GRAPHENE NANOSTRUCTURES ON ELECTRODEPOSITED CU BY CHEMICAL VAPOR DEPOSITION

[1]SHRUTIDHARA SARMA, [2]PANOSPATSALAS

[1]Department of Mechanical Engineering, Indian Institute of Technology Jodhpur, Rajasthan, INDIA-342037
[2]Department of Physics, Aristotle University of Thessaloniki, Thessaloniki, GREECE-54124

Abstract - Graphene nanostructure growth on electroplated Copper under acetylene gas flow using a low-pressure chemical vapor deposition technique has been explored in this study. Electrodeposited Cu is compatible with integrated circuit technology and therefore is explored as a substrate to synthesize graphene domains using acetylene as the precursor gas. Characterization under Scanning Electron Microscopy and Raman Spectroscopy indicates good quality bi-layer and few-layer graphene domains of circular shape, grown on electrodeposited Cu/Si substrates. Such structures are foreseen as a medium for growing continuous graphene films for temperature sensing, or for selective deposition of quantum dots with enhance luminescence.

Keywords - CVD, Electro Deposition, Graphene, Spectroscopy

I. INTRODUCTION

Graphene is a one atomic layer thick sheet of carbon atoms packed in a hexagonal lattice [1]. Graphene has motivated significant of research because of its significant properties and potential applications starting from electronics, composite materials, photovoltaics& energy storage to tissue engineering [2,4]. In terms of graphene growth too, several methods have been explored which includes mechanical exfoliation, hydrothermal self-assembly, catalytic chemical vapor deposition (CVD), carbon dioxide reduction, spin coating, nanotube slicing [5- 9] etc. Out of all, catalyst assisted CVD is considered to be the most successful and economic one for high quality growth [10, 11]. Most of the studies involving graphene growth on Cu by CVD are focused on Cu foils [12]. Moreover, a seed layer is always used to overcome adhesion issues. Electroplated Cu substrate gives a smoother surface finish and is compatible with large scale Si wafer. Here, the growth of graphene on electroplated Cu/Si without any prior smoothing/polishing and without a seed layer, is investigated.The graphene nanostructures are characterized using different characterization techniques and number of layers is determined analyzing the peaks formed in Raman spectra. The applications of the nanostructures are commented, thereafter.

II. EXPERIMENT

A. Substrate preparation by galvanic deposition

A thin layer of Cu is electroplated on a Si substrate which bears a native oxide layer (SiO_2). After initial cleaning in acetone followed by iso-propanol in an ultrasonic bath, substrates are tickled in hydrofluoric acid (HF) solution to remove the native oxide layer. The electrodeposition is done directly on the Si substrates in a plating bath of copper sulfate (CuSO4), without any seed layer. The anode is made up of a pure copper wire, while the Si substrates dipped in the solution serves as the cathode. Deposition times are varied from 3 min to 10 min. The water on the electroplated Si substrates is quickly dried using a hand-pump and inserted in to the CVD chamber (vacuum) to avoid oxidation of copper films and for further annealing.

B. Graphene synthesis with Low Pressure Chemical Vapor Deposition (LPCVD)

The LPCVD chamber consists of quartz tube coupled with a furnace, a rotary pump for evacuating, two cylinders each for the process and carbon source gases, and pressure sensors. During the graphene synthesis Argon (Ar) is used as the precursor and Acetylene (C_2H_2) as the carbon source gas. The substrates are annealed in an Ar environment at a high temperature to enable large descent terraces of Cu . Acetylene and Argon are fed at a ratio of15:100 sccm (optimized) for the synthesis and deposition temperature is varied from 850˚C to 950˚C. The base pressure is maintained at 6.3 mbar and the working pressure at 1.3 mbar. The deposition time is fixed at 6 mins and the chamber is allowed to cool back to well below 80˚C before the samples are unloaded.

C. Characterization

The graphene nanostructures are studied using a high-resolution Scanning Electron Microscope (JEOL-JSM5260 scanning electron microscope using a W-filament).

Raman spectral analysis is performed using a LabRam HR spectrometer (HORIBA) equipped with a Peltier-cooled charge coupled detector. A 100× standard objective (~1 μm focus spot) a laser power lower than 1 mW is used to avoid any laser induced heating effects, with excitation provided by the 514.6 nm line of a diode pumped solid state laser.

The Cu/Si samples (before and after graphene growth) are examined for optical reflectivity spectra, using a white light halogen source, a coaxial fiber-optic

assembly and a detector. The reflectivity spectra are normalized using a reference mirror of Silicon.

III. RESULTS AND DISCUSSIONS

A. Surface reflectivity of Cu/Si substrates

Optical reflectivity spectra of the electrodeposited Cu/Si samples, before and after the growth of graphene nanostructures are shown in Fig. 1. The times denoted shows the electrodeposition time of Cu on the Si substrates. As can be speculated from figures, higher electrodeposition time leads to thicker films as the reflectivity increases with increase in thickness of the Cu films. However, the reflectivity reduces with the formation of graphene structures on the Cu. The difference is more prominent in IR wavelength than in the visible wavelength range.

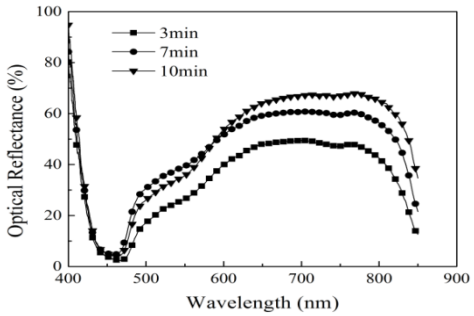


Fig. 1(a): Optical reflectivity spectra of Cu/Si samples with different electrodeposition time

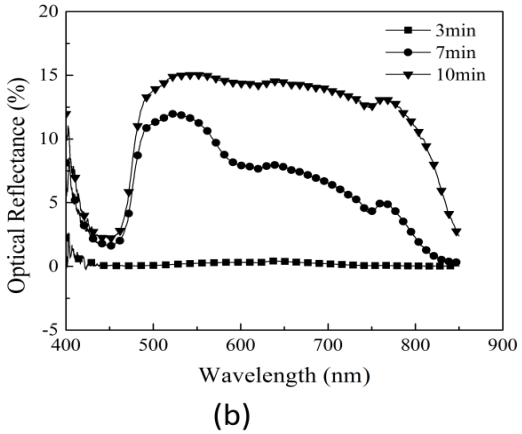


Fig. 1(b): Optical reflectivity of Cu/Si samples after graphene growth

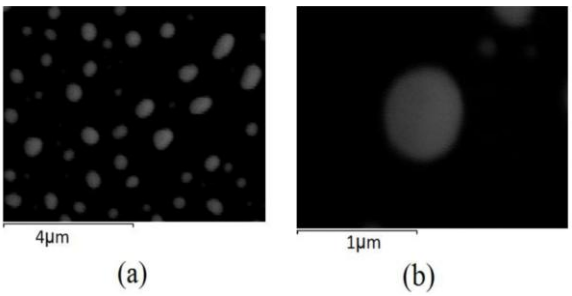


Fig. 2: SEM images of sample graphene domains at different magnification (a) 14 kX (b) 50 kX

B. Surface morphology

SEM is used to obtain images of the graphene domains on the surface of the electroplated Cu/Si without any processing. Fig. 2 shows the SEM images of sample graphene domains grown on electroplated Cu/Si surface at different magnifications. The graphene domains are randomly formed on the electroplated Cu, the electroplated Cu either consisting of single or coalesced grains. The graphene domains size in the range of 150 nm to 700nm.

C. Chemical structure

The two most significant feature in Raman spectra of graphene is the G band at ~1580 cm^{-1} and 2D band at ~2700 cm^{-1}[13]. Measurements are repeated on the same spot and at different spots on the same sample and the measured peaks are fitted with Lorentzians. Fig. 3 presents a Raman spectrum of a graphene sample grown at 850℃. Fig. 4 shows a detail analysis of 2D peak of the same sample shown in Fig. 3. Several samples are measured but spectra of all are not included due to space constraint.

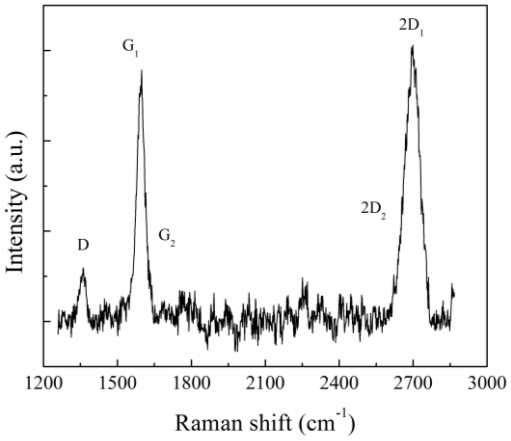


Fig. 3: Raman spectra of a sample graphene domain (G32) grown at 850˚C

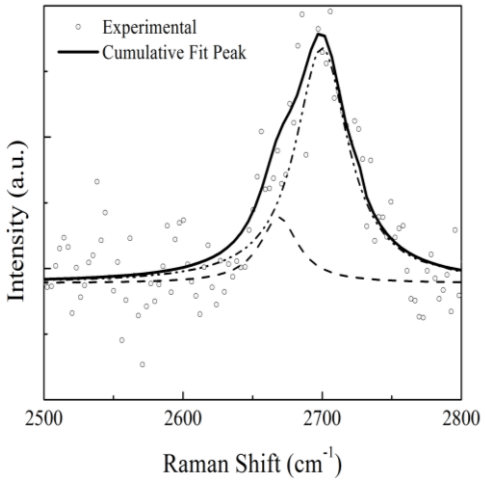


Fig. 4:2D peak of a sample graphene domain (G32) grown at 850˚C

The position of D bands (suggests defects) in the samples vary from 1352 cm^{-1} to 1363 cm^{-1} while the G

bands (suggests hexagonal lattice formation of Carbon) vary around 1588 $cm^{-1}$to 1600 cm^{-1}. The position of 2D peaks range from 2693 cm^{-1} to 2709 cm^{-1}. The 2D band (double resonance of D band) helps to determine the number of graphene layers and the quality of graphene, through its intensity and shape. The position of the bands, with the corresponding FWHM and I_{2D}/I_G ratios are listed in Table I.

The D bands are smaller in case of the graphene grown at 950℃ compared to those grown at 850℃. Very low D bands in Raman spectra are typical of high quality graphene structures implying that samples of 950 ℃ are of superior quality. The G and 2D peaks are found to shift upward in frequency with increasing number of layers. It is reported that generally accepted ratio for I_{2D}/I_Gratio for bilayer graphene is assumed between 0.8 and 1.4, whereas a ratio greater than 1.4 represents monolayer graphene. Few-layer graphene with more than three layers are generally identified with an I_{2D}/I_Gratio < 0.8 [14]. As such, the peak intensity ratio of 0.87 and 1.06 and low FWHM values of 41.26 (G peak) & 62.68 (2D peak) and 34.09 (G peak) & 50.80 (2D peak) in case of G210 and G32 samples, respectively (Table I) indicates the presence of bi layer graphene. On the other hand, a ratio of I_{2D}/I_G<0.8 confirms existence of few-layer graphene in rest of the samples. A lower FWHM suggests better homogeneity of thickness of the grown graphene.

Sample	Dep. time (min)	Temp (C)	Pos (D)	Pos (G)	Pos (2D)	FWHM (G)	FWHM (2D)	I_{2D}/I_G
G23	3	850	1359.33	1595.65	2696.95	29.89	46.41	0.81
G25	5		1358.89	1589.90	2701.10	29.79	38.04	0.69
G27	7		1352.34	1594.97	2693.46	38.29	46.64	0.54
G210	10		1352.98	1594.60	2699.46	41.26	62.68	0.87
G32	2	950	1358.85	1594.83	2702.29	34.09	50.80	1.06
G37	7		1362.81	1588.07	2709.30	27.20	50.04	0.58
G310	10		1359.77	1588.48	2702.38	26.37	31.84	0.54

Table I: Raman analysis for several graphene samples

IV. CONCLUSION

Successful growth of few-layer and bi-layer graphenenano structures have been witnessed using a combination of low-cost electro deposition and LPCVD method. The Raman spectra show lower defects (D bands) in case of samples grown at higher temperature (950℃).Semiconductor nanoparticles are known for their size dependent optical and electronic properties. Combination of such nanoparticles with graphene can add new dimensions to optoelectronic devices or photo-detectors.

The as grown graphene domains can be used for selective deposition of semiconducting nanoparticles for applications in bio-imaging or optoelectronic devices. The presence of Cuunderneath is believed to enhance the luminescence of the hybrid nanostructures. Moreover, increasing the deposition time can give continuous graphene films which can be used as temperature sensing films in thin film temperature gauges to be applied for transient measurements. Graphene films being extremely thin are expected to give instantaneous response.

ACKNOWLEDGEMENT

Authors are successful to the teams of Prof. Patsalasincluding I. Fekas, and Prof. Christofilosincluding K. Filintoglou, for helping in carrying out the experiments. Authors are also thankful to the Center of Interdisciplinary Research and Innovation of AUTh for access to the Raman instrumentation.

REFERENCES

[1] K.S.Novoselov et al.,"Electric field effect in atomically thin carbon films", Science, vol. 306, no. 5696, pp. 666-669,2004. doi: 10.1126/science.1102896

[2] W.H. Qiang, L.C. Yang, L.H. Ming and Q. He, "Graphene applications in electronic and optoelectronic devices and circuits", Chinese Physics B, vol. 22, no. 9, pp. 098106, 2013.

[3] J. Liu, Y.Xue, M. Zhang and L. Dai, "Graphene-based materials for energy applications", Materials Research Society, vol. 37, pp. 1265-1272, 2012.

[4] L. Shang et. al, "7- Graphene and graphene oxide for tissue engineering and regeneration", TheranosticBionanomaterials, Micro and Nano Technologies, Elsevier, 2019.https://doi.org/10.1016/B978-0-12-815341-3.00007-9.

[5] L. Tanget. al, "Bottom-up synthesis of large-scale graphene oxide nanosheets", Journal of Materials Chemistry, vol. 22, no. 12, pp. 5676, 2012. doi:10.1039/C2JM15944A

[6] C. Mattevi, H. Kim, andM. Chhowalla, "A review of chemical vapour deposition of graphene on copper", Journal of Materials Chemistry, vol. 21, no. 10, pp. 3324–3334, 2011. doi:10.1039/C0JM02126A

[7] A. Chakrabartiet. al, "Conversion of carbon dioxide to few-layer graphene", Journal of Materials Chemistry, vol. 21, no. 26, pp. 9491, 2011. doi:10.1039/C1JM11227A

[8] Z. Yan et. al, "Rebar graphene, ACS Nano, vol. 8, no. 5,pp. 5061-5068, 2014. doi: 10.1021/nn501132n.

[9] J. Liyinget. al, "Narrow graphene nanoribbons from carbon nanotubes", Nature, vol. 458, no. 7240, pp. 877–80, 2009. doi:10.1038/nature07919.

[10] K. Hyungkiet. al, "Copper-vapor-assisted chemical vapor deposition for high-quality and metal-free single-layer graphene on amorphous SiO2 substrate", ACS Nano, vol. 7, no. 8, pp. 6575–6582, 2013. doi: 10.1021/nn402847w

[11] A. Cortés, C. Celedón, andR. Zarate, "CVD synthesis of graphene from acetylene catalyzed by a reduced CuO thin film deposited on SiO2 substrates", Journal of the Chilean Chemical Society, vol. 60, no. 2, pp. 2911-2913, 2015.

[12] I. Pasternak et. al, "Comparison of CVD graphene grown on copper foil and PVD copper", Electronic Materials, vol. 41, no. 2, pp. 26-33, 2016.

[13] A. C. Ferrari, "Raman spectroscopy of graphene and graphite: Disorder, electron–phononcoupling, doping and nonadiabatic effects", Solid State Communications, vol. 143, pp. 47–57, 2007. doi:10.1016/j.ssc.2007.03.052

[14] P. Wadugeet. al, "Programmed synthesis of freestanding graphene nano-membrane arrays", Small, vol. 11, no. 5, pp. 597-609, 2015.doi: 10.1002/smll.201402230

★★★