

Nanographite films: structure and properties

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Abstract. Using the activated carbon fibers (ACF) as a source of nanographites, nanographite film structures of different morphology on various substrates have been grown. It was revealed from the data of Raman spectroscopy that obtained films consist basically of the same structural blocks as the initial ACF. Scanning electron microscopy (SEM) was used to study the morphology of the films. The presence of lengthy zigzag edges in nanographites, which is prerequisite for their nontrivial electronic structure and magnetic characteristics, has been established. X-ray photoelectron spectroscopy (XPS) data show that in the C1s spectra of the films in the usually observable "diffuse" structure of $p \rightarrow p^*$ shake-up satellites, p and $p+y$ plasmons, the expressed maxima appear.

1. Introduction

Nanographites belong to the large family of promising nanoscale carbon materials with carbon honeycomb net. Due to the combination of sub-miniature size and number of valuable physical properties (good electrical conductivity, high emission values, nonlinear optical characteristics and nontrivial magnetic properties) in the future they may find practical applications in various engineering fields [1]. In terms of practical application, the film structures and composites of nanographites are the most promising ones [2].

This paper presents data on the film structures of graphite particles with nanometric lateral size (≈ 3 nm) formed on various substrates. For graphite particles of that size the theory predicts a maximum contribution of edge p -electron states to the electronic structure near the Fermi level [3] and, as a consequence, fundamentally new physical and chemical properties [1].

2. Experiment

The films on silicon and copper substrates were formed from powder of nanographites obtained from polyacrylonitrile ACF by the mechanical treatment of previously purified fibers and using different experimental procedures.

The X-ray diffraction (XRD) pattern of the ACF was recorded with diffractometer ADVANCE D8 ("Bruker", Germany) using $\text{CuK}\alpha$ radiation ($\lambda = 0.15417$ nm) in the Bragg-Brentano focusing geometry. Microimages of the films were obtained with scanning electron microscope with capacity of point element analysis Hitachi S 5500 ("Hitachi", Japan). Raman spectra were obtained with RFS 100/S spectrometer ("Bruker", Germany) ($\lambda = 1064$ nm). The X-ray photoelectron spectra were measured with using the SPECS ("SPECS", Germany) instrument with nonmonochromatic $\text{AlK}\alpha$ radiation ($h\nu = 1486.6$ eV).

3. Results and discussions

The polyacrylonitrile ACF chosen as the source of nanographites are three-dimensional disordered net of them [4]. The XRD pattern of mentioned fibers may be represented as a sum of five Lorentzian lines corresponding to (002), (100), (004), (110) and (006) reflections. From the width of the (002) reflection it follows that the average domain size of the graphite in the direction perpendicular to the carbon layers $L_c \approx 0.8$ nm. From the position of that reflection the interlayer distance $d_c \approx 0.366$ nm has been calculated. Similarly, the width of

(100) reflection allows to estimate the average domain size in the plane of the carbon layers $L_a \approx 3$ nm. Therefore, according to XRD data the domains of graphite in the ACF are of nanometric sizes in all three dimensions and are presented by stacks of three (on the average) nanographenes with the interlayer distance being substantially greater than that in the macroscopic ordered graphite ($d_c = 0.335$ nm).

Application of various methods of synthesis allowed to obtain nanographite films of two types, which differ in their morphology. The Fig. 1a presents SEM images of the film on the copper substrate designated as type I film. It is a uniform (continuous) coating of tightly adjacent nanometer-sized particles and their aggregates.

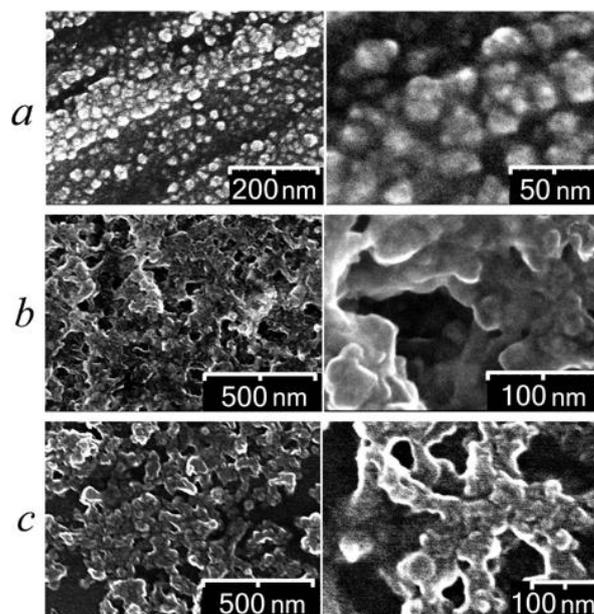


Fig. 1. SEM images of the films (at different scales): a – film on Cu substrate (type I), b – film on Cu substrate (type II), c – film on Si substrate (type II).

Fig. 1b, c show a SEM images of the films of another morphology (type II) on copper and silicon substrates. In this case the films have a porous structure. Taking into account the identity of the starting material used, it can be assumed that they are "constructed" from the same nano-sized particles as the film of type I. The element analysis carried out simultaneously with recording the SEM images of the films showed that in all cases their structural blocks represent the carbon particles.

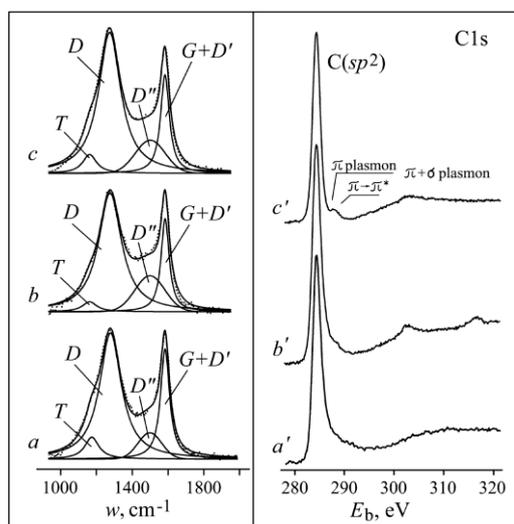


Fig. 2. Raman spectra (left): *a* – initial ACF, *b* – film of type I on Cu substrate, *c* – film of type II on Cu substrate. XPS spectra (right): *a'* – initial ACF, *b'* – film on Cu substrate (type II), *c'* – film on Si substrate (type II).

Fig. 2 a-c shows the Raman spectra of ACF and films of both types on a copper substrate in the frequency range 900–2000 cm^{-1} . The peak observed at $1598 \pm 2 \text{ cm}^{-1}$ apparently represents an unresolved superposition of the graphite component *G* and intralayer defects initiated components *D'*. Peak *D* ($\approx 1300 \text{ cm}^{-1}$) is associated with disordered and defective graphite structure. Peak *D''* ($\approx 1520 \text{ cm}^{-1}$) is caused by presence of impurity of the sp^2 -hybridized amorphous carbon in the samples [5]. Peak *T* ($\approx 1200 \text{ cm}^{-1}$) possibly is caused by disturbance of the graphene layers planarity, for instance due to changes in the type of hybridization of the valence electrons of the edge carbon atoms. The in-plane crystallite size of graphite, L_a is shown to be inversely proportional to the ratio of *D* and *G* band intensities (I_D/I_G ratio) [6]. Comparison of the Raman spectra of ACF and investigated films (Fig. 2 a-c) shows that in all of them $I_D/I_G > 1$. Taking into account the XRD data for initial ACF one may conclude that ACF and obtained films basically consist of similar structural blocks, i.e. nanographites.

In the films of type II attention is drawn to large "length" of the free edges (Fig. 1 b, c). At that, they have well expressed angulate shape, which is typical for the flat pieces of the honeycomb net of sp^2 -hybridized carbon atoms. Fig. 3 (left) shows the examples of possible corner angles and the structure of adjacent nanographene edges. It can be seen that the corners of 60° and 120° , both internal and external, are formed between segments of the adjacent nanographene edges having the same - either zigzag or armchair shapes. Corners of 90° and 150° are formed by the adjacent segments of nanographite edges, which have the different shapes. From Fig. 3 a, b it is well seen, that angles of 90° and 150° are present between edge segments of nanographene, being an external layer of nanographite - the structural block of a film with porous morphology. Consequently, nanographites, which form these films, contain extended sections of zigzag configuration of the edge carbon atoms. According to reference [1], such structure of the nanographite edges is the precondition for its nontrivial electronic structure and magnetic properties.

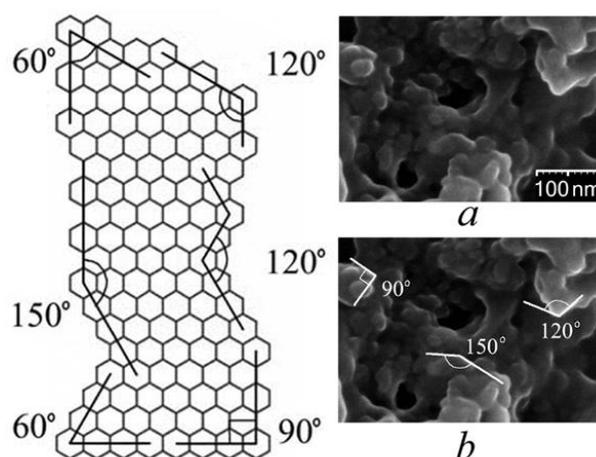


Fig. 3. Example of edge corners of idealized nanographene (left) and SEM images of type II films on Si substrate (right): *a* – original image without highlight of the corners, *b* – images with highlight of the corners.

XPS studies revealed the differences in the spectra of photoelectron characteristic losses situated at the higher binding energies with respect to the main C1s line for ACF and for the films of type II. In addition to "diffuse" structures in the areas of $p \rightarrow p^*$ shake-up losses, p and $p+y$ plasmons, being characteristic of ACF (Fig. 2, spectrum *a'*), in the spectra of type II films the expressed maxima have been found (Fig. 2, spectra *b'*, *c'*).

4. Conclusions

With using ACF as a source of nanographite, different film structures of nanographite on silicon and copper substrates have been grown and their morphologies have been studied. On the basis of microscopic data, two types of films which differ in spatial structure (packing) of nanographites on the substrates have been identified. Raman data show that films basically consist of the same structural blocks (nanographites) as initial ACF. It was concluded that there are lengthy edges of zigzag shape in nanographites forming films. It was noted that the presence of extended zigzag rows of edge carbon atoms in nanographite films is a prerequisite for their nontrivial electronic structure and magnetic properties.

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