Very thin carbon-based films for transmissive photocathodes

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Abstract. Very thin carbon-based nitrogen-doped films of different thicknesses were deposited on double-side polished sapphire substrates by RF reactive magnetron sputtering. RBS and ERD were used to determine the elemental concentration in the films, and Raman spectroscopy, to determine their chemical structure. The RBS and ERD analyses indicated that the films contained carbon, nitrogen and small amounts of hydrogen and oxygen. The Gaussian-fitted and identified Raman spectra of the films showed the D and G bands in the range 1000-1800 cm⁻¹, and the 2D and D+G bands, in the range 2500-3100 cm⁻¹. The photo-induced (pulsed laser, 266 nm) electron emission properties of the films were determined by measuring the cathodes’ bunch charge and calculating their quantum efficiency. The paper discusses the structural properties of the very thin nitrogen-doped carbon-based films deposited on a sapphire substrate with different thicknesses in view of their use as backside-illuminated transmissive vacuum photocathodes.

1. Introduction
Photoemission is one of the fundamental processes in the physics of generation of charged-particles beams. Photoinjector R&D has become a key factor in developing a technology for electron colliders and free electron lasers. In this respect, improving the photocathode function is one of the main ways to improve the injector quality. The main types of photocathodes are made of a metal and a semiconductor. Metallic photocathodes, as those using copper and magnesium, are robust, but their quantum efficiency (QE) is very low. On the other hand, the semiconductor photocathodes, GaAs(Cs), Cs₂Te and alkali antimonites have the best QE, but require a specific working environment [1]. Obtaining high-power and high-brightness radiation in free-electron lasers and future electron-positron colliders, as well as for other applications, necessitates intense electron beams with bunches having a small emittance and a large charge [2]. Cesium iodide (CsI) is a material used widely for photocathodes due to its wide band gap of 6.2 eV and low electron affinity of 0.1 eV. However, it is hydroscopic and sensitive to the air environment, which prompted the search for other materials for photocathode fabrication. Diamond and other carbon-based material have thus become interesting in...
view of preparing cold photocathodes and investigating their emission properties. Results have been reported of quantum efficiency measurements in the range 150-210 nm of photocathodes based on poly-, nano-, and single crystalline diamond [3]. Photocathodes based on diamond-rich and graphite-rich nano-diamond films working in a reflection mode have been deposited by means of the pulsed spray technology on different conductive substrates [4]. Q-carbon composite structures have been formed by pulsed laser annealing of amorphous carbon films. The optimum fabrication conditions have resulted in a dense micro-structured morphology of Q-carbon, which is important for local electric field enhancement [5]. For the purpose of transmissive photocathode production, diamond-like carbon (DLC) films have been deposited on stainless steel mesh by PECVD from the gas mixtures CH$_4$+D$_2$+Ar, CH$_4$+H$_2$+Ar, and by reactive magnetron sputtering using a graphite target and the gas mixtures Ar+D$_2$, Ar+H$_2$ [6]. Carbon materials doped with nitrogen have been reviewed emphasizing their preparation and applications in the cases of porous carbons, graphene, carbon nanotubes and fibers and carbon black [7]. All carbon materials and carbon nanostructures from three to zero dimensions (3D, 0D), such as 3D graphite or diamond, 2D graphene, 1D carbon nanotubes, and 0D fullerenes have usually been characterized by Raman spectroscopy [8].

In this paper, very thin nitrogen-doped carbon-based films were deposited by RF magnetron sputtering on sapphire substrates. RBS and ERD were used for determination of the films’ elemental concentration, and Raman spectroscopy was used to study their structural and chemical properties. The transmissive photocathodes prepared were back-side illuminated by a pulsed laser, the bunch charge was measured, and the quantum efficiency was calculated.

2. Experiment
Very thin carbon-based films were deposited on double-side polished c-plane sapphire substrates by RF (radio frequency) reactive magnetron sputtering using a graphite target and an Ar+N$_2$+H$_2$ gas mixture. The c-plane sapphire substrates were cleaned ultrasonically in acetone and deionized water, and then dried with nitrogen. The stainless steel chamber was evacuated by a turbo-molecular pump to a base pressure of 10$^{-4}$ Pa. Prior to deposition, the graphite target was treated for 5 min in argon plasma. The argon, nitrogen and hydrogen flows were 30 sccm, 8 sccm and 3 sccm, respectively. The temperature of the graphite substrate holder during the sputtering was kept at 800 °C, with the working pressure being 0.7 Pa at a magnetron input RF power of 150 W at 13.56 MHz. The carbon film thickness of the samples was as follows: VS1 (2-4 nm), VS2 (8-11 nm), VS3 (14-17 nm), VS4 (20-23 nm) and VS5 (29-32 nm). The concentration of the elements in the films was determined by RBS and ERD. For this purpose, one N-doped carbon thin film was prepared on fused silica (FS) substrate, together with sample VS5. Raman spectroscopy using a Raman microscope with a 532-nm laser was used to determine the films’ chemical and structural properties. Electron beam evaporation was used to prepare a Ti contact frame on the carbon/sapphire structures, which were then annealed in nitrogen ambient at 400 °C. The photo-induced (pulsed laser, 266 nm) electron emission properties of the very thin carbon-based films on sapphire substrates as back-side illuminated transmissive photocathodes were determined by measuring the cathode bunch charge and calculating the quantum efficiency.

3. Results and discussions
Figure 1 presents RBS a) and ERD b) spectra of a very thin carbon-based film (thickness ~ 30 nm) on an FS substrate. The RBS spectrum shows a leading edge around 580 ch corresponding to Si. The carbon leading edge is seen on the bulk of the FS profile at 320 ch; the nitrogen leading edge is observed on the bulk of FS profile at 360 ch; and the oxygen leading edge is located at 420 ch. In the ERD spectrum, the hydrogen leading edge occurs at approximately 510 ch. The elements’ concentrations were calculated from the simulated RBS and ERD spectra using the SIMNRA software. We assumed that the elemental concentrations in the films are practically the same for all samples, i.e. the film’s thickness does not affect the concentrations. The concentration data are as follows: carbon — 84 at.%, nitrogen — 11 at.%, hydrogen — 3 at.%, and oxygen — 2 at.%. The hydrogen in the gas mixture does not influence its concentration in the films due to the very high
substrate temperature during deposition; at the substrate temperature of 800 °C, it escapes from the grooves in the films. The hydrogen and oxygen in the films originated from the deposition chamber walls and from the air atmosphere.

The presence of hydrogen in the gas mixture stimulates the growth of the carbon nano-crystalline phase and etches more of the amorphous carbon, when the carbon atoms are deposited on the nucleation points. Figure 2 presents the results of Raman spectroscopy. Figure 2 a shows the dependence of the Raman spectra intensities on the thickness of the very thin carbon-based films. Figures 2 b,c,d show the deconvoluted Raman spectra of samples VS1, VS3 and VS5, respectively. The Raman spectra intensity (figure 2 a) rises with the films thickness at a constant Raman spectrometer laser power (3 mW). At this power, the laser photons interact within the full thickness of the film, i.e. a higher thickness (interaction volume) results in a higher Raman spectrum intensity. This effect is not linear. The D band around 1350 cm⁻¹ is a breathing mode of A₁g symmetry involving phonons near the K zone boundary, which is activated due to defects and disorder of sp² carbon. The G band around 1580 cm⁻¹ is a primary in-plane vibrational mode. The 2D band around 2700 cm⁻¹ is a second-order overtone of a different in-plane vibration. The D+G band around 2900 cm⁻¹ is a combination scattering peak [9]. The Raman spectra do not contain he band at 2160 cm⁻¹, which is assigned to sp³ sites and is usually present in diamond-like carbon films. For Gaussian-fitting (figures 2 b,c,d) we chose representative Raman spectra, namely, those of samples VS1, VS3 and VS5. We used four-peak fitting for the range 1000-1800 cm⁻¹ and four-peak fitting for the range 2500-3100 cm⁻¹. The peaks occurring around 1200 cm⁻¹, 1350 cm⁻¹, 1580 cm⁻¹ and 1620 cm⁻¹ are assigned to the ta-C, D, G and D’ bands, respectively. The peak ta-C can be assigned to tetrahedral amorphous carbon. The D’ band is attributed to another tensor of the A₁g mode [9]. The 2D band is represented with peaks C1 and C2. We proposed that peak C2 at 2700 cm⁻¹ be assigned to graphene-like carbon. The D+G band is represented with peaks C3 and C4; the latter (2900 cm⁻¹) can be assigned to nanosized graphene sheets. The D peak’s intensity increases with the film thickness, while the G peak intensity decreases. The Raman results demonstrate that the films start growing as graphene-like carbon, sample VS1, where one can see distinct narrow features at the 2D and D+G bands, and continue growing as graphite-like carbon [10]. These narrow and distinct features vanish in samples VS2-VS5. Table 1 presents the calculated intensity (peak area) ratios I_D/I_G, which rises with the films thickness. This can be explained by the fact that the sp² bonds predominate in a film of thickness 2-4 nm; as the film thickness increases, the percentage of sp² and sp³ bonds change, i.e., the sp³ bonds number rises, as does the disordering.
The quantum bunch charge measurements of the transmissive photocathodes prepared were performed at JINR Dubna. Before the measurement, the samples were treated by laser pulses during 20-40 min to remove surface contaminants. The electrical field applied for electron extraction was 2.0 kV/mm. The pulsed laser spot diameter was 5 mm. The bunch charge measured and the calculated QE are presented in table 1.

The best result was obtained for the transmissive photocathode with a thickness of 14-17 nm, sample VS3. The better result of sample VS1 compared to sample VS2 can be explained by the change of the structural properties of the carbon-based film from graphene-like carbon (sample VS1) to graphite-like carbon (sample VS2). We assume that the graphene-like carbon film contains similar emission centers as graphene, which is a material with excellent field emission properties [11]. The further growth of the carbon-based film, sample VS3, results in a Raman spectral shape similar to that of graphite-like nano-crystalline diamond (GNCD) [3].

Our study showed that the optimal technology for preparation of back-side illuminated transmissive photocathodes is that of sample VS3 (optimal content of sp² and sp³ bonds, disordering and thickness). The QE starts decreasing if the hickness of the carbon-based film exceed that of sample VS3. In
addition, if the film’s thickness increases, so does the $I_D/I_G$ ratio. A higher $I_D/I_G$ ratio implies more defects in the film and, thus, more recombination centers for excited electrons. This can explain the result for the QE of sample VS5, which is several times lower than that of sample VS3. Other effects also affect the QE, such as skin effect and the emission mechanism. In the case of a transmissive photocathode with a very thin carbon-based film, part of the photons interact with the photocathode material and excite electrons, and part of photons pass through the photocathode without interaction. The photo-emission characteristics depend not only on the doping and carbon film properties, but also on the film thickness. The very thin carbon-based films on sapphire substrates contain several carbon phases with different work functions. Therefore, further studies are needed of the relationship between the structural and electronic properties of very thin carbon-based films.

4. Conclusions

Very thin nitrogen-doped carbon-based films of different thickness were deposited on sapphire substrates by RF reactive magnetron sputtering. The transmissive photocathodes thus produced were used to study the photoelectron emission properties of carbon films. The carbon-based films contain C, N and small amounts of hydrogen and oxygen. The Raman results showed interesting bands assigned to graphene-like carbon, graphite-like carbon and graphite-like nano-crystalline diamond. The maximum bunch charge and QE(%)×10^4 were 2.40 nC and 23.8, respectively as measured for the sample with a film thickness of around 17 nm. In our further research, we will focus our attention on developing transmissive photocathodes based on very thin nanostructured carbon films on sapphire substrates that have the potential of increased QE.

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