論 文 の 内 容 の 要 旨

論文題目　Two-dimensional magnets grown by van der Waals epitaxy
（ファンデルワールス・エピタキシーによる2次元磁性体の研究）

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1. Introduction and motivation

After the discovery of graphene, emerging properties of two-dimensional (2D) materials with reduced thickness have attracted considerable attention both from fundamental and applied viewpoints. Among various 2D materials, transition-metal dichalcogenide (TMDC) is of particular interest due to its variety of physical properties ranging from semiconducting to metallic properties depending on the combination of transition metals and chalcogens as well as on the local lattice symmetry, providing various functionalities beneficial for electronic and optoelectronic device applications. Moreover, different magnetic properties could appear in TMDCs when intercalated with magnetic ions in a van der Waals gap, offering a good platform for research on magnetism with reduced dimensions. Current studies have been mainly done with mechanically-exfoliated nano-thick crystals from ‘top-down’ approach, while ‘bottom-up’ approach by thin film growth technique has been of growing significance to further exploration of physical properties and functionalities of TMDC and its heterostructures.

In this study, we employ molecular-beam epitaxy (MBE), the state-of-the-art technique enabling epitaxial growth of high-quality thin films and heterostructures of a wide variety of materials as verified in the research on group III-V and II-VI semiconductors. MBE has a great potential as a growth method for 2D materials research due to its unique functions like precise control of the layer number, which is essential for 2D materials research. MBE can also provide flexible combinations of intercalating elements, and TMDCs thin films with well-controlled ratio and growth speed should allow us to study magnetic properties of various 2D magnets. However, current TMDCs thin films by using MBE have been grown on conducting graphene layers formed on SiC substrates in most cases for spectroscopic studies including angle-resolved photoemission spectroscopy or scanning tunneling microscopy, and growth of large area TMDC epitaxial thin films on insulating substrates has been less successful despite its essential importance for fundamental transport studies as well as practical electronic and optoelectronic device applications.

In this study, our research motivation is to establish layer-by-layer MBE growth of TMDCs thin films on insulating substrates, and explore new transport and magnetic properties of a variety of compounds at 2D limit.

2. Film growth and characterization

In this study, commercially-available Al_2O_3 (001) single crystal is chosen as a substrate. Thin film growth was carried out in an ultrahigh vacuum chamber with a base pressure below ~ 1×10^{-7} Pa. Layer-by-layer growth mode has been confirmed by intensity oscillation of reflection high energy electron reflection (RHEED). Growth procedure has been optimized with a partly-covered amorphous buffer layer with thickness less than monolayer formed prior to film growth. We confirmed this optimized growth recipe could be broadly applicable for epitaxial growth of other TMDC thin films on Al_2O_3 substrates with high-enough crystallinity confirmed by X-ray diffraction (XRD), although lattice mismatches between films and substrates are usually very large, indicating unique nature of van der Waals epitaxy.

3. Properties of MBE-grown TMDC thin films and heterostructures

Among various TMDC thin films, we firstly investigated transport properties of 10 ML-thick WSe_2 and $TiSe_2$ thin films. WSe_2 is one of the semiconducting TMDCs. WSe_2 is chemically less active among other semiconducting TMDCs, and is suitable for future electronic and optoelectronic applications. We fabricated top-gate electric-double-layer transistors (EDLT) using ionic liquid, and characterized transistor performances by accumulating charge carriers on a surface of WSe_2. We confirmed WSe_2 film became highly conducting once electrons or holes were doped, with the minimum sheet resistance reached a few kilo-ohms, which is below the quantum resistance (h/e^2 ~ 25.8 kΩ). The number of mobile carriers and their mobilities accumulated by electrolyte gating were evaluated by Hall-effect measurements, with clear Hall signals for hole-accumulation regime with the maximum mobility of about 3 cm^2/Vs at T = 150 K, which was in the highest level reported for the first-generation CVD-grown MoS_2 thin films.

$TiSe_2$ is a semimetal, which exhibits a charge-density wave (CDW) ground state with the transition temperature of about T = 200 K in a bulk. The dimensionality effect on the electronic properties of 1T-$TiSe_2$ has been examined by angle-resolved photoemission spectroscopy, but there has been no report on transport properties of $TiSe_2$ at a few layer thickness regime. We established the growth process of $TiSe_2$ by MBE on insulating sapphire substrate and confirmed interesting "self-rotational' growth by in-plane XRD, with the epitaxial relationship of both $TiSe_2$ [100] // Al_2O_3 [100] and $TiSe_2$ [110] // Al_2O_3 [100]. We demonstrated transport measurements on $TiSe_2$ and confirmed existence of the CDW transitions down to 5 monolayers (3 nm). In addition, we found that the carrier density could be reduced by increasing the Se/Ti flux ratio during $TiSe_2$ thin film growth, leading to metal-to-insulator transition. We further found that the electron doping by EDLT also led to suppression of the CDW transitions.

To further broaden the scope of material and expand the horizons of the research area, we developed a new class of van der Waals heterostructures consisting of two sets of insulating TMDCs, group-VI WSe_2 and group-IV $TMSe_2$ (TM = Zr, Hf), by MBE, and found that those heterostructures are highly conducting despite that all the constituent materials are highly insulating. WSe_2 / $ZrSe_2$ interface exhibited more conducting behavior than WSe_2 / $HfSe_2$ interface, which could be understood by considering the band alignments between constituent materials. Moreover, by increasing Se flux during heterostructure fabrication, WSe_2 / $ZrSe_2$ interface became more conducting, reaching to nearly metallic behavior. Further improvement of the crystalline quality as well as exploring different material combinations are expected to lead to metallic conduction, providing a novel functionality emerging at van der Waals heterostructures.

4. Properties of MBE-grown magnetic TMDC thin films

The discoveries of intrinsic ferromagnetism in atomically-thin van der Waals crystals have opened up a new research field enabling fundamental studies on magnetism at 2D limit as well as development of magnetic van der Waals heterostructures. To date, a variety of 2D ferromagnetism has been explored mainly by mechanically exfoliating 'originally ferromagnetic' van der Waals crystals, while bottom-up approach by thin film growth technique has demonstrated emergent 2D ferromagnetism in a variety of 'originally non-ferromagnetic' van der Waals materials. In particular, intercalation of 3*d* magnetic ions into the van der Waals gap of TMDCs should provide a variety of 2D magnets, which is difficult to obtain by the 'top down' mechanical exfoliation method. In this study, we focus on the magnetic properties of the self-intercalated TMDCs, V_5Se_8 and Cr_3Te_4.

For the study on V_5Se_8, we found that our standard MBE process provides V_5Se_8, a self-intercalated compound having periodically-aligned V layers in between the 2D VSe_2 layers. Interestingly, those MBE-grown V_5Se_8 thin films exhibited 2D ferromagnetism with intrinsic spin polarization of the V 3*d* electrons as confirmed by the anomalous Hall effect and the X-ray magnetic circular dichroism measurements, although the bulk counterpart has been known to be an itinerant antiferromagnet. Moreover, spontaneous magnetic order was totally suppressed at 2D limit (trilayer V_5Se_8), indicating that a few-layer V_5Se_8 could be classified as an itinerant 2D Heisenberg ferromagnet with weak magnetic anisotropy.

As for a second topic, we investigated 2D ferromagnets with high Curie temperature (T_C). Recent study has revealed possible room temperature ferromagnetism in VSe_2, while there have been many discussions and enigma on the origin of its ferromagnetism. To achieve room temperature ferromagnetism, one promising candidate is chromium telluride, which has been known to possess T_c ranging from 220 K to 340 K depending on the chromium intercalation level. In this study, we grew chromium telluride epitaxial thin films by MBE, and successfully identified based on the detailed analysis on the structural and magnetic properties that the composition of our samples is Cr_3Te_4. Interestingly, we found that T_C of the as-grown samples were about 160 K, but it increased up to 310 K by post-growth annealing. Moreover, we found that T_C of the samples without annealing was almost thickness-independent down to 2D limit (bilayer). This is in sharp contrast with many other magnetic thin films including the annealed Cr_3Te_4 system, where T_C shows a decrease down to 200 K at 2D limit (trilayer).

4. Summary

We have developed a growth process of high quality TMDC thin films by MBE, and succeeded in establishing a versatile route to layer-by-layer epitaxial growth of millimeter-scale TMDC thin films and heterostructures on commercially-available insulating sapphire substrate by MBE. We have also succeeded in observing various transport and magnetic properties in TMDCs with thickness down to 2D limit. In particular, we unambiguously showed that intercalation of magnetic ions is a powerful means to broaden a lineup of 2D magnets. Based on this research, we believe that not only new 2D materials but also van der Waals heterostructures and artificial superstructures could be obtained by taking the advantage of van der Waals epitaxy, leading to a rich platform of new functional materials.