MECHANICAL PROPERTIES OF ULTRANANOCRYSTALLINE THIN FILMS DEPOSITED USING DUAL FREQUENCY DISCHARGES

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1. Introduction

The preparation of nanostructured (nanocomposite or nanocrystalline) diamond coatings is in a centre of a great industrial interest due to their extreme mechanical hardness and wear resistance, high bulk modulus, low compressibility, high thermal conductivity, low thermal expansion coefficient, broad optical transparency from the deep ultraviolet to the far infrared, high electrical resistivity, biocompatibility, etc[1–9]. Their main advantage compared to the polycrystalline diamond film is, that they can be prepared with relatively low surface roughness. Smooth diamond films with crystallite size at nanometre scale offer the potential for manufacturing a wide variety of components and structures of technological importance, with enhanced mechanical and functional properties, which cannot be realized in conventional microstructures.

The mechanical properties such as hardness, wear resistance, fracture toughness, film-substrate adhesion and thermo-mechanical stability of the coating-substrate system play always a crucial role for industrial applications of the coatings[10–13]. Therefore the main aim of the present work is to study the mechanical properties of ultrananocrystalline thin films using two different indentation techniques.

2. Experimental

The common type of microwave reactor ASTEX was used to deposit the studied films. In this reactor, microwaves are coupled into a water-cooled metal cavity through a quartz window, using an antenna, which converts the TE_{10} microwave mode in the wave-guide to the TM_{01} mode in the cavity. The inner chamber diameter is chosen so that only one microwave radial mode can be sustained in the cavity at 2.45 GHz. Substrates as large as 10 cm in diameter can be coated by positioning them on a heated stage beneath the plasma ball which forms immediately above it. This reactor was modified for the dual frequency application, i.e. application of RF power to a substrate holder to achieve the so-called bias-enhanced nucleation (BEN). The RF power of 35 W (13.56 MHz) was capacitively coupled to the central graphite plate of the substrate holder. Due to different mobility of electrons and ions this resulted in dc self-bias accelerating the ions across the sheath adjacent to the graphite plate, i.e. the substrate, causing them to sub-plant beneath the surface and create a carbon-rich layer in the topmost few layers of the substrate. This had two important effects, the initial nucleation rate was greatly increased, and the resulting diamond film was registered with the underlying substrate lattice to a much greater extent, allowing deposition of films with a preferred orientation to be grown. The orientation of diamond crystallites was studied using XRD technique.

The deposition was carried out on mirror polished (111) oriented n-doped silicon substrates in the mixture of methane (CH_4) and hydrogen (H_2) changing the CH_4 concentration. The supplied microwave power was 850 W and pressure in the reactor was 7.5 kPa. The substrate temperature, estimated by means of a pyrometer with disappearing filament, was kept in the range from 1090 to 1120 K.

A Fischerscope H100 depth sensing indentation (DSI) tester and Nano Indenter XP equipped with continuous stiffness measurement (CSM) were used to study the indentation response of ultrananocrystalline diamond films.

The optical measurements were done with Horiba Jobin Yvon ellipsometer in the spectral range from 190 to 2100 nm at the incidence angles from 55° to 75° and were evaluated using a dispersion model of optical constants based on the parameterisation of densities of states (DOS)[14].

3. Results and discussion

Nanostructured diamond films with different concentrations of methane (CH_4) in hydrogen (H_2) were studied in the present paper. According to Bachmann's[15] C-H-O gas phase concentration triangle the polycrystalline diamond can be deposited by CVD from the CH_4/H_2 gas mixtures, when the concentration of CH_4 is in the range from 1 to 3 %.

With increasing methane concentrations, the crystal sizes decrease, until above ca. 3 % CH_4 in H_2 the gas phase and the resulted films exhibit 'nanocomposite' structure and may be considered to be an aggregate of diamond nanocrystals and disordered graphite. If BEN is employed as well as growth conditions, which favour one particular orientation, highly textured films can be produced which are very closely aligned with the lattice of the underlying substrate. In case of the BEN technique the monitoring the self-bias voltage provides important information about the diamond growth. At the beginning ions impinge on the almost clean silicon surface and the self-bias voltage is nearly constant. After the surface is step by step filled by diamond nuclei the measured voltage de-

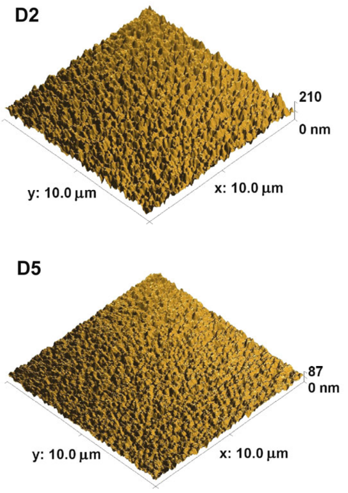

Fig. 1. **AFM images of the surfaces of sample D2 (2 % CH_4 in the deposition mixture) and D5 (10.4 % CH_4 in the deposition mixture). The analysis of AFM data yielded the RMS roughness 20.7 and 8.8 nm and autocorrelation lengths of 141 and 120 nm for D2 and D5, respectively**

creases. When the surface is completely covered the growth stage begins and the measured voltage is again constant. Sample D2 was deposited with 8.3 sccm of CH_4 mixed with 400 sccm of H_2, i. e. equivalent to 2.0 % of CH_4 in the gas phase. The nucleation stage was relatively long: it took 20 minutes. Sample D5 was, on the other hand, prepared from the mixture with higher C/H, 10.4 % (flow rates of CH_4 and H_2 were 41.7 and 400 sccm, respectively). The nucleation stage of the film D5 prepared with highest amount of CH_4 was 5 minutes.

In order to prepare the films with similar thickness in these two different gas mixtures the deposition time of the D2 and D5 was 28 and 15 min, respectively. AFM micrographs of the films D2 and D5 are shown in Fig. 1. They reveal a significant difference between the two films as concerns the surface topography. Especially in case of D5 the surface was relatively smooth and allowed optical measurements in the reflection mode. The analysis of AFM data yielded the RMS roughness 20.7 and 8.8 nm and autocorrelation lengths of 141 and 120 nm for D2 and D5, respectively.

Mechanical properties of the films D2 and D5 were studied by depth sensing indentation (DSI) test at several different final loads and by the continuous stiffness measurement (CSM) enabling the determination of the material properties continuously as the indenter moves into the surface, eliminating the need for unloading cycles. We studied not only the film hardness and elastic modulus, but also the film-substrate system indentation response in a wide range of indentation depths (20 to 3000 nm). Dependencies of the hardness and elastic modulus on the indentation depth obtained for samples D2 and D5 using these two techniques are shown in Figs. 2 and 3.

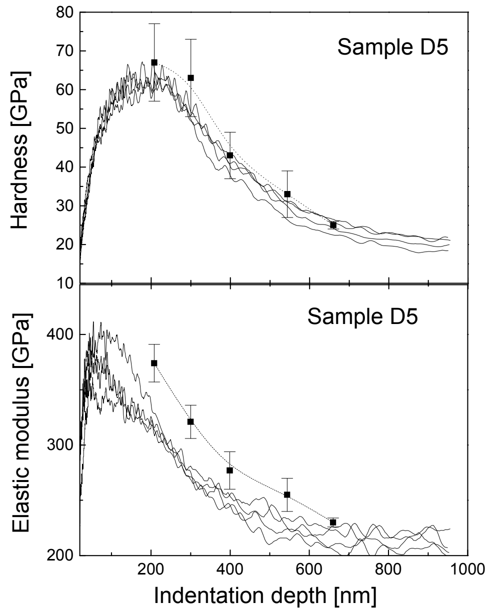

Fig. 2. **Results of mechanical tests obtained on D5 using DSI and CSM method. The lines in hardness and elastic modulus dependences belong to the selected measurements obtained using CSM technique, the scatter graphs belong to the results obtained using DSI technique**

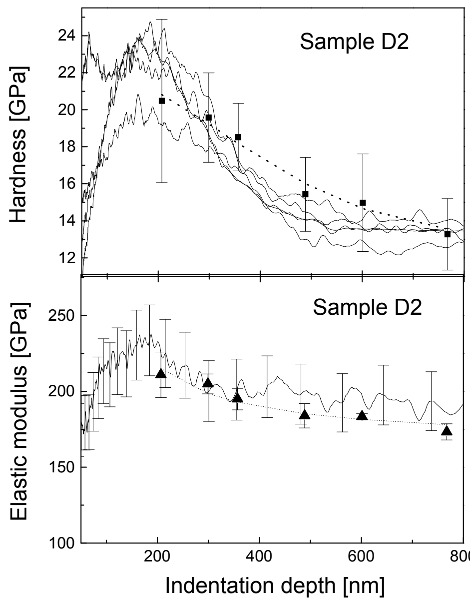

Fig. 3. **Results of mechanical tests obtained on D2 using DSI and CSM methods. The lines in hardness and elastic modulus dependences belong to the selected measurements obtained using CSM technique, the scatter graphs belong to the results obtained using DSI technique**

The influence of the substrate on the measured values was negligible up to 200 nm of indentation depth. With increasing indentation depth the influence of the substrate on the measured values increased. The combined effect of the film and substrate on the measured values of composite hardness H_c was modelled according to Battacharya and Nix[16]. The combined influence of the film and substrate on the measured elastic modulus was calculated according to Saha and Nix[17]. The results obtained with both DSI and CSM methods are in good agreement. The sample D2 exhibited the hardness around 20 GPa and elastic modulus of 220 GPa. Although the film D2 was deposited in "diamond yielding mixture" the low values of mechanical parameters suggest that it is rather a composite consisting of diamond crystals embeded in a disordered graphite matrix. The fact, that the results obtained by both DSI and CSM measurement were highly scattered confirm the previous assumption. The film D5 exhibited, on the other hand, relatively high hardness and elastic modulus of 65 and 375 GPa, respectively.

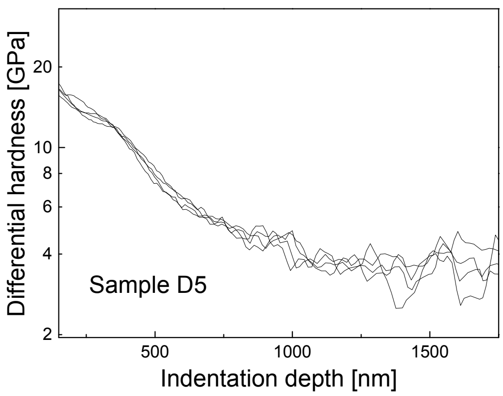

Fig. 4. **Differential hardness dependence on the indentation depth obtained on D5 using the Fischerscope tester**

Moreover, the film D5 exhibited high fracture toughness. In Fig. 4 the differential hardness $\partial L/\partial(h^2)$ (here L is the load and h is the indentation depth) dependence on the indentation depth is shown for sample D5 together with the SEM image of the indentation made at maximum load of 1 N. This dependence enables to visualise the crack creation, what appears on the dependence as an abrupt jump.

In case of the film D5 the ring/like through surface cracking begun (see SEM image in Fig. 5), when the indenter approached the film-substrate interface. We did not observe any cracks emanating from the indentation print corners or delamination around the indentation print even at indentation depths higher, than the film thickness.

For the evaluation of optical measurements on sample D5, the Rayleigh-Rice theory for roughness[18,19] and the dispersion model of optical constants based on the parameterisation of densities of states (DOS) were taken into account. The dispersion model was similar to that presented earlier for diamond like carbon films[18,19]. The refractive index was slightly lower than that of the natural diamond. The RMS

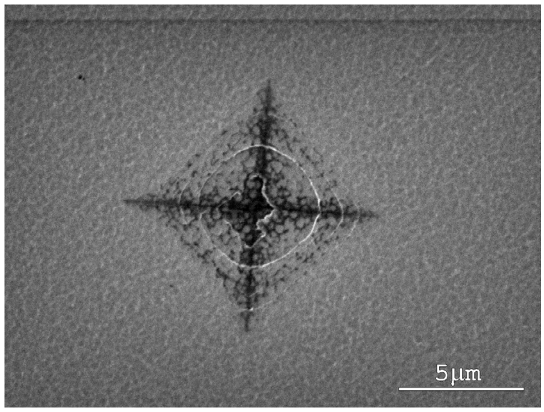

Fig. 5. **SEM image of the indentation carried out at maximum load of 1 N**

roughness and autocorrelation length for D5 were 9.1 and 73 nm, respectively. This is in a good agreement with the values found by AFM.

4. Conclusion

We have deposited a large set of diamond like carbon films with incorporation of silicon, oxygen and nitrogen. The optimum deposition conditions for deposition of smooth, hard, wear resistant thin films suitable for protection of the polycarbonate substrates were found. The film prepared under optimum conditions exhibited excellent fracture resistance and low intrinsic stress. The prepared films have all the properties needed for excellent protective coatings including high hardness, low friction coefficient, excellent chemical and thermal stability and transparency in the visible spectrum.

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V. Buršíková[a]*, O. Bláhová[b], M. Karásková[a], L. Zajíčková[a], O. Jašek[a], D. Franta[a], P. Klapetek[c], and J. Buršík[d] *([a] Department of Physical Electronics, Masaryk University, Brno, [b] University of West Bohemia, Plzeň, [c] Czech Metrologic Institute, Brno, [d] Institute of Physics of Materials, Academy of Sciences of the Czech Republic, Brno, Czech Republic):* **Mechanical Properties of Ultrananocrystalline Thin Films Deposited Using Dual Frequency Discharges**

The present paper describes the deposition of nanostructured diamond films with low surface roughness, high hardness and fracture toughness by microwave PECVD in the ASTeX type reactor from mixture of methane and hydrogen. Films were deposited on a mirror polished (111) oriented n-doped silicon substrate. The film exhibited relatively low roughness, the root mean square (RMS) of heights ranged from 20 to 9.1 nm, depending on the deposition conditions. The hardness was found to be in the range from 22 to 65 GPa and the elastic modulus ranged from 220 to 375 GPa, depending on the film structure.