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Synthesis of Large-Area 2D layered Materials and Their Heterostacking Structures

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14. ABSTRACT
Transition metal dichalcogenides (TMDs) have been recognized as a new class of semiconducting two-dimensional (2D) layered materials, which open up new opportunities in semiconductor technology for developing future 2D electronics and optoelectronics. Monolayer TMDs also feature their direct energy band gap, good carrier mobility and excellent ON/OFF current ratio when fabricated into field effect transistors, which are important properties for future low-power electronics and optoelectronics. For further applications in advanced circuits, the development of two-dimensional (2D) p-n junction is prerequisite. The research team has successfully shown the direct growth of atomically sharp p-n junction between WSe2 and MoS2. (Science, 349, 524 (2015)). This demonstrates the state-of-the-art growth in this field. The heterostructural interface presents a nice p-n junction, which is a key component for monolayer electronics.

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Abstract: Transition metal dichalcogenides (TMDs) have been recognized as a new class of semiconducting two-dimensional (2D) layered materials, which open up new opportunities in semiconductor technology for developing future 2D electronics and optoelectronics. Monolayer TMDs also feature their direct energy band gap, good carrier mobility and excellent ON/OFF current ratio when fabricated into field effect transistors, which are important properties for future low-power electronics and optoelectronics. For further applications in advanced circuits, the development of two-dimensional (2D) p-n junction is prerequisite. We have successfully shown the direct growth of atomically sharp p-n junction between WSe2 and MoS2. (Science, 349, 524 (2015)). This demonstrates the state-of-the-art growth in this field. The heterostructural interface presents a nice p-n junction, which is a key component for monolayer electronics.

Introduction: In this project, we focus on detailed mechanistic studies for the controlled growth of various lateral heterostructures. Strategic growth to achieve the direct formation of patterned devices based on various junctions shall also be carried out. The eventual project goal is to provide a foundation for the extreme scenario of future electronics, where only few strings of atoms (i.e. the 2D lateral junction) are used as the active components in electronic devices and circuits.
Details are listed below

(1) Study nucleation processes and explore methods to implant seeds at selected areas for subsequent 2DL material growth. Ideally, the growth of 1st 2DL materials can be guided by the location and shape of the seeds and the 2nd 2DL materials follows the morphology of the 1st 2DL materials.

(2) Study the epitaxial mechanism of the 2nd 2DL material on the edge of the existing 2DL materials. The epitaxial process may start from the lateral edge or the basal plane of the edge depending on the lattice, edge morphology of the 2DL materials and the growth regime (thermodynamically or kinetically controlled). Efforts will be spent to understand the mechanisms underlying the growth and lateral junction formation.

Experiment: The location-selective implement of seeds on substrates and related studies will be carried out. We will have 6 furnaces dedicated for the growth of TMD materials in Academia Sinica. Meanwhile, a customized cold wall chemical vapor deposition (CVD) system for growing wafer scale TMD has been designed and installed. In this project, we will be working on the growth of new types of various in-plane TMD-TMD structures and related devices including p-n junction diodes, bipolar junction transistors and photovoltaic cells based on TMD-TMD junctions.

- **Results and Discussion:** The 2D lateral WSe2-MoS2 heterojunction was synthesized on c-plane sapphire substrates by sequential chemical vapor deposition of WSe_2 and MoS_2 (Figure 1a), where the growth of individual TMDC material has been demonstrated. To avoid the alloy reaction observed in one-pot synthesis, we first prepare single crystalline triangular WSe_2 monolayer requiring a higher growth temperature (925 ^{O}C) and then perform the MoS2 growth at 755 ^{O}C in a separate furnace. The WSe_2 growth has been shown, where the WSe_2

seeds are formed followed by the van der Waals epitaxy on sapphire substrates. The crucial point for successful heterostructure synthesis without alloy formation is to control the relative vapor amount of MoO_3 and S during the 2nd step MoS_2 growth. The excess in Mo precursors may enhance the MoS_2 vertical growth, whereas the excess in S vapor promotes the formation of undesired WS_2 at the interface. An even worse situation is that the excess of any of the sources may result in the formation of alloy structures such as $Mo_xW_yS_zSe_t$. The morphology of in-plane heterostructures was examined by OM, PL and Raman spectroscopies. Figure 1b shows the OM image of the lateral WSe_2-MoS_2 heterojunctions. All the WSe_2 triangles in the sample are uniformly surrounded by MoS_2 and the domains for WSe_2 and MoS_2 can be distinguished from each other simply by their optical contrast. The lattice constant of WSe_2 is 5.53% larger than MoS_2, which might be one of the reasons restricting the growth of MoS_2 onto WSe_2 basal planes, but requires further studies. The Raman and photoluminescence spectra (not shown here) prove that the chemical composition of the inner WSe_2 and outer MoS_2, and these measurements also reveal the formation of seamless WSe_2-MoS_2 junctions.

STEM is used to investigate the atomic structure for the lateral WSe_2-MoS_2 junctions. Figure 1c shows the annular dark field (ADF) image obtained at the WSe_2-MoS_2 interface. The ADF-STEM signal increases with the atomic number Z by approximately Z1.7 31. Therefore, the W 74, Mo 42, Se 34, and S 16 atomic species can be clearly distinguished by their intensity. Figure 1d shows the ADF image for another location, where the atomic models corresponding to the obtained image are resolved with an atom-by-atom image quantification. One can see that an atomically sharp interface between the WSe_2-MoS_2 heterojunction is formed, where 90% of the W atoms are located at the interface bridging to two pairs of Se atoms and one pair of S atoms, as depicted in Figure 1e. In addition to the ADF image, the coherent interface is also identified by the electron energy loss spectroscopy (EELS) measurement. The EELS line scan (obtained by monitoring the EELS spectral change across the heterojunction) shown in Figure 1f-1i proves the atomically sharp change.

This observation indicates that the growth may start from the replacement of Se atoms of the WSe_2 edge by S atoms. These results demonstrate that the MoS_2 monolayer also out grows from the edge of the WSe_2 monolayer. This important feature enables the controlled growth of lateral patterns for future monolayer electronics. Based on these preliminary results, we also intend to develop the growth of the TMDs with a narrower band gap such as $MoTe_2$, WTe_2, FeS and others. These are also important components for monolayer electronics.

Most critical components in modern electronics/optoelectronics can be redesigned and produced based on this new class of 2D materials, where the great ability to tune the band gap, band offset, carrier density, carrier polarity and switching characteristics provide unparalleled control over device properties and possibly new physical phenomena. The new electronics based on 2DL materials is hence called “monolayer electronics”. Our research opens the path leading to future monolayer electronics. Also, the atomically sharp interface offers an interesting platform for the study of fundamental material science.

List of Publications and Significant Collaborations that resulted from your AOARD supported project: In standard format showing authors, title, journal, issue, pages, and date, for each category list the following:

a)papers published in peer-reviewed journals,

1. Title: Epitaxial growth of a monolayer WSe2-MoS2 lateral p-n junction with an atomically sharp interface
   Author(s): Li, Ming-Yang; Shi, Yumeng; Cheng, Chia-Chin; et al.
   Source: Science Volume: 349 Issue: 6247 Pages: 524-528 Published: JUL 31 2015
2. Title: Synthesis and structure of two-dimensional transition-metal dichalcogenides
   Author(s): Yumeng Shi; Hua Zhang; Wen-Hao Chang; et al.
   Source: {MRS} Bull. Volume: 40 Issue: 07 Pages: 566--576 Published: 2015
3. Title: Determination of band alignment in the single-layer MoS2/WSe2 heterojunction
   Author(s): Chiu, Ming-Hui; Zhang, Chendong; Shiu, Hung-Wei; et al.
   Source: Nature Communications Volume: 6 Pages: 7666 Published: JUL 2015
4. Title: Atomically Thin Heterostructures Based on Single-Layer Tungsten Diselenide and

Graphene
Author(s): Lin, Yu-Chuan; Chang, Chih-Yuan S.; Ghosh, Ram Krishna; et al.
Source: Nano Letters Volume: 14 Issue: 12 Pages: 6936-6941 Published: DEC 2014

5. Title: Spectroscopic Signatures for Interlayer Coupling in MoS2-WSe2 van der Waals Stacking
Author(s): Chiu, Ming-Hui; Li, Ming-Yang; Zhang, Wengjing; et al.
Source: Acs Nano Volume: 8 Issue: 9 Pages: 9649-9656 Published: SEP 2014
6. Title: Hole mobility enhancement and p-doping in monolayer WSe2 by gold decoration
Author(s): Chen, Chang-Hsiao; Wu, Chun-Lan; Pu, Jiang; et al.
Source: 2d Materials Volume: 1 Issue: 3 Published: DEC 2014
7. Title: Monolayer MoSe2 Grown by Chemical Vapor Deposition for Fast Photodetection
Author(s): Chang, Yung-Huang; Zhang, Wenjing; Zhu, Yihan; et al.
Source: Acs Nano Volume: 8 Pages: 8582-8590 Published: 2014
8. Title: Role of Metal Contacts in High-Performance Phototransistors Based on WSe2 Monolayers
Author(s): Zhang, Wenjing; Chiu, Ming-Hui; Chen, Chang-Hsiao; et al.
Source: Acs Nano Volume: 8 Pages: 8653-8661 Published: 2014
9. Title: Highly Flexible and High-Performance Complementary Inverters of Large-Area Transition Metal Dichalcogenide Monolayers
Author(s): Pu, Jiang; Funahashi, Kazuma; Chen, Chang-Hsiao; et al.
Source: Advanced Materials Volume: 28 Issue: 21 Pages: 4111-4119 Published: JUN 1 2016
10. Title: Janus monolayers of transition metal dichalcogenides
Author(s): Lu, Ang-Yu; Zhu, Hanyu; Xiao, Jun; et al.
Source: Nature Nanotechnology Volume: 12 Issue: 8 Pages: 744-+ Published: AUG 2017