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Quasi-2D silicon structures based on ultrathin Me_2Si (Me = Mg, Ca, Sr, Ba) films

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ABSTRACT

By means of *ab initio* calculations with hybrid functionals we show a possibility for quasi-2D silicon structures originated from semiconducting Mg_2Si, Ca_2Si, Sr_2Si and Ba_2Si silicides to exist. Such a 2D structure is similar to the one of transition metal chalcogenides where silicon atoms form a layer in between of metal atoms aligned in surface layers. These metal surface atoms act as pseudo passivation species stabilizing crystal structure and providing semiconducting properties. Considered 2D Mg_2Si, Ca_2Si, Sr_2Si and Ba_2Si have band gaps of 1.14 eV, 0.69 eV, 0.33 eV and 0.19 eV, respectively, while the former one is also characterized by a direct transition with appreciable oscillator strength. Electronic states of the surface atoms are found to suppress an influence of the quantum confinement on the band gaps. Additionally, we report Sr_2Si bulk in the cubic structure to have a direct band gap of 0.85 eV as well as sizable oscillator strength of the first direct transition.

1. Introduction

Metal and semiconducting silicides, compatible with common silicon technologies, were intensively investigated in the past [1,2]. The main focus was concentrated on transition metal silicides which were used in microelectronics [1,2]. Nowadays nanostructures of different materials are gaining much attention as they can possess properties unusual for bulk materials. In the case of silicides one-dimensional structures such as nanowires can be easily fabricated [3,4]. They display both low resistive ohmic and Schottky contacts to silicon to be used in high mobility field effect transistors based on silicide/silicon/silicide heterostructures [4].

Recent progress in exfoliation and growth techniques makes it possible to obtain a single sheet of a material, which can be viewed as a building block of bulk materials, leading to formation of two-dimensional (2D) structures. Although, there is an increasing number of materials, which can exist as 2D structures, silicides are not in that list [5]. However, it has been shown that Si-based nano-sheets could be formed by heat treatment of $CaSi_2$ precursor [6] or extracting Ca atoms from $CaSi_2$ layers on Si substrates [7,8].

Unlike transition metal silicides, where both ionic and covalent contributions to the chemical bonding are expected, semiconducting alkaline-earth metal silicides Me_2Si (Me = Mg, Ca, Sr, Ba) mainly display the ionic nature of chemical bonding as it is shown in the case of Ca_2Si by analyzing a charge transfer between atoms [9]. In addition, alkaline-earth metals having only two valence *s*-electrons can easily play a role of terminating species at a surface promoting the appearance of a 2D-like structure. In this paper by means of *ab initio* techniques we investigate whether ultrathin Mg_2Si, Ca_2Si, Sr_2Si and Ba_2Si films or a Si layer passivated by Me atoms can exist as 2D-like silicon structures.

2. Known structural and electronic properties of Me_2Si

Ca_2Si, Sr_2Si and Ba_2Si crystallize in a simple orthorhombic structure (the *Pnma* space group) [10–12]. The corresponding primitive cell is shown in Fig. 1(a). The projections of the orthorhombic structure indicate the presence of atomic layers which are perpendicular to the [010] direction and contain both Me and Si atoms (compare Fig. 1(b) and (c)) with the Me_2Si stoichiometry. Thus, for the (010) slabs it is easy to trace changes in their structure and properties by reducing film thickness layer by layer down to one monolayer (ML). While for the (100) and (001) slabs their structures have been specifically cut to have the Me_2Si stoichiometry and it is not straightforward to apply a definition of a ML to these cases because several atomic layers can form a layer with the necessary stoichiometry. Contrary to orthorhombic Ca_2Si, Sr_2Si and Ba_2Si, Mg_2Si has the anti-CaF_2 type structure with a face centered cubic lattice (the $Fm\bar{3}m$ space group, see Fig. 1(e)) [13]. In the case of $Mg_2Si(111)$ slabs one can readily identify a layered building block with the Mg_2Si stoichiometry (as selected by the rectangle in Fig. 1(f)), which

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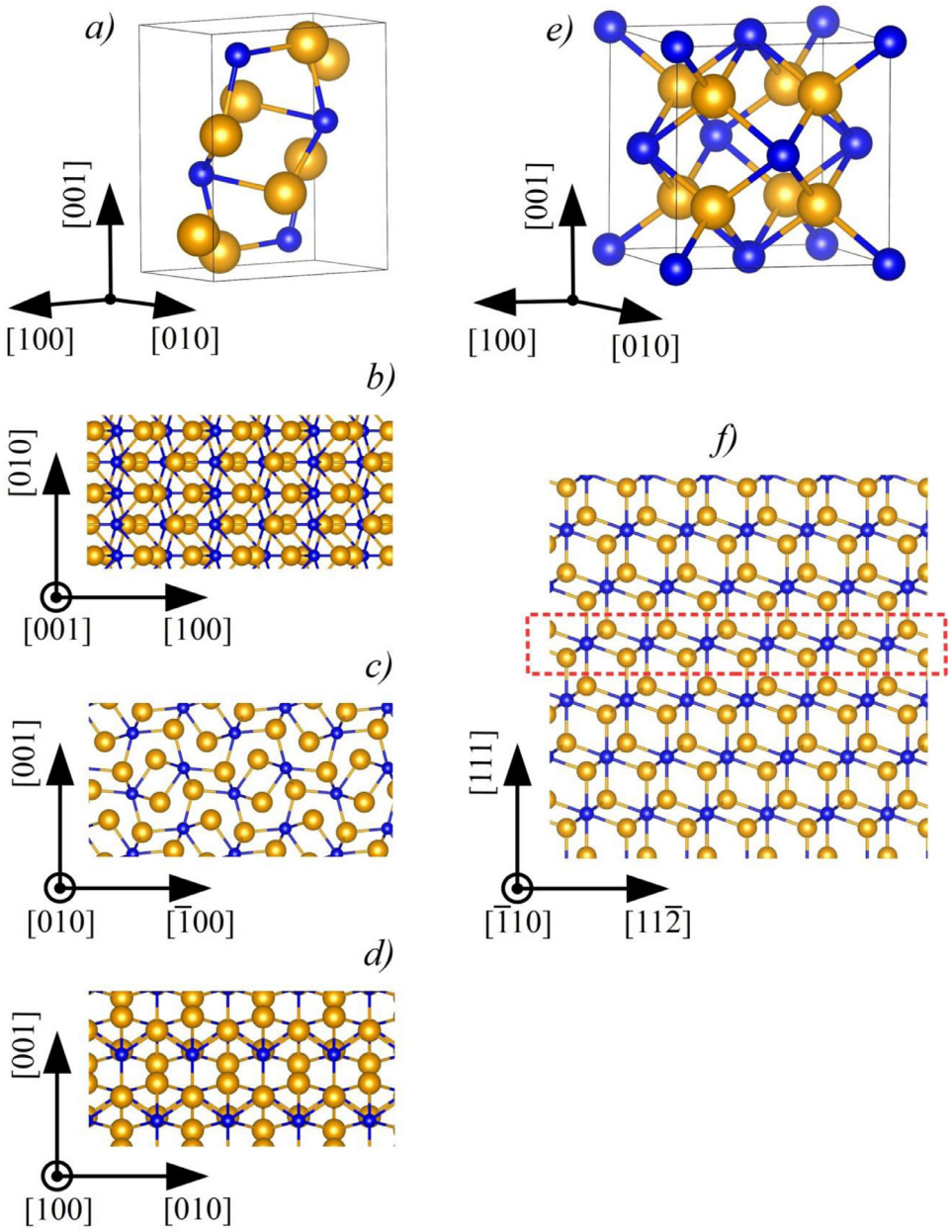

Fig. 1. (a) – the orthorhombic structure of Me_2Si bulk. (b)–(d) – the corresponding projections on (001), (010) and (100) planes of the orthorhombic Me_2Si bulk. (e) – the cubic structure of Me_2Si bulk. f) – the corresponding projection on (110) plane of the cubic Me_2Si bulk. Large in size spheres stand for Me atoms, while smaller spheres indicate Si atoms.

is characterized by a single Si layer in between of two Mg layers. Such a 2D structure is typical of some transition metal chalcogenides [5].

The results of both experimental measurements and quasiparticle calculations show that Ca_2Si has a direct band gap of 1.02 eV. For more details in the preparations and property characterizations of Ca_2Si see the recent review in Ref. [9]. In the case of Mg_2Si the indirect band gap is experimentally estimated to be about 0.65 eV [1]. In addition, according to theoretical predictions Ca_2Si in the cubic structure (isostructural to Mg_2Si) is a metastable phase with respect to the orthorhombic structure and the difference in the total energies of these two phases is rather small [14]. This metastable cubic Ca_2Si phase has a direct gap [14,15] of about 1.16 eV, as estimated by quasiparticle calculations within the GW approximation [15]. It also has a high value of the oscillator strength of the first direct transition [14,15]. In the case of orthorhombic Sr_2Si the theoretical results obtained within the generalized gradient approximation indicate it to be a semiconductor with the direct band gap of 0.35 eV [16], 0.40 eV [17], and 0.75 eV [18], while cubic Sr_2Si is reported to be unstable [18]. Optical measurements could not identify the gap value in orthorhombic Sr_2Si [16]. *Ab initio* calculations of cubic Sr_2Si and Ba_2Si obtained applying the modified Becke–Johnson exchange potential predict them to have a direct band gap of 0.72 eV and 0.42 eV, respectively [19].

3. Computational details

In this work the structural optimization of Me_2Si bulks and their ultrathin films (2–3 ML) was performed by employing the first principles total energy projector-augmented wave method (code VASP) [20–23] with the screened hybrid functional of Heyd, Scuseria, and Ernzerhof (HSE) [24–28] where the standard settings for the screening and Hartree Fock mixing parameters were used. This functional allows for better description of the exchange-correlation interaction with respect to the common local density or generalized gradient approximation (GGA). Thus, ultrathin films modeled as (001), (010) and (100) slabs