

Carbon effect on the survival of vacancies in Czochralski silicon during rapid thermal anneal

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Rapid thermal anneal (RTA) at high temperatures can be employed to introduce vacancies to control oxygen precipitation (OP) behavior in Czochralski (CZ) silicon. Such excessive vacancies survive from the recombination of silicon-interstitials and vacancies (V - I recombination) during the RTA. In this work, we aim to elucidate the carbon effect on the survival of vacancies in CZ silicon during the high temperature RTA by means of gold diffusion in combination with deep-level transient spectroscopy. It is revealed that the existence of $\sim 10^{17} \text{ cm}^{-3}$ carbon atoms significantly increases the amount of survival vacancies in the form of vacancy-oxygen (VO_m , $m \geq 2$) complexes in CZ silicon when subjected to the 1250 °C/60 s RTA. Moreover, such an increase in the number of vacancies becomes more significant with the increase in the cooling rate of RTA. The density functional theory calculations suggest that the V - I recombination is to some extent unfavorable as a carbon atom is close to the silicon-interstitial. Alternatively, it is believed that the substitutional carbon (C_s) atoms tend to trap the silicon-interstitials, thus forming C_i complexes ($C_s + I \rightarrow C_i$) in CZ silicon during the RTA. In this context, the V - I recombination is suppressed in a manner, leading to the survival of more vacancies, thus generating more VO_m complexes. Furthermore, after the 1250 °C/60 s RTA, the oxide precipitate nucleation based on the VO_m complexes is more significant in carbon-rich CZ (CCZ) silicon than in the conventional CZ counterpart. Hence, when subjected to the same OP anneal consisting of the nucleation anneal at 650 or 800 °C for 4 h and the subsequent growth anneal at 1000 °C for 16 h, CCZ silicon possesses a higher density of bulk microdefects and therefore stronger internal gettering capability than CZ silicon. However, the nucleation temperature for OP should be carefully selected as 650 °C for CCZ silicon in order to form an oxide precipitate-free denuded zone. Published by AIP Publishing. [<http://dx.doi.org/10.1063/1.4996099>]

I. INTRODUCTION

Czochralski (CZ) silicon is the base material for manufacturing integrated circuits (ICs). With the shrinkage of feature size of ICs and, meanwhile, the increase in the silicon wafer diameter, manipulating defects in CZ silicon becomes increasingly significant.^{1,2} In this regard, internal gettering (IG) associated with oxygen precipitation (OP) for the removal of detrimental metal contaminants suffering from the IC fabrication processes has always been a focus.^{1,2} Among a variety of IG processes, the one based on high temperature rapid thermal anneal (RTA) features a fast and reliable process with a lower thermal budget. Such a RTA-based IG process was designated with a trademark of “magic denuded zone (MDZ).”^{3–5} The highlight of the MDZ process manifests that OP behavior in a CZ silicon wafer is essentially dictated by the RTA-established vacancy concentration profile increasing from the surface to the bulk of the silicon wafer. Concretely, in the following OP anneal generally consisting of the nucleation anneal at a low temperature and the growth anneal at a high temperature, OP

hardly occurs within the vacancy out-diffusion region near the surface of the silicon wafer, thus forming an oxide precipitate-free zone, i.e., denuded zone (DZ) due to the lack of vacancies. However, OP is significantly enhanced in the bulk of the silicon wafer, thus forming a high density of bulk microdefects (BMDs) that play the role of gettering metal contaminants.⁶ In brief, the high temperature RTA is a viable means to build the vacancy concentration profile for tailoring the OP behavior in CZ silicon wafers.

The residual vacancies in silicon after the high temperature RTA essentially survive from the recombination of vacancies and silicon-interstitials (V - I recombination) because the equilibrium concentration of vacancies is slightly higher than that of silicon-interstitials.⁵ Actually, the V - I recombination can be interfered by the dopant/impurity atoms with appreciably high concentrations due to the interaction between the point defects and dopant/impurity atoms.⁷ In our previous report on the heavily doped (low-resistivity) CZ silicon subjected to the high temperature RTA, we have verified that a part of dopant (As/Sb) atoms combine with the vacancies to form As/Sb- V complexes in n -type CZ silicon.⁸ In contrast, a part of boron atoms trap the silicon-interstitials to form B - I complexes in p -type CZ silicon.⁹ In such two cases, the interaction between the dopant atoms and the point defects leads to

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the electrical deactivation of dopant atoms in a manner. In this work, we aim to address the effect of carbon, a neutral impurity in CZ silicon, on the V - I recombination during the high temperature RTA.

It is well known that carbon, secondary to oxygen, is an inevitable impurity in CZ silicon. While the carbon concentration has long been required to be sub-ppma in CZ silicon used for ICs, it is worth mentioning that the carbon impurity with appropriately high concentrations in CZ silicon has been found to enhance OP and to reduce the size of grown-in defects (voids).^{10–13} For the large-diameter CZ silicon wafers used for ICs, they are required to possess high IG capability and few voids. In this context, appropriately high concentrations of carbon in CZ silicon may exert beneficial effects. Therefore, it is of practical significance to clarify the carbon effect on the V - I recombination during the high temperature RTA, which remarkably affects the OP behavior and therefore the IG capability of CZ silicon. Although the theoretical studies have suggested that the silicon-interstitials are inclined to be trapped by carbon atoms,^{7,14} the experimental evidence for the interference of V - I recombination exerted by the carbon atoms in CZ silicon during the high temperature RTA is yet to be explored.

In this work, by means of gold (Au) diffusion analysis proposed by Zimmermann and Ryssel,¹⁵ we have investigated the carbon effect on the survival of vacancies that are believed to be in the form of vacancy-oxygen (VO_m , $m \geq 2$) complexes in CZ silicon subjected to the RTA at 1250 °C. It is found that after the same RTA, the CZ silicon containing $\sim 10^{17} \text{ cm}^{-3}$ carbon atoms possesses much more vacancies than the conventional CZ silicon. Therefore, the formation of bulk micro-defects (BMDs) associated with OP is remarkably facilitated in the carbon-rich CZ silicon. The mechanism underlying the carbon effect on the survival of vacancies in CZ silicon has been tentatively elucidated.

II. EXPERIMENTAL DETAILS AND CALCULATION METHODS

Two 150 mm-diameter, $\langle 100 \rangle$ -oriented, ~ 1 mm thick silicon wafers were sliced at the positions with the same distance apart from the seed-ends of two phosphorus (P)-doped CZ silicon ingots, which were grown under nearly the same nominal pulling conditions. For one CZ silicon ingot, the carbon concentration was intentionally increased by adding a certain amount of carbon nanoparticles with the sizes smaller than 20 nm into the quartz crucible together with polysilicon nuggets. Such carbon nanoparticles were gradually dissolved during the melting of poly-silicon. For the sake of convenience, the resulting CZ silicon rich in carbon impurities is designated as carbon-rich CZ (CCZ) silicon, hereafter. The substitutional carbon concentration ($[C_s]$) in the CCZ silicon wafer was $\sim 1.7 \times 10^{17} \text{ cm}^{-3}$, while that in the conventional CZ silicon wafer was below the detection limit of Fourier-transform infrared (FTIR) spectroscopy. The initial interstitial oxygen concentrations ($[O_i]$ s) in both CCZ and conventional CZ silicon wafers were $\sim 7.0 \times 10^{17} \text{ cm}^{-3}$. The aforementioned $[O_i]$ and $[C_s]$ were measured by using a Bruker IFS 66 V/S FTIR spectrometer at room temperature

with the conversion coefficients of 3.14×10^{17} and $1.0 \times 10^{17} \text{ cm}^{-2}$, respectively. The resistivity of both CZ and CCZ silicon wafers was $\sim 19 \Omega\cdot\text{cm}$. A number of specimens sized in $1.5 \times 1.5 \text{ cm}^2$ were cleaved from the aforementioned CCZ and CZ silicon wafers, respectively, for different experimental purposes. All specimens were mechano-chemically polished to a thickness of $\sim 800 \mu\text{m}$ using a Struers TegraForce-5 system.

All specimens were subjected to the 1250 °C/60 s RTA in an Ar ambient with an AccuThermo AW610 RTA system. The cooling rate from 1250 to 800 °C was varied from 60 to 7.5 °C/s for different experimental purposes. To investigate the carbon effect on the RTA-based IG process, CCZ and CZ silicon specimens were subjected to the OP anneal consisting of nucleation-growth anneal of 650 or 800 °C/4 h + 1000 °C/16 h in an Ar ambient following the 1250 °C/60 s RTA with the cooling rate of 60 °C/s. Such annealed specimens were successively wax-sealed, cleaved, and preferentially etched in Yang 1 etchant [CrO_3 (0.5 mol/l): HF (49%) = 1: 1] for 5 min. Then, the etched cleavage plane of each specimen was observed using an Olympus MX-50 optical microscope equipped with a CCD camera.

To probe the quenched-in vacancies in the bulk of CCZ and CZ silicon specimens subjected to the RTA at 1250 °C as mentioned above, the Au diffusion analysis was adopted, which is detailed as follows. ~ 100 nm thick Au films were sputtered onto the polished surfaces of CCZ and CZ specimens that had been subjected to the 1250 °C/60 s RTA with different cooling rates. Subsequently, the specimens were annealed at 750 °C for 3 h in an Ar ambient for Au interdiffusion. In order to sufficiently remove the vacancy out-diffusion zone formed during the RTA as well as the residual Au film, each specimen was mechano-chemically polished with a $\sim 150 \mu\text{m}$ thick layer. For each specimen characterized by deep level transient spectroscopy (DLTS), an ~ 100 nm thick platinum (Pt) film patterned into a 2 mm-diameter circle was sputtered onto the polished surface to form Schottky contact. In turn, the indium-gallium (In-Ga) film was pasted onto the backside to form Ohmic contact. The resulting Schottky diode was then measured by a PhysTech Fourier Transform DLTS system equipped with a helium cryostat. To acquire the DLTS spectra, the Schottky diode was applied with a reverse bias $V_R = -6$ V and a filling pulse voltage $V_P = -1$ V. The sampling period (t_w) from V_R to V_P was 204.8 ms, while the filling pulse duration t_p was 10 ms.

Density functional theory (DFT) calculations were performed using the *Vienna ab initio simulation package* (VASP). The supercell was constructed containing 216 Si atoms with the experimental lattice parameter in order to ensure that the interaction of defects in neighboring cells was negligible. The Monkhorst-Pack special k -point sampling on the 3D Brillouin zone of the supercell was $4 \times 4 \times 4$.¹⁶ Generalized gradient approximation (GGA) was employed for the exchange and correlation functional, and the core electrons were represented by the projector augmented wave (PAW) potential.^{17,18} The tetrahedron method with Blöchl corrections was used for total energy calculation, and the structure optimization process was performed with a force convergence criterion of 0.1 eV/Å. The kinetic energy cutoff was set to 400 eV.

It should be stated that the aforementioned DFT calculations generally lead to underestimated defect formation energy due to underestimation of the band gap.^{19,20} Besides, the 216-atom supercell is the lowest limit for the Frenkel pair calculations.²¹ In fact, 0.1 eV/Å is quite a rough force convergence criterion. Therefore, the results obtained in this work should be treated as the output of tentative and fast DFT calculations. Nevertheless, they are still valuable for our qualitative discussion of the carbon effect on point defects in CZ silicon.

III. RESULTS AND DISCUSSION

Figure 1(a) shows the DLTS spectra of CCZ and CZ silicon specimens subject to the 750 °C/3 h Au in-diffusion process following the 1250 °C/60 s RTA with the cooling rate of 60 °C/s. Two peaks designated as T1 and T2, respectively, appear in the DLTS spectrum of the CCZ silicon specimen, whereas only the T1 peak emerges in the DLTS spectrum of CZ silicon. The Arrhenius plots of T1 and T2 levels are shown in Fig. 1(b). The T1 peak characteristics of the majority carrier trapping center are derived to locate at $E_c - 0.56$ eV with the capture cross-section of $2.2 \times 10^{-16} \text{ cm}^{-2}$, corresponding to the acceptor level of substitutional gold (Au_s).^{22,23} As seen, the T1 peak of the CCZ silicon specimen is much stronger

than that of the CZ counterpart, indicating that the Au_s concentration is much higher in the CCZ silicon specimen. The T2 level characteristics of the minority carrier trapping center are derived to locate at $E_v + 0.38$ eV with the capture cross-section of $1.7 \times 10^{-16} \text{ cm}^{-2}$, which was believed to be pertaining to the vacancy-carbon-oxygen ($\langle V + C + O \rangle$) complexes in the report of Mooney *et al.*²⁴ Therein, the $\langle V + C + O \rangle$ complexes were suggested to be most likely due to the interaction between the substitutional carbon (C_s) atoms and the vacancy-oxygen ($\langle V + O \rangle$) complexes via the reaction $C_s + \langle V + O \rangle \rightarrow \langle V + C + O \rangle + Si_i$, where Si_i represents the interstitial silicon atom. While it is believed that the aforementioned scenario may also occur in our CCZ specimen, the origin of $E_v + 0.38$ eV needs to be further explored in the future work.

It is documented that the high temperature (e.g., 1250 °C) RTA in an Ar ambient enables the vacancies to be frozen in the bulk of the silicon wafer with a concentration of $C_v^* - C_i^*$, namely, the difference between the equilibrium concentrations of vacancies and silicon-interstitials at the working temperature of RTA.⁵ As suggested by Voronkov *et al.*, the RTA-introduced vacancies are substantially stored in the form of VO_2 complexes that are formed by the capture of vacancies by the interstitial oxygen atoms at the temperatures below ~ 1050 °C.^{25,26} The VO_2 complexes may further combine with oxygen atoms to form VO_m ($m > 2$) complexes with larger binding energies.^{27,28} Akhmetov *et al.* elaborately adopted FTIR to reveal that the VO_4 complexes with a concentration of $1.4 \times 10^{13} \text{ cm}^{-3}$ existed in the CZ silicon wafer subjected to the RTA at 1250 °C.²⁹ Nevertheless, the existence of VO_2 complexes could not be precluded. Probably, the concentration of VO_2 complexes was too low to be detected by FTIR. Actually, for the irradiated CZ silicon that contains more vacancies, the evolution of V-O complexes from VO into VO_5 with increasing annealing temperature has been verified by means of FTIR.³⁰ Therefore, it can be moderately believed that there are VO_m ($m \geq 2$) complexes in the CZ silicon wafers after the high temperature RTA.

As mentioned above, the Au or Pt diffusion analysis is an effective tool to probe the vacancy concentration. In this work, the Au diffusion was implemented in CCZ and CZ silicon specimens following the 1250 °C/60 s RTA, as described in the Experimental section. Herein, the Au diffusion is believed to proceed in the presence of VO_m ($m \geq 2$) complexes according to the aforementioned analysis. Consequently, the conversion of interstitial Au (Au_i) into Au_s is accomplished in the way expressed as $Au_i + VO_m \rightarrow Au_s + mO_i$. The resultant Au_s concentration can be measured by DLTS. In view of the analysis given by Zimmermann and Rysse,¹⁵ it is deduced that the Au_s concentration is in proportion to the concentration of VO_m complexes. As described above, the Au diffusion was carried out at 750 °C for 3 h, which was sufficiently long to enable the conversion of Au_i into Au_s to be saturated. Therefore, it can be derived from Fig. 1(a) that CCZ silicon possesses a much higher concentration of VO_m complexes than CZ silicon when subjected to the same RTA.

Figure 2 shows the binding energy (E_b) of a silicon-interstitial (I) and a vacancy (V) in different configurations.

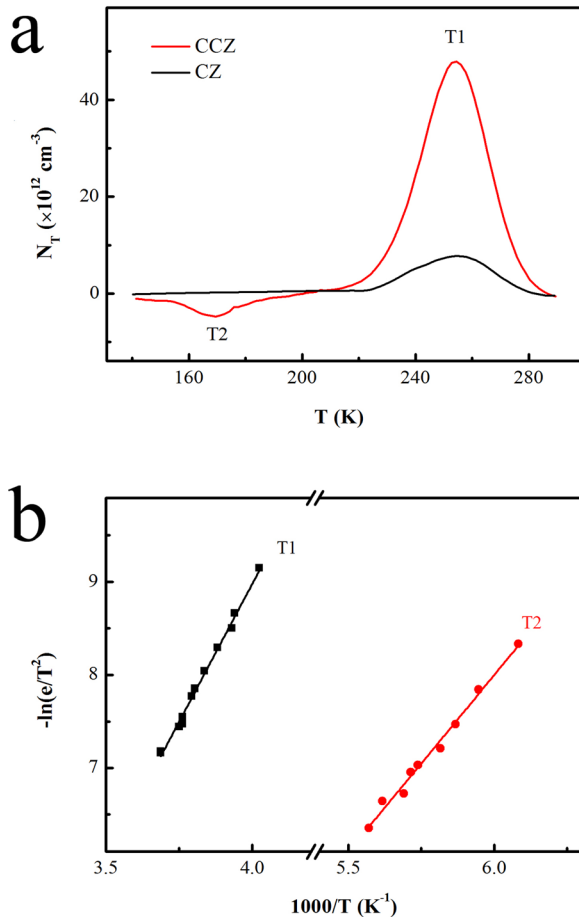


FIG. 1. (a) DLTS spectra of CZ and CCZ silicon specimens subject to the Au in-diffusion at 750 °C for 3 h following the 1250 °C/60 s RTA with the cooling rate of 60 °C/s. (b) Arrhenius plots for T1 and T2 levels shown in (a).

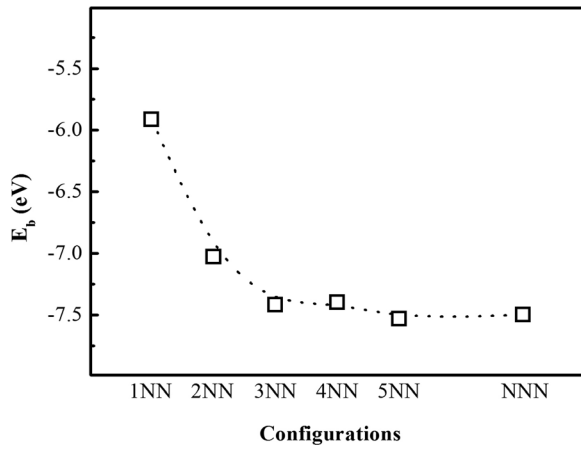


FIG. 2. Dependence of binding energy (E_b) of a silicon-interstitial and a vacancy on the configuration. From the left to the right along the x -axis, it is represented that a carbon atom locates at the 1st, 2nd, 3rd, 4th, and 5th nearest neighboring sites of a silicon-interstitial, respectively. The NNN represents that the distance between the carbon and the interstitial silicon atoms is infinite.

Here, based on the reaction $I + V \rightarrow \text{Si}$, the E_b is calculated according to the following expression:

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

where $E[\text{defect pair}]$, $E[\text{isolated defect}]$, and $E[\text{perfect}]$ represent the energies of the supercell containing the defect pair, the supercell with the isolated defect, and the perfect supercell, respectively. The negative values of E_b indicate that the recombination of the vacancy and silicon-interstitial (V - I recombination) is thermodynamically favored. The larger the absolute value of E_b , the more favorable the V - I recombination. Herein, the obtained V - I binding energy is -7.5 eV, which is consistent with that reported by Holmström *et al.*³¹ It is seen from Fig. 2 that the absolute value of the E_b in the 1NN configuration becomes abruptly smaller than those in other configurations, suggesting that the V - I recombination is to a certain extent unfavorable due to the close proximity of the carbon atom to the silicon-interstitial.

Alternatively, we can further consider the carbon effect on the V - I recombination in silicon starting from the following viewpoint. It is known that the carbon atom has a smaller covalent radius than the silicon atom and most of the carbon atoms in CZ silicon locate at the substitutional sites of the crystal lattice. In order to relieve the local tensile strain arising from the mismatch between the atomic sizes of silicon and carbon, the substitutional carbon (C_s) atoms tend to trap the silicon-interstitials, thus forming C_i complexes in the way expressed as $C_s + I \rightarrow C_i$. Mattoni *et al.* believed that the C_i complex originated as the out-product of the interaction between a silicon-interstitial and a C_s atom by a kick-out capture mechanism. By combining model-potential molecular-dynamics simulations and *ab initio* calculations, they figured out that the carbon and silicon atoms were displaced along the $\langle 001 \rangle$ direction sharing a lattice site to form a C_i complex.¹⁴ Recently, Wang *et al.* have also addressed the configuration of the C_i complex, suggesting that the Si-C dumbbell partially shares the interstitial site and, moreover,

the Si atoms surrounding the defect pair are slightly shifted off their original positions and the C atom is threefold coordinated.³² Regarding the present CCZ silicon subjected to the high temperature RTA, the C_i complexes can form, thus consuming a part of silicon-interstitials which are originally concurrent with the vacancies to constitute the so-called Frenkel pairs generated by the high temperature RTA. In this case, the V - I recombination is to some extent suppressed. It is worth pointing out that for the present CCZ silicon with the carbon concentration of $\sim 10^{17} \text{ cm}^{-3}$, the thermal equilibrium concentrations of silicon-interstitials and vacancies at high temperatures are hardly affected by the presence of carbon, according to the theoretical calculation results achieved by Sueoka *et al.* (see Fig. 13 in Ref. 7). Therefore, it is understandable that the residual vacancies and therefore the generated VO_m complexes are much more in CCZ silicon than in CZ silicon after the same RTA.

Figure 3 shows the bulk Au_s concentrations detected by DLTS for CCZ and CZ silicon specimens subjected to the Au in-diffusion process following the $1250^\circ\text{C}/60 \text{ s}$ RTA with different cooling rates. As mentioned above, the Au_s concentration is in proportion to the VO_m concentration. Therefore, it is derived from Fig. 3 that in each case the VO_m concentration is much higher in the CCZ silicon specimen than in the CZ counterpart. Moreover, the VO_m concentration in CZ silicon is slightly dependent on the cooling rate, indicating that the V - I recombination in CZ silicon is fast enough to complete even with the largest cooling rate in our work. By comparison, the Au_s concentration in CCZ silicon increases remarkably with the cooling rate, suggesting that the incorporated carbon atoms exhibit a significant influence on the V - I recombination. Sueoka *et al.* have pointed out that during the CZ silicon crystal growth the silicon-interstitials or vacancies trapped by the dopant (p -type, n -type or neutral in nature) atoms are readily released at high temperatures above the void formation temperature ($\sim 1100^\circ\text{C}$).⁷ The released vacancies or silicon-interstitials will then recombine with the corresponding counterparts. Such a scenario is also the case for the present CCZ silicon subjected to the high temperature RTA. A number of the trapped silicon-interstitials in the C_i

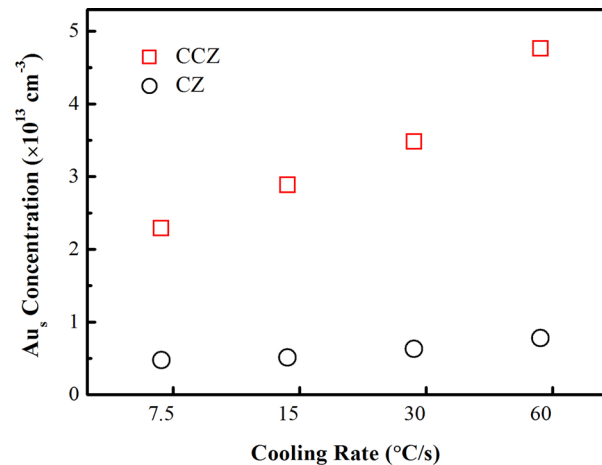


FIG. 3. DLTS-detected Au_s concentrations in CCZ silicon and CZ specimens subject to the Au in-diffusion process following the $1250^\circ\text{C}/60 \text{ s}$ RTA with different cooling rates.

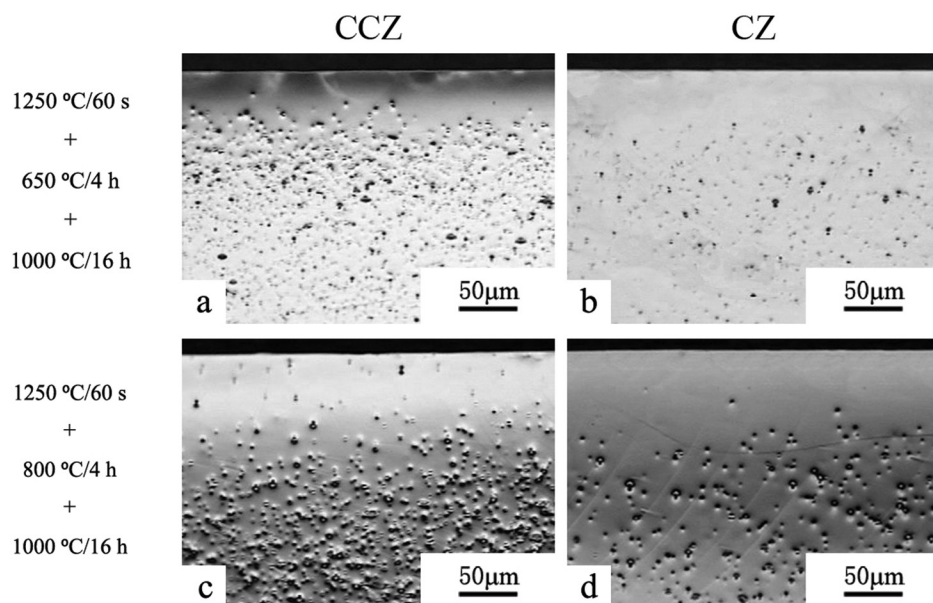


FIG. 4. Typical optical micrograph (OM) images for the preferentially etched cleavage planes of CCZ and CZ silicon specimens subjected to the nucleation (650 or 800 °C/4 h)—growth (1000 °C/16 h) two-step anneal following the 1250 °C/60 s RTA with the cooling rate of 60 °C/s.

complexes will be released during the cooling process of RTA. Understandably, as the cooling rate is smaller, the dwell time at the relatively high temperatures (i.e., >1100 °C) is longer. Thus, more silicon-interstitials can be released from the C_i complexes and then recombine with the vacancies. As a result, the residual vacancies and in turn the generated VO_m complexes are decreased in CCZ silicon. This is translated into that the Au_s concentration in CCZ silicon is lowered with the decrease in the cooling rate of RTA, as shown in Fig. 3.

Figure 4 shows the typical OM images for the preferentially etched cleavage planes of CCZ and CZ silicon specimens subjected to the nucleation (650 or 800 °C/4 h)—growth (1000 °C/16 h) two-step anneal following the 1250 °C/60 s RTA with the cooling rate of 60 °C/s. As seen, in each case the BMD density in the CCZ silicon specimen is much higher than that in the CZ counterpart. Figures 4(a) and 4(b) show that both CCZ and CZ silicon specimens exhibit a well-established DZ onto the BMDs as the nucleation anneal for OP is implemented at 650 °C. However, once the nucleation temperature is increased to 800 °C, as can be seen in Figs. 4(c) and 4(d), there are a number of defects associated with OP within the near-surface region of the CCZ silicon specimen, in contrast with the case of the CZ counterpart. The aforementioned results mean that special care should be taken to define the nucleation temperature for OP in order to obtain a DZ for CCZ silicon subjected to a prior high temperature RTA.

As has been proved above, the VO_m concentration is much higher in the CCZ silicon specimen than in the CZ counterpart after the 1250 °C/60 s RTA. Therefore, the oxide precipitate nucleation based on the VO_m complexes is more significant in CCZ silicon, leading to the higher density of BMDs. It should be mentioned that the decreased $[O_i]$ ($\Delta[O_i]$) and the BMD density of CCZ silicon specimen are hardly different from those of the CZ counterpart when subjected to the two-step anneal of 650 or 800 °C/4 h + 1000 °C/16 h without the prior 1250 °C/60 s RTA. This means that the carbon enhancement effects on OP, as reported in the previous

reports,^{10–12} hardly demonstrate in the present CCZ silicon if without the prior RTA. Accordingly, the carbon-enhanced OP during the two-step anneal following the 1250 °C/60 s RTA, as shown in Fig. 4, is essentially ascribed to the formation of more VO_m complexes resulting from the carbon-suppressed V-I recombination during the RTA. Of significance is that the generation of higher density BMDs in CCZ silicon is beneficial for the IG capability. However, the formation of DZ within CCZ silicon is heavily dependent on the nucleation temperature for OP, as shown in Fig. 4. By contrast, the DZ is readily formed in CZ silicon regardless of the nucleation temperature for OP. It is known that the vacancies out-diffuse from the bulk to the surface of a silicon wafer during the RTA and the consequent vacancy concentration profile nearly follows the error function. Turning to the present CCZ and CZ silicon specimens subjected to the 1250 °C/60 s RTA, since the bulk vacancy concentration in the CCZ silicon specimen is much higher than that in the CZ counterpart as proved above, it can be derived that the vacancy concentration in the out-diffusion region of the CCZ silicon specimen is also comparatively higher. In this context, the vacancy-assisted nucleation of oxide precipitates may be effective in the vacancy out-diffusion region of the CCZ silicon specimen. With the 800 °C/4 h nucleation anneal, certain amounts of formed nuclei are sufficiently large so that they can coarsen in the subsequent 1000 °C/16 h growth anneal, not resulting in a well-defined DZ [see Fig. 4(c)]. While with the 650 °C/4 h nucleation anneal, since the oxygen diffusivity at 650 °C is much smaller than that at 800 °C, the resultant nuclei are too small to coarsen in the subsequent 1000 °C/16 h growth anneal, leading to a desirable width of DZ in CCZ silicon, which is comparable to that in CZ silicon [see Figs. 4(a) and 4(b)].

IV. CONCLUSIONS

In summary, we have addressed the carbon effect on the survival of vacancies in CZ silicon during the high temperature RTA by means of Au diffusion in combination with DLTS. It is found that the Au_s concentration in CCZ silicon

is much higher than that in CZ silicon after the same Au indiffusion process following the 1250 °C/60 s RTA, indicating that more vacancies survive from the V - I recombination, thus generating more VO_m complexes in CCZ silicon during the RTA. Moreover, the amount of VO_m complexes generated in CCZ silicon increases significantly with the cooling rate of RTA. This is quite different from the case of conventional CZ silicon in which the amount of VO_m complexes is slightly dependent on the cooling rate of RTA. The aforementioned experimental results evidence the suppression of V - I recombination due to the incorporation of high concentration carbon atoms in CZ silicon when subjected to the high temperature RTA. The tentative DFT calculations indicate that the V - I recombination in CZ silicon becomes to some extent unfavorable as a carbon atom is adjacent to the silicon-interstitial. Alternatively, the formation of C_i complexes resulting from the interaction between the silicon-interstitials and carbon atoms, as suggested previously, can also account for the suppression of V - I recombination in CCZ silicon during the RTA. In brief, the reservoir of silicon-interstitials by the carbon atoms enables the survival of more vacancies in CCZ silicon, leading to generation of more VO_m complexes during the RTA. Such enhanced formation of VO_m complexes can facilitate the nucleation of oxide precipitates. Consequently, when subjected to the same two-step anneal (650 or 800 °C/4 h + 1000 °C/16 h) following the 1250 °C/60 s RTA, much higher density BMDs associated with OP form in CCZ silicon than in the CZ counterpart. Unfortunately, the DZ appears in CCZ silicon only as the nucleation anneal for OP proceeds at 650 °C. Such a scenario is quite different from the case of CZ silicon where the DZ definitely appears with the two nucleation temperatures as mentioned above. We believe that this work offers an insight into the manipulation of point defect behavior in CZ silicon by incorporating neutral impurity atoms, which can be applied into the defect engineering for improving the performance of CZ silicon.

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- ¹T. Sinno, E. Dornberger, W. Ammon, R. Brown, and F. Dupret, *Mater. Sci. Eng., R* **28**, 149–198 (2000).
- ²X. Yu, J. Chen, X. Ma, and D. Yang, *Mater. Sci. Eng., R* **74**, 1–33 (2013).
- ³R. Falster, D. Gambaro, M. Olmo, M. Cornara, and H. Korb, *Mater. Res. Soc. Symp. Proc.* **510**, 27 (1998).
- ⁴R. Falster and V. Voronkov, *Mater. Sci. Eng., B* **73**, 87 (2000).
- ⁵R. Falster, V. Voronkov, and F. Quast, *Phys. Status Solidi B* **222**, 219 (2000).
- ⁶X. Ma, L. Fu, D. Tian, and D. Yang, *J. Appl. Phys.* **98**, 084502 (2005).
- ⁷K. Sueoka, E. Kamiyama, and J. Vanhellemont, *J. Appl. Phys.* **114**, 153510 (2013).
- ⁸X. Zhang, C. Gao, M. Fu, X. Ma, J. Vanhellemont, and D. Yang, *J. Appl. Phys.* **113**, 163510 (2013).
- ⁹C. Gao, Y. Lu, P. Dong, J. Yi, X. Ma, and D. Yang, *Appl. Phys. Lett.* **104**, 032102 (2014).
- ¹⁰F. Shimura, R. Hockett, D. Reed, and D. Wayne, *Appl. Phys. Lett.* **47**, 794 (1985).
- ¹¹F. Shimura, *Appl. Phys. Lett.* **46**, 941 (1985).
- ¹²Q. Sun, K. Yao, J. Lagowski, and H. Gatos, *J. Appl. Phys.* **67**, 4313 (1990).
- ¹³J. Takahashi, K. Nakai, K. Kawakami, Y. Inoue, H. Yokata, A. Tachikawa, A. Ikari, and W. Ohashi, *Jpn. J. Appl. Phys.* **42**, 363 (2003).
- ¹⁴A. Mattoni, F. Bernardini, and L. Colombo, *Phys. Rev. B* **66**, 195214 (2002).
- ¹⁵H. Zimmermann and H. Ryssel, *Appl. Phys. A* **55**, 121 (1992).
- ¹⁶H. Monkhurst and J. Pack, *Phys. Rev. B* **13**, 5188 (1976).
- ¹⁷J. Perdew, J. Chevary, S. Vosko, K. Jackson, M. Pederson, D. Singh, and C. Fiolhais, *Phys. Rev. B* **46**, 6671 (1992).
- ¹⁸P. Blöchl, *Phys. Rev. B* **50**, 17953 (1994).
- ¹⁹E. Batista, J. Heyd, R. Hennig, B. Uberuaga, R. Martin, G. Scuseria, C. Umrigar, and J. Wilkins, *Phys. Rev. B* **74**, 121102(R) (2006).
- ²⁰P. Spiewak and K. Kurzydłowski, *Phys. Rev. B* **88**, 195204 (2013).
- ²¹A. Wright, *Phys. Rev. B* **74**, 165116 (2006).
- ²²C. Collins, R. Carlson, and C. Gallagher, *Phys. Rev.* **105**, 1168 (1957).
- ²³D. Lang, H. Grimmeiss, E. Meijer, and M. Jaros, *Phys. Rev. B* **22**, 3917 (1980).
- ²⁴P. Mooney, L. Cheng, M. Süli, J. Gerson, and J. Corbett, *Phys. Rev. B* **15**, 3836 (1977).
- ²⁵V. Voronkov and R. Falster, *J. Cryst. Growth* **204**, 462 (1999).
- ²⁶V. Voronkov, *J. Cryst. Growth* **310**, 1307 (2008).
- ²⁷C. Londos, I. Antonova, M. Potsidou, A. Misiuk, J. Bak-Misiuk, and A. Gutacovskii, *J. Appl. Phys.* **91**, 1198 (2002).
- ²⁸L. Murin, J. Lindström, B. Svensson, V. Markevich, A. Peaker, and C. A. Londos, *Solid State Phenom.* **108–109**, 267 (2005).
- ²⁹V. Akhmetov, G. Kissinger, and W. von Ammon, *Appl. Phys. Lett.* **94**, 092105 (2009).
- ³⁰A. Chroneos, E. N. Sgourou, C. A. Londos, and U. Schwingenschlögl, *Appl. Phys. Rev.* **2**, 021306 (2015).
- ³¹E. Holmström, A. Kuronen, and K. Nordlund, *Phys. Rev. B* **78**, 045202 (2008).
- ³²H. Wang, A. Chroneos, C. A. Londos, E. N. Sgourou, and U. Schwingenschlögl, *Sci. Rep.* **4**, 4909 (2014).