

Chemical vapor deposition of thin graphite films of nanometer thickness

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Abstract

Well-ordered graphite films with a thickness of a few graphene layers have been grown on Ni substrates by chemical vapor deposition (CVD) from a mixture of hydrogen and methane activated by a DC discharge. According to Auger, Raman and scanning tunneling microscopy (STM) data the CVD graphite film thickness is about 1.5 ± 0.5 nm. The graphene layers were perfectly adhered to the substrate surface except for upthrusted ridges of a few tens of nanometers in height. STM has revealed an atomically smooth surface with the atomic arrangement typical of graphite between the ridges. A difference in the thermal expansion coefficients of nickel and graphite is considered as a reason for the ridge formation.

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1. Introduction

Graphite is a widely used material with well-developed synthesis methods and properties investigated in detail [1]. A peculiarity of graphite is its layered structure formed by parallel two-dimensional graphene sheets weakly coupled by van der Waals interaction. Each graphene sheet looks like a hexagonal network of carbon atoms connected by strong covalent “in-plane” σ – σ bonds. The delocalized electrons appear only due to an additional π – π bonding of electronic orbitals oriented perpendicularly to the graphene plane. They are responsible for the graphite electrical conductivity which is highly anisotropic. Recently, the unconventional electric field and quantum Hall effects have been demonstrated experimentally for a single sheet of graphite–graphene [2,3]. These experiments have triggered a great interest to the graphite films containing one or a very few graphene sheets [4–7], because the unusual electron behavior is considered as a result of two-dimensional confinement of charge carriers.

Graphene can be produced by mechanical exfoliation of individual layers from the surface of highly oriented pyrolytic graphite (HOPG) crystal [2–5]. Thin heteroepitaxial graphite films consisting of a few graphene layers can be produced by graphitization of silicon carbide surface [6,8] or dissociation of ethylene gas on Ni(111) surface in ultra-high vacuum [9]. However, such “hand-made” graphene or heteroepitaxial thin films have relatively small lateral sizes and are suitable only for pure scientific studies. For deposition of extended films appropriate for practical applications a chemical vapor deposition (CVD) from activated gaseous phase could be efficient. But up to now only rather thick graphite films with a high number of structural defects were deposited by CVD technique [1].

In this paper, we describe a high yield technique of deposition of the large area graphitic films with thickness of a few graphene layers. The results of structural characterization of such films are also reported.

2. Experimental

The graphite films were grown by chemical vapor deposition technique from a hydrogen–methane gas mixture activated by DC discharge. A detailed description of the deposition facility and the growth method

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has been done elsewhere [10]. Our CVD system allows production of different types of carbon films ranging from polycrystalline diamond to carbon nanotubes. A type of the material deposited depends essentially on the methane concentration and on the substrate temperature. In this work, the process parameters corresponding to graphite phase deposition have been chosen [10]: the gas mixture composition $H_2:CH_4 = 92:8$; the total gas pressure $P = 80$ Torr; the substrate temperature of 950 °C. In these conditions the nano-graphite meso-porous layers were deposited after 1–1.5 h [10]. The deposition procedure includes pumping out the reactor chamber by a rotary pump to the base pressure value of 10^{-3} Torr followed by introduction of a pure hydrogen and ignition of DC discharge at pressure of about 40 Torr. Then the hydrogen pressure was increased up to 80 Torr simultaneously with increasing the discharge current. This procedure took about 10 min. It was followed by an introduction of the methane gas into the reactor and an increase of its content up to 8 vol%. The discharge current was fixed at value about 0.5 A/cm² being typical for the graphite phase formation [10].

Optical emission spectra (OES) measured in DC discharge plasma have revealed an important role of carbon dimers C_2 generated in the plasma near the substrate surface. The dimers may be considered as building blocks for the graphite deposit [10]. In present study the deposition time has been reduced to 5–10 min to obtain the thinner films. In our CVD system the main parameters are stabilized usually not earlier than 15 min after the process starts. Thus, the process is not completely under control during first minutes of deposition. For instance, the intensities of OES peaks (including those corresponding to C_2 dimers) are varied with time in contrast to the fixed values observed in case of the standard deposition conditions [10]. However, the deposition procedure has shown surprisingly good repeatability of the results despite of the uncontrollable character of its initial stage.

In this work, the silicon and nickel square plates with thickness of about 0.5 mm and lateral dimensions of 10×10 mm or 25×25 mm were used as substrates. The single crystalline silicon substrates have been prepared by cutting the standard polished Si(100) wafers. The nickel substrates were made by cutting of the polycrystalline Ni sheets with thickness of 0.5 mm produced by rolling. The substrates were treated in pure hydrogen DC plasma to remove the surface oxide layer before the interaction with methane started.

The CVD-deposited graphite films were studied by Raman spectroscopy using a Fourier-transform Raman apparatus Bruker FR 1 106 with excitation by a YAG:Nd laser operating at wavelength 1064 nm. A special care has been taken to avoid the material heating by laser radiation in course of measurements. For this purpose the Raman spectra were first measured with different laser power densities. The final level of the laser power density was chosen in the middle of the range where no temporal changes in the line positions and shapes were observed. Raman spectra of HOPG sample (HOPG SPI-3 GRADE supplied by SPI, West Chester, PA 19381, USA) were recorded at the same conditions to obtain the reference data.

The surface morphology was studied with a scanning electron microscopy (SEM) using LEO Supra 50 PV instrument and a scanning tunneling microscopy (STM). An Auger electron spectroscopy (AES) was used for elemental analysis of the surface. The AES and STM measurements were carried out at room temperature under ultra-high vacuum (UHV) condi-

tions in a multi-chamber setup equipped with a cylindrical mirror analyzer Riber OPS-200 (for AES), Sigma Scan GPI-300 [11] (for STM) and other instruments for the surface analysis and treatments. A basic pressure in the setup did not exceed 2×10^{-10} Torr. A preparation of W-tips for STM measurements was made by an electrochemical etching outside and a subsequent sharpening inside the vacuum chamber with Ar^+ -bombardment [12]. The samples were investigated by AES and STM in “as grown” form (without any UHV treatments).

3. Results and discussion

Our previous studies have revealed no significant difference in the structure of graphite-like materials deposited on Ni and Si substrates in CVD-process lasted 45 min or longer [10]. For the shorter deposition times (5–10 min) substantially different carbon materials have been grown onto substrates made from these two materials. To provide the identical conditions of CVD process for both types of substrates the sets of Ni and Si wafers have been located side by side on a holder in the deposition chamber. Each set consisted of four samples (10×10 mm). The films deposited onto both types of substrates looked very smooth and continuous, but their morphologies were different. The SEM images of films grown on both substrates are shown in Fig. 1.

The film grown on Si substrate consists of numerous tiny grains (more clearly seen under the higher resolution) and looks more or less homogeneous over the whole sample. The film deposited on Ni has a specific morphology with the smooth surface areas separated from each other by out-of-plane extrusions. A typical size of the smooth surface regions is about 1 μ m. The ridges between such regions form their own net on the film surface. The SEM image obtained for the tilted sample (Fig. 1c) shows a formation of the net of ridges at the boundaries of the smooth micron-size areas. Some of the surface regions look like swells formed by the film partially exfoliated from the substrate. An example of such swelling is marked by arrow in Fig. 1c. The films grown onto nickel contain also the ball-like structures on the surface. An origin of these structures is unclear. Taking in account an absence of any non-carbon inclusions shown by AES we suppose that these balls are the islands of amorphous carbon.

The films grown have been analyzed by Raman scattering spectroscopy. Fig. 2 shows the typical Raman spectra of films grown on Si (Fig. 2(1)) and Ni (Fig. 2(2)) – solid

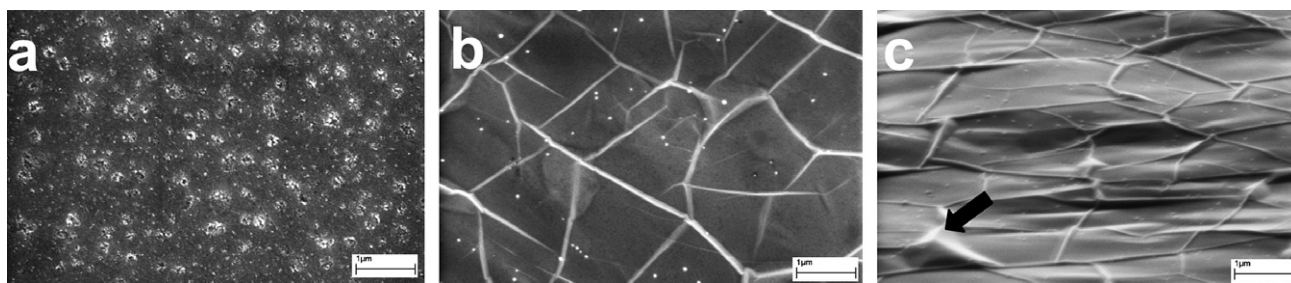


Fig. 1. The SEM images films grown in identical CVD conditions on Si (a) and Ni (b and c) substrates. The image (c) has been obtained with the sample tilt of 75° .

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