

Low Temperature Interfacial Graphene Growth Using Thin Metal Catalyst and Solid Carbon Films

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Graphene is a two-dimensional (2D) material consisting of a single layer of sp^2 -bonded carbon atoms arranged in a hexagonal lattice. This structure gives graphene excellent electronic and mechanical properties. One of the interests in the semiconductor industry for graphene is for use as a diffusion barrier^[1]. Current methods of graphene synthesis use temperatures above 750°C, hydrocarbon gases such as CH_4 and C_2H_2 ^[2], and thick metal catalyst layers, (usually greater than 200 nm)^[3]. The graphene formed by these methods requires a multi-step manual transfer process that often causes film damage and leads to high defect density in the transferred graphene films. In this report, a method for synthesizing interfacial graphene using thin carbon and catalyst layers at low temperatures is presented. This method allows the top layer formations to be etched away and leaves the graphene formed on the substrate behind.

To investigate the effects of carbon and catalyst thicknesses on the graphene growth using the annealing method, two different types of samples were prepared, 5nm of amorphous carbon with 20nm of nickel and 10nm amorphous carbon with 40nm of nickel. The amorphous carbon was deposited on the surface of an SiO_2/Si wafer via thermal evaporation. The layer of nickel catalyst was then deposited on the surface of the amorphous carbon using direct current (DC) magnetron sputtering. These samples were annealed at 450°C under argon for 1-10 minutes. A sample of each combination of carbon and nickel was annealed for each time increment, for a total of 20 samples. After annealing, the graphene formed on the surface of the catalyst through carbon diffusion was removed by a PMMA transfer process and the catalyst was then etched away with iron (III) chloride, leaving only the interfacial graphene formations on the surface of the substrate. Raman spectra and images of the samples before and after the etching process were collected with a HORIBA Jobin Yvon LabRAM Raman spectrometer using an Ar⁺ laser (532 nm), and a scanning electron microscope (SEM).

Figure 1(a) and 1(b) show an optical micrograph and an SEM image, respectively. They are the representative results obtained in this experiment. This sample contained 5nm of carbon and 20nm of Ni and was annealed for 10 minutes. The observation suggests that the thin film of amorphous carbon was mostly intact. However, there were areas where the characteristic graphene Raman signals were observed. These graphene formations are the dark purple spots in figure 1(a) and the dark grey spots in figure 1(b). The sparse graphene formations are likely the result of the limited amount of catalyst and carbon present to allow the conversion into graphene.

The Raman spectra of the graphene formations are shown in figure 1(c) and 1(d), where three characteristic peaks, -D, G, and 2D are labeled. Note peak D provides information about the defect density, the G peak provides information about the sp^2 bonding of neighboring carbon atoms, and the 2D peak provides information about the number of graphene layers. For comparison, monolayer graphene was grown on a copper substrate by thermal decomposition of methane at 800°C^[2]. To analyze the Raman results, the full width at half maximum values of the 2D peak were measured and compared. Monolayer sample was measured to be 37.76 cm^{-1} [Figure 1(c))-red line] and the annealed amorphous carbon sample

was measured to be 80.83 cm^{-1} [Figure 1(c)-blue line]. The Raman spectra of graphene formations [blue lines in figure 1(c) and 1(d)] suggest that they are multi-layer graphene indicated by a higher FWHM value^[4]. In addition, the trough between the D and G peaks in figure 1(d) reduces in height starting from the as-deposited sample (grey line), to the after annealing sample (orange line) and finishing with the multi-layer island sample (blue line). Comparing the multi-layer graphene Raman spectrum to that of high-quality monolayer graphene in figure 1(c) also shows a slight peak shift in all peaks of interest. This suggests possible defects and strain within the sheets of graphene^[5]. The Raman 2D to G peak intensity map in figure 2(b) gives a graphical representation of the distribution of graphene signals across the area outlined on the optical micrograph in figure 2(a). The lighter the color on figure 2(b) indicates a higher 2D:G peak ratio indicative of fewer layers while the dark color indicates a lower ratio, indicative of an increased number of layers^[4].

The characterization of the remaining samples indicated that if the annealing temperature is kept at 450°C , samples annealed for less than 10 minutes, and those with thicker carbon films showed no evidence of graphene signal. However, when annealing temperature is higher than 450°C with a carbon thickness of 5nm and a nickel thickness of 20nm, more graphene formations are observed. These results suggest that it is important to understand the synergistic effects of the annealing temperature of amorphous carbon as well as the catalyst in order to optimize the annealing method for interfacial graphene growth. This preliminary investigation suggests that it is possible to convert amorphous carbon into graphene using a nickel catalyst and single-step annealing process. The diffusion of carbon into nickel during heating and precipitation during cooling results in island-style growth of multi-layer graphene. This research is ongoing to further investigate the role of annealing temperature and annealing time as well as carbon and catalyst thickness with respect to the grain sizes of the graphene formations^[6].

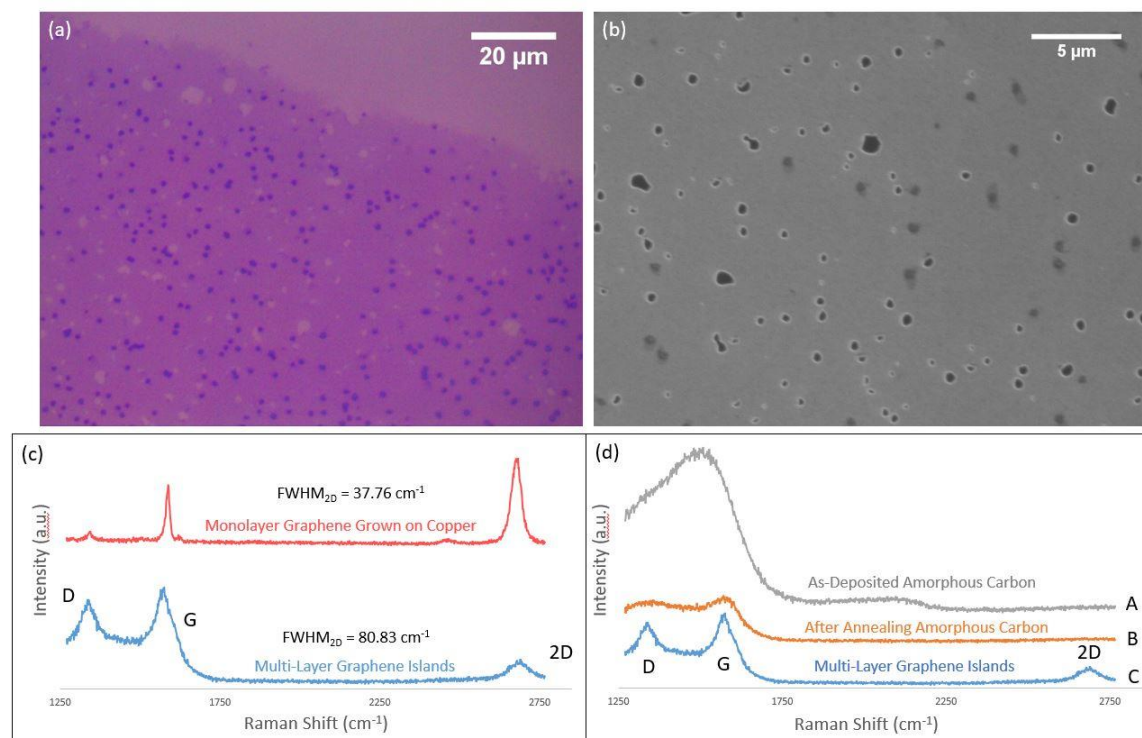


Figure 1. (a) Optical micrograph of showing amorphous carbon (purple film), graphene islands (dark purple spots) and the underlying SiO₂ (light purple). (b) SEM of the same area at higher magnification,

graphene is the small grey areas, grey background is the amorphous carbon and the very dark areas are holes in the amorphous film showing SiO₂. (c) Raman for multi-layer islands and monolayer grown on copper. (d) Raman signal comparison of as-deposited amorphous carbon (A), after annealing amorphous carbon (B), and multi-layer islands (C).

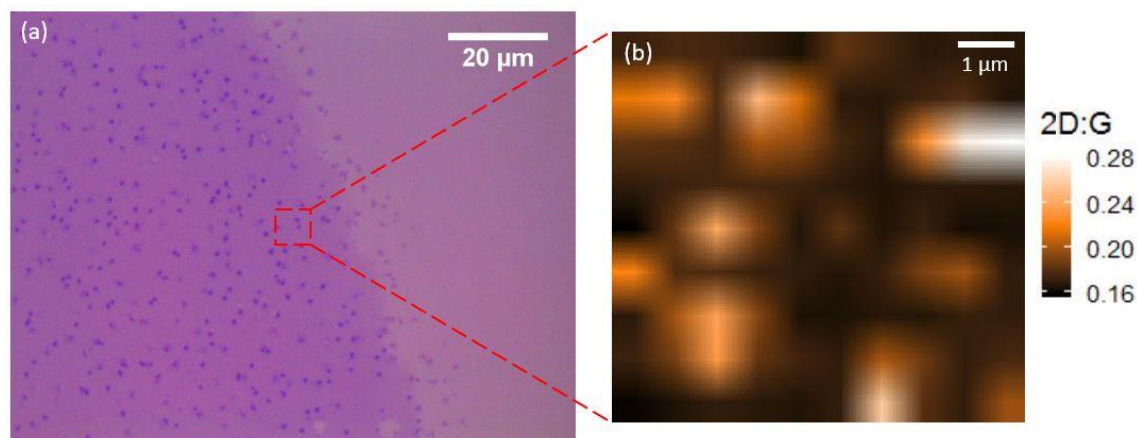


Figure 2. (a) Optical micrograph the same sample, dark spots are multi-layer graphene islands. (b) Raman peak intensity map for the area indicated by the red box. Brighter areas have a larger 2D:G peak ratio, indicating fewer layers.

References

- [1] H. Hirai, H. Tsuchiya, Y. Kamakura, N. Mori, M. Ogawa, Electron Mobility Calculation for Graphene on Substrates, *Journal of Applied Physics*, 116, (2014), 083703
- [2] L.F. Lampert, R. Caudillo, T. Lindner, J. Jiao, C-Plane Sapphire and Catalyst Confinement Enable Wafer-Scale High-Quality Graphene Growth, *The Journal of Physical Chemistry*, 120, (2016), p. 26498-26507
- [3] Z. Sun, Z. Yan, J. Yao, E. Beitler, Y. Zhu, J.M. Tour, Growth of Graphene from Solid Carbon Sources, *Nature*, 468, (2010), p. 549-552
- [4] A.C. Ferrari, J. Robertson, Interpretation of Raman Spectra of Disordered and Amorphous Carbon, *The American Physical Review B*, 61, (2000), p. 095-107
- [5] J. Zabel, R.R. Nair, A. Ott, T. Georgiou, A.K. Geim, K.S. Novoselov, C. Casiraghi, Raman Spectroscopy of Graphene and Bilayer under Biaxial Strain: Bubbles and Ballons, *ACS Nano Letters*, 12, (2012), p. 617-621
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