Materials Chemistry and Physics 222 (2019) 165–172

Contents lists available at ScienceDirect

Materials Chemistry and Physics

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

Theoretical investigation of lattice dynamics, dielectric properties, infrared reflectivity and Raman intensity spectra of Nowotny chimney-ladder semiconducting silicide Ru_2Si_3

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HIGHLIGHTS

- *Ab-initio* calculations of lattice dynamics and dielectric properties of Ru_2Si_3.
- *Ab-initio* calculations of Infrared reflectivity and Raman spectra of Ru_2Si_3.
- Significant Raman intensities are obtained for modes 91, 231 and ~479 cm^{-1}.
- Born effective charges and IR activity are found to be largest for mode 422 cm^{-1}.

ARTICLE INFO

Keywords:
Semiconducting silicide
Thermoelectric materials
Solar cell materials
Ab-initio calculations

ABSTRACT

Semiconducting silicides are highly promising materials for applications in thermoelectric, photovoltaic and optoelectronic devices. Here, using *ab-initio* density functional theory, the lattice dynamics, dielectric properties, Infrared (IR) refletivity and Raman intensity spectra of Nowotny chimney-ladder semiconducting silicide Ru_2Si_3 are investigated. The zone-center phonon mode frequencies are found to be in the range 80–510 cm^{-1}. The Born effective charge tensor, oscillator strength and Infrared activity is found to largest for the mode with frequency 422 cm^{-1} which is primarily contributed by displacements of Si atoms. The largest Raman activity is obtained for mode with frequency 479 cm^{-1} which is also dominated by vibrations of Si atoms. Modified Becke-Johnson (MBJ) exchange potential is used to compute the band gap of Ru_2Si_3 which improves the band gap by ~8% as compared to that obtained using LDA. The computed Infrared reflectivity and Raman intensity spectra are expected to provide benchmark first-principles theoertical results for comparison with the experiments.

1. Introduction

Over last few decades, metal silicides have been explored intensively due to their wide range of technological applications. In particular, metallic silicides have played a very important role in the development of silicon-based integrated microelectronic device technology [1–5]. In complimentary metal-oxide-semiconductor (CMOS) devices, silicides are being exploited as gate metallization, low-resistivity interconnects, Ohmic contacts etc. due to their low resistivity, good thermal stability, low contact resistance, and good process compatibility of silicon. In addition, many silicides can also be grown epitaxially on silicon thereby providing extra advantage and functionality [2,3,6,7]. Silicides based Schottky-barrier photodiodes and detectors are also being used in systems such as infrared imaging and multi-wavelength pyrometry [4]. Besides technological applications, many silicides also exhibit diverse interesting physical phenomena and properties which make them attractive for fundamental scientific investigation. For instance, quantum non-Fermi liquid behavior and critical phase transition have been reported in silicides of manganese arising due to strong electronic correlations [8,9]. Though majority of silicides are metallic conductors, there are few silicides which are semiconductors having band gaps in the range of 0.1–1.3 eV [10]. These semiconducting silicides have also attracted a lot of attention in recent years due to their potential applications as optoelectronic materials which can be exploited in systems such as infrared detectors, light sources, electro-optic very large scale integrated circuit interconnects etc. [11,12]. Further, semiconducting silicides have also been found promising as materials for applications in thermoelectric and photovoltaic devices [13–15]. Among the semiconducting silicides, orthorhombic ruthenium silicide, Ru_2Si_3, has generated considerable

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https://doi.org/10.1016/j.matchemphys.2018.09.081
Received 29 January 2018; Received in revised form 10 August 2018; Accepted 30 September 2018
Available online 03 October 2018
0254-0584/

interest for its potential applications in optoelectronic and thermoelectric devices [10,16,17]. For silicon based optoelectronics, it is essential to find silicon based light emitters. However, efficient silicon based light emitting diodes (LED) are not available despite the considerable research in this field. In particular, light emitting diodes in the near-infrared at ~1.5 μm wavelength which correspond to absorption minimum in glass fibers, are technologically important. The band gap of Ru_2Si_3 has been found to be direct with magnitude between 0.7 and 1.2 eV [16–18]. Thus, the light emission in Ru_2Si_3 is expected to be in near-infrared, thereby making Ru_2Si_3 a promising silicon based material for light emission. Ru_2Si_3, has also attracted attention as a potential thermoelectric material for applications at high temperatures due to its enhanced thermoelectric performance [19,20]. Thermoelectric materials can be used in various applications such as solid state cooling, waste-heat recovery, power generation, air conditioning, refrigeration etc. The performance of a thermoelectric material is evaluated from dimensionless parameter$ZT = S^2\sigma T/\kappa$, where S is Seebeck coefficient, σ is electrical conductivity, κ is thermal conductivity and T is absolute temperature. Since high value of ZT indicates the high efficiency, thermoelectric materials having large electrical conductivity and/or low thermal conductivity are desired in order to exhibit high efficiency. Seebeck coefficients for nominally intrinsic polycrystalline Ru_2Si_3 has been reported and found to be either negative and positive at low and high temperatures respectively, undergoing a change in sign at ~600–700 K; or uniformly positive, with S increasing with temperature [19,21]. The maximum value of Seebeck coefficient S_{max} is reported to vary between ~190 mV/K [13] and ~550 mV/K [14]. Over last few years, several experimental studies on Ru_2Si_3 have been reported. Thermoelectric properties were reported by Okamoto et al. [22] whereas directional thermoelectric properties were reported by Simkin et al. [19]. Lenssen et al. [18] and Chang et al. [23] reported electrical and optical characterization of epitaxial Ru_2Si_3 films grown on Si(111) and Si(001) substrate by molecular beam epitaxy. Physical and electrical properties of sputtered Ru_2Si_3/Si structures were reported by Jelenkovic et al. [24].

Despite the technological importance of Ru_2Si_3, reported theoretical studies on this system are scarce. Further, to best of our knowledge, only few theoretical studies of electronic band structure, optical and transport properties have been reported [25–28]. Here in this article, we present a comprehensive first-principles theoretical study of 1) Lattice dynamics 2) Infrared (IR) reflectivity spectrum 3) Raman intensity spectrum 4) Born-effective dynamical charge tensors 5) Frequency dependent dielectric permittivity and 6) phonon mode contribution to static dielectric constant of room temperature orthorhombic Ru_2Si_3. The zone-center phonon modes, IR reflectivity and Raman spectrum of Ru_2Si_3 are computed in order to investigate lattice dynamics and related structure-property relations associated with it. As is well known known, the Infrared (IR) and Raman spectroscopic techniques can be very effectively exploited to study structural and dynamical properties of materials as they are able to provide precise information of ionic configurations and local distortions in crystal structures [29,30]. In particular, the Raman spectroscopy can be used to obtain information about structural changes and/or new phases; even in systems which lack long-range structural ordering such as amorphous materials and liquids. Raman spectroscopy is also an excellent nondestructive method which can be used to determine the strain in the films during device fabrication [31].

This paper is organized as follows. Theoretical details are presented in section II with computational methodology presented in section II A. The crystal and electronic structure of Ru_2Si_3 are discussed in section II B. The zone-center phonon modes, Born dynamical charges of ions, dielectric properties are discussed in section II C-E. Infrared reflectivity and Raman intensity spectrum are discussed in II F and II G. Finally, conclusions are presented in section III.

2. Theoretical details

2.1. Computational methodology

Density functional calculations (DFT) are performed within local density approximation (LDA) as implemented in the PWscf package [32]. The Troullier-Martins (TM) form of norm-conserving pseudo potential (NCPP) is used to approximate the core-valence electron interaction [33]. The Kohn-Sham wavefunctions are expanded using plane wave basis set with a kinetic energy cutoff of 60 Ry. The Brillouin zones of orthorhombic cell is sampled using a 4 × 5 × 8 Monkhorst-Pack k-point mesh. The self-consistency in calculations is achieved by converging total energies to 10^{-6} eV/cell. The structures are relaxed by minimizing the force on each atom to 10^{-2} eV/Å or less. The DFT-Linear response scheme with iterative Green's function approach of density-functional perturbation theory is used to compute zone-center phonon modes, Born-effective charge tensors, dielectric permittivity tensors etc. [32,34,35]. The band gap is also calculated using the modified Becke-Johnson (MBJ) scheme [36,37] using projected augmented wave (PAW) potentials as implemented in VASP package [38].

2.2. Crystal and electronic structure of Ru_2Si_3

The crystal structure of Ru_2Si_3 belongs the family of compounds Ru_2X_3 (X = Si, Ge, or Sn). At low temperature below ~1000 °C, Ru_2Si_3 crystallizes in orthorhombic structure with *Pbcn* space group symmetry (No. 60). As temperature becomes higher than ~1000 °C, the structure changes to tetragonal with *P*4*c*2 space group symmetry (No. 116) via a first order reversible and diffusionless phase transition [39,40]. The gradual phase transformation takes place over a wide temperature range whereby the Ru atoms remain undisplaced, while the Si atoms are displaced and pass through the intermediate orthorhombic phase *Pb*2*n* (No. 30). The structure of high temperature tetragonal phase has the general chemical formula M_nX_{2n-m}, where M is transition metal element, X is element in group 13 or 14, n and m are integers. This structure is known as 'Nowotny chimney-ladder' compound structure [41] in which the unit cell consists of subcell of M (Ru) atoms arranged in square array as in β-Sn type structure (chimney) and subcell of X (Si) atoms arranged as in coupled helices (ladders). The tetragonal Ru_2Si_3 'Nowotny chimney-ladder' structure with $n = 2$ and $m = 1$ consists 20 atoms in the unit cell [19,39]. The chimney and ladder are aligned along the [001] or c-axis of the tetragonal unit cell. Since the chimney-ladder unit cell is composed of n and m subcells of M and X atoms respectively, the [001] or c-axis can be expressed as the least common multiple of the c-axis dimension of subcell of M and X atoms, i.e, $c = n\ c_M = m\ c_X$. The X/M atomic ratio of the chimney–ladder compound M_nX_{2n-m} can also be expressed in terms of c_X/c_M ratio as [22,41]:

$$\frac{X}{M} = \frac{2n-m}{n} = 2 - \left(\frac{c_X}{c_M}\right)^{-1} \quad (1)$$

The low-temperature orthorhombic Ru_2Si_3 phase arises through the distortion of the Si and Ru subcells from the chimney-ladder structure, which results in doubling of the unit cell along the [100] or a-axis. The unit cell of orthorhombic Ru_2Si_3 is shown in Fig. 1 and consists 40 atoms. As can be seen, the unit cell consists Ru atoms at three inequivalent crystallographic sites (Ru1, Ru2, Ru3) and Si atoms also at three inequivalent crystallographic sites (Si1, Si2, Si3). The computed and experimental lattice constants and fractional atomic coordinates of orthorhombic Ru_2Si_3 are presented in Table 1 and Table 2. As can be seen, the computed values of lattice constants and fractional atomic coordinates are in good agreement (< 2%) with reported theoretical and experimental values [25–28]. The energy bands of orthorhombic Ru_2Si_3 along the high symmetry directions in the Brilliouin zone are shown in Fig. 2, while the total and partial density of states (DOS) are shown in Fig. 3. The valence band maximum (VBM) is set at 0.0 eV. As can be seen, the valence band in the energy range from ~ −6 eV to