayatissa, A. Sumant, J. Tucek, et al., *Diamond Relat. Mater.* 10 (2001) 1952.
- [5] V. Malcher, A. Mrska, A. Kromka, A. Satka, J. Janik, *Curr. Appl. Phys.* 2 (2002) 201.
- [6] X.T. Zhou, H.L. Lai, H.Y. Peng, C. Sun, W.J. Zhang, N. Wang, et al., *Diamond Relat. Mater.* 9 (2000) 134.
- [7] Riccardo Polini, Fabio Bravi, Giorgio Mattei, Giancarlo Marcheselli, Enrico Traversa, *Diamond Relat. Mater.* 11 (2002) 242.
- [8] M. Vojs, J. Pavlov, J. Janik, A. Satka, *Proceedings of 9th International Workshop on Applied Physics of Condensed Matter APCOM 2003*, 2003, p. 44.
- [9] Sadao Takeuchi, Sumitsugu Oda, Masao Murakawa, *Thin Solid Films* 398–399 (2001) 238.
- [10] Michael D. Whitfield, James A. Savage, Richard B. Jackman, *Diamond Relat. Mater.* 9 (2000) 262.
- [11] Shane A. Catledge, Paul Bakera, John T. Tarvin, Yogesh K. Vohra, *Diamond Relat. Mater.* 9 (2000) 1512.
- [12] A. Shane, M.Y. Liao, X.M. Meng, X.T. Zhou, J.Q. Hu, Z.G. Wang, *J. Cryst. Growth* 236 (2002) 85.
- [13] N. Jiang, S. Kujime, I. Ota, T. Inaoka, Y. Shintani, H. Makita, A. Hatta, *J. Cryst. Growth* 218 (2000) 265.