Theoretical investigation on surface/interface optimization and property analysis of novel 2D materials

論 文 の 内 容 の 要 旨

論文題目　　Theoretical investigation on surface/interface optimization and property analysis of novel 2D materials
（新奇2次元材料の表面／界面最適化と物性解析に関する理論研究）

氏　　名　　倪　澤遠

Layered 2D materials have existed for ages, but not until the beginning of this century have the researchers realized the true potential of them. Their reduced dimension and the accompanied exotic properties, like ultra-clean surface, flatness, flexibility, transparency, superconducting phenomenon, and topological electronic structure, are possible to lead the world to break the bottleneck in microelectronics and energy converting technology. In recent years, the family of 2D materials has been rapidly expanded to monoelemental layers (silicene, phosphorene, etc.), transition metal dichalcogenides (TMD) and MXenes, towards future applications in microelectronics, light emission, and energy storage. Nevertheless, the understanding of novel 2D materials in their surfaces/interfaces, such as 2D materials with substrate interaction and surface relaxation, is still far from thorough. In this dissertation, we use the first-principles calculations to investigate the surface/interface properties of novel 2D materials, including germanene, stanene and WTe_2, and use materials informatics search for exploring the optimal interfaces to preserve the geometry and exotic properties of germanene and stanene. The word “optimization” in the title means both geometric optimization of surface/interface structure (by DFT) and selection of optimal interfaces (by materials search).

In Chapter 1, a brief introduction about Moore’s law, novel 2D materials in general, germanene and stanene, WTe_2, and topological insulators is given. We point out that germanene and stanene are more suitable for spintronic devices compared to graphene due to their larger spin-orbit coupling (SOC), but they still lack semiconducting substrates that can preserve their Dirac-cones and band gaps in experiment. They are also topological insulators with non-trivial Z_2 invariant and chiral edge state (or quantum spin Hall effect) in their intrinsic forms. We also point out that WTe_2 has unsaturated magneto resistance at an external magnetic field over 50 T, but the surface relaxation and its impact still remain untouched.

In Chapter 2, the methodologies used in this work are introduced, including the density functional theory (DFT), Z_2 topological invariant calculation, and materials search by data mining.

In Chapter 3, the research about group III monochalcogenides (MX) as suitable substrates for germanene is presented. By using DFT, we find that germanene can preserve its low-buckled geometry and Dirac-cone-like band structure on MX like in its free-standing case in the most energetically preferable configuration considering the van der Waals (vdW) interaction (Figure 1a). Furthermore, germanene on GaTe and InSe is semiconducting with a band gap of 0.14 ~ 0.16 eV predicted by hybrid functional calculations (Figure b). The effective masses at the Dirac point of germanene remain as small as 0.05 ~ 0.06 times the free electron mass, leading to an ultrahigh carrier mobility estimated to be up to 2.2×10^5 $cm^2V^{-1}s^{-1}$. The band splitting caused by the SOC can be up to 42 meV, which suggests that this system may have potential for room temperature quantum spin Hall material. Molecular dynamics calculations show that germanene's structure on MX will not be destroyed under 500K. In addition, we find that multilayer MX can also serve as a suitable substrate for germanene, so the (001) surface of bulk MX may be a good candidate.

In Chapter 4, the materials search for the suitable substrates for germanene and stanene is presented. We use data mining to filter out suitable 2D substrate candidates for germanene and stanene that can preserve their geometric structures and Dirac-cones. After that, DFT calculations are performed to examine whether the substrate is truly suitable. According to our calculation, germanene can preserve its Dirac-cone on CdI_2, ZnI_2, GeI_2, MgI_2 and GaGeTe with stable quasi-free-standing structures (Figure 2a). We have also found two suitable substrates for stanene, namely PbI_2 and CaI_2, using the same method. The discovered substrates are all real materials, some of which has been used before as the substrate for vdW epitaxial growth, like CdI_2 and PbI_2. Moreover, atomically thin film of PbI_2 has been synthesized experimentally. We have performed geometry optimization and then investigate the phonon dispersions, band structures and Z_2 invariants of the germanene-substrate systems. The distance between the substrates and germanene is rather large (>3 Å) after optimization with a very small binding energy of ~15 meV/Å^2. On suitable substrates, supported germanene preserves Dirac-cone-like band structure near the K point with a small band gap opened (Figure 2b), whose size ranges from nearly zero to about 0.18 eV. Interestingly, the effective mass of germanene has almost perfect linear relationship with the band gap size (Figure 2c), and the Z_2 invariant of germanene is also changed from 1 to 0 on most substrates (Figure 2d), indicating the occurrence of a topological phase transition of

germanene, although the interaction is vdW-like. To explain the above phenomenon and the different Z_2 on different substrates, we fit the DFT bands of the supported germanene by the tight binding Hamiltonian of free-standing germanene under external fields and find that the substrate acts mainly like a pseudoelectric field. The external Rashba coefficient and the charge transfer between germanene and the substrate are found to have linear relationship with the pseudoelectric field strength. (Figure 2c)

In Chapter 5, the surface relaxation of WTe_2 is investigated. In experiment, which is not a part of this dissertation but is introduced briefly, tensor low-energy electron diffraction (LEED) analysis determines that WTe_2 has finite surface relaxation with a damped oscillation in the buckling of crystallographic atomic planes z_1~z_6 (Figure 3a, left). In this work, such damped oscillation is verified by the DFT calculation of a 7-layer WTe_2 slab (Figure 3a, right). Furthermore, the presence the surface reconstruction will affect the band structure, Fermi surface and the ratio of electron and hole carriers of the surface of WTe_2. The surface-projected bands at the Γ point with surface reconstruction are slightly left up compared to bulk-like structure. Corresponding to the evolution of the band structure, the topology of the rings at the Fermi surface differs as well (Figure 3b, c). The ratio between electron and hole carriers is also changed by the surface relaxation. One of the surface is electron-rich, while the other is hole-rich. With the surface relaxation, the electron-rich surface will have higher ratio, i.e. more electron-rich, and the hole-rich one will have lower ratio, i.e. more hole-rich. These results demonstrate that the surface relaxation has non-negligible impact on the electronic structure and possibly also on the magnetoresistance according to the two-band model.

In summary, interface optimization of germanene and stanene and the surface relaxation of WTe_2 are investigated in this dissertation. Several suitable substrates are found for germanene and stanene by materials search, and their effect is explained as the pseudoelectric field. Finite surface relaxation of WTe_2 is confirmed, which affects the band structure, Fermi surface, and electron/hole concentration of the surface.