Optimization of the Growth of Graphene on Cu Foil Substrates by Chemical Vapor Deposition

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Introduction

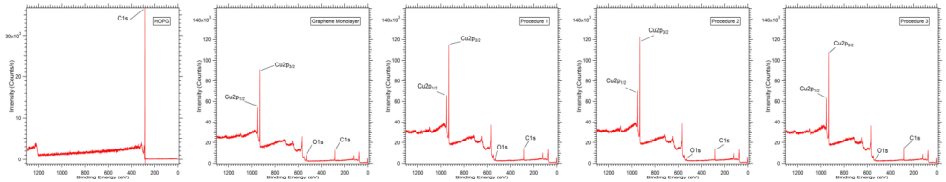
The most common method for producing large area graphene films is by performing chemical vapor deposition (CVD) on Cu foil substrates [1]. The reason for using Cu as a substrate is that it has a very low solubility for C at the temperature that the CVD is performed, which ensures a self-limited growth of a single monolayer of graphene. The goal of this research project is to determine the optimal procedure for producing graphene films with a low defect density on Cu foil substrates. The graphene films were grown on 99.8% pure Cu foils 0.001" thick, 0.25" wide, and 6" long. The Cu films were heated by passing a current through the film, and the temperature was monitored using a disappearing filament optical pyrometer. The precursor used was ethylene (C_2H_4).

Methods

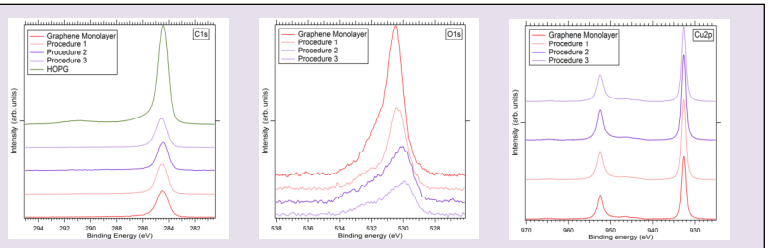
Three methods were used to grow the graphene films. The initial step in each growth process was to anneal the Cu foil in 1 x 10^{-5} Torr of H_2 at 800 °C for 30 min to remove the native oxide. The first growth procedure involved annealing the film in 1 x 10^{-6} Torr of O_2 at 500 °C for 10 min after the initial H_2 anneal to remove residual carbon from the surface of the Cu foil, followed by annealing in 1 x 10^{-5} Torr of H_2 at 800 °C for 10 min to remove chemisorbed oxygen from the surface from the previous anneal in O_2. The growth of the graphene film was then performed by introducing 5 mTorr of H_2, 5 mTorr of C_2H_4, and 5 Torr of Ar and annealing at 850 °C for 30 min. The second growth procedure also used the oxygen treatment to remove residual carbon but did not use H_2 during the graphene growth process. The third growth procedure did not use the oxygen anneal to remove residual carbon and used H_2, C_2H_4, and Ar during the graphene growth. The reason for not doing the O_2 anneal was to determine how residual carbon might affect the subsequent graphene growth.

XPS Results

Overview Spectra



Elemental Peaks

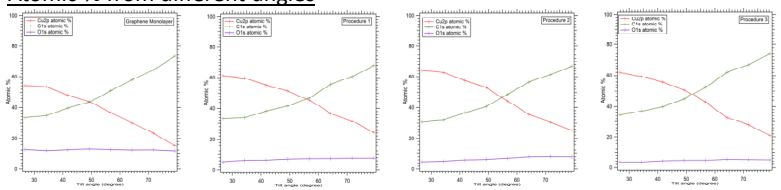


Sample	Peak BE	Intensity (Counts/s)	Atomic %
Graphene Monolayer	284.49	16492.99	13.48
Procedure 1	284.53	17171.65	14.03
Procedure 2	284.46	16210.49	13.25
Procedure 3	284.58	16434.67	13.43
HOPG	284.43	56061.22	45.81

Sample	Peak BE	Intensity (Counts/s)	Atomic %
Graphene Monolayer	530.53	10599.08	41.72
Procedure 1	530.37	5939.38	23.38
Procedure 2	530.15	5522.5	21.74
Procedure 3	530.07	3342.03	13.16

Sample	Peak BE	Intensity (Counts/s)	Atomic %
Graphene Monolayer	932.65	205449.56	20.44
Procedure 1	932.68	271425.23	27.01
Procedure 2	932.66	283547.9	28.22
Procedure 3	932.67	244482.01	24.33

Atomic % from different angles

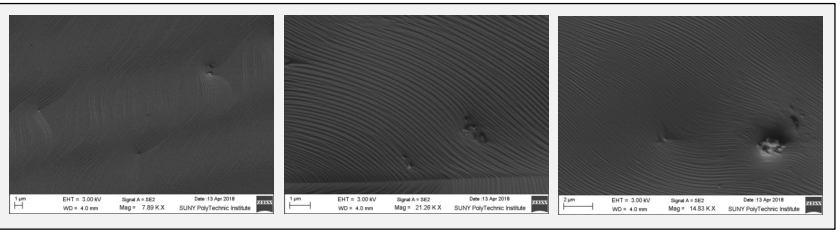


Analysis

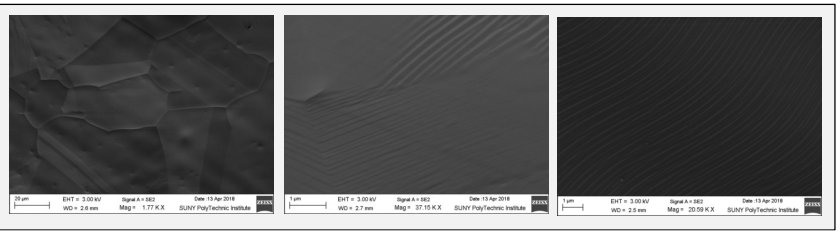
The films were characterized using angle-resolved X-ray photoelectron spectroscopy (AR-XPS). A previous study by P. Tyagi et al. has shown that AR-XPS can be used to determine graphene coverage[2]. In addition, scanning electron microscopy (SEM) was used to determine the topography of the graphene films grown on the Cu substrate.

SEM Results

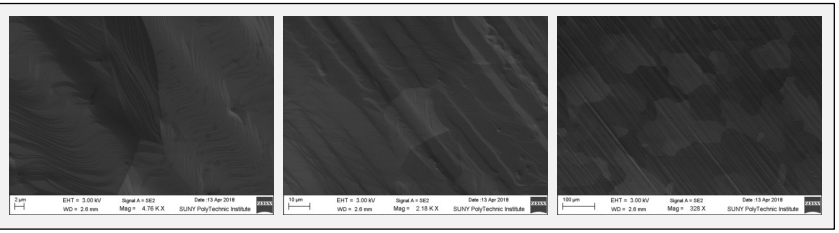
Procedure 1
- H_2 anneal in $1 * 10^{-5}$ $Torr$ at 800^oC for 30 minutes
- O_2 anneal in $1 * 10^{-6}$ $Torr$ at 500^oC for 10 minutes
- H_2 anneal in $1 * 10^{-5}$ $Torr$ at 800^oC for 10 minutes
- Growth: 5 $mTorr$ H_2, 5 $mTorr$ C_2H_4, 5 $Torr$ Ar. Annealed at 850^oC for 30 minutes



Procedure 2
- H_2 anneal in $1 * 10^{-5}$ $Torr$ at 800^oC for 30 minutes
- O_2 anneal in $1 * 10^{-6}$ $Torr$ at 500^oC for 10 minutes
- H_2 anneal in $1 * 10^{-5}$ $Torr$ at 800^oC for 10 minutes
- Growth: 5 $mTorr$ C_2H_4, 5 $Torr$ Ar. Annealed at 850^oC for 30 minutes



Procedure 3
- H_2 anneal in $1 * 10^{-5}$ $Torr$ at 800^oC for 30 minutes
- Growth: 5 $mTorr$ H_2, 5 $mTorr$ C_2H_4, 5 $Torr$ Ar. Annealed at 850^oC for 30 minutes



Future work

Future studies might include measuring the growth kinetics of graphene by varying the C_2H_4 partial pressure and measuring the effect of the purity of the Cu foil on the nucleation of the graphene.

Growth kinetics of graphene could be measured and compared on other metal substrates.

Conclusion

All three methods produced a single monolayer of graphene. For the high vacuum system used in this experiment, the introduction of H_2 during the growth did not affect the graphene growth process. This indicates that the vacuum conditions were sufficient to prevent incidental oxidation of the Cu foil during growth.

Growing graphene without the oxygen pre-treatment resulted in a rough surface topography. This indicates that residual carbon adversely affects the graphene growth process.

References

[1] D. Dikin, S. Stankovich, E. Zimney, R. Piner, G. Dommett, G. Evmenenko, S.B. Nguyen, and R. Rodney, Nature **447**, (26AD).

[2] P. Tyagi, Z.R. Robinson, A. Munson, C.W. Magnuson, S. Chen, J.D. Mcneilan, R.L. Moore, R.D. Piner, R.S. Ruoff, and C.A. Ventrice, Surface Science **634**, 16 (2015).