



# Graphene fabrication via carbon segregation through transition metal films

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## ABSTRACT

A detailed study of graphene growth process via segregation of carbon atoms through a 16 nm-thick metal film is presented. Two different transition metals – Co and Ni – are deposited on a highly-oriented pyrolytic graphite (HOPG) substrate. It is demonstrated that annealing of the systems leads to segregation of carbon atoms from the substrate to the surface. X-ray photoemission studies show that in both cases a metal-rich carbide phase is formed in a near-surface area, which after a low-temperature annealing transforms into carbon-rich carbide phase. After further increase of the annealing temperature this carbide phase is transformed into graphene mono- and multilayers. Low energy electron diffraction measurements show that at the final stage a large part of the sample is covered with highly-ordered graphene domains, however a lot of small variously oriented domains can also be seen. It is shown that graphene on Co/HOPG is formed at comparable temperatures to that on Ni/HOPG, and it has better ordered surface.

## 1. Introduction

Graphene is one of the most promising materials designed to set a new vector for the development of modern electronics. The combination of graphene with various substrates made it possible to propose the implementation of the basic elements of nanoelectronics and spintronics: a spin filter [1], a photodetector [2], a transistor [3], an element of the device for spin signal transmission [4]. A key obstacle to massive introduction of graphene into nanoelectronics is the lack of highly efficient and cost-effective methods of synthesis at low temperatures [5]. Among methods of graphene synthesis, the most extensive use was made of the chemical vapor deposition (CVD) method [6–8]. The mechanism of catalytic reaction on the surface is self-limiting, and multilayer structures are not formed [6,7]. An important restriction for the use of CVD is the limited choice of substrates. It has been found that graphene can be formed on various faces of transition metals (Re, Ir, Pt, Ru, Rh, Pd, Co, Ni, Fe) [9,10]. However, CVD method cannot be performed on semiconductor and dielectric substrates. To overcome this obstacle, other methods, which include some stages of the CVD method such as dissolution or accumulation of carbon atoms on the surface, are designed. One of such methods is based on the segregation process, when carbon atoms float to the surface and arrange into graphene [11,12].

It would be interesting to compare process of graphene synthesis via different methods. For example, graphene growth on SiC goes by sublimation of Si atoms from the step edges on the surface [13]. Carbon atoms migrate on the terraces and form graphene islands which grow

during annealing and corresponding removal of Si layers. Typical growth temperature is in the range of 1200–2000 °C. Second, even more popular growth mechanism, CVD, still has uncertain nature, most interest is usually devoted to CVD on Ni(111) surface [14–17]. It is generally assumed that carbonaceous molecules decompose at the Ni surface at the substrate temperature of 400–600 °C with simultaneous dissolving of carbon atoms inside the Ni film. The following cooling to room temperature leads to segregation of the dissolved carbon atoms to the surface due to decreasing solubility of carbon in the bulk nickel and to accumulation of monolayer graphene (MG) atop Ni(111) [14,15]. However there is another point of view on the mechanism of CVD growth. It assumes that carbon atoms from decomposed molecules react with Ni and form nickel carbide in the surface region of a sample. Further annealing and cooling to room temperature leads to transformation of the formed carbide phase into graphene [16,17]. Segregation-based methods can have different source of carbon atoms: SiC substrate [18], a carbon layer deposited on SiO<sub>2</sub>/Si substrate [19] or highly-oriented pyrolytic graphite (HOPG) substrate [11], but the procedure of synthesis is always the same. A metal (mostly Ni) layer is deposited on the carbon-containing substrate, and the system is annealed to certain temperature. Elevated temperatures cause C atoms to segregate from the substrate to the surface where they arrange into graphene layer during the cool-down step due to decreasing solubility of carbon in the metal film.

Recently we have studied growth of graphene by segregation on thin metal (Ni, Gd) films deposited on a HOPG substrate [12,20,21]. It has been shown that the synthesis process includes formation of a

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surface carbide phase (both on Ni and Gd films), which transforms into graphene at certain temperatures. The disadvantages of this method may include the high temperature of graphene synthesis on a Gd film (1000–1100 °C) [21], and the presence of a multidomain structure on a Ni film [12,20].

In this paper, a cobalt film is taken, since it combines advantages of the two above-mentioned cases. Graphene on Co has a better-ordered structure than on Ni [22]. At the same time, the temperatures of graphene growth on Co and Ni are comparable [22,23]. It is also worth noting that Co has the greatest magnetic moment among 3d-metals, and the graphene formed on it should be highly spin-polarized, which should make it suitable for spintronics devices.

## 2. Experimental techniques

Graphene synthesis was studied by analysis of X-ray photoemission (XPS) spectra, taken at different stages of the growth process. Information about the quality of the surface and about the perfection of the crystalline structure of graphene was obtained by low energy electron diffraction (LEED). The experiments were conducted in the Resource Center “Physical methods of surface investigation” of Research Park of Saint Petersburg University using a Thermo Fisher Scientific Escalab 250Xi spectrometer and in Russian-German laboratory at BESSY II synchrotron facility (Helmholtz-Zentrum, Berlin).

A HOPG sample was used as a substrate for experiments. The sample surface was cleaned by a preliminary cleavage in atmosphere with a following degassing in UHV (about  $3 \times 10^{-9}$  mbar) at a temperature of  $\sim 750$  °C for an hour. The quality of prepared surface was controlled by LEED and XPS.

We deposited a Co film on a clean HOPG surface kept at room temperature. The thickness of the film was 160 Å, approximately the same as the thickness of Ni film, which was previously studied [12]. We used electron-beam evaporator (Prevac EBV 40A1), the deposition rate was 1–1.5 Å/min, as estimated by quartz microbalance. Such thickness was chosen to form uniform film and to maximally reduce the contribution of the signal from HOPG substrate to the XPS spectrum of the system [12,20].

Graphene was synthesized as proposed in [11] in the following way. During annealing of the Metal/HOPG system carbon atoms from the HOPG substrate segregate through the film to the surface and arrange into graphene layer. Sample was annealed consistently by an electron bombardment at a set of temperatures in the range 250–350 °C for 15 min, pressure in the chamber was better than  $5 \times 10^{-9}$  mbar. The temperature of the system was controlled using a Keller MSR PZ20 AF02 singlebeam infrared pyrometer and a thermocouple mounted directly on the sample.

The XPS measurements were conducted at Russian-German beamline at the BESSY II synchrotron facility. The energy of a beam was 350 eV, with the energy resolution  $< 0.15$  eV.

Raman measurements were conducted at the resource Center for Optical and Laser Material Research of Research park of Saint-Petersburg University. Raman spectra were recorded ex-situ by Horiba T64000 spectrometer using 532 nm laser line. The laser power at the sample under a  $100\times$  objective was kept at 4 mW. A diffraction grating of 600 grooves/mm was used giving a point-to-point spectral resolution of  $0.5 \text{ cm}^{-1}$ .

## 3. Experimental results and discussion

The synthesis process was studied by analysis of C 1s photoemission line. Fig. 1. presents a modification of the C 1s photoemission line with deconvolution on spectral components for clean HOPG surface, after Co layer deposition and after following annealing at various temperatures (240–350 °C). We will denote the spectral components as follows:  $C_B$  (285.5 eV),  $C_G$  (284.8 eV),  $C_A$  (284.5 eV),  $C_D$  (283.9 eV),  $C_E$  (283.3 eV),  $C_F$  (282.6 eV). The C 1s line of HOPG substrate was fitted with a

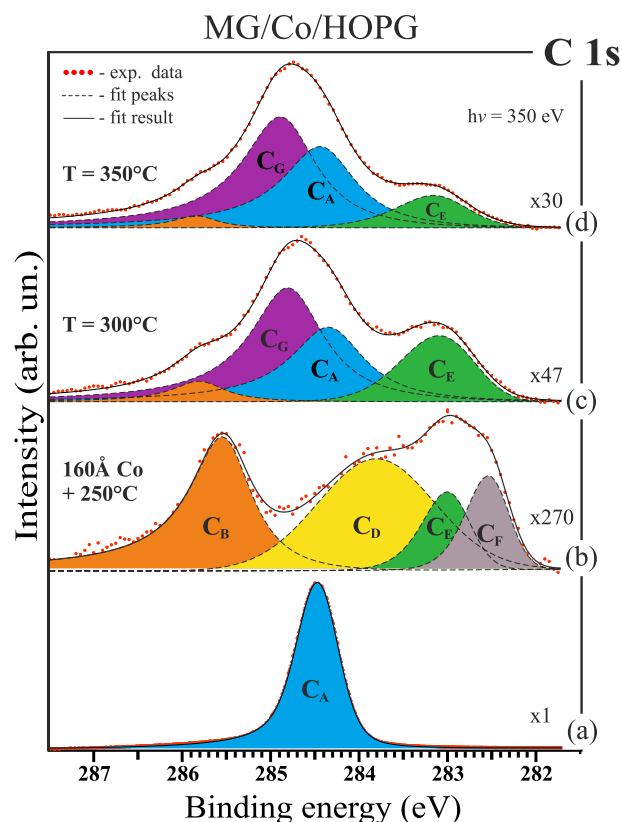


Fig. 1. Modification of the C 1s core spectrum measured at different stages of the formation of the studied system: (a) for the initial HOPG substrate; (b) after Co film deposition followed by annealing at 250 °C; (c, d) after annealing at temperatures between 300 and 350 °C respectively. Duration of all annealings was 15 min. Spectral components are denoted as:  $C_A$  –  $sp^2$ -hybridized carbon,  $C_B$  –  $sp^3$ - hybridized carbon,  $C_D$  – carbon dissolved in Co,  $C_E$  and  $C_F$  –  $Co_2C$  and  $Co_3C$  carbides correspondingly,  $C_G$  – graphene.

convolution of Mahan, Gauss and Lorentz lineshapes. All other peaks, including  $C_A$  peak at latter stages of experiment, were fitted with product of asymmetric Gaussian and Lorentzian lineshape of the same width and unit height. Appendix B presents the details on peak fitting and layer thickness calculation.

### 3.1. Graphene on Co film

The C1s spectrum of the initial HOPG surface (Fig. 1.a) has a one-component structure, the binding energy of the component is 284.5 eV ( $C_A$ ) which is typical for single crystal graphite and HOPG [24].

After deposition of Co layer on the clean HOPG substrate followed by annealing at 250 °C (Fig. 1.b), the  $C_A$  component disappears from the spectrum, which means that the formed film is uniform. Indeed, assuming that the intensity of the substrate decreases exponentially with the thickness of a film, the intensity of XPS signal from the substrate should be less than the experimental error (noise) after passing the 160 Å-film. The substrate peak may be seen only if the film is non-uniform, and some areas on the surface are uncovered or covered with much thinner Co layer. Such choice of the film thickness, which fully attenuates the substrate contribution in the structure of the XPS C1s line, allows us to analyze the later stages of graphene synthesis without referring to the contribution from the substrate.

The spectrum of C 1s line in the Fig. 1.b consists of 4 components:  $C_B$  (at 285.5 eV),  $C_D$  (283.9 eV),  $C_E$  (283.3 eV) and  $C_F$  (282.6 eV). According to the literature [25–27],  $C_B$  component may correspond to the  $sp^3$ -hybridized carbon atoms in carbon-containing molecules adsorbed on the surface. The  $C_D$  component stands for the carbon atoms dissolved

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