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Synthesis of graphene by liquid precursors at lower temperatures

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Abstract

Benzene, toluene, and xylene can be liquid precursors for graphene and carbon nanotube synthesis. However, the growth mechanisms can have greater variances for different carbon allotropes. In the case of graphene, Cu can be the catalyst for dehydrogenation and provides a weakly-coupled substrate for 2-dimensional graphene nucleation and growth. In the case of carbon nanotubes, Fe nanoparticles are essential to catalyze the C-C bonds breaking and dissolve carbon before the precipitation of a graphene cap over the catalyst particle where a tube forms. Controlling the precursor feed rate is crucial for a successful synthesis. In this research, we developed a low-pressure CVD system and a bubbler to control the feed rate of liquid precursors. The goal is to correlate the precursor molecules' feed rate with the nucleation of graphene flakes to achieve a uniform layer of graphene at millimeter scale. Successful low temperature synthesis of graphene will open up enormous opportunities on device applications.

Introduction

Graphene, one extremely useful form of carbon allotropes, is a 2-dimensional monolayer form of carbon arranged in a honeycomb lattice. The unique electronic, chemical, and optical properties of a single layer carbon atoms have led to a great deal of research since the seminal publication in 2004.[1] The typical carbon feedstock for graphene synthesis by chemical vapor deposition (CVD) is methane. However, the stability of methane requires a very high temperature (above 1000 °C) to decompose to synthesize graphene (and carbon nanotubes [2]). Such a high temperature has made the synthesis costly and difficult to integrate graphene into conventional device fabrication processes. Interestingly, it has been reported more recently that liquid aromatic molecules such as toluene and benzene can generate graphene on Cu foils at temperatures between 300 and 600 °C.[3,4] These results should generate enormous interest both in academia to investigate the fundamental mechanisms and industry to scale up production. However, to the best of our knowledge, no follow-up research has appeared in the literature. It is likely that the results are difficult to reproduce because the window for successful synthesis in the parameter space is very narrow. Given the existing equipment and experience in carbon nanotube synthesis by CVD at Dr. Shen's laboratory, the objective of this research was to explore the growth parameter space of nucleation and growth of graphene using toluene and xylene as the precursor on single crystal Cu film by atmospheric pressure CVD (APCVD) and low pressure CVD (LPCVD).

Cu substrates

The atomic structure of Cu(111) surface is a hexagonal lattice with a lattice constant of 2.55 Å while graphene has a honeycomb structure with a lattice constant of 2.46 Å. Therefore, it is reasonable to expect Cu(111) a suitable surface for the epitaxial growth of graphene.[5] It is too costly to use single crystal Cu to synthesize graphene because the substrate will be etched off to transfer the graphene to a Si wafer for device applications. Alternatively, thin films deposition on α -Al₂O₃ (0001) substrate could generate a single-crystal Cu(111) surface, because the α -Al₂O₃ (0001) surface has a hexagonal lattice with a lattice spacing of 2.75 Å. However, thin Cu film could be damaged by Cu evaporation at the high temperature needed for methane in LPCVD. Therefore, Cu foils of 25 μ m in thickness are the common substrate for graphene growth. Perhaps because of the very weak interaction between C and Cu, once graphene starts to nucleate, the underlying crystal orientation may not be critical for a continuous graphene growth.

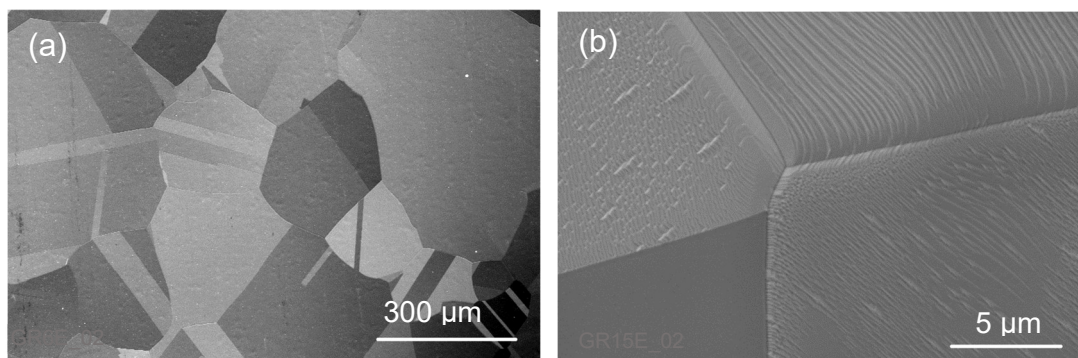


Fig. 1 The morphology of Cu foil (127 μ m thick) after a 950 °C hydrogen anneal for 15 min (a) without and (b) with a HCl dip before the hydrogen anneal.

We have prepared both Cu foil and Cu(111) thin films in this research. The foils were electropolished first to improve the surface smoothness.[3] There is always a layer of oxide on the surface of Cu once it is exposed to air. With oxide on the surface, Cu cannot catalyze precursor molecules to nucleate graphene. The standard procedure to remove oxide is to anneal the sample in hydrogen at high temperatures. Figure 1(a) shows Cu crystal grains in different orientations after annealing in a gas flow of $H_2:Ar=100:300$ sccm at $950^\circ C$ for 15 min. However, an extra 1-min dip in 50% HCl made drastic changes of the surface morphology after hydrogen annealing. With a HCl dip, Fig. 1(b) shows step bunching in each crystal grain. The step bunching indicates that HCl dip really helps to remove oxide which cannot be completely removed by hydrogen anneal alone.

Cu(111) surfaces were prepared by sputtering 500 nm of Cu film on $\alpha-Al_2O_3$ (0001) surfaces at $73-86^\circ C$. Note that even at such a low substrate temperature, sputter coating creates a Cu(111) surface with a twin structure. Without a HCl dip, hydrogen-annealing leads to some step bunching (could be higher than 10 nm at some places) as shown in Fig. 2(a). The two shades in the image is a result of the twin crystal structure. After a HCl dip, H_2/Ar -annealing leads to more and different step bunching and thermal grooves between the two twin regions as shown in Fig. 2(b).

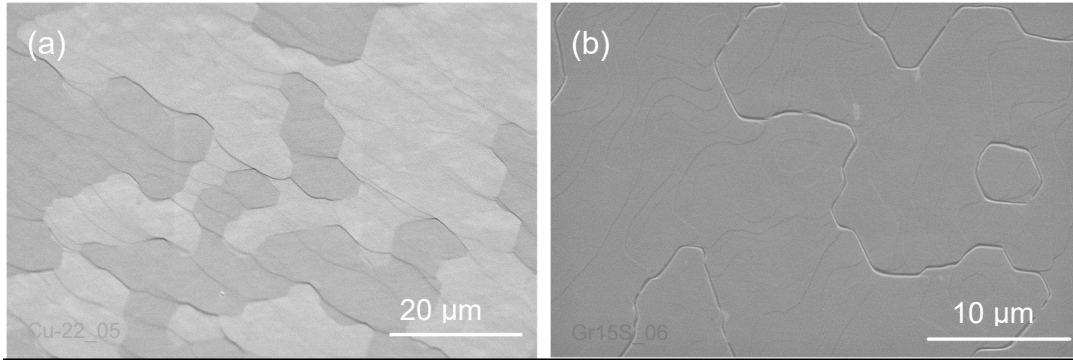


Fig. 2 The morphology of sputtered Cu (111) surfaces (a) without and (b) with a HCl dip followed by $H_2: Ar=100:300$ sccm anneal at $950^\circ C$ for 15 min.

To test the oxide layer effect, Cu-sputtered samples preserved in a vacuum chamber were annealed in H_2/Ar with and without HCl dip. We find that in this case, HCl dip makes no difference, which is plausible because the oxide layer should be very thin from a very short exposure to air. More surprisingly, step bunching follows triangular lattice of the Cu(111) surface as shown in Fig. 3. More work will be needed to understand the cause.

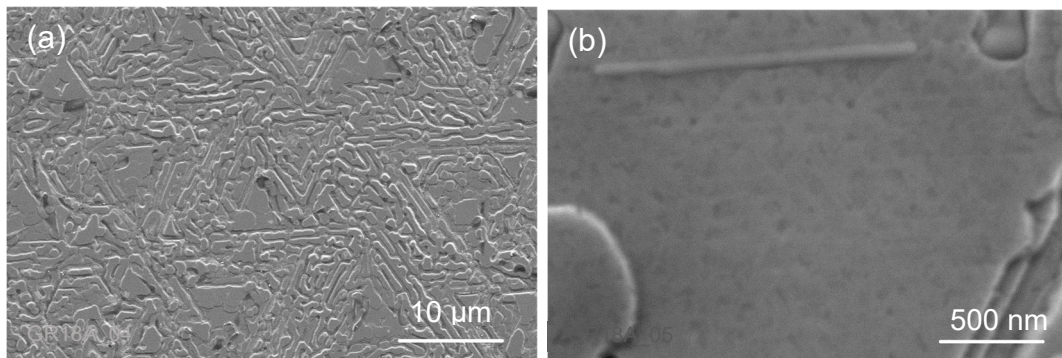


Fig. 3 The morphology of 400-nm sputtered Cu (111) surfaces preserved in vacuum after a $H_2: Ar=100:200$ sccm anneal at $950^\circ C$ for 15 min.

Graphene synthesis by toluene in APCVD

Experimental

Both the 520-nm sputtered Cu film on α -Al₂O₃ (0001) substrates and 127- μ m thick Cu foils were used in the toluene growth experiments. The samples were dipped in 50% HCl for 1 min to remove oxide. After rinsed with DI water and dried in nitrogen, the sample was sent in the CVD reactor immediately for an hydrogen anneal at 950 °C for 15 min in the flow of H₂:Ar=100:200 sccm. When the furnace temperature has lowered to the growth temperature (300-500 °C), toluene was injected into the reactor by a syringe pump at a rate of 0.5 mL/h. The gas mixture was changed to H₂ at 20 sccm. The sample was positioned at the rear end of the tube furnace to give the precursor maximal dwell time to decompose thermally. After growth, a mixture of H₂:Ar=50:200 sccm was used to cool the reactor to room temperature.

Result

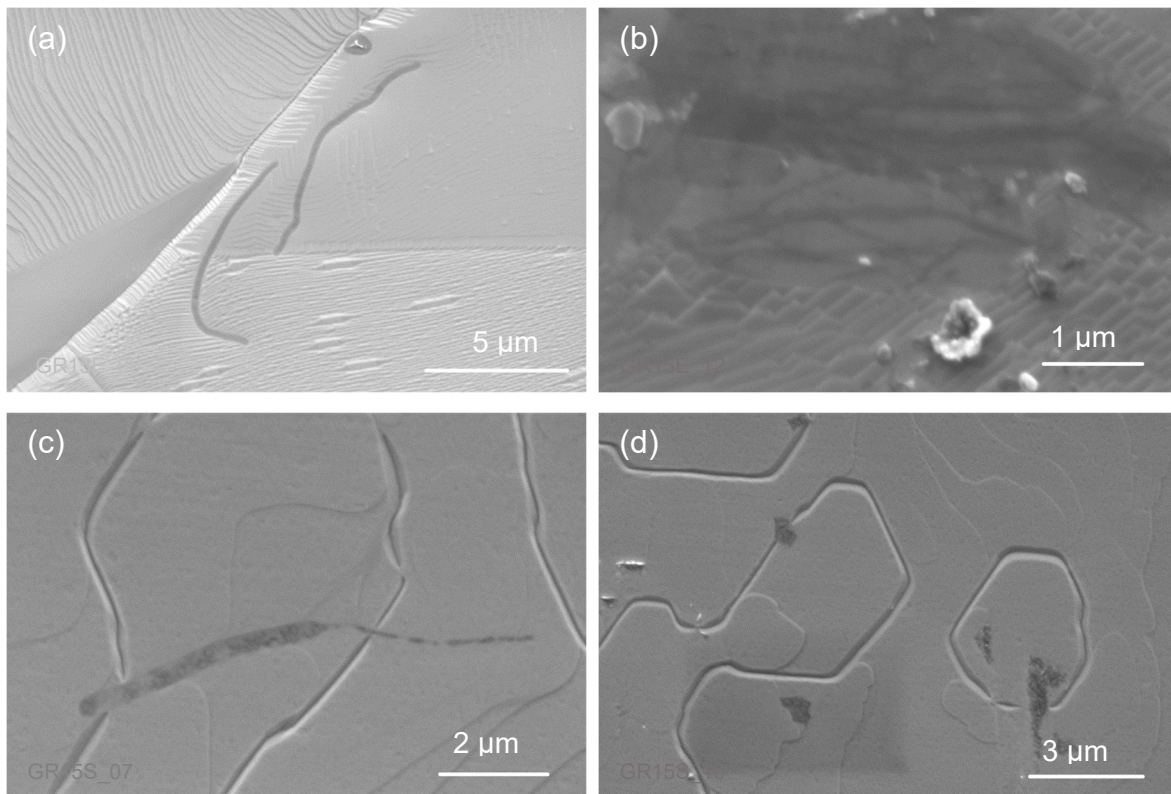


Fig. 4 Carbon ribbons and patches formed on (a)-(b) Cu foil and (c)-(d) sputtered Cu film on sapphire (0001) substrates by toluene at 400 °C in APCVD with a H₂ flow of 20 sccm.

1. Isolated carbon ribbons and patches were found on both Cu foil and Cu film samples after toluene APCVD at 400 °C. (Fig. 4) It is beyond the SEM resolution to determine the thickness of the foil, but from the electron transparency and the folding shown in Fig. 4(b), the thickness must be in nanometers. From the fact that the carbon features interrupt the step bunching, we suspect that these features could be formed during hydrogen annealing and not a result of toluene CVD, because the Cu surface cannot be altered at 400 °C.

2. Large scale carbon features were observed on the sputtered Cu film sample when the furnace temperature was raised to 500 °C. (Fig. 5) It is plausible that the darker shade represents more layers of graphene while the lighter shade represents fewer layers. It is not clear what the darker dots are in Fig. 5(c). EDS analyses indicate a high C-content in the dark regions and much higher C-content in the bright regions of Fig. 5(d). It is not clear if this patch was formed before or during the toluene CVD,

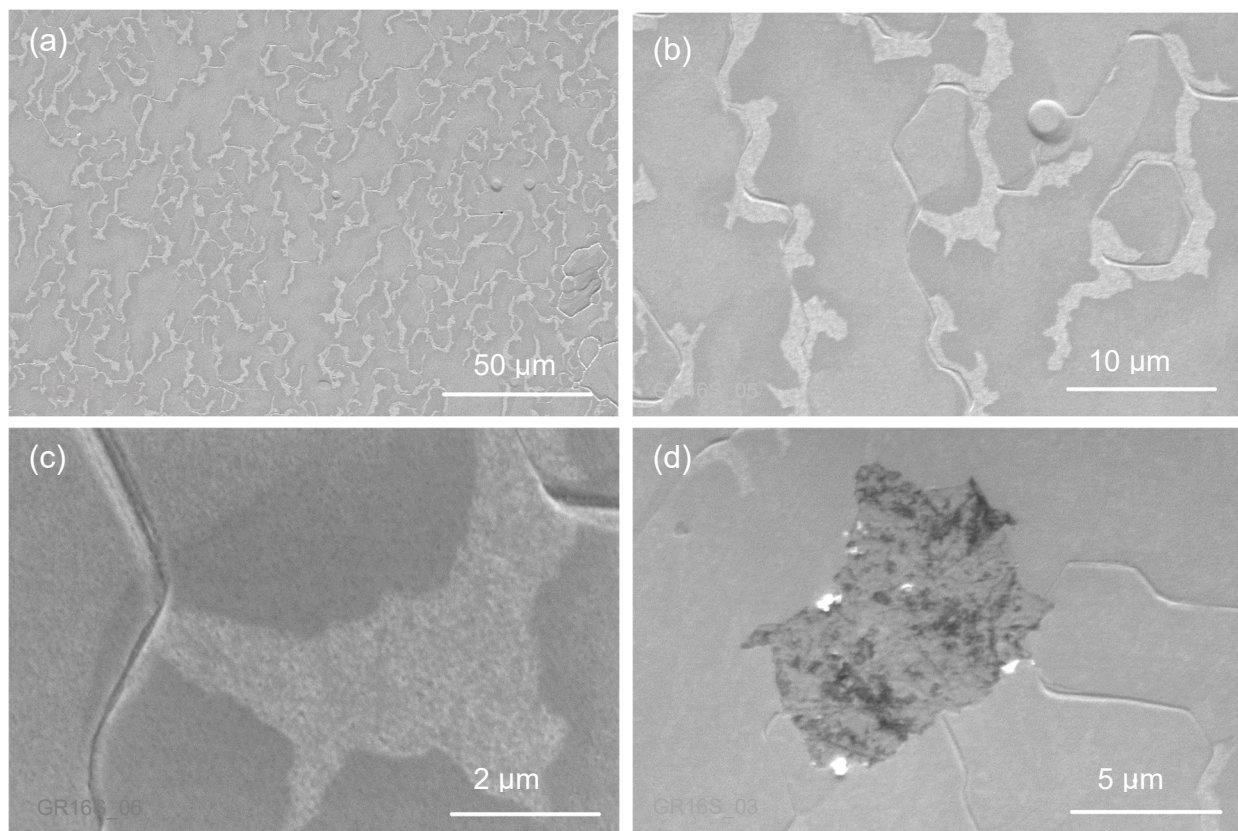


Fig. 5 (a)-(c) Large scale carbon features formed on sputtered Cu film on sapphire (0001) substrate by toluene at 500 °C in APCVD with a H₂ flow of 20 sccm. (d) A patch of carbon of various thickness on the same sample. The bright regions are lumps of carbon.

Develop a LPCVD system

Trace oxygen could be a problem for graphene nucleation on Cu because Cu is so easily oxidized. Therefore, most groups use LPCVD to synthesize graphene or use very high gas flow in APCVD to reduce contamination. To adapt our APCVD system to low pressure operations, we need to control the precursor flow and use proper pumping system to maintain the reactor pressure below 10 Torr. Toward this goal we designed a bubbler as shown in Fig. 6. After filling the liquid precursor into the bubbler, air can be pumped out by a few freeze-and-thaw cycles through valve 2 and the needle valve to pumps. Valve 1 will allow the carrier gas (Ar or H₂) to mix with precursor to the reactor through the needle valve. The flow rate of the carrier gas can be regulated by a mass flow controller. Alternatively, the precursor flow by the pressure difference between the saturation

vapor pressure of the bubbler and the low vacuum of the reactor can be adjusted by the needle valve. The bubbler can be used for any liquid precursor for LPCVD processes and can be connected to another port of the CVD system for APCVD processes.

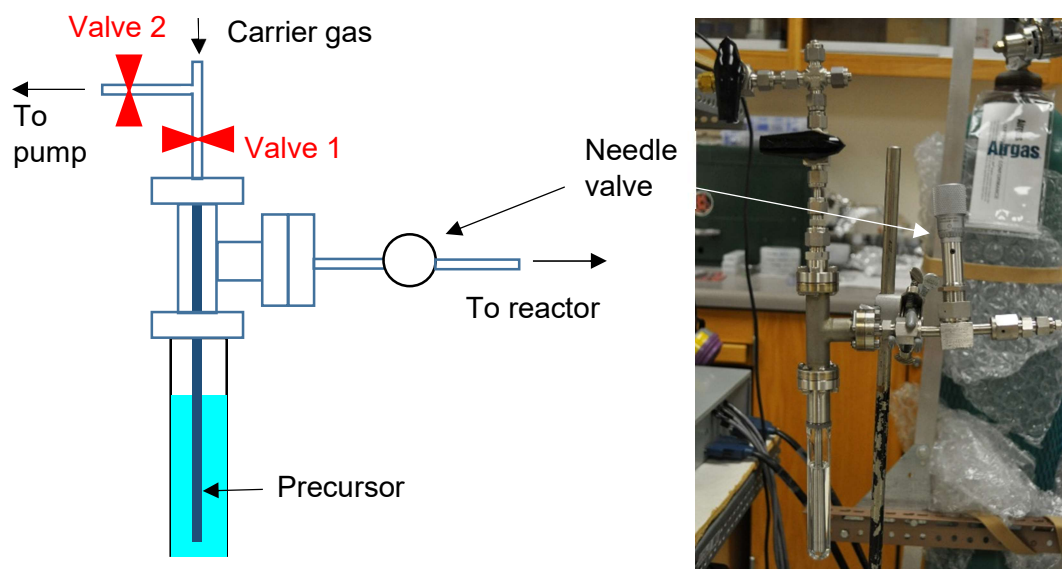


Fig. 6 The schematic and a picture of the bubbler for LPCVD and APCVD processes.

Conclusion

The question of why aromatic liquid precursors can synthesize graphene at low temperatures is still outstanding. We have explored the Cu substrate preparation and APCVD synthesis, but the graphene nucleation rate is still too low. Many more experiments are needed to get a reproducible recipe to synthesize a uniform layer of graphene for device applications.

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