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STUDY OF THE CVD GRAPHENE TRANSFERRED FROM COPPER TO GOLD SUBSTRATE

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Graphene, two-dimensional form of graphite, is characterized by its remarkable chemical, optical, thermal and mechanical properties. The graphene form and support substrate are keys for graphene applications. Here we report chemical vapor deposition of single layer graphene on copper substrate and then transferred on gold substrate. We studied the effects of the transfer process on the graphene properties. Graphene/substrate interaction induces modifications in graphene structure. The characterization of graphene on catalyst and target substrate was performed by Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM) and Raman spectroscopy for confirm the presence of graphene after transfer. The results indicated the great potential for application, special for medical devices.

Keywords: Chemical Vapor Deposition, Graphene, Gold, SEM, AFM, Raman spectroscopy

1. Introduction

Carbon has many allotropic forms — from old known diamond and graphite to more new faces as graphene, carbon nanotube and fullerenes [1, 2], and all of them are intensively investigated in the last decade for various applications [3-5]. Graphene has received extensive attention due to its remarkable properties, such as good optical transmittance, large surface area and high electric conductivity. It can play a significant role in electronic devices, biosensors or energy sources. Today, the synthesis of graphene is the most important sector for graphene application [6]. Since 2004, year of graphene discovered, different synthesis methods have been reported: epitaxial growth [7], chemical synthesis [8], mechanical exfoliation [9], chemical vapor deposition [10,

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11] and chemical exfoliation [12, 13]. Chemical vapor deposition (CVD) is the most favorable technique for large-scale graphene production with the ability to control number layers of graphene. After obtaining CVD graphene on metal catalyst, the transfer process is required to translate the graphene film into the target substrate, in function of applications [14]. It is crucial that graphene quality continues to exist during the transfer. Many techniques are reported to transfer CVD graphene, but transfer based on the polymer support is widely reported [15, 16]. Poly (methyl methacrylate) (PMMA) is the most used polymer as a carrier material in the transfer process of graphene to target substrate. This method may introduce defects or residues in the graphene structure, or structural modifications such as cracks in the layer [17, 18]. For a clean transfer, is very important to remove the PMMA residues from the graphene surface and carefully captured with the target substrate to avoid packaging.

Gold nanomaterials are currently used in a substantial number of biomedical applications including medical fields because of their remarkable surface Plasmon optical properties and photothermal effects. The excellent biocompatibility and resistance to corrosion make gold a true material for medical devices. The research for new medical uses of gold is focused on the anticancer and antimicrobial properties of the gold materials [19, 20]. The ability of the gold nanostructures to integrate into biological systems due to unique properties, such as: increased targeting selectivity, enhanced tumor uptake, low immunogenicity, rapid transport kinetics and their optical properties has been exploited on a large scale for early diagnosis [21, 22], cancer targeting imaging [23, 24] and photothermal cancer therapy [25]. Recent studies focus on theranostics platforms that combine diagnostic detection and therapeutic functions in a single procedure. Gold, used with successfully as theranostics agent, is a good candidate for the theranostics platform based on graphene, so, we study the transfer of graphene on the gold substrate [26]. Graphene on gold substrate provides an excellent combining for theranostics platform.

In this paper, we study step by step the graphene synthesis on copper catalyst and transfer to gold substrate, for quality investigation. Raman spectroscopy is the most useful method for the characterization of graphene characteristics, such as: number of graphene layers, detecting defects, strain effects, interaction between graphene and support layer. The graphene Raman spectra have three characteristic peaks: D band (around 1300-1400 cm^{-1}), G band (around 1580 cm^{-1}) and 2D band (around 2600-2800 cm^{-1}). When graphene is transferred on a substrate, the interface interaction may introduce modification in the band structure [27, 28]. The graphene morphological characterization on copper and gold substrate is investigated by scanning electron microscopy. Atomic Force Microscope (AFM) is used for graphene topography, for evidence the presence of graphene layer before and after transfer.

2. Experimental methods

2.1 *Substrate pretreatment*

The copper foil from Graphene Platform Co., with a thickness of 35 µm was used as a catalyst for graphene synthesis. Copper foil, 99.95% purity, is subjected as a pre-cleaning process: acetic acid, deionized water and isopropyl alcohol (Sigma Aldrich). The samples were dried with nitrogen gas and then introduced into the Nanofab system.

2.2 Methods

The chemical vapor deposition method requires the formation of a graphene film on a copper foil by a chemical reaction of vapor-phase precursors: methane and hydrogen. Reactions of graphene formation were initiated by heating at 1080˚C. The graphene synthesis by thermal CVD method includes five steps: introducing the sample into the reaction chamber in argon atmosphere, heating at optimal temperature, thermal treatment at 1080˚C, growth in precursor's presence and cooling down. In our study, the graphene was grown in a flow of 5 sccm H_2 and 10 sccm CH_4.

After the growth process of graphene on copper substrate, the sample is coated with a uniform PMMA film. The sample is subjected to a heat treatment at 120˚C for 2 minutes. The transfer method is based on chemical etching in the presence of hydrochloric acid activated by peroxidase water. After copper foil etching, the graphene/PMMA is rinsed with deionized water, and then captured with target substrate. The polymer is removed in acetone. The sample is subjected in deionized water, and for reside removal it is heated at high temperature. This method is feasible to transfer graphene to another substrate rapid and with high quality. The graphene with PMMA support layer is a very thin and flexible film with packaged tendency. To avoid cracking or separating in the graphene layer is important to place the sample in the center of gold substrate.

The characterization methods are used to demonstrate the graphene synthesis on copper metal and then track the structure modification on gold substrate. Raman spectroscopy was used to characterize graphene from the structural point of view. We used a high-resolution spectrometer LabRam HR 800 (Horiba Jobin Yvon, Japan) in the wavenumber 4000-400 cm^{-1}, for the bond configuration study. Scanning electron microscopy has been used for morphological characterization of graphene on different substrates with a FEI Nova NanoSEM 630 system (FE-SEM). For the evaluation of graphene film coatings and surface morphology has been performed with an Ntegra Aura Scanning Probe Microscope (NT_MDT Spectrum Instruments), operated in SemiContact (intermittent-contact) mode. ETALON series HA_NC AFM probes

(NT-MDT), 235 kHz resonant frequency, 12 N/m force constant were used in the measurements.

3. Results and discussions

First characterization, for certify the material synthesis is Raman spectroscopy. The Raman spectra were obtained with the red laser: 633 nm.

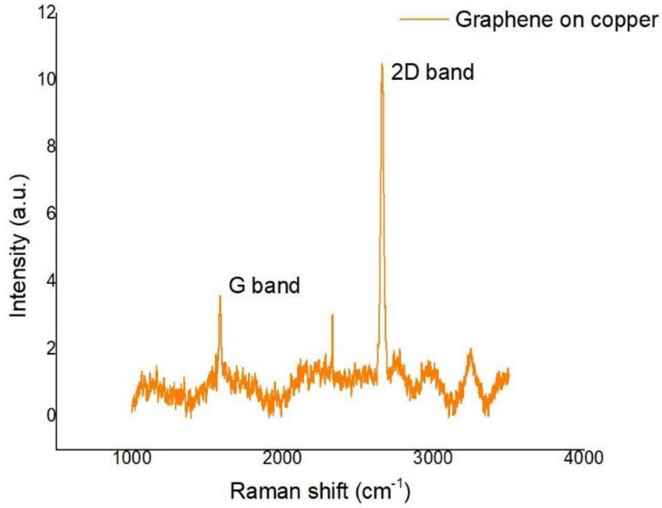

Fig. 1- Raman spectrum of graphene on copper

In Fig. 1 is presented the Raman spectrum of graphene on copper foil after CVD process. The number of graphene layers is determined by the intensity ratio of characteristic bands: G and 2D. Is observed appearance of the G and 2D bands characteristic to graphene. Defects band is not present, indicating an increase with a low density of defects in the graphene lattice. In the case of graphene obtained on copper, the Raman data reported in Table 1, indicate the formation of single layer graphene expressed by ratio of 2.93. It can be noticed that this value is maintained after the transfer on the gold substrate, with reduced changes due to manipulation of the sample.

In the transfer process, we observed a good adherence between graphene and gold substrate, could be due to the strong electrostatic interface interaction. The combination of graphene monolayer and gold substrate can be a promising SERS substrate for detection and therapy.

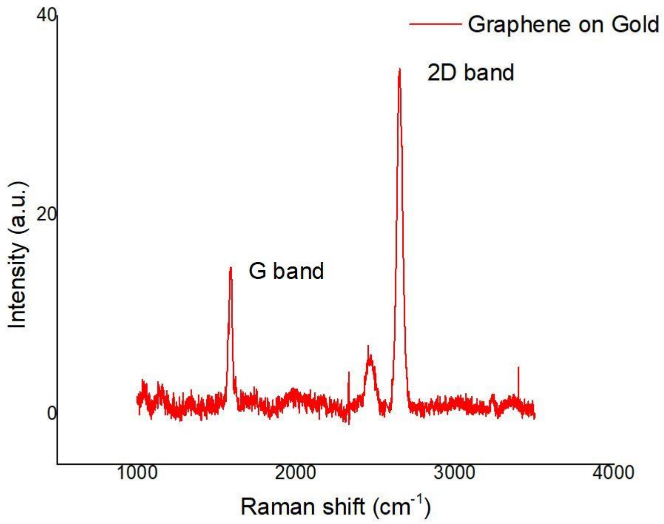

Fig. 2- Raman spectrum of graphene on gold substrate

Raman spectra of graphene on gold substrate show a good transfer of graphene monolayer without defects. It is observed an increase in intensity with approximately three times. Fig. 2 shows the Raman spectrum in the 2450 cm^{-1} wavenumber, due to a double resonant Raman scattering explaining by interface between the gold substrate and the graphene layer.

Table 1

Comparative Raman characteristics

Sample	G band		2D band		I_D/I_G	I_{2D}/I_G
	Raman shift (cm^{-1})	Intensity (a.u)	Raman shift (cm^{-1})	Intensity (a.u)		
Graphene on Cu	1583.2	7	2660.4	13	0	2.93
Graphene on Au	1589.6	13	2653.3	34	0	2.83

Table 1 shows the Raman assignments of the bands and the data for graphene quality analysis on copper and gold substrate. The qualitative indicator (I_{2D}/I_G) remains roughly the same. This value indicates a wet chemical method has a high quality, without polymer residue. This method opens the possibilities for medical applications based on graphene in the gold substrate. Full width at half maximum (FWHM) of the G band of graphene on copper foil is around 21 cm^{-1}, without change after transfer on gold substrate. FWHM line width of 2D band indicates an increase after transfer, with a 40 cm^{-1} value. This difference between FWHM for 2D band higher than equilibrium value indicates the existence a disorder in the graphene lattice due to transfer manipulation. An important aspect for the graphene on gold substrate is the very well elimination of PMMA. Correlation between the layers number in the graphene on copper and on the gold substrate suggests a good transfer on the target substrate, suitable for applications. The increase of the intensity on the gold substrate establishes the existence of a SERS- plasmonic gold effect amplifying the Raman lines characteristic of the graphene.

Scanning electron microscopy was used to study the morphology of graphene on copper substrate and then transferred to gold substrate for interface analysis.

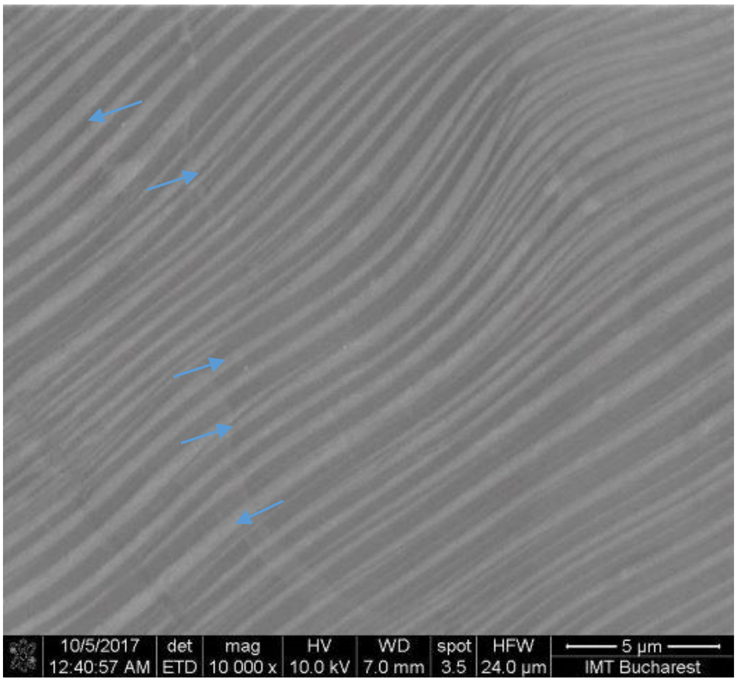

Fig. 3- Micrograph of monolayer graphene CVD on copper foil

Fig. 3 clearly indicates the graphene monolayer grown with large domains, around 80 µm on copper foil with the size of 2 cm x 2 cm. The copper presents wrinkles, without influence in graphene structure. The arrows indicate the graphene domains.

We investigate the coating and uniformity of graphene on the catalyst substrate after CVD process. Also, SEM micrograph on gold substrate confirmed the graphene transfer with large area. Fig. 4 shows micrograph of transferred graphene on the gold substrate. The arrows indicate the boundary between the graphene layer and the gold substrate.

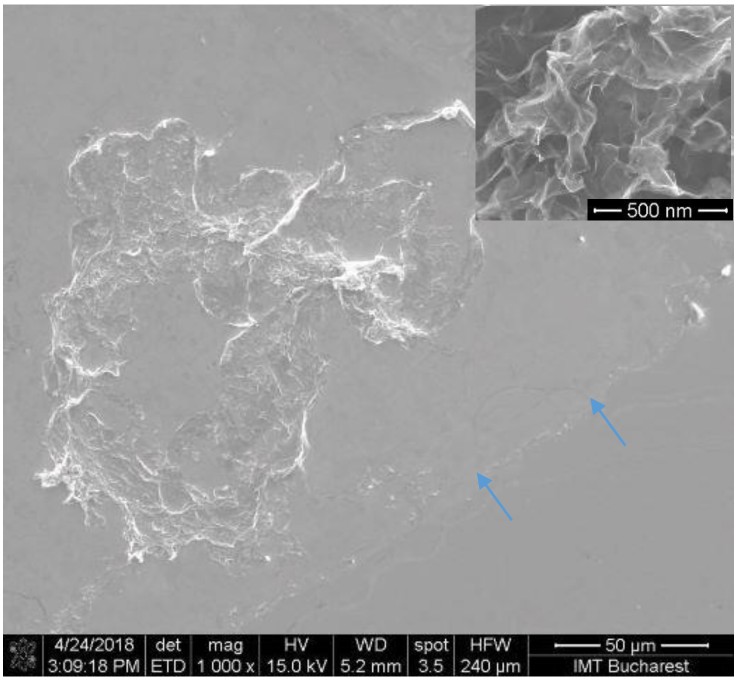

Fig. 4- Micrograph of monolayer graphene on gold substrate

In the SEM micrograph on the gold substrate a zone appears with graphene folded due to sample package tendency. Due to its properties, graphene has an affinity for the dielectric substrate and adheres excellently to gold, but in the air it has a very high tendency to pack.

For graphene topography and structural properties, we used the AFM characterization. The graphenes supported on copper a) or gold b) are morphological evidenced in Fig. 5.

a) b)

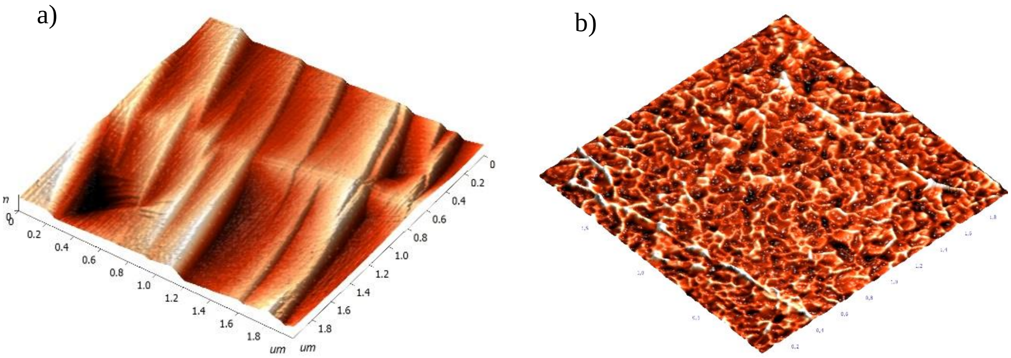

Fig. 5- 3D AFM of graphene on a) copper and b) gold

The graphene topography depends on the type of the substrate and the quality of the graphene surface. The difference between the graphene topography on a) the copper and b) the gold substrate is clearly influenced by the uniformity of the substrate support. Graphene follows the morphology of the substrate, on copper presents wrinkles due to copper surface roughness, while on gold is folded. Both images were acquired on the same scan area: 2 μm x 2 μm. In both cases, because of the appreciable values of the substrate roughness, the graphene morphology is dictated by the topography of the underlying substrates. For the copper substrate, both large (about 10 nm in height) and small (~ nanometer) quasiregular steps could be noticed in the AFM image. As steps do not show up on initial copper foil, prior to graphene deposition, we presume that these steps are due to surface "reconstruction" of polycrystalline Cu under the high temperature processes involved in the CVD process of graphene. The graphene on gold shows a completely different morphology, as in this case graphene was transferred on the gold surface, after being chemically deposited on initial copper substrate. The graphene roughly follows the gold film grain-like morphology. However, typical peculiarities differentiate its morphology from that of the bare gold film: smoothing of the surface features, rounded edges and typical wrinkles and folds point to the presence of the graphene layer on the scanned area.

4. Conclusions

Graphene on copper foil was successfully prepared by chemical vapor deposition. The resulting graphene monolayer was synthesized with a defect free which is relevant for application. Graphene monolayer transferred on a gold substrate without polymer residue and with high quality was identified by Raman spectroscopy. SEM and AFM characterizations are complementary to Raman data, which provide information about graphene presence and morphology on the target substrate. The graphene morphology is identified by SEM images on copper, and then a folded graphene layer was observed when it is transferred on gold substrate.

Graphene on the gold substrate, with high quality and SERS effect, is an ideal candidate for medical imaging and biosensors, as applications. Graphene high surface area and with possibility to number layer control has important advantages in the functionalization and applications uses. The gold substrate enhances the graphene properties. This experimental paper shows the possibility of obtaining graphene on gold substrate, with high quality and good properties, which can be used in biosensors and medical imaging.

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