Applied Surface Science xxx (2013) xxx–xxx

Contents lists available at SciVerse ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Influence of the graphene substrate on morphology of the gold thin film. Spectroscopic ellipsometry study

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ARTICLE INFO

Article history:
Received 16 April 2013
Received in revised form 17 June 2013
Accepted 27 June 2013
Available online xxx

Keywords:
Graphene
Gold film
Cluster structure
Variable angle spectroscopic ellipsometry
Optical properties
Drude–Lorentz model
Bruggeman effective medium approximation

ABSTRACT

In metal optics gold assumes a special status because of its practical importance in optoelectronic and nanooptical devices, and its role huge increases when occurs combination of gold with two-dimension materials. We performed spectroscopic ellipsometry measurements on evaporated gold, and gold–graphene nanostructures to determine the optical dielectric function across a broad spectral range from 250 to 1000 nm. It was found that the deposition of gold film on the quartz substrate covered by graphene flake leads to significant changes in structural and dielectric properties of thin gold layer. Such changes can be explained by increasing of the gold cluster size. The model fit of the ellipsometric data demonstrates that the bilayer "graphene-gold" nanostructure can be described as a uniform optically homogeneous layer with modified optical properties. We can suggest that graphene flake creates a matrix for epitaxial alignment of the crystalline structure of the gold film during its growing. Effective doping of the graphene by free electrons of the gold clusters tends to decrease the optical contrast at the graphene-gold interface.

1. Introduction

Amongst the wide spectrum of potential applications of graphene [1–3], 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. Indeed, graphene's suitability for high-speed photodetection was demonstrated in an optical communication link operating at 10 Gbit/s. However, the photocurrent generation mechanism in graphene-based photodetectors and solar cells 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) placed on top of graphene. Incident light, absorbed by such nanostructures, can be efficiently converted into plasmonic oscillations, which lead to a dramatic enhancement of the local electric field.

Moreover, Au is one of the most widely used metals for a range of graphene applications, including making contacts to circuits [4], electrochemical catalysis [5], biosensors [6], and studying interfaces [7]. In order to further miniaturize such nanostructures exist huge interest in metallic nanostructures (contacts) with sizes of the order of 10 nm or less. So direct observation of gold behavior on grapheme – for example, nucleation, cluster coalescence, epitaxial alignment and continuous coverage forming – in particular by ellipsometry, transmission electron microscopy (TEM), is one of the key requirements to understand the nature of the interaction, and to gain a better understanding of the properties of metal contacts on suspended single-layer graphene and their effect on macroscopic dielectric and optical properties of metal-grapheme structure. Comparison of structures, optical and dielectric properties of the gold films deposited on graphene and significantly different substrate at the stable conditions can give additional information on the metal-graphene interaction.

It is known that very thin layers of evaporated gold do not form a complete surface coverage but the structure of separated gold islands. Such naturally occurred metal nanostructures were a subject of extensive study in 1970–1980th before the term "nanostructure" was introduced. Interest to nano-island nanostructures was recently revived due to their promising applications in nanoelectronic devices in which two dimension materials (flakes of graphene, MoS_2, WS_2, BN) interact with metallic contacts [3]. There can also be interesting fundamental study of the optical properties such conductive nanostructures of very small length scales approximately about of 10 nm. This demands us to describe the optical response of structures that are too large to treat using quantum

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http://dx.doi.org/10.1016/j.apsusc.2013.06.156

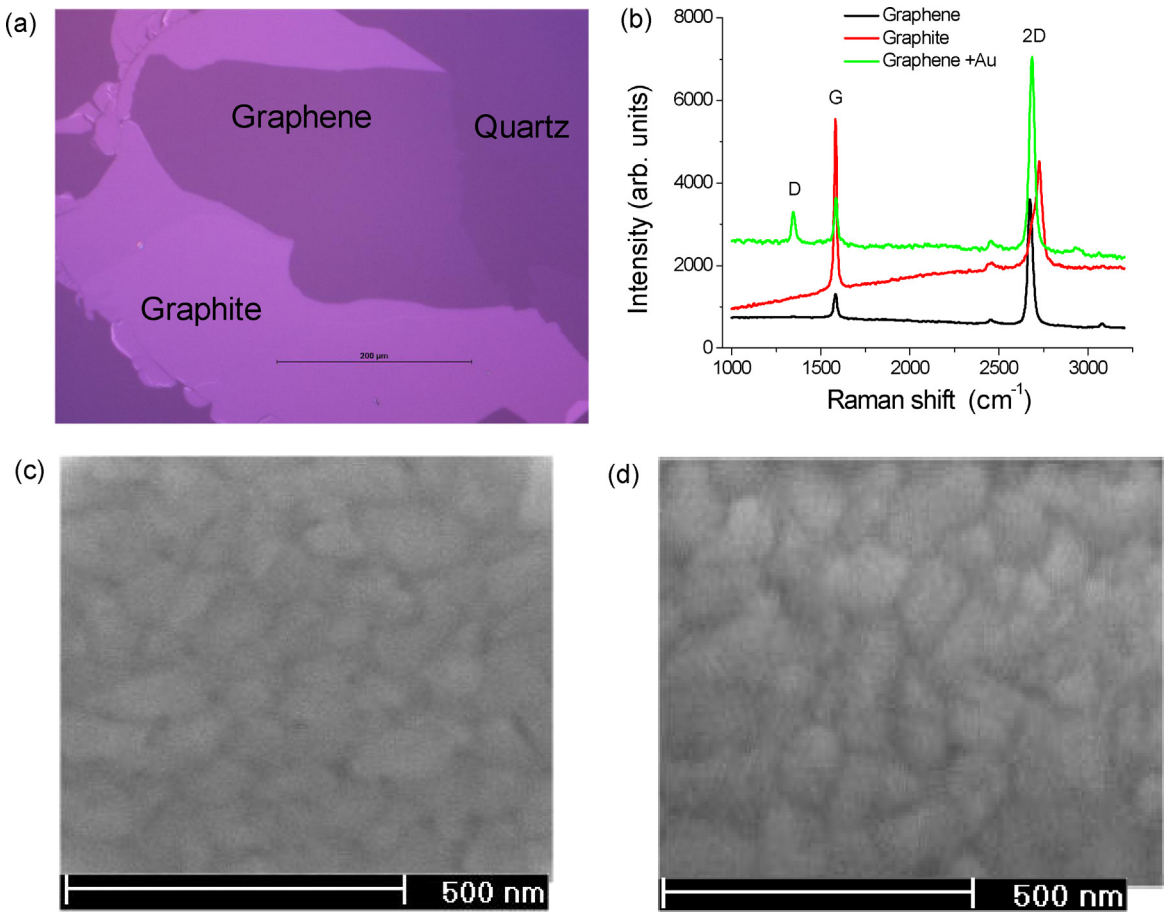

Fig. 1. Optical image of a graphene flake on quartz before Au deposition (a); comparison the main Raman bands of graphene and graphite on top of thick quartz substrate (λ_{exc} = 514 nm) (b). A clear evolution of these peaks is seen when moves from thick to monolayer. Thin gold layer causes the increase of the intensity of main peaks (G and 2D) in spectra; SEM images of a thin gold film deposited on quartz (c) and quartz–graphene (d) structures.

mechanics, yet too small for local continuum electrodynamics to be valid.

Hence, characterizing and understanding optical properties of gold nanoclusters for accurate prediction of the effective behavior on the optical devices are important. In this study, we employed ellipsometry as a nanometrology tool to study the optical response of the films deposited on single layer of graphene. Effective medium theory (Bruggeman approximation) with a Drude–Lorentz model was employed to treat Au nanocluster as a thin film. Furthermore, we extended our investigation to explore the potential application of ellipsometry and effective medium model as a tool to quantify the gold–graphene atomic interactions. Our approach provides a powerful and convenient tool to investigate the optical response of structures at the nanometer length scale.

2. Preparation of samples and methods of investigation

2.1. Sample preparation

The single layer graphene (SLG) was prepared by use of micromechanical exfoliation of graphite on top of quartz substrate. As the substrate we used quartz cut from microscope slides of sizes 22 mm × 22 mm and thickness of 0.7 mm. Graphene flakes have been prepared on a quartz substrate in order to improve graphene visibility [4,8,9]. Just before use quartz substrate was ultrasonically cleaned in heated acetone then ethanol. Note that in order to improve the stick between the quartz and graphene the substrate was treated by argon plasma etching. The single layer nature of our flakes was confirmed by a combination of optical contrast image (Fig. 1a) and characterized by micro-Raman spectroscopy under ambient condition (Fig. 1b). Raman spectroscopy is a highly specific technique used to detect and identify the SLG [10]. Raman spectra were recorded with a Renishaw RM1000 spectrometer. It is well known that graphene is characterized by a set of Raman peaks: a G peak at ~1580 cm^{-1} due to the in-plane vibrational E_{2G} mode at the Brillouin zone center and a 2D peak at about ~2700 cm^{-1} due to two phonon intervalley scattering [10]. In our experiment line scans was done for 514 nm laser excitations. Fig. 1b demonstrates significant changes of intensity and shape of both G and 2D bands of graphene layer in comparison to the thick (graphite) layer. We performed the measurements with high aperture objective (spot size of 1 μm) in several areas of samples (approximately five) in order to check homogeneity of the samples and to carry out surface averaging.

The gold thin films were produced by electron-beam evaporation of pure (99.99%) gold on quartz substrate covered by graphene at a pressure of about 2×10^{-4} Pa. Growth of the metal film was monitored by a calibrated quartz microbalance (CQM), at an approximately growth rate of 0.3–0.4 nm/s. Note that rapidly evaporated films reproduce the surface smoothness of the substrate and film a smooth homogeneous surface.

After deposition of the gold thin film we again measured the Raman spectra of graphene. It was shown (Fig. 1b) that the Raman signals from SLG covered by of Au film are enhanced by the plasmonic resonances of the gold nanoclusters. We measured an enhancement factor F as the ratio of Raman counts (of a given

Please cite this article in press as: A.M. Kostruba, Influence of the graphene substrate on morphology of the gold thin film. Spectroscopic ellipsometry study, Appl. Surf. Sci. (2013), http://dx.doi.org/10.1016/j.apsusc.2013.06.156