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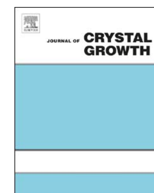

Thermal equilibrium concentration of intrinsic point defects in heavily doped silicon crystals - Theoretical study of formation energy and formation entropy in area of influence of dopant atoms-

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A B S T R A C T

It is well known that p-type, neutral and n-type dopants affect the intrinsic point defect (vacancy *V* and self-interstitial *I*) behavior in single crystal Si. By the interaction with *V* and/or *I*, (1) growing Si crystals become more *V*- or *I*-rich, (2) oxygen precipitation is enhanced or retarded, and (3) dopant diffusion is enhanced or retarded, depending on the type and concentration of dopant atoms. Since these interactions affect a wide range of Si properties ranging from as-grown crystal quality to LSI performance, numerical simulations are used to predict and to control the behavior of both dopant atoms and intrinsic point defects. In most cases, the thermal equilibrium concentrations of dopant-point defect pairs are evaluated using the mass action law by taking only the binding energy of closest pair to each other into account. The impacts of dopant atoms on the formation of *V* and *I* more distant than 1st neighbor and on the change of formation entropy are usually neglected. In this study, we have evaluated the thermal equilibrium concentrations of intrinsic point defects in heavily doped Si crystals. Density functional theory (DFT) calculations were performed to obtain the formation energy (E_f) of the uncharged *V* and *I* at all sites in a 64-atom supercell around a substitutional p-type (B, Ga, In, and Tl), neutral (C, Ge, and Sn) and n-type (P, As, and Sb) dopant atom. The formation (vibration) entropies (S_f) of free *I, V* and *I, V* at 1st neighboring site from B, C, Sn, P and As atoms were also calculated with the linear response method. The dependences of the thermal equilibrium concentrations of trapped and total intrinsic point defects (sum of free *I* or *V* and *I* or *V* trapped with dopant atoms) on the concentrations of B, C, Sn, P and As in Si were obtained. Furthermore, the present evaluations well explain the experimental results of the so-called "Voronkov criterion" in B and C doped Si, and also the observed dopant dependent void sizes in P and As doped Si crystals. The expressions obtained in the present work are very useful for the numerical simulation of grown-in defect behavior, oxygen precipitation and dopant diffusion in heavily doped Si. DFT calculations also showed that Coulomb interaction reaches approximately 30 Å from p (n)-type dopant atoms to *I* (*V*) in Si.

1. Introduction

It is well known that p-type, neutral and n-type dopants affect the intrinsic point defect (vacancy *V* and self-interstitial *I*) behavior in single crystal Si. By the interaction with *V* and/or *I*, (1) growing Si crystals become more *V*- or *I*-rich [3,5,14,20,2,23], (2) oxygen precipitation is enhanced or retarded [20,18], and (3) dopant diffusion is enhanced or retarded [7,11], depending on the type and concentration of dopant atoms. In case (1), a reduction of the radius of the oxidation induced stacking fault (OSF) ring in CZ-Si was observed in case of B doping higher than ~1×10^{18} B cm^{-3}[5]. High concentrations of P, As, or Sb doping make the crystal more *V*-rich [14]. In case (2), oxygen precipitation is enhanced by B or C doping [18] while it is retarded by P or As doping [20]. In case (3), B diffusion is mediated by self-interstitials [7] while Sb diffusion is mediated by vacancies in Si [11].

Since these interactions affect a wide range of Si properties ranging from as-grown crystal quality to LSI performance, numerical simulations are used to predict and to control the behaviors of both dopant atoms and intrinsic point defects [14,8]. In most cases, the thermal equilibrium concentrations of dopant-point defect pairs are evaluated using mass action law by taking only the binding energy of the closest pair to each other into account [14]. The impacts of dopant atoms on the formation of *V* and *I* more distant than 1st neighbor and on the change of formation entropy are usually neglected. In a previous study

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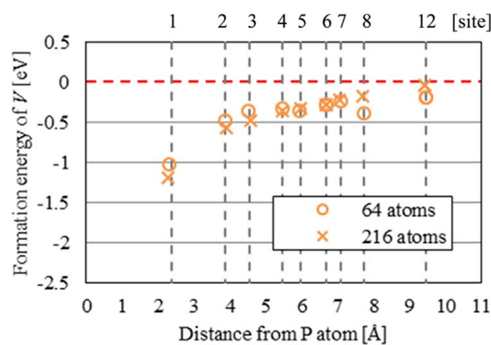

Fig. 1. (color online) Comparison of the calculated change of V formation energy E_f^V at each site around the central P atom in 64-atom and 216-atom Si supercells. The dotted lines at 1st to 8th, and 12th site indicate the distance from P atom before ionic coordinates are relaxed.

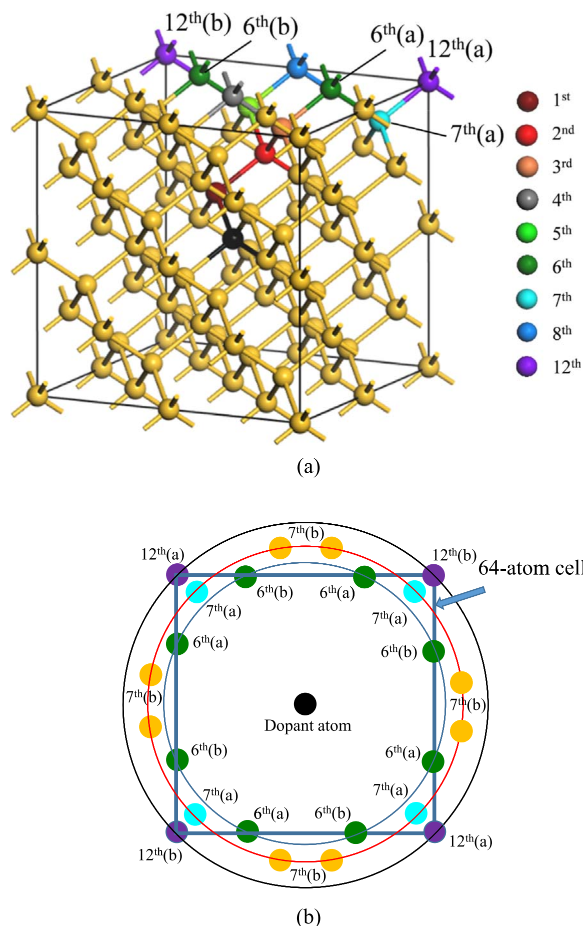

Fig. 2. (color online) (a) 64-atom calculation cell with V sites classified according to the distance from the dopant atom in the center (black). (b) Supplementary illustration for 6th, 7th and 12th sites on circles with dopant atom (black) at the center and 64-atom supercell.

of the authors [17], an appropriate model of V and I behavior in a growing single crystal Si was proposed based on density functional theory (DFT) calculations of the formation energy (E_f) of V and I up to 5th neighboring sites from the dopant atom. To understand the dopant impact more precisely, even more distant sites should be considered as the E_f of V (I) at 5th site from n-type (p-type) dopant are still decreasing. Also the change of formation (vibration) entropies of V and I should be considered.

In this study, we have evaluated the thermal equilibrium concentrations of intrinsic point defects in heavily doped Si crystals. DFT calculations were performed to obtain E_f of the uncharged V and I at all

Table 1
Distance and coordination number of each V site around a central dopant atom before optimization of geometry in a Si 64-atom supercell with cell size of 10.937 Å.

No. V site from dopant atom	Distance from dopant atom (Å)	Coordination number
1st	2.37	4
2nd	3.87	12
3rd	4.53	12
4th	5.47	6
5th	5.96	12
6th (a)	6.69	12
6th (b)	6.69	12
7th	7.10	4
8th	7.73	12
12th (a)	9.40	4
12th (b)	9.40	4

sites in a 64-atom supercell around the substitutional p-type (B, Ga, In, and Tl), neutral (C, Ge, and Sn) and n-type (P, As, and Sb) dopant atoms. The formation entropies (S_f) of free I, V and I, V at 1st neighboring site from B, C, Sn, P and As atoms were also calculated with the linear response method. The dependences of the thermal equilibrium concentrations of trapped and total point defects (sum of free I or V and I or V trapped with dopant atoms) on the concentrations of B, C, Sn, P and As in Si are obtained. Furthermore, the experimental results of so-called "Voronkov criterion" in B and C doped Si, and also the observed void sizes in P and As doped Si crystals are explained. The expressions obtained in the present work are very useful for the numerical simulations of grown-in defect behavior, oxygen precipitation and dopant diffusion in heavily doped Si. The maximum distances of Coulomb interaction from p (n)-type dopant atoms to I (V) are also clarified.

2. Calculation details

DFT calculations were performed within the generalized gradient approximation (GGA) for electron exchange and correlation, using the CAmbridge Serial Total Energy Package (CASTEP) code [1]. The wave functions were expanded with plane waves, and the ultra-soft pseudopotential method [22] was used to reduce the number of plane waves. The cut-off energy was 340 eV. The expression proposed by Perdew et al. [15] was used for the exchange-correlation energy in the GGA. Density mixing [9] was used to optimize the electronic structure and Broyden Fletcher Goldfarb Shanno (BFGS) geometry optimization [6] was used to optimize the atomic configurations. The convergence condition to optimize the electronic structure was set to a change in total energy that was smaller than 5×10^{-7} eV/atom. The convergence conditions to optimize the geometry were set to a change in total energy that was smaller than 5×10^{-6} eV/atom, atomic force that was smaller than 0.001 eV/Å, and stress in the cell that was smaller than 0.001 GPa.

In the present study, we considered only neutral intrinsic point defects. The cell size of a perfect 64-atom Si supercell after its geometry optimization was 10.937 Å. Periodic boundary conditions were used to calculate perfect and defect-containing Si crystals. k-point sampling was performed at 2×2×2 special points in a Monkhorst-Pack grid [12]. In a single crystal Si, the thermal equilibrium concentrations of V and I, even near melting temperature, are well below 5×10^{15} cm^{-3}[14]. For such low concentration, the calculation cell should be surrounded by perfect cells. Therefore, the calculations for the dopant and/or intrinsic point defects were performed by using a cubic supercell with the same cell size as for perfect crystals. Preliminary calculations were performed to confirm the reliability of a calculation cell of 64-atoms. Fig. 1 shows the comparison of the results obtained for 64-atom and 216-atom supercells for the change of V formation energy E_f at 1st to 8th, and 12th site from the P atom doped in Si crystal. The dotted black lines at

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