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SEM and Raman analysis of graphene on SiC(0001)

K. Grodecki[a,*], I. Jozwik[a], J.M. Baranowski[a,b], D. Teklinska[a], W. Strupinski[a]

[a] Institute of Electronic Materials Technology, 133 Wolczynska Str., 01-919 Warsaw, Poland
[b] Faculty of Physics, University of Warsaw, Pasteura 5, 02-093 Warsaw, Poland

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ABSTRACT

Graphene grown by a sublimation technique was studied by Scanning Electron Microscopy (SEM) and micro-Raman spectroscopy. The measurement area of a sample was marked and investigated using both systems, as a result of which SEM images were directly compared with Raman maps. In this work we show that a correlative analysis of Energy Selective Backscattered electrons detector (EsB), In-Lens figures and Raman maps of shape and intensity of the 2D band is adequate to determine graphene layer thickness with the precision of SEM and reliability of Raman spectroscopy.

1. Introduction

One of the most important aspects of graphene characterization is to measure the number of graphene layers in a proper and precise manner. There are many methods available, including optical measurements (Ivanov et al., 2014; Ni et al., 2007) as well as Low Electron Energy Microscopy (LEEM) (Hibino et al., 2008; Virojanadara et al., 2008) and ellipsometry (De Heer et al., 2011). LEEM is a very precise technique but it takes a long time to measure and analyze the sample. Optical measurements may be very fast but it is necessary to use reflectance, not absorption (Ivanov et al., 2014), and it is quite complicated to analyze the thickness of graphene structure.

Raman spectroscopy is a widely used tool to characterize graphene structures (Ferrari et al., 2006; Mohiuddin et al., 2009; Nyakiti et al., 2012; Röhrl et al., 2008; Yan et al., 2007). Measuring Full Width at Half Maximum (FWHM) of the 2D band one can calculate how many layers are on the sample (Ferrari et al., 2006; Malard et al., 2009; Nyakiti et al., 2012). Nevertheless, lateral resolution of Raman maps is always limited by diffraction. It is possible to use a confocal microscope or a confocal immersive objective to analyze a very small spot but still it is very hard or impossible to obtain resolution better than 0.1 μm.

A Scanning Electron Microscope equipped with an in-lens detector was already used to analyze graphene thickness but only for exfoliated graphene (Albrektsen et al., 2012; Kochat et al., 2011). Calculating the number of layers by an in-lens SEM system is difficult and complicated, especially if graphene thickness is changing from one sample area to another, like for graphene grown on 4H-SiC(0001). Raman spectroscopy is a much more reliable and faster tool to determinate the number of graphene layers.

In this paper we present a method enabling the determination of graphene thickness with the precision of SEM and reliability of Raman imaging.

2. Materials and methods

Graphene was grown using a commercial horizontal CVD hot-wall reactor (Aixtron VP508) on 4H-SiC(0001) semi-insulating on-axis Cree 10 × 10 mm SiC substrates cut out from a 4″ wafer. The substrate was first etched in H_2 at 1600 °C. Then, hydrogen was replaced by argon and the process of sublimation began. Before Raman maps acquisition, small marks were made on the sample surface using a diamond pen in order to navigate on the sample. Afterwards, the measurement area was chosen close to the mark point using a preview camera in a Raman Microscope. Raman maps were performed by the Renishaw in via Raman Microscope, using 532 nm excitation wavelength and a 0.9 NA objective with magnification ×100. The measurement area was 60 × 40 μm with a 0.25 μm step in both directions. The thicknesses of graphene structures were determined using Lorentz fitting for the area and FWHM of the 2D band. To measure both parameters wire 3.4 software was used. In this case the areas having no graphene on the sample caused some problems because in general the software always fits some void functions. Therefore, spectra with no 2D have some 2D band fitted to a very small area, which means that in certain

* Corresponding author.
E-mail address: Kacper.grodecki@itme.edu.pl (K. Grodecki).

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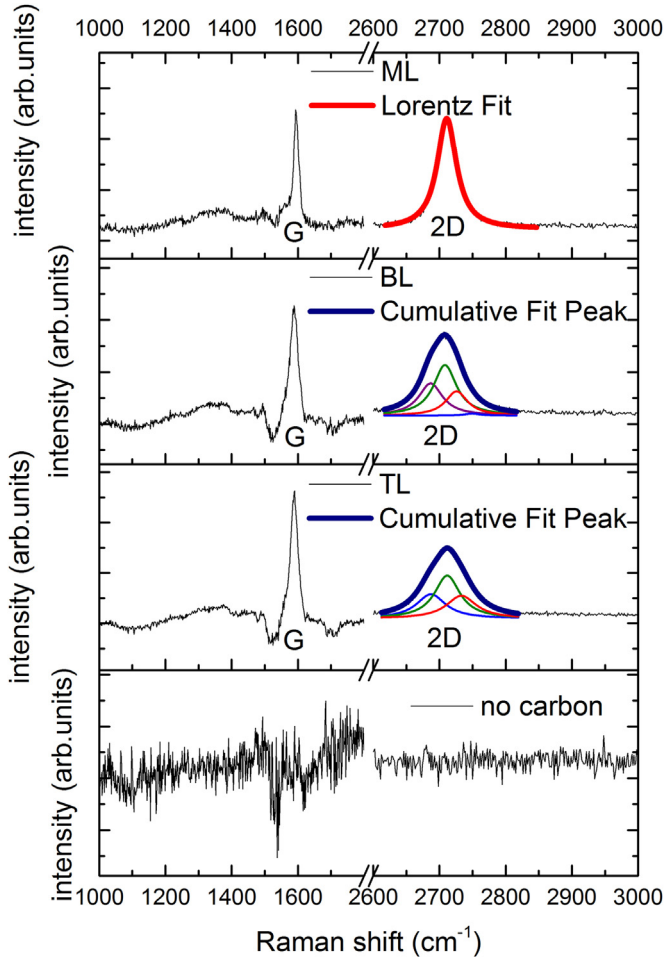

Fig. 1. Raman spectra of (a) graphene ML—2D band is fitted by one Lorenzian peak, (b) BL graphene—2D band is fitted by four Lorenzian peaks, (c) TL graphene 2D band is fitted by three Lorenzian peaks, (d) place without graphene—there is no 2D band and no other graphene band. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

places the FWHM of the 2D band has no physical meaning. That is why, the thickness of graphene structures was determined based on both the FWHM 2D band and the 2D band area.

The next step was to perform low-kV (~0.5 keV) SEM imaging in correlation with Raman maps. We used an Auriga Cross Beam Workstation (Carl Zeiss) equipped with an In-Lens secondary electrons detector (In-Lens SE) detector and an EsB and low-loss Backscattered Electrons (low-loss BSE) detector, both positioned on the optical axis of the unique Gemini column integrated with the beam booster. Thanks to the lens design and its strong dispersion in the reverse imaging plane, the SEs and BSEs are separated in real time and projected to the individual detectors. In front of the entry of the BSE detector there is an energy filtering grid with retarding potential that can be applied from 0 to 1500 V.

3. Results and discussion

Shape and intensity of the Raman 2D band were used to determine the thickness of graphene structure on the sample (Fig. 1). The rules for the determination of the number of graphene layers are different for graphene structures grown on both 4H-SiC(0001) and 6H-SiC(0001) and for exfoliated graphene structures (Nyakiti et al., 2012; Ferrari et al., 2006). The range of about 30–45 cm^{-1} is characteristic of monolayer graphene (ML) fitted by one Lorenzian (Nyakiti et al., 2012) in Fig. 1a. FWHM from 45 to 60 cm^{-1} is bilayer graphene (BL) fitted by four Lorenzian peaks (Nyakiti et al., 2012) in Fig. 1b. FWHM from 60 to 75 cm^{-1} is trilayer graphene (TL) fitted by three Lorenzian peaks in Fig. 1c (Malard et al., 2009). Regions with higher FWHM were treated as four graphene layers. Additionally in some unclear situations the 2D band area was used to verify the number of layers. For instance regions with a very small 2D band area were treated as no-graphene places (Fig. 1d).

Fig. 2 presents the SE and BSE SEM images and Raman maps of the FWHM 2D band and 2D band area of the same sample area collected using a correlative technique. In the case discussed, the secondary electrons image acquired by the In-Lens detector and the backscattered electrons image in the EsB detector present very similar features. However, the low-loss BSE image contrast is based mostly on the compositional (the nature of molecular bonds in this case) and thickness contrast, while the In-Lens SE image contrast is strongly influenced by different surface parameters such as conductivity, work function, crystal orientation etc. Image b in Fig. 2 shows clearly the graphene thickness increase on the edges of the

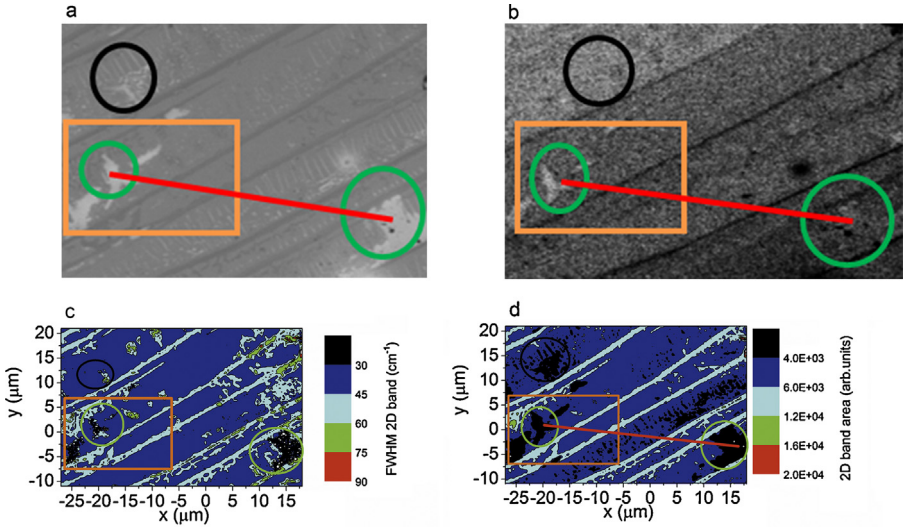

Fig. 2. Images of (a) SEM In-Lens, (b) SEM EsB and Raman maps of (c) FWHM 2D (d) area 2D band. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

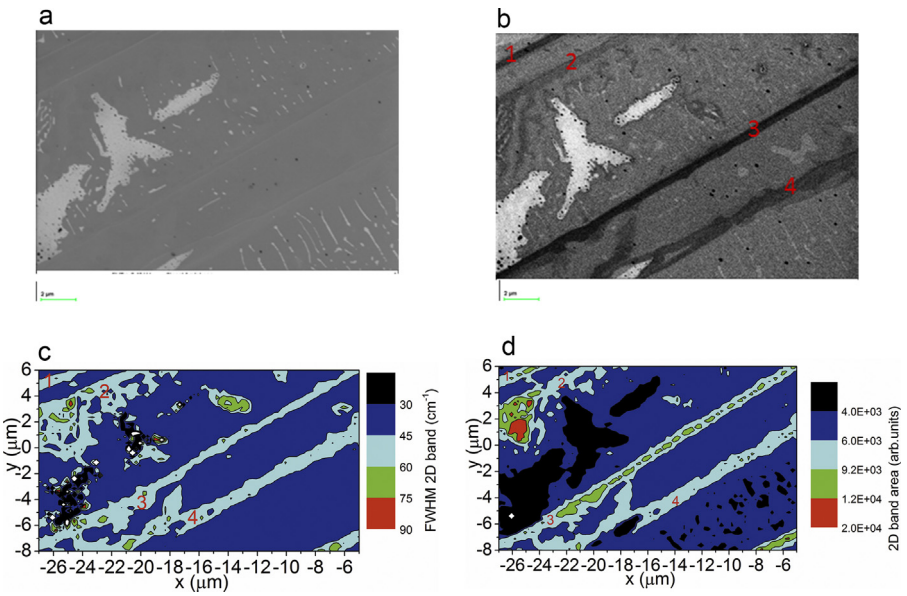

Fig. 3. Images of (a) SEM In-Lens, (b) SEM EsB and Raman maps of (c) FWHM 2D (d) area 2D band. Images are made in the area of orange rectangle marked in Fig. 2. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

terraces, which are favorable sites for graphene growth. The brighter areas marked with circles (both black and green) are places without graphene, showing compositional contrast of the substrate in comparison to the graphene layers. The correlation with Raman maps is direct (see Fig. 2a–d), with only one exception—the feature on the right circled in green. It has the same character as other features when observed in the In-Lens SE detector, but it is hardly visible in the BSE image. At the same time point, the Raman maps show no graphene in the analyzed area. One of the possible explanations of the darkening of this area is as follows: due to the very high level of contamination during the observed growth of the layer, the image becomes darker and darker from the top-left to down-right corner of the image, which is a typical phenomenon, very often observed in low-kV SEM imaging.

On the FWHM 2D band map (Fig. 2c) a large area in blue corresponding to ML may be treated as terraces and most of the thicker layer as step edges (Grodecki et al., 2012). The 2D band area map (Fig. 2d) was calibrated in such a way as to have places without graphene of the same shape as in the case of SEM In-Lens (Fig. 1a) and have other regions (blue, cyan and green) in the same place as for the FWHM 2D band map (Fig. 2c). Regions marked as ML have a smaller 2D area (Fig. 2d blue color) than regions marked as bilayer (cyan), trilayer (green) and four layer (red) graphene.

In the 2D area map, areas without graphene structures are black. Two of these places were marked with a green circle (Fig. 2). Both places are well-seen in the SEM images and are also marked with green circles. The shape of these places on the 2D band area map and the corresponding SEM image is the same. In addition, the distance between them, marked with a red line (both red lines have the same length), is very similar. Because of some error and imperfections in the Raman measurement table there may be a slight discrepancy between these maps. While watching the places without graphene structures one can see that on the FWHM 2D map some of these places are seen as black (below 30 cm^{-1}), whereas others (marked with a black circle) as blue (30–45 cm^{-1}). This means that it is better to use both FWHM 2D band area 2D in the case of samples with places without graphene. In those regions there is always some fit of 2D band—the area is then very small, but FWHM is outside the physical interpretation and may be very different (like black or white on the FWHM 2D map). So analyzing in such regions area of 2D band should clarify if there is a place without graphene or some errors

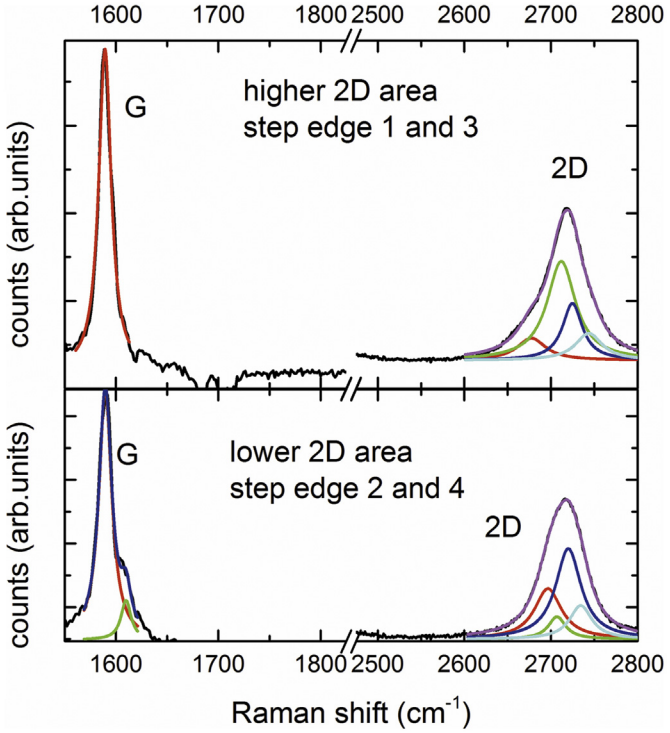

Fig. 4. Raman spectra from step edges with (a) higher 2D band area from step edge 1 and 3 (b) lower 2D band area from step edge 2 and 4. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

in fitting procedure. There may also be a buffer layer in these areas. The buffer layer is known to have a planar structure of graphene and be bounded to the SiC surface covalent bonds. (Strupinski et al., 2015). Nevertheless Raman spectra (Fig. 1d) invalidate the existence of the buffer layer in the above mentioned regions (Strupinski et al., 2015).

Figures above are adequate for estimating the thickness of graphene structures, at the same time showing agreement between SEM and Raman maps and making it possible to do proper calibra-

tion of the 2D area map. On the other hand, the spatial resolution of SEM images can be much higher than in the case of Raman maps.

For a more precise analysis, the SEM high magnification image of the region marked in Fig. 2 with an orange rectangle was collected and is presented in Fig. 3:

The SEM images shown in Fig. 3a and b present bright regions without graphene (just as in the case of the region marked with green circle in Fig. 2). Raman map of the 2D area (Fig. 3d) also confirms the absence of graphene structures in this region. 90% of terraces are covered by ML. When the region of ML for the FWHM 2D map is 30–45 cm^{-1}, the map shows ML having a shape, which is the most similar to objects distinguished by the contrast change in the SEM images (Fig. 3b). The 45–60 cm^{-1} region for the bilayer covers the whole region of the step edges and some additional regions which are darker in the SEM image.

Four step edges are visible in the EsB SEM image (Fig. 3b marked by numbers 1, 2, 3, 4). Two of them are much darker (1 and 3), while the other two are brighter (2 and 4). All of them are represented as a bilayer on the FWHM 2D map (cyan regions). However, two darker step edges in the SEM image have a slightly higher 2D band area (green spots). On the other hand, the 2D band on spectra from the step edge with a bigger 2D band area is classical bilayer graphene (Fig. 4a) with a slightly asymmetric band, fitted with four Lorentzian lines.

The second spectrum with a smaller 2D band area may be fitted with four Lorentzian peaks (Fig. 4b). This suggests that a slight difference in the SEM image shade does not have to mean different thickness. In Fig. 4a the G band is fitted with one Lorentzian, whereas in Fig. 4b with two Lorentzians, which suggest different carriers concentration as it was observed for bilayer graphene (Yan et al., 2009).

4. Conclusions

In conclusion, a comparison of Raman FWHM and the 2D band area maps with the secondary and low-loss backscattered SEM images was made. We showed that by analyzing all images together one can measure the thickness of a graphene structure more precisely than only by Raman spectroscopy. It is however important to keep in mind that these both techniques are complementary, but have different origins of contrast. Therefore, either slight or substantial differences linked with conductivity and other dissimilarities between graphene and a SiC substrate may emerge.

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