Abstract of Ph.D. thesis

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X-ray studies of graphene layer systems grown by sublimation and CVD methods

Graphene is a material that combines many of interesting physical properties, including: very high mechanical strength, high mobility of carriers and large thermal conductivity. It seems that graphene has the potential to be widely used in the production of sensors, supercapacitors, solar cells, touch screens or composite materials. In addition, due to its unique band structure (linear energy dependence of the wave vector) high hopes are associated with graphene as far as its use in electronic applications is concern. But to make this possible it is necessary to develop a method for the reproducible production of large-area grapheme which will have a homogeneous structural quality as well as the consistent number of layers. For this purpose it is necessary to develop experimental methods which allow the characterization of the structural quality and the thickness and number of layers of graphene layers stacks.

X-ray diffraction has been used as one of the standard experimental methods used to study the structure of graphite powders from the forties of the 20th century. However, nowadays X-ray diffraction measurements are used in studies of graphene only occasionally. In most of the cases the synchrotron sources are used, while the X-ray tube as the radiation source was employed only in study of samples in powder form. There are no reports showing that standard laboratory X-ray sources were used to study graphene layers stacks grown on the SiC substrate. Therefore, this thesis has been mainly devoted to the X-ray measurement of graphene layers stacks on SiC substrates obtained with the X-ray diffractometer.

Diffraction signal recorded from the graphene layer stacks is very weak, especially from the thin ones (less than 5 layers). Therefore, it was necessary to use a Bragg mirror, which increases the intensity of the incident beam by almost one order of magnitude. This made it possible to carry out measurements with satisfactory signal statistics in less than 12 hours. Another crucial element of the measurement system was to prepare a sample holder that can help to eliminate the necessity of gluing the sample. This allowed to minimize the background signal from the sample holder, thereby significantly improved the signal to the background ratio.

This work also presents method that successfully allows recording diffraction signal from the graphene layer stacks. In particular, a symmetrical reflection from SiC substrate was used to correct and adjust the angular position corresponding to the diffraction signal from graphene layers.

In this thesis the graphene layer stacks grown by sublimation and CVD methods on silicon carbide substrates (4H or 6H polytypes) and on silicon or carbon side were primarily studied. For samples of thick graphene layer stacks the 0002, 0004 and 0006 reflections were recorded by $\omega/2\theta$ scans. Then each peak was fitted with Gaussian or Voigt profile which allows obtaining the angular position of the maximum intensity and the FWHM of the peak. Using the Bragg's law and the determined values of angular positions of the maximum intensity, the interplanar spacing d_{0002} was calculated for each sample. The value of the d_{0002} corresponds to the average distance between successive graphene layers. Using the Scherrer formula and FWHM values the average thickness and number of grapheme layers can be obtained for thick stacks (more than 5 graphene layers). The three methods of grapheme stack thickness estimations: Scherrer formula (X-ray measurements), Raman spectroscopy and optical absorption were compared. This allowed estimating the value of K coefficient (Scherrer), which for thick graphene layers stacks gives results consistent with those obtained with two other methods. It was found that using the Scherrer formula for thin graphene layer stacks (less than 5 layers) becomes problematic, and the d_{0002} obtained from Bragg's law is incorrect.

For samples of thin graphene layer stacks it was necessary to develop a new analysis method of measurement data from which one could derive the correct values of d_{0002}, the number of layers and surface coverage by graphene stacks. For this purpose the mathematical model based on the so-called Yang's approximation was used. This model was used to calculate the diffraction intensity of recorded 0002 reflections. One can use this model for non uniform surface coverage by graphene stacks as well as for stacks with different lattice constants.

The most important part of this work was connected with the study of graphene intercalated with hydrogen. For the measurements three samples of graphene stacks grown by sublimation on 4H-SiC substrate (Si side) were selected, of which two were further intercalated with hydrogen. One of the intercalated samples was later annealed at 1000°C. In a similar manner three samples of CVD graphene were also prepared. From the X-ray diffraction measurements of 0002 reflection and from the theoretical calculations it was found that graphene layers intercalated by hydrogen have a d_{0002} value greater when compared to the samples of non intercalated graphene. This means that the hydrogen goes between the graphene planes, resulting in an increase of the interlayer spacing. X-ray measurements presented in this thesis showing the interlayer intercalation of hydrogen are the first result that properly illustrates the intercalation process. Our results also show that by annealing the samples at high temperatures we can evacuate hydrogen from graphene stacks. The sample after annealing at 1000°C has values of d_{0002} typical for non intercalated graphite (AB stacking).

The CVD process of graphene growth on 4H-SiC substrate (Si side) has been analyzed as a function of growth time. It was found that extended duration of the growth process leads to the growth of thin graphene layers stacks as well as the local formation of very thick carbon structures with a different lattice spacing.

In addition, using the high resolution X-ray diffraction and X-ray topography, polytypes stability of SiC substrates was investigated. In the case of SiC substrates used in the growth of graphene layers the presence of any additional polytypes of SiC was not revealed.

Simulation method of X-ray diffraction profiles used in this thesis for graphene layers stacks can also be applied to other layered materials, such as BN or MoS_2, which in recent years have attracted the attention of research community.