Growth of high quality graphene on sub-300 nm thick copper thin films

Joon Hyong Cho, Michael Cullinan
Mechanical Engineering Department, The University of Texas at Austin, Austin, TX 78712
joonyboy@utexas.edu

Jason Gorman
National Institute of Standards and Technology, Gaithersburg, MD 20899

Chemical vapor deposition (CVD) of graphene on copper thin films is a promising graphene fabrication method since it can be integrated to conventional micro/nano fabrication processes. This enables large area production of graphene with low manufacturing costs. However, graphene is generally grown on relatively thick copper films (~1 μm thick) due to stability and agglomeration issues of Cu thin films at the temperatures required for CVD growth (~ 1000 ºC).[1] Use of these thick Cu films results in overuse of material and prohibits further potential integration of graphene in wafer scale manufacturing. Our paper reports graphene growth on very thin (250 nm thick) Cu films through use of a nickel adhesion layer.

For large area production of graphene, graphene is grown directly using CVD method on E-beam evaporated thin Cu film with thicknesses of 1 μm, 750 nm, 500 nm, and 250 nm. 50 nm of nickel is used to enhance adhesion at the SiO_2/Cu film interface. During CVD graphene growth process, a 50 mTorr chamber pressure is maintained while constantly flowing 200 sccm of H_2 and 500 sccm of Ar inside the vacuum tube. When furnace temperature reaches 1000ºC, 2 sccm of CH_4 is introduced for 5 min. to initiate graphene growth. After the growth, the sample is pulled out of furnace heat zone for rapid cooling. Graphene/Cu/SiO_2 sample was spin-coated with PMMA A4 and the Cu film was etched with 0.5M ammonium persulfate (APS) solution for two days. This slow etching technique prevented abrupt dissolving of Cu film hence letting the PMMA/Graphene film remain on SiO_2 surface. The Graphene/SiO_2 surface was then dried and thermal treatment to promote adhesion between the two layers and the PMMA was then removed using acetone.

The quality of the graphene was investigated using scanning electron microscopy (SEM) and Raman spectroscopy. I_{2D}/I_G peak ratio from Raman spectra indicates that majority of the surface is covered with monolayer graphene. The graphene also exhibits extremely low defect rates as shown by the I_D/I_G peak ratio even from the thinnest Cu film of 250 nm thickness. The coverage of the graphene from Cu film of 250 nm thickness is lower than with the thicker Cu film but this may be improved through further optimization of the growth recipe. The results presented in this paper show the possibility of low defect, high quality monolayer graphene growth on Cu film thickness below 250nm.

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[1] M. P. Levendorf, C. S. Ruiz-Vargas, S. Garg, and J. Park, Nano Lett. **9**, 12, 4479 (2009).

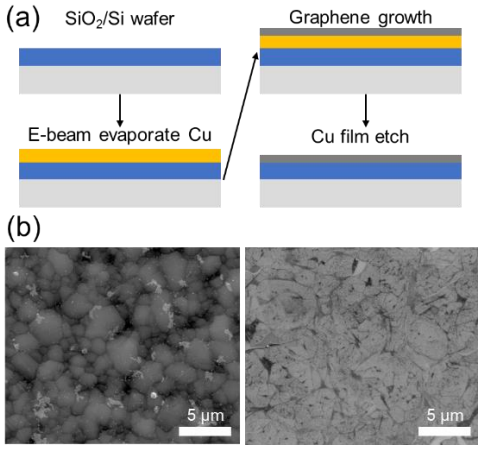

Figure 1: (a) Process flow for graphene growth on thin Cu film (b) SEM image of graphene before Cu film etch of 1000 μm thickness (left) and after Cu film etch (right)

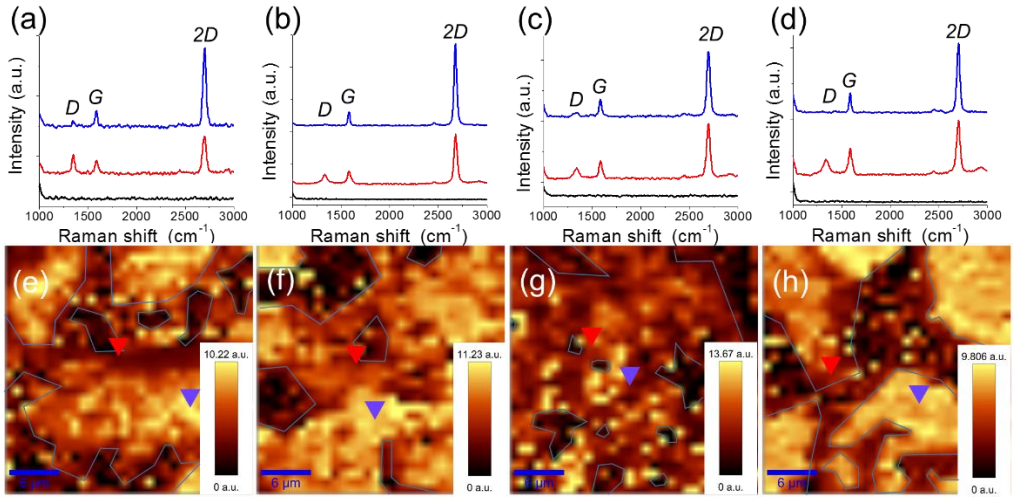

Figure 2: (a)-(d) Typical 532 nm laser excited Raman spectra of CVD-grown graphene after Cu etching. Each spectra line color presents data harvested from the same colored arrow on Raman map below. Graphene samples are grown on Cu film of thickness 1 μm, 750 nm, 500 nm, and 250 nm from left to right respectively. (e)-(h) 30 μm^2 scale I_{2D}/I_G intensity Raman map of graphene grown on Cu film with same thicknesses change. Blue arrows point continuous graphene layer and red arrows point graphene near boundary region. Solid sky-blue lines represent graphene boundaries.

Cu thickness (nm)	Surface roughness, R_a (nm)	I_{2D}/I_G	I_D/I_G	Coverage (%)
1000	77.46	4.8	.81	62.0
750	110.02	5.3	.44	80.3
500	116.49	4.1	.80	84.1
250	111.70	3.9	.28	53.7

Table 1: Average surface roughness of Cu film, ratio of Raman 2D peak intensity over G peak intensity on complete monolayer graphene, and average ratio of D peak intensity over G peak intensity of overall graphene according to corresponding Cu thicknesses in 30 μm^2 Raman map