Retarded oxygen diffusion in heavily phosphorus-doped Czochralski silicon: experiments and first-principles calculations

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Abstract
The effect of heavy phosphorus (P) doping on oxygen diffusion in Czochralski (Cz) silicon has been experimentally and theoretically investigated. It is experimentally found that the oxygen diffusion in heavily P-doped Cz silicon is retarded, with a diffusion activation energy which is ∼0.12 eV larger than that of its lightly P-doped counterpart. First-principles calculations suggest that the P–O complexes in the –P–Si–O–Si–configuration can form in heavily P-doped Cz silicon, leading to the trapping of interstitial oxygen (O_i) atoms at the twelve equivalent second-nearest neighbors of the P atoms. Furthermore, the calculated increase of the oxygen diffusion activation energy, taking account of the trapping effect of such P–O complexes, is in accordance with the experimental result. This indicates that the retarded oxygen diffusion in the heavily P-doped Cz silicon can be ascribed to the trapping of O_i atoms associated with the formation of the aforementioned P–O complexes.

(Some figures may appear in colour only in the online journal)

1. Introduction

Oxygen is the primary impurity that is not deliberately introduced but unavoidable in Czochralski (Cz) silicon. The relevance of oxygen to device fabrication is due primarily to the internal gettering of metal contaminants, which is associated with oxygen precipitation (OP) [1, 2]. Evidently, oxygen diffusion is one of the dominant factors for OP, and it has thus received intensive investigation in the past few decades. It is well recognized that the oxygen atom occupies an interstitial Si–Si bond site in the silicon lattice, forming a Si–O–Si configuration and, moreover, the oxygen diffusion is via the hopping of the oxygen atom from one

interstitial Si–Si bond center to another [3–5]. Intuitively, this oxygen diffusion process in Cz silicon may be disturbed by a dopant of high concentration. Ono *et al* [6] found that the oxygen diffusion in Cz silicon at 800 °C was retarded by both heavy boron (B) and arsenic (As) doping but not by heavy antimony (Sb) doping. They attributed the retarded oxygen diffusion to the existence of dopant–oxygen complexes rather than the charge and size effects arising from the dopants. Takeno *et al* [7] furthermore verified the retarding effects of heavy B and As doping on oxygen diffusion at 500–800 °C. In contrast, they also observed distinct retarded oxygen diffusion in heavily Sb-doped silicon. At high temperatures such as 1125 and 1200 °C, the oxygen

diffusion in Cz silicon was also found to be retarded by the heavy B and As doping [8]. To reveal the physical origin underlying the retarded oxygen diffusion in the heavily doped silicon, first-principles calculations have been performed to explore the interaction between interstitial oxygen (O_i) and dopant atoms. It is revealed that in the heavily As-doped Cz silicon the As atoms can interact with the O_i atoms at the second-nearest neighbors, forming the most stable –As–Si–O–Si–type of complexes, which are believed to trap the O_i atoms, thus reducing the oxygen diffusivity [9].

In recent years, heavily phosphorus (P)-doped Cz silicon has increasingly exhibited its technological importance due to its even lower resistivity with respect to that of the heavily As-doped silicon [10, 11]. Likewise, the oxygen diffusion in the heavily P-doped Cz silicon is of fundamental and technological concern. Unfortunately, this issue has not been essentially addressed as yet. In this work, the oxygen diffusion behaviors in lightly and heavily P-doped Cz silicon have been comparatively investigated in the temperature range of 800–1100 °C. It is found that the oxygen diffusion in the heavily P-doped Cz silicon is retarded, with a diffusion activation energy ∼0.12 eV higher than that of the lightly doped counterpart. First-principles calculations suggest that the P–O complexes in the –P–Si–O–Si–configuration can form in the heavily P-doped Cz silicon, resulting in the trapping of O_i atoms at the twelve equivalent second-nearest-neighbor (2NN) sites of the P atoms. Moreover, the calculated variation of the diffusion activation energy due to the trapping effect of such P–O complexes is essentially in accordance with the experimental result, indicating that the retarded oxygen diffusion in the heavily P-doped Cz silicon is due to the trapping of O_i atoms as a result of forming the aforementioned P–O complexes.

2. Experimental details and the theoretical method

In the experiment, two groups of specimens were sliced from six-inch ⟨100⟩-oriented, heavily and lightly P-doped Cz silicon wafers with the P concentrations of ∼5×10^{19} and 1×10^{15} cm^{-3}, respectively. Here, the doping concentrations were derived from four-point resistivity measurements. The initial oxygen concentrations in the heavily and lightly P-doped wafers were 1.07×10^{18} and 9.32×10^{17} cm^{-3}, measured by secondary-ion mass spectroscopy (SIMS) and Fourier transformation infrared (FTIR) spectroscopy, respectively. The specimens were annealed at 800 °C for 32 h, 900 °C for 8 h, 1000 °C for 30 min and 1100 °C for 20 min in an argon atmosphere. Note that the lightly and heavily doped samples were simultaneously annealed at each temperature in the same furnace. After the annealing, the samples were dipped into a dilute HF solution (HF(49 wt%):H_2O = 1:10 in volume) for 2 min to remove any oxide layers. The oxygen out-diffusion depth profiles in the specimens were measured by SIMS using a CAMECA IMS 4f system. Here, the primary beam was a Cs$^+$ ion beam with the energy of 14.5 keV, resulting in a sputtering rate of 5 nm s^{-1}. The sputtering area covered 250×250 μm^2, while the area analyzed was 30 μm in diameter. The depth of the sputter crater was 8 μm. The oxygen

concentration was converted using a relative sensitivity factor obtained from the analysis of oxygen-implanted standard silicon that had been calibrated against a NIST certified FTIR reference standard (NIST SRM 2551). The detection limit of the oxygen was 5×10^{16} cm^{-3}, which was checked by analysis of a float zone silicon wafer.

First-principles calculations were performed with CASTEP program based on the density functional theory with ultrasoft pseudopotentials [12]. We adopted the widely used 64-atom supercells to define the interactions between the substitutional P and O_i atoms with different configurations in the silicon lattice. The lattice constant of the supercell is 10.86 Å, which is large enough for neglecting the influence from the impurities in the neighboring supercell. The generalized gradient approximation (GGA) using the Perdew–Burke–Ernzerhof [13] exchange–correlation functional was implemented. Moreover, a large cutoff energy of 380 eV coupled with a $2 \times 2 \times 2$ Monkhorst–Pack [14] scheme for the Brillouin zone sampling was used during structure optimization. The convergence of the structure relaxation was tested and ensured.

3. Results

Figure 1 shows the out-diffusion depth profiles of normalized oxygen concentrations in the lightly and heavily P-doped Cz silicon specimens annealed at 800, 900, 1000 and 1100 °C, respectively. It can be seen that the oxygen diffusion is retarded in the heavily P-doped silicon at each temperature. Moreover, the retarding effect becomes weaker at higher temperatures. Note that for the lightly or heavily P-doped Cz silicon the oxygen out-diffusion depth profile at each temperature investigated herein can be fitted with the following error function equation:

$$\frac{C(x)}{C_B} = \frac{C_S}{C_B} + \left(1 - \frac{C_S}{C_B}\right) \text{erf}\left(\frac{x}{2\sqrt{Dt}}\right) \tag{1}$$

where C_S and C_B are the surface and bulk oxygen concentrations, respectively, D is the oxygen diffusivity, x is the depth from the surface, and t is the annealing time. The calculated oxygen diffusivities at different temperatures for the lightly and heavily P-doped Cz silicon are listed in table 1. As can be seen, at each temperature the oxygen diffusivity of heavily P-doped Cz silicon is smaller than that of lightly P-doped Cz silicon. Therefore, it is believed that the oxygen diffusion in the heavily P-doped Cz silicon is dictated by a certain mechanism different from that operating in the lightly P-doped counterpart.

The dependence of oxygen diffusivity on temperature can be expressed by the following equation:

$$D = D_0 \exp\left(-\frac{E_A}{kT}\right) \tag{2}$$

where D is the oxygen diffusivity, D_0 is the diffusion prefactor, and E_A is the diffusion activation energy. Figure 2 shows the fitted curves for the oxygen diffusivities in the temperature range of 800–1100 °C according to equation equation (2) for the lightly and heavily P-doped Cz silicon. We
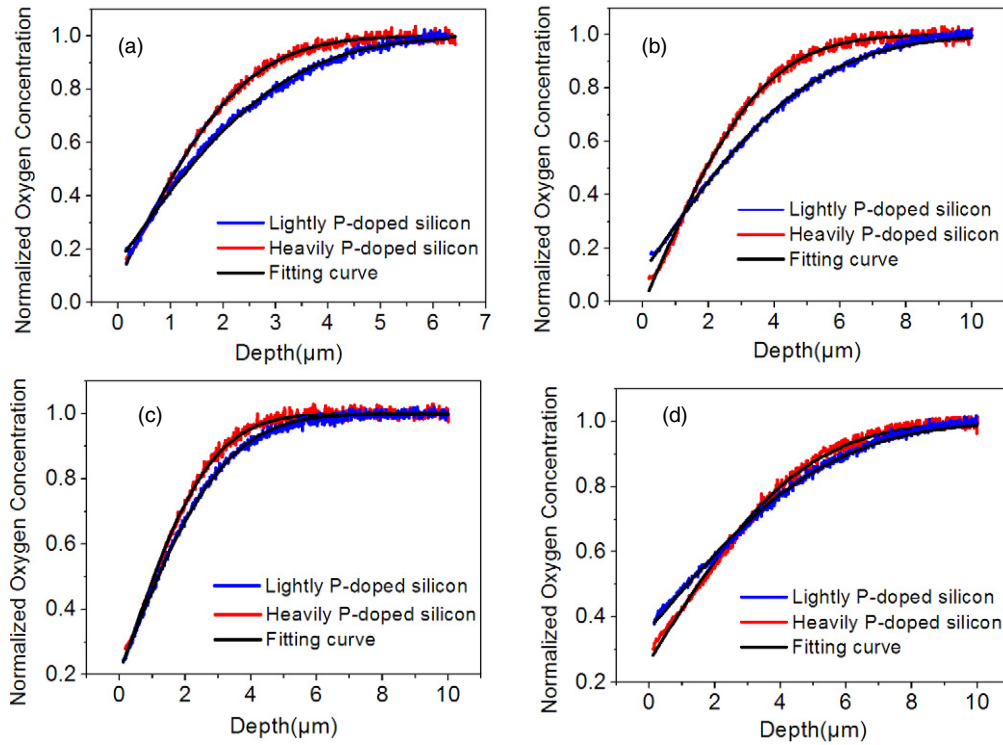
Figure 1. Depth profiles of the normalized oxygen concentrations and calculated fitting curves for the lightly and heavily P-doped Cz silicon specimens annealed at (a) 800 °C for 32 h, (b) 900 °C for 8 h, (c) 1000 °C for 30 min and (d) 1100 °C for 20 min.

Table 1. Oxygen diffusivities calculated by fitting the out-diffusion profiles with equation (1) for the lightly and heavily P-doped Cz silicon.

	Diffusivity (cm^{-2} s^{-1})			
	800 °C	900 °C	1000 °C	1100 °C
Lightly P-doped	2.52×10^{-13}	3.05×10^{-12}	1.68×10^{-11}	8.87×10^{-11}
Heavily P-doped	1.44×10^{-13}	1.40×10^{-12}	1.25×10^{-11}	5.60×10^{-11}

also show Mikkelsen's data [15] as the dashed line in figure 2 for reference. From figure 2, the oxygen diffusion prefactor D_0 and the diffusion activation energy E_A for either kind of silicon can be derived. The temperature dependences of the oxygen diffusivities for the lightly and heavily P-doped Cz silicon are respectively expressed as follows:

$$D_{LP} = 0.08^{+0.06}_{-0.04} \exp(-2.43 \pm 0.07 \text{ eV}/kT) \text{ cm}^{-2} \text{ s}^{-1}$$

$$D_{HP} = 0.14^{+0.13}_{-0.07} \exp(-2.55 \pm 0.07 \text{ eV}/kT) \text{ cm}^2 \text{ s}^{-1}$$

where D_{LP} and D_{HP} represent the oxygen diffusivities of the lightly and heavily P-doped Cz silicon, respectively. As can be seen, the optimum value of the oxygen diffusion activation energy for the lightly P-doped silicon is 2.43 eV, in good agreement with Mikkelsen's result [15]. It is known from the above two expressions that the optimum value of the oxygen diffusion activation energy for the heavily P-doped Cz silicon is 0.12 eV higher than that for the lightly P-doped Cz silicon. Intuitively, the retardation effect is attributed to the trapping of O_i atoms by the P atoms through the formation of certain P–O complexes. In the following, first-principles calculations will reveal the most energetically favorable configuration of the P–O complex.

Table 2. Energies of binding (E_b) between a substitutional P atom and an O_i atom with different configurations in the silicon lattice, as shown in figure 3.
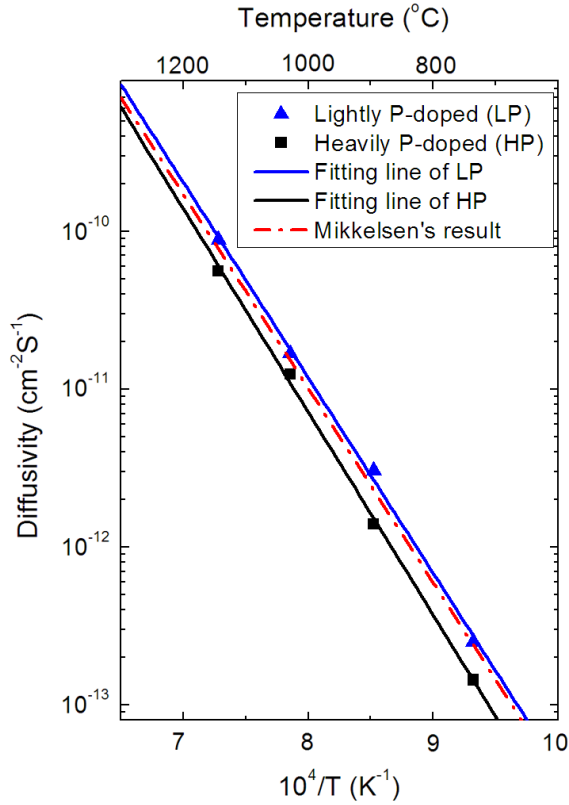
Configuration	(a)	(b)	(c)	(d)	(e)
E_b (eV)	0.29	−0.28	−0.01	0.02	−0.17

Figure 3 shows the different configurations for one substantial P atom interacting with an O_i atom, which locates at the first-, second- and third-nearest neighbors (1NN, 2NN and 3NN respectively) of the P atom. The energy of binding between the P and O_i atoms is given as follows:

$$E_b = E[\text{Si}_{63}\text{PO}] - E[\text{Si}_{63}\text{P}] - E[\text{Si}_{64}\text{O}] + E[\text{Si}_{64}] \quad (3)$$

where E_b is the binding energy, $E[\text{Si}_{63}\text{PO}]$ is the energy of the supercell containing a P atom and an O_i atom, and $E[\text{Si}_{63}\text{P}]$, $E[\text{Si}_{63}\text{O}]$ and $E[\text{Si}_{64}]$ are the energies of the supercells with a P atom, an O_i atom, and the pristine one, respectively.

Table 2 lists the calculated energies of binding between the P and O_i atoms with different configurations in the silicon lattice, as shown in figure 3. Here, the binding energy taking a negative value means that the interaction between the P
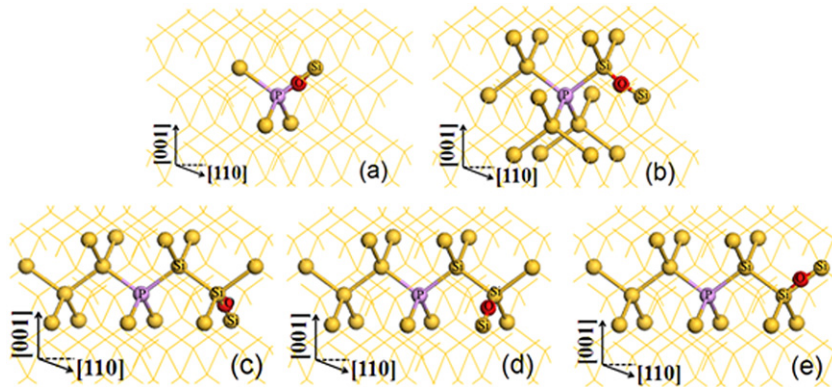
Figure 2. Oxygen diffusivities in the lightly and heavily P-doped Cz silicon as a function of temperature. All diffusivities for either kind of Cz silicon can be fitted with equation (2), as shown by the solid curves. Mikkelsen's result [15] (dashed line) is also shown for reference.

scenario is similar to that for the interaction between the As and O_i atoms in the heavily As-doped Cz silicon [9]. As the O_i atom moves to the 3NN sites of the P atom, the interaction between the P and O_i atoms becomes remarkably weakened. Therefore, in the heavily P-doped Cz silicon, the O_i atoms can be incorporated into the P–O complexes of the –P–Si–O–Si– configuration due to the energy of binding between the O_i and P atoms therein. In other words, a P atom can act as a trapping center for the O_i atoms, which is located at the 2NN sites of the P atom. Note that one P atom has twelve equivalent 2NN sites because of the geometric symmetry of the silicon lattice. Imaging the oxygen diffusion in the heavily P-doped Cz silicon, overall, the O_i atoms are inevitably captured by the P atoms at their 2NN sites to form the above-mentioned P–O complexes. Then O_i atoms have to overcome an additional energy barrier to be released from the P–O complexes and subsequently diffuse to the next sites. In other words, the oxygen diffusion activation energy is increased due to the trapping of O_i atoms by the P atoms in the heavily P-doped Cz silicon. The increase in oxygen diffusion activation energy, ΔE, can be estimated by using the following expression which is modified on the basis of the theory in [16]:

$$\Delta E = E_b \frac{n f_T \exp(E_b/kT)}{1 + n f_T \exp(E_b/kT)} \qquad (4)$$

where E_b is the energy of binding between the O_i and P atoms, n is the number of trapping sites around a P atom, and f_T is the ratio of the trapping center density to the lattice site density. Here, $n = 12$, $E_b = 0.28$ eV and $f_T = 1 \times 10^{-3}$. Therefore, the estimated ΔE ranges over 0.07–0.04 eV at 800–1100 °C. Actually, besides the above-mentioned twelve equivalent 2NN trapping sites, certain 3NN sites of the P atom still exhibit a trapping effect on O_i atoms, which is, however, weaker than that of 2NN trapping sites. It should be noted that density functional theory (DFT) based on the generalized gradient approximation (GGA) and localized density approximation (LDA) tend to underestimate the binding energies of defects in silicon [17]. Consequently, the actual ΔE resulting from the trapping of O_i by the

and O_i atoms and resulting P–O complex is energetically favorable. Clearly, the direct P–O bonding is not favorable with the highest energy. The most energetically favorable P–O complex consists of a P atom and its 2NN O_i atom in the –P–Si–O–Si– configuration (see figure 3(b)), with a binding energy of 0.28 eV. In such a configuration, the P atom interacts with the O_i atom indirectly via a Si atom in between. This

Figure 3. Configurations of the substitutional P atom and O_i atom in silicon supercells: (a) the O_i atom at the first-nearest-neighbor (1NN) site of the P atom, i.e. –P–O–Si–; (b) the O_i atom at the second-nearest-neighbor (2NN) site of the P atom, i.e. –P–Si–O–Si–; ((c)–(e)) the O_i atom at the third-nearest-neighbor (3NN) site of the P atom, i.e. –P–Si–Si–O–Si–. The yellow, pink, and red balls represent Si, P and O atoms, respectively.
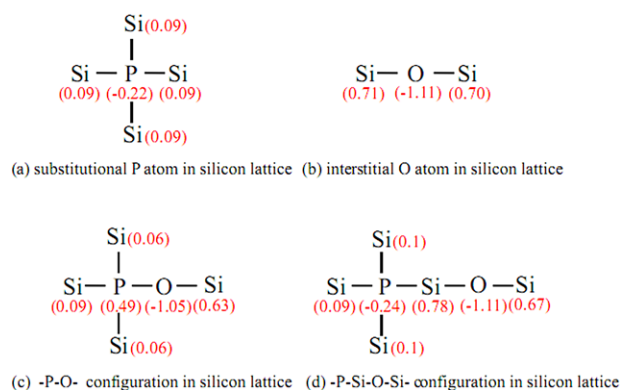
Figure 4. Electron population analysis for the Si, P and O_i atoms with different configurations in the silicon lattice. The red numbers with negative and positive values represent the gain and loss of electrons, respectively.

P atoms should be larger than that estimated according to equation (4). In other words, the experimentally determined value of ΔE, i.e. 0.12 eV as mentioned above, is quite close to those derived from the first-principles calculations. In view of this fact, it is reasonable to believe that the trapping of O_i atoms via the formation of P–O complexes primarily in the –P–Si–O–Si– configuration is the origin for the retarded oxygen diffusion in the heavily P-doped Cz silicon.

Using Mulliken population analysis [18, 19], we defined the electron population of the Si, P, and O_i atoms with different configurations in the silicon lattice. As shown in figures 4(a) and (b), the substitutional P or O_i atom in the silicon lattice captures electrons from the nearby Si atoms, thus possessing negative charges. In turn, the Si atoms around the P or O_i atoms are positively charged. Therefore, the substitutional P or O_i atom is stable due to Coulomb attraction to the silicon lattice. Figure 4(c) indicates that as the O_i locates at the 1NN site of the substitutional P atom in the silicon lattice, the P atom becomes positively charged because it loses charge to the O_i atom which has a larger electron affinity. Simultaneously, the three silicon atoms around the P atom are positively charged. In this context, Coulomb repulsion occurs between the Si and P atoms, indicating that the P–O complex in the form of –Si–P–O–Si– is not electrostatically favorable. When the O_i atom locates at the 2NN site of the P atom, as shown in figure 4(d), both P and O_i atoms are negatively charged while the surrounding Si atoms are positively charged, indicating an electrostatic stability of the P–O complex in the –P–Si–O–Si– configuration. This is in agreement with the calculated binding energies described above.

4. Conclusion

In summary, we have comparatively investigated the oxygen diffusion in lightly and heavily P-doped Cz silicon at temperatures ranging from 800 to 1100 °C. It is experimentally found that oxygen diffusion in the heavily P-doped Cz silicon is retarded, with an additional diffusion activation energy of 0.12 eV. This experimental result implies that the trapping of O_i atoms by the high concentration of P atoms is a possible mechanism for the retarded oxygen diffusion. By means of first-principles calculations, it is derived that P–O complexes in which the O_i atoms are located at the 2NN sites of P atoms, namely, in the configuration of –P–Si–O–Si–, can form in the heavily P-doped Cz silicon. As the O_i atoms are captured by the P atoms, the oxygen diffusion is retarded. The theoretically derived diffusion activation energy that considers the trapping effect of the P–O complexes is quite close to our experimental result. On the basis of this agreement, the formation of P–O complexes is proposed to be the origin of the retarded oxygen diffusion in heavily P-doped Cz silicon.

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