Exploration and Creation of New Two-dimensional Materials on Substrates by First-principles Calculations and Experiments

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Gallium selenide (GaSe) is a layered post-transition metal monochalcogenide with a 2 eV band gap which is also known to be a good nonlinear optical material owing to the non-centrosymmetry of its trigonal prismatic crystal structure. A GaSe monolayer is composed of four atomic layers in a Se-Ga-Ga-Se sequence. The investigation of the GaSe(0001) thin films our group has recently succeeded the growth on Ge(111) substrates by molecular beam epitaxy (MBE) revealed that the existence of two novel two dimensional (2D) structures. The Ge(111) substrate is terminated by a buckled GaSe two-dimensional (2D) honeycomb structure with the same lattice parameter as the Ge(111) substrate. In addition, separated by a van der Waals gap, a new GaSe polymorph in which the monolayers have a trigonal-antiprismatic structure, was found near the Ge(111)/GaSe(0001) interface. In this thesis, the physical properties of these two novel 2D materials were investigated by means of ab initio calculations and experiments. The study of the GaSe half-layer is motivated by the fact that it is a 2D material with a structure resembling that of silicene and similar 2D materials and giving rise to interesting electronic states. Unlike transition metal dichalcogenides, the physical properties of metal monochalcogenides have to be explored in detail. In particular, it is important to clarify the influence of the crystal symmetry on the fundamental physical properties.

Chapter 1 is a general introduction of the thesis whereas chapters 2 and 3 give descriptions of the computational and experimental methods, respectively.

Chapter 4 presents the investigation by means of first-principles calculations of the difference in structural stability, electronic structure and optical properties between the conventional prismatic phase of GaSe (called P-phase) and the recently discovered antiprismatic phase (AP-phase). Although the equilibrium lattice parameter of AP phase is almost the same as that of the P-phase GaSe, the AP-phase is more stabilized than P phase by tensile stress in the in-plane direction. The stabilization mechanism is attributed to the difference in the Se-Se repulsive interaction between the two phases. Nudged elastic band(NEB) and molecular dynamics(MD) calculations, indicate that the AP-phase GaSe is unlikely formed by a phase transition from the P-phase, but rather by the direct nucleation of the AP-phase during the growth. This suggests that the AP-phase of GaSe can be grown by nonequilibrium processes which is consistent with our previous experimental study. Although the band structures of both phases are similar, small variations in the optical properties are found for photon energies above 2eV, which are due to different inter-band transition.

Chapter 5 addresses the study of the GaSe half layer terminating the Ge(111) substrate. First principles calculations reveal the existence of a Dirac cone-like dispersion near the Γ point The analysis of the pseudo-atomic orbital contribution shows that the Dirac cone is caused by the interaction between the half-layer GaSe and the surface states of Ge(111). The calculated electronic structures of GaSe half layers on substrates such as Si(111) and InSb(111)B feature no Dirac cone like dispersion which suggests that the Ge (111) surface plays an important role in its emergence.

Chapter 6 presents the preparation of GaSe half-layers samples by MBE and the characterization of their electronic properties. The valence band dispersion was determined by angle resolved photoemission spectroscopy (ARPES). The experimental spectra are consistent with the results of first-principles calculations shown in chapter 5. The fact that the top of the valence band is located at the Fermi level indicates that the system is p-doped. Although the Dirac point is located above the Fermi level and thus cannot be seen, the band predicted to originate from from the half-layer GaSe was observed. The characterization of the electronic states after exposure to ambient air showed that the GaSe half-layer is not robust against oxidation and needs a protective layer.

By revealing the physical properties of AP-phase GaSe and GaSe half-layer on Ge(111), this thesis contributes to a new variety in 2D materials. The revelation of the physical properties of AP-phase GaSe is a major step in the exploration of metal monochalcogenides and their polymorphes and will give insightful indications for to the search of similar novel materials. In addition, the discovery of the existence of a AP-phase GaSe possibly coexisting with the the P-phase and possessing different optical properties, is expected to help analyzing the results of the characterization of the optical properties of GaSe thin films. The discovery of the unique electronic structure of GaSe half-layer is expected to guide the design of new two-dimensional materials taking advantage of the interaction with the substrate.

Keywords: GaSe, Layered materials, MBE, DFT, Dirac cone