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Structure and electronic properties of transition metal dichalcogenide MX_2 (M = Mo, W, Nb; X = S, Se) monolayers with grain boundaries

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HIGHLIGHTS

- Atomistic structures of GBs in MX_2 (M = Mo, W, Nb; X = S, Se) monolayer were identified.
- Stability of GBs in the MX_2 (M = Mo, W, Nb; X = S, Se) monolayer were studied.
- Electronic properties of GBs in the MX_2 (M = Mo, W, Nb; X = S, Se) monolayer were studied.
- Defect levels induced by the GBs are located within the band gap of semiconducting MX_2.
- NbS_2 and $NbSe_2$ remain as metallic materials within grain boundaries.

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ABSTRACT

Layered transition metal dichalcogenides with unique mechanical, electronic, optical, and chemical properties can be used for novel nanoelectronic and optoelectronic devices. Large-area monolayers synthesized using chemical vapor deposition are often polycrystals with many dislocations and grain boundaries (GBs). In the present paper, atomic structure and electronic properties of MX_2 (M = Mo, W, Nb; X = S, Se) with the GBs were investigated using first principles based on density functional theory. Simulation results revealed that the zigzag-oriented GBs (which consist of pentagon/heptagons (5-7) pairs) were more stable than the armchair-oriented GBs (which consist of pentagon/heptagons (5-7-5-7) pairs). The GBs induced defect levels are located within the band gap for the semiconductor materials of MX_2 (M = Mo, W; X = S, Se) monolayers, and the NbS_2 and $NbSe_2$ remained as metallic materials with GBs. Results provided a possible pathway to build these nano-layered materials into nanoelectronic devices.

1. Introduction

Dimensionality plays an important role in determining the fundamental properties of materials. Changes in the interlayer coupling, degree of quantum confinement, and symmetry will lead to dramatic differences in electronic properties of the materials. For example, two dimensional (2D) graphene shows an extraordinary linear dispersion for charge carriers and other unique physical properties compared with bulk graphite [1,2]. The discovery of the graphene obtained by mechanical exfoliation of graphite sparked tremendous interest in 2D nanomaterials [3]. The 2D nanomaterials are also promising candidates for nanoscale and flexible electronic applications, such as low-power, high-frequency, and flexible nanodevices [4–6]. The presence of a gap in the electronic band is an essential requirement for the realization of common electronic devices such as transistors. The lack of an intrinsic band gap for the graphene limits its application in logic electronics [7]. It is necessary to find other 2D materials with a finite band gap. Layered transition metal dichalcogenides (TMDs), MX_2, (where M and X correspond to transition metal and chalcogen, respectively, e.g. MoS_2), have emerged as competing materials for nanoelectronics.

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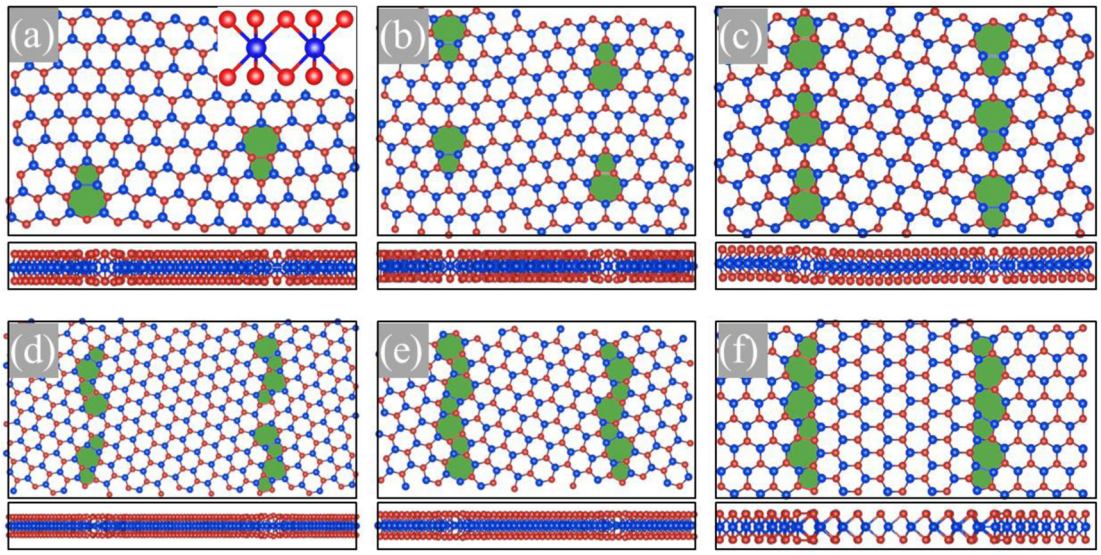

Fig. 1. Top view and side view of the atomistic structure of MX_2 monolayers with GBs. The blue and red balls represent the M and X atoms, respectively. (a)–(c) zigzag- and (d)–(f) armchair-oriented GBs. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

The monolayer of MX_2 consists of a covalently bonded slab of X-M-X layer [8], which typically has an average thickness of 6–7 Å, and consists of a hexagonally packed layer of metal atoms sandwiched between two layers of chalcogen atoms. Electronic properties of the TMDs vary from semiconducting (e.g., WSe_2) to superconducting (e.g., $NbSe_2$). The semiconducting monolayer TMDs, such as MoS_2, $MoSe_2$, $MoTe_2$, WS_2, and WSe_2, etc., were predicted to exhibit a direct band-gap in the range of 1–2 eV [9]. The indirect to direct band-gap transition of MoS_2 has been confirmed by the strong photoluminescence in a thinned monolayer [10,11]. The chemistry of MX_2 compounds thus offers opportunities for exploring nanoelectronics beyond graphene and opening up new fundamental and technological pathways for inorganic 2D materials. Such monolayer systems not only have a direct band-gap with highly desirable optical properties, but also possess a high carrier mobility for potential applications in nanoelectronics. For examples, a monolayer of MoS_2 has been successfully employed to fabricate low-power field effect transistors [5], logic circuits [12], and phototransistors [13]. The hexagonal symmetry, large spin-orbit coupling, and lack of inversion symmetry of the monolayer MoS_2, give rise to a band

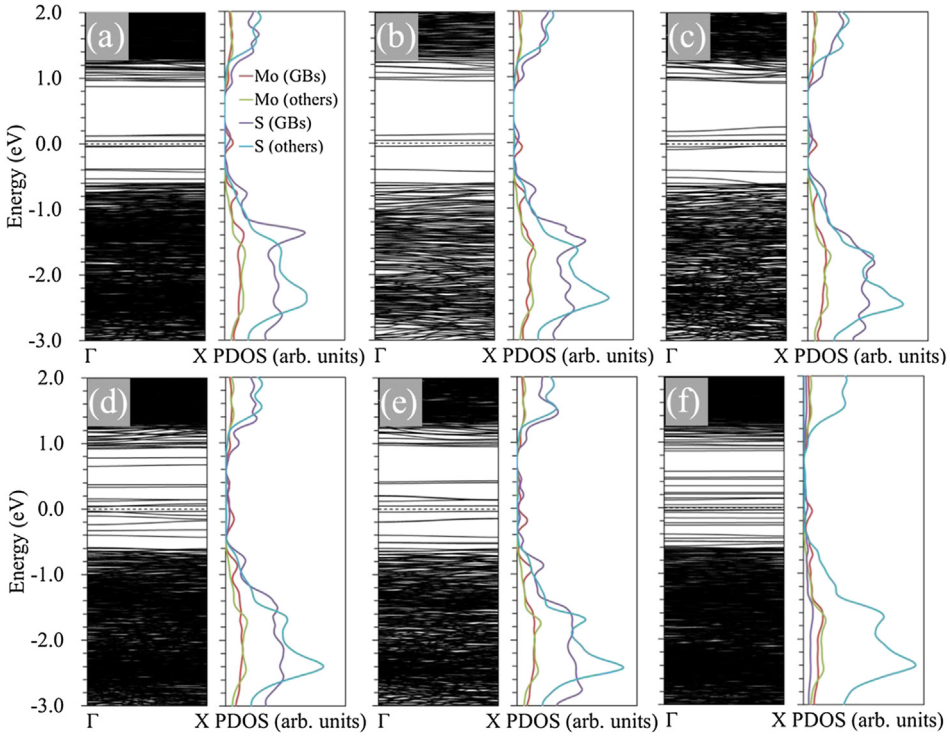

Fig. 2. Band structures along the GBs and site projected density of states (PDOS) of the MoS_2 monolayer with GBs. Fermi energy is set to be 0 eV. (a)–(f) correspond to the atomic structures of (a)–(f) in Fig. 1.