Comparison of CVD graphene grown on copper foil and PVD copper

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Abstract: Graphene synthesis by the CVD method performed on the surface of copper is one of the most promising techniques for producing graphene for low cost and large scale applications. Currently, the most commonly used Cu substrate for graphene growth is foil, however, there is still a need to find new substrates and improve the quality of graphene layers. Sputtered Cu films on insulating substrates are considered as an alternative. Here we show the properties of graphene grown by the CVD method on thin copper foil and PVD copper films on Si/SiO_2 substrates. We compare data on the properties of graphene films transferred from different copper substrates onto SiO_2/Si substrates. We note that graphene grown on sputtered Cu films creates a multilayer form on the boundaries which can be identified on micro-Raman maps and in SEM images.

Key words: graphene on copper foils, PVD copper films, grain boundaries, Raman spectroscopy

Porównanie własności grafenu otrzymanego metodą CVD na folii miedzianej oraz warstwie PVD miedzi

Streszczenie: Wytwarzanie grafenu metodą CVD na podłożach miedzianych jest jedną z najbardziej perspektywicznych metod otrzymywania grafenu ze względu na niski koszt podłoża oraz szerokie możliwości zastosowania w przemyśle. Obecnie najczęściej stosowanym do wzrostu grafenu podłożem miedzianym jest folia, jednakże ciągle istnieje potrzeba znalezienia nowego podłoża tak by poprawić jakość warstw grafenu. Jako alternatywę rozważa się cienkie warstwy miedzi wytwarzane metodami PVD osadzane na nieprzewodzącym podłożu. W niniejszym artykule przedstawiamy własności grafenu wytwarzanego metodą CVD na cienkiej folii miedzianej oraz na warstwach miedzi osadzonych na Si/SiO_2. Porównujemy także wyniki otrzymane dla przeniesionych warstw grafenu z obu rodzajów próbek.

Słowa kluczowe: grafen na folii miedzianej, warstwy PVD miedzi, granice ziaren, spektroskopia ramanowska

1. Introduction

Graphene on a copper substrate has attracted great 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]. The most popular approach to the fabrication of graphene on copper substrates is epitaxial growth on foils [3], single crystals [4] and on deposited thin films on dielectric surfaces using carbon precursors [5 - 6]. All these methodologies have their advantages. High purity copper foil used as a substrate is available in different thicknesses and sizes, from one square centimeter pieces to one square meter sheets. On the other hand, Cu deposited on SiO_2 is more controllable in the crystallographic context and cost-effective due to the fact that usually its thickness ranges between 200 and 500 nm.

In this work we compare the properties of graphene grown by the CVD method on different substrates, namely thin copper foil and sputter-deposited copper on a Si/SiO_2 substrate. We collate data on the properties of graphene films transferred from different copper substrates onto dielectric ones. We show that the grain size in the case of sputtered Cu films is much smaller than for Cu foil and we present its influence on the quality of the transferred graphene films.

2. Experimental

The graphene films were synthesized by chemical vapor deposition on the surface of 12 μm thick copper foils. To obtain graphene of top quality we use the Aixtron VP508 horizontal CVD hot wall reactor (formerly known as the Epigress system). This device ensures perfect temperature distribution without the thermal gradient effect, laminar gas flow, pyrometrically-controlled temperature, ultra high purity of applied hydrogen, argon and propane as well as precise control of the pressure, partial pressure and gas flows.

At first, the samples were pretreated at 1000 °C under an Ar gas flow and then H_2 gas flow at the pressure of 100 mbar. The purpose of this step was to improve the quality and enlarge the grain size of Cu foil. Afterwards, both C_3H_8 and H_2 gas were introduced into the reactor for 2 minutes. Finally, the copper substrates covering the graphene films were cooled down to room temperature in an Ar atmosphere. Samples of graphene on the PVD copper substrate were prepared outside our laboratory.

To transfer graphene onto the SiO_2 substrate, graphene on Cu foil was covered with a thin layer of poly (methyl methacrylate) (PMMA) by a spin-coating method. The PMMA layer served as a support preventing the graphene film from collapsing during copper etching. Then we removed graphene from the backside of copper foil to avoid impurities between the top and lateral graphene films formed during copper etching. Next, the PMMA/graphene stack was immersed in an aqueous solution of ammonium persulfate. In the case of graphene on PVD $Cu/SiO_2/Si$, the whole structure was put in the solution of ammonium persulfate after covering graphene with PMMA. When Cu was completely etched, the PMMA/graphene stack was floating on the surface of the solution. To clean the PMMA/graphene stack, we used the modified RCA cleaning method [7]. Next, the PMMA/graphene stack was fished by the SiO_2 substrate and they were all gradually heated at above 150 °C in an air atmosphere to make full contact. At the end, the PMMA layer was carefully removed by acetone.

The characterization of graphene on copper includes Raman spectroscopy, confirming the formation of graphitic structures, as well as SEM and AFM imaging, showing the morphology of the graphene/Cu interaction. Further assessment of the properties of transferred graphene is performed with Hall measurements in the van der Pauw configuration and a novel contactless microwave technique that utilizes a single post dielectric resonator operating at 13.1 GHz [8 - 9].

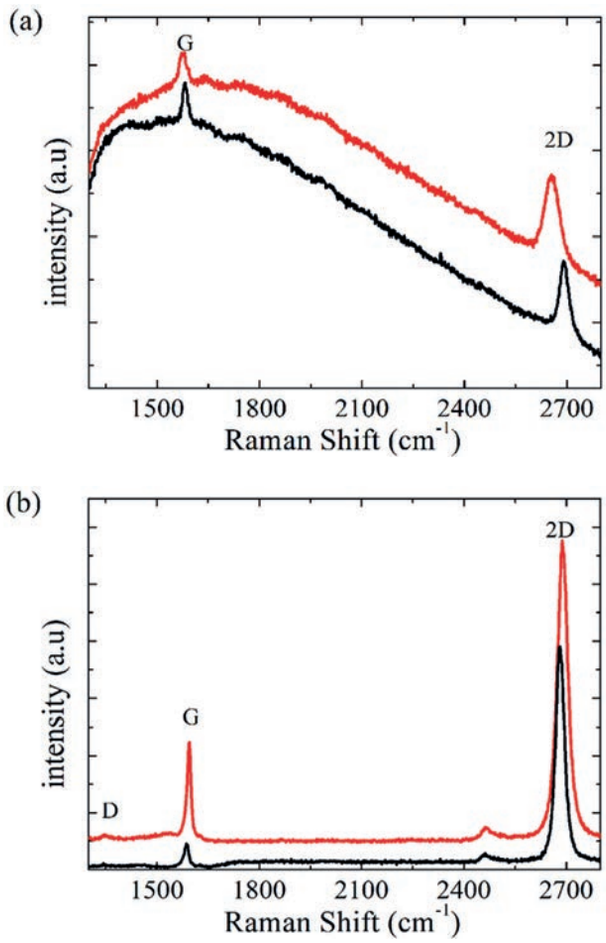

Fig. 1. Raman spectra for (a) graphene grown on copper foil (black) and the PVD copper film (red) and (b) graphene transferred to SiO_2 from copper foil (black) and the PVD copper film (red).

Rys. 1. Widma ramanowskie (a) grafenu na foli miedzianej (czarna linia) i warstwy PVD miedzi (czerwona linia) oraz (b) grafenu przeniesionego na SiO_2 z folii miedzianej (czarna linia) i z warstwy PVD miedzi.

3. Results and discussion

As regards the characterization of the obtained graphene films, in the first step we aimed at confirming their quality by performing Raman spectroscopy measurements. The Micro-Raman experiments were done in back-scattering geometry, using a Renishaw in via Raman Microscope, with a x100 objective and a 532 nm Nd:YAG laser as an excitation source.

In Fig. 1a Raman spectra for graphene on both copper substrates with a background characteristic of copper are shown. For these spectra, the G (1590 cm^{-1}) and 2D (2690 cm^{-1}) bands are clearly visible, which confirms the presence of a graphene structure in both measured samples [10]. A typical position of the 2D band for graphene grown on copper foil is higher than for the PVD copper film, which suggests higher strain for graphene grown on copper foil. Moreover, we investigated the transferred graphene films obtained on both kinds of copper substrates. Figure 1 b presents Raman spectra confirming the presence of a transferred graphene monolayer on SiO_2. Low Full Width at Half Maximum (FWHM about 30 cm^{-1}) of the 2D band for both graphene layers presented in Fig. 1b as well as much higher intensity of the 2D band by comparison with the intensity of the G band are characteristic of a single layer of graphene. Very low D bands on both spectra are typical of high quality graphene structures.

Next, we investigated the Raman spectroscopy results in more detail and performed a structural analysis of the graphene layers. Spatial Raman mapping was carried out on two different scales, namely on a macro-scale (a few mm^2) to show the average graphene parameters and on a micro-scale (a few μm^2) to analyze the homogeneity and continuity of the graphene structure. The laser spot diameter on the sample surface was approximately 0.3 μm.

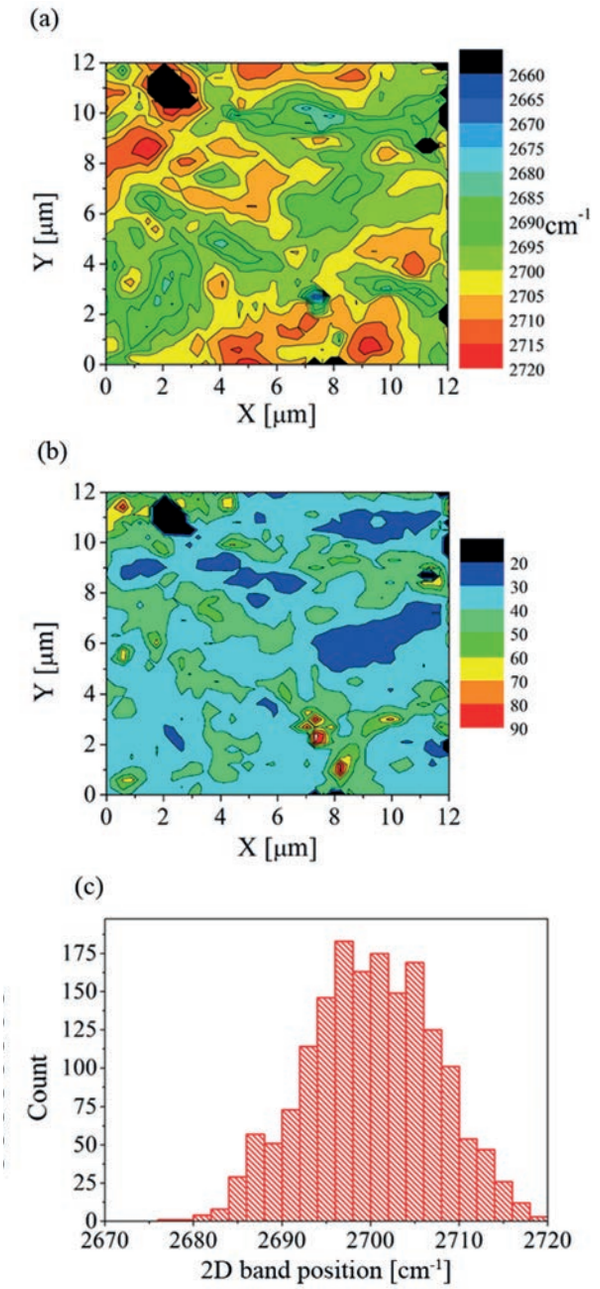

Fig. 2. Raman maps of (a) 2D band position, (b) FWHM of the 2Dband, (c) histogram of the 2D band position for graphene on Cu foil.
Rys. 2. Mapa ramanowska (a) pozycji pasma 2D, (b) FWHM pasma 2D, (c) histogram pozycji pasma 2D dla grafenu na folii Cu.

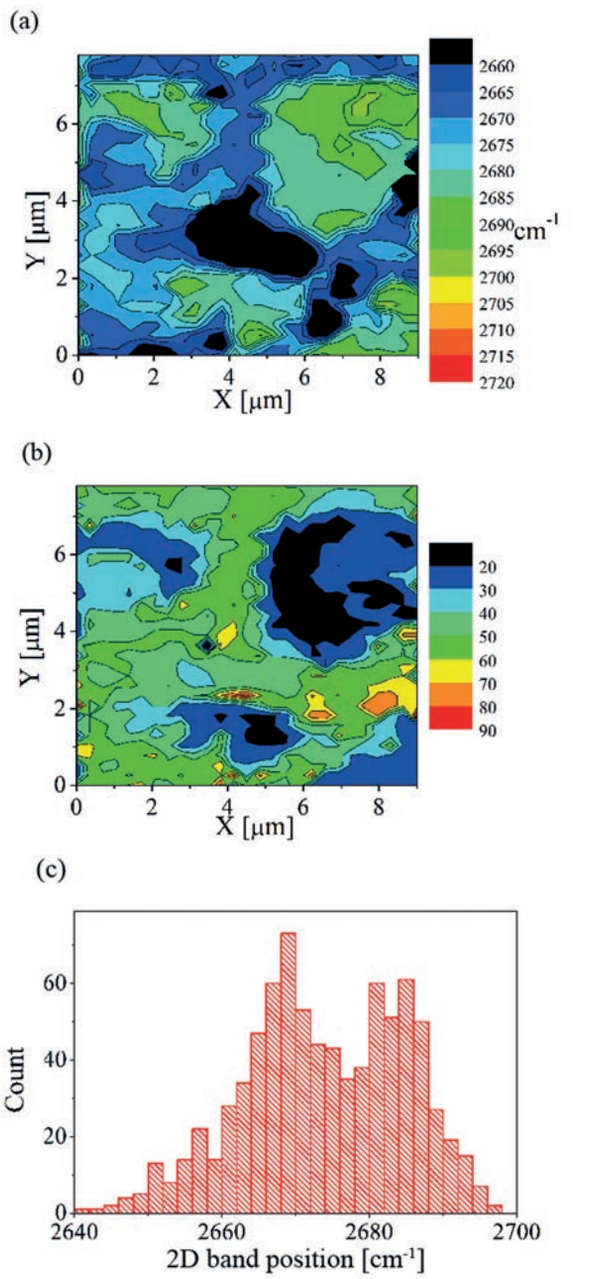

Fig. 3. Raman maps of (a) 2D band position, (b) FWHM of the 2D band position, (c) histogram of the 2D band position for graphene on the PVD Cu film.
Rys. 3. Mapa ramanowska (a) pozycji pasma 2D, (b) FWHM pasma 2D, (c) histogram pozycji pasma 2D dla grafenu na warstwie PVD miedzi.

The Raman spectra and histograms for graphene on Cu foil and the PVD Cu samples are shown in Fig. 2a, b, c and 3a, b, c, respectively. Fig. 2a and b present the maps of the 2D band position and FWHM of the 2D band. There are no visible regularities when changing the positions of both the 2D band and FWHM, which suggests there being no pattern of changes in the graphene structure in the sample. In Fig. 3a and 3b, for PVD Cu samples, the regions with higher 2D band energy (Fig. 3a) are in the same position in which the FWHM of the 2D band (Fig. 3b) is lower. Moreover, two different types of areas are prominent on these maps. One of them is characterized by high 2D band energy and low FWHM of the 2D band, whereas the other has inverse regularities. This indicates the presence of two different types of graphene regions in this sample.

For graphene on Cu-foil, the changes in the 2D band position are less significant, (Fig. 2c) i.e. between 2680

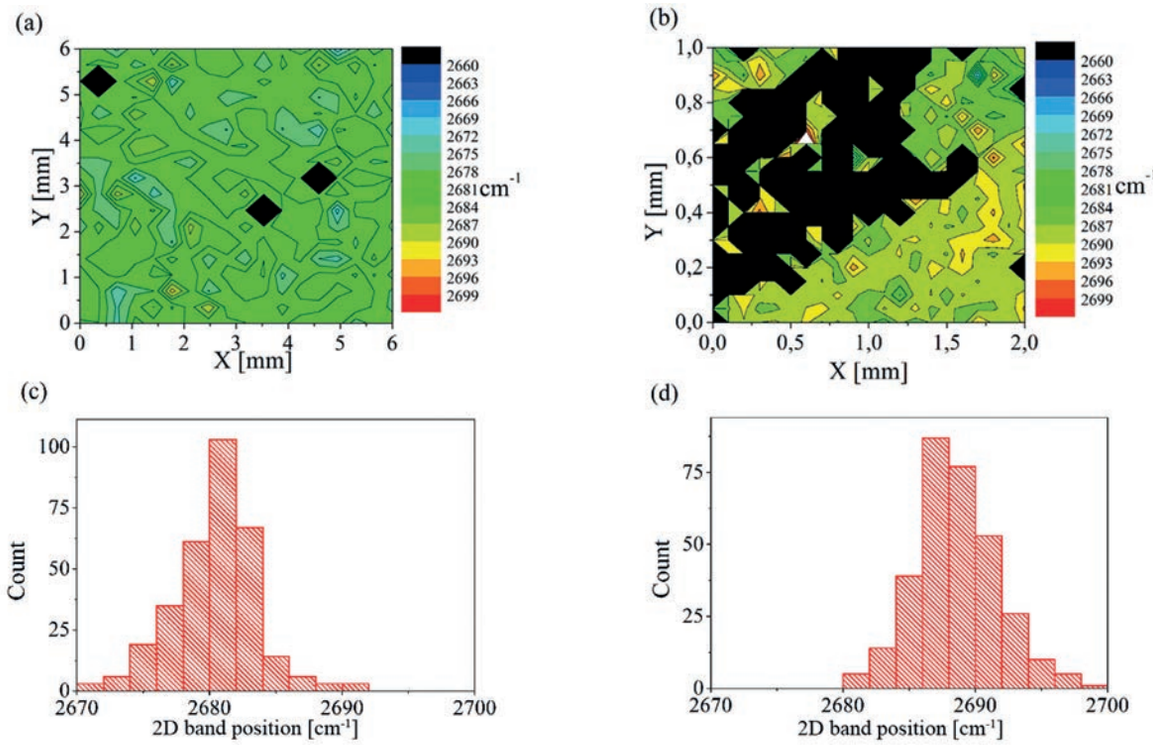

Fig. 4. Raman maps and histograms of the 2D band position for graphene transferred from (a), (c) Cu foil (6x6 mm) (b), (d) PVD Cu (1 x 2 mm).
Rys. 4. Mapy ramanowskie oraz histogramy pozycji pasma 2D dla grafenu przeniesionego z (a), (c) folii miedzianej (6 x 6 mm) (b), (d) warstwy PVD miedzi (1 x 2 mm).

and 2720 cm^{-1}, with a maximum difference of 40 cm^{-1}. For graphene on the PVD Cu film sample, the difference is 60cm^{-1} and varies between 2640 and 2700 cm^{-1}. In consequence, it can be stated that the homogeneity of graphene on Cu - foil is higher than in the case of graphene on the PVD Cu film. This takes place mainly because of the fact that both PVD copper grains and their boundaries exert a strong influence on the morphology of the surface on which graphene is synthesized, which is revealed by the 2D band position and maps of the FWHM of the 2D band.

The Raman maps of the 2D band position of graphene transferred from Cu foil are presented in Fig. 4a and c. The average 2D band position is 2680 cm^{-1}, which is the value for freestanding graphene. It suggests that the graphene layer transferred from Cu foil is averagely relaxed. On the basis of the map shown in Fig. 4b and presenting the 2D band position for graphene transferred from PVD Cu, it can be stated that slightly compressive strains are observed [11]. It is also well seen that graphene transferred from Cu foil covers the entire substrate, whereas for graphene transferred from PVD Cu there are places without graphene (black areas).

Comparison of the maps done for graphene grown on Cu and graphene transferred onto SiO_2 mainly suggest relaxation of stress in graphene structures. Homogeneity of graphene grown on Cu foil is preserved for graphene transferred on SiO_2. Differences in the graphene structure grown on the PVD film may stem from not fully covering the graphene structure after its transfer onto the SiO_2 substrate.

To explain the noticeable differences between the behavior of graphene on Cu foil and the PVD Cu film, both grown and transferred, we used complementary topographic characterization methods, namely AFM and SEM. We checked the influence of substrate morphology and the graphene-Cu interaction by analyzing the surfaces of graphene/copper foil and graphene/PVD copper films.

In Fig. 5 (a and b) one can find AFM images taken over an area of 5 x 5 μm^2 which present the morphology of the graphene/Cu surface. The roughness of graphene on Cu foils is R_q = 7.43 nm, which is higher than the roughness of the graphene/PVD Cu interface, the value of which is R_q = 4.05 nm.

To demonstrate the topography of our samples, SEM imaging is applied. At first, we investigate the surface of graphene covering Cu foils (Fig. 6a) and PVD Cu films (Fig. 6b). Thanks to the ESB (Energy Selective Backscattered) detector and ultra-low energy of an electron beam, the value of which is 0.5 kV, it is possible to perform imaging, revealing the atomic number contrast of the surface of the sample. One can notice that copper grains are significantly larger on copper foil than on PVD copper. The size of the copper grains on the Cu film ranges between dozens and hundreds of micrometers, while on PVD Cu it is just over a dozen of micrometers.

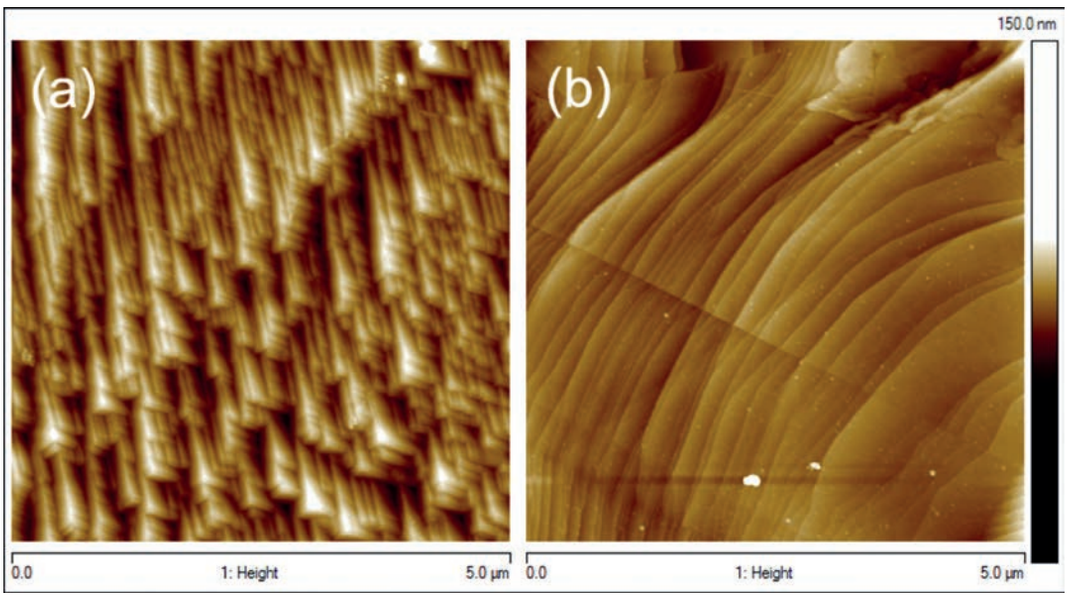

Fig. 5. AFM images of the surfaces of (a) graphene/Cu foil, (b) graphene/PVD Cu film.
Rys. 5. Obrazy AFM powierzchni (a) grafen/folia miedziana, (b) grafen/warstwa PVD miedzi.

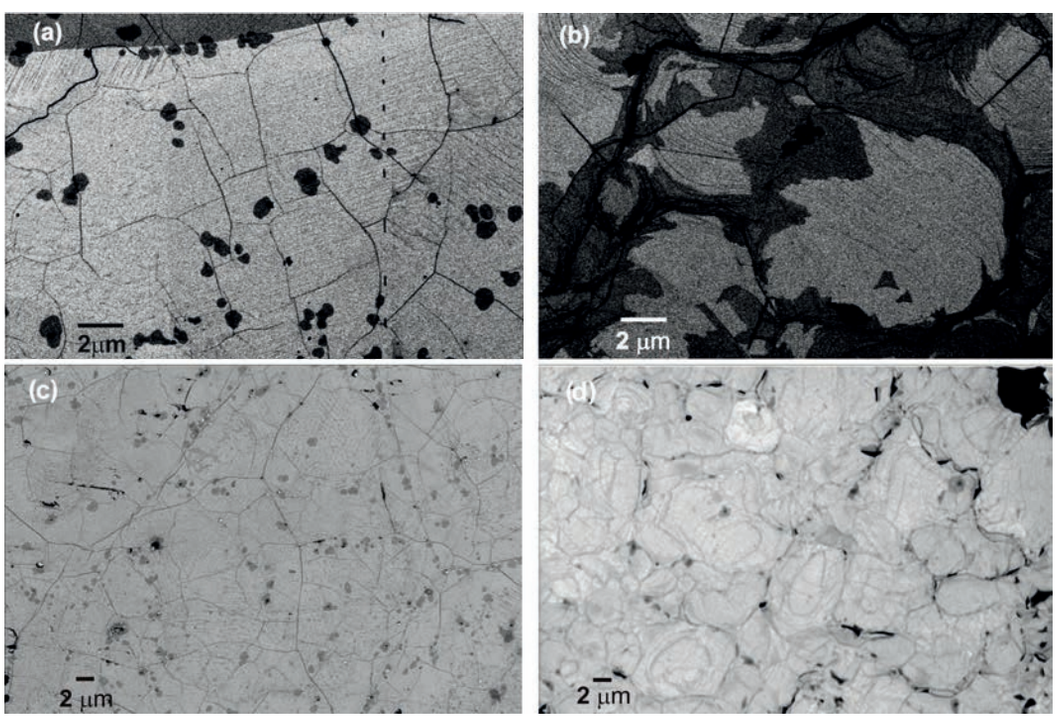

Fig. 6. SEM image of graphene grown on (a) Cu foil and (b) PVD Cu film and graphene transferred to silicon dioxide samples from (c) copper foil and (d) PVD copper.
Rys. 6. Obrazy SEM grafenu syntetyzowanego na (a) foli miedzianej oraz (b) warstwy PVD miedzi a także grafenu przeniesionego na dwutlenek krzemu z (c) folii miedzianej oraz (d) warstwy PVD miedzi.

Moreover, in the case of Cu foil, both on it and on its boundaries there are just a few spots where we can observe additional graphene layers – the dark dots in the images. In the case of graphene grown on PVD copper we observe an extensive number of multilayer graphene formations around the grains, which evidently corresponds with the already shown Raman maps. The previously observed region with higher 2D band energy and lower FWHM 2D energy is related with the additional layers of carbon films, whereas lower 2D band energy and higher FWHM of the 2D energy with the monolayer of graphene.

The SEM image of the morphology of the transferred graphene films indicates that when graphene is transferred from Cu foil, its surface is flat and continuous (Fig. 6c). Moreover, we cannot observe distinct grain boundaries in the case of this film. When it comes to graphene peeled

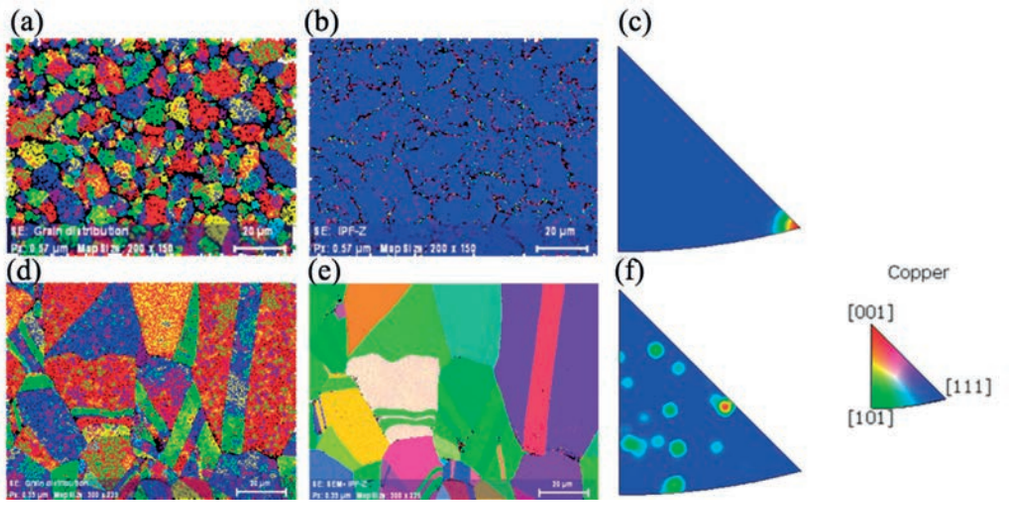

Fig. 7. EBSD maps of Cu grains distribution of a) PVD Cu film and d) Cu foil. Inverse pole figure EBSD maps of b) PVD Cu film and e) Cu foil. Stereographic projection for c) PVD Cu film and f) Cu foil.
Rys. 7. Mapy EBSD rozkładu ziaren miedzi (a) warstwy PVD miedzi oraz (d) foli miedzianej. Graficzne przedstawienie orientacji ziaren (b) warstwy PVD miedzi oraz (e) foli miedzianej. Rzut stereograficzny (c) warstwy PVD miedzi oraz (f) folii miedzianej.

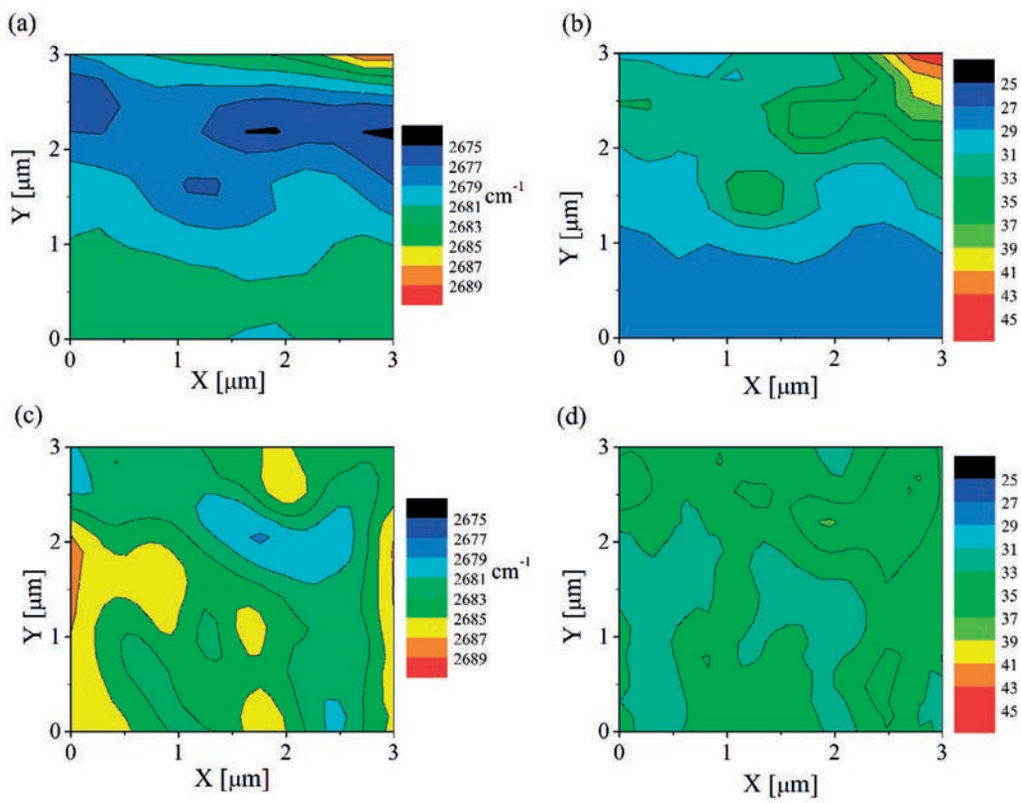

Fig. 8. Raman maps of (a) 2D band position, (c) FWHM of the 2D band for graphene transferred from Cu foil and (b) 2D band position, (d) FWHM of the 2D band for graphene transferred from the PVD Cu film.
Rys. 8. Mapy ramanowskie (a) pozycji pasma 2D, (c) FWHM pasma 2D grafenu przeniesionego z folii miedzianej oraz (b) pozycji pasma 2D, (d) FWHM pasma 2D grafenu przeniesionego z warstwy PVD miedzi.

off the PVD copper substrate, we noticed that the surface of graphene has a complex topography, with tangible grain boundaries and wide cracks, which is shown in Fig. 6d. Both the cracking on the boundaries as well as mechanical damage during the whole experiment account for discontinuities in the graphene layers. These results confirm the features mentioned when commenting on the Raman maps, where there were a lot of places without graphene layers (black areas) on the map of the 2D band position.

In addition, we performed EBSD (Electron Backscatter Diffraction) maps presenting the Cu grain distribution of sputtered Cu films and Cu foil, which demonstrate dif-

ferences in the crystallographic orientation of the copper grains on both copper substrates (Fig. 7). We note that the PVD Cu film is highly textured and the preferred orientation of copper grains is (111). It is also showed that high quality graphene can be successfully obtained using Cu (111) films and that the Cu (111) crystallographic orientation is the most suitable surface for graphene synthesis [12 - 13].

The AFM and EBSD results, revealing lower roughness for graphene on PVD Cu films and the desired crystallographic orientation for PVD Cu surface, suggest that graphene fabricated on this kind of substrates should have enhanced properties when compared with graphene on copper foils. Therefore, we checked how graphene behaves inside the copper grains. The micro-Raman maps were taken over 3 x 3 μm^2 areas on graphene films transferred from Cu foil and the PVD Cu film (Fig. 8).

The comparison of Fig. 8a and fig. 8c shows that the strain level is similar in the case of graphene on both Cu foil and PVD Cu film. However, the dispersion of the 2D band position is lower for graphene on the PVD Cu film. Changes of the 2D band position are 6 cm^{-1} and 10 cm^{-1} for graphene on the PVD Cu film and Cu foil respectively. For FWHM of the 2D band the changes are 5 cm^{-1} for the PVD Cu film and 19 cm^{-1} for Cu foil. Lower FWHM of the 2D band for PVD Cu foil suggests a better homogeneity of thickness in comparison with the results obtained for the second sample. In both instances the average thickness is comparable, with the average FWHM of the 2D band of about 32 cm^{-1}. In conclusion, micro-Raman maps prove that in a micro-scale the quality of graphene on the PVD Cu film is slightly higher than on Cu foil.

The equivalence of sheet resistance assessed with the microwave dielectric resonator measured on 1 cm^2 samples was 1164 Ω/□ and 9006 Ω/□ for copper foil and PVD copper respectively. In the case of graphene transferred from PVD copper, there is a direct link between high sheet resistance and the interrupted graphene films. Van der Pauw Hall measurements in 300 K showed the following results: μ = 644 cm^2/Vs, ρ = 1600 Ω/□ and p - type concentration of 6E12 cm^{-2} for graphene transferred from Cu foil and non-measurable in the case of graphene transferred from PVD Cu. The dielectric resonator method allows the assessment of the equivalence of the sheet resistance of single layer graphene even if it is discontinuous. At this point standard DC conductivity measurement methods, e. g. Hall method, may fail, which was observed for a discontinued graphene layer transferred from PVD Cu. Instead, we assessed its sheet resistance with the microwave method.

4. Conclusions

We investigated graphene grown on two kinds of copper substrates and we showed that graphene achieved according to the mentioned methods is a monolayer carbon film with a proven quality. Additionally, we found that much smaller grains, and hence more invasive boundaries, are obtained on PVD Cu films, compared to those on Cu foils. On a macro-scale this affects the transferred graphene films. On the other hand, we revealed that inside the grains the quality of graphene on PVD Cu is slightly better than in the case of Cu foil, which encourages us to further develop the synthesis of graphene on PVD Cu.

Acknowledgements

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