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Yu-Chuan Lin

Properties of Synthetic Two-Dimensional Materials and Heterostructures

Doctoral Thesis accepted by Pennsylvania State University, State College, PA, USA

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Supervisor's Foreword

Two-dimensional (2D) materials are arguably one of the most popular research fields in solid-state materials science over the past two decades. This material system is a true "2D" building block, thinner than 1 nm, with wafer-scale lateral dimensions that could provide the foundation for next-generation materials engineering. Their versatility for material functionalities and heterogeneities is interesting and inspires many ideas.

Furthermore, their ability to couple individual properties to generate new and novel properties has led to a wide variety of scientific breakthroughs. Most 2D materials are known as van der Waals (vdW) materials, a class of materials whose structures are highly anisotropic and whose surfaces are terminated with vdW bonds. They can be placed on any foreign surface without significant changes in their intrinsic materials properties; they can be stacked to form high-quality interfaces with other 2D materials whose lattice constant is not necessarily matched. This is where the focus of Yu-Chuan Lin's thesis research begins: with the integration of disparate 2D materials to explore novel properties that arise from their combination. Heterostructures like the ones described in Yu-Chuan's thesis have enabled hundreds of groundbreaking results in physical sciences since their first reports in 2011. In order to make vdW heterostructures technologically relevant, we must move on from mechanical exfoliation and transfer to a practical level where we can create them in an atom-by-atom, bottom-up approach.

Yu-Chuan's doctoral research at the Pennsylvania State University focuses on the growth, integration, and properties of vdW heterostructures, with an emphasis on transition metal dichalcogenides and graphene. Yu-Chuan has incorporated materials synthesis techniques, materials chemistry, and a variety of characterization techniques into his research in order to build a comprehensive study on synthetic vdW heterostructures. His graduate research on vertical vdW heterostructures out of various atomic layers has led to "firsts" in the field, including the first directly grown vdW heterostructure with epitaxial graphene, the first demonstration of novel properties in advanced heterostructures not seen before in manually stacked materials, and the first to conclusively show the importance of defects in the vertical transport of these structure. He demonstrated novel multilayer heterostructures and elucidated electronic transport and optical coupling across multiple 2D interfaces. In addition to his vdW heterostructures work, the independent investigation in his thesis also focused on epitaxial WSe_2, grown by MOCVD processes. He sufficiently elaborated the reasonings behind everything we see in MOCVD, including growth mechanisms, surface chemistry, and device performance. The implication of his thesis has advanced our understanding on the synthesis sciences and properties of nanomaterials, as the articles embedded in the content of this thesis has been cited more than 400 times. Needless to say, this thesis provides sustainable knowledge and information, as we are brainstorming to grow better 2D materials, better 2D interfaces in the future.

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Preface

Graphene and other two-dimensional semiconductors have established a completely new research field, "2D materials" that covers all of subjects related to fundamentals and applied sciences, engineering, biology, medicine, and so forth. Their layered crystal structures and anisotropic properties are utilized to create new properties. From an electrical perspective, they are promising candidates for the low-power and flexible electronics because of their ultrathin nature, excellent electrical properties, and excellent mechanical flexibility.

While they are considered as dreamful materials by many of us, many researchers may encounter a few difficulties when studying them: The size of 2D materials prepared by mechanical exfoliation is limited. Besides the size limitation, tapes used during exfoliation usually leave polymer contamination on the surface of 2D materials. Therefore, some of researchers in this field has moved on to grow 2D materials directly on substrates, instead. Ultimately, we are hoping to synthesize 2D materials as large as we want and also be able to control properties and functionality at where exactly we want to for a variety of applications and practical use. However, several questions need to be answered first, such as the following: How to make them scalable and large area? How to control or reduce defect density of 2D materials during growth? How to integrate them with dissimilar but preferable substrates? This thesis was meant to answer some of these questions, hoping it would move the frontier of the synthesis sciences of 2D materials forwards.

This book covers two types of materials integration in the context of 2D transition metal dichalcogenides and graphene. They are (*1*) vertical integration of 2D layers for van der Waals (vdW) heterostructures and (*2*) scalable, lateral growth of WSe_2 on insulating substrates. The first two chapters cover fundamental knowledge and a brief overview on 2D transition metal dichalcogenides (TMDC) and graphene, vdW heterostructures, thin-film techniques and examples. Chapter 3 has two sections that cover the properties of synthetic WSe_2: The first is about the first demonstration of the metallic-organic chemical vapor deposition process for WSe_2, and the second covers a more sustainable process for WSe_2 on insulating substrates and also a completed study on the properties of WSe_2. Chapter 4 discusses the synthesis of MoS_2 on graphene and how morphology and quality of graphene template impact the nucleation and growth of MoS_2 and other TMDC. Chapters 5 and 6 discuss epitaxial relationship between WSe_2 and graphene, vertical electronic transport through their heterointerface, and modulation of the carrier concentration of graphene for electrical contact. In Chap. 7, resonant tunnel diodes made of TMDC bilayer (MoS_2/WSe_2 and WSe_2/$MoSe_2$) is thoroughly discussed, including materials preparation, properties, and its electronic transport.

Oak Ridge, TN, USA Yu-Chuan Lin

Acknowledgments

I gained valuable research experience and also obtained professional skills during my time in Department of Materials Science and Engineering at The Pennsylvania State University. After five years of hard work and some sleepless nights, I acheived one of my career objectives here: obtaining a Ph.D. degree. However, I would not have made it if there were no a good mentor and a group of wonderful and important friends who came alone at my graduate school. I would like to acknowledge Professor Joshua Robinson for offering me opportunities to exploit novel layered materials and their optoelectronic and providing me the necessary support and guidance for the success of it. He is a great mentor and always a wonderful academic father with good nature and enormous patience to me. I would like to recognize both Dr. Amy Robinson and Professor Joshua Robinson for offering me teaching assistant opportunities so I can interact with undergraduate students at Penn State, providing them short courses and laboratory instruction.

I would also like to recognize Professor Lain-Jong Li who first introduced me to materials science research when I was pursuing a master's degree in Department of Physics at National Taiwan University and also thank Professor Joan Redwing and Dr. Sarah Eichfeld for introducing me to metal-organic chemical vapor deposition for 2D semiconductors. I am thankful to my past and current colleagues at graduate school for assistance in research and insightful discussion. In particular, I would like to express my appreciation to Dr. Ganesh Bhinamapati, Brian Bersch, Kehao Zhang, Shruti Subramanian, Natalie Briggs, Jennifer DiStefano, Maxwell Wetherington, Chia Hui Lee, Lorrain Hossaine, Donna Deng, and Dr. Bhakti Jariwala for their instrumental help and collaboration within the group. I also thank my supportive collaborators outside Penn State, they are Professor Robert Wallace, Professor Susan Fullerton-Shirey, Professor Randall Feenstra, Professor Kyeongjae Cho, and their students and postdocs for unselfish collaboration and input on our collaborations in the Center for Low Energy Systems Technology (LEAST). I am also grateful to the LEAST program for its funding support for my graduate research and stipend.

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Contents

Parts of this thesis have been published in the following articles:

1. Lin Y-C, Ghosh RK, Addou R, Lu N, Eichfeld SM, Zhu H, Li M-Y, Peng X, Kim MJ, Li L-J, Wallace RM, Datta S, Robinson JA (2015) "Atomically thin resonant tunnel diodes built from synthetic van der Waals heterostructures," *Nat. Commun.* 6:7311. https://doi.org/10.1038/ncomms8311
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