INVESTIGATION OF DIAMOND FILMS IN DOUBLE BIAS-ENHANCED DEPOSITION ON MOLYBDENUM

VILIAM MALCHER[1]*, ALEXANDER KROMKA[1], VIERA DUBRAVCOVÁ[1], MICHAL KUBOVIČ[1]

Diamond films were deposited on Mo and Si substrates in a double bias-assisted chemical vapor deposition reactor employing a bias-enhanced nucleation. The deposition process was subdivided into two steps: the pre-treatment step (i.e. bias-enhanced nucleation with two bias voltages) and the growth step (electron-enhanced diamond growth). To investigate separately the nucleation process, we varied the deposition parameters only during the pre-treatment and kept all of them at the constant during the growth step. The deposition parameters, which result in the homogeneous formation of continuous diamond films on Si, yield only low nucleation density on Mo. An increase in the nucleation density (N_D) was achieved by raising the negative biasing of the Mo substrate. The continuous diamond film on Mo was achieved under high ion current density and was also slightly enhanced by increase of methane concentration (2% CH_4 in H_2).

Key words: diamond films, micro-Raman spectra, double bias-assisted hot filament CVD method, nucleation, molybdenum

VÝSKUM DIAMANTOVÝCH VRSTIEV VYRASTENÝCH NA MOLYBDÉNE METÓDOU DVOJITÉHO PREDPÄTIA

Depozícia diamantových vrstiev sa uskutočnila na Mo a Si substrátoch v reaktore s chemickou depozíciou z pár s dvojitým predpätím, s podporou nukleácie prostredníctvom napätia. Depozičný proces bol rozdelený na dve etapy: predúprava (t.j. podpora nukleácie cez dve napätia) a rast (diamantový rast bol podporený bombardovaním substrátu elektrónmi). Aby bolo možné preskúmať nukleačný proces oddelene, menili sa hodnoty depozičných parametrov iba počas predúpravy a v priebehu rastu zostali nezmenené. Depozičné parametre, ktoré viedli k vytváraniu homogénnej spojitej vrstvy na Si, dávali iba nízku nukleačnú hustotu na Mo substráte. Vzrast nukleačnej hustoty (N_D) sa dosiahol zvýšením záporného predpätia na Mo substráte. Spojitá diamantová vrstva na Mo sa dosiahla pri vysokých iónových hustotách prúdu a pri mierne zvýšenej koncentrácii metánu (2 % CH_4 v H_2).

[1] Department of Microelectronics, Faculty of Electrical Engineering and Information Technology, Slovak University of Technology, Ilkovičova 3, 812 19 Bratislava, Slovak Republic

* corresponding author, e-mail: malcher@elf.stuba.sk

1. Introduction

Diamond has a number of unique and desirable properties for electronic and industrial applications. The high cost of natural diamond limits its practical applications. However, the recent developments in the field of chemical vapor deposition (CVD) techniques of diamond films have made it as a useful material with reasonable cost.

In the recent years, the deposition techniques for diamond thin-film growth have been progressing rapidly. A detailed review of the various methods used for fabrication of diamond films can be found in Dischler and Wild [1]. One of the major problems associated with chemical vapor deposition of diamond films on silicon and metal substrates is a low nucleation density in the absence of nucleation pretreatments. Yugo et al. [2] first suggested the bias-enhanced diamond nucleation in microwave plasma CVD (MPCVD). In the negative bias-enhanced nucleation step, a high nucleation density can be achieved by bombarding of the Si substrate with positive ions of hydrogen and hydrocarbons [3]. However, the beneficial effect of ion bombardment observed in MPCVD cannot be obtained easily in a hot filament CVD (HFCVD). The predominantly thermal nature of the hot filament process means that there are very few gas-phase ions presented in the HFCVD, and this reduces efficiency of the substrate to improve nucleation and growth rates or to induce oriented growth. Even simply biasing of the substrate is not expected to produce enough ion bombardment for heteroepitaxial diamond nucleation as the concentration of ions is too low. For these reasons, Zhou et al. [4] and Kromka et al. [5] have developed a new process to obtain high density diamond nucleation via a double bias-assisted HFCVD.

In this paper, the deposition of diamond films on molybdenum and silicon substrates was prepared by the double bias-assisted hot filament CVD method. The diamond films were investigated by optical microscopy and micro-Raman spectroscopy.

2. Experimental details

Diamond films were synthesized by chemical reactions of methane and hydrogen gas using the double bias-assisted hot filament CVD reactor. The experimental apparatus is schematically shown in Fig. 1. A conductive grid was installed at about 6 mm above three tungsten filaments 0.6 mm in diameter. With this arrangement, a stable plasma can be generated between the grid and the hot filaments. Ions in the plasma are then driven to the substrate by the negative substrate bias voltage.

Unpolished Mo and mirror-polished Si wafers were used as substrates which were placed on water-cooled molybdenum substrate holder (70 mm in diameter). Before the deposition process, the filaments were treated in methane-hydrogen atmosphere (1% CH_4 in H_2) until they were completely carbonized. The substrates

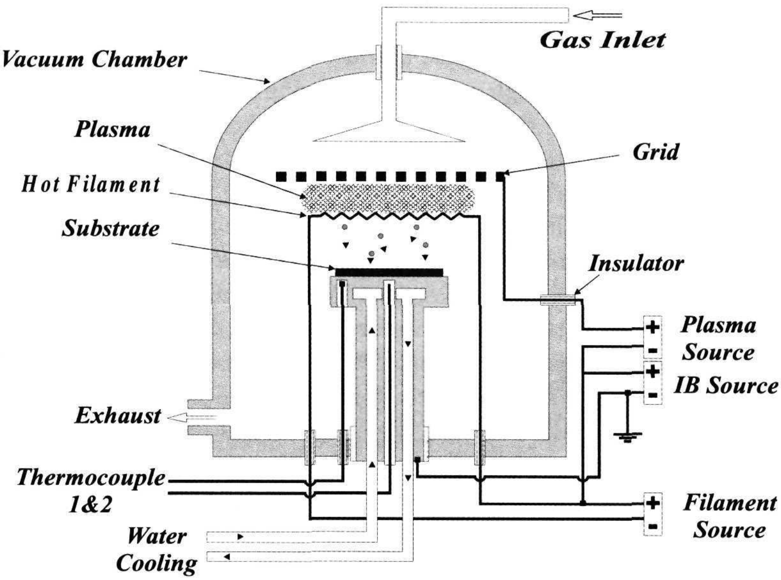


Fig. 1. A schematic diagram of HFCVD apparatus.

were ultrasonically cleaned in bath of acetone for 10 min before loading into the reactor. The deposition process was subdivided into two steps: (1) the bias-enhanced nucleation (pre-treatment) and, (2) the diamond growth step. The nucleation step was performed at negative biasing of substrate. The growth step was realized at positive substrate bias of +100 V with respect to the filaments. Detailed nucleation and growth parameters are listed in Table 1.

The surface morphology of the diamond thin films was investigated by optical microscopy. The as-grown films were characterized by using micro-Raman spec-

Table 1. The parameters of nucleation and growth of diamond films

	Nucleation	Growth
Total flow rate [sccm]	303	303
Methane conc. [vol.%]	1, 2	1
Filament temp. [°C]	2000	2000
Substrate temp. [°C]	650	650
Pressure [Pa]	2000	3000
Grid voltage with respect to the filaments [V]	+100	+100
Substrate voltage with respect to the filaments [V]	−150, −200	+100
Duration [h]	2	5

troscopy. Micro-Raman spectra were carried out by means of a Dilor system (Jobin Yvon/Spex/Dilor, Horiba Group) working with a He-Ne laser (632.817 nm), which was focused on the sample to a spot size ~1 μm in diameter at the sample surface in the backscattering geometry. An ISA Labram equipment was used for Raman measurements. For all measurements, a confocal hole diameter of 200 μm, a spectrograph entrance slit of 150 μm, and a 1800 grooves/mm diffraction grating were employed.

3. Results and discussion

Fig. 2 shows an optical photograph of the diamond films deposited on Mo and Si under bias substrate −150 V with respect to the filaments (1% CH_4 in H_2). No continuous film was deposited on Mo plate. The diamond deposit consists of a small number of crystals randomly localized over the substrate surface. It means the nucleation density was quite low. Fig. 3 represents micro-Raman spectrum of a diamond grain grown on the Mo surface. The Raman spectrum shows a diamond peak from the grain. There is also a non-diamond carbon band at approximately 1520 cm^{-1}. The differences in the diamond films on the two different substrate materials become readily apparent if the depositions performed under the same conditions are compared. However, an increase of substrate bias from −150 to −200 V in the gas phase during the nucleation stage leads to the substantial increasing of N_D for Mo (Fig. 4). The continuous film can be deposited on Mo after a slight increase in the methane concentration (2% CH_4 in H_2) at −200 V as it can be seen in Fig. 6. In comparison to the observations made for Si substrate, the Raman spectrum consists of higher amount of non-diamond phase (Fig. 7). However, such

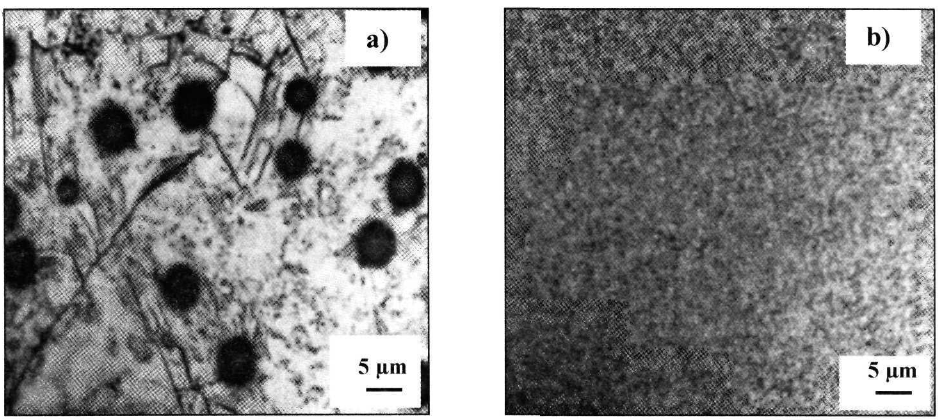


Fig. 2. Optical images of as-grown diamond films wafers with −150 V bias voltage pretreatment (1% CH_4 in H_2): a) Mo, b) Si.

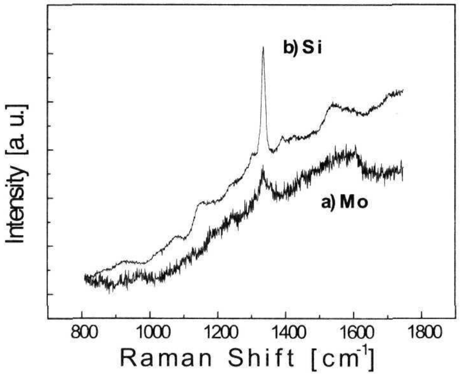
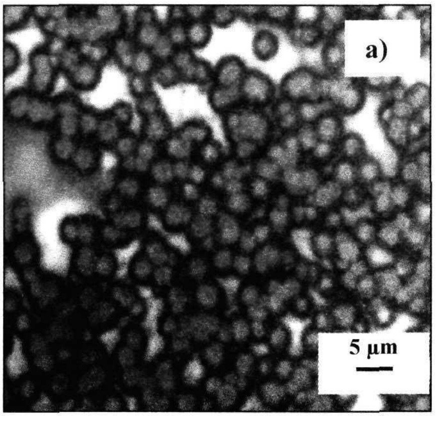


Fig. 3. Raman spectra of diamond films deposited under −150 V bias voltage pre-treatment (1% CH_4 in H_2): a) Mo, b) Si.



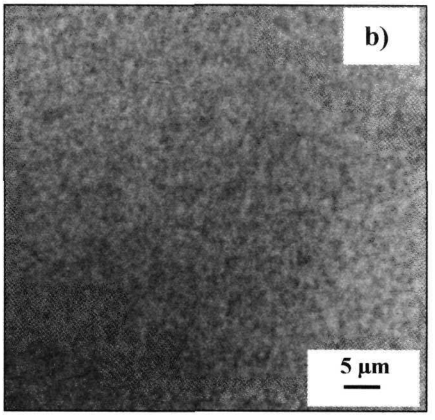
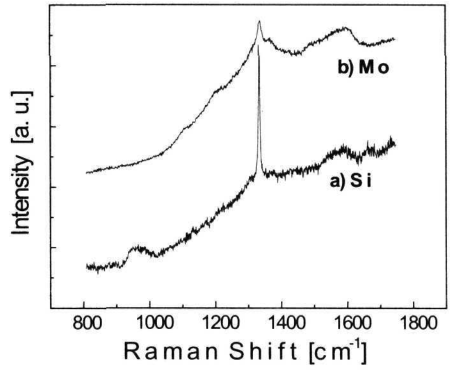


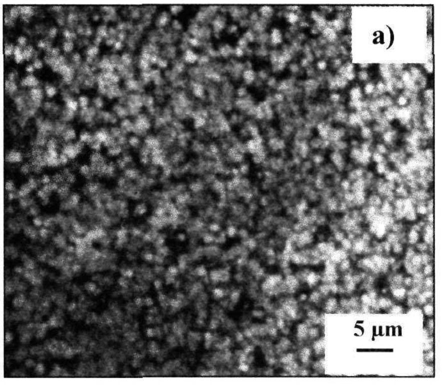
Fig. 4. Optical images of as-grown diamond films with −200 V bias voltage pre-treatment (1% CH_4 in H_2): a) Mo, b) Si.

deposition conditions are still better than those published by Wang et al. [6], where the continuous films can be formed after 12 h growth at methane concentration higher than 5%.

In this study, we eliminated seeding with diamond particles or scratching in the pre-treatment step. The main differences between scratching and bias-enhanced nucleation are: with scratching, the nucleation centers are introduced in ex-situ process and the bias-enhanced nucleation process is used to create the nucleation centers by an in-situ deposition process and is therefore much more sensitive to the substrate material properties [7]. We have included an investigation of the influence of ion bombardment on the formation of the pre-treatment layer on Mo.

Fig. 5. Raman spectra of diamond films deposited under −200 V bias voltage pre--treatment (1% CH_4 in H_2): a) Si, b) Mo.





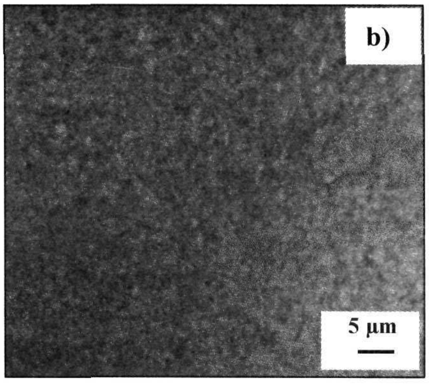


Fig. 6. Optical images of as-grown diamond films wafers with −200 V bias voltage pre--treatment: a) Mo, b) Si. The methane concentration was 2% in hydrogen during the nucleation stage.

The ion bombardment of the substrate does not change substantially the quality of the diamond film and enhances the nucleation density as it can be transparently seen for the Mo substrate.

Despite the simplicity of the different diamond film growth techniques, the nucleation process is still not well understood. A good knowledge of the mechanisms involved in nucleation could increase the range of different substrates capable of being diamond coated and also lead to a better control of the properties of diamond films. The theory of the nucleation mechanism in the HFCVD lies outside the scope of the present work. Several mechanisms have been proposed for the nucleation enhancement with the substrate bias [8, 9], but a full understanding is still lacking.

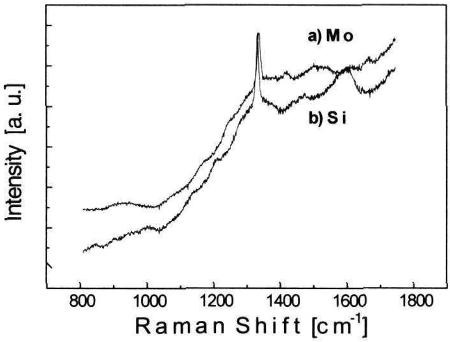


Fig. 7. Raman spectra of diamond films deposited under −200 V bias voltage pre--treatment (2% CH_4 in H_2): a) Mo, b) Si.

4. Conclusions

The continuous diamond films on Mo substrate were achieved under high bias voltage of substrate and at slightly enhanced methane concentration during the nucleation stage in the double bias-assisted hot filament CVD reactor. We have found that the uniformity of as-grown diamond films on Mo increased with increasing bias voltage. This result implies a possibility to grow CVD diamond films on temperature-sensitive materials, like steels. Deposition of diamond films on steel could also require a use of the intermediate layers (for example metals) to enhance and improve the adhesion between the diamond film and steel material. For this reason, first we need to deposit continuous diamond film on a metal matrix. It seems that further technological developments could be carried out by the double bias-assisted HFCVD-diamond technology.

Acknowledgements

The authors would like to express their gratitude to J. Král for technical support in preparing the samples. This work has been supported by the grant 1/7629/20 "Study of Deposition and Properties of Diamond Films Prepared by CVD Method".

REFERENCES

[1] DISCHLER, B.—WILD, CH. (Eds.) : Low-Pressure Synthetic Diamond: Manufacturing and Applications. Berlin Heidelberg, Springer-Verlag 1998.
[2] YUGO, S.—KAMAI, T.—KIMURA, T.—MUTO, T.: Appl. Phys. Lett., *58*, 1991, p. 1036.
[3] JIANG, X.—KLAGES, C. P.: Diamond Relat. Mater., *2*, 1992, p. 1112.
[4] ZHOU, X. T.—LAI, H. L.—PENG, H. Y.—SUN, C.—ZHANG, W. J.—WANG, N.—BELLO, I.—LEE, C. S.—LEE, S. T.: Diamond Relat. Mater., *9*, 2000, p. 134.
[5] KROMKA, A.—VEIS, P.—BEDERKA, S.: In : Proceedings ELITECH'99. The 2nd Conference on Electrical Engineering and Information Technology. Bratislava, STU 1999, p. 135.
[6] WANG, W. L.—LIAO, K. J.—GAO, G. C.: Surface Coat. Technology, *126*, 2000, p. 195.

[7] REINKE, P.—KANIA, P.—OELHAFEN, P.: Thin Solid Films, *270*, 1995, p. 124.
[8] ROBERTSON, J.—GERBER, J.—SATTEL, S.—JUNG, K.—EHRHARDT, H.: Appl. Phys. Lett., *66*, 1995, p. 3287.
[9] LEE, S. T.—LIN, Z.—JIANG, X.: Materials Science Engineering, *25*, 1999, p. 123.

Received: 7.5.2001
Revised: 26.6.2001