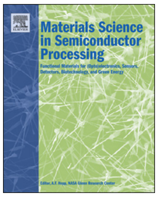
Materials Science in Semiconductor Processing 31 (2015) 251–255

Contents lists available at ScienceDirect

Materials Science in Semiconductor Processing

journal homepage: www.elsevier.com/locate/mssp



First-principles calculations of phonon and thermodynamic properties of $OsSi_2$

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ARTICLE INFO

Available online 18 December 2014

Keywords:
Silicides
Phonons
Thermodynamic properties
First-principles calculation

ABSTRACT

The structure, lattice dynamics, and some thermodynamic properties of orthorhombic $OsSi_2$ were investigated using a first-principles density functional theory (DFT). Linear response theory was used to calculate the phonon dispersion relation and phonon density of states for $OsSi_2$ as well as its infrared and Raman active mode frequencies. In this study, the thermodynamic properties, including vibrational entropy (S_{vib}), constant-volume specific heat (C_v), and Debye temperature (Θ_D), were predicted theoretically and discussed.

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1. Introduction

Semiconducting transition silicides have gained considerable attention as potential candidates for optoelectronics, photovoltaics, and thermoelectrics [1]. In particular, to date, iron disilicide (β-$FeSi_2$), an environmentally friendly, non-toxic, low-cost material made from abundant elements found in the Earth's crust, has been extensively investigated [2–5]. Despite the fact that osmium disilicide ($OsSi_2$) has a crystal structure identical to that of β-$FeSi_2$, very few experimental and theoretical studies have been reported for $OsSi_2$ [6–11]. Fig. 1 shows the crystal structure of $OsSi_2$, containing 16 Os and 32 Si atoms per unit cell. The crystal structure of $OsSi_2$ belongs to a base-centered orthorhombic in the *Cmca* (No. 64) space group, with lattice constants of $a=10.1496$ Å, $b=8.1168$ Å, and $c=8.2230$ Å [12]. There are two crystallographically inequivalent sites (Os_I, Os_{II}, Si_I, and Si_{II}) for both the Os and Si atoms in $OsSi_2$. Both the Os_I and Os_{II} atoms are surrounded by 8 nearest-neighbor Si atoms with slightly different distances, and have the crystallographic point symmetries 2 (C_2) and m (C_s), respectively. Migas et al. [9] reported on the optical properties of isostructural β-$FeSi_2$, $OsSi_2$, and two ternary compounds, $Os_{0.5}$ $Fe_{0.5}Si_2$ and $Fe_{0.5}Os_{0.5}Si_2$, in which the Fe_I or Fe_{II} sites were replaced by Os in the β-$FeSi_2$ structure, respectively, according to the first-principles calculations. They noted the potential for band-gap engineering by composition owing to the $Os_{0.5}$ $Fe_{0.5}Si_2$ having a predicted direct band-gap, while β-$FeSi_2$, $OsSi_2$, and $Fe_{0.5}Os_{0.5}Si_2$ have indirect band-gaps. Moreover, the elastic properties such as elastic constants, bulk modulus, shear modulus, and Young's modulus of $OsSi_2$ were investigated using the first-principles calculations [10,11].

In our previous paper, we reported the detailed lattice-dynamical properties of β-$FeSi_2$ based on first-principles calculations [13]. The calculated vibrational entropy, specific heat, and Debye temperature of β-$FeSi_2$ from these calculations are in agreement with previous experimental data. At a finite temperature, numerous physical properties of solids are greatly influenced by the solid's crystal vibration. Accordingly, it is vital to investigate the vibrational properties of $OsSi_2$. However, as far as we know, few experimental and theoretical studies on the phonons of $OsSi_2$ have been reported. In this study, we report on the detailed lattice-dynamical properties of $OsSi_2$, including the phonon dispersion relations, the phonon density of states, the infrared (IR) and Raman active phonon frequencies, the Born effective charge, and the thermodynamic properties, based on first-principles calculations.

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http://dx.doi.org/10.1016/j.mssp.2014.11.049
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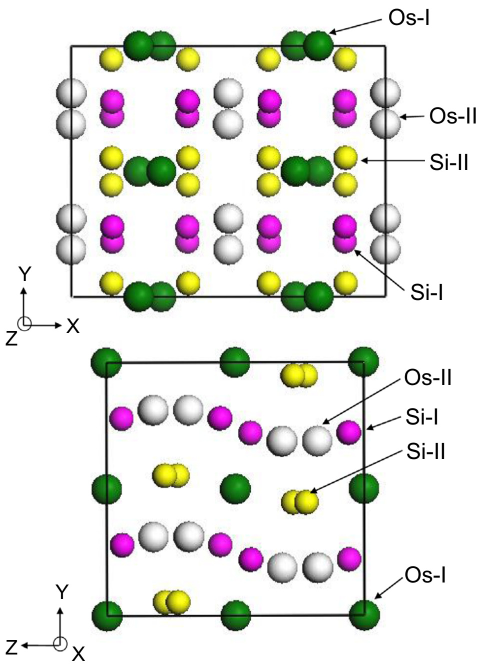

Fig. 1. The $OsSi_2$ unit cell. The large spheres represent Os and the small spheres represent Si. There are two crystallographically inequivalent sites for both types of atoms (Os_I, Os_{II}, Si_I, and Si_{II}).

2. Computational details

We used the CASTEP (Accelrys Inc.) software package [14] to perform the density-functional theory (DFT) plane-wave pseudopotential calculations within local density approximations (LDA). The norm-conserving pseudopotential, generated using the optimization scheme of Lin et al. [15], was utilized. The valence electron configurations of the Os and Si atoms were $5d^6 6s^2$ and $3s^2 3p^2$, respectively. The Ceperley–Alder form of the exchange correlation potential, as parameterized by Perdew and Zunger [16], was used in the LDA. A base-centered orthorhombic primitive cell having 24 atoms (4 Os_I, 4 Os_{II}, 8 Si_I, and 8 Si_{II}) was built. The total energy of the unit cell converged to better than 1 meV/atom using the valence electron wave functions in a plane wave basis, with a kinetic energy cutoff of 560 eV. The density mixing method was used for electronic minimization. In the geometry optimization and lattice-dynamical calculations, the Brillouin-zone integrals were performed using the Monkhorst-Pack grids [17] of a $3 \times 3 \times 2$ mesh with a 0.05 $Å^{-1}$ k-point spacing. The linear response method [18–20] was applied after the geometrical optimization to calculate phonons, including the longitudinal optical/transverse optical (LO/TO) splitting. A convergence of the calculated phonon frequencies was better than 1 cm^{-1}.

3. Results and discussion

Table 1 shows the calculated lattice parameters and fractional atomic coordinates of the $OsSi_2$ in this study, compared with those obtained from previous experiments [12]. The difference in the three lattice parameters a, b, and c, between the calculated values herein and those obtained from previous experiments are −0.8%, −0.9%, and −0.9%, respectively, within the range of typical errors in LDA. The calculated fractional atomic coordinates (x, y, z) of the Os_I, Os_{II}, Si_I, and Si_{II} atoms are consistent with previous experimental results [12].

Fig. 2 shows the calculated phonon dispersion relations of $OsSi_2$. The special high-symmetry points of the Brillouin zone (BZ) are denoted by $\Gamma(0, 0, 0)$, $Z(0, 0, 0.5)$, $T(-0.5, 0.5, 0.5)$, $Y(-0.5, 0.5, 0)$, $S(0, 0.5, 0)$, and $R(0, 0.5, 0.5)$. The phonon frequencies are obtained at these special high-symmetry points, as well as at other intermediate points. All of the calculated phonon frequencies are positive, suggesting that the $OsSi_2$ is dynamically stable throughout the BZ. It is clear that the some frequencies at the Γ point depend strongly on direction ($\mathbf{q} \rightarrow 0$ along $\Gamma - Z$, $\Gamma - Y$, and $\Gamma - S$) due to the LO-TO splitting in the anisotropic $OsSi_2$ crystal.

Table 2 shows the calculated phonon frequencies from this study of the $OsSi_2$ at the Γ point. As the primitive cell contains 24 atoms, there are 72 vibrational modes at the Γ point: 3 acoustic and 69 optical. The $Cmca$ space group has the crystal point group D_{2h} in the Schoenflies notation [21]. Therefore, the phonon modes of $OsSi_2$ can be classified as 3 acoustic ($B_{1u}+B_{2u}+B_{3u}$), 36 Raman-active ($9A_g+9B_{1g}+9B_{2g}+9B_{3g}$), 25 IR-active ($9B_{1u}+9B_{2u}+7B_{3u}$), and 8 silent modes ($8A_u$) [13,22]. The IR-active phonon mode frequencies (B_{1u}, B_{2u}, and B_{3u}) are split by the LO–TO splitting, which is computed based on the dynamic Born effective charge [23].

The calculated dynamic Born effective charge tensors (Z^*) and static Mulliken charges for the Os_I, Os_{II}, Si_I, and Si_{II} of the $OsSi_2$ are shown in Table 3. All of the off-diagonal components of the Z^* for Os_I, Os_{II}, Si_I, and Si_{II} come to zero or negligible values. On the other hand, the diagonal elements of the Z^* for the Os_I, Os_{II}, Si_I, and Si_{II} are not symmetric $(Z^*_{xx} \neq Z^*_{yy} \neq Z^*_{zz})$ and have large values,

Table 1
Comparison between $OsSi_2$'s structural properties calculated in this study with those obtained in previous experiments [12]. The deviations from the experimental data are shown in parentheses.

Structural parameters			Calculated	Experimental [12]
Cell parameters	a (Å)		10.0660 (−0.8%)	10.1496
	b (Å)		8.0445 (−0.9%)	8.1168
	c (Å)		8.1487 (−0.9%)	8.2230
	V ($Å^3$)		659.85 (−2.6%)	677.43
Atomic coordinates	Os_I (8d)	x	0.2147	0.2142
		y	0	0
		z	0	0
	Os_{II} (8 f)	x	0	0
		y	0.1881	0.1881
		z	0.1818	0.1812
	Si_I (16 g)	x	0.3717	0.3699
		y	0.2222	0.2208
		z	0.0588	0.0591
	Si_{II} (16 g)	x	0.1270	0.1280
		y	0.0526	0.0534
		z	0.7241	0.7252

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