Title	層状III族モノカルコゲナイド薄膜のファンデルワールスヘテロ界面微細構造に関する研究
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Atomistic Study on van der Waals Heterointerface Structures of Layered Group-III Monochalcogenide Thin Films

Takahiro Yonezawa

Owing to a wide range of physical properties tunable through their composition, the number and stacking of layers, and the intralayer structures, layered materials (LMs) are of great interest for various applications in electronic, optical and thermoelectric devices. The absence of dangling bonds at the surface of individual layers allows LMs for being epitaxially grown on various templates via weak van der Waals (VDW) interaction regardless of the lattice mismatch, which is called "VDW epitaxy (VDWE)". Since the 1980's, a lot of examples of growth of LMs on different materials by VDWE have been reported. However, the growth of large-scale single-crystalline films remains a key challenge. Also, the atomic structure near the film-substrate interface is poorly documented, in spite of its strong influence on the crystallographic structure of the LMs thin films. In this study, gallium and indium selenide (GaSe and InSe) thin films were grown on semiconducting substrates such as Ge(111) and GaAs(111) by molecular-beam epitaxy (MBE). GaSe and InSe are semiconducting LMs with great expectations for optical and electronic devices. The thin film structures were analyzed using X-ray diffraction (XRD), reflection high-energy electron diffraction (RHEED), scanning tunneling microscopy (STM), atomic force microscopy (AFM) and scanning transmission electron microscopy (STEM).

Chapters 1 and **2** of the thesis give, respectively, a general introduction of this research and a description of the experimental methods.

Chapter 3 presents the investigation of the VDWE growth of GaSe and InSe thin films. The thin films were grown with the substrate temperature $T_{sub.}$ between 300 °C and 550 °C and with different ratios of the evaporation rates of Se and Ga or In. The growth of single crystalline thin films was found to require a fine tuning of the growth conditions. Ga- and In-rich conditions gave rise respectively to Ga droplets and to elongated crystallites in the InSe thin films. In contrast, Se-rich phases like Ga_2Se_3 or α-, β-, γ-In_2Se_3 and In_3Se_4 form under Se-rich or low $T_{sub.}$ conditions. The growth of single-phase GaSe thin films was found to require Se-rich conditions and $T_{sub.}$ set between 400 °C and 550 °C. Almost perfect single-phase InSe thin films with the best crystallographic quality were obtained for balanced evaporation rates of In and Se and a relatively high $T_{sub.}$ of 500 °C. GaSe and InSe thin films were grown with (Ga, In)Se(0001) // Ge(111) and (Ga, In)Se$[11\bar{2}0]$ // Ge$[1\bar{1}0]$ epitaxial relationships. In addition, a strong temperature dependence of the terrace shape of the GaSe thin films was found: The shape of the terrace edges changes from rounded hexagonal to triangular when T_{sub} is increased from 400 °C to 500 °C.

In **chapter 4**, suitability of sample thinning process based on focused-ion beam milling for plan-view STEM observations of Moiré patterns resulting from the overlapping of a LM thin film and a substrate is demonstrated. Then, an accurate determination of the local variation of the in-plane orientation of GaSe thin films with respect to the Ge(111) substrate by means of STM and plan-view STEM is presented. The Moiré pattern observed by plan-view STEM confirms an almost perfect GaSe$[11\bar{2}0]$ // Ge$[1\bar{1}0]$ epitaxial relationship. Meanwhile, Moiré patterns observed by STM indicate the existence, locally at the interface, of small in-plane deviations from this orientation. These results indicate that the local misorientations of LMs at the nucleation stage disappear with the increased number of layers.

In **chapter 5**, the investigation of the atomic structures near the interface between the GaSe or InSe thin films and the Ge(111) or GaAs(111) substrates observed by cross-sectional STEM is presented. Strain-free GaSe and InSe thin films were grown with the same optimized condition on Ge(111) and on the As face of GaAs(111). The epitaxial relationship of (Ga, In)Se(0001) // GaAs(111) and (Ga, In)Se$[11\bar{2}0]$ // GaAs$[1\bar{1}0]$ was adopted. The dangling bonds of the Ge(111) were terminated by a half GaSe or InSe monolayer and those of the GaAs(111) were terminated by Se atoms. The GaSe and InSe individual layers adopted the expected trigonal prismatic structure, but also a non-prismatic (NP) structure, which has not been reported yet. Since the NP layers were formed regardless of the type of substrate and the lattice mismatch, it is likely that they are stabilized by the growth conditions: Single-phase NP GaSe thin films were grown with Se-rich conditions and low T_{sub}. The rounded hexagonal shape of GaSe islands shown in chapter 3 can be explained by the formation of the NP GaSe phase in the thin film.

These achievements contribute to a better knowledge and understandings of the structures of GaSe and InSe thin films, their growth conditions and formation mechanism in VDWE. The discovery of novel NP GaSe and InSe phases suggests that the world of LMs is much richer than expected.

Keywords: GaSe, InSe, VDW epitaxy, STEM, Moire pattern, Layered materials, MBE, SPM