

SURFACE CHEMISTRY AT THE NANOMETER SCALE

Thesis by

Peigen Cao

In Partial Fulfillment of the Requirements

for the Degree of

Doctor of Philosophy



California Institute of Technology

Pasadena, California

2011

(Defended April 29, 2011)

© 2011

Peigen Cao

All Rights Reserved

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 Nagarath, 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 SiO₂ 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.

Table of Contents

Acknowledgements.....	iii
Abstract.....	vi
Table of Contents.....	viii
List of Figures.....	xi
List of Tables.....	xiv
Chapter 1 Thesis Overview	1
Chapter 2 Chlorine-Terminated Silicon(111) Surfaces.....	8
2.1 Introduction.....	8
2.2 Wet-chemical preparation of Cl-terminated Si(111) surfaces	10
2.3 STM results.....	11
2.4 STS results	16
2.5 Conclusion	20
2.6 References.....	21
Chapter 3 Azidation of Silicon(111) Surfaces.....	23
3.1 Introduction.....	23
3.2 Experimental.....	24
3.2.1 Materials and methods.....	24
3.2.2 Instrumentation	25
3.2.3 Surface coverage calculations.....	26
3.3 XPS and IR analysis.....	29
3.4 STM and STS analysis.....	35
3.5 Conclusion	37
3.6 References.....	37
Chapter 4 Electrical Properties of Graphene Wrinkles and Nanoribbons.....	41

4.1	Introduction	41
4.1.1	Wrinkles in graphene	41
4.1.2	Graphene nanoribbons	43
4.2	Experimental	45
4.2.1	Fabrication of graphene sheets.....	45
4.2.2	Fabrication of graphene nanoribbons.....	47
4.3	Structural and electrical characterizations of graphene wrinkles.....	51
4.4	Electron transport in graphene nanoribbons.....	59
4.5	Conclusion.....	64
4.6	References	65
Chapter 5 Imaging through Graphene Templating.....		69
5.1	Introduction	69
5.1.1	Water.....	69
5.1.2	Organic molecules	71
5.2	Experimental	72
5.2.1	Materials	72
5.2.2	Sample preparation	73
5.2.3	Identification of graphene layers	74
5.2.4	Atomic force microscopy.....	76
5.3	Water on mica	77
5.4	THF and cyclohexane on mica.....	89
5.5	Conclusion.....	101
5.6	References	103
Chapter 6 Quartz Tuning Fork Based Low Temperature Atomic Force Microscopy		108
6.1	Introduction	108
6.2	Experimental	117
6.2.1	Pre-amplifier	117
6.2.2	Low noise measurements.....	118

6.2.3	Tuning-fork-tip assembly.....	120
6.3	Results	121
6.3.1	Noise performance	121
6.3.2	Quality factor	126
6.3.3	Topographic images.....	127
6.4	Conclusion.....	128
6.5	References	128

List of Figures

Figure 2.1. Large-field view of STM topographic images	13
Figure 2.2. Close-up STM images with atomic resolution	14
Figure 2.3. Schematics of the structure of steps on Cl-terminated Si(111) surfaces	15
Figure 2.4. Scanning tunneling spectroscopy of Cl/Si(111)	17
Figure 2.5. Schematic illustration of energy bands	18
Figure 3.1. A schematic showing the two-step chlorination/azidation surface synthetic process	23
Figure 3.2. XPS analysis of azide-terminated Si(111) surfaces	29
Figure 3.3. ATR-IR data from azide-terminated Si(111) surfaces	31
Figure 3.4. Kinetics of azidation of Si(111) surfaces	32
Figure 3.5. Stability of azidated Si(111) surfaces against air oxidation	33
Figure 3.6. Morphology evolutions following the two-step chlorination/azidation process	34
Figure 3.7. Identification of surface chemical groups on azidated Si(111)	36
Figure 4.1. Process flow schematics for the fabrication of graphene sheets	45
Figure 4.2. Raman spectrum and STM topography of a typical graphene sample	46
Figure 4.3. Locating the graphene sheet in STM	48
Figure 4.4. Representative bright-field optical images following the GNR fabrication process	50
Figure 4.5. STM topographs of graphene wrinkles	52
Figure 4.6. Comparison of STM topographs of a graphene wrinkle and a “flat” part of the same graphene sheet, obtained at positive and negative sample biases	56
Figure 4.7. Scanning tunneling spectroscopy study of a graphene wrinkle	57
Figure 4.8. Conductance measurements of graphene nanoribbons	60
Figure 4.9. Linear dependence of GNR resistance on ribbon length	62

Figure 4.10. Mobility and current on/off ratio analysis	63
Figure 5.1. Few-layer graphene sheets are most readily observed through transmission optical microscopy	74
Figure 5.2. Identification of numbers of graphene layers in a representative sample	75
Figure 5.3. Raman spectrum of a monolayer graphene sheet deposited on a mica surface that was in equilibrium with a THF vapor	76
Figure 5.4. Graphene visualizes the first water adlayer on mica surface at ambient conditions	77
Figure 5.5. Comparison of the roughness of different surfaces	78
Figure 5.6. Additional AFM images of graphene deposited on mica and SiO ₂ substrates under ambient conditions	80
Figure 5.7. AFM phase images indicate the island-like plateau structures are under the graphene sheets	81
Figure 5.8. Stability of the graphene-fixed water patterns	83
Figure 5.9. AFM images of graphene deposited on mica at RH ~2%, revealing the influence of surface defects on water adlayer nucleation	85
Figure 5.10. AFM images of graphene deposited on mica at RH ~90%, revealing the structure of the second water adlayer	87
Figure 5.11. Graphene templating illustration (a) and representative measurements of adsorbed adlayer thicknesses (b,c)	90
Figure 5.12. AFM images of graphene-templated THF adlayers reveal both structural and dynamical information	92
Figure 5.13. Water adsorption on TMCS-functionalized mica surfaces at ambient conditions	94
Figure 5.14. AFM images of graphene-templated cyclohexane adlayers	97
Figure 5.15. Possible structural models for THF and cyclohexane adlayers	99
Figure 6.1. A schematic of AFM detection systems	109
Figure 6.2. A scheme of the relevant spatial distances in dynamic AFM	111
Figure 6.3. A schematic of the low-noise detection system	118

Figure 6.4. Quartz-tuning-fork-tip assembly	120
Figure 6.5. Low noise detection scheme.....	121
Figure 6.6. Noise performance.....	124
Figure 6.7. Excitation curves for quality-factor measurements	126
Figure 6.8. Frequency-modulated AFM topographic images.....	127

List of Tables

Table 6.1. Comparison of noise floor at room temperature for three types of amplifiers	123
---	-----