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Mengxi Liu

Controlled Synthesis and Scanning Tunneling Microscopy Study of Graphene and Graphene-Based Heterostructures

Doctoral Thesis accepted by
Peking University, Beijing, China

Springer

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ISSN 2190-5053 ISSN 2190-5061 (electronic)
Springer Theses
ISBN 978-981-10-5180-7 ISBN 978-981-10-5181-4 (eBook)
https://doi.org/10.1007/978-981-10-5181-4

Library of Congress Control Number: 2017952510

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Printed on acid-free paper

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The registered company is Springer Nature Singapore Pte Ltd.
The registered company address is: 152 Beach Road, #21-01/04 Gateway East, Singapore 189721, Singapore

Supervisors' Foreword

Since the Nobel Prize for physics in 2010 was awarded to Prof. Geim and Prof. Novoselov for their '*ground-breaking experiments regarding the two-dimensional material graphene*,' dramatic research progress in graphene has been witnessed, such as the controllable synthesis, the deep understanding of the chemical and physical properties, and the broad application prospects. The unique electronic property of high carrier mobility makes graphene a potential material in future electronics. However, the Dirac-type band structure of graphene with zero bandgap limits its application in electronic devices. It is of great importance to develop techniques to open a gap in the band structure of graphene.

This thesis provides a series of experimental work in fabricating well-designed nanostructures to modulate the band structure of graphene, involving vertically coupled bilayer graphene and lateral heterostructure with the 'white graphene' hexagonal boron nitride (h-BN). It shows how to synthesize bilayer graphene with different interlayer rotation angles on Rh substrates *via* a combined chemical vapor deposition and segregation process. The obtained bilayer graphene generates different moiré patterns and thus induces van Hove singularities near Fermi level, which is observed by atomic-resolved scanning tunneling microscopy/spectroscopy. In addition, it puts forward an efficient way to modulate the bandgap of graphene by creating a heterostructure with h-BN. It shows how to control the domain shape, domain size and near 100% zigzag-dominated boundary linking type of heterostructures. The mechanism of bandgap opening of h-BN-G heterostructure is discussed based on experimental results and theoretical calculations.

Beijing, People's Republic of China — Prof. Zhongfan Liu
June 2015 — Prof. Yanfeng Zhang

Abstract

Graphene, a novel two-dimensional atomic crystal, has attracted serious attention because of its unique physical properties, such as high carrier mobility, high Young's modulus, high thermal conductivity, and low optical absorption. Due to these excellent properties, graphene has been considered as a potential material for applications on electronics, optics, and composite materials. However, it is negative for graphene to show high performance in logic circuits because graphene is a semimetal material with zero bandgap at Fermi level. Therefore, tuning the energy band structure of graphene near Fermi level is highly favorable.

On one hand, the energy band structure of graphene is highly dependent on its stacked order. Bernal-stacked bilayer graphene shows zero bandgap between valence and conduction bands with a quadratic dispersion. Upon an electric field applied perpendicular to the bilayer graphene would cause a bandgap opening. For non-Bernal stacked bilayer graphene, the saddle points in the energy band structure lead to a divergence in the density of states, as known as a van Hove singularity, which would give rise to new phase of matter, such as superconductivity, magnetism, or charge density wave.

On the other hand, diverse approaches were developed for opening the bandgap of graphene. The existing methods include gate-induced method, substrate-induced method, etching graphene layer into graphene nanoribbons or nanomeshes, patterned hydrogen adsorption and chemical doping. However, most approaches lead to the decreasing of carrier mobility of graphene, which goes against the application on devices. Theoretical calculations predicted that the heterostructure of graphene and hexagonal boron nitride (h-BN) would be the most effective way to open the bandgap of graphene and maintain the high carrier mobility spontaneously.

On the basis of the energy band engineering of graphene, this thesis mainly encompasses two parts: The one is the synthesis of non-Bernal-stacked graphene and the new electronic states near the Fermi level; the other is the designed fabrication of hexagonal boron nitride–graphene heterostructure and the electronic structure on the interface.

1. Controlled Growth of Graphene on Rh Substrates and the Generation of van Hove Singularities

(1) Controlled Growth of Graphene on Rh Substrates
Large-scale uniform graphene was synthesized on high carbon solubility substrates of Rh foils using an ambient pressure chemical vapor deposition method. It was interestingly to be found that, by increasing the cooling rate after the growth process, the thickness of graphene could be tuned from multilayer to bilayer and even to monolayer. Besides, there were plenty of wrinkles formed on graphene grown on Rh substrates, and the wrinkles usually encircled into nearly hexagonal or quadrilateral shapes. The wrinkles were proposed to be a consequence of compressive stress during the cooling process because of the different thermal expansion coefficients of graphene and Rh substrates. Based on these results, a segregated growth mechanism was put forward for graphene growth on Rh foils and it was emphasized that carbon atoms mostly segregated from Rh grain boundaries, with a little portion of Rh steps and terraces.

(2) Scanning Tunneling Microscopy Study of Graphene on Rh Substrates
With the aid of scanning tunneling microscopy, the bilayer graphene on Rh substrates was found that preferred to stack deviated from the Bernal stacking geometry, resulting in the formation of moiré patterns. The moiré periods decreased with the increasing twisted angles between the coupled graphene bilayer. Interestingly, the robust van Hove singularities were observed on various graphene moiré patterns near the Fermi level by scanning tunneling spectroscopy. More importantly, the energy difference between the two van Hove singularities (ΔE_{VHS}) increased with the increasing twisted angles, indicating that the van Hove singularities on twisted bilayer graphene were angle-dependent on Rh substrates. Besides, the strain caused by graphene wrinkles strongly affected the local energy band structures of the twisted bilayer graphene, resulting in the decreasing ΔE_{VHS} with the lattice deformations increasing. Moreover, along a graphene wrinkle, the states condensed into well-defined pseudo-Landau levels, which mimic the quantization of massive Dirac fermions in a magnetic field of about 100 T. These results suggest that twisted bilayer graphene could induce the electronic states near Fermi level, and strained bilayer graphene could be an ideal platform to realize the high-temperature zero-field quantum valley Hall effect.

2. Controlled Growth of h-BN-graphene Heterostructures and the Electronic States on the Interface

(1) Controlled Growth of Quasi-freestanding h-BN-graphene Heterostructures
Monolayer graphene and h-BN were synthesized separately on weakly coupled Ir(111) substrate using an ultrahigh vacuum chemical vapor deposition method. With the aid of scanning tunneling microscopy, it was found that the layer corrugation of h-BN was much greater than that of graphene on Ir(111)

(graphene: h-BN = 1:7), which was a challenge for the two analogues linking together to form a seamless monolayer. By using a two-step growth method, two kinds of h-BN-graphene in-plane heterostructures, h-BN@G heterostructure and G@h-BN heterostructure, were synthesized on Ir(111) substrate. Graphene and h-BN could overcome the differences in layer corrugation and form in-plane monolayer heterostructure. The grain sizes of graphene and h-BN could be controlled by tuning the growth temperature.

(2) Atomic Structures and Electronic States on the Interfaces of the Heterostructures
An atomically sharp zigzag-type boundary has been found to dominate the patching interface between graphene and h-BN, as evidenced by high-resolution scanning tunneling microscopy. The formation of zigzag-type boundaries simply related to the edge of the pre-deposited graphene or h-BN domains, excluding the effects from growth sequences, domain sizes, domain shapes, and substrates. Scanning tunneling spectroscopy studies showed that the graphene and h-BN tended to exhibit their intrinsic electronic structures near the patching boundary with no doping effects from each other. It suggests that h-BN behaves as an insulator in the heterostructure and does not change the intrinsic electronic structure of graphene. However, the existing of h-BN domains presents important influences on the electronic structure of the heterostructure. Firstly, the AB-symmetry of graphene lattices was broken because of the appearance of h-BN domains, leading to the bandgap opening of graphene. Secondly, the seamless boundaries between graphene and h-BN domains decreased the electronic scattering of graphene edges, which confirmed the high carrier mobility of graphene. The present work offers a deep insight into the h-BN-graphene heterostructures both geometrically and electronically together with the graphene energy band engineering.

Keywords Graphene · Segregated growth · van Hove singularity · h-BN-graphene heterostructure · Energy band engineering · Scanning tunneling microscopy

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Acknowledgements

The research was supported by the Ministry of Science and Technology of China (973 program 2011CB921903, 2011CB933003, 2012CB933404, 2012CB921404 and 2013CB932603) and the National Natural Science Foundation of China (NSFC 21603045, 51290272, 21073003, 51222201, 51121091, and 11304053).

The investigations described in this thesis were mostly carried out in the Center for Nanochemistry, Peking University (PKU). Some investigations were carried out in National Center for Nanoscience and Technology (NCNST) and Beijing Normal University (BNU).

I would like to thank the following people who have contributed to this thesis:

- Prof. Zhongfan Liu and Prof. Yanfeng Zhang for supervising and guiding me on this thesis. Thank you for leading me to the magic world of STM and graphene.
- Prof. Jin Zhang, Prof. Hailin Peng, and Dr. Xie, who give us the nice research environment in CNC, Peking University.
- Prof. Lin He and Dr. Wei Yan in Beijing Normal University, who carried out the STS measurement presented in Chap. 3.
- Prof. Yuanchang Li, who carried out the DFT calculations presented in Chap. 4.
- Prof. Xiaohui Qiu and Dr. Pengcheng Chen for offering me the opportunity to do the STS measurement of h-BN-G interface in National Center for Nanoscience and Technology of China. Now, I am an Assistant Professor working with Prof. Qiu in NCNST!
- Dr. Yabo Gao, Dr. Teng Gao, who taught me how to use STM and other instruments.
- Dr. Jingyu Sun and Dr. Face for sharing attitude on scientific research.
- Dr. Qiucheng Li, Dr. Yue Qi, Dr. Xiebo Zhou, and Dr. Jianping Shi.
- My parents and parents-in-law for their powerful support!
- Dr. Donglin Ma, my soul mate and my husband. Thank you for…all!

Contents