

論文の内容の要旨

論文題目 Growth of high-quality graphene by alcohol CVD method
(アルコールCVD法による高品質グラフェンの合成)

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Graphene is a promising material for many future applications due to its unique properties, such as high carrier mobility and high mechanical strength. Chemical vapor deposition (CVD) method is the popular procedure for graphene synthesis due to its advantages in graphene quality, layer-number control, and large size products. Despite the excellent work done by other groups, there are still many challenges to overcome. Especially, the control of number of layers is insufficient, the defect level of graphene is much higher than that of mechanically exfoliated ones, and the mechanism of growth is not fully understood. Conventionally, almost all the successful graphene growth works employ methane as carbon source, but considering the history of our group on the synthesis of clean and single-walled carbon nanotubes using from ethanol precursor, I believe ethanol may bring some new insight on solving these three challenges and prove to be an even more suitable carbon source for graphene. The ultimate objective of this thesis is, based on the understanding of mechanism, to realize synthesis of wafer-sized, single-crystal graphene from ethanol.

To start with, after learning the principles of alcohol catalytic CVD (ACCVD), and the basic knowledge of Raman spectroscopy in graphene, we conducted our trials on Ni substrates. With optimized CVD conditions, we prove that ethanol as a replacement carbon source is equally capable in the synthesis of high-quality, single-layer graphene, and at some aspects, even with better performance. By Scanning Raman spectroscopy, we find that Single-layer, bi-layer and twisted

bi-layer graphene dominate the sample grown from ethanol, with a total percentage of >70%. The mechanism behind the CVD growth is explored *via* carbon-isotope labeling. With sufficient evidence, we proposed the surface-adsorptive process to explain the growth of graphene from ethanol on Ni substrates.

Next, the CVD growth of graphene on Cu substrates using ethanol as carbon source is discussed. We turned our attention to Cu substrates, as we realized due to the high solubility of C in Ni, the formation of bi-layer and multilayer graphene seems to be unavoidable. With optimized conditions, we were able to synthesize large-scale single-layer homogeneous graphene films on Cu foils. Small Raman D bands at random locations indicate the low defect level. With parametric study, we show that the formation of bi-layer and multi-layer graphene can be restrained by lowering the CVD reaction pressure. To solve the problem of high-temperature etching, we utilized Cu pockets. By Cu pockets and raising growth temperature, graphene with higher quality, i. e., fewer contamination, bigger graphene domain

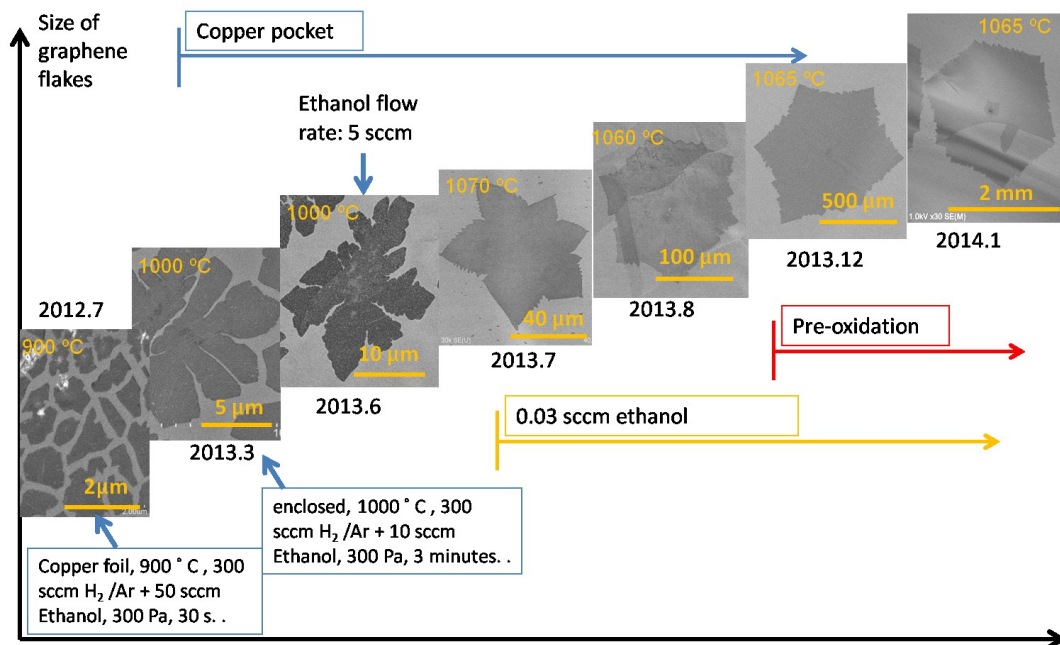


Figure 1, Approaches to graphene large single crystals. The main condition change is CVD reaction and the approximate date of the sample is provided.

size, more dominant single layer, is synthesized. Furthermore, we find the growth can be self-limited, giving us a much bigger window and thus better control of the good quality of single-layer graphene. Based on the observations, we propose the mechanism of a diffusion-limited growth procedure to explain graphene growth on Cu from ethanol.

My main contribution as a doctoral candidate is the synthesis of graphene large single crystals using ethanol as precursor. Here, we propose and investigate several key processes for increasing the size of graphene flakes using ethanol as CVD precursor, including heating without H_2 , extremely small flow rate (0.03 sccm), and pre-oxidation. The effect of each step is shown in Figure 1. The influence of each CVD parameter is carefully investigated, including flow rate and partial pressure of carbon source, reaction temperature, CVD duration, and

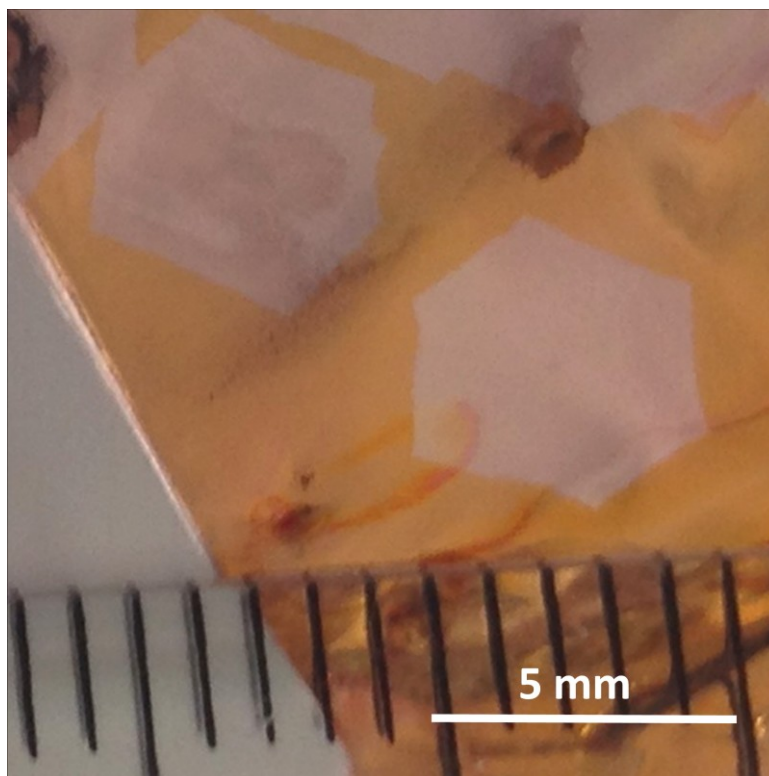


Figure 2.. Photograph of 5mm graphene single crystals on Cu foil. Graphene/Cu foil is heated in air at $180^{\circ}C$ for 5 minutes to oxidize the Cu surface that is not covered by graphene, in order to create contrast.

oxidation level. These systematic studies give us a good insight on how to control the growth behavior, and provide us evidence for demonstrating a growth mechanism that emphasizes the role of oxygen in controlling the nucleation density. Raman maps and selected area electron diffraction (SAED) observation help us to understand the quality and morphology of graphene flakes, and we are proudly proclaim that we grow single-crystal graphene flakes with relatively easy procedure, and the size of our biggest graphene single-crystal sample is 5 mm (Figure 2), which is one of the biggest individual hexagonal-shaped graphene single crystals in the whole world. Besides, the proposed mechanism based on experiment evidences would create an enlightening prospect for the possible realization of wafer-scale single-crystal graphene in the future.