First-principles Calculations on the Electronic Structure and Optical Properties of Mg$_2$Si Epitaxial on Si (111)

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Abstract

The electronic structure and optical properties of Mg$_2$Si for the epitaxial relationship Mg$_2$Si (111)//Si (111) are calculated by using the first-principles pseudopotential method based on the density functional theory. The results show that Mg$_2$Si is the most steady state when the lattice parameter $a$ of the primitive cell is 0.4522 nm; Mg$_2$Si is an indirect semiconductor with the band gap of 0.2261 eV; the valence bands of Mg$_2$Si near the Fermi surface are composed of Si 3p, Mg 3s, 3p and the conduction bands are mainly composed of Mg 3s, 3p as well as Si 3p; the static dielectric function is 18.7369.

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1. Introduction

There has been increasing attention to the semiconducting silicides which are composed of non- or less toxic and abundantly natural elements in the earth’s crust for the applications to photoelectronic and thermoelectric devices. These silicides belong to the most promising materials for the modern solid-state electronics because of their technological compatibility with silicon, high thermal stability, resistance to oxidizing and aggressive media, and chemical inertness. These silicides are called ecologically friendly semiconductor materials [1]. Mg$_2$Si belongs to one of the most promising ecologically friendly semiconductor materials.

The first calculations of the band structures of Mg$_2$Si were made in the early 1960s. P. M. Lee [2] calculated the electronic energy-band spectra of magnesium silicide and magnesium germanide in 1964. N. O. Folland [3] applied the self-consistent method to calculate the energy band structure of Mg$_2$Si in 1967. In 1969, M. Y. Au-Yang [4] used the empirical pseudopotential method to calculate the band structures and dielectric function of Mg$_2$Si and predicted the indirect band gap to be 0.53 eV. The early empirical pseudopotential calculation of F. Aymerich [5]

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was 0.49 eV in 1970. D. M. Wood [6] calculated the band structures, equilibrium lattice constants, and electronic charge densities of MgSi using self-consistent pseudopotential band theory within the local-density formalism in 1986. J. L. Corkill [7] applied the ab initio pseudopotential method to MgSi in 1993 and predicted the indirect band gap to be 0.118 eV. P. Baranek [8] calculated the electronic structure, lattice parameters, phonon frequencies at the Brillouin zone center, and first-order elastic constants at the ab initio Hartree–Fock level using either all-atomic-electron basis sets or basis sets associated with core pseudopotentials. B. Arnaud [9] used GW approximation (GWA) based on an all-electron full-potential projector-augmented-wave method to calculate the electronic properties of semiconductors. Y. Imai [10] used the first-principles pseudopotential method to calculate the electronic structure and densities of states of MgSi in 2002 and predicted the indirect band gap to be 0.28 eV. Q. Chen [11] used the first-principles pseudopotential method to calculate the electronic structure, densities of states and optical properties of MgSi in 2008.

However, no studies have been done for MgSi/Si (111) system to our knowledge. In the present paper, we give the results of the calculation of the electronic structure and optical properties of MgSi/Si (111).

2. Computational details

The calculations have been done using CASTEP (Cambridge Serial Total Energy Package) developed by Payne et al. [12], which is the first-principles pseudopotential method based on the density-functional theory (DFT) [13] to describe the electron-electron interaction, a pseudopotential description of the electron-core interaction, and a plane-wave expansion of the wave-functions. As for the method of approximation to the exchange-correlation term of the DFT, the gradient corrected exchange-correlation functional was used. We expanded the valence electronic wave functions with the plane-wave basis set and set the cutoff energy $E_{\text{cut}}=380$ eV for the plane wave, which converges the total energy of unit cell to better than 1 meV/atom. The electron-ion interaction is described by Vanderbilt's ultrasoft pseudopotentials [14].

The intermetallic silicide MgSi is the only stoichiometric silicide in Mg-Si system. MgSi has an anti-CaF$_2$ type structure (Fm3m, No.225) with the lattice constant of 0.635 nm [15]. The Si atoms occupy fcc sites and the eight Mg atoms are at the points $\pm (1/4, 1/4, 1/4)a$ in the unit cell, where $a$ is the lattice constant. The crystal structure of MgSi is shown in Figure 1.

![Figure 1 Crystal structure of MgSi](image-1.png)  
![Figure 2 Relation curve of the lattice parameter a and the total energy of MgSi primitive cell](image-2.png)

3. Results and discussion

3.1 System optimization

Structural matching is one of the main factors to determine the quality of an epitaxial growth. The geometrical concept of the lattice match for any pair of crystal lattices in any given crystal direction has been proposed by Zur et al. [16,17]. A small lattice mismatch is a favorable prerequisite for epitaxial layer growth. For good quality epitaxial layers, the lattice mismatch between the silicide and the silicon substrate is typically less than 3% [18].

MgSi has a cubic structure which is similar to silicon but with a larger lattice parameter. For $a=0.635$ nm a side of the unit cell on the MgSi (111) $1 \times 1$ surface is 0.449 nm, that is about 1.3% longer than 0.4434 nm, which is
times the surface lattice parameter of the ideal Si (111)1 surface (0.384 nm). Due to the small lattice mismatch, high-quality epitaxial growth of Mg<sub>2</sub>Si onto monocrystalline silicon appears to be possible.

In order to gain the stable structure, we let $b=c=0.4434$ nm and calculate the total energy of the primitive cell near $a=0.449$ nm. Figure 2 shows the relation curve of the lattice parameter $a$ and the total energy of Mg<sub>2</sub>Si primitive cell. As shown in Figure 2, the most steady state is $a=0.4522$ nm.

### 3.2 The band structure

According to the optimization results, the calculated band structure is plotted in Figure 3, where the dotted line represents the Fermi level. As shown in Figure 3, Mg<sub>2</sub>Si is an indirect-gap semiconductor with $E_g=0.2261$ eV and the direct-gap is $1.8831$ eV. The valence band maximum is located at the $\Gamma_{15}$ point, whereas the conduction band minimum is located at the $X_1$ point.

![Figure 3 The calculated band structure of Mg<sub>2</sub>Si](image1)

### 3.3 The density of states

![Figure 4 The total densities of states of Mg<sub>2</sub>Si (a) and the partial densities of states of Mg (b) and Si (c)](image2)
The calculated partial densities of states for Mg$_2$Si is shown in Figure 4. According to the calculations, the s states of Si have a pronounced effect only on the first valence band, whereas their effect near the Fermi level is minor; therefore their spectra are excluded from consideration. The dominant contribution to the valence band is made by the s and p states of Mg hybridized with p states of Si. The lower conduction band is characterized by the hybridization of all states of Si and Mg, the total contribution of Mg states being greater than the total contribution of Si. Therefore, the valence bands of Mg$_2$Si near the Fermi surface are composed of Si 3p, Mg 3s, 3p and the conduction bands are mainly composed of Mg 3s, 3p as well as Si 3p.

### 3.4 The optical properties

The dielectric function is an important parameter for the material, because it is the fundamental feature of the linear response to an electromagnetic wave and uniquely determines the propagation behavior within the radiation. Figure 5 shows the calculated real part $\varepsilon_1(\omega)$ and the imaginary part $\varepsilon_2(\omega)$ of dielectric function for Mg$_2$Si. The calculated static dielectric function $\varepsilon_1(0)$ is 18.7369. In Figure 5, there are four obvious peaks in the $\varepsilon_2$ curve at the energy range of 0~4 eV. Peaks $E_1$ (2.2762 eV), $E_2$ (2.4955 eV), $E_3$ (2.7514 eV) and $E_4$ (3.3728 eV) correspond with $X'\rightarrow X_1$ and $L'\rightarrow L_1$, $X'\rightarrow X_3$, $\Gamma'\rightarrow \Gamma_2^*$, $L'\rightarrow L_3$ transitions in Figure 3 respectively.

### 4. Conclusions

The electronic structure and optical properties of Mg$_2$Si for the epitaxial relationship Mg$_2$Si (111)//Si (111) are calculated. The results show that Mg$_2$Si is the most steady state when the lattice parameter $a$ of the primitive cell is 0.4522 nm; Mg$_2$Si is an indirect semiconductor with the band gap of 0.2261 eV; the direct transition is 1.8831 eV; the valence bands of Mg$_2$Si near the Fermi surface are composed of Si 3p, Mg 3s, 3p and the conduction bands are mainly composed of Mg 3s, 3p as well as Si 3p; the static dielectric function is 18.7369.

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