

Suppression of boron-oxygen defects in Czochralski silicon by carbon co-doping

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We have investigated the influence of carbon co-doping on the formation of boron-oxygen defects in Czochralski silicon. It is found that carbon can effectively suppress the formation of boron-oxygen defects. Based on our experiments and first-principle theoretical calculations, it is believed that this effect is attributed to the formation of more energetically favorable carbon-oxygen complexes. Moreover, the diffusion of oxygen dimers in carbon co-doped silicon also becomes more difficult. All these phenomena should be associated with the tensile stress field induced by carbon doping in silicon. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4914889>]

Crystalline silicon solar cell is moving toward high efficiency and low cost. However, the currently terrestrial solar cells fabricated from boron-doped Czochralski silicon (CZ-Si) are suffering from light-induced degradation (LID) phenomenon with efficiency loss up to 2–3%, due to the formation of boron and oxygen (B-O) defects. The B-O defects are usually formed under the injection of excess carriers introduced by either illumination or forward bias, which have strong recombination activity for carriers.^{1–3} It has been reported that after an annealing process in the dark at 200 °C, the carrier lifetime can be recovered, but the subsequent illumination can cause the formation of B-O defect again.⁴ The saturated defect concentration (N_{∞}^*) of B-O complexes is primarily proportional to the boron concentration (N_B) and to the square of the interstitial oxygen concentration ($[O_i]^2$).^{5,6} Therefore, Schmidt *et al.* proposed a B_sO_{2i} model, in which the formation of B-O defect is formed by the fast-diffusion of an oxygen dimer (O_{2i}) towards an immobile substitutional boron atom (B_s) based on the recombination-enhanced diffusion mechanism.⁷ However, the linear dependence of N_{∞}^* on the hole concentration p_0 (instead of N_B) has been extensively demonstrated in the dopant compensated CZ silicon, which obviously conflicts with the standard B_sO_{2i} model.^{8–11} Therefore, a modified B_sO_{2i} model based on a short-distance range diffusion was recently presented by us, which can well explain the experimental results obtained from the compensated p -type Si and n -type Si.¹²

Recently, the strategies of suppressing the LID phenomenon have been extensively studied, including boron-free doping,^{13–15} low oxygen level atoms (FZ-Si), optimized post-heat processing¹⁶ and the regeneration treatment.¹⁷ Germanium (Ge) co-doping in silicon has been found to effectively suppress the formation of B-O complexes by our group.¹⁸ However, carbon located at the same group as Ge and Si has earlier been reported to suppress the generation of doubly thermal donors (TDs) which might also originates from oxygen dimers in CZ silicon.^{19,20} Therefore, how carbon

co-doping in CZ silicon influencing the formation of B-O complexes is quite interesting to be investigated.

The purpose of this manuscript is to understand the effect of C co-doping on the formation of B-O defects in CZ silicon. The experimental results show that carbon co-doping can reduce the concentration of B-O defects, as a result of the formation of more energetically favorable carbon-oxygen (C-O) complexes. The results pave a way to the suppression of B-O defects in CZ silicon.

Three 6-in., p -type (B -doped, 1–3 Ω cm) $\langle 100 \rangle$ oriented CZ silicon crystals with different carbon concentrations (CCZ-Si) were pulled under similar growth conditions. Meanwhile, an exclusively B -doped conventional crystal without intentional carbon co-doping was grown as a reference. After slicing the crystals, all the samples were pre-annealed in Ar ambient for 30 min at 650 °C to eliminate grown-in TDs. Afterwards, the concentrations of boron ($[B_s]$ s) in these samples were derived from four-point probe measurement according to ASTM F723. The oxygen concentrations ($[O_i]$ s) and carbon concentrations ($[C_s]$ s) were determined by Fourier transform infrared spectroscopy (FTIR) at room temperature, with a calibration factor of $3.14 \times 10^{17} \text{ cm}^{-2}$ and $1 \times 10^{17} \text{ cm}^{-2}$, respectively. The oxygen dimer concentrations ($[O_{2i}]$ s) were measured by FTIR at 10 K with a spectral resolution of 1 cm^{-1} .

For the carrier lifetime measurements, all the samples were firstly etched to remove the saw damages and then subjected to a double-surface passivation with plasma-enhanced chemical vapor deposited silicon nitride ($\text{SiN}_x\text{:H}$) films. Meanwhile, a gallium (Ga) doped sample ($\sim 2 \Omega$ cm) was subjected to the same process for inspecting the stability of surface passivation. Afterwards, the samples were annealed at 250 °C for 30 min in dark circumstance and then illuminated under a halogen lamp with an intensity of 30 mW/cm^2 at 70 °C for 48 h. The evolutions of the sample carrier lifetime (τ_d) were measured by the quasi-steady-state photoconductance (QSSPC) technique. The saturated defect concentration N_{∞}^* can be obtained via $N_{\infty}^* = 1/\tau_d - 1/\tau_0$, where τ_0 is the carrier lifetime measured after 250 °C/30 min annealing.

The first-principle calculations are performed using the CASTEP density-functional-theory code²¹ with the Perdew-Burke-Ernzerhof (PBE) Generalized Gradient Approximation

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(GGA) density functional²² and ultra-soft pseudopotentials. The host crystal is represented by a periodic supercell with 216 host atoms and a Gamma point was used to sample the Brillouin Zone.²³ A plane-wave cutoff energy of 440 eV is employed throughout. The variation of total energies with the number of k points and the cutoff energy are tested to ensure the convergence. The binding energy (E_b) can be achieved from the total energy of the pair/complex and its dissociation products in separate supercells, i.e., $E_b = E_{\text{pair/complex}} - \sum (E_{\text{dissociation products}})$. Oxygen dimers are placed at different interstitial sites near the substitutional C atom (C_s) to establish the atomic models for the calculation.

Since the saturated defect concentration N_{∞}^* is proportional to the boron concentration $[B_s]$ and the square of the oxygen concentration $[O_i]^2$,^{5,6} the N_{∞}^* can be normalized as the form of $N_{\infty}^*/([B_s][O_i]^2)$ to exclude the variation of B and O_i levels in different samples. Figure 1 shows the values of $N_{\infty}^*/([B_s][O_i]^2)$ in those degraded samples as a function of the C concentration ($[C]$) on a single-logarithmic scale in CCZ silicon. Note that the N_{∞}^* in the Ga-doped sample keeps near zero during the entire illumination, indicating that the $\text{SiN}_x\text{:H}$ layer is fairly stable. One can see that the values of $N_{\infty}^*/([B_s][O_i]^2)$ rapidly decrease with an increase of $[C]$, which means that the CCZ silicon will have a smaller N_{∞}^* than the CZ silicon with the same $[B]$ and $[O_i]$. This clearly proves that carbon co-doping in CZ silicon can effectively suppress the formation of B_sO_{2i} defects, even with a low C concentration of $5 \times 10^{15} \text{ cm}^{-3}$. In our previous study, a Ge concentration of larger than 10^{19} cm^{-3} is usually needed to suppress the formation of B-O complexes in the Ge co-doped CZ silicon.¹⁸ This implies that C co-doping is more efficient than Ge co-doping to suppress the B-O complexes in CZ silicon.

Figure 2 shows the typical IR absorption spectra of the conventional CZ silicon and CCZ silicon with a C concentration of $3.4 \times 10^{17} \text{ cm}^{-3}$ measured at 10 K. Here, it should be stressed that the $[O_i]$ s are almost the same in both kinds of the samples. One can see that the intensities of vibrational IR absorption bands associated with O_{2i} , 1012, 1060, and 1105 cm^{-1} ,²⁴ are significantly lower in the CCZ sample than

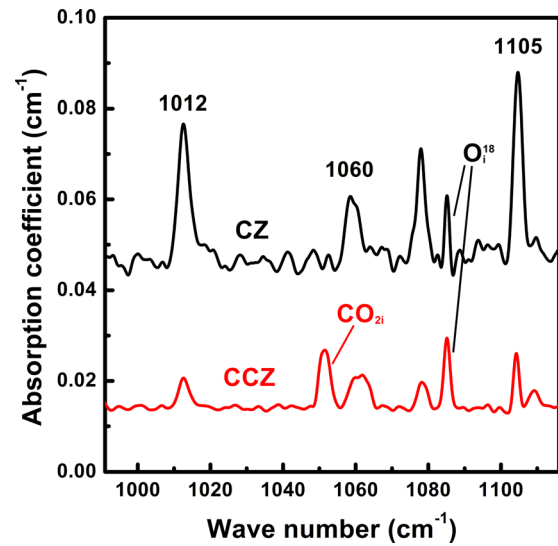


FIG. 2. Infrared absorption spectra for the conventional CZ and CCZ silicon with a C concentration of $3.39 \times 10^{17} \text{ cm}^{-3}$ measured at 10 K. The spectra are shifted on the vertical axis for clarity.

those in the conventional CZ sample. This indicates that there exists a much lower concentration of O_{2i} in the CCZ silicon. Meanwhile, an obvious infrared absorption band of 1052 cm^{-1} associated with the local vibrational mode of $C_s\text{-}O_{2i}$ bond,^{25,26} is also found in the CCZ sample. It suggests that most of the O_{2i} may form C_sO_{2i} complexes with C_s in the CCZ sample. In fact, carbon, as an isovalent impurity with a smaller tetrahedral radius than silicon, can essentially induce considerable tensile stress in silicon lattice.²⁷ As a consequence of stress compensation, it is supposed that the O_{2i} is more energetically favorable to diffuse into the C tensile stress field and then form C_sO_{2i} . This might reduce the concentration of free O_{2i} available to pair with boron atoms and therefore suppress the formation of B_sO_{2i} complexes in CCZ silicon.

Figure 3 shows the values of normalized $[O_{2i}]/[O_i]^2$ as a function of the $[C]$ in CCZ silicon. Note that the O_{2i} concentration is obtained by integrating the intensity of 1012 cm^{-1} in the FTIR spectra. The normalized $[O_{2i}]/[O_i]^2$ can

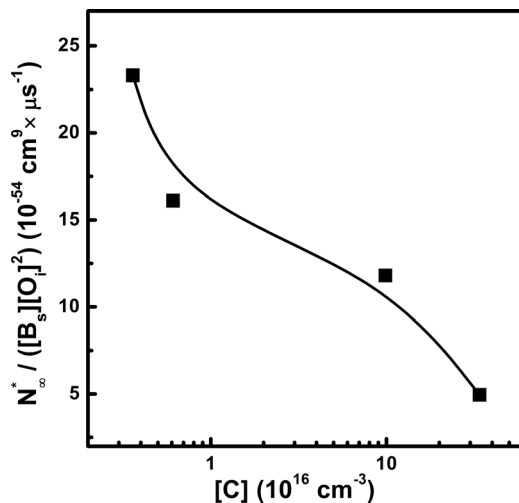


FIG. 1. The values of $N_{\infty}^*/([B_s][O_i]^2)$ for the samples as a function of C concentration after complete generation of B-O defects at 70°C . The solid line is guide to the eye.

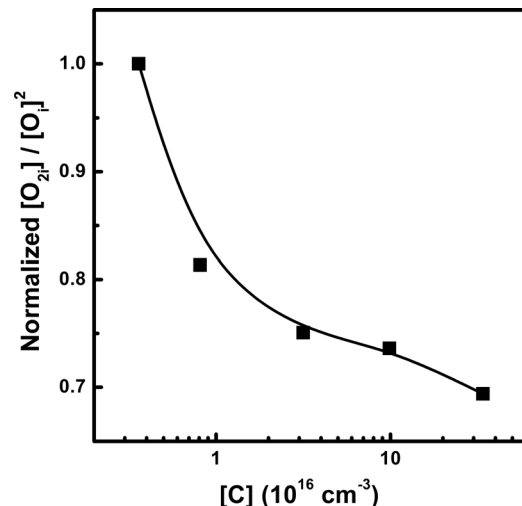
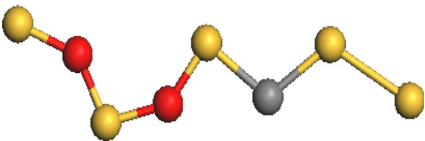
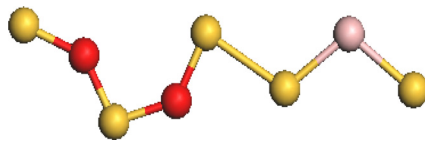


FIG. 3. The $[O_{2i}]/[O_i]^2$ in the CCZ silicon as a function of C concentration. The solid line is guide to the eye.

TABLE I. The most stable C_sO_{2i} and B_sO_{2i} configurations, together with their binding energies. Red, yellow, grey, and pink balls represent O, Si, C, and B atoms, respectively.

Complex		
E_b (eV)	-0.42	-0.15

eliminate the effect of various $[O_i]$ s in CCZ samples since the $[O_{2i}]$ is proportional to the $[O_i]^2$.^{6,7} It can be seen that the values of normalized $[O_{2i}]/[O_i]^2$ decrease with an increase of $[C]$, which exactly coincides with the results of B-O complexes above. This indicates that a higher concentration of C can cause a lower $[O_{2i}]$ and therefore suppress the formation of B_sO_{2i} defects in CCZ silicon. However, it should be mentioned here that C co-doping in CZ silicon with extremely high concentrations above 10^{18} cm^{-3} is not practical, since carbon can also enhance the nucleation of high density oxygen precipitates which might strongly reduce the carrier lifetime.²⁸ In the worst case, high concentration of carbon can react with silicon to form silicon carbide inclusions, which might increase the leakage current and therefore deteriorate the performance of solar cells.^{29,30}

We have further verified the reaction probability between carbon and O_{2i} in CCZ silicon by the first-principle calculation. It is found that both C_s and B_s tend to bond with O_{2i} and then form the stable complexes with a negative binding energy of -0.42 and -0.15 eV, respectively (see Table I). This means that the O_{2i} is more likely to bond with

the C_s and form a more energetically favorable C_sO_{2i} complex in CCZ silicon. Therefore, it is believed that only a portion of O_{2i} will be expected to take part in the formation of B_sO_{2i} complexes in CCZ silicon. Since the formation of B-O complexes in the conventional CZ silicon can be supposed as a process of oxygen dimers moving towards the immobile substitutional borons atom via $B + O_{2i} \leftrightarrow BO_{2i}$, the O_{2i} migration energy (E_m) barrier is also interesting to be known. In order to investigate the E_m of O_{2i} in CCZ silicon, two migration paths of O_{2i} through $\langle 110 \rangle$ chain in a silicon super-cell containing a substitutional isovalent atom C were considered. One is the $\langle 110 \rangle$ chain with a C atom in it, labeled by “W,” and the other is the $\langle 110 \rangle$ chain with a C atom nearby, labeled by “L.” The diffusion jumps along the W chain are numbered by 1–4 and those along the L chain by 1’–4’, as shown in Figure 4. The calculation results show that the values of E_m for electronically neutral O_{2i} diffusing along the W and L chain are 3.24 and 1.78 eV, respectively. If the O_{2i} is single- and double-positively (+1 and +2) charged, the E_m are further improved. Nevertheless, the E_m of O_{2i} in CCZ silicon should be larger than that in the conventional CZ silicon, 1.30–1.50 eV.^{31,32} Thus, it can be concluded that C doping can make the O_{2i} more difficult diffuse towards the B_s , which could be also associated with the tensile stress field of C in CZ silicon.

In summary, we have demonstrated that C co-doping in CZ silicon can effectively suppress the formation of B-O complexes. The saturated defect concentrations of both B-O complexes and O_{2i} decrease with an increase of C concentration. Furthermore, it is found that this suppression effect is mainly ascribed to the formation of more energetically favorable C_sO_{2i} complexes. Meanwhile, the diffusion of O_{2i} in CCZ silicon is more difficult than that in CZ silicon. It is believed that CCZ silicon could become one of promising candidates for fabricating silicon solar cells with low LID effect in practical PV industry if carbon concentration is well controlled, since the carbon doping method is quite simple and cheap.

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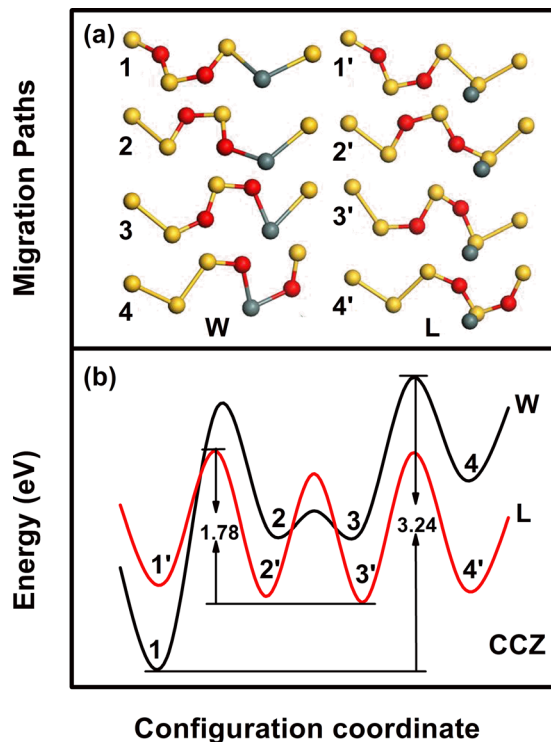


FIG. 4. (a) Migration paths of O_{2i} through $\langle 110 \rangle$ chains with a C atom (W) and without a C atom (L). The representative atoms of the balls are the same as Table I. (b) The configuration-coordinate diagram for O_{2i} diffusing through $\langle 110 \rangle$ chains with C atom (W) and without C atoms (L).

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