CAPILLARY AND MECHANICAL PROPERTIES OF DOPED NANOCRYSTALLINE DIAMOND FILMS

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Introduction

To study the interaction of diamond films with liquid media as a function of the film surface chemical state is important for the film applications as electrochemical electrodes in electrochemistry, hermetic coatings for bioimplants, sensors. A possibility to grow diamond films with nanoscale grain size and their doping allows the development of materials with unique properties.

Here we present the data on wettability and mechanical properties of nitrogen-doped ultra-nanocrystalline diamond (UNCD) films as a function of the doping level and surface chemical modification (hydrogenation, oxidation).

Results and discussion

Smooth (surface roughness R_a<40 nm) UNCD films 0.8-3.5 μm in thickness with the grain size of the order of 10 nm were deposited onto Si substrates using a microwave plasma CVD in $Ar/2\%CH_4/5\%H_2$ mixtures with addition of N_2 in different concentrations - from zero to 25% in a manner close to that reported by D. Gruen [1].

Highly N-doped films were electrically conductive, with resistivity in the range of $10^0 - 10^{-2}$ Ohm_cm. The Raman spectra obtained at excitation wavelength 514,5 nm (Fig.1) showed three wide lines (1140 cm^{-1}, 1350 cm^{-1} and 1550 cm^{-1}) typical for nanocrystalline diamond.

We modified the film surface properties by oxidation in air (500ºC, 30 min) and hydrogenation in a microwave plasma (microwave power 3,6 kW, pressure 60 Torr, substrate temperature 600ºC, exposure time 15 min). The film topography was analyzed with an Ultra Objective atomic force microscope (SIS, Germany).

The contact angles on the films for the liquids of different polarities (water, μ = 1,84 D and glycerine, μ = 0,28 D) were measured by a sessile drop technique (drop diameter 0,5 – 1 mm) in air at room temperature 20±3 ºC.

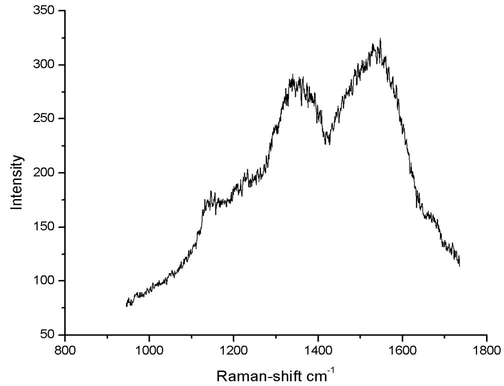

Fig.1. Raman spectrum of an UNCD film doped with 10% N_2.

The nanohardness tests were carried out using a Nano Indenter-II (MTS Systems Corporation) with a trihedral Berkovich indenter at maximum loads of 1 and 5 mN and the load rate of 0,2 mN/s. During the test the load-indenter displacement dependence was measured. The hardness was determined from the indent depth under the load, and the elastic modulus was found from the unloading curve. The accuracy of measurements of the indent depth and indentation load were ±0,04 nm and ±75 nN, respectively.

Our results show that the water contact angle (Fig. 2) on as-grown UNCD films monotonically decreases from 72º to 40º with the increase of nitrogen concentration in the gas mixture from 0 to 25%. Hydrogenation makes the film surface hydrophobic, which is caused by the surface passivation due to the hydrogen chemisorption. The effect is more pronounced for the low-doped films. The oxidation transforms the UNCD film surface into the extremely hydrophilic one (θ<5º) for all samples, which is caused by the surface activation due to chemisorption of oxygen–containing functional groups.

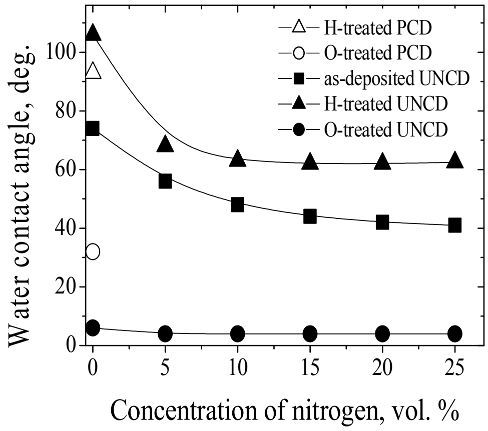

Fig. 2. Water contact angle on UNCD vs. nitrogen concentration in the gas mixture in comparison with the data for polycrystalline diamond (PCD) films [2].

It should be noted, that oxidized *poly*crystalline diamond films (see Fig. 2) and single crystals typically show much higher values (θ=32º) [2].

Adsorption of oxygen and oxygen-contained functional groups on the film surface is of critical importance for wettability with the water. The adsorptivity may be changed by film doping. The lower the Fermi level of the film surface, the lower the surface adsorptivity for acceptor (oxygen) molecules. The donor impurity (nitrogen) increases the Fermi level, intensifying the surface adsorptivity with respect to oxygen, which improves the wettability.

Mechanical tests have shown that the hardness and elastic modulus decrease with increase of nitrogen concentration in plasma during deposition process (Table 1, Fig 3). The maximum hardness (about 30 GPa) is for undoped films. It's assumed that N-content in the film correlates with that in plasma.

Table 1. Hardness and elastic modulus of UNCD films (at load of 5 mN).

N_2, %	E, GPa	H, GPa
0	248 ± 104	28,3 ± 16,6
5	329 ± 117	22,6 ± 6,7
10	340 ± 109	21,2 ± 5,0
15	290 ± 121	18,0 ± 4,9
20	179 ± 29	13,0 ± 4,1
25	136 ± 48	9,0 ± 4,0

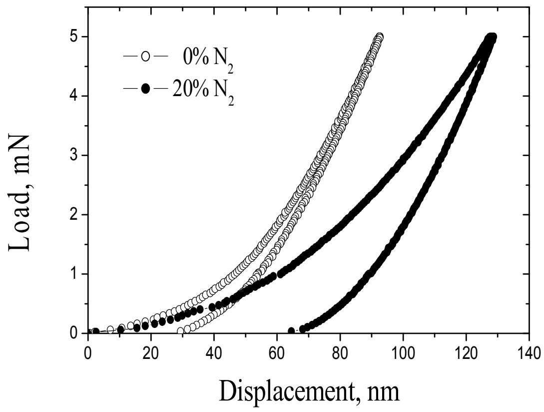

Fig. 3. Load-displacement curve for UNCD films grown at 0% and 20% N_2 content in plasma.

Summary and conclusions

On the whole, the tendencies of water wettability of chemically modified UNCD films similar with those observed earlier for diamond single crystals and PCD films [2]. However, the variations in the UNCD films wettability induced by treatments in oxygen and hydrogen are significantly wider than for PCD films because the structure of UNCD films is much more finely granular and developed, which affects the adsorption processes on the surface. The changes in electronic properties of UNCD by nitrogen doping may also play a role in adsorption process.

The appreciable surface roughness or very high hydrogen content of the film (up to 6 at%) leads to the underestimated values of hardness (the maximal value is 57,5 GPa) and elastic modulus.

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References

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