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Characterization of thin graphite layers and graphene by energy dispersive X-ray analysis

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ABSTRACT

Ultrathin graphite and few layer graphene fragments were obtained by mechanical exfoliation on copper surface and characterized by scanning electron microscopy, the energy dispersive X-ray spectroscopy and Raman spectroscopy. In order to achieve higher sensitivity on surface carbon layers the low-energy probing (1 keV) by the energy dispersive spectroscopy was used. Data of the energy dispersive X-ray spectroscopy allows to obtain well distinct levels of carbon and to determine a minimum step level relating to one graphene layer. Raman spectra shows apparent contribution of the D-peak, indicating radiation damage after conventional medium electron microscopy investigations. The weak effect of radiation damage has also been revealed after low-energy (2 keV) observation and energy dispersive X-ray measurements using 1 keV primary electron beam.

1. Introduction

The scientific and technological significance of graphene is linked with its good combination of both unique physical and mechanical properties. It is well known, that graphene is being very promising material for applications in modern and future nanotechnologies and can be used in many types of sensors and devices in many application areas. Therefore, graphene, in spite of its recent availability for experimental investigations [1] is an object of great interest for many researches [2–8].

Unfortunately, identification and characterization of ultrathin graphite and graphene fragments after mechanical production from highly oriented pyrolytical graphite can be performed with some limitations and difficulties. Moreover, as for graphene, its fragments are usually dispersed among more thicker few-layers and thin graphite pieces on a substrate surface. Discovering the few-layer graphene fragments in SEM or in optical microscope usually includes selecting some areas of the surface with nano-objects by the secondary electron image contrast differences. Using of analytical methods for characterization of ultrathin graphite and graphene is not widespread till present. Taking into account that during SEM investigations radiation structural defects can be produced [3,7,9,10] in this paper we have focused on the using the combination of the low-energy SEM investigations with energy dispersive X-ray analysis and Raman spectroscopy by nondestructive searching and characterizing thin graphite and graphene fragments, arranged on a copper substrate.

2. Experimental and results

Thin graphite and graphene pieces were arranged on a copper substrate due mechanical exfoliation of highly oriented pyrolytical graphite [1]. Copper poly-crystal substrate was as $10 \times 10 \times 0.5\ mm^3$ plate after fine mechanical polishing with using diamond emery past. All graphite fragments were initially observed with an optical microscopy. We have supposed that large difference of atomic numbers between carbon and copper make it easier to select ultrathin carbon fragments by SEM Quanta 3D 200i dual system. All composition measurements were performed with the help of the EDAX Ametek system built in SEM. Raman scattering measurements were performed by NT-MDT NTegra confocal spectrometer at room temperature in backscattering geometry using the 473 nm line of a semiconductor laser. The spectrometer was calibrated using the frequency of the optical phonon peak ($1332\ cm^{-1}$) of mono crystalline diamond. The scattered light was dispersed and detected with cooled charge couple device detector.

The main operating regime, which was used by SEM observations: $V=20$ keV (the probe size was equal to 2 nm, with the beam current 0.12 nA) by the conventional medium-energy SEM operation and $V=2$ keV by searching graphene in low-energy mode in order to avoid radiation damage. The EDX measurements were conducted by the low-energy primary electron beam. We have taken into account that a maximum value of ionization cross-section for a K-level with a binding energy E_b corresponds to the relation $V/E_b \approx 3$–4 [11]. As for carbon $E_b=285$ eV, so the energy of the primary electron beam as large as 1 keV was selected. The number of X-rays emitted is approximately proportional to the size of the volume that is subjected to irradiation.

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Proportionality between graphene stack thickness and the signal of the EDX X-ray detector is observed if spot area, current and value of e-beam energy are kept constant. During all EDX measurements parameters were used as follows: spot of 2 nm diameter, 1 keV e-beam energy and the beam current 0.12 nA.

The composition of the copper surface free of graphite flaks, determined by the EDX technique at the energy of the electron

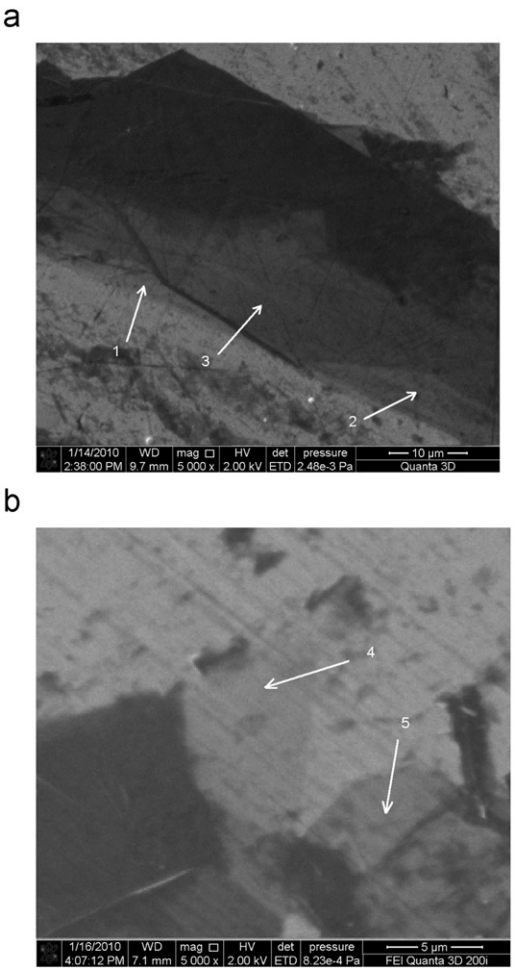

Fig. 1. SEM images of graphite flakes with the marked areas.

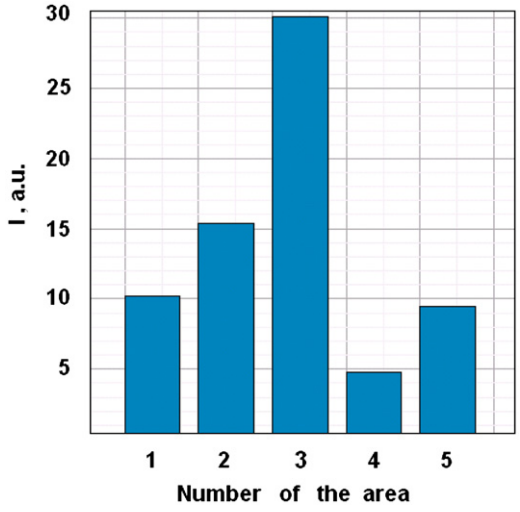

Fig. 2. The carbon EDX intensities from the marked areas presented in Fig. 1.

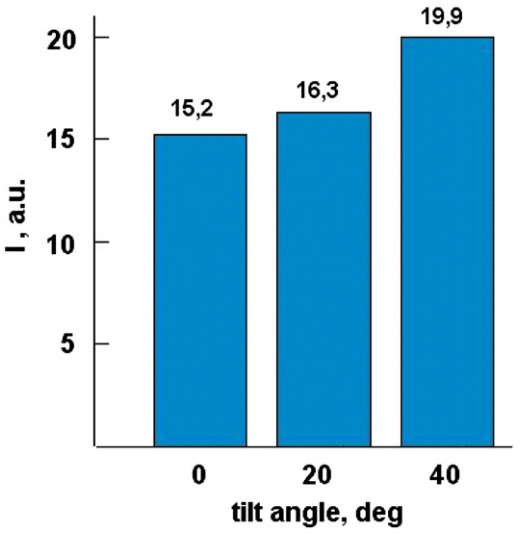

Fig. 3. A typical dependence of the EDX intensity on tilt angle (the measurements were performed on the area 2).

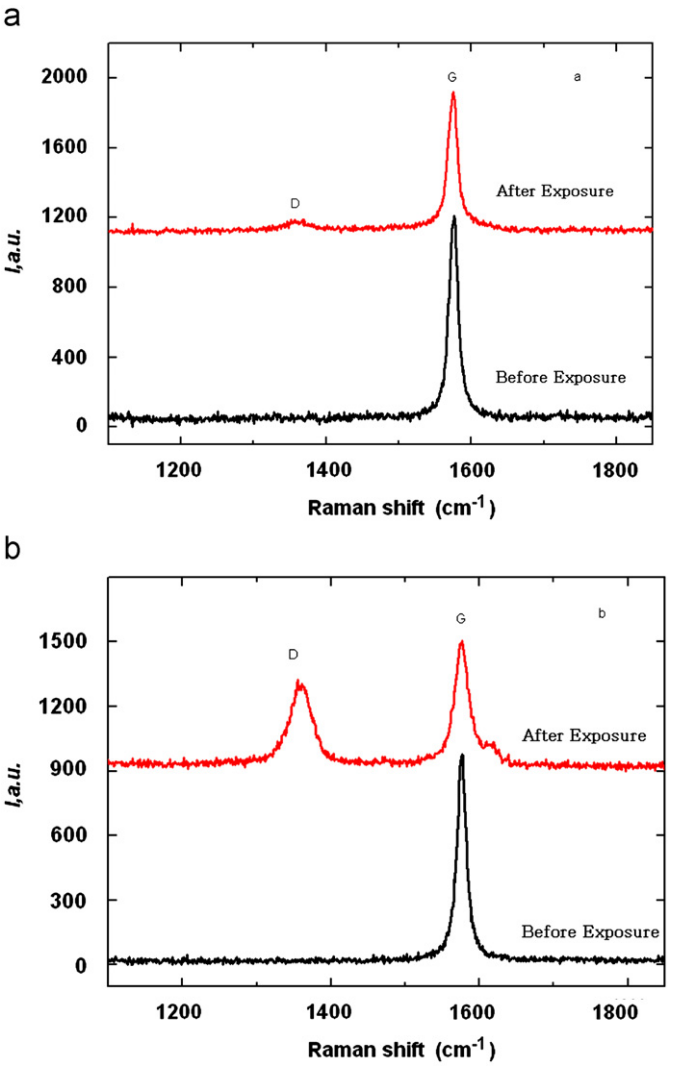

Fig. 4. (a) Raman spectra of sample before and after low-energy (2 and 1 keV) beam irradiation during the EDX measurements and (b) Raman spectra after observation with medium-energy (20 keV) beam.

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beam 2 keV was as follows: Cu- 46%, C -44%, O-10% (at%). The level of the background surface impurity of carbon was nearly constant on the surface with very low variations ($\approx 2\%$).

Fig. 1(a,b) presents typical image of areas with carbon layers on surface obtained by using low-energy primary electron beam (2 keV). One can see several areas which are well distinguished on the contrast. Fig. 2 presents EDX intensities of carbon at marked areas after background subtraction. The background level, measured in the same arbitrary units was equal to 14.0 ± 0.3.

EDX signal was recorded in 5 different points for every fragment. The accuracy of the data presented in Fig. 2 is equal to 5%. One can see that all histograms in Fig. 2 show obviously discrete structure and are approximately multiples of 5 a.u., and moreover, the minimum intensity level which corresponds to the layer with a minimum contrast (the fragment 4) is also equal to 5 ± 0.1 a.u. It would be reasonable to suppose, that this minimum intensity level corresponds to single graphene layer.

In order to confirm that we deal with very thin layers of graphite, the additional measurement of the EDX intensities by different angles θ between the normal to the surface investigated and the electron beam direction were performed (Fig. 3). One can see, that data presented are in a fine agreement with a "$I_0/\cos\theta$"-dependence, where I_0 is the intensity of carbon at $\theta=0$. It confirms that in our case the thikness of the fragment investigated is less than the depth of X-rays generation from carbon K-level (285 eV) for 1 keV electron beam, which is less than nearly 1 nm [11]. Fig. 4 presents typical Raman spectra of the fragments investigated. It is known, that graphite mono-crystal has a single Raman active mode, which is zone center mode at nearly 1580 cm^{-1} labeled "G" for graphite. Disordered graphite has a second mode at around 1350 cm^{-1} labeled "D" for "disorder". It corresponds to the breathing vibrations of rings at the graphitic cluster. This mode is forbidden in perfect graphite and only becomes active in the presence of disorder. Fig. 4 allows to compare effect of low- and medium-energy electron beams. In pristine fragment one can see only the distinct G peak near 1585 cm^{-1}, that indicates the high quality of crystalline structure. After using the low-energy probe (2 keV SEM-observation and 1 keV EDX measurements), the Raman spectrum reveals G- and weak D-peak, which indicates the low contribution of a defect structure . One can see, that after using the medium-energy regime of observation (20 keV), D-peak is obviously much more larger. This result is in a good agreement with data, recently reported in [10] about a radiation damage observed in graphene structure under SEM observations.

3. Conclusion

We have placed on the copper surface thin graphite and graphene fragments obtained by mechanical exfoliation and used low-energy scanning electron microscopy, energy dispersive X-ray and the Raman spectroscopy to characterize carbon nanostructures. Well distinguished discrete steps between carbon peak intensities, obtained by the low-energy dispersive X-ray spectroscopy was interpreted as indicating to variation of the depth equal to one or a few graphene layers.

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