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Theoretical study of two-dimensional boron silicide from first-principles

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ABSTRACT

Using first-principles calculations and evolutionary algorithm, we predict two honeycomb (P1- and C2-type) structures of BSi with two-atom thickness. Phonon spectrum calculations show that both structures are thermodynamically stable. A weak covalent bonding interaction between B atoms along [001] direction plays a very important role in structure stability of P1- and C2-type BSi. P1-type BSi is semi-metallic, while C2-type exhibits a semiconductor band structure and has a good absorption of photons in the range of 1.5–2.5 eV that is very promising for photoelectric applications. An e_{22} piezoelectric coefficient of 1.65×10^{-10} C m^{-1} is predicted for C2-type BSi, which makes it a potential candidate for piezoelectric applications at nano-scale. Moreover, three-phonon interactions are adopted to evaluate phonon lifetimes, phonon linewidths and lattice thermal conductivity. Although both P1- and C2-type BSi have a similar honeycomb structure and same elements, the maximum lattice thermal conductivity of P1-type BSi is around 6 times higher than that of C2-type BSi. Additionally, P1-type BSi exhibits remarkably higher phonon lifetimes than C2-type BSi.

1. Introduction

In the past decades, the two-dimensional materials [1–13] have attracted many attentions of researchers due to their unique properties such as extremely high mobility, superconductivity, magnetism, lubrication, catalytic activity and hydrogen storage. Especially, graphene [14] with a one-atom-thick honeycomb structure opens up a new era in the research fields of material science, physics and chemistry. However, the semi-metallic (zero-bandgap) characteristic of graphene greatly hinders its technological applications in the fields of piezoelectric generators, solar cells and semiconductor devices. Some efforts [15–17] are devoted to open its energy gap, while making graphene become a photoelectric device is still a challenging job. Another interesting property of two-dimensional materials is piezoelectricity. Recently, the piezoelectric response has been reported experimentally in single-layer MoS_2 [4,18] and graphene nitride nanosheets [19]. The theoretical results reveal that graphene oxide [20], transition metal dichalcogenides [6], single-layer hexagonal BN and doped graphene [21] exhibit piezoelectricity as well. It is known that the most two-dimensional structures are made of III-V, IV-VI elements and metal oxides [6,7,19,22]. Up to now, the two-dimensional materials made of B and Si elements have been not found experimentally. These prompt us to search for new two-dimensional (2D) materials with an intrinsic gap and composed of B and Si, and then study their optical, piezoelectric and thermal properties.

Here, we perform first-principles calculations combined with evolutionary algorithm to look for new 2D structures composed of B and Si. Two 2D structures of boron silicide with the two shells and hexagonal unit are found. Our results reveal that the two structures are thermodynamically stable among all candidates investigated in this work. We show that, P1-type BSi is semi-metallic, while C2-type BSi has a semiconductor electronic structure suitable for photoelectric devices. The P1-type BSi exhibits remarkably higher phonon lifetimes and lattice thermal conductivity than C2-type one. Furthermore, piezoelectric coefficient e_{22} of C2-type BSi is predicted to be about 1.65×10^{-10} C m^{-1}. This finding would make it a promising piezoelectric material for nano-scale electromechanical system.

2. Calculation details

In order to search for the preferable structures of BSi, we perform first-principles calculations using the QUANTUM-ESPRESSO package [23] and evolutionary algorithm USPEX [24]. The local density approximation and Troullier-Martins norm conserving pseudo-potentials [25] are adopted to treat the exchange correlation energy. We treat three valence electrons for B ($2s^2 2p^1$) and four for Si ($3s^2 3p^2$). An energy cutoff of 952.4 eV is used in all calculations, and the convergence thresholds for energy and force are

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set to 6.8×10^{-6} eV and 1.3×10^{-4} eV/Å, respectively. Meanwhile, the k-points spacing of 0.033 $Å^{-1}$ is used to sample Brillion zone in all calculations. Phonon dispersions, phonon lifetimes, phonon linewidths and lattice thermal conductivity are obtained using the supercell method implemented in the phono3py [26] software. The piezoelectric coefficients are calculated through density functional perturbation theory performed by the ABINIT [27]. The quasiparticle absorption property of C2-type BSi is calculated by solving the *GW*-Bethe-Salpeter (BSE) equation and using the BerkeleyGW [28–30]. The schematic images of the crystal structure and electronic function are depicted by the VESTA [31].

3. Structure and electronic properties

The calculated lattice parameters within the local density approximation (LDA) for 2D BSi are listed in Table 1. The comparison with the generalized gradient approximation (GGA) results shows good coincidence between these two functionals (see Table S1). The $4 \times 4 \times 1$ primitive supercells of P1- and C2-type BSi are the two-atom-thick honeycomb structures as shown in Fig. 1. The thickness of P1-type BSi is about 1.86 Å, smaller than the value of C2-type one (about 1.89 Å). Due to smaller lattice parameters, the cohesive energy of P1-type BSi is larger than that of C2-type BSi. In both structures, each Si atom has three nearest neighbors B in the 2D plane (i.e. (0 0 1) plane), and both Si and B have sp^2 bonding in this plane. Along the [0 0 1] direction, the B—B and B—Si bond distances of P1-type BSi are about 1.9 and 2.14 Å, respectively, which are different from those of C2-type BSi (1.89 and 2.38 Å). Due to significant differences in the two structures, the P1- and C2-type BSi are expected to exhibit the different electronic characters.

The B atom usually exhibits sp^2 bonding in its compound [32], and Si usually has a sp^3 bonding with another atom. In this work, the predicted P1- and C2-type BSi per formula unit with seven valence electrons form the stable 2D structures, which are different from BN that has eight valence electrons. These two structures are unusual, so the analysis of bonding between atoms is necessary for understanding their characteristics.

The electronic localization function (ELF) proposed by Becke and Edgecombe [33] is based on the Hartree-Fock pair probability of parallel spin electrons, and can be used to analyze the electron pairing and local property, e.g. lone pair electrons and covalent bonding. The ELF distribution of P1- and C2-type BSi are given in Fig. 1(c) and (d), respectively. It can be seen that the bonding electrons appear between the Si and B atoms in the (0 0 1) plane, but not between the Si and B (or Si and Si) atoms in the [0 0 1] direction, so the Si atoms in both P1- and C2-type BSi have only sp^2 hybridization. This is different from the case of bulk Si that exhibits sp^3 bonding between the Si atoms. Moreover, the bonding electrons are very few between the B—B atoms along the [0 0 1] direction, suggesting that the covalent bonding of the B—B atoms is very weak. In C2-type BSi, the hybridization of sp^2 orbitals of the B and Si atoms shows a remarkably anisotropic character. The two of

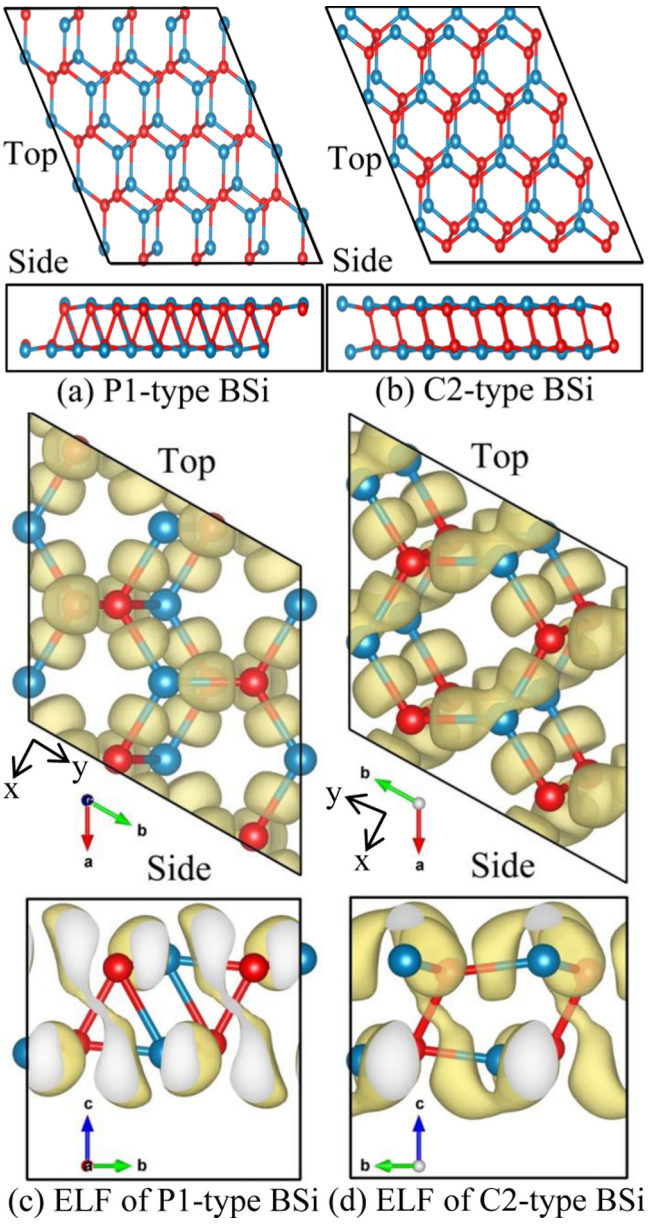

Fig. 1. Top and side views of two-dimensional (a) P1- and (b) C2-type BSi. Darkcyan and red balls represent Si and B atoms, respectively. The calculated electronic localization function for (c) P1- and (d) C2-type BSi. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

three sp^2 covalent electronic density are close to Si due to the stronger electronegativity of Si than B.

To further analyze the bonding of both structures, we perform the crystal orbital Hamilton population calculations implemented

Table 1
Calculated lattice parameter of P1- and C2-type BSi.

Struct.	Space group atom	Lattice parameters (Å and degree) LDA(Troullier-Martins)		
BSi	P-1	$a = 3.4030$ $b = 3.4048$ $c = 17.0609$ $\alpha = \beta = 90$ $\gamma = 60.193$		
	B	0.91242	0.43400	0.04918
	Si	0.24354	0.76374	0.05998
BSi	C2	$a = 3.4335$ $b = 5.8435$ $c = 17.7777$ $\alpha = \beta = \gamma = 90$		
	B	0.86140	0.41552	0.54585
	Si	0.64992	0.25047	0.43954