Application Note

Fusion 500™

In Situ Atomic Structure Manipulation of Graphene

Introduction

Scientists are strongly motivated to control the electronic properties of graphene to expand its potential in nanoelectronics applications. Several synthesis methods exist that yield high quality graphene sheets, such as chemical vapor deposition, reduction of graphite oxides and arc discharge. However, it is difficult to modify the material structure to obtain the desired electrical properties using these methods alone. Post-synthesis treatments such as Joule heating, preferential edge cutting and e-beam manipulation offer promising results, which can alter the properties of graphene in controlled and reproducible ways.

The structural defect density in graphene can change the electrical properties and intentionally introducing or repairing specific types of defects at desired locations can lead to novel behavior and devices. Individual point defects and arrays of point defects (line-defects) can exist in the graphene lattice. Point defects typically manifest as hexagons rotated 90° and pentagon-octagon pairs, and a line-defect can contain a 5-7-7 cluster at its immobile end, 5-5-8 pairs within the line, and an unstable 5-6 cluster at the opposite end. These line defects, which are generated via Joule heating, enable unique electronic behavior. Valleytronics, an emerging field of data processing, makes use of local band gap minima and maxima created by this type of line defect. Valleytronics — analogous to spintronics, which discriminates between spin up and spin down electrons — discriminates and “filters” electron-based on momentum. It has processing speed advantages over classical electronics and spintronics, it is temperature insensitive and does not require magnetic fields, which can introduce instability. Self-repair and lattice reconstruction also can occur via Joule heating, where certain areas of the graphene sheet can heat up to 2000K. Reducing the defect density in graphene yields enhanced and tunable electrical conductivity for use in nanoelectronic devices.

Transmission electron microscopy (TEM) enables scientists to investigate materials at the atomic level, and combines spatial resolution with analytical tools to enable a broad range of capabilities. With a TEM equipped with *in situ* systems that apply specific and precise external stimuli, researchers can study dynamic material phenomena in graphene and other two-dimensional materials. *In situ* systems also make atomic scale structural manipulation possible, and combined with imaging and analysis creates a nanoscale laboratory in the TEM.

The Protochips Fusion system enables heating and electrical biasing in the TEM with easy to use software and versatile MEMS sample supports called E-chips. The E-chip devices are well suited for graphene and other two dimensional materials, because they feature a flat surface on which a sample is placed. The software precisely applies and measures electrical stimuli, so images and electrical data are easily correlated. Fusion features a patented, ultra-stable heating membrane design for routine atomic scale resolution at sustained temperatures of up to 1200 °C.

Experiment

In this application note, we present two experiments that demonstrate *in situ* capabilities. In the first experiment, Chen et al. in the Zettl group at UC Berkeley and Lawrence Berkeley National Lab transferred single layer graphene to E-chips and made electrical contacts via electron beam lithography. Electrical current was applied to individual graphene sheets to achieve temperatures up to 1300K resulting in individual line-defects characterized at ultra-high resolution. The experiments were done using the TEAM 0.5 at the National Center for Electron Microscopy at the Lawrence Berkeley National Lab, operating at 80 kV in bright field TEM mode. The researchers applied exit-wave reconstruction techniques to image series to resolve the atomic scale detail required for precise quantitative defect analysis.

In the second experiment, Qi et al. in the Johnson group at University of Pennsylvania applied electrical current using slow voltage ramping rates to individual graphene nanoribbons resulting in Joule heating up to 2000K where self-repair starts to occur. The researchers correlated structural changes in the nanoribbons observed at high resolution with electrical measurements, including structural recrystallization, reduction of defect density, electrical conductance, mobility and current density. An FEI Titan at Brookhaven National Lab was used in bright field TEM mode, operating at 300 kV.

Discussion

Defect Generation

Due to the two-dimensional nature of graphene, individual point defects and an array of point defects (line-defects) can form. In this experiment, researchers introduced line defects to individual sheets of graphene with atomic precision using Joule heating. These defects consistently nucleated near a free edge of graphene due to higher atom mobility there. In this case, the free edge is the perimeter of a hole generated by focused electron beam irradiation, as shown in Figure 1. Under appropriate biasing conditions the defect nucleates with a 5-6 pair, which propagates in the general direction of the applied current where ejection of one carbon atom results in formation of the next 5-5-8 pair, leaving an immobile end consisting of a stable 5-7-7 defect and a line defect consisting of 5-5-8 pairs. Note the line defect can recede from the edge nucleation point as demonstrated in Figure 1b. In a valleytronic device, the defect allows electrons to pass through the defect depending on their momentum and acts as a “valley valve” analogous to a spin valve.

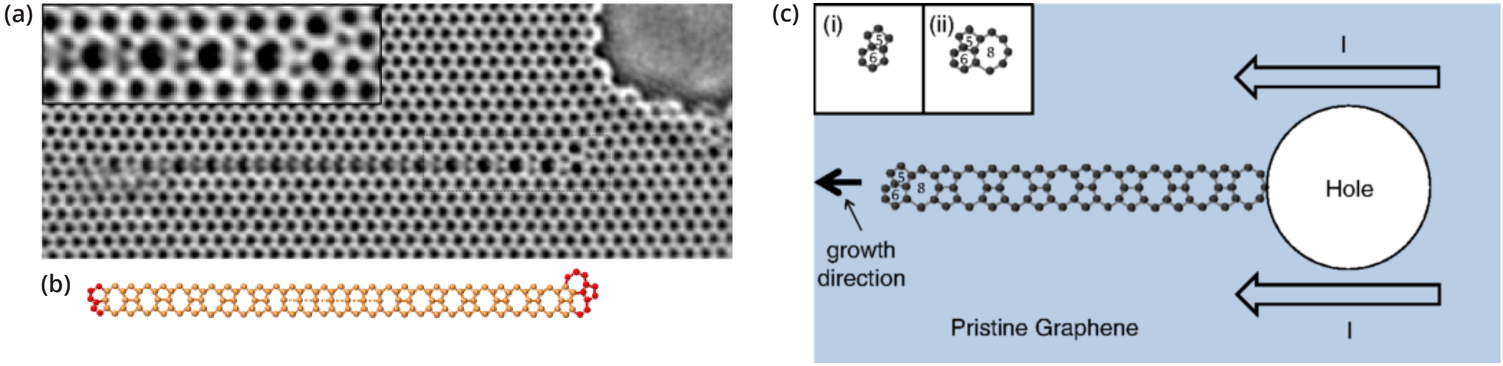

Figure 1: Reconstructed exit-wave phase image of a 5-5-8 line-defect in graphene. (a) Overview of the line-defect formation close to the free edge of graphene. (b) and (c) progression of growth of the line-defect upon application of electric field.

Lattice Reconstruction

Under increasing electrical bias and Joule heating, the graphene structure change occurred primarily along the crystal edges. The initial resistance of the nanoribbon was 19 kΩ, and decreased to 8 kΩ during the recrystallization and annealing process, as the width reduced from 8.2 to 5.4 nm (Figure 2h). Recrystallization transformed the initial curved edge morphology to a faceted morphology (Figure 2a-g). Sharp edges showed increased susceptibility to recrystallization where an increase in local heating likely occurs allowing for greater heat dissipation, which was supported by simulations. Enhanced conductance (Figure 2i-j) was attributed to improved carrier transport from the lower number of scattering centers present in the recrystallized nanoribbons. As the width shrunk to below 5 nm, the nanoribbon experienced electrical breakdown and failure. The authors conclude that the structure of the nanoribbon is tunable via controlled biasing; when a specific resistance,

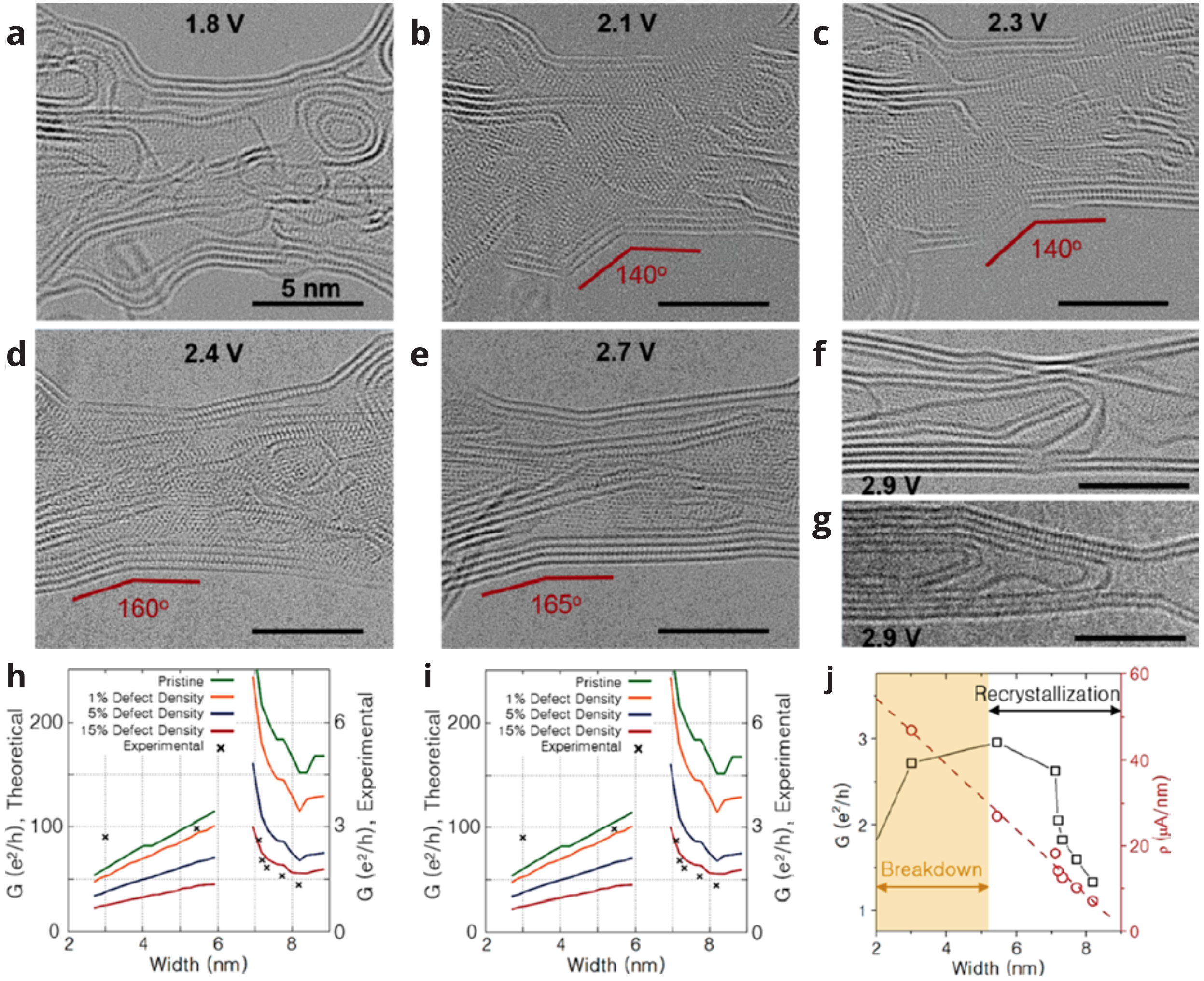

Figure 2: (a-g) Current-induced recrystallization in few-layer graphene sheets upon application of Joule heating. Scale bar is 5 nm in all images. (h-j) Evolution of electrical properties, resistance (contact resistance subtracted), intrinsic conductance and current density.

and thus structure, is reached the voltage is cut and the desired nanoribbon structure preserved.

The results demonstrate that crystallinity plays a major role in the electrical performance of graphene, and used for the fabrication of atomically sharp graphene sheets with superior transport properties.

Applications

As-grown graphene is an excellent candidate in many applications, but before widespread use in nanoelectronics, optics and catalysts can occur, further structural modifications and correlated property measurements are required. Additionally, motivated by growth in the graphene-based applications, researchers are studying other two-dimensional materials such as BN, MoS_2, WS_2, which have unique properties promising for many applications.

The Fusion system is the essential tool for precise and accurate electronic measurements at the pico- and nanoAmp scale, with ultra stable heating for atomic-scale resolution at high temperatures. Fusion is compatible with nearly every TEM on the market today, and combined with user-friendly software, a variety of E-chip designs and versatility of possible experiments it expands the research capabilities of your lab to study next generation materials and devices. Contact us to discuss the full range of capabilities of the Fusion platform with the thermal and electrical biasing E-chip sample supports. We can be reached at (919) 377-0800 or contact@protochips.com.

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