Crystallization of Thin Copper Films on Silica Substrate for Graphene Growth


The synthesis of graphene on thin copper film deposited on quartz substrate is reported. The copper films are fabricated with different thickness of 300 and 1150 nm and then crystallized during thermal annealing that occurs at temperature of 950 and 1000 °C for 30 or 90 min. The size of copper grains increases with increasing of the temperature and the time of annealing that results in increasing of graphene film size. The deposited copper films are studied by electron backscatter diffraction and synthesized graphene films are analyzed by Raman spectroscopy and scanning probe microscopy. Proposed phase contrast mode of the scanning probe microscopy demonstrates high lateral resolution and sensitivity to the presence of graphene with different number of layers. It is found that graphene monolayer is preferably formed on the surface of copper grains with orientation [111] and proposed techniques can be used for the analysis of the evolution of graphene growth.

1. Introduction
The synthesis of graphene films of high quality with reproducible physical properties on a metal foil (Cu, Ni) demands high requirements for the crystalline structure of the latter. It is a challenging task to implement reproducible synthesis of graphene on comparatively thin catalytic substrates. The growth of high-oriented thin copper films on a single-crystal substrate allows to solve this problem. The crystalline structure of the substrate, on which the growth of the metal film occurs, determines the direction of recrystallization during its annealing. In this paper, we investigate the effect of grain orientation of thin copper films and their crystallization on the synthesis of graphene by means of a Raman spectroscopy and scanning probe microscopy (SPM). For this purpose, we deposited thin polycrystalline copper film on the polished silica substrate and annealed the wafer in different conditions before graphene formation process.

2. Experimental Section
A copper film was deposited on quartz substrate in a UNIVEX 300 vacuum chamber at a pressure of 10⁻³ mbar by passing an electric current through a molybdenum boat with copper metal pieces. The quartz substrate was washed in a potassium dichromate and annealed at 580 °C for surface cleaning before the metal deposition. The cleaned quartz substrate was placed in a vacuum chamber, pumped to a pressure of 10⁻⁵ mbar with simultaneous heating to a temperature of 150–2000 °C to remove adsorbed gases and water vapor from the surface. The molybdenum boat was heated up to 1700–2000 °C and the copper evaporated and sputtered on the target substrate. The thickness of the deposited layer was 300 and 1150 nm and was determined by the mass of metal placed into the boat.

Graphene film was synthesized by standard chemical vapor deposition technology from a mixture of hydrogen and methane at a temperature of from 950 to 1000 °C but without any gas flow in the chamber, at stationary rarefied atmosphere of hydrogen and methane.[5,6] We used a standard commercial vacuum tube furnace with 32 mm of inner diameter of quartz tube and 30 cm of uniform temperature heating zone. Graphene synthesis was occurred under the following procedures: at first, a copper film...
on quartz was annealed in hydrogen in a vacuum chamber at a pressure of 100 mbar and a temperature of 950 or 1000 °C for 30 or 90 min. These parameters are the key points for copper film crystallization and grain formation, that is demonstrated in Section 3. Further, methane was launched into the chamber at a concentration of 5%, namely, introduction 5 mbars of methane inside the chamber with 100 mbars of hydrogen. A constant temperature the same as during annealing process was maintained for 2 min, then the heater was turned off and the vacuum chamber cooled to room temperature within 8 h.

The main distinguishing feature of the described technology is the absence both of gas flows and of argon during the synthesis of graphene. It is known that for the synthesis of high-quality graphene, the correct ratio of precursor concentration and synthesis time must be achieved. The lower the methane concentration, the longer it takes of graphene synthesis. Also during long-term synthesis and low methane concentration, graphene formation was observed on all copper surfaces regardless of the orientation of the crystals of copper. But at short time regime with high concentration of methane, graphene is synthesized only in the most catalytically active areas, that is, on the copper crystallites with a particular orientation. In our experiment, we chose a regime with a sufficiently high concentration and a short synthesis time, that leads to rapid selective graphene synthesis. After synthesis process the samples of a graphene film on the surface of a copper film were examined using micro Raman spectrometer Horiba LabRAM HR Evolution using 100-times optical objective. The wavelength of the probe diode laser was 532 nm and the power was 14 mW.

The surface morphology of the samples was studied by Ntegra Spectra M SPM. A noncontact monocrystal silicon probe with a tip radius of 10 nm was used. Because of the large differences in the relief (≈100 nm) of the copper film after its annealing and the small thickness of the synthesized graphene film (≈1 nm), we used the SPM phase-contrast mode. Scanning the surface in tapping mode (“tapping” with a probe tip with a resonant frequency on the sample surface) SPM, allows minimizing inelastic deformations as a result of reducing the contact time of the probe tip with the sample surface. Amplitude of oscillations is relatively large, and the probe tip is in direct contact with the surface of the sample only for short time, during which it is affected by the forces of intermolecular attraction and repulsion. Phase contrast mode allows one to obtain information about the local nano-inhomogeneity of the properties of the surface layers of the investigated sample. The phase shift of the resonant oscillations of the cantilever is fixed when the conditions for the elastic interaction of the probe with the sample surface are changed. Measurements in the phase contrast mode reveal changes in the microhardness (microelasticity) of investigating material, which makes it possible to detect the carbon film on surface and to distinguish the area of graphene with different number of layers.

At the same time, the interpretation of the phase contrast image is complicated due to the impact of elastic repulsion, contact and non-contact adhesion on the cantilever. To reduce the specific contribution of adhesion forces to the dissipation of the energy of the oscillating cantilever tip, that is, to the resulting picture of the phase image, we chose contactless silicon probes with greater rigidity (cantilever force constant 12–20 N m⁻¹), and therefore with greater initial probe energy.

A dual-beam scanning electron microscope FEI Versa FEG equipped by Hikari electron backscatter diffraction (EBSD) Camera was used for the grains orientation characterization. Diffraction patterns were acquired at 20 kV accelerating voltage and 4 nA beam current.

3. Results and Discussion

The annealing of catalytic substrate goes before graphene formation for removing natural oxide layer from the copper and, as it was noted in Section 2, for crystallization of deposited copper film. SPM topographical map of copper films with thicknesses of 300 and 1150 nm after deposition on quartz substrate and before thermal annealing and graphene growth is shown in Figure 1. Deposited copper films look homogeneous and very smooth, however small particles with mean diameter of about 150 nm have appeared after increasing the thickness up to 1150 nm. Annealing of copper film with a thickness of 300 nm at temperature of 950 °C leads to the formation of separated islands of micron-sized drops on the surface of quartz substrate (Figure 2a). This is the evidence of the melting–dispersion process occurring in a thin film on an inert substrate. It involves several competing physicochemical processes, such as local melting, shape optimization as a...
result of a decrease in the surface area, crystallization, and melting of the remaining film, and its kinetics in copper films with thicknesses ranged from 10 to 100 nm can be found elsewhere.\cite{16} The observed melting point for thin copper films is lower than the experimental melting temperature of 1085 °C for bulk material by over 100 °C.\cite{17} The decrease of the melting temperature can be assigned to the film thickness of nanoscale size and the reduced pressure in the chamber. According to Gromov et al. the melting temperature of a copper film 50 nm thick was lower than the handbook value by over 250 °C.\cite{18} With increasing of copper film thickness up to 1150 nm, a copper recrystallization starts in all used annealing modes, resulting in formation of grains of different size and orientation. Figure 2b–d show the images of the surface morphology obtained by the SPM for samples with thickness of 1150 nm for different temperatures (Figure 2b at 950 °C, Figure 2c, d at 1000 °C) and times (Figure 2b,c – 30 min, Figure 2d – 90 min) of annealing procedure. With an increase of both the temperature and the duration of annealing, the average crystal size of the film and the efficiency of graphene synthesis are increasing.

Studying the surface of the film by the SPM in the phase contrast mode and by the Raman spectroscopy allows not only determining the localization regions of the carbon material on the substrate, but also detecting areas with different numbers of crystalline layers of carbon material.\cite{14} Figure 3 presents images of the copper film surface relief with the thickness of 1150 nm and 90 min annealed at 1000 °C (Figure 3a) and the lateral distribution of the oscillation phase of the probe (phase contrast mode) (Figure 3b). Figure 3a indicates rough surface of the grain with number of steps and cracks, so this routine technique does not allow to register the presence of graphene layers and to recognize the amount of layers. However the phase imaging (Figure 3b) shows the difference in the microhardness of areas indicating with numbers of 1, 2, and 3. Changes in both the carbon film thickness and the condition of its surface lead to changes in the phase shift of the probe oscillations.\cite{19} Graphene is hydrophobic and with an increase of the number of monolayers, the hydrophobicity of multilayer regions increases as well.\cite{20} Thus, changes in the thickness of both the carbon material itself and the layer of water adsorbate on its surface lead to changes in the phase response to the impact of the cantilever needle. The subsequent comparison of the SPM phase-contrast mode measurements with the Raman spectroscopy measurements (Figure 4) allows to determine the area of the samples with different numbers of graphene layers and further usage only the SPM for fast recognizing the thickness of graphene with resolution of about 10 nm, corresponded to the tip diameter.

In the study of graphene areas, characteristic graphene peaks were found at a Raman shift of 1580 cm$^{-1}$ (G-peak) and 2670 cm$^{-1}$ (2D-peak) (Figure 4). The first peak characterizes the sp2-hybridization of carbon and is the main peak in graphene and graphite. The 2670 cm$^{-1}$ band is responsible for the two-phonon interaction in graphene and makes possible to determine the amount of layers from 1 to 5 in the graphene film.\cite{21–23} It is clearly seen that a film with a thickness of one atom is formed in region 1, a narrow peak (bandwidth < 25 cm$^{-1}$) in the region of 2670 cm$^{-1}$ and a ratio I$_{2D}$/I$_G$ more than two are observed in this case. And region 2 is characterized by a low-intensity and wide 2D peak, which indicates a graphene film with a thickness of more than 5 layers. It should be noted the absence of D-peak at 1350 cm$^{-1}$ of Raman shift, which corresponds to defects in graphene film, and it means that there is no defects in graphene film synthesized on copper film. The Raman spectra presented in
Figure 4 correspond to the areas from Figure 3a,b: in area 1 – graphene monolayer, in area 2 – few-layer graphene and no graphene in area 3.

To study the correlation of the graphene synthesis with the copper grains orientation, we obtained a grain orientation map using EBSD of the sample surface (Figure 3d). The boundaries between different crystallites are clearly visible in Figure 3d and correlate to surface morphology obtained by the SPM and depicted in Figure 3a. It is clearly seen that graphene monolayer is formed only on the part of the grain with orientation \{111\}, close to its edges. And more than 5 layers are observed in the central part of the grain. This is in a good agreement with previous works and gives us reason to believe that growth of graphene begins in the middle of the grain.\cite{9,24} Obtained results open new possibilities for study and further development of the graphene synthesis on thin copper films.

4. Conclusions

In conclusion, we have optimized parameters of synthesis to obtain high quality graphene on thin copper film. Raman spectroscopy and EBSD technique indicate that graphene monolayer is preferably formed on the surface of the crystallite orientation \{111\}. SPM technique in the phase contrast regime proved to be quite sensitive to the presence of graphene with different number of layers, and can be used as rapid alternative method for graphene diagnostic despite on the surface roughness. Proposed in this work the combination of techniques demonstrates the potential for fast diagnostic of the synthesis of graphene.

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Conflict of Interest

The authors declare no conflict of interest.
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