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Full Length Article

Enhancement of absorption in vertically-oriented graphene sheets growing on a thin copper layer

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ABSTRACT

The optical properties and surface structure of graphene films grown on thin copper Cu (1 μm) layer using chemical vapour deposition method were investigated via spectroscopic ellipsometry and nanoscopic measurements. Angle variable ellipsometry measurements were performed to analyze the features of dispersion of the complex refractive index and optical conductivity. It was observed significant enhancement of the absorption band in the vertically-oriented graphene sheets layer with respect to the bulk graphite due to interaction between excited localized surface plasmon at surface of thin Cu layer and graphene's electrons. Scanning tunneling microscopy measurements with atomic spatial resolution revealed vertical crystal lattice structure of the deposited graphene layer. The obtained results provide direct evidence of the strong influence of the growing condition and morphology of nanostructure on electronic and optical behaviours of graphene film.

1. Introduction

Amongst the wide spectrum of potential applications of graphene [1,2], ranging from transistors and chemical-sensors to nanoelectromechanical devices and composites, the field of photonics and optoelectronics is believed to be one of the most promising. Graphene monolayers exhibit unique properties due to conjugation of π-electrons along all honeycomb crystal lattice and two dimension structures density of states with "ultrarelativistic" electrons and holes. These unique characteristics allow graphene to be used as a basic material in a variety of different nanoscale devices. Indeed, microchips which are made using graphene can operate in terahertz frequency range [1]. However, the photocurrent generation mechanisms in graphene-based optoelectronic nanostructures suffer from the two main problems: (i) low light absorption of graphene (2.3% of normal incident light); (ii) difficulty of extracting photoelectrons (only a small area of the *p-n* junction contributes to current generation). One possible way of overcoming these restrictions is to combine the graphene with plasmonic nanostructures (for example, thin film of noble metal Ag, Au, Cu). Incident light, absorbed by such nanostructures, can be efficiently converted into plasmonic oscillations, which lead to a dramatic enhancement of the local electric field on top layer of graphene. The ability of such nanostructures to concentrate and manipulate optical energy on subwavelength scales can be improved by using a vertically-oriented graphene (VG) sheets. Recently the vertically fabricated graphene nanosheets become one of the popular 3D carbon structure materials [3,4], which has been applied to various applications of field emitters [5], supercapacitors [6] and selective biosensor [4]. The VG sheets can be directly grown on the plasmonic electrode using a chemical vapour deposition (CVD) method and function as the optical sensing structure. CVD approach can serve as a simple and one-step method to prepare graphene-based optical sensor devices and can be a better alternative route to drop-casting methods that are commonly used to fabricate graphene and carbon nanotube devices. It was shown that directly grown VG on the plasmonic electrode reach higher stability and repeatability than the drop-casting method [4].

Another key attribute includes the material's properties being dependent on the substrate (electrode) properties. The atoms of substrate diffuse to the graphene layer and change its local electronic properties. The copper substrate can be used as an electrode in nanoscale devices because of copper's high electrical conductivity and relatively low price then in the production. Large single-layer graphene films ranging in size of centimeters can be grown on copper substrates by CVD [3,4]. The copper films covered with one to several graphene layers may exhibit distinct plasmonic response and yield the improved characteristics. They demonstrate

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stable characteristics and can also be used in plasmonic devices [7]. Plasmons in a graphene-metallic substrate system may display a rather complicated picture. For example, the electromagnetic response of graphene and the spectrum of collective plasmon excitation were studied as a function of wave vector and frequency [8]. The quasiparticle dynamics of the sheet plasmons in epitaxial grown graphene layers on SiC(0001) has been studied as a function of temperature including intrinsic defects action as well as influence of multilayers and carrier density [9]. The graphene can be used as transient electrodes in computer screens because of its high optical transmittance and simultaneous high electrical conductivity.

Hence, characterizing and understanding optical properties of vertically-oriented graphene sheets grown on a plasmonic Cu electrode for accurate prediction of the effective behavior in the optical devices are important. In this study, we employed ellipsometry as a nanometrology tool to study the optical response of the graphene thin film deposited on a copper layer. Using ellipsometric measurements with consecutive numerical simulations we can determine optical constants (namely refractive index n and absorption index k and including optical conductivity $\sigma(\omega) = nk\omega/2\pi$, ω is an angular frequency of light) from ellipsometric data for a monolayer graphene in a wide spectral range. These data can indicate graphene's optical absorption as well as high frequency optical conductivity. Thus in this study we have performed spectral ellipsometric measurements for the vertically-oriented graphene monolayers deposited on a copper film substrate. In such nanostructures the VG can be also successfully employed to protect Cu against corrosions and chemical reactions. We will concentrate on the plasmonic geometries of the formed nanostructure which utilize the localized surface plasmons on a top of Cu substrate and enhance an absorption in graphene monolayer. Such graphene coating provides not only a corrosion barrier but also allows to realize the targeted bio-functionalization of its surface in the case of biosensing.

2. Preparation of samples and methods of investigation

First, the copper films with thickness of 1 μm were produced by electron-beam evaporation at a base pressure of about 10^{-5} mTorr and growth rate of 0.3 nm/s (film thickness was monitored by calibrated quartz microbalance). As an electron-beam target we used 99.99% Cu from Sigma-Aldrich. A thin adhesion layer of Cr with thickness of about 1.5 nm was evaporated onto a substrate before copper. The quartz substrates of sizes 25 × 25 mm^2 and thickness of 1 mm were used for all the studied samples. The substrates were ultrasonically cleaned in heated acetone and isopropanol before deposition. Second, large size (10 × 10 mm^2) graphene films were grown on Cu film by using the CVD method [3,4]. A 1-μm thick Cu on quartz was placed inside a quartz tube and then heated up to 1000 °C with a H_2 flow at rate of 20 cm^3/min and a pressure of 200 mTorr. To remove the native oxide layer, the Cu film was first annealed at 1000 °C during 30 min. Then a gas mixture of H_2 and CH_4, with flow rates of 20 and 40 cm^3/min, respectively, was introduced into the chamber. CVD growth was performed at a pressure of 600 mTorr during 30 mins. Finally, the CVD chamber was rapidly cooled to the room temperature in hydrogen atmosphere. Usually the monolayer graphene film grows on a thick Cu substrate (Cu foil with thickness of ∼50 μm). Here we have tested a thin Cu film (∼1 μm) as substrate for CVD graphene preparation.

To investigate the structure of the VG alignment graphene on the copper layer optical high resolution and scanning electron microscope (SEM) techniques were employed at first stage. For precise surface topology study at sub-nanometer scale the microscope INTEGRA NT-MDT was used in the scanning tunneling microscopy (STM) regime. Measurements of the STM images have been done in Constant Current Mode as described in Refs. [10,11]. Scanning tunneling microscopy spatial resolution reached up to 0.1 nanometers. In order to obtain direct surface profiles the experiments were performed using the measurement regime with constant tunneling current.

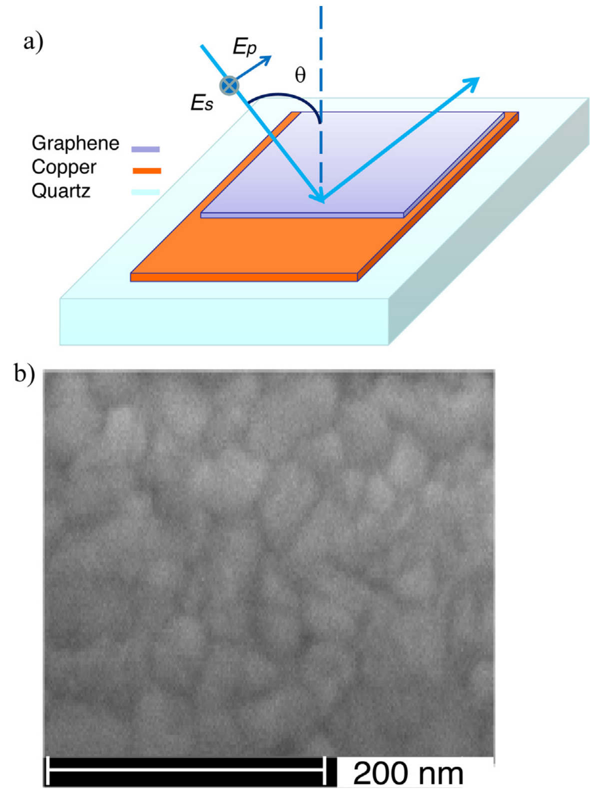

Fig. 1. (Color online.) Schematic representation of experimental setup for spectroscopic ellipsometry (a). SEM images of a surface Cu film deposited on a quartz substrate (b).

In order to check the quality of graphene film on top of Cu layer we have used Raman spectroscopy. Raman spectra were recorded by a Renishaw RM1000 spectrometer with the excitation wavelength of 514.5 nm. To find optical absorption we have also used spectroscopic ellipsometry a measurement because of the aim of this work is to elucidate optical properties of graphene monolayers grown on copper film. Spectral ellipsometric measurements were performed in λ = 250–1000 nm spectral region applying Beattie technique [12–14]. The azimuth of the restored polarisation Ψ and the phase shift Δ between p- and s- components of a polarisation vector E were measured at different values of light incidence angle θ from 45° to 75° with step of 5 deg. A schematic representation of experimental setup is presented in Fig. 1a. The ellipsometric parameters Ψ and Δ are defined as $\Psi \exp \Delta = r_p/r_s$, where r_p and r_s are the reflection coefficients for the light of p- and s- polarizations [13]. Measurements have been performed consistently for the substrate and for relatively large samples, see Fig. 1a and modeled by method based on the Fresnel coefficients for multilayer films. It is worth to notice that the effective optical thickness of thin layers can deviate from "geometrical" thickness of the sample. It was shown [15] that the optical thickness of graphene layer which gave the best fit changed from sheets to sheets was varying about of 30% around the value of the interlayer distance of graphite. In this study we have fixed the thickness of graphene layer to 2.35 nm in our calculations (we consider 7 layers in VG, which is equal to 7×0.335 = 2.35 nm of thickness). We tested our installation on thick flakes of highly ordered pyrolytic graphite fabricated on top of quartz substrate.