Investigation of Straight-Edge Graphene Grown via Segregation on Ni(110) using Scanning Tunneling Microscopy

Jill Wenderott
Physics, University of Kansas, Materials Science and Engineering, University of Michigan

NNIN iREU Site: National Institute for Materials Science (NIMS), Tsukuba, Ibaraki, Japan
NNIN iREU Principal Investigator: Dr. Daisuke Fujita, National Institute for Materials Science, Tsukuba, Ibaraki, Japan
NNIN iREU Mentor: Dr. Keisuke Sagisaka, National Institute for Materials Science, Tsukuba, Ibaraki, Japan
Contact: jwenderott@gmail.com, fujita.daisuke@nims.go.jp, sagisaka.keisuke@nims.go.jp

MATS

Abstract and Introduction:

Controlling the size and shape of graphene grown on metal surfaces is key to utilizing graphene in future applications. Despite having three-fold symmetry, graphene was found to grow in rectangular shapes and with straight edges on the Ni(110) surface. The focus of this project was to clarify the growth mechanism of graphene on the Ni(110) surface by observing the edges of graphene with atomic resolution. Two samples were investigated in this project: pristine Ni(110) and carbon-doped Ni(110). It is known from prior work that nickel contains a small amount of impurity sulfur that will segregate and reconstruct on the surface in a c(2×2) pattern upon annealing. This c(2×2) pattern is hypothesized to be responsible for the rectangular shape of graphene by acting as a template for graphene growth.

Graphene was grown via surface segregation by heating and then cooling the carbon-doped nickel sample. The subsequently segregated graphene was characterized with various surface characterization techniques, including scanning tunneling microscopy (STM). It was found at the atomistic level that the leading edge of graphene grows in stair-stepping fashion and the reconstructed c(2×2) sulfur on the surface of Ni(110) experiences stress during the growth of graphene, as indicated by circuitry patterns seen with STM. The density of the sulfur stress patterns changes with the size and density of graphene flakes, further confirming a direct relationship between the sulfur stress patterns and the growth of graphene.

Methods:

Carbon was doped into a nickel sample at 800°C and in high vacuum for three weeks. The sample was placed in an ultra-high vacuum chamber and heated to 1000°C for one minute and cooled to prompt segregation of graphene. The cooling rate during segregation was manipulated to determine which yielded graphene with the best crystallinity. Upon segregating graphene, the sample was moved into the ultra-high vacuum STM chamber and measured at liquid nitrogen temperature (78K). These STM measurements provided an atomistic survey of the sample.

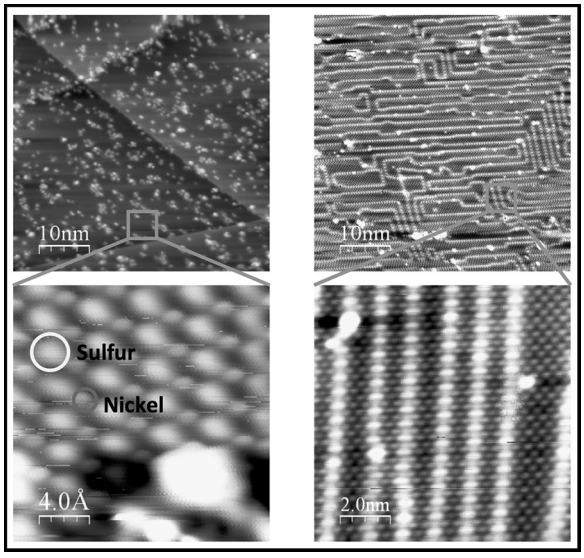

Figure 1: Sulfur on Ni(110) pristine (leftmost images), on C-doped Ni(110) (rightmost images).

The sample was also measured with low-energy electron diffraction (LEED), which showed the average crystal structure of the surface in reciprocal space, and Auger electron spectroscopy (AES), which revealed the chemical composition of the surface. Furthermore, helium ion microscopy, atomic force microscopy (AFM) and scanning electron microscopy (SEM) were used to look at the distribution and average size and shape of graphene flakes. All of these techniques allowed for a macroscopic view of the sample that, once paired with STM images, painted a more complete picture of the graphene growth mechanism on Ni(110).

Results and Conclusions:

The c(2×2) sulfur patterns on the pristine Ni(110) and the carbon-doped Ni(110) were first inspected to elucidate any differences. It was noted that STM images of the pristine Ni(110) surface confirmed the existence of sulfur arranged in

c(2×2) pattern. The carbon-doped Ni(110) STM images also showed surface sulfur, but it was observed that sulfur was stressed in such a way that it produced intricate circuitry patterns (see Figure 1). As graphene was later found on the same sample, it was inferred that the growth of graphene was straining the c(2×2) sulfur either by competing with sulfur for placement on the Ni(110) surface or effectively "pushing" sulfur out of the way during its growth.

Next, graphene and the borders between graphene and sulfur on the carbon-doped Ni(110) were investigated. Fast-Fourier transforms of STM images of graphene showed certain areas of graphene to be highly-ordered, though in several cases highly-ordered graphene bordered semi-ordered graphene (see Figure 2). It was found that decreasing the cooling rate during segregation from 10°C/sec to 3°C/sec increased the ratio of well-ordered graphene to semi-ordered graphene, but decreasing the cooling rate to 0.6°C/sec resulted in multi-layer graphene. Thus, a balance was struck between cooling slow enough to produce well-ordered graphene and not cooling so slowly that multi-layer graphene was formed.

Regarding the borders between c(2×2) sulfur and graphene, it was found that graphene grew in a stair-stepping fashion down to the atomistic scale with STM (see Figure 3). This lent support to the hypothesis that graphene is using sulfur as a template for growth. It was also confirmed that graphene segregated was composed entirely of carbon and the surface surrounding it was covered in sulfur via AES.

Finally, it was observed that as the area of graphene on the nickel surface increased, the stress patterns of the c(2×2) sulfur experienced greater compaction (see Figure 4). When multi-layer graphene was grown, the stress patterns appeared the most compacted, implying that sulfur's presence on the surface of nickel was potentially directing the growth of graphene. It was postulated that monolayer graphene segregated laterally across the surface of nickel compacting sulfur. When sulfur could not be pushed closer together, the graphene began to grow vertically away from the surface. The use of an element such as sulfur to direct and/or quench the growth of graphene would be a breakthrough in graphene research, but more studies are needed to confirm these preliminary findings.

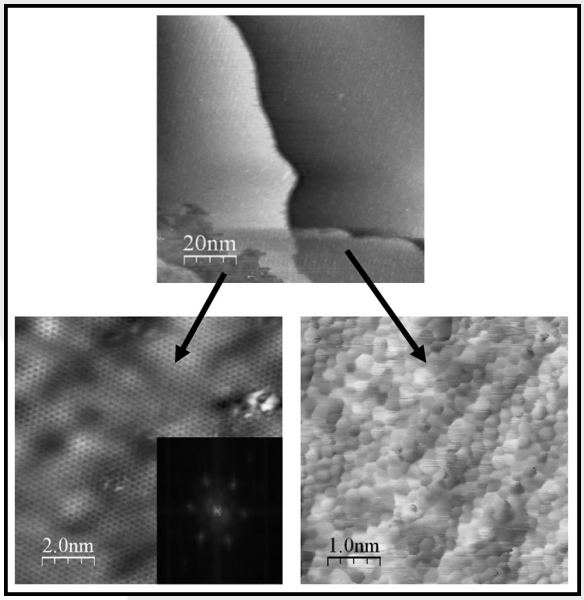

Figure 2: Well-ordered graphene (left) bordering semi-ordered graphene (right).

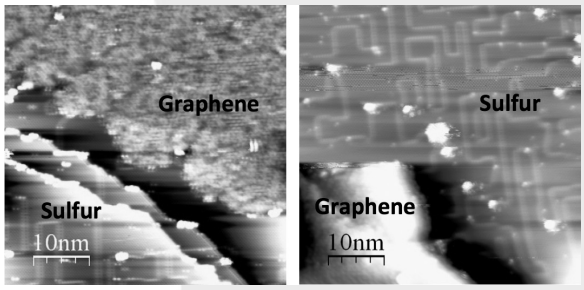

Figure 3: Borders between graphene and c(2×2) sulfur on Ni(110).

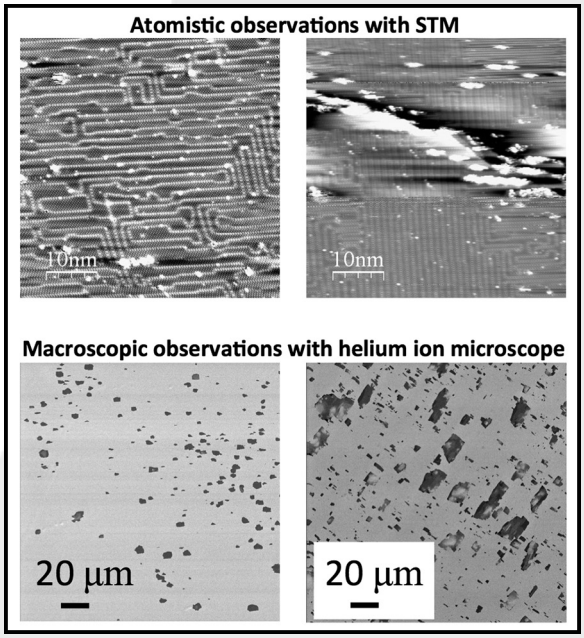

Figure 4: Comparison of sulfur stress patterns (top) to area of graphene growth (bottom), with the leftmost images corresponding to one sample and the rightmost images corresponding to another sample.

Future Work:

Theoretical modeling, such as density functional theory, is necessary to support experimental data collected thus far. The relative surface energies of sulfur and carbon on nickel should be considered to help clarify the mechanism of graphene growth. More experimental studies, such as segregation of graphene on nickel after sputtering sulfur from the surface, should also be conducted.

Acknowledgments:

This project would not have been possible without many parties' support. Many thanks are owed – the National Nanotechnology Infrastructure Network International Research Experience for Undergraduates (NNIN iREU) Program and National Science Foundation, for funding; H. Guo, for helium ion microscope measurements; K. Matsushita, for atomic force microscope measurements; and T. Kusawake, for tungsten tip preparation instruction.