Growth of Graphene on Various Substrates

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Abstract:

Graphene is a single layer of graphite. Its unique properties consist of chemical stability, high tensile strength, flexibility, and high thermal conductivity. These properties make graphene suitable for future applications such as hydrogen storage, lighter prosthetics, and flexible electronics. Past methods of graphene preparation such as exfoliation are efficient for lab purposes, but are not suited for mass production. With applications in mind, suitable substrates and methods for large quality graphene growth are necessary. This project focused on which methods of graphene growth are suitable for different substrates. Graphene was grown by the following methods: simple chemical vapor deposition (CVD), hot filament CVD, and radio-frequency plasma CVD. The methods were selected because they provide the option to use various substrates under unique conditions. From these methods, graphene growth was attempted on the following substrates: copper, 3C-silicon carbide on silicon, nickel, nichrome, and nickel films on 3C-silicon carbide. These substrates were selected for their strength, ductility, and resistance to corrosion and heat. The grown films were characterized using scanning electron microscopy (SEM) and Raman spectroscopy. Raman results have confirmed graphene on nickel films on 3C-silicon carbide, diamond nanoseeded nichrome, nickel foil, and annealed nickel foil by the hot filament CVD method. Ultimately, these results may uniquely contribute to the mass production of graphene on potentially any substrate.

Introduction:

Graphene growth is a fairly new technology and many growth methods are currently being evaluated. Popular techniques to form graphene include exfoliation, sublimation of silicon carbide, and CVD onto metal foils [1-3]. Exfoliation requires physically removing multiple layers of graphene to obtain single layer. The sublimation method is limited to silicon carbide and requires transferring to other substrates. CVD is practiced on metal foils at high temperatures to get quality graphene. Unfortunately, this limits graphene growth to only a select few substrates; of which, have little favorability for graphene applications. Enhanced CVD processes like hot filament CVD (HFCVD) and radio-frequency plasma CVD (RFCVD), which uses hot filaments or a plasma to disassociate hydrocarbon gases, allow graphene to be grown on more substrates over a broader range of temperatures. With help from the filaments or the plasma, graphene growth no longer relies on the substrates to be at high temperatures. Enhanced CVD can grow graphene directly onto various substrates, which eliminates the transfer process and is valuable for mass production of high quality large area graphene.

Experimental Procedure:

In this work, graphene was grown on various substrates by the following methods: simple CVD, RFCVD, and HFCVD. The growth conditions are given in Figure 1. The various substrates (copper, 3C-silicon carbide on silicon, nickel, nichrome, and nickel films evaporated on 3C-silicon carbide) were pretreated through sonication in 1) trichloroethylene, 2) acetone, and 3) methanol for three minutes each. In pretreating the substrates, copper and nickel were annealed *in situ* under H_2 at ~ 1000°C from ~ 0-40 min. Additional trials were completed using other substrate pretreatments conditions namely: non-*in situ* annealed copper, unannealled substrates, and UV radiated substrates. With conventional CVD, graphene growth was attempted on copper and nickel substrates with the following growth conditions: H_2/CH_4 = 3 at ~ 1000°C for 10 min. With RFCVD, graphene growth was attempted on all substrates with the following growth conditions: Ar/CH_4 = 19 at ~ 1000°C for 5-10 min. With HFCVD, graphene growth was attempted on all substrates with

Growth Conditions	Simple CVD	RFCVD	HFCVD
Substrate Temperature	1000°C	1000°C	0-750°C
Filament Temperature	N/A	N/A	2100-2300°C
Gas Flowrates (sccm)	H_2=5 CH_4(5%)=35	N/A	H_2=30; 50 CH_4(5%)=5;10
Gas Ratio H_2/CH_4	3	N/A	5; 60; 125
Gap Distance	N/A	N/A	15-45mm
Plasma Intensity	N/A	250-300 Watts	N/A
Pressure	0.3 Torr	1.3E-4 Torr	20-35 Torr
Anneal Time (min)	45 min	0-30 min	0-40
Growth Time (min)	10 min	5-10 min	5-10min

Figure 1: Graphene growth conditions for simple CVD, radio-frequency plasma CVD, and hot filament CVD.

the following growth conditions: H_2/CH_4 of 5, 60, and 125 from 5-10 min. Additionally, the substrate and filament temperatures for HFCVD were 0-750°C and 2100-2300°C, respectively. Uniquely, HFCVD's substrate temperature range was trialed for lower temperature growth.

Results and Conclusions:

The substrates were characterized using Raman spectroscopy and scanning electron microscopy (SEM). CVD and RFCVD method did not yield any graphene films. Raman results have confirmed graphene by HFCVD on nickel films on 3C-silicon carbide (Figure 2). The results correspond to multi-layer graphene. The SEM image of graphene grown on nickel films on 3C-silicon carbide shows graphene grain sizes on the order of 1-3 μm (Figure 3). Similar Raman results confirmed graphene by HFCVD on the following other substrates: diamond nanoseeded nichrome, nickel foil, and annealed nickel foil. The SEM image of graphene grown on nickel foil shows graphene grain sizes on the order of 30-40 microns (Figure 4).

Improper annealing of the copper substrate may explain the lack of graphene on copper. Lack of graphene by RFCVD may be due to the substrate temperature being significantly lower than the thermocouple reading due to heat loss. Future research will require a more extensive evaluation of the growth conditions for each system and what substrate properties are important in the formation of graphene. Also some effort will be required to increase grain size.

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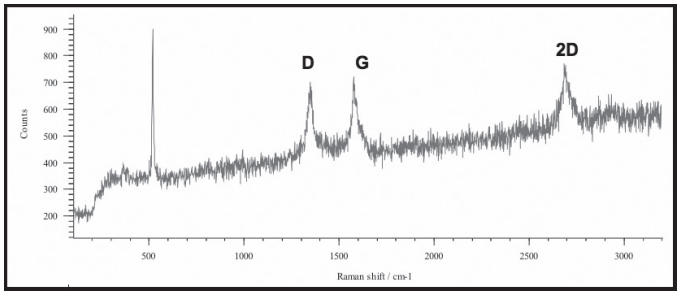

Figure 2: Raman spectroscopy results for 100 nm Ni film evaporated on SiC on Si grown by HFCVD.

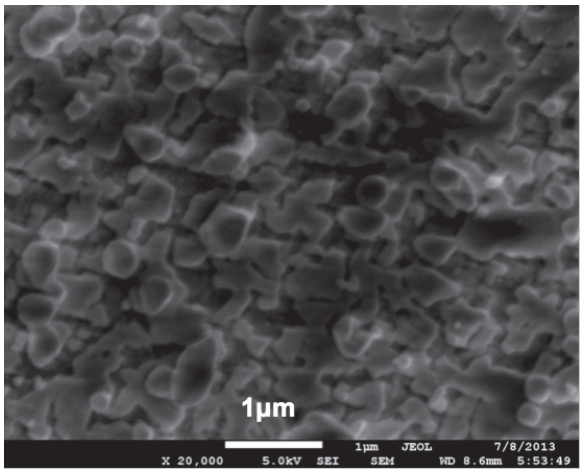

Figure 3: SEM image of graphene grown by HFCVD on 100 nm Ni film on SiC on Si.

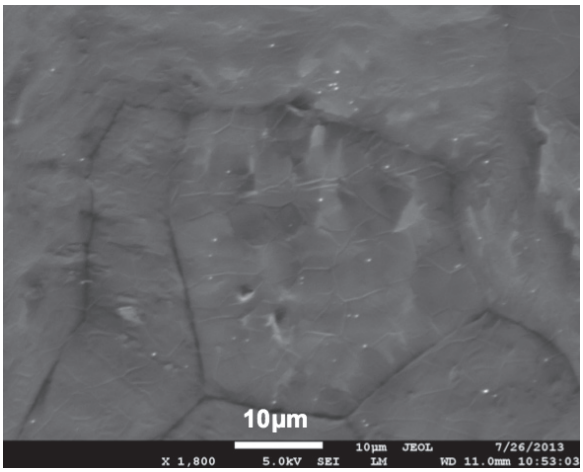

Figure 4: SEM image of graphene grown by HFCVD on Ni substrate.

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