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The Effect of Plasma on Graphene Quality in an Inductively Couple Plasma Chemical Vapor Deposition Reactor

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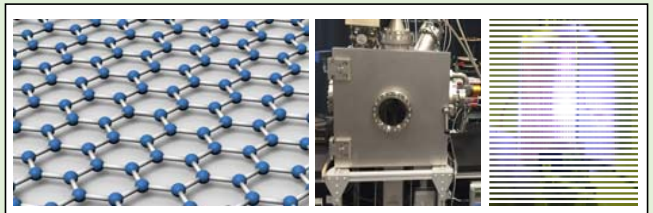
Graphene and its Market Limitations

Since its discovery in 2004, graphene and its material properties have excited researchers and entrepreneurs alike. Its single atom thick, honeycomb-like crystal structure (Figure 1 (a)) gives rise incredibly high electrical conductivity, mechanical strength, thermal conductivity, 97% optical transparency and molecular impermeability, to name a few. Currently, industrial scale graphene applications are limited by many factors including preventative high temperature growth requirements. To address this limitation, the development of growth regimes using an Inductively Coupled Plasma Chemical Vapor Deposition Reactor (ICP CVD) (Figure 1 (b-c)) could lead to a break through understanding of the methods needed to bring graphene to scale.



a b c

Figure 1 Graphene Structure (a), ICP CVD Reaction (b) and Plasma (c) Chamber

Chemical Vapor Deposition (CVD)

A commonly used method to grow graphene is through CVD, a process through which a gaseous precursor mixture is decomposed by an activation energy and deposited on a substrate. Thermal CVD, using heat as its activation energy, is capable of producing extremely high quality graphene. If similar quality graphene is to be produced through CVD, an alternate source of energy must be supplied to reduce the temperature. To that end, the ICP CVD reactor uses induction to create a plasma and deionize the precursor gas prior to contact with the substrate. With a combination of appropriate growth parameters, growth temperature may eventually be substantially reduced.

Raman Spectroscopy Characterization

Graphene's quality is generally evaluated by three main factors: minimal defects, a single layer and large crystal domains. To characterize graphene's quality, Raman spectroscopy is a quick and reliable method. In Raman spectroscopy, monochromatic light is shone on a substance and the reflected light is evaluated for Raman scattering, or changes in the color of the light. The resulting spectra indicates information about the chemical composition and bond structure of the substance. Figure 2 (a) shows a Raman spectrum of pristine graphene with its three primary peaks, D, G and 2D, labeled. A low ratio of the intensity of the D to G peak (I D:G) indicates low amounts of defects. A ratio of the intensity of 2D to G peak (I 2D:G) approaching or greater than 1.25 and a full width, half maximum of the 2D peak (FWHM 2D) of 30 or less indicate monolayer graphene. Further investigation is needed to make crystal size determinations.

Plasma Characterization

To determine the effects of the applied power on the precursor mixture, hydrogen and acetylene, Ultra Violet/Visible (UV Vis) spectra of the light given off by the plasma was measured and evaluated. Sufficient energy applied to the gas forces electrons to be removed from their previous energy state releasing a photon of the same change in energy. The UV Vis spectra can be used to signal a type of decomposition is occurring in the precursor mixture.

Experimental Procedure

After identifying a semi successful growth parameter set of 600 ˚C, 150 watt plasma power, 5 minute growth time and 15:1 hydrogen to acetylene mixture on a 15/260 nm nickel/copper Si/SiO_2 substrate, UV Vis spectra were taken and of plasma of the same gas mixture for plasma power 100 – 400 watts. Three graphene growths were conducted at 300, 325 and 375 watts. Two more growths were conducted at the 150 watts with compositions of 7.14:1 and 3.57:1 hydrogen to acetylene. UV Vis spectra of their respective plasma was also collected. Raman analysis of all graphene was conducted.

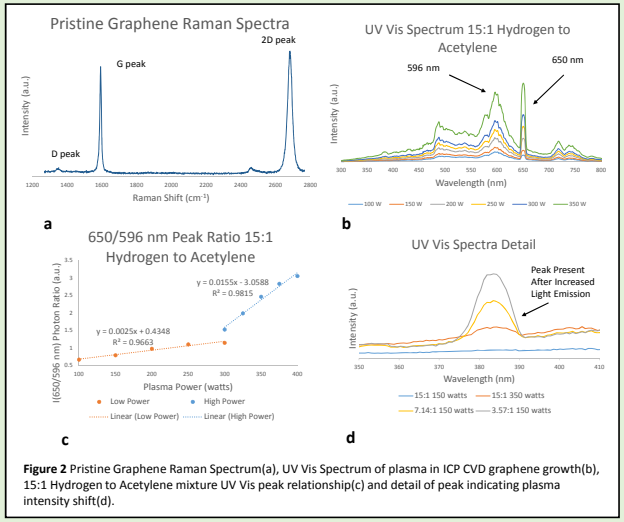


Figure 2 Pristine Graphene Raman Spectrum(a), UV Vis Spectrum of plasma in ICP CVD graphene growth(b), 15:1 Hydrogen to Acetylene mixture UV Vis peak relationship(c) and detail of peak indicating plasma intensity shift(d).

Results

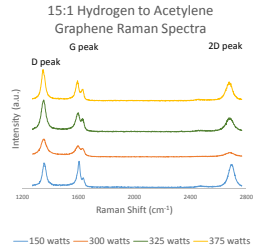
Figure 2 (b) shows spectra collected from 15:1 hydrogen to acetylene at increasing power. While collecting a UV Vis spectra of the plasma, a visible sharp increase in the light intensity was observed. Analysis of the spectra showed the existence of peak at approximately 385 nm consistent with powers after the shift in intensity (Figure 2(d)). Analyzing the spectra showed strong linear relationships between the ratio of the 650 to 596 nm peaks (I(650:596nm)) and the plasma power; however, a drastic difference in rate of change was observed before and after the shift (Figure 2(c)).

Results continued

Figure 3 (a-b) show a chart summarizing the Raman peak ratios and the spectra for the 15:1 hydrogen to acetylene growths at increasing plasma powers. Before the shift, increasing the power leads to an increase of defect density and a decrease in the tendency towards monolayer. After the shift, increasing power leads to a slight decrease in defect density and a slight decrease towards the tendency of monolayer.

Power	Stage	I(D/G)	I(2D/G)	2D FWHM
150	Before Shift	0.94	0.88	58
300	Before Shift	1.65	0.37	76
325	After Shift	1.71	0.72	68
375	After Shift	1.60	0.94	62

a



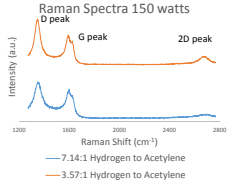
b

Figure 3 15:1 hydrogen to acetylene Raman analysis summary(a) and individual spectra(b).

The plasma light emission given off by reduced hydrogen ratio mixtures at 150 watts visibly similar to after the shift. The presence of the 385 nm peak in the UV Vis spectra confirmed the shift (Figure 2(d)). When the high power equation was applied to I(650:596nm) ratio for the reduced hydrogen mixtures, the comparative powers were 410 and 420 watts respectively. Figure 4 (a-b) show a chart summarizing the graphene Raman peaks and spectra respectively. Taking into consideration the comparative plasmas of the higher hydrogen to acetylene ratio, each growth has a much reduced tendency towards monolayer. Additionally, the 7.14:1 ratio growth has a defect density outside of the expected range.

Mixture	Stage	Plasma Comparison	I(D/G)	I(2D/G)	2D FWHM
7.14:1	After Shift	410	1.28	0.13	160
3.57:1	After Shift	420	1.55	0.27	94

a



b

Figure 4 7.14:1 and 3.57:1 hydrogen to acetylene Raman analysis summary(a) and individual spectra(b).

Conclusions

Changes in plasma reactions driving ICP CVD graphene growth result in changes to the quality of the graphene, both in its defect density and tendency towards monolayer growth. Plasma manipulated through increase of power are subject to gradual changes in the reactions as well as drastic shifts after a threshold is met. Trends in graphene quality, defects and monolayer tendency, were observed to be oppositely correlated after the power threshold was met. It seems likely drastic changes in plasma can have drastic effects on graphene grown with these reactions. However important the role of plasma may be on graphene quality, it alone is not sufficient to fully dictate the quality of graphene it produces. Reduced ratio hydrogen to acetylene mixtures subjected to 150 watts of power generated similar plasma to over 400 watts of the higher hydrogen to acetylene ratio. The reduced ratio mixtures produced graphene with differences in the defect density and tendency towards monolayer. Additionally, the Raman peak ratios do not fit the expected trends when compared to the high power, high hydrogen to acetylene ratio growths. It is likely that in addition to the affect plasma plays on the growth, the ratio of gases also plays a role. If graphene growth temperature reduction is to occur due to plasma generation, a more detailed understanding of the mechanisms it drives must be achieved.

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