

Microwave PECVD of Nanocrystalline Diamond with RF Induced Bias Nucleation

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Nanocrystalline diamond film was deposited by microwave CVD in the ASTeX type reactor on a mirror polished (111) oriented n-doped silicon substrate. The deposition mixture consisted of 9 % of methane in hydrogen. The applied microwave power (2.45 GHz) and pressure were 850 W and 7.5 kPa, respectively. The substrate temperature was 1090 K. The diamond nucleation process was enhanced by rf induced dc self-bias of -125 V. The film exhibited very low roughness (rms of heights 9.1 nm). Its hardness and elastic modulus were 75 and 375 GPa, respectively. The optical constants were determined by combination of spectroscopic ellipsometry and reflectometry employing the Rayleigh–Rice theory for the roughness and the dispersion model of optical constants based on the parameterization of densities of states. The deposition rate was 57 nm/min including the 5 min nucleation step.

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1 Introduction

Nanocrystalline diamond (NCD) films are in the center of interest because they keep advantageous properties of polycrystalline diamond films without having their drawback - high surface roughness. Relatively smooth NCD films with crystal sizes in the nanometer scale range are highly desirable in e. g. tribological, optical, electronic and biomedical applications. There are several proposed ways how to deposit NCD by chemical vapor deposition (CVD). Most employed growth process is based

on inert gas dilution in conventional hot filament or microwave plasma CVD systems [1, 2, 3]. Other authors deposited NCD from the gas mixture rich of CO₂ [4] or applying a dc bias to the substrate in a hot flame system [5]. The bias enhanced nucleation (BEN) combined with a higher than normal C/H ratio during the nucleation phase was first time proposed for the CVD of diamond already by Yugo *et al.* [6]. Recently, Seo *et al.* [7] have shown that the rms roughness of NCD deposited by microwave CVD can be decreased down to 53 nm using this approach. In present paper we deposited NCD in microwave CVD enhanced by the dc self-bias that was induced by application of rf voltage to the substrate. We investigated an effect of methane/hydrogen ratio kept constant during both, the nucleation and growth phases.

2 Experimental

The experimental apparatus was a conventional bell jar (ASTeX-type) reactor [8] operating at the frequency of 2.45 GHz, modified for the application of rf power to a substrate holder. The deposition was carried out on mirror polished (111) oriented n-doped silicon substrates in the mixture of methane (CH₄) and hydrogen (H₂) changing the CH₄ 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. The rf power of 35 W (13.56 MHz) was capacitively coupled to the central graphite plate of the substrate holder (Fig. 1). The outer graphite ring served as a grounded electrode. 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. Ion bombardment, related to the dc self-bias, enhanced a necessary diamond growth nucleation step.

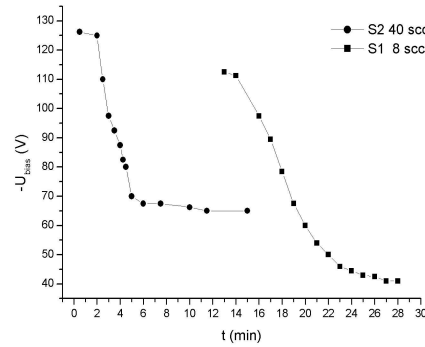
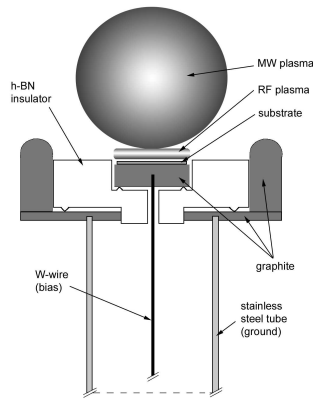


Fig. 1. Modified substrate holder

Fig. 2. Time dependence of the rf induced self-bias for bias enhanced nucleation.

The surface morphology of the deposited films was studied by scanning electron microscopy (SEM) with the JEOL 6460 and field emission cathode JEOL JSM 6700F microscopes. The surface morphology was quantitatively studied also by atomic force microscopy (AFM) with the scanning probe microscope Explorer. The root-mean square (rms) value of heights and autocorrelation length related to the surface roughness [9] were determined by the self-developed software, Gwydion. Mechanical properties such as film hardness and elastic modulus were determined by depth sensing microindentation with the FISCHERSCOPE H100 XYp tester. Optical constants, i. e. refractive index (n) and extinction coefficient (k), as well as film thickness were determined by the combination of variable angle spectroscopic ellipsometry and near-normal spectroscopic reflectometry. The spectral dependences of ellipsometric quantities were measured using the Jobin Yvon UVISEL spectroscopic ellipsometer within the wavelength region 230–850 nm. The spectral dependences of the reflectance were measured by the Perkin Elmer Lambda45 spectrophotometer 45 within the spectral region 190–1000 nm.

3 Results and Discussion

Two films, S1 and S2, with different concentrations of methane (CH_4) in hydrogen (H_2) were studied in present paper. According to Bachmann *et al.* [10] the polycrystalline diamond can be deposited by CVD from the gas mixtures defined by certain areas of the C-H-O gas phase concentration triangle. In the mixture containing solely C and H, the diamond may be grown only in the hydrogen-rich sector of this diagram where $\text{H}/(\text{H}+\text{C})$ is 0.98 at minimum. This means that for the CH_4/H_2 mixture the concentration of CH_4 should not exceed 4 %. Sample S1 was therefore deposited in 8.3 sccm of CH_4 mixed with 400 sccm of H_2 , i. e. 2.0 % mixture. Sample S2 was, on the other hand, prepared from the mixture with higher C/H, 9.4 % (flow rates of CH_4 and H_2 41.7 and 400 sccm, respectively). In order to prepare the films of similar thicknesses in these two different gas mixtures the deposition time of the S1 and S2 was 28 and 15 min, respectively.

In case of the BEN technique the monitoring of the self-bias provides important information about the diamond growth. Since the dc voltage with respect to the ground is measured outside the reactor its value is influenced by the growth of a dielectric diamond film. Time dependences of this voltage for both the studied depositions, S1 and S2, are shown in Fig. 2. In the first minutes, ions impinging on the almost clean silicon surface (first constant part of the graph) displace preferentially carbon atoms deposited in the form of sp^2 (graphite) and leave on the surface the majority of sp^3 carbon clusters (diamond nuclei) [11]. In next several minutes, the surface is filled by these diamond nuclei and the measured voltage decreases. When the surface is completely covered the growth stage begins (last constant part of the graph). Therefore, the voltage-time dependence inform us about the nucleation and is the first indication that the experiment can proceed towards a successful deposition of diamond film.

Comparing the voltage dependence on time for the depositions S1 (8.3 sccm of

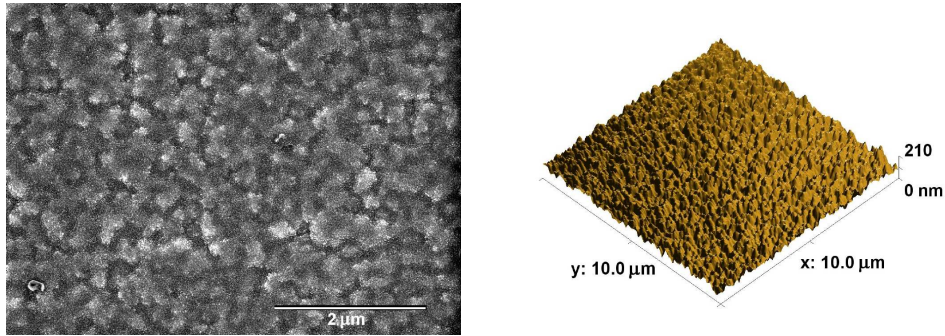


Fig. 3. SEM (left) and AFM (right) micrographs of sample S1 (8.3 sccm of CH₄).

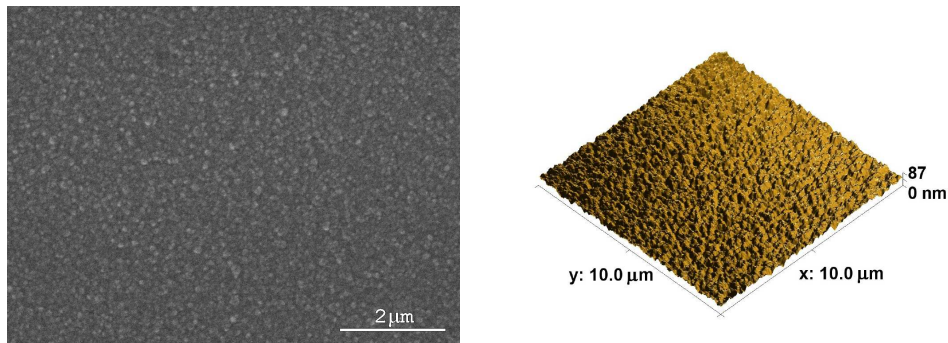


Fig. 4. SEM (left) and AFM (right) micrographs of sample S2 (41.7 sccm of CH₄).

CH₄) and S2 (41.7 sccm of CH₄) we can see that the nucleation phase was finished in between 15. and 20. minute for S1 whereas it took only 5 minutes in case of S2. SEM and AFM micrographs of the films S1 and S2 are given in Figs. 3 and 4, respectively. They revealed a significant difference between these two films as concern the surface topography. Especially in case of S2 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 S1 and S2, respectively.

For the evaluation of optical measurements on sample S2, the Rayleigh–Rice theory for roughness [12] and the dispersion model of optical constants based on the parameterization of densities of states (DOS) were taken into account. The dispersion model was similar as that presented earlier for diamond like carbon films [13]. The paper dealing with more detailed analysis of the optical characterization of the NCD films is under preparation. Spectral dependencies of optical constants, n and k , for the film S2 are shown in Fig. 5. The refractive index was slightly lower than that of natural diamond (compare obtained 2.28 with tabulated 2.417 at 589.3 nm). The rms roughness and autocorrelation length for S2 were 9.1 and 73 nm, respectively. This is quite good agreement with the values found by

AFM. The film thickness evaluated from the optical measurements was 856 nm.

Mechanical properties of the films S1 and S2 were studied by depth sensing microindentation at different final loads. The dependencies of the hardness and elastic modulus of the whole system, i. e. a diamond film on the silicon substrate, on the load are in Fig. 6. The sample S1 exhibited the hardness below 20 GPa and elastic modulus of 180 GPa. The film thickness estimated from the load dependencies was 100–200 nm. Although the film S1 was deposited in "diamond yielding mixture" the low values of mechanical parameters suggest that is rather a composite consisting of diamond crystals embedded in a graphite matrix. The film S2 exhibited, on the other hand, relatively high hardness and elastic modulus of 75 and 375 GPa, respectively.

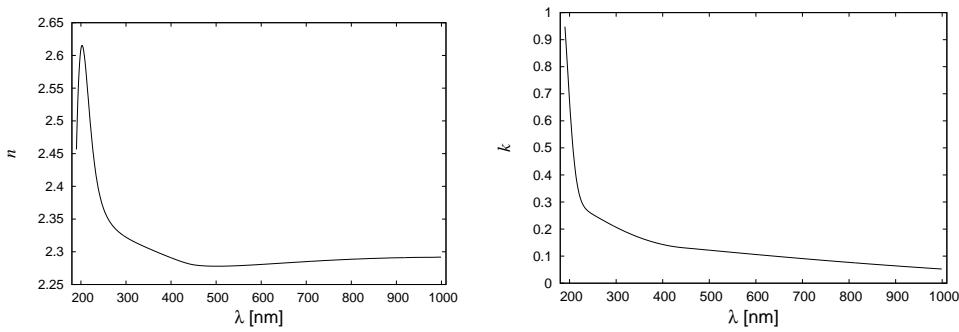


Fig. 5. Spectral dependencies of refractive index (left) and extinction coefficient (right) of nanocrystalline diamond film S2.

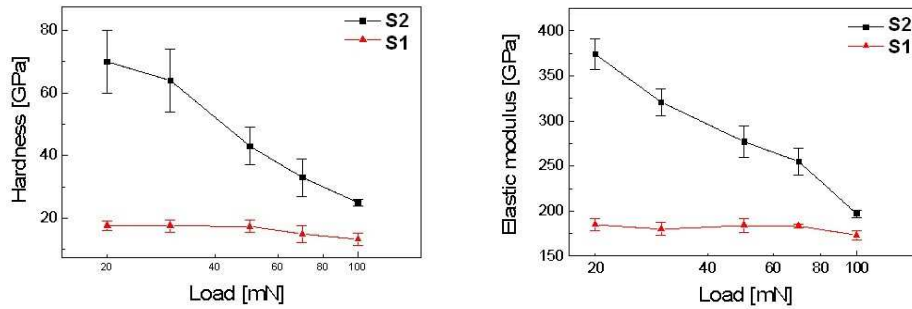


Fig. 6. Load dependencies of hardness (left) and elastic modulus (right) measured by depth sensing indentation technique on samples S1 and S2.

4 Conclusions

We have successfully deposited nanocrystalline diamond film using microwave PECVD process in the 9 % CH₄/H₂ mixture with bias enhanced nucleation step.

The film exhibited very low roughness (rms of heights 9.1 nm). Its hardness and elastic modules were 75 and 375 GPa, respectively. The deposition rate was 57 nm/min including the nucleation step of 5 min.

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