

Metal based Synthesis of Graphene by Pulsed Laser Deposition Technique

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Abstract— Pulsed laser deposition technique was used to investigate the effect of cobalt and silver on the fabrication of graphene layers on silicon substrate at 500°C temperature. A uniform and layer by layer deposition of the graphene film has been identified by Atomic Force Microscopy. Micro Raman spectroscopy revealed that by increasing graphite content there is decrease in I_D/I_G ratio and increase in I_{2D}/I_G ratio which is indicative of the formation of low defect, monolayer and few layer graphene.

Index Terms— Graphene, Pulsed Laser Deposition, Raman Spectroscopy, Atomic force Microscopy.

1 Introduction

Graphene is a flat, 2D monolayer of sp^2 hybridized carbon atoms tightly packed in closed hexagonal crystal structure [1]. In regular hexagon graphene layer C-C bond length is 0.142nm while interplanar spacing is of the order of 0.335 nm [2]. Graphene can be wrapped up into 0D fullerene C_{60} , rolled into 1D nanotube CNT and also stacked into 3D graphite (C) [1].

In microelectronics, graphene is proved to be a good replacement of silicon due to its strong bonding and unique electronic, thermal and mechanical properties [2]. All these inspiring and attractive graphene's properties need high availability of controllable and reliable fabrication techniques. In literature, mono and few-layer graphene has been fabricated by many methods such as micromechanical cleavage (drawing) method [3], thermal decomposition and metal induced graphitization [4,5], graphite oxide reduction [6], molecular beam epitaxy (MBE) [7], chemical vapor deposition (CVD) [8] and the most recently by pulsed laser deposition (PLD) technique [9,10].

Carbon deposition on metal has been gaining attention as an alternative graphene fabrication method. Growing interest of graphene formation on metal occur due to its reduced temperature, less rigorous vacuum conditions and easily transferring of graphene to other arbitrary substrates by dissolving the metal layer [11]. This paper describes the fabrication of few-layer graphene by PLD technique at 500°C substrate temperature.

A limited amount of carbon was deposited on cobalt (Co) and silver (Ag) thin films at 500°C substrate temperature by pulsed laser ablation of graphite. High energetic carbon species form a solid solution of C-Co or C-Ag into the Co and Ag metals used respectively.

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During natural cooling of deposited films till room temperature, carbon precipitated out from solid solutions and

a crystalline hexagonal carbon layer appears at the top surface. In this comparative study, effect of Co and Ag metals on the quality of graphene was discussed.

2 Experimental

In this experiment few-layer graphene has been deposited by using cobalt-graphite (Co-C) and silver-graphite (Ag-C) targets on n^+ silicon (100) substrate. Cobalt and silver were used as catalyst. Co-C and Ag-C has been prepared by embedding cobalt disc into the graphite disc and after Co-C deposition, cobalt was replaced by silver in the same graphite disc. Schematic of targets Co-C and Ag-C is shown in Fig. 1. Targets were mounted on motorized target holder placed in stainless steel chamber which was evacuated to a pressure of 10^{-5} torr. A KrF excimer laser (248 nm, 20 mJ, 20 Hz) was focused at an angle of 45° on targets Co-C and Ag-C. Silicon is placed in parallel configuration with targets at a distance of 2cm. Schematic of the experiment is shown in Fig. 2.

Experiment was done in two steps. In 1st step, chamber was evacuated with base pressure of the order of 10^{-5} torr in three hours. After that 5000 shots from KrF excimer laser (248 nm, 20 mJ, 20 Hz) were given to cobalt (Co), ablated material was deposited on silicon substrate. Then substrate (Si) temperature was raised to 500 °C for 1 hour and metal particles arrange uniformly to provide matrix for carbon atoms. In 2nd step, after heating substrate to 500 °C, graphite came in front of KrF excimer laser by using electric stepper motor. 200 laser shots were given to graphite and the ablated graphite particles were deposited on heated Co-Si substrate. Finally, carbon was precipitated out from metal-carbon solid solution on natural cooling upto room temperature and adsorbed energetic carbon atoms form crystalline hexagonal structure which leads to the formation of few-layer graphene. 1st step and 2nd step were repeated by giving 5000 shots to cobalt and 500 shots to graphite respectively. Same procedure was adopted by taking silver as a catalyst and graphite as carbon source.

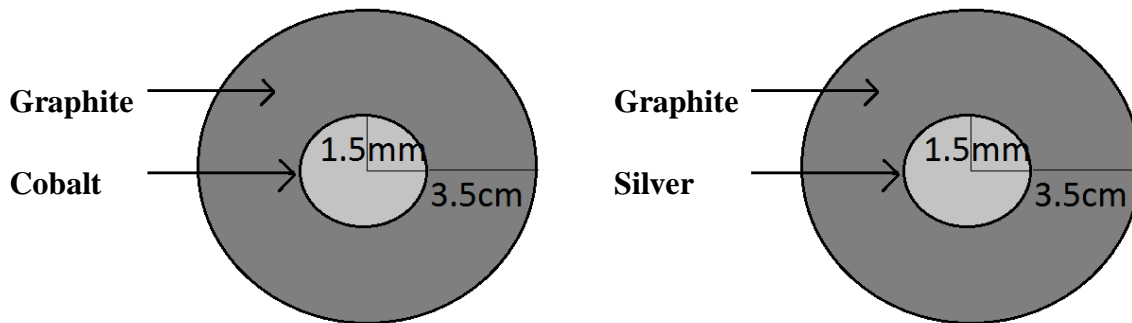


Fig. 1. Schematic of Co-C and Ag-C target assembly

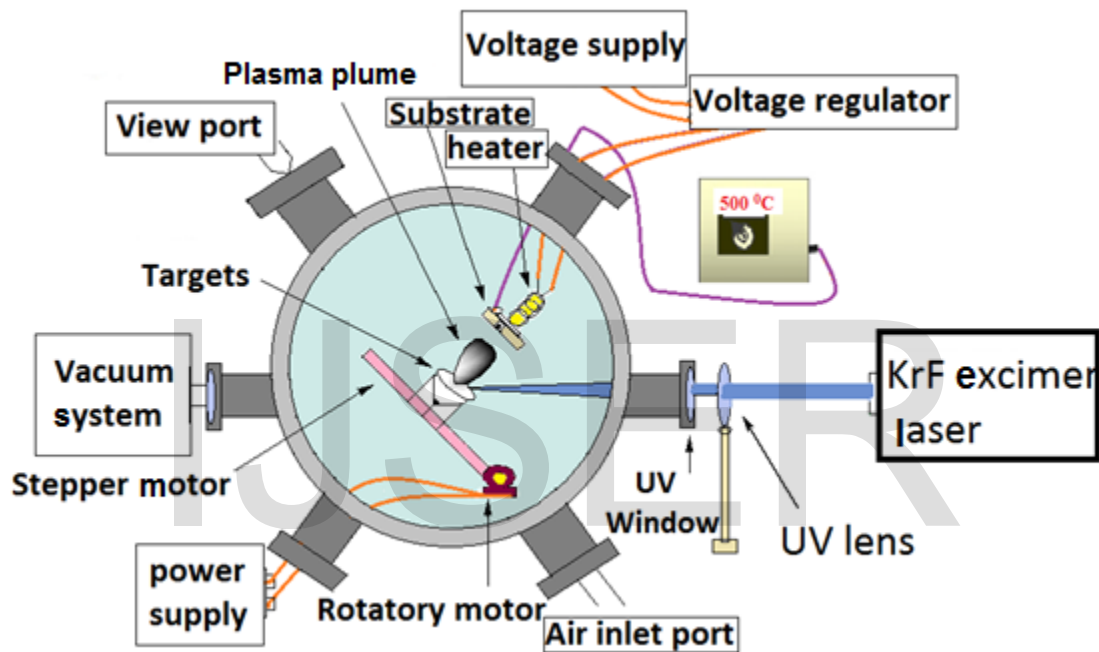


Fig. 2. Schematic of experimental setup

3 Results and discussion

These fabricated films were then analysed by Raman spectroscopy for structural analysis while surface topography of deposited films were explored by Atomic Force Microscopy (AFM).

3.1 Raman analysis

Fig. 3 shows the spectra of Raman analysis of films grown with (a) Co: 5000 shots, C: 200 shots, (b) Co: 5000, C: 500 shots, (c) Ag: 5000 shots, C: 200 shots and (d) Ag: 5000

shots, C: 500 shots. All the Raman spectra show three common prominent graphene peaks. These are D peak, G peak and 2D peak which occurs at $\sim 1330\text{ cm}^{-1}$, $\sim 1588\text{ cm}^{-1}$ and $\sim 2670\text{ cm}^{-1}$. D-band mostly appears due to asymmetric breathing mode of sp^2 carbon structure [12]. The D and 2D peaks are due to double resonant scattering processes [13]. The D peak is absent in perfectly crystalline graphene. G peak measures the degree of graphitization, it is non-dispersive and occurs due to in-plane bond stretching of sp^2 hybridized carbon atoms [12].

In all Raman spectra, there appears a side peak with G peak at $\sim 1519\text{ cm}^{-1}$. This is SiC peak which occurs due to the direct interaction of carbon particles with silicon substrate. The occurrence of 2D peak confirms the formation of graphene.

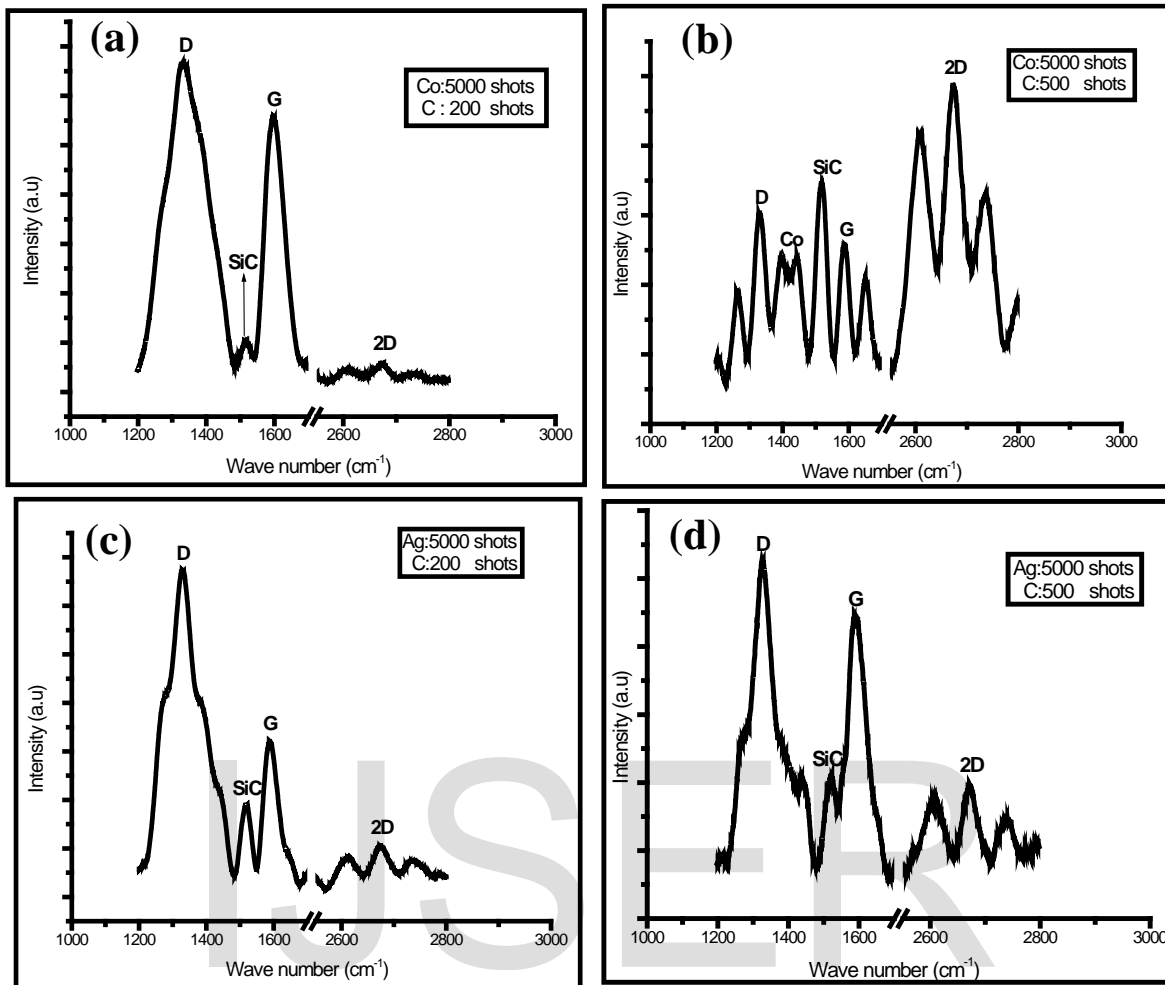


Fig. 3: Raman analysis of films grown with (a) Co: 5000 shots, C: 200 shots, (b) Co: 5000, C: 500 shots, (c) Ag: 5000 shots, C: 200 shots and (d) Ag: 5000 shots, C: 500 shots.

However, the shape and intensity of 2D peak describes the number of graphene layers or graphene thickness. For monolayer graphene, 2D band has single symmetric peak while in bi-layer 2D peak splits into 4 peaks. Splitting occurs due to four double resonance scattering processes. For the case of monolayer graphene there is only one double resonance scattering process. As the number of layers increases, the number of doubly resonance processes also increases and the shape moves towards graphite spectra [14]. As such, looking at Raman spectra it can be seen that monolayer and few-layer graphene has been fabricated. Table I shows Raman data analysis of monolayer and few layer graphene growth on cobalt and silver metals with different graphite shots at 500 °C substrate temperature. From Raman data of films grown with C: 200 and C: 500 shots on metals, I_{D/I_G} ratio indicates disorder and defects. These defects are produced due to

clustering of carbon atom upon cooling. As carbon concentration on catalyst cobalt increases there is a decrease in I_{D/I_G} ratio which shows that less defects are produced. It is observed that I_{D/I_G} ratio decreases on increasing carbon concentration which depicts phase transition in structure from non- sp^2 to sp^2 bonding. Hence, less defects and more crystalline graphene layers are produced by taking graphite 500 shots on metals.

Intensity ratio of 2D and G band (I_{2D/I_G}) is sensitive to number of graphene layers. I_{2D/I_G} for film with Co: 5000 shots and C: 200 shots is 0.115 [9] which translates to the formation of few-layer graphene (< 10 layers) while I_{2D/I_G} ratio for the film grown at Co: 5000 shots and C: 500 shots is 1.890 [15] which confirms the formation of monolayer graphene. For monolayer graphene 2D-peak intensity should be double than that of G-peak intensity i.e. $I_{2D/I_G} \approx 2$ [9].

Table I. Raman analysis data of monolayer and few-layer graphene.

Metals	No. of laser shots		Intensity ratio	
	Graphite		I_D/I_G	I_{2D}/I_G
Cobalt	5000	200	1.187	0.115
Co	5000	500	1.17	1.890
Silver	5000	200	2.07	0.343
Ag	5000	500	1.183	0.446

For as-grown films with Ag: 5000 shots and C: 200 shots I_{2D}/I_G ratio is 0.343. This value indicates the formation of < 5 layers graphene. Film with Ag: 5000 shots and C: 500 shots show I_{2D}/I_G ratio is 0.446 which translates to the formation of few-layer graphene (< 5 layers) [16].

Raman analysis confirms the formation of few-layer graphene on both cobalt and silver transition metals at 500 °C substrate temperature by PLD. However, cobalt as a catalyst facilitates monolayer graphene synthesis with less structural defects as compared to that of silver catalyst.

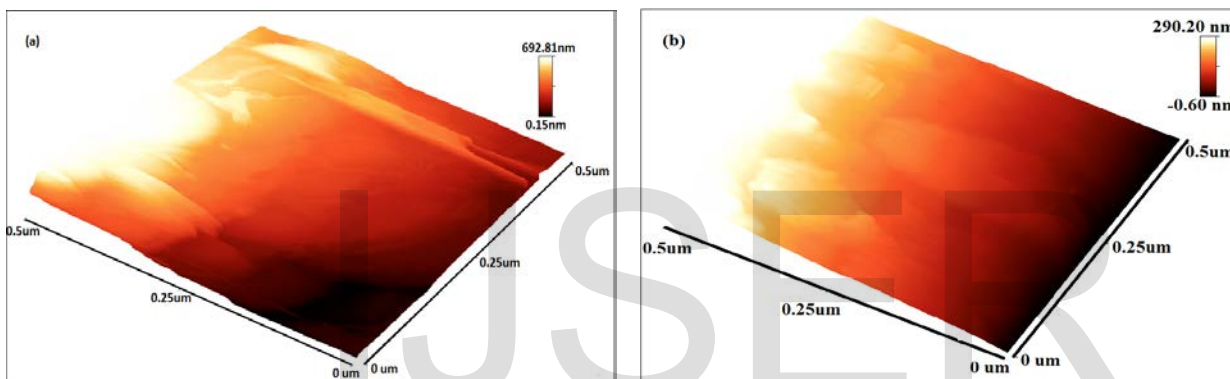
3.2 AFM analysis

The topography of monolayer and few-layer graphene grown by pulsed laser deposition is characterized by using AFM (Veeco) operated in non-contact mode. 3D AFM

image of films grown at (a) Co: 5000 shots and C: 200 shots, (b) Co: 5000 shots and C: 500 shots, (c) Ag: 5000 shots and C: 200 shots and (d) Ag: 5000 shots and C: 500 shots is

Cobalt: 5000 shots and graphite: 200 shots

Cobalt: 5000 shots and graphite: 500 shots



Silver: 5000 shots and graphite: 200 shots

Silver: 5000 shots and graphite: 500 shots

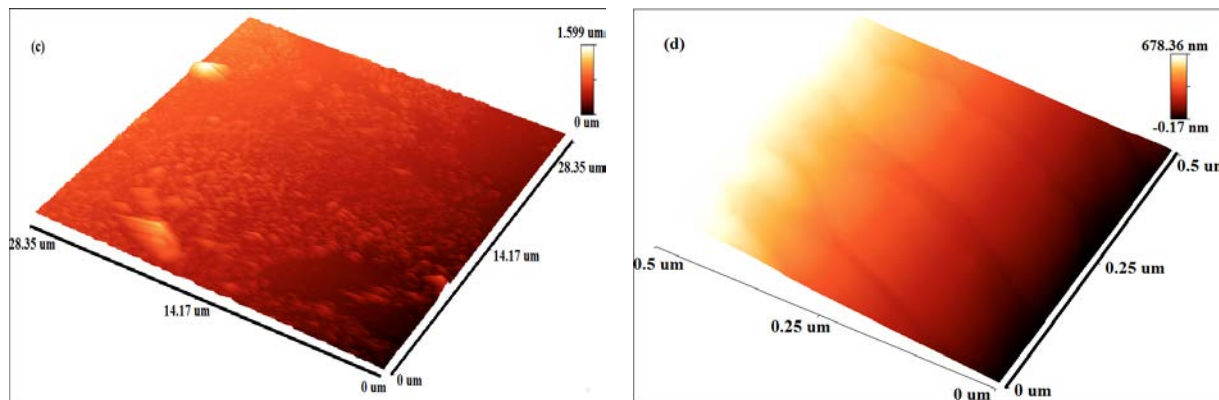


Fig. 4: AFM analysis of film grown at (a) Co: 5000 shots and C: 200 shots, (b) Co: 5000 shots and C: 500 shots, (c) Ag: 5000 shots and C: 200 shots, (d) Ag: 5000 shots and C: 500 shots.

shown in Fig. 4. Fig. 4(a, b, d) shows different layered patterns which can be distinguished from color contrast bar given in AFM images. Black region in the 3D image is the reference silicon surface. Red region corresponds to metal

deposition at 500°C while light yellow color indicates carbon particles segregation on metal which results in monolayer Fig. 4(b) and few-layer Fig. 4(a, d) graphene formation. Total thickness of deposited films in Fig. 4(a, b,

d) is 678, 291 and 695nm respectively. In Fig. 4(c) film prepared with silver and low carbon concentration (200 laser shots) shows some aggregates of carbon atoms immersed in catalyst. Surface patterns shows nucleation which results in the formation of discrete metal islands which grow with low carbon species absorption and finally converged to form few-layer graphene film. This shows that the solubility limit decreases at low concentration of carbon particles on metals as insufficient carbon atoms accumulate on metal surface and forms few-layer graphene (Fig. 4(a, c)). However, by increasing carbon concentration at 500°C on cobalt and silver, the solubility of carbon in metals increases which results in the formation of uniform

monolayer graphene and few-layer graphene. In comparison, carbon films grown on cobalt has more uniform layered patterns with fewer defects as compared to carbon films grown on silver catalyst.

4 Conclusions

Formation of few-layer graphene on transition metals cobalt and silver was investigated. By increasing graphite content on cobalt and silver, low-defect few-layer and monolayer graphene can be successfully obtained at 500°C substrate temperature. However, cobalt as a catalyst facilitates monolayer graphene synthesis with less structural defects as compared to that of silver as catalyst.

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