

Graphene Synthesis by CVD on Copper Substrates

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Abstract and Introduction:

Graphene is an extremely interesting and potentially important material with unique and desirable physical characteristics. A few of the practical applications envisioned for graphene include semi-conductor applications, optoelectronics (solar cells, touch screens, liquid crystal displays), graphene based batteries/super-capacitors, and thermal management. To achieve some of these goals though, large, high-quality graphene is needed [1]. Our research focused on synthesis of monolayer graphene on 25 μm thick copper (Cu) substrates, which allowed for lateral growth on the scale of many centimeters; various measurements showed predominantly uniform, monolayer graphene.

The graphene was grown using chemical vapor deposition (CVD) with methane and hydrogen gas in a tube furnace vacuum system. The as-grown graphene was characterized using a scanning electron microscope (SEM) to understand growth at different conditions and to find desired growth parameters. The graphene films were then transferred to SiO_2/Si wafers for further characterization by optical microscopy and micro Raman spectroscopy. To date, we have seen that higher temperature growth results in a faster growth rate with generally higher quality graphene coverage and that the growth mechanism is based on surface adsorption.

Experimental Procedure:

Graphene samples were grown on 25 μm thick copper foil in a quartz tube furnace system using a CVD method involving methane and hydrogen gases [2]. Under vacuum conditions of 10 mtorr, the furnace would be heated with a 2 sccm flow of H_2 present. Temperatures that were tested ranged from 800°C to 1050°C. After 40 minutes of

heating to allow the copper foil to anneal, a flow of 35 sccm of methane would be introduced for a growth time ranging from 30 seconds to 15 minutes. A quick cooling method was used ($\sim 300^\circ\text{C}/\text{min}$) after growth, and the methane and hydrogen gas flows were continued throughout the cooling process. The graphene films on copper were then characterized using SEM images. After transferring the films to Si/SiO_2 wafers through polymethyl methacrylate (PMMA) coating and iron (III) nitrate etching [2,3], the films would be further analyzed by optical microscopy and Raman spectroscopy.

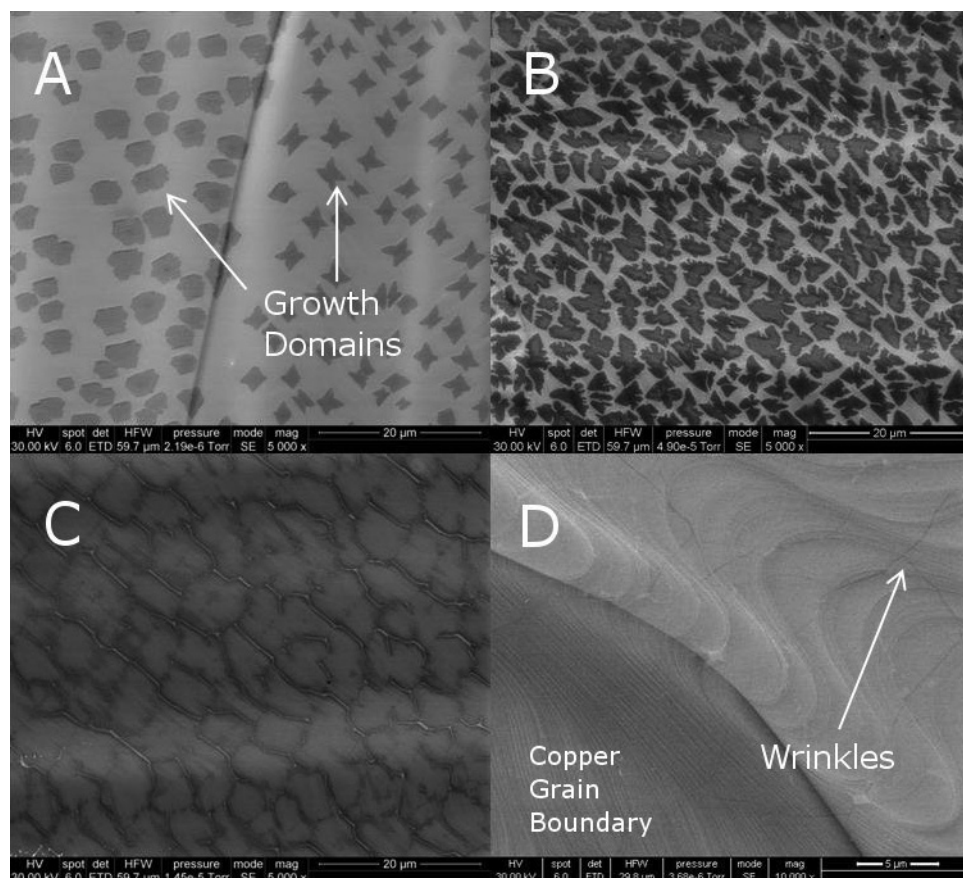


Figure 1: Growth for 10 minutes - clockwise starting with A, growth temperatures of 900, 950, 1000, and 1050°C, respectively.

Results and Discussion:

The graphene films that were grown on the copper substrates were predominantly uniform monolayer graphene; on the scale of many centimeters, with minimal defects/multilayer flakes. The uniform monolayer growth can be attributed to a surface adsorption growth mechanism due to carbon's low solubility in copper [4].

The growth mechanism consists of carbon nucleation sites adsorbing to the copper surface and then growing with addition of carbon to the edges of these growth domains. This growth mechanism, as opposed to a precipitation-based mechanism, allows for the monolayer growth, with very little of the multilayer growth that is seen for precipitation-based growth [4]. The growth domains can be seen in Figure 1, with the domains increasing in size from additional carbon atoms being adsorbed to the edges of the nucleation sites until the domains join, forming graphene (Figure 1d). These figures also display the temperature effect on the growth of the graphene sheets. The images show that increasing temperature (in the range we studied) while holding growth time constant results in significantly faster growth at the higher temperatures, with generally larger domains. This shows that the growth rate of the graphene is highly dependent on the temperature of growth and that full high-quality coverage is apparently more easily achieved at these higher temperatures.

Figure 2 shows Raman spectroscopy results obtained on a transferred graphene film. The spectrum has large, symmetrical G and 2D peaks indicating the presence of monolayer graphene [5]; additionally, the absence of the D peak suggests that defects are minimal [5]. The main defects found while characterizing the sheets were wrinkles (Figure 1d, which are due to the difference in the coefficients of thermal expansion between the graphene and copper [4]) but the full coverage and lack of multilayer flakes shows progress in the growth of high quality and monolayer growth.

Conclusion and Future Work:

Large, uniform monolayer graphene sheets can be grown on copper substrates by the thermal CVD method used, and these sheets are able to be transferred to other substrates. We

also determined that higher temperatures allow for faster growth and large growth domains from observing samples with sub-full layer coverage; the data support growth by surface nucleation and surface adsorption at the edges of growing domains. At longer growth times, the monolayer graphene does not add layers to form multi-layer graphene sheets strongly arguing against precipitation-based growth.

Future research on CVD growth of graphene on metals such as Cu can hopefully lead to larger growth domains and improved physical characteristics. Improved electrical properties may also be able to be achieved through some form of doping to create n or p type films. Finally, achieving uniform bi-layer or other n-layer graphene with control of n, vs. only monolayer graphene, is an exciting challenge.

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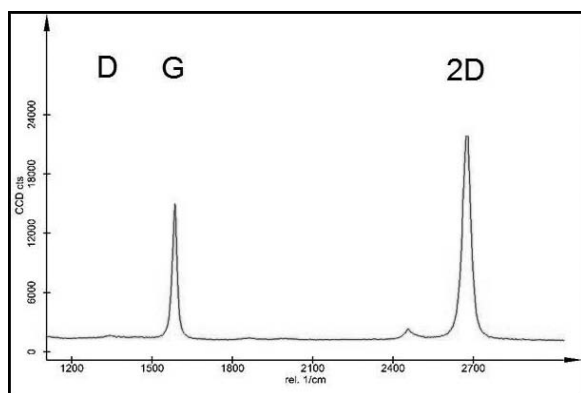


Figure 2: Raman spectrum of a graphene sample.

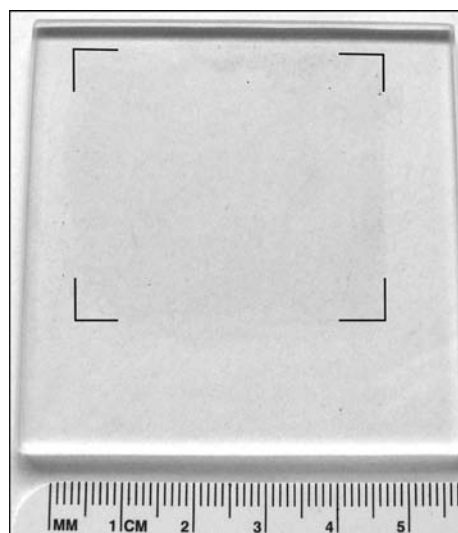


Figure 3: Transferred graphene, 4.5 × 4.5 cm².