First principle band calculations of Mg$_2$Si thin films with (001) and (110) orientations

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We investigate the surface band structure in Mg$_2$Si thin films using the first principle band structure calculations. When the film is stacked along the [001] direction, surface band structures appear inside quantum confinement band structures originates from the bulk band structure. When the film is stacked along the [110] direction, the semiconductor gap retains while a direct band gap appears.

1. Introduction

Magnesium silicide, Mg$_2$Si has been known as a promising candidate for the thermoelectric applications at mid-range temperature (600-900 K). The fundamental semiconducting properties of bulk crystalline have been investigated thoroughly such as the band gap properties [1], and electrical properties and the Seebeck effect [2]. The band structure of Mg$_2$Si has been discussed theoretically [3,4]. The Mg$_2$Si film fabrication has been demonstrated by several works, including the (111) texture by molecular beam epitaxy (MBE) [5–7], and the (110) texture by the MBE [8]. The deposition of Mg-Si films is fabricated by ion beam sputtering [9], Mg$_2$Si thin films are grown on Si(111) by the solid-phase annealing method [10,11]. The thin films are prepared by the radio-frequency magnetron sputtering, and measured the Seebeck coefficient [12]. The thin film is also grown by an industrial rapid thermal annealing [13]. Recently, the origin of the p-type conductivity in thin films of Mg$_2$Si is investigated [14]. The experimental results show that the possible Mg$_2$Si thin films are the (001), (110), and (111) surfaces.

The first principle calculations of Mg$_2$Si thin films have been performed in recent works. Liao et al. investigate surface electric properties of Mg$_2$Si thin films with the (001) surface [15]. The band structure and the local density of states are calculated to point out the difference between the Si-terminated surface and Mg-terminated surface. Balout et al. investigate thermoelectric properties of Mg$_2$Si thin films with the (001), (110), and (111) surfaces for various film thicknesses [16]. Migas et al. investigate the band structure of mono-layer Mg$_2$Si with the (111) surface as well as the mono-layers of Ca$_2$Si, Sr$_2$Si, and Ba$_2$Si [17].

In thin films, quantum confinement effect emerges, and the electronic states are quantized. This leads to a sharper density of states profile, and it would be favorable for thermoelectric characteristics. In addition, recent studies of the topological materials show that there appears the surface electronic state inside the band gap. This also helps to improve the thermoelectric properties. In this work, we focus on the surface band structure in Mg$_2$Si thin films with the (001) and (110) surfaces for various film thicknesses. Although the band structures of the (001) and (110) surfaces have been investigated theoretically [15,16], the nature of the surface band structure has not been addressed in detail. For this purpose, we investigate the first principle calculations to clarify the difference in the surface band structures between the films with (001) and (110) orientations, and the film thickness dependence of the band structure and the density of states with the Si-terminated and Mg-terminated films.
2. Method

Mg$_2$Si crystal structure is categorized in Fm-3m (225) space group. We consider the thin film stacked along [001] and [110] directions as shown in Figs. 1 (a) and (b). The direction of the stacking of the atomic layers is indicated in the figure. The electronic structures are calculated within the density functional theory (DFT) framework using the WIEN2K program which performs the calculation using the full potential, linearized augmented planewave (FLAPW) and local orbital methods [18]. We used the general gradient approximations (GGA) proposed by Perdew, Burke and Ernzerhof [19]. The calculations have been done for pure Mg$_2$Si crystal structure with the lattice constant $a=6.35$ Å. We use $R_K_{\text{max}} = 7.0$, $25 \times 25 \times 1$ $k$-mesh points for thin film calculations. Energy convergence is set to 0.0001 Ry. Figure 1(c) shows the band structure of the bulk Mg$_2$Si crystal. Mg$_2$Si is a semiconductor with an indirect band gap [20,21] between the $\Gamma$ point and the X point.

Fig. 1. Mg$_2$Si thin film structures along [001] (a) and [110] (b) directions. The film stacking direction is indicated by the black arrow. (b) Band structure of bulk Mg$_2$Si crystal.

3. Results

Now we investigate the band structure of Mg$_2$Si thin films. For the films along the [001] direction, the surface layers consist of either Si atoms or Mg atoms, each of which is referred as Si or Mg terminated film, respectively. For the [110] direction, the surface layers consist both of Mg and Si atoms. The band structures for these thin films are shown together with thin film atomic arrangements next to each band diagram in Fig. 2. For the [001] direction, the band structures consists of two parts: The surface band structures indicated by the red arrows while the quantum confinement band structures are indicated by the blue arrows.

For the [110] direction, the surface band is not clear and almost merged with the quantum confinement band structure. Note that a direct band gap appear at the $\Gamma$ point. The appearance of the direct band gap at the $\Gamma$ has been pointed out in Ref. [17] in the film with the (111) surface. This result is in contrast to the bulk crystal result, where only the indirect gap appears [20,21]. This point will be an advantage for photo detection devices using Mg$_2$Si [22–24].

To understand the surface electronic states, we now consider the layer resolved density of states (L-DOS) for thin films stacked along the [001] direction; Figure 3 shows the L-DOS of
Fig. 2. Thin film atomic arrangement and band structure for the [001] direction with Mg terminated film (a), and Si terminated film (b) and the [110] direction (c). The red arrows indicate the surface band structures while the blue arrows indicate the quantum confinement states. Band energy is shown in units of eV.

Fig. 3. Layer resolved density of states of Mg$_2$Si thin film stacked along [001] direction with Si terminated surfaces. Mg$_2$Si with Si terminated film while Figure 4 shows the L-DOS of Mg$_2$Si with Mg terminated film. A common feature in both cases is that large L-DOS at the Fermi energy appears near the surface layers and L-DOS is suppressed as the atomic layer moves to the center of the film. This result indicates that the surface band structure in Fig. 1 actually originates from the surface electronic states.

There is a qualitative difference in the L-DOS results. For the Si terminated film, both Si and Mg atoms have large L-DOS around the Fermi energy near the surface layers. For the Mg terminated film, L-DOS changes its magnitude near the Fermi energy. The large DOS at the Fermi energy generally leads to instability. This means the Mg terminated film is more stable than the Si terminated film. This conclusion is consistent with the result in Ref. [15].

Finally, we show another evidence of the surface band structure; The surface band structure should be unchanged under the change of the film thickness. Figure 5 shows the band calculations along the [001] direction with several different film thicknesses as indicated by atomic arrangement shown next to the band diagram; The surface band structures are un-
Fig. 4.  Layer resolved density of states of Mg$_2$Si thin film stacked along [001] direction with Mg terminated surfaces.

Fig. 5. Thin film atomic arrangement and band structure with different film thicknesses for the [001] direction films with Mg and Si terminated surfaces.

changed against the film thickness changes. Quantum confinement band structure shows, on the other hand, that the energy separation of the sub-bands decreases as the film thickness increases because of the confinement over the film.
4. Conclusions

We performed the first principle band structure calculations in Mg$_2$Si thin films stacked along the [001] direction both with Si-terminated and Mg-terminated surfaces, and [110] direction aiming at understanding the surface band structure of Mg$_2$Si films. Clear surface band structures appear in the [001] direction films. The surface band structures can be directly detected by an angle-resolved photoemission spectroscopy. We calculate the layer resolved density of states and the band structure for various film thicknesses. These results show that the surface band structure comes form the electronic states near the surface atomic layers.

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