博士論文（要約）

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）

王　越

Abstract

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. 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. Our main results are:

- Demonstration of film growth procedure: We succeed in developing a fundamental route to well-controlled growth of high-quality TMDC thin films on insulating substrates with desired thickness and crystallographic orientation by molecular-beam epitaxy (MBE). 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 Al2O3 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.

- Transport properties of TMDCs thin films: WSe_2 and $TiSe_2$ thin films are synthesized with high crystallinity. We fabricated top-gate electric-double-layer transistors (EDLT) on WSe_2 using ionic liquid, and characterized transistor performances. We confirmed WSe_2 film became highly conducting once electrons or holes were doped, 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. We 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.

- 2D ferromagnetism in TMDCs thin films: we focus on the magnetic properties of the self-intercalated TMDCs, V_5Se_8 and Cr_3Te_4. For 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. For Cr_3Te_4, we successfully identified its phase based on the detailed analysis on the structural and magnetic properties. 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, thickness dependence of these annealed and non-annealed samples showed significant difference.