

Plasma enhanced chemical vapor deposition of deuterated diamond like carbon films for photocathode application

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Abstract: The influence of diamond like carbon films properties on quantum efficiency of prepared transmission photocathodes has been investigated. DLC films were deposited on silicon substrate and stainless steel mesh by PECVD using methane, argon and hydrogen or deuterium gas mixtures. Photocathodes prepared with deuterated DLC film have higher quantum efficiency than photocathodes prepared with hydrogenated DLC film and photocathode quantum efficiency rise up with deuterium and hydrogen flow rate.

Keywords: diamond like carbon films, plasma deposition, transmission photocathode

1. Introduction

Diamond-like Carbon (DLC) is a disordered carbonaceous material composed of hydrogen and carbon, which is bonded in sp^2 and sp^3 electronic configurations. The properties of diamond-like carbon (DLC) are strongly affected by the amount of carbon atoms bonded in sp^2 and sp^3 electronic hybridizations. Also the amount of incorporated hydrogen and oxygen plays an important role in the final properties of DLC films [1]. The film deposition process is usually achieved using empirical methods. Plasma-enhanced chemical vapor deposition (PECVD) with mixed gases containing H_2 and hydro-carbons such as CH_4 is often employed for film deposition [2]. When using CH_4/H_2 as a source gas to prepare a-C:H films, the origin of the H in the films is often unknown. The H may originate from H_2 or from CH_4 . Deuterium (D) is useful for investigating H incorporation into a-C:H films. The probability of dissociation would be different on D_2 and H_2 because of their different dissociation energies (36113 cm^{-1} - H_2 ; 36743 cm^{-1} - D_2), but D would help understand H attitude during the deposition from CH_4/H_2 [3]. Deuterated amorphous carbon films (a-C:D) deposited by plasma enhanced chemical vapor deposition (PECVD) using deuterated hydrocarbons as precursor gases were investigated [4] and some specific applications, like storing ultra cold neutron devices [5] or neutron mirror [6] were published. Electron field emission from diamond, diamond like carbon, carbon nanotubes and nanostructured carbon is compared [7]. Electron emission from carbon materials has been based on two effects: field enhancement from conducting nanostructures and barrier lowering due to the negative electron affinity of diamond surfaces [8]. The results of the external Quantum Efficiency (QE) measurements, in the range 150–210 nm, of Poly-, Nano- and Single-Crystalline Diamond (PCD,

NCD and SCD) film photocathodes (PCs) are reported and discussed [9].

In this paper, the influence of diamond like carbon films properties on quantum efficiency of prepared transmission photocathodes based on stainless steel mesh coated with DLC film were investigated. DLC films were prepared by standard PECVD technology with deuterium and hydrogen as reactive gas. The properties of films were investigated by RBS, ERD and RAMAN measurement techniques. Properties of prepared photocathodes were performed by measurement of quantum efficiency.

2. Experiment

Diamond like carbon films were deposited on silicon (Si) substrate and stainless steel mesh by plasma enhanced chemical vapor deposition (PECVD) from gas mixture CH_4+D_2+Ar and CH_4+H_2+Ar . Mesh grid: stainless steel wire with diameter 0.03 mm; the size of a cell 0.04 mm. Prior to deposition, standard cleaning was used to remove impurities from the silicon surface and stainless steel mesh. Before film deposition Si substrate and mesh was cleaning in argon RF plasma at $U_{sb}=-400\text{ V}$, 10 minutes. The methane, deuterium (hydrogen) and argon were introduced into reactor through the shower head. Gases were flown vertically toward the samples on bottom electrode connected with RF power 150 W at frequency 13.56 MHz. The flow rates of CH_4 , $D_2(H_2)$ and Ar gases were 15 sccm, 8 sccm and 10 sccm, respectively for sample PD1(PH1), 15 sccm, 16 sccm and 10 sccm, respectively for sample PD2(PH2) and 15 sccm, 24 sccm and 10 sccm, respectively for sample PD3(PH3). Deposition pressure was 10 Pa. The substrate holder temperature during deposition was $100\text{ }^\circ\text{C}$. DLC films were deposited on both size of mesh at the same deposition conditions. DLC films on Si substrate were used for structural characterisation as PD and PH sample. Stainless steel mesh

with DLC films were used for PD and PH transmission photocathode. Concentrations of elements in the films were analyzed using Rutherford backscattering spectrometry (RBS) and elastic recoil detection (ERD) analytical method simultaneously. Raman measurements of DLC films were performed by using a Thermo Fisher Scientific DXR Raman microscope with 532 nm laser. The G and D peaks were fitted with two Gaussians and the intensity is calculated as the peak's area. The transmission DLC coated mesh type photocathode quantum efficiency testing was performed at JINR Dubna. The 15 ns UV laser pulses (quadrupled Nd:YAG laser, 266 nm) with laser spot size ≤ 5 mm are used to backside illuminate the DLC film coated mesh as photocathode. To draw the electrons from the DLC film coated mesh photocathode a negative voltage was placed on the cathode. This voltage was kept at roughly 10-12 kV. The bunch charge is measured by using Faraday cup (FC). The FC was connected to the ground through the measuring capacitor with a math cable; voltage on charging capacity (U_c) was monitored by 500 MHz oscilloscope.

3. Results and discussion

The concentrations of species in samples are presented in Tab. 1. From the concentration results for PD samples we can conclude that the concentration of carbon and deuterium increase with increase deuterium flow rate and eliminate concentration of hydrogen. In the case of PH samples concentration of elements in the films were very similar. Figure 1 shows the measured and simulated RBS and ERD spectra for samples PD2 and PH2. In Fig. 1 (a), we can see the leading edge at ~ 500 ch corresponding to the Si at the interface of the film. The slight difference of the edge position between the samples can be attributed to differences in film thickness. The peaks corresponding to C are observed on the profile of the bulk Si at around ~ 320 ch. Two peak-like profiles were observed in the ERD spectra (Fig. 1 (b)) for sample PD2. H and D appeared at different channels because of differences in the

Table 1 Concentration of species in DLC films determined by RBS and ERD methods.

Sample	C (at.%)	D (at.%)	H (at.%)	O (at.%)
PD1	65	14	19	1-2
PD2	67	17	14	1-2
PD3	69	18	11	1-2
PH1	68	-	30	1-2
PH2	68	-	31	1

PH3	70	-	30	-
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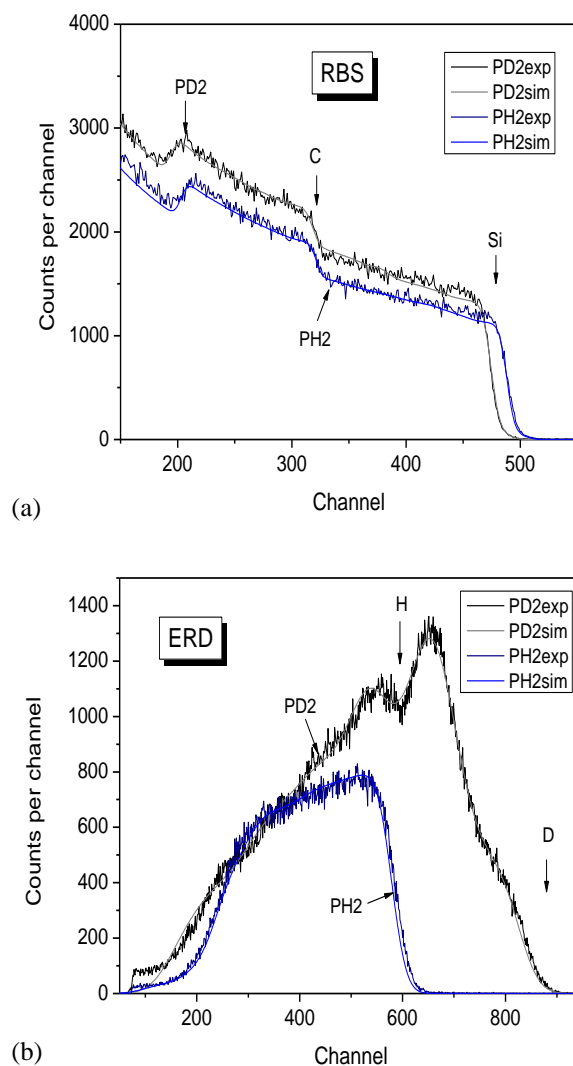


Fig. 1 Experimental and simulated spectra RBS (a) and ERD (b) for samples PD2 and PH2.

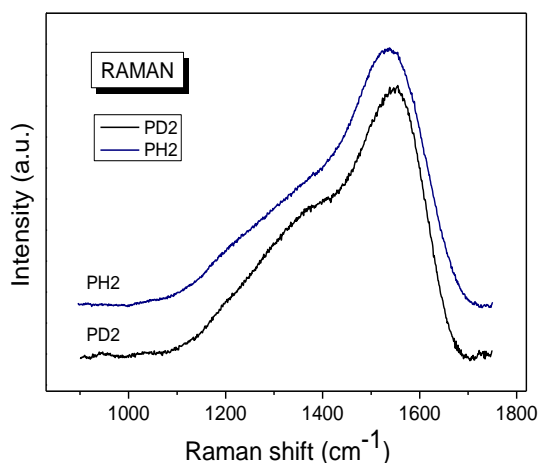
mass ratio. The leading edge of H occurred at approximately ~ 640 ch, whereas the leading edge of D occurred at approximately ~ 890 ch. Figure 2a) shows the experimental correct baseline Raman spectra of samples PD2 and PH2. All disordered carbons show common features in their Raman spectra in $800\text{--}2000$ cm^{-1} region, the so called G and D peaks, which lie at around 1560 and 1360 cm^{-1} , respectively, for visible excitation. The G peak is due to the bond stretching of all pairs of sp^2 atoms in both rings and chains. The D peak is due to the breathing modes of sp^2 atoms in rings and it is activated by disorder [10]. Figure 2b) shows Raman spectrum of deuterated DLC film on Si substrate, sample PD2, which were Gaussian-fitted and identified as D and G band conversion. We used only two main peaks Gaussian

fitting. The G peak and D peak are located at the two positions 1553 cm^{-1} and 1385 cm^{-1} , respectively. The intensity ratio $I(D)/I(G) = 1.493$, and was determined after fitting analysis of the spectrum. The peaks position and intensity ratios are presented for all samples in Tab. 2. In the case of samples PD the G peak position was found to shift to higher frequencies than in the case of sample PH. This can be attributed to the reduction of sp^2 sites of aromatic rings. The D peak position was found to shift to higher frequencies for samples PD than in the case of sample PH. In general, the D peak position will increase with increasing disorder for the double-Gaussian fit. Two factors can shift the D peak. On one hand, smaller aromatic clusters have higher modes and shift D upwards. On the other hand, a decrease in number of ordered aromatic rings on passing from nanocrystalline graphite to a-C lowers D and reduces its intensity, due to softening of the vibrational density of states. From the Raman spectra, $I(D)/I(G)$ ratio is higher for the samples PD prepared with deuterium gas.

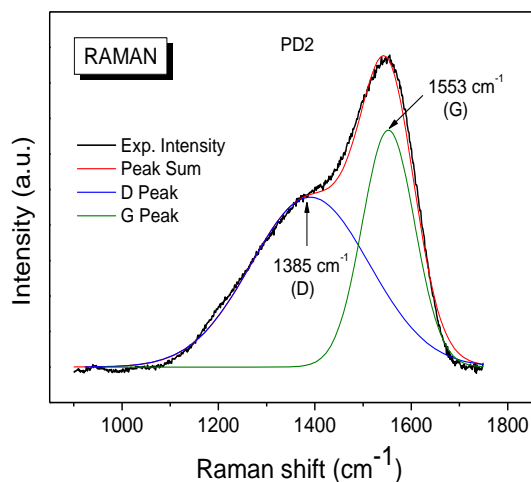
DLC films for samples PD2, PH2 (a) and Raman spectrum of sample PD2 (b) with fitting of the experimental curve by Gaussian center G and D.

Table 2 Raman spectroscopy results, D and G peak positions and $I(D)/I(G)$ ratio.

Sample	D - peak position (cm^{-1})	G - peak position (cm^{-1})	Intensity ratio $I(D)/I(G)$
PD1	1382	1551	1.443
PD2	1385	1553	1.493
PD3	1390	1556	1.541
PH1	1375	1544	1.133
PH2	1377	1545	1.211
PH3	1381	1553	1.498



(a)



(b)

Fig. 2 Experimental (correct baseline) Raman spectra of

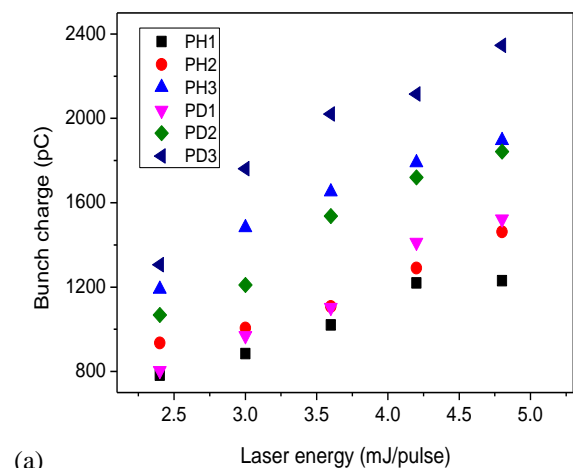
Figure 3a) shows the bunch charge as a function of the laser energy for all prepared photocathodes. The bunch charge increased from 1068 to 1842 pC as the laser energy increased from 2.4 to 4.8 mJ for PD2 photocathode. In the case of PH2 photocathodes, the bunch charge increased from 935 to 1462 pC. For PD and PH photocathode the bunch charge increase with increasing flow rate of deuterium or hydrogen, respectively. Increase in the laser energy indicates increase in the number of photons causing photoemission, which leads to the increase in the number of photoelectrons produced at the cathode surface. The bunch charge intensity trend of the six type photocathodes reported in Fig. 3 evidences a dependence of the photoemission properties on the graphitic component inside the DLC films.

The quantum efficiency was calculated from the measured laser energy and the measured cathode charge using the formula:

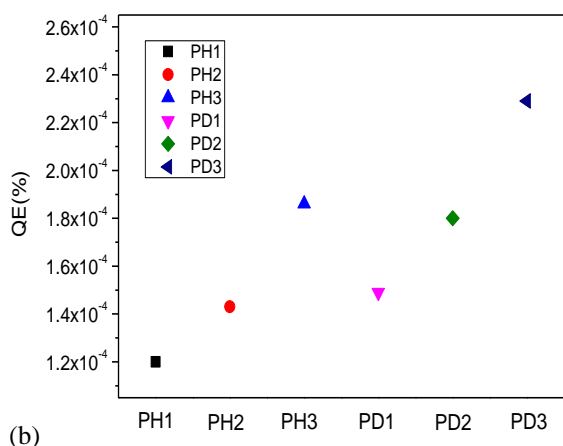
$$QE = \text{Charge} / (\text{Laser Energy}) \times (\text{Photon Energy}),$$

where the photon energy is 4.66 eV for the quadrupled Nd:YAG laser at wavelength 266 nm. The quantum efficiency had been 2.29×10^{-4} (PD3 photocathode), 1.8×10^{-4} (PD2), 1.49×10^{-4} (PD1) and 1.86×10^{-4} (PH3 photocathode), 1.43×10^{-4} (PH2), 1.2×10^{-4} (PH1). Figure 3b) shows the quantum efficiency as a function of technology parameters of prepared photocathode. On the basis of the present results it can be conclude that the QE of PD photocathodes is higher than QE of PH photocathodes at the same flow rate of deuterium or hydrogen. Moreover, QE results can be also directly connect with the intensity $I(D)/I(G)$ ratio of D and G peaks in Raman spectra. The intensity $I(D)/I(G)$ ratio of PD films is higher than for PH films at the same flow rate of deuterium or hydrogen. $I(D)/I(G)$ ratio can indirectly determine the content of sp^2

and sp^3 bonds. However, higher value of $I(D)/I(G)$ ratio corresponds with higher quantum efficiency of diamond like carbon film coated mesh type transmission photocathode. The emission mechanism in DLCs has been difficult to understand. Experimental evidence suggests that the main barrier to emission in DLC is large and at the front surface. The barrier lowering requires some types of heterogeneity [2]. In our case, the obtained results show, that heterogeneity can be deliberately introduced into DLC by deuterium mix in working gases.



(a)



(b)

Fig. 3 Bunch charge versus laser energy for all photocathodes (a), quantum efficiency as a function of parameters technology of DLC film coated mesh type transmission photocathodes (b).

4. Conclusions

We have investigated the structural properties of DLC films prepared by plasma enhanced chemical vapor deposition with deuterium and hydrogen in gas mixture on Si substrate and stainless steel mesh for transmission photocathode. RBS and ERD analysis indicated that the films contain carbon, hydrogen, deuterium and small amount of oxygen. Raman spectra of DLC films show the D and G

band conversion which were Gaussian-fitted and identified. In the case of samples PD the G peak position was found to shift to higher wave number than in samples PH at the same flow rate of deuterium or hydrogen. The D peak position was found to shift to higher frequencies for samples PD than in the case of samples PH. In general, the D peak position will increase with increasing disorder for the double-Gaussian fit. The emission process from diamond like carbon films, excited with near-UV radiation, seems to be governed mainly by the intensity ratios $I(D)/I(G)$. A further study is underway to investigate the nature of deuterium on the structural and surface properties of deuterated DLC film together with the quantum efficiency of prepared DLC coated mesh type transmission photocathode.

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