Effect of tin on point defects and oxygen precipitation in Czochralski silicon: Experimental and theoretical studies

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The effect of tin (Sn)-doping on point defects and oxygen precipitation (OP) in Czochralski (CZ) silicon has been investigated by experiment and theoretical calculations based on density functional theory (DFT). It is found that Sn plays different roles in affecting OP according to the amount of introduced vacancies. That is, Sn suppresses OP in vacancy-lean CZ silicon but promotes OP in vacancy-rich CZ silicon. The effects of Sn-doping on the formation and annihilation of point defects as well as on the evolution of vacancy- and oxygen-related complexes have been systematically studied using DFT calculations. Based on the experimental and theoretical results, it is postulated that Sn atoms in silicon act as vacancy reservoirs which modify the formation and annihilation of vacancies as well as the evolution of vacancy-related complexes. The mechanism for the different roles of Sn in affecting OP is discussed based on the DFT calculations. © 2013 American Institute of Physics. [http://dx.doi.org/10.1063/1.4794531]

I. INTRODUCTION

Oxygen is the primary impurity inevitably incorporated into Czochralski (CZ) silicon during crystal growth. The supersaturated oxygen atoms will form oxygen precipitates and even induce secondary defects such as dislocations and stacking faults during the device fabrication process. Such oxygen precipitates and secondary defects, overall termed as bulk micro-defects (BMDs), are important for internal gettering (IG) in CZ silicon.[1–3] Appropriate control of oxygen precipitation (OP) can enhance the IG capability and improve the mechanical strength of CZ silicon wafers.[4] Moreover, the oxygen atoms will interact with the point defects including vacancy (V) and silicon self-interstitial (I), which in turn exert an influence on OP in CZ silicon.[5] In order to control the defects and therefore to improve the quality of CZ silicon wafers, specific impurities are intentionally co-doped into CZ silicon crystals. This is the so-called "impurity engineering," which has involved the co-doping of nitrogen, carbon, or germanium.[6–9]

Recently, Sn-doped CZ (SCZ) silicon has attracted considerable attention. The isovalent Sn impurity is electrically inactive itself in silicon and can be doped into silicon with a high concentration. Sn-doping endows silicon with prominent radiation hardness, which has trigged a lot of research interests.[10–12] Moreover, the oversized Sn atoms are suitable for strain compensation in heavily boron-doped silicon wafers which are the basic substrate materials for power devices.[13] Furthermore, Sn-doping is also expected to be desirable for impurity engineering of CZ silicon. Therefore, it is necessary to gain an insight into the impact of Sn-doping on point defects and OP in CZ silicon.

Sn atom has a covalent radius of 1.40 Å, larger than that (1.17 Å) of Si. As a result, Sn atoms can act as efficient vacancy traps in silicon. The combination of Sn atoms with vacancies suppresses the formation of vacancy-oxygen (VO) complexes (A-centers) and di-vacancies (V_2), which are the main electrically active defects, introduced in CZ silicon by the particle irradiation.[11–14] The resulting SnV complex has a special split-vacancy configuration in which Sn atom resides in a position halfway between two normal silicon atom sites.[15] Two donor levels at $E_V + 0.35$ eV (Ref. [15]) and $E_V + 0.07$ eV (Ref. [16]) as well as two acceptor levels at $E_C - 0.21$ eV and $E_C - 0.50$ eV (Ref. [17]) were assigned to the SnV complex. Density functional theory (DFT) calculations and Fourier transform infrared (FTIR) measurements of the electron-irradiated CZ silicon revealed that Sn-doping reduces the formation of the VO and in turn the VO_2 defects due to the generation of SnVO complexes.[10–12,18] Furthermore, the formation of VO_n complexes which are considered to be the heterogeneous nucleation centers of oxygen precipitates is affected by the Sn-doping.[19] Besides the vacancy-related defects, carbon- and oxygen-related complexes such as C_iO_i and C_iC_s are also identified to be suppressed in SCZ silicon. The above observations are attributed to the lattice strain induced by the Sn-doping.[11] Based on the DFT calculations, Chroneos proposed a method of doping the oversized dopants such as Pb, Zr, or Hf to suppress the formation of VO defects in CZ silicon.[12] It is also found that OP in SCZ silicon is enhanced during the single-step annealing at temperatures 400–900 °C for 100 h in N_2 atmosphere, which is attributed to the formation of Sn-V pairs.[20] Moreover, the formation of thermal donors is reported to be suppressed in SCZ silicon.[21,22] In a word, the doped Sn atoms significantly affect the evolution of oxygen-related defects and actively interact with the vacancies in CZ silicon.

In this work, we have experimentally investigated the OP behaviors of CZ and SCZ silicon wafers subjected to low-high two-step anneals without and with prior rapid thermal processing (RTP) at different high temperatures. It is shown that the co-doped Sn atoms play different roles in

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affecting OP in CZ silicon wafers with varying amounts of vacancies injected by the RTP. The influence of Sn atoms on point defects and the interactions of Sn atoms and vacancies or vacancy-related clusters have been studied by means of DFT calculations. Based on the experimental and theoretical results, we have proposed that the Sn atoms in silicon can serve as vacancy reservoirs, governing the transformation between the free vacancies and vacancy-related complexes under different conditions. In consequence, OP in CZ silicon is modified by Sn-doping in a manner.

II. EXPERIMENTAL DETAILS AND CALCULATION METHODS

Two kinds of specimens were sliced from 4 in. $\langle 100 \rangle$-oriented conventional CZ and SCZ silicon wafers, respectively. The Sn concentration in SCZ silicon is $\sim 5 \times 10^{17} \, cm^{-3}$, measured by second ion mass spectroscopy (SIMS) using a CAMECA IMS 4f system. The initial interstitial oxygen concentrations in the CZ and SCZ wafers were $\sim 8.7 \times 10^{17} \, cm^{-3}$, measured by a Brucker IFS 66 V/S FTIR spectrometer at room temperature using the conversion coefficient of $3.14 \times 10^{17} \, cm^{-3}$. The carbon concentrations in the CZ and SCZ silicon wafers were below the detection limit of FTIR spectroscopy. For either CZ or SCZ silicon, the specimens were divided into four groups. One group was annealed at $1000 \, ^\circ C$ for $30 \, min$ for investigation of oxygen out-diffusion. The oxygen out-diffusion depth profiles were measured by SIMS using the CAMECA IMS 4f system. While, the other three groups were annealed to generate oxygen precipitates. The related annealing procedures are detailed in Table I. It should be mentioned that the CZ and SCZ silicon specimens were simultaneously annealed in argon atmosphere. After the annealing, the samples were dipped into a dilute HF solution [HF (49 wt. %):$H_2O = 1:10$ in volume ratio] for $2 \, min$ to remove any oxide layers. The BMD densities in the CZ and SCZ silicon specimens were measured by a Semilab SIRM-300 Scanning infrared microscope (SIRM).

DFT calculations were performed using ultrasoft-pseudopotentials method as implemented in the CASTEP code.[23–25] The DFT exchange-correlation potential was described by generalized gradient approximation (GGA) using the Perdew-Buerke-Ernzerhof function.[26] Structure optimization was performed with a large cutoff energy of $380 \, eV$ and a $2 \times 2 \times 2$ Monkhorst-Pack[27] scheme for the Brillouin zone sampling. Periodic supercells containing 64 diamond structure tetrahedral sites were relaxed under constant volume conditions (with a lattice dimension of $10.86 \, \text{Å}$) and constant pressure conditions (zero pressure), respectively. The convergence
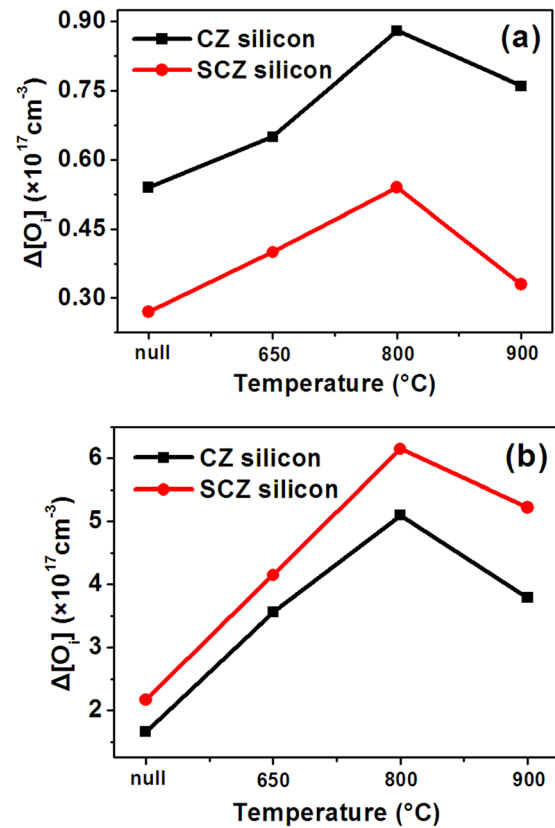

FIG. 1. Decreases in O_i concentrations for the CZ and SCZ silicon specimens subjected to the single-step anneal at $1000 \, ^\circ C$ for $16 \, h$ (labeled as "null" in the x-axis) and the two-step anneal of (650, 800, and 900) $^\circ C/8 \, h$ + $1000 \, ^\circ C/16 \, h$, without (a) and with (b) the pretreatment of RTP at $1250 \, ^\circ C$ for $60 \, s$.

tolerance of the structure relaxation was confined to $5.0 \times 10^{-6} \, eV$ for the energy and $5.0 \times 10^{-4} \, \text{Å}$ for the maximum displacement.

III. RESULTS

A. Effect of Sn-doping on OP

Figure 1 shows the decreases in interstitial oxygen (O_i) concentrations ($\Delta[O_i]$s) in the CZ and SCZ silicon specimens after low-high two-step anneal without and with the RTP pretreatment, respectively. Note that *null* in x axis in Fig. 1 represents that no nucleation anneal was performed before the $1000 \, ^\circ C$ anneal. It can be seen that the most significant nucleation for OP occurs at $800 \, ^\circ C$ in both CZ and SCZ silicon specimens. The $\Delta[O_i]$s in the SCZ silicon specimens are always smaller than those in the CZ silicon specimens, as shown in Fig. 1(a), indicating a suppression effect of

TABLE I. Annealing procedures for OP in the CZ and SCZ silicon specimens (*null* represents no nucleation anneal).

	RTP		Nucleation anneal		Growth anneal	
	Temperature ($^\circ C$)	Duration (s)	Temperature ($^\circ C$)	Duration (h)	Temperature ($^\circ C$)	Duration (h)
1	…	…	null, 650, 800, 900	8	1000	16
2	1250	60	null, 650, 800, 900	8	1000	16
3	1050–1250	60	800	4	1000	16

Sn-doping on OP. However, when a RTP pretreatment at 1250 °C for 60 s is applied, the $\Delta[O_i]$s in the SCZ silicon specimens become larger than those in the CZ silicon specimens, as shown in Fig. 1(b). Figure 2 shows the depth profiles of BMD densities in the CZ and SCZ specimens subjected to the two-step anneals with the nucleation anneals at 650 and 800 °C, respectively, following the RTP at 1250 °C for 60 s. As can be seen, the BMD densities in the SCZ silicon specimens are much higher than those in the CZ silicon specimen. Moreover, it is derived from the comparison between Figs. 1(a) and 1(b) that the prior RTP significantly enhances OP in either CZ or SCZ silicon. The results revealed in Figs. 1 and 2 demonstrate the various roles of Sn-doping in OP under different conditions. That is, the Sn-doping exhibits a suppression effect on OP without the RTP pretreatment while an enhancement effect on OP with the RTP pretreatment at 1250 °C.

Since the RTP at high temperature injects vacancies into silicon,[28,29] it is believed that the different effects of Sn-doping on OP in CZ silicon, as mentioned above, are most likely related to the vacancies. To further verify this point, the CZ and SCZ silicon specimens were subjected to 800 °C/4 h + 1000 °C/16 h anneal following the RTP at different temperatures ranging from 1050 to 1250 °C. The resultant $\Delta[O_i]$s in the CZ and SCZ silicon specimens are shown in Fig. 3. As can be seen, the $\Delta[O_i]$s in the SCZ silicon

FIG. 3. Decreases in O_i concentration for the CZ and SCZ silicon specimens subjected to the two-step anneal of 800 °C/4 h + 1000 °C/16 h following the RTP at 1050, 1100, 1150, 1200, and 1250 °C for 60 s, respectively.

specimens are larger than those in the CZ silicon specimens when the RTP temperature is higher than 1100 °C. However, as the RTP temperature decreases, the difference between the $\Delta[O_i]$s of CZ and SCZ silicon specimens is reduced. Note that the $\Delta[O_i]$ in the SCZ silicon falls below that in CZ silicon when the RTP temperature is 1050 °C, indicating the suppression effect of Sn-doping on OP, similar to the case as revealed in Fig. 1(a).

B. Effect of Sn-doping on oxygen diffusion

Figure 4 shows the normalized oxygen concentration depth profiles in the CZ and SCZ specimens annealed at 1000 °C for 30 min. It can be seen that the oxygen concentration profiles in the CZ and SCZ specimens are almost the same, indicating that the oxygen diffusion is hardly influenced by the Sn-doping at the level of $5 \times 10^{17}\,\mathrm{cm}^{-3}$. Since the concentrations of Sn and O_i in silicon are nearly comparable ($5 \times 10^{17}\,\mathrm{cm}^{-3}$ for Sn and $8.75 \times 10^{17}\,\mathrm{cm}^{-3}$ for O_i), it is derived from the above result that the Sn and O_i atoms have no direct interaction. However, considering the large strain field existing around the oversized Sn atoms, this scenario may not be the case if a much higher concentration of Sn atoms is doped into CZ silicon.
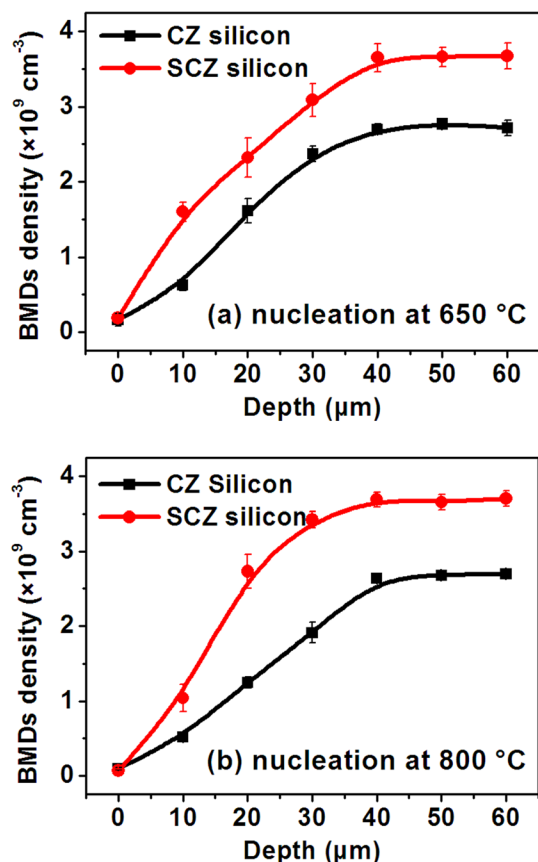

FIG. 2. BMD density depth profiles in the CZ and SCZ silicon specimens subjected to the two-step anneal of 650 and 800 °C/4 h + 1000 °C/16 h, respectively, following the RTP at 1250 °C for 60 s.
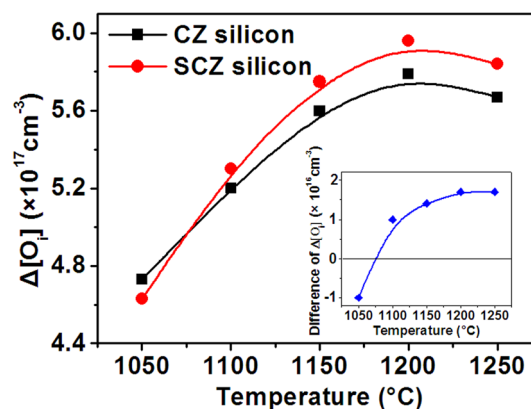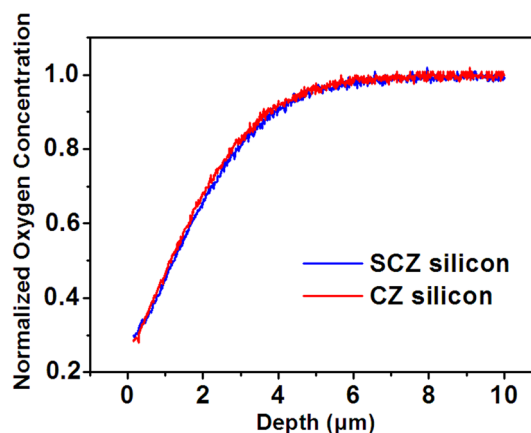

FIG. 4. Normalized oxygen concentration profiles in the CZ and SCZ silicon specimens annealed at 1000 °C for 30 min in Ar atmosphere.

C. Effect of Sn-doping on the point defects

The optimal lattice site for silicon self-interstitials is ascertained to be the hexagonal interstitial site, which is in accordance with previous calculations.[30] Herein, only the neutral defects are taken into consideration. The formation energy of the neutral defects is calculated by

$$E_f = E_{defect} - \sum n\mu_i, \tag{1}$$

where E_{defect} is the supercell energy containing defects, n is the number of atoms in the supercell, and μ_i is the chemical potential of a silicon atom in bulk silicon, which is calculated from a 64-atom supercell.

Figure 5 shows the values of formation energy of self-interstitials (E_I^f) calculated under constant pressure and constant volume conditions, respectively. It can be seen that the E_I^f values for pristine silicon are 3.32 and 3.68 eV, calculated under constant pressure and constant volume conditions, respectively. They are close to the E_I^f of 3.80 eV calculated by Leung *et al.*[30] As a Sn atom is introduced into the supercell, the E_I^f is increased, ranging from 4.36 to 4.51 eV with increasing the distance from 2.7 to 5.4 Å between the Sn and interstitial silicon atoms under the constant volume condition. The same trend is also found in the case calculated under the constant pressure condition, although the numerical values are somewhat different. In the following, unless otherwise mentioned, the discussions will be based on the values obtained under the constant volume condition if the same trend is revealed by both calculation conditions.

Since the concentration of self-interstitials follows the Arrhenius equation, it is expected that the increase of 0.68–0.83 eV in formation energy will lead to significantly suppressed formation of self-interstitials if a large amount of Sn atoms are incorporated into the silicon. Of course, the calculated result as mentioned above does not really reflect the actual situation in our SCZ silicon. However, the tendency predicted by the DFT calculation for the generation of silicon self-interstitials is reasonable for the SCZ silicon used in this work.

Figure 6 shows the binding energy (E_b) of a vacancy and a self-interstitial. In calculating E_b, the reaction process
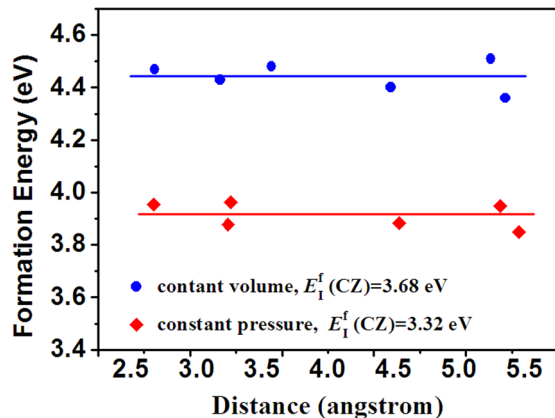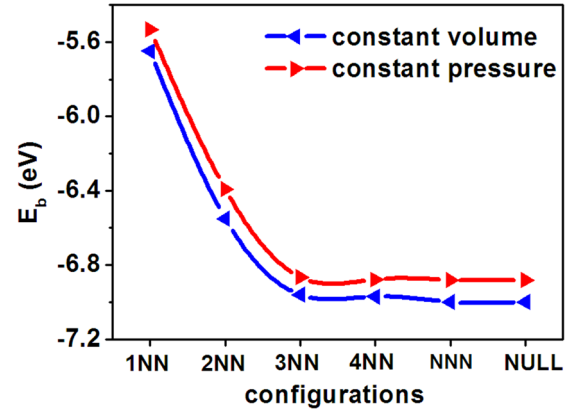

FIG. 6. Binding energy (E_b) of a vacancy and a self-interstitial in different configurations. From the left to right along the x-axis, it is represented that a Sn atom locates at the 1st, 2nd, 3rd, and 4th nearest neighboring sites of a vacancy, respectively, and is infinitely separated from a vacancy (NNN). NULL represents no Sn atom.

$$I + V \rightarrow Si \tag{2}$$

is taken into account. The binding energy E_b is calculated according to

$$E_b = E[\text{defect pair}] - \sum E[\text{isolated defect}] + E[\text{perfect}], \tag{3}$$

where $E[\text{defect pair}]$ and $E[\text{isolated defect}]$ represent the energies of the supercells containing the defect pair and isolated defect, respectively; and $E[\text{perfect}]$ stands for the energy of a perfect supercell. The negative values of E_b indicate that the recombination of vacancies and self-interstitials (V-I recombination) are energetically favored. The larger the absolute value of E_b, the easier the V-I recombination is. In Fig. 6, the NNN in the x axis represents the case of a Sn atom being infinitely separated from a vacancy and the NULL means no Sn atom presented in silicon. The absolute values of E_b in both cases of NNN and NULL are nearly the same and the largest, indicating that the most favored recombination occurs in the absence of Sn atoms. As the Sn atom progressively approaches the vacancy, the absolute value of E_b decreases, suggesting that the V-I recombination is retarded around the Sn atoms.

Table II shows the binding energies calculated under constant volume condition for the different vacancy-related complexes. It can be found that the SnV complex has a large binding energy of -1.26 eV, while those of V_2 and VO complexes are even larger. It is understood that the formation of SnV complexes is facilitated by the strain-relief, while the V_2 complexes are formed as a result of reducing the dangling bonds from eight to six in number. In the case of VO complexes, both stress-relief and reduction in dangling bonds

FIG. 5. Formation energies of self-interstitials in the case of introducing a Sn atom into the silicon lattice.

TABLE II. Binding energies calculated under constant volume conditions for vacancy-related complexes.

Complex	VO	V_2	SnV	SnVO	SnV_2	VO_2
E_b (eV)	-1.68	-1.56	-1.26	-2.28	-2.81	-2.78

occur. However, the reduction in the dangling bonds does not occur during the movement of a vacancy toward another vacancy or an O_i atom, which is driven by strain-relief to reach the minimum energy. In order to compare the vacancy-capture capabilities of the Sn atom, oxygen atom, and vacancy itself, we have calculated the changes in energies as a vacancy moves toward the Sn atom and another lattice defect (vacancy or oxygen atom, denoted as V/O hereafter). Herein, the reference energy is defined when the vacancy is located at an infinitely separated site. We first calculate the energy as the vacancy moves from the infinite site to the midpoint between the Sn atom and V/O. Then, we calculate the changes in energies as the vacancy moves toward the Sn atom and V/O starting from the midpoint, respectively. Figure 7 shows the absolute values of the decreases in total energies ($\Delta E_{abs.}$) for different configurations consisting of Sn and O/V. As can be seen, in terms of energy loss, the formation process of V_2 complexes is the most probable, followed with those of SnV and VO complexes in turn. However, because the vacancy concentration is several orders of magnitude lower than those of Sn and O_i atoms, the probability of forming the V_2 complex is much smaller than that of forming SnV or VO complex. Despite that the trends shown in Fig. 7(b) are somewhat different under constant pressure and constant volume conditions, the above-mentioned viewpoint is all the same. Actually, it has been reported that the Sn atom is about a factor of 5 more efficient than the O_i atom in trapping the vacancy.[17] Therefore, the formation of SnV complexes prevails over that of VO complexes. Experimentally, the existence of SnV complexes in
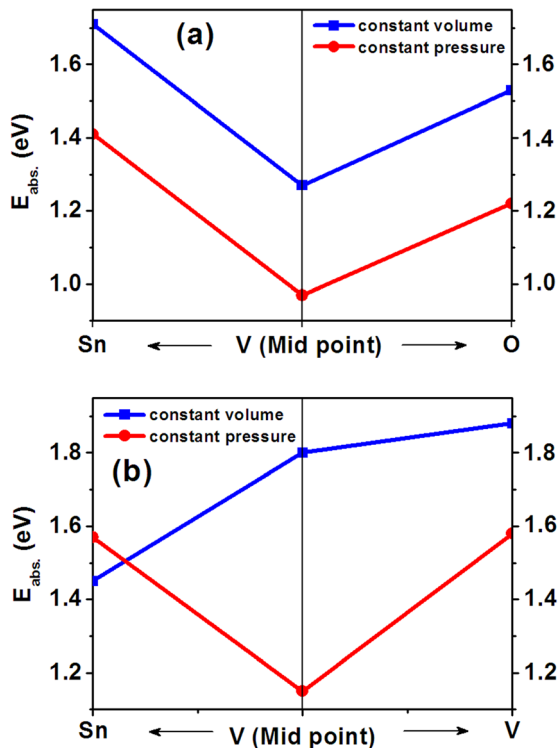
SCZ silicon has been confirmed by electron paramagnetic resonance (Ref. 15), DLTS (Ref. 31) and infrared absorption measurements.[32]

Figure 8 shows the absolute values of the decreases in total energies ($\Delta E_{abs.}$) for the movements of V_2 and VO complexes toward a Sn atom from an infinitely separated site, respectively. It is indicated that the V_2 and VO complexes are energetically favorable to combine with the Sn atoms to form the SnV_2 or SnVO complexes. Moreover, the calculated binding energies of SnV_2 or SnVO complexes are also shown in Table II. It can be derived from the binding energies that the SnV_2 and SnVO complexes are more stable than the VO complex and comparable to the VO_2 complex.

IV. DISCUSSIONS

A. On the point defects

The equilibrium concentration of vacancies in the doped silicon is given as

$$C_V^{eq} = C_{V0}^{eq} \exp(k\{(V_i - V_{Si})n\}), \qquad (4)$$

where C_{V0}^{eq} is the equilibrium concentration in intrinsic silicon, k reflects the size difference between the dopant and Si atoms, and n is the dopant concentration.[33] It can be derived from Eq. (4) that the doping of oversized atoms in silicon results in a higher equilibrium vacancy concentration. Actually, it has been proved that Ge-doping increases the equilibrium vacancy concentration.[34] Moreover, it is estimated that the Sn-doping at $\sim 1 \times 10^{18}\,cm^{-3}$ leads to an increase in vacancy concentration by 2.4%.[33] The reason for this increase in vacancy concentration is twofold, i.e., the decreased formation energy and the suppressed V-I annihilation. The Sn-Si bond length is stretched to 2.56 Å, larger than that of intrinsic Si-Si bond length (2.35 Å). The elongated Sn-Si bond is much easier to be broken than the Si-Si bond by the high temperature anneal. Furthermore, the strain field induced by the oversized Sn atoms favors the vacancy formation. In this work, the vacancy formation energy at the 1NN site of a Sn atom is calculated to be 2.18 eV for SCZ silicon, which is 1.25 eV smaller than that for CZ silicon. This vacancy formation energy of 2.18 eV is quite close to the experimentally derived value of 2.20 ± 0.13 eV

FIG. 7. Absolute values of the decreases in total energies ($\Delta E_{abs.}$): (a) a vacancy moves toward a Sn atom or an O_i atom from the midpoint, (b) a vacancy moves toward a Sn atom or a vacancy from the midpoint. Herein, the reference energy is defined when the vacancy is located at an infinitely separated site.
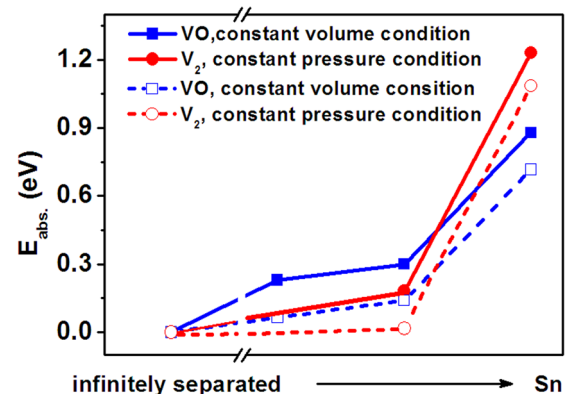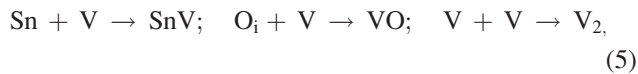

FIG. 8. Absolute values of the decreases in total energies ($\Delta E_{abs.}$) when the V_2 and VO complexes move toward a Sn atom from an infinitely separated site, respectively.

for the Ge-doped CZ silicon with a concentration of $6.5 \times 10^{20}\,\mathrm{cm}^{-3}$.[34]

Vacancy annihilation is due to the recombination with silicon self-interstitials. The formation of SnV complexes is actually a way of preserving vacancies. The negative values of binding energy shown in Fig. 6 indicate that the V-I recombination is an exothermic process. The V-I recombination is suppressed as the vacancy moves toward the Sn atom, as indicated in Fig. 6. In other words, the Sn-doping prevents the vacancies from being annihilated due to the formation of SnV complexes. Therefore, the Sn atoms in silicon can be regarded as the vacancy reservoirs.

B. On the evolution of Sn-related complexes

It has been revealed that vacancies are energetically favored to generate around the Sn atoms, leading to the formation of SnV complexes. Moreover, the formation of V_2 and VO complexes is also favorable from the thermodynamic point of view. Nevertheless, the formation of SnV complexes prevails in SCZ silicon, as analyzed in the above. This has also been derived by Nylandsted Larsen *et al.*[17] The reported diffusion activation energy of VO complex is $\sim 2.0\,\mathrm{eV}$,[35] close to that of O_i atom. It is thus suggested that the VO complex and the O_i atom may have comparable diffusivities. The VO complexes will be probably captured by the Sn atoms to form the SnVO complexes. Likewise, the mobile V_2 complexes can also be captured by the Sn atoms, resulting in the formation of SnV_2 complexes. The evolution of different complexes can be expressed as follows:

$$\mathrm{Sn} + \mathrm{V} \rightarrow \mathrm{SnV}; \quad \mathrm{O_i} + \mathrm{V} \rightarrow \mathrm{VO}; \quad \mathrm{V} + \mathrm{V} \rightarrow \mathrm{V_2}, \tag{5}$$

$$\mathrm{SnV} + \mathrm{O_i} \rightarrow \mathrm{SnVO}; \quad \mathrm{VO} + \mathrm{O_i} \rightarrow \mathrm{VO_2}, \tag{6}$$

$$\mathrm{Sn} + \mathrm{VO} \rightarrow \mathrm{SnVO}; \quad \mathrm{Sn} + \mathrm{V_2} \rightarrow \mathrm{SnV_2}. \tag{7}$$

It has been confirmed that the VO_2 (Refs. 36 and 37) and SnVO (Ref. 18) complexes can be evolved from the VO and SnV ones along with the increase of annealing temperature. More complicated V_mO_n complexes are formed at even higher temperature at a price of consuming the simple complexes.[36,37] Therefore, it is derived that the simple complexes such as VO and SnV ones are the building blocks for the more complicated complexes and even clusters formed at higher temperature.

In SCZ silicon, the formation of SnV, SnVO, and SnV_2 complexes is somewhat similar to that of VO_2 complexes, which is accomplished during the RTP. The vacancies generated at high temperature are fast diffusers in silicon. They can be readily captured by the Sn and O_i atoms. Actually, a part of vacancies is generated around the oversized Sn atoms. In this context, the above-mentioned different complexes are generated. During the subsequent nucleation anneal at low temperature (e.g., 650–800 °C), more oxygen atoms aggregate onto the complexes evolved from the SnV, SnVO, and SnV_2 ones, resulting in more complicated clusters which further evolve into oxygen precipitate nuclei. A similar story for the VO_2 complexes acting as the heterogeneous nucleation precursors for OP has been elucidated by Falster and Voronkov.[5]

C. Homogeneous nucleation of OP in SCZ silicon

For SCZ silicon, we have evaluated the interactions between Sn and O_i atoms by DFT calculations. It is found that the O_i atoms are unable to aggregate around the Sn atoms because the Sn-O complexes are not energetically favorable to form. Therefore, in the absence of vacancies in SCZ silicon, the Sn atoms will not be involved into the heterogeneous nucleation of OP. Therefore, in the SCZ silicon received no prior RTP, the nucleation of OP is dominated by a homogeneous process. The OP process can be expressed as

$$(1 + \mathrm{y})\,\mathrm{Si} + 2\mathrm{O_i} \rightarrow \mathrm{SiO_2} + \mathrm{yI} + \mathrm{strain}, \tag{8}$$
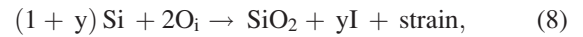
where "I" is the self-interstitials emitted from the growing oxygen precipitates in order to release the strain, and y is the number of the self-interstitials. Obviously, if the emission of self-interstitials is suppressed, then OP is suppressed. On the other hand, if a number of self-interstitials have existed in CZ silicon due to certain reasons, then OP is also suppressed.

Since Fig. 4 shows that the Sn-doping at the level of $\sim 5 \times 10^{17}\,\mathrm{cm}^{-3}$ in our specimens has no essential influence on oxygen diffusion, it is known that the suppressed OP in SCZ silicon, as shown in Fig. 1(a), does not relate to the oxygen diffusion. According to the theoretical results given in Fig. 5, the Sn-doping increases the formation energy of silicon self-interstitials. In other words, the emission of self-interstitials from the growing oxygen precipitates is suppressed. Moreover, the Sn-doping induces strain in the silicon lattice due to the oversize of Sn atoms. It has been reported that the substitution of a Si site by a Ge atom in the silicon lattice is roughly equivalent to the introduction of 0.04 self-interstitials with respect to strain.[34] Considering the covalent radius of Sn (1.41 Å) is even larger than that of Ge (1.22 Å), it is estimated that a substitutional Sn atom in silicon lattice is equivalent to introducing ~ 0.2 self-interstitials. In view of the above analysis, the suppression effect of Sn-doping on OP, as shown in Fig. 1(a)), can be understood.

D. Heterogeneous nucleation of OP in SCZ silicon

The high temperature RTP applied on CZ silicon injects a number of vacancies which are involved into the heterogeneous nucleation of OP in the subsequent thermal cycles.[28,29] It is reported that the vacancies introduced by the RTP at 1250 °C reach a concentration of $\sim 10^{13}\,\mathrm{cm}^{-3}$ in CZ silicon.[38] In the conventional CZ silicon, the injected vacancies combine with O_i atoms to form the VO_2 complexes which act as the precursors for the heterogeneous nucleation of OP and, moreover, provide space for relief of strain arising from OP.

When the interaction between the vacancies and the Sn atoms reach equilibrium, the concentration of free monovacancies C_V will be in equilibrium with the concentration of vacancy-related species (C_{VO} for VO complexes and C_{SV} for SnV complexes):[39]

$$C_V/C_{VO} = C_V^e/C_{VO}^e; \quad C_V/C_{SV} = C_V^e/C_{SV}^e, \tag{9}$$

where C_V^e, C_{VO}^e, and C_{SV}^e are equilibrium concentrations of free vacancies, VO complexes and SnV complexes, respectively.

Since both the concentrations of VO and SnV complexes are correlated with the vacancy concentration, we have

$$\frac{C_V}{C_V^e} = \frac{C_{VO}}{C_{VO}^e} = \frac{C_{SV}}{C_{SV}^e}. \qquad (10)$$

It can be derived from Eq. (10) that an equilibrium state will be achieved among the residual free vacancies, the SnV and the VO complexes. Considering the vacancies are preferentially generated around the Sn atoms during the high temperature anneal, the SnV complexes will dominate over other vacancy-related complexes. Therefore, according to Eq. (10), the concentrations of V and VO complexes are affected by the Sn-doping.

In the case of RTP at high temperature (e.g., 1250 °C), the Sn-assisted vacancy generation and the free mono-vacancy generation occur simultaneously. In this context, enough free mono-vacancies are left to reach equilibrium with the SnV and VO complexes. The SnV complexes and VO complexes further capture the O_i atoms to form more stable SnVO and VO_2 complexes which can develop into the heterogeneous nuclei for OP. Moreover, the formation of SnV complexes reduces the amount of substitutional Sn atoms in silicon. Therefore, the suppression effect of Sn atoms on the formation of self-interstitials is to a certain extent relieved. In a word, the enhanced OP in SCZ silicon with respect to that in CZ silicon, as shown in Fig. 3, is due to the additional heterogeneous nuclei initiated from the SnV complexes.

In the case of RTP at relatively low temperature (e.g., 1050 °C), OP in the conventional CZ silicon is dominated by the VO_2-assisted heterogeneous nucleation. In SCZ silicon, nearly all of the vacancies exist in the form of SnV complexes in the very early stage of RTP. In order to reach the equilibrium between the SnV and V species, the SnV complexes have to be dissociated to some extent, releasing free mono-vacancies. However, this process should conquer an energy barrier. As a result, the subsequent formation of the VO and in turn the VO_2 complex in SCZ silicon is not as energetically favorable as that in the conventional CZ silicon. The residual SnV complexes can evolve into the SnVO complexes, based on which the heterogeneous nucleation of OP occurs. Therefore, OP in SCZ silicon with the prior RTP at 1050 °C is enhanced in comparison with that in SCZ silicon received no prior RTP, which can be derived from the comparison between Figs. 1(a) and 3. In SCZ silicon, however, the substitutional Sn atoms, a part of which are returned from the dissociation of SnV complexes as mentioned above, suppress the emission of silicon self-interstitials from the growing oxygen precipitates. Therefore, with the same prior RTP at relatively low temperature of 1050 °C, OP in SCZ silicon is somewhat weaker than that in CZ counterpart, as shown in Fig. 3.

V. CONCLUSIONS

In summary, the effect of Sn-doping on OP in CZ silicon has been experimentally investigated. Moreover, the effect of Sn-doping on the evolution of point defects has been revealed on the basis of DFT calculations. It is found that OP can be either suppressed or enhanced by the Sn-doping, determined by the amount of vacancies existing in CZ silicon. DFT calculations reveal that the formation energy of silicon self-interstitials is increased due to the presence of Sn atoms. On the other hand, the equilibrium vacancy concentration is increased by the Sn-doping due to the decreased vacancy formation energy and the retarded V-I annihilation. Moreover, the Sn atoms are more efficient than the O_i atoms in capturing free mono-vacancies. The resulting SnV complexes further evolve into more stable SnVO and SnV_2 complexes, which are supposed to serve as the heterogeneous nucleation precursors for OP. Combining the experiments and theoretical calculations, it is believed that in the vacancy-rich SCZ silicon the SnV and VO complexes coexist and further evolve into the heterogeneous nucleation precursors, leading to the enhanced OP. In the vacancy-lean SCZ silicon, the formation of SnV complexes dominates over that of VO complexes. The SnV complexes can further evolve into the heterogeneous nucleation centers for OP. However, the residual substitutional Sn atoms in the silicon lattice suppress the emission of self-interstitials from the growing oxygen precipitates. In this context, OP in SCZ silicon is weaker than that in CZ counterpart. It is supposed that the Sn atoms in silicon serve as the vacancy reservoirs which modify the formation, annihilation and evolution of the vacancies and related complexes. It is thus deduced that the Sn-doping may also exert a profound influence on void formation in CZ silicon. Moreover, a well-defined IG process can be developed for CZ silicon with proper Sn-doping in combination with desirable RTP. Furthermore, it is expected that SCZ silicon could be applied into the electronic devices with well radiation-hardness.

[1]S. M. Hu, Appl. Phys. Lett. **36**, 561 (1980).
[2]K. Wada, H. Nakanishi, H. Takaoka, and N. Inoue, J. Cryst. Growth **57**, 535 (1982).
[3]F. Shimura, H. Tsuya, and T. Kawamura, J. Appl. Phys. **51**, 269 (1980).
[4]S. M. Hu, Appl. Phys. Lett. **31**, 53 (1977).
[5]R. Falster and V. V. Voronkov, Mater. Sci. Eng. B **73**, 87 (2000).
[6]F. Shimura, R. S. Hockett, D. A. Reed, and D. H. Wayne, Appl. Phys. Lett. **47**, 794 (1985).
[7]A. Karoui and G. A. Rozgonyi, J. Appl. Phys. **96**, 3264 (2004).
[8]A. Karoui, F. S. Karoui, G. A. Rozgonyi, and D. Yang, J. Appl. Phys. **96**, 3255 (2004).
[9]D. Yang, J. Chen, X. Ma, and D. Que, J. Cryst. Growth **311**, 837 (2009).
[10]A. Chroneos and C. A. Londos, J. Appl. Phys. **107**, 093518 (2010).
[11]A. Chroneos, C. A. Londos, E. N. Sgourou, and P. Pochet, Appl. Phys. Lett. **99**, 241901 (2011).
[12]A. Chroneos, C. A. Londos, and E. N. Sgourou, J. Appl. Phys. **110**, 093507 (2011).

[13]C. Claeys, E. Simoen, V. B. Neimash, A. Kraitchinskii, M. Kras'ko, O. Puzenko, A. Blondeel, and P. Clauws, J. Electrochem. Soc. **148**, G738 (2001).

[14]B. G. Svensson, J. Svensson, J. L. Lindström, G. Davies, and J. W. Corbett, Appl. Phys. Lett. **51**, 2257 (1987).

[15]G. D. Watkins, Phys. Rev. B **12**, 4383 (1975).

[16]G. D. Watkins and J. R. Troxell, Phys. Rev. Lett. **44**, 593 (1980).

[17]A. Nylandsted Larsen, J. J. Goubet, P. Mejlholm, J. Sherman Christensen, M. Fanciulli, H. P. Gunnlaugsson, G. Weyer, J. Wulff Petersen, A. Resende, M. Kaukonen, R. Jones, S. Öberg, P. R. Briddon, B. G. Svensson, J. L. Lindström, and S. Dannefaer, Phys. Rev. B. **62**, 4535 (2000).

[18]L. I. Khirunenko, O. A. Kobzar, Yu. V. Pomozov, M. G. Sosnin, N. A. Tripachko, V. P. Markevich, L. I. Murin, and A. R. Peaker, Phys. Status Solidi C **0**, 694 (2003).

[19]C. A. Londos, A. Andrianakis, D. Aliprantis, E. N. Sgourou, and H. Ohyama, Phys. Status Solidi C **8**, 701 (2011).

[20]W. Wijaranakula, J. Appl. Phys. **69**, 2737 (1991).

[21]V. B. Neimash, A. Kraitchinskii, M. Krasko, O. Puzenko, C. Claeys, E. Simoen, B. Svensson, and A. Kuznetsov, J. Electrochem. Soc. **147**, 2727 (2000).

[22]Yu. V. Pomozov, M. G. Sosnin, L. I. Khirunenko, and V. I. Yashnik, Semiconductors **34**, 994 (2000).

[23]P. E. Blöchl, Phys. Rev. B **50**, 17953 (1994).

[24]D. Vanderbilt, Phys. Rev. B **41**, 7892 (1990).

[25]M. D. Segall, P. J. D. Lindan, M. J. Probert, C. J. Pickard, P. J. Hasnip, S. J. Clark, and M. C. Payne, J. Phys.: Condens. Matter. **14**, 2717 (2002).

[26]J. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).

[27]H. J. Monkhorst and J. D. Pack, Phys. Rev. B **13**, 5188 (1976).

[28]R. Falster, D. Gambaro, M. Olmo, M. Cornara, H. Korb, Mater. Res. Soc. Symp. Proc. **510**, 27 (1998).

[29]R. Falster, M. Cornara, D. Gambaro, M. Olmo, and M. Pagani, Solid State Phenom. **57–58**, 123 (1997).

[30]W.-K. Leung, R. J. Needs, and G. Rajagopal, Phys. Rev. Lett. **83**(12), 2351–2354 (1999).

[31]M. L. David, E. Simoen, C. Claeys, V. Neimash, M. Kras'ko, A. Kraitchinskii, V. Voytovych, A. Kabaldin, and J. F. Barbot, J. Phys: Condens. Matter. **17**, S2255 (2005).

[32]A. Brelot, IEEE Trans. Nucl. Sci. **19**, 220 (1972).

[33]K. Tanahashi, H. Harada, A. Koukitsu, and N. Inoue, J. Cryst. Growth **225**, 294 (2001).

[34]J. Vanhellemont, M. Suezawa, and I. Yonenaga, J. Appl. Phys. **108**, 016105 (2010).

[35]M. Furuhashi and K. Taniguchi, Appl. Phys. Lett. **86**, 142017 (2005).

[36]C. A. Londos, A. Andrianakis, V. Emtsev, G. A. Oganesyan, and H. Ohyama, Mater. Sci. Eng. B **154**, 133 (2008).

[37]C. A. Londos, A. Andrianakis, E. N. Sgourou, V. V. Emtsev, and H. Ohyama, J. Appl. Phys. **109**, 033508 (2011).

[38]M. Jacob, P. Pichler, H. Ryssel, and R. Falster, J. Appl. Phys. **82**, 182 (1997).

[39]V. V. Voronkov and R. Falster, Mater. Sci. Semicond. Process. **5**, 387 (2002).