Application Note

Atmosphere™

In Situ Few Layer Graphene Etching Using Iron Nanoparticles

Introduction

Graphene, a two-dimensional material with unique chemical and electrical properties is extensively studied for applications in electronics, optics and catalysis. One area of current research focuses on creating and isolating graphene nanostructures with well-defined shapes along specific crystallographic orientations. Single layer graphene nanoribbons and nanopatterned few layer graphene (FLG) flakes are of particular interest in nanoelectronics and catalysis, because they enable new, useful devices and applications. However, creating these structures requires a well-controlled method of fabrication.

Graphene nanoribbons exhibit markedly different electronic behavior depending on size and exposed edge type. For example, zigzag-edged nanoribbons (Figure 1A) are considered a "half-metal", and act as a metal or insulator depending on the electron spin polarization. This behavior is important for spintronic applications, and useful in devices such as spin valves in computer memory. Armchair-edged nanoribbons (Figure 1B) may either be metallic or semiconducting depending on their width, and are useful in field effect transistors and other semiconductor applications. Pristine zigzag and armchair-edged nanoribbons are crucial for taking full advantage of graphene's unique properties.

Graphene and FLG catalyst activity in gas-phase reactions is highly dependent on the available surface area. However, graphene and FLG tend to restack upon drying due to van der Waals forces, which significantly reduce the specific surface area and surface accessibility. Consequently, these systems are not well-adapted for catalyst applications, particularly for gas-phase reactions. Catalytic nanopatterning of FLG using metal nanoparticles overcomes this limitation by creating nanochannels on the FLG surface with enhanced accessibility. These nanochannels favor the development of new anchorage sites on the FLG surface where metallic and/or oxide active phases can adhere.

Creating nanoribbons out of SLG and FLG with pristine zigzag or armchair edges, or with a highly porous structure, is challenging. Patterning methods using electron beam lithography, or a scanning tunneling microscopy tip, result in ribbons of insufficient quality. Other chemical etching techniques also result in ribbons with imprecise edges. Metal nanoparticles, such as Ni, Fe, Pt, Co and Ag, can etch channels on graphite and graphene surfaces with pristine edges when exposed to oxygen, hydrogen, CO_2 or water vapor at elevated temperatures. To date, this method is the only way to pattern graphene along particular crystallographic directions in order to leave edges consisting of only zigzag or armchair chirality. Recently, researchers demonstrated that varying the reaction temperature, reaction time and nanoparticle size can result in different channel properties, where higher temperatures and/or longer reaction times and smaller nanoparticles can lead to differences in channel length and width. Therefore, the nanoparticle type, size and temperature offer some control over the etch process.

Graphene etching results are usually characterized in the transmission electron microscope (TEM), which offers the resolving power required to view materials at the atomic scale and identify important properties such as crystal orientation. Etching experiments require exposure to a controlled gas and high temperature environment, which is not practical in a typical TEM because it requires high vacuum to operate. Rather, etching is done in a separate reactor, and the results characterized later in the TEM. To better understand the behavior of the etching process, researchers must see the reaction occur in real time. A controlled gas and temperature source must be introduced into the microscope itself, so the reaction and characterization can occur simultaneously.

The Protochips Atmosphere 200 Gas E-cell system combines the reaction chamber and sample analysis tool. Researchers can now expose samples to a highly controlled gas environment up to 1 atm while applying temperatures to 1000 °C inside the TEM. The holder-based closed cell design converts nearly any TEM into an environmental TEM with no modifications to the microscope. It also features a fully automated, software-controlled gas handling system. Atmosphere uses a patented thin film ceramic heating for ultra-stable high-resolution imaging and closed loop temperature control for accurate heating regardless of the gas environment.

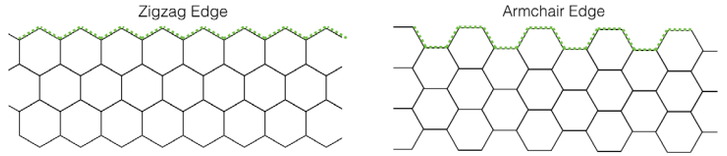

Figure 1: A) graphene nanoribbon with an exposed zigzag edge as indicated by the green dotted line and B) Graphene nanoribbon with an exposed armchair edge.

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Experiment

At DSI-IPCMS-CNRS/University of Strasbourg, France, G. Melinte, Dr. S. Moldovan and Prof. O. Ersen used Atmosphere to visualize the FLG etching process under relevant reaction conditions. The researchers exposed the sample to 150 Torr of H_2 at elevated temperatures inside the TEM to first reduce the Fe_3O_4 nanoparticles to metallic Fe, which was used as the etching catalyst. Figure 2 shows the nanoparticle reduction from Fe_3O_4 to metallic Fe. Figure 3 shows the associated EEL spectrum (background subtracted) of the Fe_3O_4 phase at 400 °C, and the graphene EEL spectrum (raw). After reduction, the environment conditions were adjusted to 900 °C and 600 Torr H_2, which match the conditions required to initiate the etching process. The experiment was carried out in a JEOL 2100F operating at 200 kV using bright field TEM mode.

Discussion

The IPCMS researchers previously demonstrated the FLG etching process with metallic Fe nanoparticles using *ex situ* techniques. To better understand the etching process, *in situ* experiments using the same materials were carried out using Atmosphere. In this case, the Fe nanoparticle catalyzes the reaction of hydrogen with carbon from graphene edges forming methane (CH_4), and proceeds as follows:

$$C_{(FLG)} + 2H_2 \rightarrow CH_4 \text{ (on the nanoparticle surface)}$$

The reaction can be understood as the reverse of catalytic carbon nanotube growth. The reaction is the driving force for particle movement and removal of carbon atoms at the leading catalyst-graphene interface. The schematic shown in Figure 4 visually describes how the reaction occurs. The nanopatterning is initiated only when the nanoparticles are in contact with a FLG edge, as the C-H reaction can start only if the C atoms from the edge are not part of a closed hexagon. A movie showing the reaction taking place *in situ* is available in Figure 5. It is generally accepted that the H_2 molecules dissociate first on the metal nanoparticle surface before they are brought into contact with the C atoms. After one row of carbon atoms is removed, the nanoparticle will move to regain contact with the edge leaving an etch track behind.

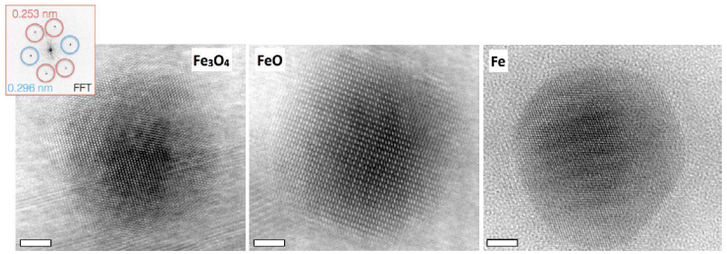

Figure 2: *In situ* reduction of iron oxide to metallic iron. The left BF-TEM image show a Fe_3O_4 nanoparticle. The crystal structure of this nanoparticle was determined by the FFT, show in the inset. The center image is a partially reduced FeO nanoparticle after exposure to 150 Torr of H_2 at 700 °C. The right image is a fully reduced, metallic Fe nanoparticle after exposure to 150 Torr of H_2 and 800 °C. The scale bar is 2 nm in each image.

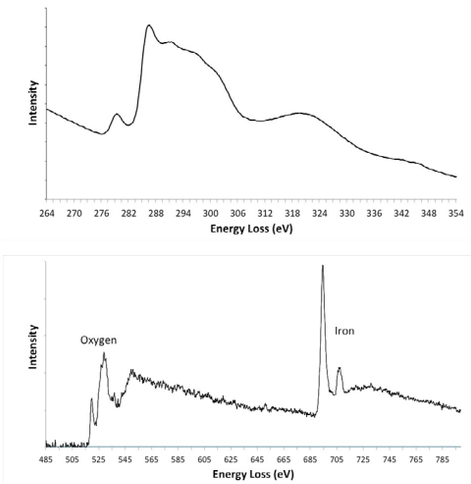

Figure 3: EELS analsysis of iron oxide nanoparticles and FLG material. The top image shows the carbon edge from the FLG material. The bottom image shows the oxygen and iron edges from the iron oxide nanoparticles present in the sample.

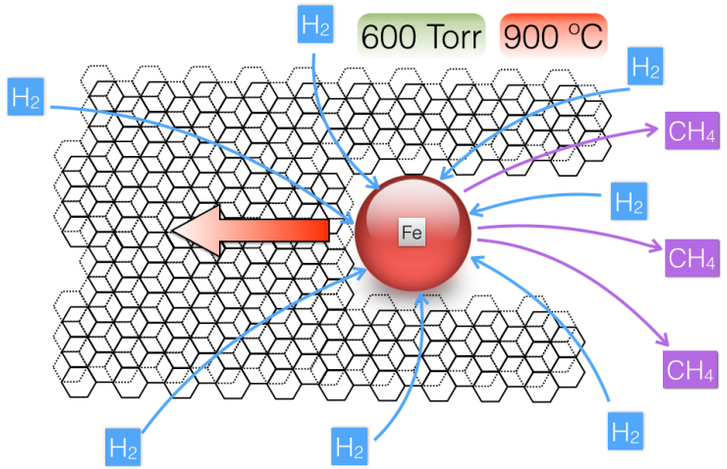

Figure 4: Schematic of the etch reaction. The iron nanoparticle catalyzes a reaction between H_2 and carbon from the FLG material to create methane, CH_4. This reaction removes carbon from the lattice and the iron nanoparticle moves forward.

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A complete understanding of the etching process must take into account the material dynamics. Changes in particle facets, support defects, and structural and morphological evolution upon etching are key issues that must be considered. The researchers succeeded in reproducing the etching process and visualized the dynamic process at high resolution using Atmosphere. More research is necessary to explore the exact conditions for the process initiation and to control the etching speed.

Applications

Graphene and FLG are promising materials for a variety of applications spanning nanoelectronics, optics, catalysis, and composites. Before widespread adoption is realized, the fabrication process and large-scale synthesis must be well understood. The results described here show that the process can be directly visualized and conditions tuned to better understand the behavior. These results represent a subset of possible application areas that can be explored with the Atmosphere system. The surface and bulk evolution of various types of nanoparticles can be viewed in real time under different reaction conditions, similar to the iron oxide to metallic iron reduction example. Nanoparticles often strongly interact with their support. For example, the interaction may give rise to different diffusion and coalescence behavior, and this can now be directly viewed under specific gas environments at the atomic scale. Probing the composition and electronic structure of materials is also possible using EELS analysis, as demonstrated here.

Atmosphere gives researchers the ability to analyze material behavior at atomic scale under real-world reaction conditions, without compromising resolving power of the TEM. Contact us to discuss the full range of capabilities of the Atmosphere 200 Gas E-cell system for your applications. We can be reached at (919) 377-0800 or contact@protochips.com.

play video

Figure 5: BF-TEM image of a FLG flake after a reaction has occurred. Trenches along specific crystallographic directions are readily apparent.

References:

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