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A microscopic study investigating the structure of SnSe surfaces

Sang-ui Kim, Anh-Tuan Duong, Sunglae Cho, S.H. Rhim *, Jungdae Kim *

Department of Physics and EHSRC, University of Ulsan, Ulsan 680-749, South Korea

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ABSTRACT

SnSe has been widely studied due to its many potential applications that take advantage of its excellent thermoelectric, photovoltaic, and optoelectronic properties. However, experimental investigations into the microscopic structure of SnSe remain largely unexplored. Herein, for the first time, the atomic and electronic structures of SnSe surfaces are studied by a home-built low temperature scanning tunneling microscope (STM) and density functional theory (DFT) calculations. The cleaved surface of SnSe is comprised of covalently bonded Se and Sn atoms in zigzag patterns. However, rectangular periodicity was observed in the atomic images of SnSe surfaces for filled and empty state probing. Detailed atomic structures are analyzed by DFT calculations, indicating that the bright extrusions of both filled and empty state images are mostly located at the positions of Sn atoms.

1. Introduction

When a material is synthesized with low dimensionality, new physical properties that are radically different from the bulk can emerge. One of the most representative examples is graphene, which exhibits Dirac fermion behavior that is not found in highly-ordered pyrolytic graphite (HOPG) [1,2]. Recently, layered chalcogenide materials (LCMs), such as MoS_2, SnSe, and WSe_2, have been intensively studied due to their potential applications for next generation devices [3–6]. Each layer of an LCM is coupled by weak van der Waals interactions, just like HOPG. This means that a simple mechanical exfoliation method that was developed for graphene can also be applied to prepare two-dimensional LCMs.

Among the various LCMs, SnSe is a IV–VI semiconductor with a band gap of 0.89 eV [7]. Single-crystal SnSe usually exhibits p-type characteristics. SnSe is well-known for its high stability and elemental abundance in the earth's crust. Recently, SnSe has attracted extensive attention for a variety of potential applications due to its excellent physical properties [8–10]. For example, Zhao et al. reported exceptional thermoelectric properties of SnSe single crystals, which showed $ZT = 2.6 \pm 0.3$ at 923 K; here, Z is a figure of merit and T is the absolute temperature [5]. They attributed such a high ZT value to the remarkably low thermal conductivity at high temperatures. Substantial enhancements in the quantum efficiency and short-circuit current density were observed in photovoltaic devices utilizing SnSe nanocrystals [11]. SnSe is also considered to be a promising lead-free chalcogenide for a variety of optoelectronic applications [12,13]. Even though many of the papers that have investigated SnSe have proposed a variety of potential applications, surprisingly little information is available regarding the microscopic structure of SnSe surfaces [14].

In this report, the surface of single-crystal SnSe was investigated via a home-built low temperature scanning tunneling microscope (STM) [15]. Along the cleaved plane, Se and Sn atoms are connected by strong covalent bonds in zigzag formations (see Fig. 1). Clear atomic images of cleaved SnSe surfaces were observed at the filled and empty state measurements. The atomic structures revealed the periodicity of a rectangular unit cell. Additionally, for the first time, detailed atomic structures were analyzed based on density functional theory (DFT) calculations. We found that only Sn atoms are visible on STM topographic images for both filled and empty state probing. This can be attributed to the structural buckling between Sn and Se atoms.

2. Experiment

Single-crystal SnSe was synthesized by a temperature gradient growth method. High purity (99.999%) tin (Sn) and selenium (Se) powders were loaded into a two-layer quartz ampoule and sealed under vacuum ($<10^{-4}$ Torr). The sealed ampoule was then mixed and loaded into a vertical furnace. The temperature was slowly increased up to 930 °C and maintained for 10 h. Finally, the temperature was slowly cooled down to room temperature. Experiments were conducted in a home-built low temperature STM system at a base pressure $<1.0 \times 10^{-10}$ Torr [15]. A single-crystal SnSe sample was transferred into the STM chamber and cleaved in-situ to obtain clean surfaces. Tungsten tips were prepared by electrochemical etching and cleaned with electron beam heating for STM measurements. All STM experiments were carried out at 78 K.

First-principle calculations have been performed using the full-potential linearized augmented plane wave (FLAPW) method [16], as implemented in flair [17]. An STM image is calculated from a slab consisting of two layers which has total four atomic monolayers. To remove spurious interactions between layers, the vacuum distance is

* Corresponding authors.
E-mail addresses: sonny@ulsan.ac.kr (S.H. Rhim), kimjd@ulsan.ac.kr (J. Kim).

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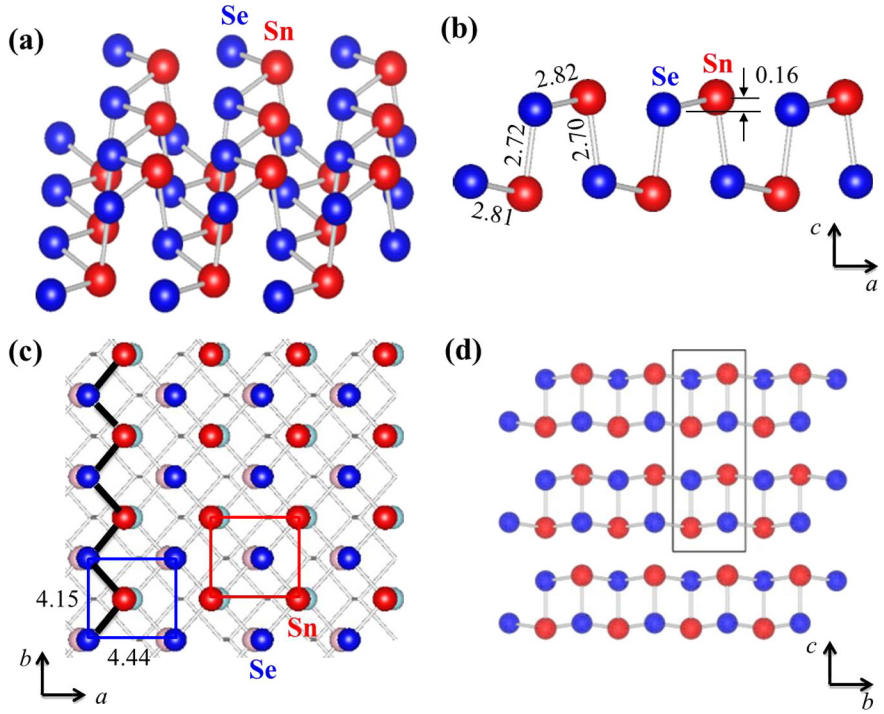

Fig. 1. (a) A perspective view of one SnSe layer. (b) The cross-sectional view presents the buckling structure of the SnSe layer. The lengths of each Se-Sn bond are provided in angstroms. (c) Top-view of SnSe, where Se and Sn atoms at the top layer are shown in blue and red balls, respectively. Two identical rectangular unit cells of Se and Sn atoms are marked as blue and red boxes, respectively. The zigzag bonds of Se and Sn atoms are indicated by black thick lines. The given numbers indicate the size of a unit cell in angstroms. (d) Side-view of SnSe. The box presents the bulk unit cell. Van der Waals stacking direction is chosen as c-axis. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

taken to be 20 Å. Brillouin zone summation is done with a $9 \times 9 \times 3$ k mesh. Generalized gradient approximation (GGA) by Perdew, Burke, and Ernzerhof (PBE) parameterization [18] is adopted for the exchange-correlation potential. The atomic coordinates are fully relaxed with a force criterion of 0.001 eV/Å. Simulated STM images are obtained from iso-density contours of 10^{-5} e/a_B^3, where a_B is the Bohr radius. This corresponds to the constant current mode in experiment [19,20].

3. Results and discussion

Perspective views of the SnSe structure, space group *Pnma*(#62), are provided in Fig. 1. One layer of SnSe consists of two-atom-thick structures along the *ab*-plane. Each layer is formed by strong covalent bonding between Se and Sn atoms, while weak van der Waals forces hold these layers together [21]. The structure of SnSe is identical to that of black phosphorus with the exception that Sn atoms are slightly buckled upward in the *c*-direction [22]. It should be noted that Se and Sn atoms are connected in a zigzag fashion along the *ab*-plane, as shown in Fig. 1(c). Fig. 2(a) shows the XRD spectrum of single-crystal SnSe along the cleavage plane, which shows a well-oriented structure along the *c*-axis. SnSe was cleaved inside a UHV chamber to obtain uncontaminated surfaces, which are critical for STM experiments. Clean SnSe (001) surfaces were confirmed from the STM topographic image shown in Fig. 2(b). At room temperature, the crystal structure of SnSe can be understood as a distorted NaCl structure (orthorhombic structure) [10].

Clear atomic images along the cleavage plane were measured by STM for both filled and empty state probing. We found that not all atoms were resolved in the observed STM images compared with the zigzag surface structures of the *ab*-plane in Fig.1(c). Fig. 3(a)–(c) presents the STM topographic images observed in empty states with various sample biases. Instead of a zigzag pattern, a rectangular unit cell (see the black box in Fig. 3(a)) can be found in the empty state

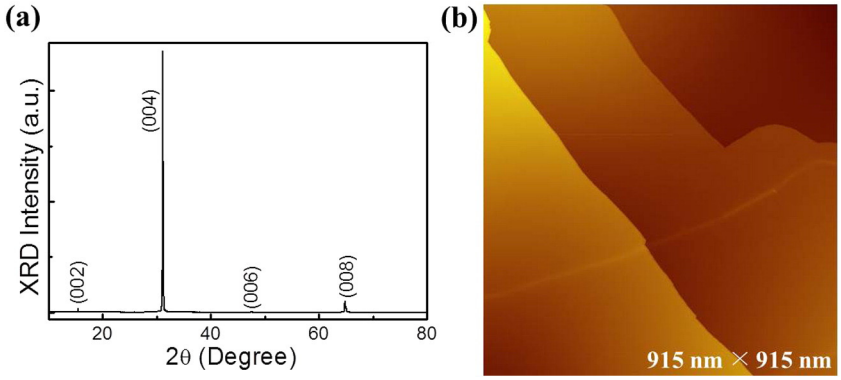

Fig. 2. (a) XRD spectrum of SnSe along the cleavage plane. (b) STM topographic image obtained from the in-situ cleaved (001) surface of SnSe (V_{sample} = 2.5 V, $I_{tunneling}$ = 30 pA).