Synthetic Metals 209 (2015) 461–467

Contents lists available at ScienceDirect

Synthetic Metals

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

The effect of annealing temperature and time on synthesis of graphene thin films by rapid thermal annealing

Jovana Prekodravac[a,*], Zoran Marković[a], Svetlana Jovanović[a], Milica Budimir[a], Davor Peruško[a], Ivanka Holclajtner-Antunović[b], Vladimir Pavlović[c], Zois Syrgiannis[d], Aurelio Bonasera[e], Biljana Todorović-Marković[a]

[a] Vinča Institute of Nuclear Sciences, University of Belgrade, Mike Alasa 12-14, 11001 Belgrade, Serbia
[b] Faculty of Physical Chemistry, University of Belgrade, Studentski trg 12-16, 11158 Belgrade, Serbia
[c] Joint Laboratory for Advanced Materials, Serbian Academy of Sciences and Arts, 11000 Belgrade, Serbia
[d] Dipartimento di Scienze Farmaceutiche, Università degli Studi di Trieste, P.le Europa 1, 34127 Trieste, Italy
[e] Humboldt-Universität zu Berlin, Institut für Chemie, Brook-Taylor-Straße 2, D-12489 Berlin, Germany

ARTICLE INFO

Article history:
Received 18 May 2015
Received in revised form 13 August 2015
Accepted 15 August 2015
Available online 4 September 2015

Keywords:
Thin films
Graphite
Graphene
Rapid thermal annealing

ABSTRACT

In this paper, we performed synthesis of graphene thin films by rapid thermal annealing (RTA) of thin nickel–copper (Ni/Cu) layers deposited on spectroscopic graphite as a carbon source. Furthermore, we investigated the effect of annealing temperature and annealing time on formation and quality of synthesized graphene films. Raman spectroscopy study showed that annealing at lower temperatures results in formation of monolayer graphene films, while annealing at higher temperatures results in formation of multilayer graphene films. We used Raman mapping to determine the distribution of graphene sheets. Surface morphology of graphene thin films was investigated by atomic force microscopy and scanning electron microscopy with EDS probe.

1. Introduction

Graphene is a single-atom-thick sheet with sp^2 hybridized carbon network hexagonally arrayed [1]. Recently graphene was described as the thinnest material in our universe [2]. Graphene is transparent, extremely strong and rigid material with high elasticity and surface area, high charge carrier mobility at room temperature and high thermal conductivity [3–6]. Due to structural, electrical, mechanical and chemical properties, graphene has attracted remarkable attention by research community [7–12]. These properties enable the usage of this material for nanoelectronic applications, bioelectronic, gas sensors, hydrogen storage devices, lithium batteries and supercapacitors [13–19].

Novoselov et al. [9] produced graphene for the first time in 2004, from graphite by mechanical exfoliation. Since then, graphene has been synthesized in many different ways. There are several primary synthesis methods for producing graphene, however all of these methods come with drawbacks as well. The drawbacks are mainly related to the time required for the synthesis and price of used method, or quality of obtained graphene films. Today, the most used methods are chemical vapor deposition (CVD), the epitaxial growth on silicon carbide, liquid exfoliation of graphite crystals, chemical reduction of graphene oxide and rapid thermal annealing (RTA) [20–28].

In this paper, we present graphene synthesis by RTA method in vacuum from thin Ni/Cu layers deposited on polished polycrystalline spectroscopic graphite as a carbon source. The samples were annealed at different annealing temperatures and with different annealing times in order to investigate the effect of annealing temperatures and annealing time on formation and quality of monolayer and multi-layer graphene films.

2. Materials and methods

2.1. Sample preparation

Samples were prepared by cutting the graphite spectroscopic electrodes (99.999% purity, Ringsdorff Spektralkohlestäbe, höchster Reinheit, SGL Carbon, Germany) into small pieces with diameter of 12.5 mm. Sample surface was polished with diamond pastes. Ni/Cu metal films were then deposited on graphite substrates in a single vacuum run, without heating of the graphite substrates. The deposition was carried out by direct-current (DC) sputtering (Balzers Sputtron II system, Switzerland) using 1.3 keV

* Corresponding author.
E-mail address: prekodravac@vinca.rs (J. Prekodravac).

http://dx.doi.org/10.1016/j.synthmet.2015.08.015
0379-6779/

argon (Ar) ions and 99.9% pure Ni and Cu targets. The base pressure in chamber was 7×10^{-6} mbar and the Ar partial pressure during deposition was 1×10^{-3} mbar. The first deposited thin metal layer was Ni with deposition rate of 9.5 nm/min and the second one was Cu with deposition rate of 16 nm/min. Thickness of individual thin Ni and Cu films, measured by profilometry, were 50 nm for Ni and 700 nm for Cu [29].

The samples were annealed in a vacuum furnace (TorVac system, United Kingdom), at different annealing temperatures, at 600 °C, 700 °C, 800 °C and 900 °C for 30 min followed by rapid cooling. Another set of samples was annealed at 900 °C for different annealing times: 30 min, 2 h and 3 h.

2.2. Sample characterization

Raman spectra of as-deposited and annealed samples were obtained by DXR Raman microscope (Thermo Scientific) using a 532 nm laser as excitation source. The laser power was kept at 2 mW to avoid heating of the sample with a pixel-to-pixel spectral resolution of 1 cm^{-1}.

The distribution of graphene sheets was obtained by Raman mapping with Renishaw inVia 15 Reflex, equipped with three laser sources and directly interfaced to a confocal microscope Leika DM-LM. The excitation radiation was generated by a Nd:YAG laser (532 nm), He–Ne laser (632.8 nm) and a Ti: sapphire laser (785 nm). The scanned area of the sample was 15×25 μm^2.

Surface morphology of as-deposited and annealed Ni/Cu thin films was analyzed with atomic force microscopy (AFM). AFM measurements were performed using Quesant microscope (Ambios Technology, USA) operating in tapping mode in air at room temperature. All images were obtained at 1 Hz, with 512×512 pixels image definition over different square areas. The average size of objects in AFM images and root mean square roughness (RMS) were determined by Gwyddion software [30].

The morphology of the films was characterized by scanning electron microscopy (SEM, JEOL JSM-6390LV) in vacuum at room temperature, with 15 kV acceleration voltage. Samples elementary composition was obtained with energy dispersive spectroscopy (EDS, Oxford Aztec X-max). The scanned surface area was 1×1 mm^2.

3. Results and discussion

3.1. Raman spectroscopy

Raman spectroscopy is very important tool for the study of different allotropes of carbon, since it is very sensitive to geometric structure and bonding within molecules. The Raman spectra of graphene show two main bands designed as the G and 2D bands. The third, D band may also be apparent in graphene Raman spectra if there are defects present in carbon lattice [31]. The G band is sharp and appears at around 1587 cm^{-1}. The existence of G band corresponds to the in-plane vibration mode involving the sp^2 hybridized carbon atoms that comprise the graphene sheet. With the G band position, one can determine the number of layers present in the sample. However, the G band position can be affected by temperature and doping thus, intensity of the G band is more accurate way to determine graphene thickness. The D band is disorder or the defect band that appears at around 1350 cm^{-1} and it has been attributed to in-plane A_{1g} zone edge mode. The intensity of the D band can indicate the quality of graphene. By specifying intensity ratio of D and G bands (I_D/I_G) it is possible to define the level of defects present in the sample [31]. The 2D band is sharp, appears at around 2680 cm^{-1}, and it is the result of a two phonon lattice vibration process. Therefore intensity of 2D band can be used to determine graphene layer thickness based on the 2D and G bands intensity ratio (I_{2D}/I_G) [32–33]. If the intensity ratio of these bands is two or higher, single layer graphene is present in the sample.

In Fig. 1 we present Raman spectra of Ni/Cu thin films annealed at different annealing temperatures for 30 min. In Raman spectra of the samples annealed at 600 °C and 700 °C, sharp 2D band at ~2700 cm^{-1} is more intense than the G band. Based on 2D-to-G intensity ratio (I_{2D}/I_G), ~3.57 and ~1.72 respectively (Table 1), it was suggested the formation of monolayer graphene films in these samples. By fitting these 2D bands with one Lorentzian it was confirmed the formation of single layer graphene. Full width at half maximum (FWHM) was ~26 cm^{-1} for samples annealed at 600 °C, and ~37 cm^{-1} for samples annealed at 700 °C, which is characteristic for the single layer graphene [34].

Raman spectra of samples annealed at 800 °C and 900 °C showed some changes in 2D band shape and intensity. Here, intensity of the G band is much higher than intensity of the 2D band, while its shape is less symmetric which is characteristic for multilayer graphene. The presence of multilayer graphene was also confirmed with 2D-to-G intensity ratio (I_{2D}/I_G) presented in Table 1, where I_{2D}/I_G intensity ratio for the samples annealed at 800 °C was ~0.64, while in samples annealed at 900 °C it amounts ~0.36. FWHM values for samples annealed at 800 °C were ~71 cm^{-1}, and ~77 cm^{-1} for samples annealed at 900 °C which is characteristic for multilayer graphene [34].

From I_{2D}/I_G intensity ratio in Table 1, it was confirmed that annealing at 600 °C and 700 °C leads to the formation of single layer graphene films, while annealing at 800 °C and 900 °C results in formation of multilayer graphene films. Here, it can also be seen

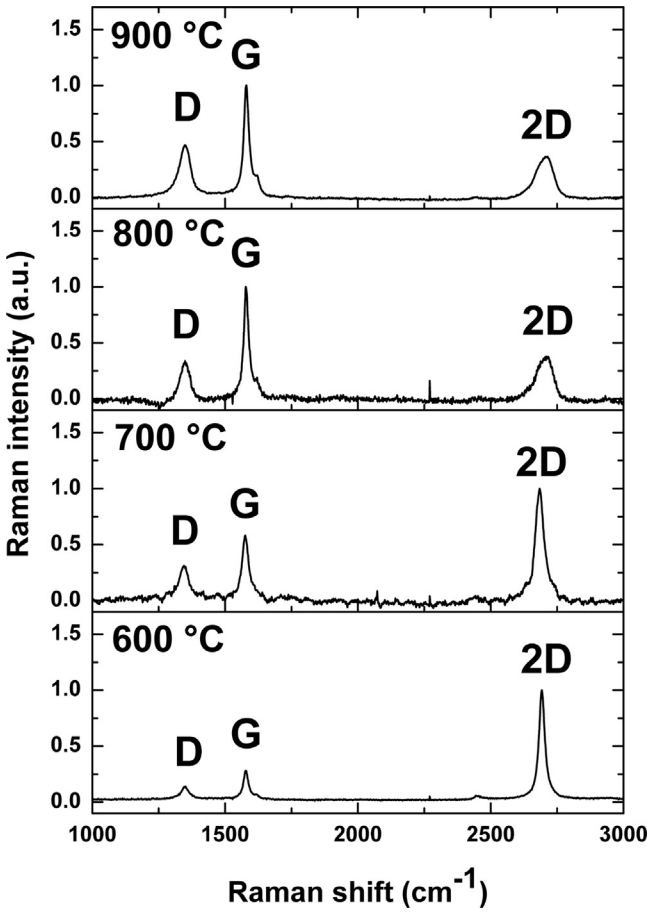

Fig. 1. Raman spectra of Ni/Cu thin films annealed at 600 °C, 700 °C, 800 °C and 900 °C in vacuum for 30 min.