Characterization of nanocrystalline diamond/amorphous composite carbon films prepared by PECVD technology


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Abstract

Nanocrystalline diamond/amorphous composite carbon films were deposited by plasma enhanced chemical vapour deposition method. The concentrations of species in the films were determined by RBS (Rutherford backscattering spectrometry) and ERD (elastic recoil detection) methods. The RBS results showed the main concentrations of C in the films. The concentration of hydrogen was approximately 20 at.%. Chemical compositions were analyzed by FTIR spectroscopy. IR results showed the presence of C-H specific bonds. Film was used for photocathode application. The original quantum efficiency of prepared photocathode at energy of FH 15,6 mJ was 1,43x10⁻⁶  %.

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1. Introduction

Nanocrystalline diamond, ultrananocrystalline diamond or amorphous carbon embedded NCD (NCD/a-C) films, have advantages of having higher surface flatness, high hardness, high wear resistance, high thermal conductivity, low friction coefficient, high electrical resistance, high optical transparency, high electron emission efficiency and excellent chemical inertness. The properties of deposited films are generally characterized by powerful ex-situ techniques that are commonly available, for instance Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM), Transmission Electron Microscopy (TEM), Raman spectroscopy or X-ray Diffraction (XRD). Diamond films have been extensively investigated in field electron emission (FEE) [1], [2]. J.E. Yater et al. showed that grains may impede electron transport in diamond films and argued that the reduction of grain sizes is important for diamond film to be used as a cold cathode electron source [3]. This mechanism is actually similar as recently proposed conduction channel model, in which the grain boundary area can act as electron conduction channel in

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diamond field electron emission. In the electron conduction model, the diamond grain boundary plays the main role, as grain boundaries of diamond film consist of sp² phase. The sp²-bonded regions are of low electrical resistivity and act as an electron transport path, which facilitates the field electron emission. The plasma was electrically studied by a Langmuir probe in PECVD system [4]. There are several carbon-based photo cathodes, like polycrystalline diamond, hydrogenated amorphous carbon and nanostructured fullerene films. Polycrystalline diamond photocathodes are chemically inert, have a high damage threshold but also a low QE of 10⁻⁶. Hydrogenated diamond photocathodes have the highest QE’s of 8·10⁻⁴ for 213 nm wavelength, but have low damage threshold and become oxidized after irradiation.

In this study, we investigated properties of nanocrystalline diamond/amorphous composite carbon (NCD/a-C) films prepared by plasma enhanced chemical vapor deposition (PECVD). The properties of films were investigated by RBS, ERD and IR measurement techniques. Property of prepared photocathode was performed by measurement of quantum efficiency.

2. Experiments

The methane was introduced into capacitively coupled plasma reactor through the shower head, which is also an upper electrode with 20 cm diameter. Gas was flown vertically toward the substrate on bottom electrode connected with RF power 150 W and frequency 13.56 MHz. A p-type silicon wafer with resistivity 2-7 Ωcm and (100) orientation was used as the substrate for the carbon films. Prior to deposition, standard cleaning was used to remove impurities from the silicon surface, and the 5% hydrofluoric acid was used to remove the native oxide on the wafer surface. The wafer was then rinsed in deionized water and dried in nitrogen ambient. The flow rate of CH₄ gas was 40 sccm. The deposition temperature was for sample P1 – 400 °C and P2 – 500 °C. Spectroscopic ellipsometry was used for film thickness measurements and results are: for samples P1 -315 nm and P2 -325 nm. The concentration of species in the carbon films was determined by Rutherford backscattering spectrometry (RBS). Chemical compositions were analyzed by infrared spectroscopy. The concentration of hydrogen was determined by the elastic recoil detection (ERD) method. For this purpose the ⁴He⁺ ion beam from a Van de Graaff accelerator at JINR Dubna was applied. The energy of E = 2.3 MeV was chosen. The target was tilted at an angle α = 15° with respect to the beam direction and the recoiled protons were measured in forward direction at an angle θ₁ (30°) by a surface barrier detector. The quantum efficiency (QE) testing of prepared photocathode was performed at JINR. At one side of the cathode test facility vacuum chamber a fused silica window is mounted that transmits UV light. The vacuum condition was 4x10⁻⁹ mbar. The 15 ns UV laser pulses (quadrupled Nd:YAG laser) are used to illuminate the (NCD/a-C) film as photocathode. Laser spot size 5 mm. During testing, the laser energy was monitored using a calibrated portion of the signal that was picked off from the main beam. To draw the electrons from the cathode a positive voltage was placed on the anode-extractor. This voltage was kept at roughly 5 kV. The photocathode current is measured by using an oscilloscope.

3. Results and discussion

An example of plasma optical emission spectrum generated by a CH₄ glow discharge is shown in Fig. 1. By using OES the CH(X²Π) radical number density using actinometry method and plasma composition are determined [5]. Figure 2 a) show RBS spectra of two samples P1 and P2 with different deposition conditions of the deposited carbon films. The (NCD/a-C) films contained C, H and also other species which were under the detection limit of RBS method. In Fig. 2 b) are plotted ERD spectra obtained from the deposited layers which contain different amounts of incorporated hydrogen. From ERD measurement, it follows that the concentration of hydrogen in thin films depends on the deposition conditions. ERD analyses made on prepared layers show that amount of incorporated H was decreased from 21 at.% to 17 at.% with increasing of deposition temperature. The values were obtained by computer modeling of measured spectra and compared with the results obtained from the Si reference sample implanted with H. In the case of sample P1 the concentration of hydrogen and carbon are 21 and 75 at.% respectively. The concentrations of H and C in sample P2 are 17 and 77 at.%, respectively. The FTIR spectra, figure 3, revealed the main absorption region between 1200-1600 cm⁻¹ and 2800-3150 cm⁻¹. The most important result is that the sp³ hybridization is stronger in the sample deposited at higher temperatures.
Fig. 1. Optical emission spectrum of CH$_4$ glow discharge at 10 Pa with small amount of Ar for actinometry method.

Fig. 2. RBS spectra of (NCD/a-C) films deposited onto a silicon substrate a) and ERD spectra of recoiled hydrogen obtained with 2.3 MeV $^4$He$^+$ b). The spectra were measured on (NCD/a-C) films deposited at different temperature.
Fig. 3. The IR spectra of a-C:H films for samples P1(400 °C) and P2(500 °C) in the range of 1200-1600 cm⁻¹ and 2800-3150 cm⁻¹.

At lower wave numbers for the low temperature sample the sp² CH olefinic related peak is more pronounced compared to the high temperature case. For both samples beside the sp³ bonds sp² and graphite like related peaks can be assigned. In FTIR-SE, as in the case of SE the parameters ψ and Δ are defined from the ratio ρ of the complex reflection coefficients for s and p polarization, respectively [6].

The photocathode current is measured by using an oscilloscope as a voltage on resistance 47 Ω, see Fig.4. QE is defined as ratio of numbers of emitted electrons and injected laser photons. QE in % is expressed with the conventional parameters as QE [%] = 123,8 I / λP, where I is emitted current of the electron beam in mA, λ is wave length of the laser light in nm, P is power of the laser light in Watt. In our case: I = 0.85 A; λ = 266 nm; P = 0.4 MW. The original quantum efficiency at energy of FH 6 mJ had been 1x10⁻³ %.

Fig. 4. The (NCD/a-C) photocathode current pulse-red line and synchronization pulse-blue line.
4. Conclusion

The RBS results showed that the concentration of C in the films dependent a little on the deposition temperature. The concentration of hydrogen dependent on deposition temperature and increases from 17 to 24 at.% with decreasing of deposition temperature. The results presented above demonstrate that 2.3 MeV $^4$He$^+$ ERD analyses may be successfully used to measure the hydrogen concentration. FTIR results showed the presence of C-H specific bonds. The original quantum efficiency of prepared photocathode at energy of FH 6 mJ was $1\times10^{-3}$ %.

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