Chemical Vapor Deposition of Graphene on Copper at Reduced Temperatures

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ABSTRACT

A preliminary study on reduced temperature chemical vapor deposition of graphene on copper substrates was performed. Graphene's exceptional mechanical strength, very high electrical and thermal conductivity, and stability at atomic layer thicknesses, generates potential for a broad range of applications, from nanodevices to transparent conductor to chemical sensor. Of the techniques demonstrated for graphene formation, chemical vapor deposition is the sole process suitable for manufacturing large area films. While large area film deposition of graphene has been shown on metal substrates, this process has been limited to high temperatures, 900-1000C, which increases the cost of production and limits methods of integrating the graphene with other material structures. In this work, CVD of graphene on copper foil was performed over a range of temperatures (650 - 950C) on substrates as large as 5 x 15 cm in a horizontal tube reactor. Depositions were performed using both CVD and Plasma-Enhanced CVD (PECVD), and the results are compared for both techniques. Quality of graphene films deposited with and without plasma enhancement was characterized by micro Raman spectroscopy.

Keywords: Graphene, Chemical vapor deposition, low temperature growth

1. INTRODUCTION

Graphene's unique electronic and thermal properties make it a candidate for use in a large array of potential applications including optics, electronics, sensors and solar energy. The high carrier mobility and ambipolar nature make it a strong candidate for high speed transistors,[1] while low optical absorption allows its use as a transparent electrode.[2,3] Its high sensitivity to absorbed molecules also creates strong sensing capabilities.[4]

Recently, there has been intense research activity to investigate and develop graphene based nanoscale devices. A critical need exists for robust and reliable production tools, for high quality graphene film growth. Mechanical exfoliation of graphite has been the traditional method of preparing graphene for characterization or further device processing. This process is not scalable, resulting in small flakes of graphene with somewhat random distribution on the desired substrate. Sublimation growth using SiC substrates has proven to be an effective method for production of larger area, thin graphene layers. In this process, Si is sublimated from the surface of the SiC material at high temperatures, leaving behind free carbon atoms. These C atoms then form graphene on the SiC surface. The method produces excellent results for sensing applications, due to SiC's intrinsically large resistance and the high quality layers of graphene produced but also requires very high temperatures. Such sensors have been demonstrated to effectively detect NOx selectively from other automobile exhaust gases.[4] The method however does not allow for transfer to other substrates, eliminating the potential for integration with traditional CMOS electronics and processing. The process temperatures and SiC substrate also prohibit direct growth of graphene onto Si or other more practical substrates. Integrated devices need wafer scale deposition with processes compatible with CMOS techniques while maintaining high quality and uniform thin films with controllable thicknesses.[5]

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Figure 1. Graphene growth system, showing plasma at right and RF power supply below.

2. CVD DEPOSITION OF GRAPHENE

Catalytic chemical vapor deposition (CVD) of graphene promises to produce material with a broad range of possible applications. This method has been demonstrated on a wide range of transition metals,[6,7] as well as on insulating substrates such as Al_2O_3 and quartz. The process is highly scalable and compatible with existing semiconductor processing methods used in industry. The process has already produced large-scale sheets of graphene useable as transparent electrodes.[3] Ni and Cu have been the predominant transition metal materials used for catalyzed growth of graphene sheets. For growth on Ni, C is dissolved in the material at high temperatures and precipitates out during cool down. This method can produce mulit-layer sheets of graphene depending on the time spent at high temperature in the presence of carbon. In copper, the solubility of C is significantly reduced, in this case graphene forms predominantly due to surface reactions, providing a limit to the graphene thickness as a result.[5,7] Copper substrate are shown to produce high quality single layer graphene sheets with only a small percentage of area having multiple layers and the layers are continuous across the surface of the copper substrate. Growth on copper is typically done by decomposing CH_4 over Cu at 1000 C.

After deposition, graphene can be transferred to other substrates using an additional layer to support the graphene and subsequently removing the underlying copper substrate through wet etching. CVD of graphene on Cu has prodcued high mobilities and optical transparency along with large area growth.[5] High-quality, single-layer uniform graphene sheets have also been grown on polycrystalline copper foils and evaporated Cu layers. The low cost of copper and ease of etching make it an attractive substrate for graphene growth.[5] Pretreatment of copper foils has been found to be important in obtaining large graphene domains. The substrates must be free of debris and contaminants on the surface and prior to deposition, films are annealed in H_2 to remove CuO.

There is a strong desire to enable the production of graphene sheets at lower temperatures. Lowering the temperature decreases production costs by lowering the thermal budget of process runs and requiring less expensive equipment. Additionally, the demonstrated of growth on thermally deposited Cu films could potentially open the door to direct growth on existing Si chips or the pre-patterned growth. The copper films can be removed following graphene deposition using wet etching techniques, leaving the patterned graphene behind on the desired substrate. A decrease in growth temperature however must not sacrifice quality of the film.

2.1 Growth System Design

The graphene discussed here was grown a system designed and built by Structured Materials Inc. Growth takes place in a three inch diameter, three-zone horizontal quartz tube reactor. CH_4 is used as the C source and H_2 as the reducing gas. For the work presented, growth is carried out at low pressure (less than 1 Torr) though atmospheric pressure growth has been achieved in the system using Ar as a carrier gas. For PECVD growth, a plasma source is located upstream from the substrate and excites both CH_4 and H_2 at the inlet of the quartz tube. The upstream location excites the gases away from the substrate and no plasma is present where growth

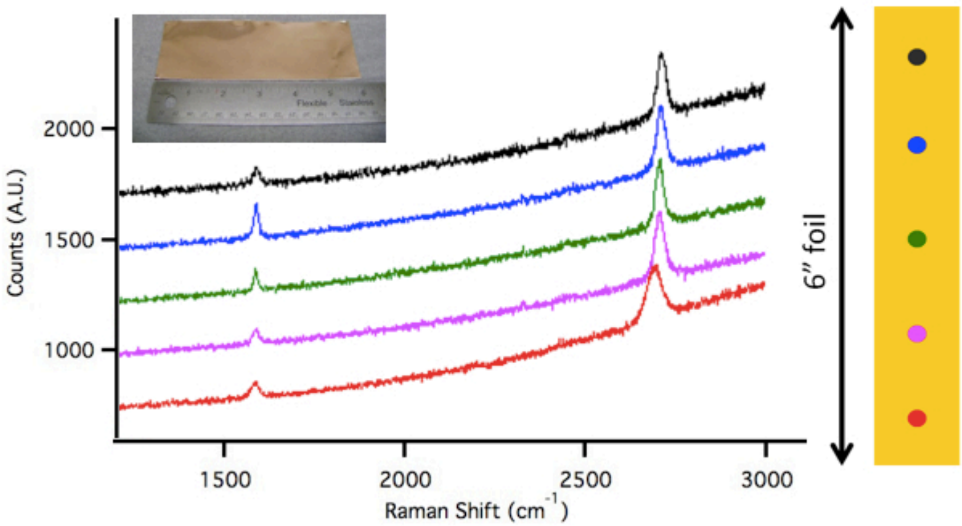

Figure 2. Raman spectra measured across graphene grown on a copper foil substrate at 990 C for 20 minutes.The left indicates the position along the foil strip for each measurement. The inset shows a photo of the copper foil after growth

takes place. The plasma is excited using a copper coil located around the quartz tube at the inlet. For the work presented here the plasma is excited at 450 kHz. Substrates used are 0.05 mm thick and 150 mm wide annealed copper foil (Goodfellow Cambridge Ltd OFHC 99.95%) cut into 6" long pieces. Fig. 1 shows the physical system, including an image of a plasma generated at the gas inlet, upstream of growth.

In this paper we describe results of growth runs obtained in the described system including initial results from plasma enhanced growth, down to 650 C. The Cu foil is cleaned in acetone and isopropyl alcohol before being loaded into the growth chamber. Prior to the introduction of CH_4, any CuO that has formed on the surface is removed by annealing at elevated temperature under H_2 flow. Graphene is subsequently grown by introducing CH_4 at the desired growth temperature and maintaing the flow for between 5 and 20 minutes. The samples are cooled under H_2 flow before removal.

3. GROWTH RESULTS

In this work we present preliminary results from tests using plasma enhancement techniques to reduce the growth temperature of graphene on Cu while maintaining higher quality films and uniformity. To evaluate the film quality, micro Raman spectra were measured at several locations on each growth sample. Additionally, we have started to explore the effects of plasma enhancement on standard growth recipes and found indications that an upstream plasma may improve uniformity of large area growth.

Our system has produced high quality growth on copper under typical growth conditions. Fig. 2 shows a set of Raman spectra of graphene grown at 990 C with a ratio of H_2/CH_4 of 2.6 (49 and 19 sccm respectively). The samples are cleaned, placed in the quartz furnace and ramped up to an annealing temperature of 950 C under 25 sccm of H_2 at a pressure below 1 Torr. The spectra show no D peak (1350 cm^{-1}), indicative of high quality films. A strong 2D peak (2700 cm^{-1}) is present with a 2D/G peak ratio of 4 and a full-width-half-maximum (FWHM) of the 2D peak of about 35 cm^{-1}, characteristic of single layer, high quality graphene. The films also demonstrate a reasonably high level of uniformity across the copper foil, as seen in Fig. 2, with only small variations in measured spectra at all positions across the sample. The system has also demonstrated high quality growth at atmospheric conditions, using Ar as the carrier gas.

To investigate the effects of plasma enhancement, identical growths were completed with and without plasma enhancement during the growth. Both the H_2 and the CH_4 are excited as they enter the quartz tube, as shown

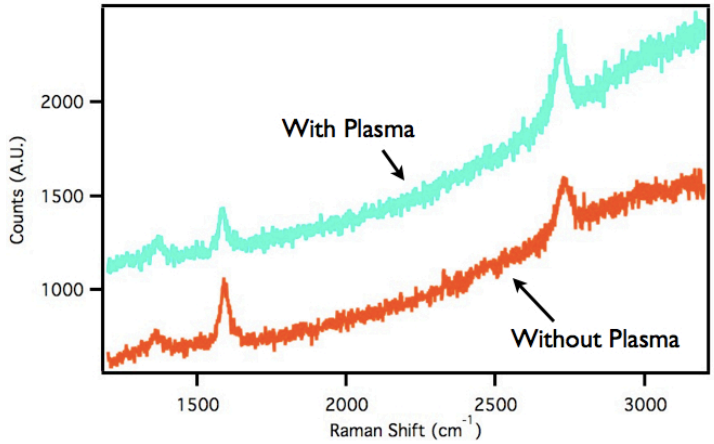

Figure 3. Raman spectra of sample grown with and without plasma enhancement

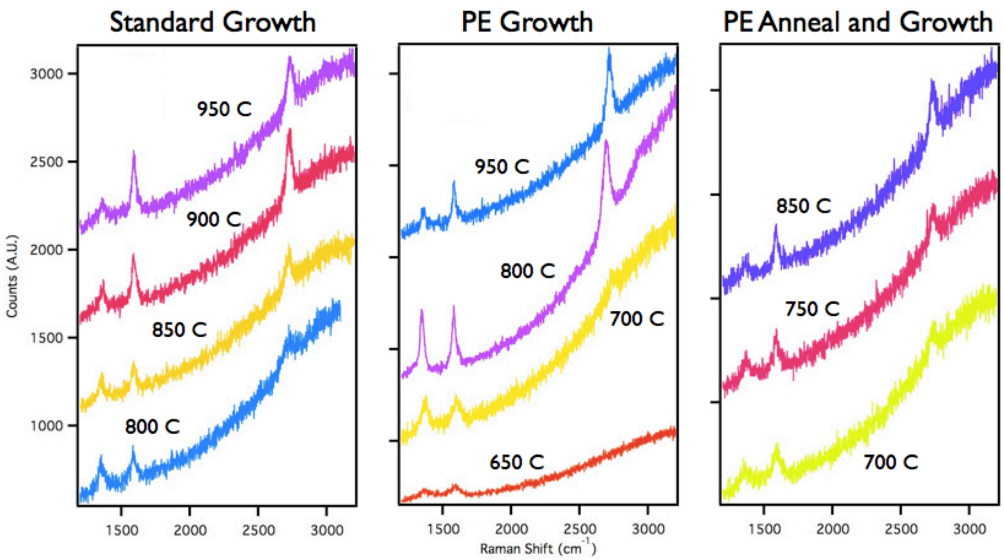

Figure 4. Representative Raman spectra from samples grown at varying temperatures and using three separate techniques. Standard growth is done at the stated temperature and a H_2/NH_4 flow ratio of 1, PE growth is under identical conditions with the introduction of plasma enhancement during the growth stage, PE anneal and growth adds plasma enhancement to the annealing stage as well as the growth stage.

in Fig. 1. Molecules that remain excited upon reaching the Cu foil should require less energy to undergo the decomposition needed to leave C on the surface and thus form graphene. Fig. 3 shows two Raman spectra grown at 950 C with a H_2/CH_4 flow ratio of 1. The upper spectra is from a sample grown with plasma enhancement while the lower is measured from graphene grown without using plasma enhancement. Both samples show an average 2D/D ratio near 4 and FWHM values of the 2D peak near 65 cm^{-1}. The plasma enhanced sample has a somewhat larger 2D/G ratio of 2 compared to 1 for the non-enhanced sample. The initial results based on the spectra shown as well as results from several other growth runs, indicate that introduction of plasma enhancement techniques may improve growth under typical growth conditions, with a limited number of preliminary runs indicating some improvement. An average of all results at higher temperature only indicate a small improvement, within error in most cases. A more thorough evaluation is needed to optimize and evaluate the technique more rigorously.

To investigate the effects of plasma enhancement on lower temperature deposition, several growth runs were

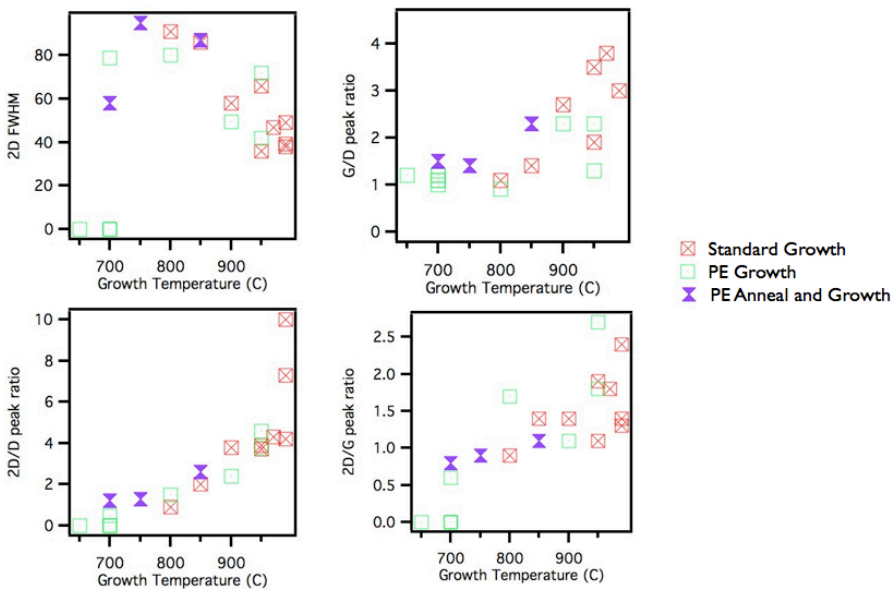

Figure 5. Plots 2D FWHM, G/D peak ratio, 2D/D peak ratio and 2D/G peak ratio as a function of growth temperature for the three methods discussed.

completed at varying temperatures. Three types of recipes were explored, the first using no plasma enhancement, the second using plasma enhancement during the growth cycle only and the final using plasma during both the annealing stage and growth stage. No plasma was used during cooling. For growth where plasma is used in both the annealing and growth stages, the annealing temperature is held at the growth temperature instead of 950 C which is used in the other two methods. Fig. 4 shows Raman spectra from each growth type at differing temperatures. For each type, the quality of the resulting films decreases with decreasing growth temperature. The standard growth recipe did not produce results below 800 C, the plasma enhanced methods however showed evidence of a 2D peak down to 700 C. These initial results do provide some indication of potential improvements in growth at lower temperatures when using plasma enhancement. Comparing the standard and plasma enhanced growth at 800 C, the plasma enhanced spectra shows a decided larger 2D/G ratio and 2D/D ratio, indicating higher quality film. Furthermore, comparing plasma enhanced growths at 700 C, show that the introduction of the plasma during annealing appears to further increase film quality. At the lowest temperature of 650 C, no graphene is present in any growth method tested. No additional measurements were performed to inspect uniformity of the films, so the differences in the Raman spectra may also be attributed to other factors and further investigation is needed to fully understand the plasma effects.

Fig. 5 provides plots of several figures of merit for the Raman spectra vs growth temperature for all three growth types at varying temperatures. For evaluation of peak ratios and FWHM, each spectra was fitted to a Lorentzian for each peak along with a LogCubic baseline. In spectra with lower signals, significant errors were introduced due to the presence of noise in the measurement. The 2D peak was fitted to a single Lorentzian in each case. We see an obvious degradation of film quality as the growth temperature is decreased. The 2D/D ratios decrease as expected with decreasing temperatures. The samples with plasma enhancement in both the anneal and growth stages do show a slightly increased ratio at 750 and 700 C, as is also the case with the G/D peak ratios. The improved quality at 800 C in the plasma enhanced sample is also evident, showing larger ratio values as well as a lower FWHM. The limited number of runs and measurement noise prevent a strong conclusion on the effects of plasma enhancement techniques but the data does provide some indication that with further refinement this method may be used to produce graphene at reduced temperatures.

A more surprising result that emerged from the analyzed Raman spectra was the possibility that the plasma enhancement improved uniformity of the samples. For each sample, Raman spectra is measured at several points along the copper foil. In many cases under standard growth conditions, a spectra taken at a far end of the sample

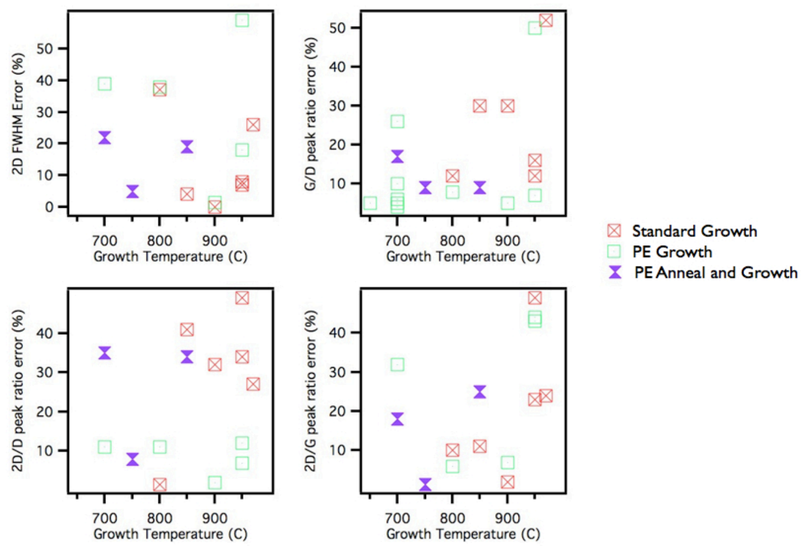

Figure 6. Plots of the errors in 2D FWHM, G/D peak ratio, 2D/D peak ratio and 2D/G peak ratio as a function of growth temperature for the three methods discussed. Error is calculated as the percentage difference between the maximum and minimum value for each value.

may provide a significantly different result from one taken at the center for the sample. From the limited data available it was observed that the introduction of plasma enhancement appeared to increase uniformity across the sample. Fig. 6 shows the percentage difference between the maximum vs minimum value measured for each parameter as a function of temperature on a given sample. In particular in measurements of the G/D and 2D/D peak ratios, the plasma enhanced samples had an increased uniformity across the entire sample. Again, the small number of samples grown prevent a strong correlation from being identified but the slight indication makes it an important result to be further explored in future growths.

4. SUMMARY AND CONCLUSION

We have presented some preliminary results in work using plasma enhancement techniques to improve graphene film growth on copper at reduced temperatures. Within the limited number of runs and measurements, there are some indications of improvements at lower temperature, as can be seen in the Raman spectra presented at 800 C and 700 C. The plasma provided small improvements in several figures of merit, including the 2D/D peak ratio. There is some indication that the plasma increases uniformity across the large copper foils, however this is based on limited Raman data at selected points. A more thorough analysis of the surface using mapping techniques or imaging may allow a better assessment of the possible improvements. Future work will require the incorporation of additional film quality metrics, including imaging to evaluate the uniformity of the films as grown. Further exploration into the plasma effects should also entail positioning the plasma source closer to the substrate and varying the frequency of excitation to investigate possible effects and improvements in film quality. The results presented provide an initial basis for an in-depth exploration of plasma enhancement techniques for reduced temperature growth in large scale graphene production systems.

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