Fundamental Studies of the Synthesis of Graphene Using Plasma Enhanced Chemical Vapor Deposition Processes

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Abstract and Introduction:

Graphene, the two-dimensional form of carbon, has a linear electronic dispersion with high electronic mobility. Much research has utilized graphene in high performance devices to realize practical applications [1]. However, these innovative devices require large, uniform and high crystallinity graphene sheets. In plasma enhanced chemical vapor deposition (PECVD), the decomposition process of hydrocarbon atoms is facilitated by the plasma as opposed to by thermal decomposition, allowing for low temperature synthesis [2]. This is the reason that PECVD growth is well suited for the mass production of graphene wafers.

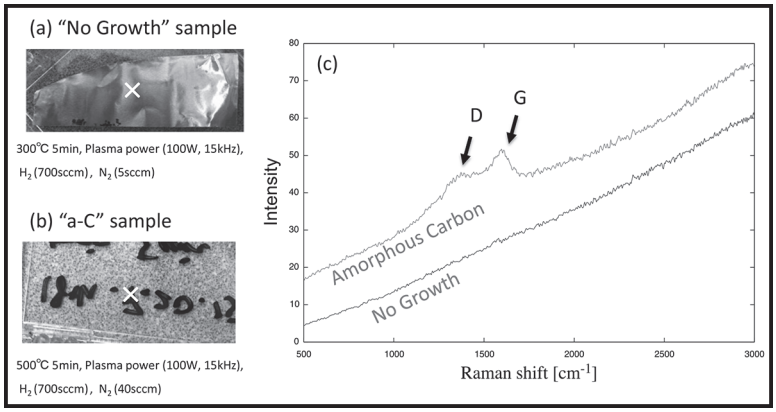

Figure 1: (a) and (b) Optical images after the PECVD growth, and (c) Raman spectra taken from grown samples.

Low crystallinity of graphene grown using PECVD is a barrier to realize practical applications [1]. D. A. Boydm, et al., improved PECVD graphene synthesis by using a mixed gas of nitrogen and methane in hydrogen plasma [3]. They claimed high quality graphene synthesis was achieved with copper etching by CN^- radicals. In addition, the bottom side of copper foils was used to grow graphene to inhibit the direct plasma exposure. High quality graphene synthesis was achieved at low temperature. The nitrogen has an impact pre growth, but the role during growth is not understood. In this study, we investigated the synthesis of graphene using PECVD with nitrogen to realize reproducible synthesis of high quality graphene wafers.

Experimental Procedure:

Growth occurred on the bottom side of copper foils elevated by small silicon wafer pieces in a Black Magic (Aixtron) PECVD furnace. The copper was cleaned before synthesis for 10 minutes under a 700 sccm hydrogen and 100 sccm nitrogen flow at 300°C in a 40W DC plasma. After cleaning, a mixture gas of nitrogen and methane in hydrogen plasma was used for growth with a total pressure of 23 mbar. Growth temperature ranged from 300°C to 700°C and flow rates of methane and nitrogen were controlled in the range of 5 to 40 sccm. Samples were analyzed with Raman spectroscopy (Thermo Nicolet Alemga XR dispersive Raman utilizing 488 nm laser wavelength).

Results:

The optical images of two samples under different growth conditions are shown in Figure 1(a) and (b). One is an "amorphous carbon (α-C)" sample and the other is a "no growth" sample. Typical Raman spectra are shown in the right side of Figure 1(c). Using these spectra, we evaluated the crystallinity of the deposited carbon on copper foils. At 300°C, no carbon was deposited on the foil, as evidenced by the lack of D (1350 cm^{-1}) and G (1580 cm^{-1}) peaks, whereas at 500°C, α-C was deposited, evidenced by the broad D and G peaks and lack of 2D (2700 cm^{-1}) peak. The cause of the "no growth" condition can be due to either the low adsorption coefficient of carbon species or the existence of carbon etchants.

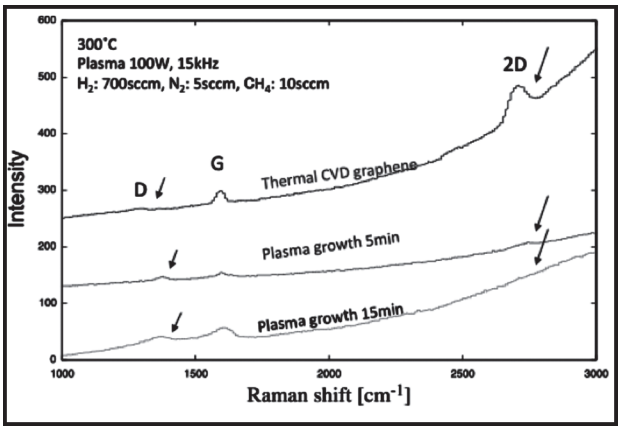

Figure 2: Raman spectra taken from a thermal CVD graphene sample and post plasma growth samples for 5 and 15 minutes.

To verify these possibilities, we put pre-grown thermal CVD graphene samples into the "no growth" condition. The graphene surface was face down and placed on wafer pieces for elevation. Figure 2 shows Raman spectra taken from a thermal CVD graphene sample showing a clear 2D peak and a small D peak. From the Raman spectrum, this graphene is found to have good crystallinity.

This sample was separated into two pieces, and each of them processed in the "no growth" condition for 5 and 15 minutes respectively. As a result, it was found that graphene was etched under these growth conditions, which explain the disappearance of the 2D mode and the appearance of the D peak.

The possible etchants are reactive hydrogen or CN- radicals. In these experiments, the copper foils were etched and deposited on the chamber walls of the PECVD furnace. The primarily etchant of copper species in the plasma condition are the CN^- radicals. The CN^- radicals are generated by a reaction between reactive C and reactive N, reducing the available carbon species for graphene synthesis. Thus, the balance of methane to nitrogen is an important factor to determine the carbon deposition regime. Additionally, hydrogen is known to etch carbon, which also contributes to the carbon deposition regime [4]. In this research, we did not successfully synthesize graphene, but we hypothesize that a transition regime (shown in Figure 3) exists in which graphene growth is possible at low temperatures.

Conclusions and Future Works:

In this research, we attempted to grow graphene on copper foils using the PECVD method with a mixture of nitrogen and methane in hydrogen plasma. We found two regimes: the "carbon etching" regime and the "α-C deposition" regime. These conditions were achieved by varying the ratio of methane flow to nitrogen flow. While no graphene growth was observed, future work will investigate the hypothesized transition region.

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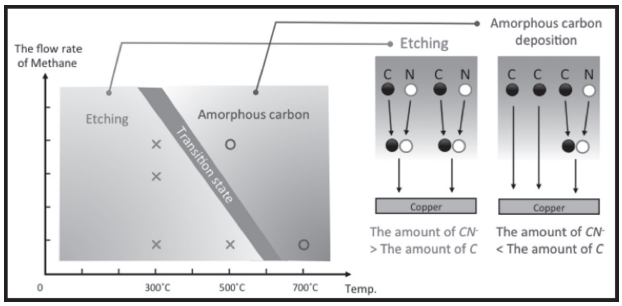

Figure 3: The plot of growth condition and the characteristics of deposited carbon.