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## Theoretical Investigation of Neutral Point Defects in CoSi<sub>2</sub>

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### Abstract

Using a first-principle plane-wave ultrasoft pseudopotentials method based on the generalized gradient approximations (GGA), atomic geometry, bulk modulus and Mulliken population of CoSi<sub>2</sub> have been investigated to offer a formation mechanism of the Co-Si compound. The formation energies of point defects depend on the atomic chemical potentials of Co and Si. Generally, the calculated formation energies of Co vacancy and interstitial are smaller than those of Si vacancy and interstitial, respectively, indicating that the diffusion via Co vacancy and interstitial are strongly favored in CoSi<sub>2</sub>.

### 1. Introduction

The increasingly shrinking of MOSFET critical size triggers to apprehend the details of vacancy, interstitial, dislocation, boundary, surface and interface of CoSi<sub>2</sub>, which significantly influence sub-90nm devices performance, by means of more advanced theoretical methods so as to provide more science instruction to IC process [1].

In the paper, first-principle method has been used to cast light on the formation of point defects in CoSi<sub>2</sub>, the silicide extensively used as local interconnects, gate metallization and Salicide in IC devices.

### 2. Details of the simulation

CASTEP (Cambridge Serial Total Energy Package), the first-principle pseudopotential method based on the plane-wave basis, has been used in this study [2]. The density functional is treated by GGA with parameterized exchange-correlation potential and the cut-off energy (340 eV) of the plane-wave basis set was used throughout [3]. The tolerances were set as follows:  $2 \times 10^{-6}$  eV/atom for the total energy, 0.001 Å for the root mean square atomic displacement, 0.05eV/ Å for the root mean square atomic force, and 0.1GPa for the root mean square stress, respectively. The 2a×2b×c supercell (a,b,c are lattice constants of CoSi<sub>2</sub>) was relaxed to obtain the theoretical equilibrium structures by geometry optimization. The interstitial or vacancy was created by adding one atom into or remove one atom from the relaxed supercells. In order to decrease inter-cell defect interactions, only first and second neighbor atoms were permitted to relax during energy optimization. Finally, the simulation results were analyzed.

### 3. Results and Discussion

As listed in the Table 1, the calculated lattice constants are very close to the experimental values with the slight errors being less than 1% due to the usage of the GGA approximation. Moreover, the bulk modulus from our calculation in table 2 is in good agreement with the previous theoretical and experimental values and predicts that 240GPa is far from the values available and can't reflect CoSi<sub>2</sub> elastic properties. The simulation result agreeing fairly well with the experimental values implies that the CASTEP

can be utilized to investigate CoSi<sub>2</sub> with reasonable accuracy.

The formation energies of neutral interstitial ( $\Phi$ ) and vacancy ( $\Omega$ ) are of importance and are defined as

$$\Phi = E_D + \mu_x - E_P \quad (1)$$

$$\Omega = E_D + \mu_x - E_P \quad (2)$$

where  $E_I$  and  $E_D$  and  $E_P$  are total energies of supercells with one interstitial, one vacancy and no defect, respectively, and  $\mu_x$  ( $x=Si$  or  $Co$ ) is the atom chemical potential which are restrained by three constraints:

$$\mu_{Si} \leq \mu_{Si}(bulk) \quad (3)$$

$$\mu_{Co} \leq \mu_{Co}(bulk) \quad (4)$$

$$2\mu_{Si} + \mu_{Co} = \mu_{CoSi_2}(bulk) \quad (5)$$

The formation energies shown in Fig. 1 have been calculated out using the values listed in Table 3. At Si-rich limit,  $\Phi$  for Si and Co interstitial are 2.2 and 0.61eV while those are 3.07 and -1.12eV at Co-rich limit, from which it is obvious that Co interstitial exhibits the lower formation energy than Si interstitial. The formation energies of Si vacancy are 2.39 and 1.53 eV at Si-rich and Co-rich limits and those of Co vacancy are 0.56 and 2.29eV at Si-rich and Co-rich limits, respectively. In general,  $\Omega$  of Co vacancy is smaller than that of Si vacancy. Hence, the calculated formation energies indicate that the formation of Co vacancy and interstitial is more favorable than that of Si vacancy and interstitial, according with the general accepted experiments that Co atoms are dominant diffusion species though there were still arguments about whether Si atoms are the dominant species [4,5]. According to tantalum marker layers experiment, Diale *et al.* assumed that self-diffusion process occurs via a vacancy mechanism that a vacancy flux towards the Co surface is associated with the observed flux of Co from Co surface towards the silicide/Co interface [6]. What's more, it is noticed that Si vacancy is more favorable to form than Si interstitial and the formation energy of Co interstitial is less than that of Co vacancy. It is supposed from our simulation that Si vacancy flux help the diffusion of Co interstitials.

After forming interstitial or vacancy in CoSi<sub>2</sub>, the neighbor atoms are relaxed by shifting of the distances to point defect from  $d_0$  to  $d_1$  and their corresponding Mulliken charges are adjusted from  $e_0$  to  $e_1$  due to orbital rebounding and the structural rearrangement, as listed in Table 4. The introduction of interstitials results in greater atom relaxation amount than that of vacancies. Generally speaking, it can be also concluded by analysis of the data in Table 4 that the first-nearest neighbor atoms approach to vacancy by the absence of steric repulsion resulting from the existence of vacancy and move away from interstitial while the presence of interstitial in CoSi<sub>2</sub>. Furthermore, the calculated densities of states exhibit little discrepancies after propagating point defects in CoSi<sub>2</sub> and the average Mulliken

charge of Si and Co atoms nearly don't change in the whole supercells.

#### 4. Conclusion

In short, the formation of Co and Si vacancy and interstitial has been investigated to illustrate the properties of intrinsic point defects in  $\text{CoSi}_2$ . Co point defects show smaller formation energies and are easier to form than Si point defects and Si vacancy is more favorable to form than Si interstitial so that Co point defects are dominant diffusion species with the assistance of Si vacancy in solid reaction between Si and Co bilayer.

#### Acknowledgment

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#### Reference

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Table 1. Experimental and calculated lattice constants and structural data.

Compound	Structure	Space number	atom	Atom coordinate	a (Exp.)	a (Calc.)
c-Co	A3 (Mg)	P6 <sub>3</sub> /mmc	Co	(0,0,0)	2.51Å <sup>[7]</sup>	2.48Å
c-Si	A4 (Diamond)	Fd <sub>3</sub> m	Si	±(0.125,0.125,0.125)	5.431Å <sup>[7]</sup>	5.37Å
$\text{CoSi}_2$	C1 (CaF <sub>2</sub> )	Fm <sub>3</sub> m	Co	(0,0,0)	5.365Å <sup>[8]</sup> , 356Å <sup>[9]</sup>	5.31Å

Table 2. Experimental and theoretical bulk moduli (GPa).

B	$c_{11}$	$c_{44}$	$c_{12}$	$c_{11}-c_{12}$	Reference
182	227	100	156	71	In this work
201.8	273	97.4	166	107	Calc. <sup>[10]</sup>
200.2	273	100	164	109	Calc. <sup>[10]</sup>
187±30					Exp. <sup>[11]</sup>
171.5±3.	224	85	145	79	Exp. <sup>[12]</sup>
240±5					Exp. <sup>[13]</sup>
169±5	228	83	140	88	Exp. <sup>[14]</sup>

Table 4. First and second neighbors' coordinate and Mulliken population.

Model	Neighbor	No.	$d_0(\text{\AA})$	$d_I(\text{\AA})$	$\delta_d(\%)$	$e_0$	$e_I$
$I_{\text{Co}}$	Si	8	2.323	2.420	+4.18	-0.26	-0.26
	Co	4	2.682	2.610	-2.68	+0.52	+0.48
	Co	2	2.682	2.682	0	+0.52	+0.403
$I_{\text{Si}}$	Si	8	2.323	2.454	+5.64	-0.26	-0.26
	Co	4	2.682	2.550	-4.92	+0.52	+0.53
	Co	2	2.682	2.682	0	+0.52	+0.55
$V_{\text{Co}}$	Si	8	2.323	2.315	-0.34	-0.26	-0.20
	Co	8	3.794	3.747	-1.24	+0.52	+0.52
	Co	4	3.794	3.761	-0.87	+0.52	+0.53
$V_{\text{Si}}$	Co	4	2.323	2.202	-5.21	+0.52	+0.31
	Si	4	2.683	2.730	+1.75	-0.26	-0.2
	Si	2	2.683	2.683	0	-0.26	-0.12

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Table 3. Calculated total energies.

Model	Total energy (eV)
$\text{Co}_{16}\text{Si}_{32}$ (perfect crystal)	-20214.2770
Co	-1044.5051
Si	-108.5800
$\text{Co}_{17}\text{Si}_{32}$ (defective crystal with $I_{\text{Co}}$ )	-21259.5545
$\text{Co}_{16}\text{Si}_{33}$ (defective crystal with $I_{\text{Si}}$ )	-20320.3118
$\text{Co}_{15}\text{Si}_{32}$ (defective crystal with $V_{\text{Co}}$ )	-19167.4863
$\text{Co}_{16}\text{Si}_{31}$ (defective crystal with $V_{\text{Si}}$ )	-20103.3057

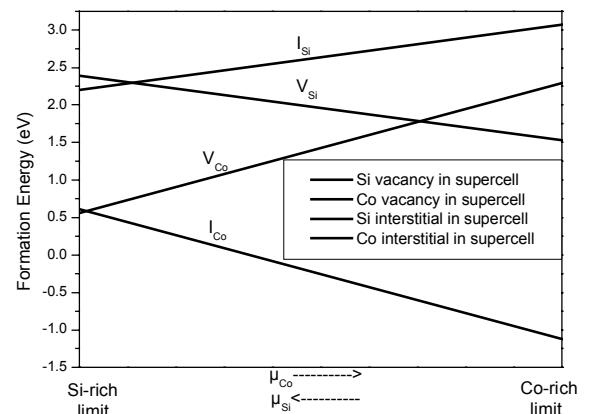


Fig. 1. Formation energies of point defects in  $\text{CoSi}_2$ .