SURFACE CHEMISTRY AT THE NANOMETER SCALE

Thesis by

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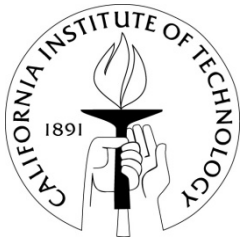
In Partial Fulfillment of the Requirements

for the Degree of

Doctor of Philosophy



California Institute of Technology

Pasadena, California

2011

(Defended April 29, 2011)

Acknowledgements

There are many people to whom I would like to express my gratitude. First and foremost I would like to thank my advisor, Professor Jim Heath. I'm so grateful for his constant support and guidance during my graduate studies. His intensive enthusiasm to the pursuit of science has always been inspiring me and motivating me to think creatively about the experiments. I would also like to thank Jim for providing access to the resources that are imperative for much of my research work. I'm very grateful to have the opportunity to have worked with him.

I would also like to thank my committee members, Professor Aron Kuppermann, Professor Nate Lewis, and Professor Dan Weitekamp, who are all inspiring scientists and have guided me through my Ph.D. study.

In the Heath group, a lot of the current and past members have helped me tremendously during the past years. Dr. Hongbin Yu, a former postdoc in the group, taught me most of the basic experimental techniques when I first joined the lab, and I've learned a lot from him while working with him on the low-temperature atomic force microscopy project. Dr. Ke Xu, a former graduate student of the Heath group, has been a terrific friend and a constant source of inspiration and ideas. He collaborated with me on most of my research projects and was enormously generous with his time. I'm deeply impressed by his instincts about the experiments and have learned a lot from him. I would particularly thank Dr. Rosemary Rohde and Dr. Heather Agnew, who taught me the basic glove-box skills and infrared spectrometer techniques, and have also been always willing

to discuss the silicon functionalization project. Joey Varghese collaborated with me closely on the graphene-templated imaging project. I learnt a lot from him, and enjoyed his friendship. Thanks to Dr. Bonnie Sheriff, Dr. William Dichtel and Clara Ji-Hyun Cho on the microcontact printing project. Special thanks to Drs. Yi Luo, Guanglu Ge, Ryan Bailey, Kris Beverly, Ezekiel Johnston-Halperin, Pin Wang, Woon-Seok Yeo, Dunwei Wang, Mike McAlpine, Rong Fan, Lidong Qin, Habib Ahmad, Akram Boukai, John Nagarah, Erica Delonno, Johnny Green, Yuri Bunimovich, Jang Wook Choi, Young-Shik Shin, Gabriel Kwong, Udi Vermish, Ophir Vermesh, Slobodan Mitrovic and Steven Millward for useful discussions and assistance with experiments. I thank Dr. Qihui Shi, Dr. Ann Cheung and Dr. Jun Wang, Jen-Kan Yu, Douglas Tham, Ruo-Gu Huang, Chao Ma, Wei Wei, Kiwook Huang, Alex Sutherland, Ahrundhati Nag, Kaycie Butler, Jessica Pfeilsticker and other labmates for helpful discussions. I also thank Kevin Kan, Diane Robinson and Amy Crown for keeping the lab running at high efficiency.

Beyond the Heath group, I would also like to thank many other people who helped me and added tremendous depth to my education and experience at Caltech. I'm so grateful to Dr. Lauren Webb, a former graduate student in the Lewis group, who introduced me to the silicon functionalization project. I also learned a lot in collaboration with Dr. Santiago Solares from Goddard group on the functionalization project. Discussing with him was always a pleasure for me. I thank Professor George Rossman for helpful discussions and assistance in using the micro-Raman spectrometer. I would also like to thank Professor Franz J. Giessibl (Universitaet Augsburg) for great help in the low-temperature AFM project and generously providing their q-plus setup and valuable

suggestions. I thank Dr. Cameron Hughes and Dr. Andrew Beyer from Yeh group for helpful discussions on the AFM project.

I'd like to thank Dr. Matt Traub for help in using XPS; Dr. Chi Ma for his help with the SEM system; Dr. Guy DeRose and Bophan Chhim for training and assistance of using the facilities in the KNI; Dr. Kate Plass for making samples for STM measurements; Dr. Bruce Brunschwig and the Caltech Molecular Materials Research Center (MMRC) for assistance in using the equipment therein.

Thanks also go to Dian Buchness, Laura Howe and Agnes Tong for help with the departmental paperwork, especially during my candidacy exam and graduation. Thanks to Jim Endrizzi, Athena Trentin, Laura Kim and Daniel Yoder in ISP for their help with my visa paperwork. Thanks to Rick Gerhart and Mike Roy for their help with my glassware and machine work.

I'd also like to thank all my friends who enriched my life here at Caltech; they are Drs. Ling Shi, Changlin Pang, Chengzhong Zhang, Yong Hao, Tao Liu, Yu Liu, Fan Yang, Bolin Lin, Xin Guo, Shu Miao, Xiao Lu, Chih-Kai Ko, Xiaojie Gao, Wei Ji Ma, Siyang Zheng, I-Ren Li, Min-Shir Lin, Hsin-Ying Chiu, Valerie Norton, Hao Jiang, Jigang Wu, Zhipu Jin, John Matson, Yan Xia, Seokmin Jeon, Changshi Lao, Mo Li, Bo Li, Kechun Zhang, George Ouyang, Peera Jaru-Ampornpan, Jinyu Chen, Tingwei Mu, etc.

Finally, I'd like to express my deep gratitude to my parents and my wife for their endless love, support and encouragement. None of this would have been possible without them.

Abstract

This thesis describes research towards understanding surface chemical and physical processes, as well as their effects on the underlying substrate properties, at the nanometer and atomic scales. We demonstrate a method to tune the density of etch pits on Si(111) during the chlorination process so as to change the surface reactivity. Subsequent grafting of an azide group to replace chlorine demonstrates an example of non-oxidative passivation of silicon surfaces with new functionalities. Depending upon the solvent used in the azidation process, it is shown to yield different azidation kinetic rates, different final azide coverages, and different surface-area distributions. Scanning tunneling spectroscopy studies show that both chlorination and azidation processes significantly modify the surface electronic structures, with the former leading to a non-zero density of states at the Fermi level.

Our studies on a new class of corrugation, i.e., wrinkles, in exfoliated graphene on SiO_2 show that a "three-for-six" triangular pattern of atoms is exclusively and consistently observed on wrinkles, suggesting the local curvature of the wrinkle is a perturbation that breaks the six-fold symmetry of the graphene lattice. Lower electrical conductance is also found on the top of wrinkles compared to other regions of graphene. The wrinkles are characterized by the presence of midgap states, which is in agreement with recent theoretical predictions. A general method is also reported for reliably fabricating ultrahigh-density graphene nanoribbon (GNR) arrays. We have clearly observed how the properties of GNRs evolve as a function of number of graphene layers.

The band gap (and so the on-off ratio) decreases as the number of layers increases. These results suggest that, in addition to single layer graphene, properties of GNRs of different thicknesses can also be harnessed for engineering GNRs as different building blocks towards FET applications.

A novel imaging technique, graphene-templated scanning probe microscopy, has been developed and applied for the study on the condensation process of water and small organic molecules on mica. We found that these molecular adlayers grow epitaxially on the mica substrate in a layer-by-layer fashion. In particular, submonolayers of water form atomically flat, faceted islands of height 0.37±0.02 nm, in agreement with the height of a monolayer of ice. The second adlayers also appear ice-like, and thicker layers appear liquid-like. This general mechanism, however, is not universal. Exclusively three-dimensional droplets of water are observed on chemically modified (hydrophobic) mica surfaces, suggesting a 3D growth mechanism.

This thesis also includes my work on the design of a quartz-tuning-fork-based force sensor and related electronics for applications on low-temperature atomic force microscopy. Results show that the force-sensor-global-feedback circuit detector system induced lowest noise floor. The high detection sensitivity of this system demonstrates its ability to be used in frequency-modulated AFM at cryogenic temperatures. Surface topographic imaging of H-terminated Si(111) has been achieved at low temperatures.

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