PHOTO-INDUCED ELECTRON EMISSION OF NANOSTRUCTURED CARBON THIN FILM BASED TRANSMISSION PHOTOCATHODES AT DIFFERENT ELECTRIC FIELD

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Abstract. Very thin nanostructured carbon films were deposited on quartz substrate by reactive magnetron sputtering using graphite target and gas mixture of Ar and reactive gas N2 or N2+H2. Film thicknesses were in the range of 20–25 nm. Rutherford backscattering spectrometry and Elastic recoil detection analytical method determined the concentration of elements in the films. Scanning electron microscopy scanned the surface morphology of carbon films. Raman spectroscopy was used for chemical structural properties determination of very thin carbon films. Raman spectra intensities were fitted with Gaussian peaks. The photo-induced (pulsed laser - 266 nm) electron emission properties of very thin nanostructured carbon films were investigated by the measurement of cathode bunch charge at different electric field and calculate quantum efficiency. The influence of different electric field on the photo-induced electron emission characteristics of prepared transmission photocathodes are discussed.

Keywords

Electric field, electron emission, magnetron sputtering, nanostructured carbon film.

1. Introduction

For each accelerator facility, e.g. the future electron-ion collider and the light source, the development of the photo injector is a key technology. Carbon-based materials are suitable thin film photocathode to use in electron emitting structures. Amorphous and nanocrystalline carbon films can exist in different kinds of matrices. Upon investigating the field emission behaviours of graphite-like carbon film, amorphous carbon film, and graphene sheets embedded carbon film, graphene sheets embedded carbon film exhibited an enhanced performance [1]. Compares the electron field emission from nanostructured carbon, diamond, diamond-like carbon, and carbon nanotubes [2]. Microwave plasma chemical vapour deposition deposits diamond-graphite nanohybrid films on Si substrates. An increase of deposition temperature from 730 °C to 830 °C leads to remarkable changes in morphology and microstructure, namely from a typical planar UltraNanoCrystalline Diamond (UNCD) film at 730 °C to a novel Nanocrystalline Diamond/Graphene NanoWall (ND/GNW) film at 830 °C. Moreover, the electron field emission is significantly enhanced on a ND/GNW film [3]. The carbon nitride was synthesized using microwave plasma...
chemical vapor deposition from a CH$_4$–N$_2$ gas system. Crystalline carbon nitride is expected to be an emitter with a high emission stability and a long lifetime, because it is composed of carbon and nitrogen with high oxidation resistance and its sharp shape facilitates the occurrence of electron emission [4]. Plasma-Enhanced Chemical Vapor Deposition (PECVD) technique with gas mixtures CH$_4$+D$_2$+Ar, CH$_4$+H$_2$+Ar and reactive magnetron sputtering using a pyrolytic graphite target and gas mixtures Ar+D$_2$, Ar+H$_2$ were used for diamond-like carbon films deposition on the stainless-steel mesh to use it for the transmission photocathode fabrication [5]. Q-carbon composite structures was formed by pulsed laser annealing of amorphous carbon films. The electron field emission properties of the Q-carbon were improved with temperature by lowering the turn-on field and increasing the current density [6] and [7]. The performances and operation lifetime of field emission cathodes made by spray-coating, three different nanocarbon materials: Carbon NanoTubes (CNTs), Carbon NanoCoils (CNCs) and Graphene (GE), were compared. The CNTs had the benefits of the lowest turn-on field, CNCs exhibited the most stable cycle-to-cycle repeatability and a significantly longer life-time than CNTs and GE under a continuous high-current-density operation [8]. The calculations reveal that graphene edges functionalized by H, OH, and COOH results in relatively large emission current for a wide range of electric field. Potential barrier decreased caused by the dipoles compared before functionalization [9]. Photocathodes composed of rich-graphite and rich nanodiamond films were deposited by pulsed spray technology on different conductive substrates. The photocathodes quantum efficiency values at 140 nm working in reflection mode was in the range from 26.8 to 47 % [10]. Authors investigated pulsed-laser-induced electron emission properties of very thin nanostructured carbon films deposited by reactive magnetron sputtering technology on quartz and sapphire substrates. Prepared transmission photocathodes on sapphire substrates exhibited better results than those prepared on quartz substrates [11]. Raman spectroscopy is generally used to characterize all carbon materials from zero to three dimensions (0D, 3D), such as 0D fullerenes, 1D carbon nanotubes, 2D graphene, and 3D graphite or diamond [12]. Pulsed laser induced electron emission from materials is interesting for fundamental and applied research. Intense electron beam sources with bunches having a small emittance and large charge required to obtain high-brightness and high-power radiation for electron-positron colliders and for other application [13].

The aim of this paper is to study the performance of very thin nanostructured carbon (ns-carbon) film-based transmission photocathodes at different electric field. Carbon films were prepared by reactive magnetron sputtering using argon and nitrogen or nitrogen + hydrogen as reactive gases. RBS (Rutherford Backscattering Spectrometry), ERD (Elastic Recoil Detection), SEM (Scanning Electron Microscopy) and Raman techniques were used to investigate the structural properties of films. The photo-induced electron emission properties of ns-carbon films were investigated by measurement of the bunch charge and calculate Quantum Efficiency (QE).

2. Experiment

Very thin ns-carbon films were prepared on quartz substrates by reactive magnetron sputtering using argon (flow 30 sccm) and nitrogen (8 sccm) or nitrogen (8 sccm) and hydrogen (flow 3 or 6 sccm) as reactive gases. Magnetron target was high purity pyrolytic graphite of 76 mm in diameter and 3 mm thick planar disk. The substrate and target were separated by 80 mm. The vacuum chamber was pumped down to 5 · 10$^{-4}$ Pa by a turbomolecular pump. Substrate holder temperature for samples were: QO1–600 °C, QO2–700 °C, QO3–800 °C, QO4–900 °C, QH1–800 °C (hydrogen flow 3 sccm) and QH2–800 °C (hydrogen flow 6 sccm). Carbon film was deposited at a working pressure 0.7 Pa and magnetron input RF power 150 W at 13.56 MHz. A quartz crystal thickness monitor tracked the film thickness during magneton sputtering. Film thickness was in the range 20–25 nm. Concentration of elements in the films was determined by RBS and ERD analytical methods. SEM (HV = 30 kV) scanned surface morphology of very thin ns-carbon films. Raman spectroscopy using a Raman microscope with 532 nm wavelength laser at power 3 mW was used to determine structural chemical properties of ns-carbon films. Raman spectra were acquired from 850 to 3750 cm$^{-1}$. The D band, G band and 2D band were fitted with Gaussian peaks. The backside illuminated transmission photocathode testing was performed at JINR Dubna [14]. To draw the electrons from the ns-carbon film coated quartz transmission photocathode a negative voltage was applied on the cathode to obtain electric field 0.5, 3.0, 4.0 and 5.0 kV·mm$^{-1}$.

3. Results and Discussions

Figure 1 shows experimental and simulated RBS and ERD (inlet) spectra of N-doped ns-carbon film prepared on Si substrate in the same technological conditions as sample QO3. In this case, the thickness of film was 80 nm. We proposed that substrate temperature in the range 600–900 °C does not significantly influences the concentration of elements. The leading edge
by RBS spectrum for Si is observed around 650 ch. The leading edges of Carbon, nitrogen and oxygen on the bulk Si profile are observed at 360, 420 and 470 ch, respectively. The leading edge (ERD inlet) for Hydrogen was at 610 ch, approximately. The concentration of elements (calculated using program SIMNRA) in the N-doped ns-carbon films were practically the same for all samples, which were: carbon - 82 at. %, nitrogen - 14 at. %, hydrogen - 2 at. %, oxygen - 2 at. %. Hydrogen fully escapes from growing film at the substrate temperature over than 600 °C. Oxygen and Hydrogen concentration could be a result of desorption from the stainless-steel vacuum chamber wall after magnetron sputtering and from air in the atmosphere.

Figure 2 shows SEM micrographs of samples prepared at different temperature. Surface morphology of samples QO1 and QO2 (Fig. 2(a) and Fig. 2(b)) are practically fully amorphous, rather smooth and compact without significant changes of amorphous structure. Surface morphology of sample QO3 (Fig. 2(c)) changes to mixture of amorphous structure and ultra-nanoscale flakes. Surface morphology of amorphous structure and nanoscale thickness flakes of random arrangement we can see on the surface of sample QO4 (Fig. 2(d)).

Figure 3 shows SEM micrographs of samples prepared at temperature 800 °C and different flow of hydrogen added to gas mixture. Surface morphology of nano-scale thickness flakes of random arrangement is shown on the surface of sample QH1 and can be compared with the surface morphology of sample QO4 i.e., added hydrogen in gas mixture modifies parameters of film growth resulting the same surface morphology than sample prepared at higher temperature without hydrogen in gas mixture. Adding more hydrogen, sample QH2, results in higher dimension of nano-scale thickness flakes of random arrangement. At the start of

Figure 4 shows Raman spectra of samples QO1, QO2, QO3, QO4, QH1 and QH2 in the wavelength range 900–3750 cm\(^{-1}\). Raman spectra shapes of ns-carbon films on quartz substrates change with increasing deposition temperature and adding hydrogen to the gas mixture. The D band and G band became distinct and narrow with increasing deposition tempera-
ture. The bands 2D and D+G became clearer with increasing deposition temperature. These effects continue in the case of samples QH1 and QH2 prepared with hydrogen in gas mixture. We can see the most distinct and narrow D band and G band and clearest 2D and D+G bands in the case of sample QH2. Because more hydrogen in the gas mixture results in more etched amorphous carbon and then stimulate the growth of the crystalline graphitic structures.

![Raman spectra](image_url)

**Fig. 4:** Raman spectra of samples QO1, QO2, QO3, QO4, QH1 and QH2.

Figure 5 show deconvoluted Raman spectra of sample QO4 and QH1 that were chosen on the base of comparable structural properties (RBS, ERD, SEM, Raman) and obtained results of photoelectron emission properties. We used four peaks fitting in the range 1000–1800 cm\(^{-1}\) and another four in 2500–3300 cm\(^{-1}\). Peak intensities that occur at 1180 cm\(^{-1}\) and 1680 cm\(^{-1}\) can be assigned to the ta-C and D\(^{'}\) band, respectively. The ta-C band is assigned to sp\(^3\)-bonded tetrahedral carbon and the D\(^{'}\) band is attributed to another tensor of the A1g mode. Peak intensities that occur at 1340 cm\(^{-1}\), 1590 cm\(^{-1}\) are assigned to D and G bands, respectively. The D band is a breathing mode of A1g symmetry involving phonons near the K zone boundary, which is activated due to defects and disorder of sp\(^2\) carbon and the G band is a primary an in-plane vibrational mode. The 2D band represent peaks P1 and P2. The 2D band is a second-order overtone of a different in-plane vibration. We proposed that peak P2 at 2710 cm\(^{-1}\) is assigned to graphene-like carbon [11]. The D+G band is a combination scattering peak and is represented with peaks P3 and P4 [15]. Peak P4 at 2910 cm\(^{-1}\) can be assigned to nanosized graphene sheets [16].

Figure 6 shows dependences of measured bunch charge and calculated QE (%) on the electric field at pulsed laser energy 3.9 mJ, repetition rate 10 Hz and pulse duration 15 ns. Bunch charge rose up with electric field for all samples. In the case of samples QO4, QH1 and QH2, the plots show linear behavior up to electric field 3 kV·mm\(^{-1}\). It can be explained that the surface potential barrier decreased with increasing electric field resulting increasing value of bunch charge. At higher electric field (> 3 kV·mm\(^{-1}\)), the value of bunch charge start to change to saturation behavior. It can be explained that the electric field penetration start surpasses the surface potential barrier. In the case of samples QO3, QO2 and QO1, the bunch charge values plots show practically linear behaviors with small deviation in the whole voltage range. Measured bunch charge of samples QO1, QO2 and QO3 was lower than at sample QO4, which value of bunch charge and calculate QE (%) was 16.08 nC and 85.22 · 10\(^{-4}\), respec-
tively at electric field $5.0 \text{ kV} \cdot \text{mm}^{-1}$. Sample QH2 exhibit the best value of bunch charge and calculate QE (%) and was $19.88 \text{nC}$ and $105.16 \cdot 10^{-4}$, respectively at electric field $5.0 \text{ kV} \cdot \text{mm}^{-1}$. Results also showed that optimal substrate temperature for deposition of very thin ns-carbon films would be in the range 800–900 °C. Interesting behaviours of measured bunch charge exhibit samples QH1 and QH2. Value of bunch charge was slightly higher for sample QH1 up to electric field near 2 $\text{kV} \cdot \text{mm}^{-1}$. At higher electric field than 2 $\text{kV} \cdot \text{mm}^{-1}$, the measured bunch charge was slightly higher for sample QH2. We proposed that this effect is connected with the different content of various carbon phases in the very thin ns-carbon films. It is disputable to compare the QE results in this study with those in other works [10] and [17] due to differences in the configuration and parameters of photocathode measurement systems and the properties of carbon-based materials.

4. Conclusion

We have investigated photo-induced electron emission properties at different electric field of very thin N doped ns-carbon films on quartz substrate. Carbon films contain C, N and small amount of hydrogen and oxygen. SEM results showed changes of surface morphologies with substrate deposition temperature from fully amorphous structure to structure of nanoscale thickness flakes of random arrangement. Dimension of nanoscale thickness flakes of random arrangement rose up at higher hydrogen flow. Raman results showed interesting bands assigned to ns-carbon films. Bunch charge and QE rose up with electric field. Highest value of measured bunch charge and calculated QE (%) were at electric field $5.0 \text{ kV} \cdot \text{mm}^{-1}$ for all samples. The best value of bunch charge and calculate QE (%) was $19.88 \text{nC}$ and $105.16 \cdot 10^{-4}$, respectively for a QH2 back-side illuminated transmission photocathode. Reported results in this study call for detailed studies to optimize technology of very thin ns-carbon films for back-side illuminated transmission photocathode.

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Author Contributions

J.H. supervised the project, performed samples technology and wrote original draft and final version of the manuscript. Both V.S. and A.K. performed Raman spectroscopy of samples. E.K. studied surface morphology of films by SEM. A.P.K. performed RBS and ERD spectroscopy. M.A.N. measured bunch charge and calculated quantum efficiency.

References


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