Scanning electron microscope at low voltage operation – a unique characterization tool for graphene layers

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Abstract: Graphene grown on Cu foils by chemical vapor deposition (CVD) technique has been investigated using commercially available scanning electron microscope at low voltage operation. The optimized conditions of SEM imaging carried out in a double-channel mode (registering secondary electrons type 1 (SE1) and backscattered electrons (BSE) images in a single scan) allowed for the visualization of typical features of graphene on Cu, such as folds, cracks and add-layers. The mechanism of thickness contrast observed in the BSE images was described in terms of low loss-BSE detection. Antioxidant qualities of graphene sheets on metallic substrate were confirmed by the ability of observation of the channeling contrast in Cu substrates at primary electrons energy of 0.5 keV.

Key words: graphene, graphene characterization, low-kV scanning electron microscopy

Skaningowy mikroskop elektronowy pracujący w zakresie niskich wartości napięcia przyspieszającego jako unikatowe narzędzie do charakteryzacji warstw grafenu

Streszczenie: Próbki grafenu otrzymywanego metodą chemicznego osadzania z fazy gazowej na podłożach Cu poddano badaniom przy użyciu komercyjnego skaningowego mikroskopu elektronowego (SEM) pracującego w zakresie niskich wartości napięcia przyspieszającego. Optymalizacja warunków obrazowania SEM prowadzona w trybie dwukanałowym (rejestracja obrazów SE1 i BSE podczas tego samego skanu) pozwoliła na wizualizację typowych cech grafenu na Cu takich jak fałdy, pęknięcia i dodatkowe warstwy. Mechanizm kontrastu związanego ze zmianami liczby warstw grafenu obserwowanego w obrazach BSE został przedstawiony w oparciu o detekcję elektronów BSE o niskich stratach energii. Przeciwutleniające właściwości grafenu na metalicznych podłożach zostały potwierdzone poprzez możliwość obserwacji kontrastu kanałowania elektronów w podłożach Cu przy energii elektronów pierwotnych rzędu 0,5 keV.

Słowa kluczowe: grafen, charakteryzacja grafenu, niskoenergetyczna skaningowa mikroskopia elektronowa

1. Introduction

Graphene on a copper substrate has attracted broad attention of researchers and industrialists all over the world, mostly due to its high quality and the possibility of achieving a monolayer graphene film which can be efficiently transferred and easily implemented in mass production [1 - 2]. Various unique properties of graphene have created high expectations for a number of applications in emerging technologies [3 - 4]. Nevertheless, graphene layers are atomically thick, and the overall electronic properties of a sample are determined by the number of layers present. Therefore, it is of great importance to be able to experimentally determine the number of graphene layers in a sample, particularly for device fabrication. Characterization of graphene films is essential for the quality control purposes. Common techniques include optical microscopy [5 - 7], atomic force microscopy [8 - 9], Raman spectroscopy, transmission electron microscopy [12 - 14], Auger electron spectroscopy [15], etc. Scanning electron microscopy (SEM) is getting more popular for imaging graphene because it is a rapid, non-invasive and effective imaging technique which is complementary to most other techniques. Particularly, many electronic applications require uniform and defect free graphene in large area. SEM has the advantages in detecting impurities, ruptures, folds, voids and discontinuities of synthesized or transferred graphene on a variety of substrates. However, SEM imaging of graphene is challenging, mainly due to the fact that the ultra-thin graphene film is *transparent* to sufficiently high energy of electron beam. Hence SEM images easily display the morphologies of the substrate beneath the graphene, not the graphene itself. Low beam energy is required to image graphene and an efficient, high performance electron detector is required for detecting low energy electrons which provide the best contrast and topographic sensitivity. Imaging graphene with a low beam voltage field emission scanning electron microscope (LV FE-SEM) is very promising because of its unique combination of high resolution, a small beam/specimen interaction volume, enhanced contrasts and the capability of revealing more surface details [16 - 20].

2. Experimental procedure

Graphene single- (SL) and multilayers (ML) grown by chemical vapor deposition (CVD) method on polycrystalline Cu substrates were subjected to SEM investigation

with low energy (less than 1 keV) electrons using Auriga CrossBeam Workstation (Carl Zeiss) equipped with the In-lens SE (true SE1) detector and Energy selective Backscattered electrons (EsB, low-loss BSE) detector, both positioned on the optical axis of the Gemini® column. In front of the entry system on the axis of the BSE detector there is an energy filtering grid integrated into the electron optical detection system, that can be adjusted in its retarding potential from 0 to 1500 volts. This grid allows only BSEs with energies greater than the grid energy to be detected. The energy of the primary electrons was adjusted to effectively reveal all the features of the studied samples in terms of graphene characterization. The presence of graphene has been independently confirmed by Raman spectroscopy measurements.

3. Results and discussion

The contrast in the images of SE1 detector (especially at low kV operation) is usually driven by the differences in the topography of the sample, thanks to the angular distribution of these electrons, as well as the small interaction volume [21]. However, other factors, such as sample surface potential, work function or crystallinity may strongly influence the contrast mechanisms as well. In most cases, it is rather unusual that only one factor will take control over the mechanism of contrast generation, so one should keep in mind that the origin of the observed contrast may by the result of phenomena superposition.

The design of the semi-in-lens detector of backscattered electrons applied in the system used, assures the imaging with low-loss BSE (LL-BSE), i.e. these electrons which were scattered in the single events almost elastically at high angles. Typically, the contrast in the images of LL-BSE is sensitive even to slight changes in the composition of the analyzed samples. However, when applied to imaging at low primary energies, it allows for visualization of the information from the few very first atomic layers of the sample. In case of thin films, the contrast becomes sensitive to the number of atomic layers.

Graphene and multilayers graphene samples are perfect candidates for imaging with the use of SE1 and BSE electrons in SEM at low kV operation, and the other way round: low kV SEM seems to be a perfect tool for graphene imaging. What it takes, is the ability of the operator to apply optimum imaging conditions and be able to serve with reasonable interpretation of the images after all. That causes SEM not only a tool for imaging, but rather a system for research application.

The typical scanning electron microscopy images of graphene grown on copper foil recorded at primary beam energy of 0.5 keV are presented in Fig.1.

Image in Fig. 1a reveals the presence of cracks in the graphene sheet, which most probably are generated during the cooling of the sample after the growth process. The bare copper in this region has been oxidized after the contact with air, and appears as bright lines in the image (red arrows). The same cracks are represented by dark lines in the image of BSE (compare Fig. 1b). However, there are many more dark lines visible in the BSE image (yellow arrows), which originate from the folds of the graphene sheet on the copper surface. The presence of the folds is the result of differences in the thermal expansion coefficient of Cu substrate and graphene sheet. Both, cracks and folds, appear dark in the BSE image, thus it would not be possible to differentiate between them, unless the SE1 image was recorded in parallel with the BSE image. In many cases of the results concerning the graphene imaging by SEM, which can be found in the literature, the authors rely on the BSE or SE2 (SE type 2) images to acquire information on the graphene structures. In the outcome, some of the features of graphene sheets may be

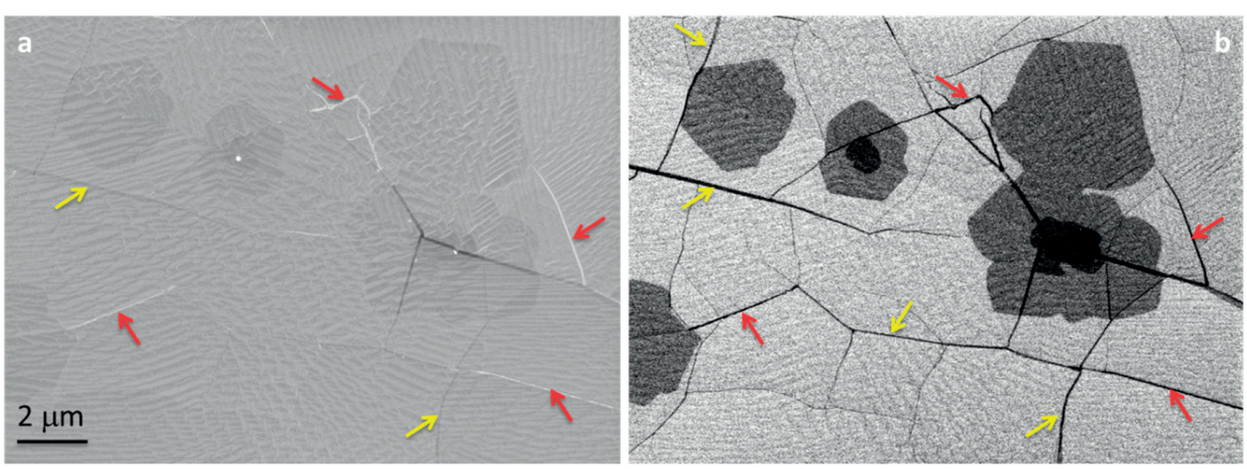

Fig. 1. SEM images of graphene grown over the Cu substrate: (a) – SE1 image, (b) – BSE image; cracks and folds in graphene sheet marked with red and yellow arrows, respectively.
Rys. 1. Obrazy SEM grafenu na podłożu Cu: (a) – obraz SE1, (b) – obraz BSE; pęknięcia i fałdy w warstwie grafenu oznaczono odpowiednio czerwonymi i żółtymi strzałkami.

misinterpreted [18, 20]. Only by comparative analysis of the two images taken at the same time in two channels (SE1 and BSE) it is possible to determine the origin of individual lines in the BSE image, as presented herein.

Similarly, it is necessary to perform image recording in a dual-channel mode to see other features typical for the CVD-grown graphene over a Cu substrate, i.e. add-layers. The add-layers are hardly visible in the SE1 image, but they can be clearly seen in the BSE image. The contrast is governed by the changes in the thickness of the graphene sheet over the substrate, namely the number of add-layers.

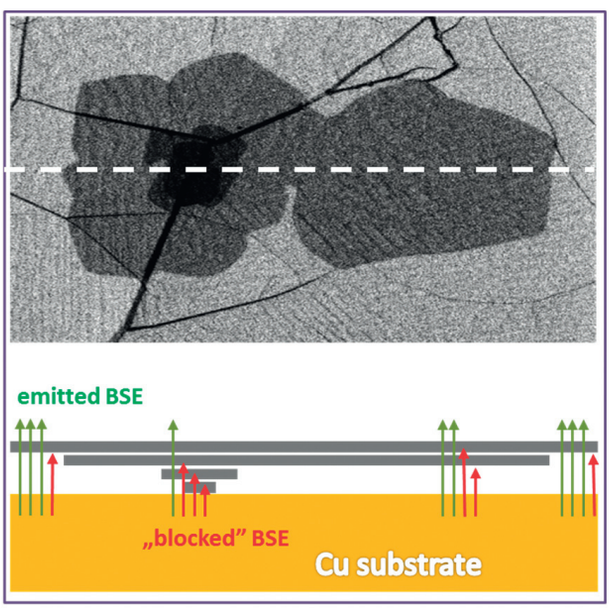

Fig. 2. Schematic representation of thickness contrast mechanism in LL-BSE image of graphene on Cu substrate (not in scale).
Rys. 2. Schematyczna reprezentacja mechanizmu kontrastu w LL-BSE związanego ze zmianą liczby warstw grafenu na podłożu Cu (nie w skali).

A reduction in the landing energy will result in smaller electron penetration depth and hence more information of interest will come from the surface [21]. By definition and because of the physical processes, the low-loss BSE must come from the outermost layers of the surface. The greater discrimination applied with the filtering grid to the smallest energy loss possible, the more the detection signal originates from the surface layers. Using this principle, the thinnest films on the surface, down to monolayers, can be imaged. In the case considered, most of the BSE are still generated within the Cu foil (Fig. 2). The reduction of the net signal to the smallest energy losses increases the contrast dramatically. At such circumstances, even the presence of additional single atomic layer on the surface (single add-layer) becomes a serious obstacle for the BSE on their way to the detector. Thus the regions of the sample covered with additional layers will be represented by the decreased intensity of BSE signal, i.e. dark parts in the image. In case of graphene on Cu, these will be discrete changes, thus informing about the number of layers. The proposed description of thickness contrast mechanism in LL-BSE images is also applicable to folds of graphene sheet, which in fact can be considered as local increase in the number of layers.

It is worth to note, that add-layers (schematically shown in Fig. 2) are placed below the continuous sheet of graphene. This finding has been previously reported by [22 - 23] and is widely accepted by the technologists.

Another interesting feature present in the low-kV BSE images of graphene on Cu is the contrast observed

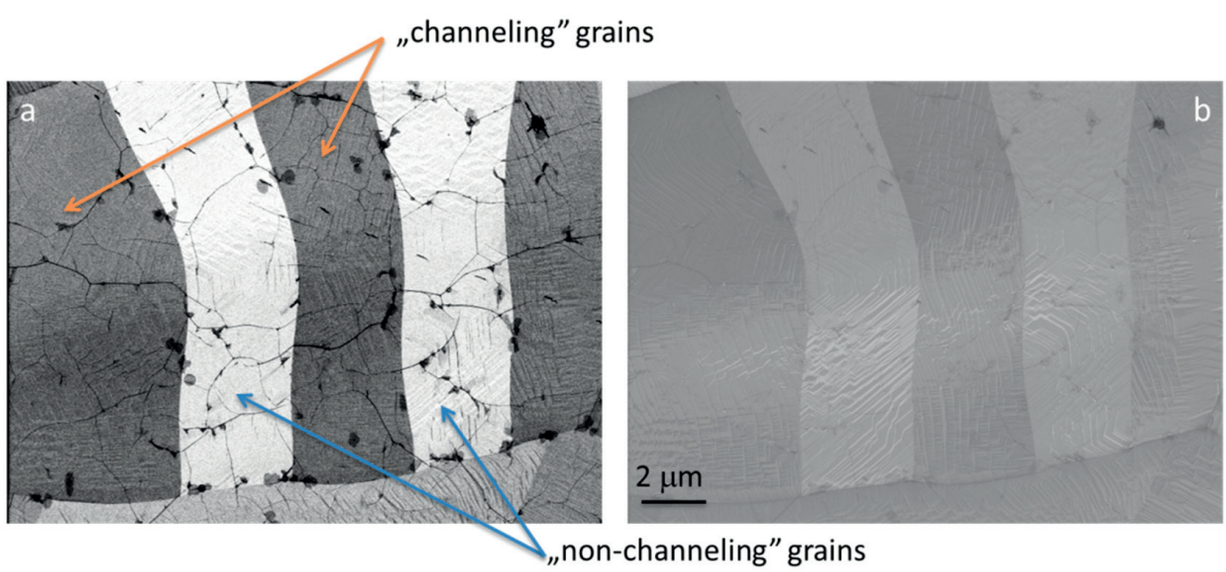

Fig. 3. Channeling contrast in the Cu grains under graphene clearly visible in BSE image: (a) channeling grains appear darker than non-channeling grains; (b) SE1image of the same fragment of the sample: weak channeling contrast.
Rys. 3. Kontrast kanałowania elektronów w polikrystalicznym podłożu Cu pokrytym grafenem widoczny w obrazie BSE: (a): ziarna kanałujące jawią się jako ciemniejsze niż ziarna niekanałujące; (b) obraz SE1 tego samego fragmentu próbki: słaby kontrast kanałowania.

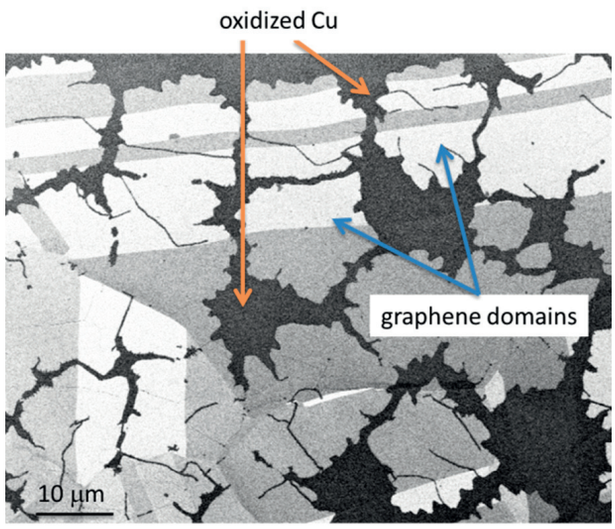

Fig. 4. SEM image (BSE) of the initial phase of graphene growth over polycrystalline Cu substrate; channeling contrast is observed only in the regions covered with graphene, in contrary to the fragments of oxidized Cu.
Rys. 4. Obraz SEM (BSE) grafenu na podłożu Cu we wczesnej fazie wzrostu; kontrast kanałowania obserwowany tylko w obszarach pokrytych grafenem, w przeciwieństwie do fragmentów utlenionej Cu.

for the Cu grains in polycrystalline substrate. The value of the backscattering coefficient in the individual grains of material is orientation-dependent [24]. The scattering is lowest for the grains which main crystallographic axis is aligned with the primary beam direction, and so is the intensity of BSE signal.

The strongly-misoriented grains are characterized by high scattering coefficient, thus the signal registered in the BSE image over such grains is very strong (Fig. 3). Analogous, however much weaker, contrast can be observed in SE1 image as well. In this case the signal intensity is more dependent on the work function of electrons from the individual grains (Fig. 3b).

The type of contrast described above, called channeling contrast, can be observed at low primary beam energies only when the surface of the studied sample is crystalline, free from defects, oxides and perfectly clean. Coverage of the copper surface with graphene ensures that all of these requirements are fulfilled. The best example of the antioxidant properties of the graphene on the metallic substrate can be observed in the image of the sample in the initial phase of growth, when the graphene forms micro--domains. In contrast to the parts of Cu surface covered with graphene, oxidized (by the contact with air) fragments of copper do not present any contrast in-between the individual grains.

In order to find optimum set of the primary electron beam parameters suitable for graphene on Cu observation, the series of images was recorded in parallel mode (SE1 and BSE simultaneously) with an application of beam energies ranging from 0.5 keV to 10 keV. Fig. 5 presents a set of images registered for the same fragment of the sample at different imaging conditions.

Typical features of the graphene film on Cu substrate, such as folds, cracks in graphene foil and add-layers, are visible in all of the SE1 images even at the beam energy as high as 10 keV (Fig. 5a – e). Despite the fact, that all the features are visible in the image at 10 keV (Fig. 5e), the information they bring may be misinterpreted, as both, cracks and folds appear to be alike. From the images presented in Fig. 5, only the one registered at 0.5 keV-beam operation allows to clearly distinguish between aforementioned features (Fig. 5a). On the other

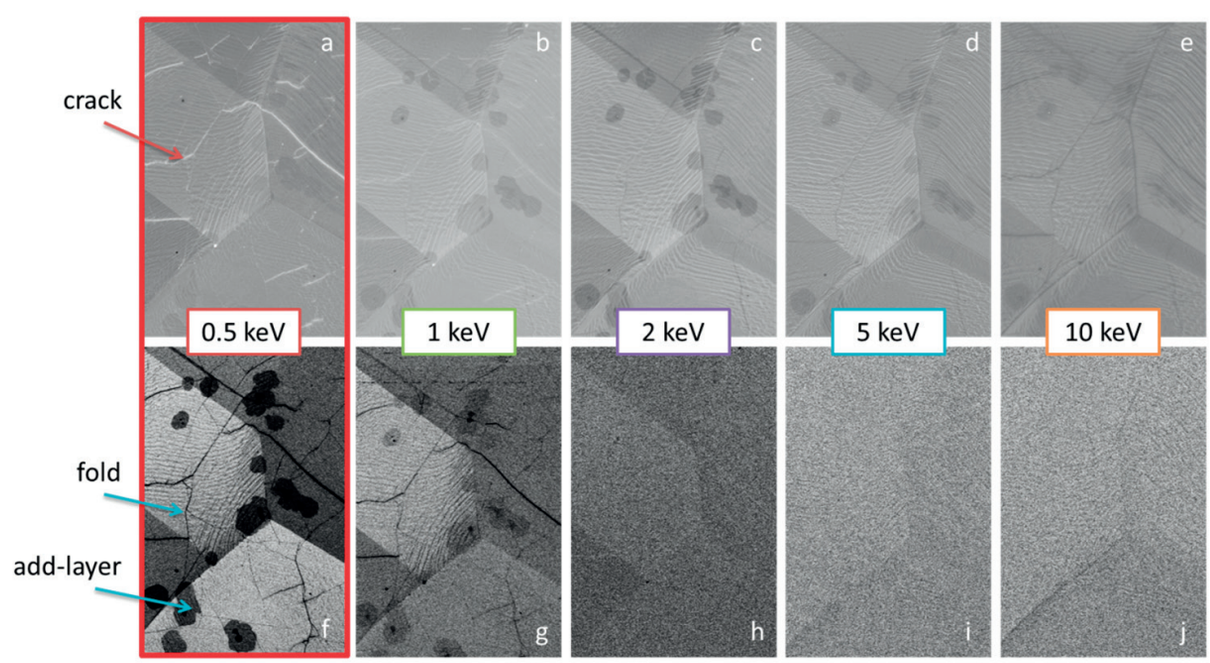

Fig. 5. Set of SE1 and BSE images of graphene grown on Cu, obtained at different values of energy of primary electron beam.
Rys. 5. Obrazy SE1 i BSE grafenu na podłożu Cu, uzyskane przy różnych wartościach energii elektronów pierwotnych.

hand, SEM imaging in a single mode (SE1 either BSE) is insufficient to gather full available information about the sample. The add-layers are not (or hardly) visible in the SE1 mode at 0.5 keV. That is why it is necessary to perform double-channel signal registration during SEM imaging (SE1 and BSE). At the primary beam energy above 1 keV, the BSE images contain no useful information on the graphene on the Cu substrate, only residual information on the existence of grains in the substrate. That is caused by the loss of information delivered by the BSE which encounter multiple Rutherford scattering and their increased penetration depth. Only by the application of low energy of the primary beam and selection of the low-loss BSE from the remainder of the whole electron spectrum it becomes possible to limit the information which originates from the outermost shallow region on the surface.

4. Summary and conclusions

The SEM imaging must be performed in such a way, that images collected will provide as much information about the studied sample as possible. One of the fundamental conditions is to optimize microscope settings and to give reasonable interpretation of the images. That is why understanding the contrast in the recorded images is so important. The samples studied in this work were the layers of graphene obtained by CVD method on Cu substrates. The influence of SEM imaging conditions on the quality of information gathered by this technique has been considered. The results of this study demonstrate undeniably high utility of low energy scanning electron microscopy in the observation and characterization of graphene layers on various substrates. The advantages of SEM technique are: it is fast, non-destructive, non--contact, allowing for examination of relatively vast areas on the sample, and there is no need of special sample preparation. High-resolution SEM imaging makes it much more precise method of characterization in terms of features which become "invisible" for other techniques, i.e. Raman spectroscopy due to poor resolution of the latter. The practical aspect of the work presented here is the development of a novel method of low-kV SEM characterization of thin materials, which will serve as a rapid characterization tool of graphene layers obtained in the laboratory, and can be used for graphene produced on an industrial scale, as well.

Acknowledgment

Author would like to thank Dr. Iwona Pasternak (Institute of Electronic Materials Technology, Poland) for preparation of graphene samples used in this study. This work was partially sponsored by the Polish Ministry of Science and Higher Education, in the frame of the research project entitled „Examination of graphene by SEM in terms of the identification of the numbers of graphene layers" held at the Institute of Electronic Materials Technology.

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