

MODIFICATION OF THE GLASS-LIKE CARBON SURFACE PROPERTIES BY ION IRRADIATION

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Introduction

Glass-like carbon (GC) is the polymeric form of carbon¹ produced from the precursor polymer by the progressive coalescence of stabilized polymer chains in the temperature region between 400 and 1000 °C. The association and linkage of the polymer chains and the consequent material properties, can be modified during the carbonization process² in which precursor material pyrolysis occurs and/or by introduction of the heteroatoms into the material prior³ or after^{4, 5, 6} carbonization. The possibility of preparing GC with controlled structural and surface properties is important since it permits the new areas of the material application.

Low-energy nitrogen ion implantation of graphite⁷ and diamond surface,^{8, 9} diamond-like carbon films,¹⁰ glass-like carbon coatings¹¹ and amorphous carbon thin films¹² yield predominantly amorphous CxNy product, sometimes with H incorporated into the structure. Our approach was to use glass-like carbon and precursor polymer carbonized at different temperatures as a target exposed to the N-ion beam irradiation. The experiments are expected to reveal the carbonization stage where irradiation has the highest influence to the structural and surface properties of the target material.

Experimental

Four samples were chosen for the experiment: phenol-formaldehyde polymer precursor heat-treated at 150 °C, two samples partially carbonized with heating rate 10 °C/h under flowing nitrogen to 500 and 700 °C as well as GC sample carbonized at 1000 °C under same conditions. The samples were in the form of 0.5 mm thick plates (5x20 mm). The samples width of 5 mm allowed the simultaneous exposure of four samples to the N⁺ ions in a single experiment.

The irradiation experiments were performed at the channel for the modification of materials of the Tesla Accelerator Installation¹³ at the Vinča Institute. The channel uses an

electron cyclotron resonance ion source.¹⁴ N⁺ ions, generated in the ion source, were extracted at 15 kV and transported through the beam line section to the target chamber where four samples were placed at the target holder and irradiated at a dosage of 1×10^{17} ions cm⁻². Total weight loss during ion irradiation was measured.

Irradiated samples were examined using scanning electron microscope Philips XL series, EDX analyser (Philips XL-EDX) and X-ray diffractometer. Surface functional groups were studied using FTS 6000 spectrometer (Bio-Rad, Cambridge, Mass), utilizing an attenuated total reflectance accessory (SensIR Technologies DuraSamplIR) with a silicon sampling crystal in single bounce configuration and sampling area of 0.44 mm².

After the ion irradiation and examination, samples were carbonized in flowing nitrogen atmosphere to 1000 °C with heating rate 10 °C/h in order to produce GC. Carbonized samples were characterized by X-ray structural analysis.

Characterization of the irradiated samples

The weight loss during irradiation is presented in Figure 1 as a function of final temperature during sample preparation. The values of weight loss (%) in Figure 1 are

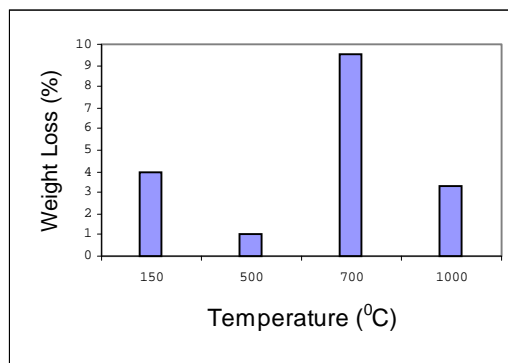


Figure 1. The weight loss after the irradiation as a function of the sample preparation temperature

corrected for the unite surface area exposed to N^+ ion irradiation. The weight losses close to 4% were observed for polymer precursor as well as for the GC sample carbonized up to 1000 °C. However, two intermediate samples (partially carbonized polymers) show extremely different behavior. The minimum weight loss of 1% is obtained for the sample heated up to 500 °C. The sample heated up to 700 °C shows the maximum weight loss 9.5%. The scanning electron microscopy (SEM) revealed typical changes at the surface induced by N^+ ion beam irradiation. It was observed that the surfaces of tree samples with 4% or less weight loss exhibit relatively smooth surface. The weight loss from these samples is clearly the result of the sputtering effect. As an example, the scanning electron micrograph of GC sample (1000 °C) is presented in Fig. 2a. The undamaged surface area in Fig. 2a was covered with the sample holder during ion irradiation experiment. At the surface exposed to the ion beam the craters formed are due to the sputtering.

SEM of the sample heated up to 700 °C, one with the maximum weight loss close to 10%, shows the serious damage induced by ion irradiation. The extensive surface cracking presumably produced by a contraction of the surface layer are clearly visible in Fig. 2b. Therefore, the maximum weight loss of the sample heated up to 700 °C is the joint effect of the sputtering and surface decline.

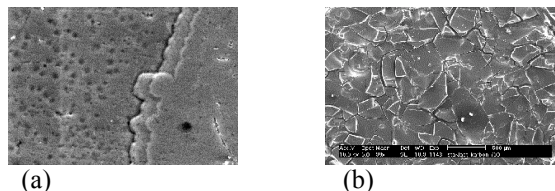


Figure 2. Scanning electron micrographs of GC surface (a) and the surface of partially carbonized sample at 700 °C (b) after ion beam irradiation

The contraction of the surface and consequent cracking observed only for the sample preheated up to 700 °C was the indication that N atoms could be incorporated into the sample during irradiation. Therefore, the structure and elemental composition of the samples before and after irradiation were examined in order to outline the changes due to ion irradiation.

X-ray diffraction profiles of the irradiated samples are presented and compared with the diffraction profiles of the same samples before irradiation in Fig. 3. Ion irradiation of the polymer precursor (Fig. 3a) resulted in the increase intensity of the non-crystalline broad diffraction profile (at 2θ 18) due to the interatomic distances in the polymer structure. Hence, the ion irradiation promotes the crosslinking of the polymer chains. The structural changes observed for CG and partially carbonized samples at 500 and 700 °C (Fig. 3b) are resembling. The diffraction profile

(002) at 2θ 23.4 is not seriously affected by N ion irradiation showing that the micro crystallites size is not disrupted. Therefore, the number of graphene plains and the interlayer distance remained almost invariable after ion irradiation. However, the reduced intensity of the (10) diffraction indicates that the graphene plains are obstructed by N ion beam irradiation, showing that N-ions are incorporated into the graphene layers.

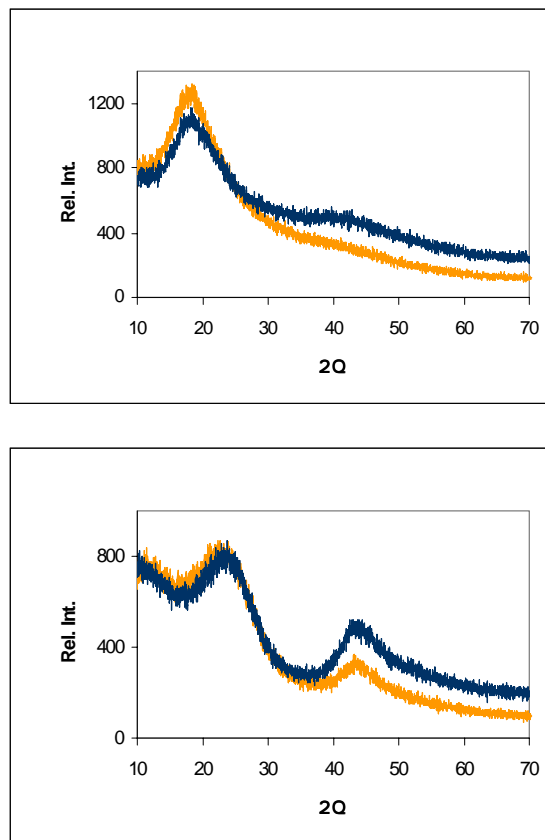


Figure 3. X-ray diffraction profiles for the precursor polymer (a) and partially carbonized sample to 700 °C (b) before (black trace) and after irradiation (red trace)

EDX analysis of the samples showed the significant increase of nitrogen content at the surface after irradiation. In Fig. 4, EDX spectrum of the original sample pretreated at 700 °C is presented with black line. The most abundant peak in the spectrum is due to the C $K\alpha$ X-ray emission line. The second peak, which corresponds to O $K\alpha$, confirms the presence of the oxygen complexes expected at the surface.¹⁵ The EDX spectrum of the same sample recorded after N-ion irradiation (red line) shows a single broad peak with maximum displaced from the position corresponding to C $K\alpha$ emission line. The deconvolution of this composite peak revealed the presence of carbon (C $K\alpha$) and nitrogen (N $K\alpha$) emission lines. Nitrogen distribution at the surface was not uniform, but fluctuating

from few up to maximum 40%. It is interesting to point out that the amount of oxygen has been significantly decreased after ion irradiation, although irradiated sample has been exposed to air for few weeks before recording the spectrum.

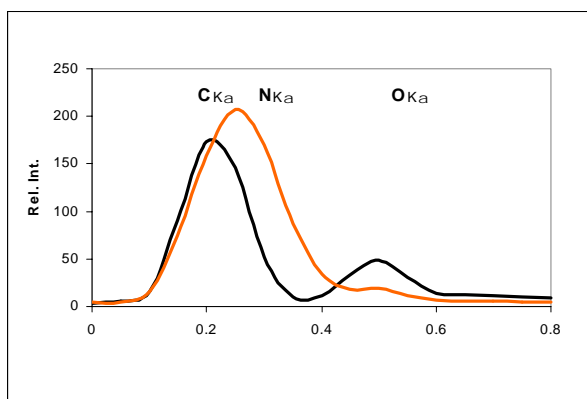


Figure 4. EDX analysis of the sample treated at 700 °C (black trace) and the same sample after irradiation (red trace). The expected positions of C, N and O K α emission lines are marked.

FT-IR spectra reveal the changes of the surface functional groups after N-ion irradiation. To illustrate typical changes of the functional groups observed at the surface, IR spectra of the sample prepared at 500 °C before (black) and after irradiation (red) are compared in Figure 5. The absorption peaks corresponding to the C-H stretch of sp³ hybridized C atoms at 2920 and 2850 cm⁻¹ are extensively reduced, yet the signals corresponding to the aromatic structure (at 1580, 870 and 788 cm⁻¹) are significantly increased after ion irradiation. The absorption peaks corresponding to the oxygen complexes (pronounced peaks corresponding to C=O stretching at 1740, 1710 and 1650 cm⁻¹ and O-H stretching at 3229.200 cm⁻¹) are substantially reduced after ion irradiation. The lack of oxygen at the surface of irradiated samples is also observed in EDX spectrum.

The most significant data for establishing the presence of nitrogen atoms after irradiation, are the changes in the peaks shape in the regions around 3400, 1470 and 1200 cm⁻¹. In the spectrum of irradiated sample it is possible to distinguish a peak due to N-H₂ stretching (at 3417 cm⁻¹) in addition to the peak at 1430 cm⁻¹ (N-H bending). The peak at 1202 cm⁻¹ gave the definitive confirmation of the presence of N-H bonds; this is a combination band of asymmetric C-N stretching and N-H bending due to the presence of primary aliphatic amines. Carbonyl surface groups, present at the original surface, were mainly replaced with C-N-H groups after ion irradiation. The IR data demonstrate that N ions implantation induces dramatic changes in the chemical composition of the material surface.

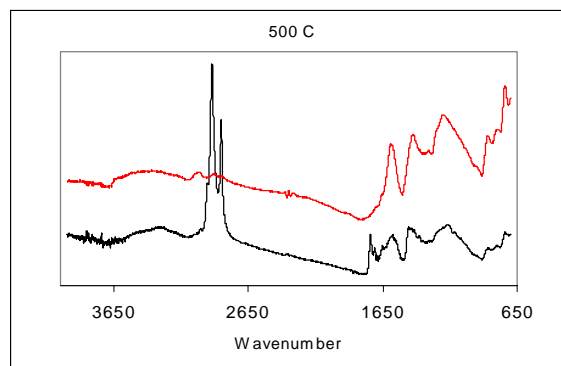


Figure 5. IR spectra of the sample prepared at 500 °C before (black) and after irradiation (red)

Characterization of the irradiated and subsequently carbonized samples

Irradiated samples were carbonized in nitrogen atmosphere with heating rate 10 °C/h to 1000 °C. Samples preheated at 150, 500 and 700 °C were powdered during the carbonization; only the sample carbonized up to 1000 °C was not completely disintegrated but severely damaged. The X-ray diffraction profiles of the carbonized samples are presented in Fig. 6.

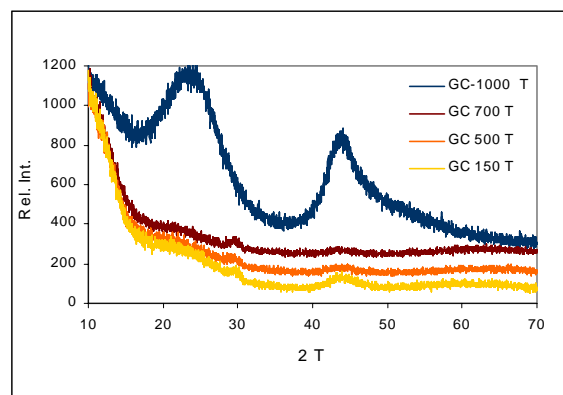


Figure 6. X-ray diffraction profiles of the irradiated samples after carbonization

The diffraction profiles for powdered samples (150, 500 and 700 °C) are very weak. The 100 profile (at 2θ 43.6°) is clearly visible only for the polymer sample but almost completely lost in the spectrum of the samples preheated up to 500 and 700 °C showing the degradation of graphene layers during subsequent carbonization. The diffraction profiles at 2θ 23.4° of three powdered samples are diffuse showing the destruction of the micro-crystallites in the bulk of the samples. The structural damage caused during the irradiation affected thermal stability of these samples. Only the X-ray diffraction profiles of both, irradiated and

subsequently carbonized GC samples, prepared at 1000 °C, are similar showing that the bulk of the sample was not seriously disrupted neither by irradiation nor by subsequent heat treatment.

Conclusion

In order to investigate the influence of the irradiation to the process of glassy carbon formation, samples produced at the different temperatures were exposed to the N⁺ ion beam. N⁺ ion irradiation induced structural changes. Oxygen complexes, present at the surface of the original samples, were almost completely replaced with C-N-H groups after ion irradiation.

Irradiated samples were carbonized to 1000 °C. The structural damage caused during the irradiation affected thermal stability of all samples. The powdered carbonization products were obtained for all samples except for GC. The structure of GC sample was not seriously disrupted neither by irradiation nor by subsequent heat treatment.

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