

# Infrared defect dynamics – radiation induced complexes in silicon crystals grown by various techniques

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Radiation induced point defect-light element impurity complexes, basically  $C_iO_i$ , are used widely for lifetime control in power devices for hybrid cars. Recently, not only CZ, but also FZ and epitaxial wafers have been examined as candidates. It has been suggested by luminescence study that  $C_iO_i$  behaved differently during annealing in crystals from different origins. The behavior of  $C_iO_i$  (and VO) during annealing was examined by highly sensitive infrared absorption spectroscopy (IR).  $C_iO_i$  concentration ( $[C_iO_i]$ ) after irradiation depended strongly on the growth techniques and as-grown carbon ( $[C]$ ) and oxygen ( $[O]$ ) concentrations. In the basic C-rich MCZ

case,  $C_iO_i$  and VO reacted with each other and decreased steadily with annealing temperature increase. They mostly disappeared at 400 °C. In low  $[C]$  CZ case,  $C_iO_i$  residual ratio ( $RR = \alpha_{400^\circ C} / \alpha_{RT}$ ,  $\alpha$  is the absorption coefficient) was higher, probably due to low reaction probability of much lower  $[C_iO_i]$  with VO. In FZ silicon,  $C_iO_i$  residual ratio was low, probably due to rapid break. Thus, IR made systematic and quantitative analysis compared to the luminescence study. In nitrogen-doped FZ silicon, NV was observed in as-grown crystals.  $N_2$  was modified by irradiation and complicated reaction took place with V or I by annealing. This would affect the  $C_iO_i$  behavior.

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**1 Introduction** Silicon crystals have been used mainly for LSIs. Recently, power devices, especially those for hybrid cars, have become important application [1]. Today, radiation induced complexes  $C_iO_i$  are used widely for improving performance of inverters for mobile cars [1]. The behavior of radiation induced light element impurity-intrinsic point defect complexes such as  $C_iO_i$  has long been analyzed, mainly on high carbon concentration ( $[C]$ ) samples under high dose irradiation [2]. It, however, has become practically important to understand the behavior in

high quality low  $[C]$  substrates under low dose irradiation. In addition, CZ silicon was the main substrate to date, but FZ and epitaxial silicon are also the candidates for power device substrates now. The behavior of  $C_iO_i$  and the effect on device performance has usually been analyzed by photoluminescence (PL) and cathodoluminescence (CL) or deep level transient spectroscopy (DLTS) [1]. Since these methods can detect only a fraction of these complexes, we have used infrared absorption measurements which can detect almost all complexes and is quantitatively reliable. We

have, in fact, established highly sensitive, quantitative and systematic infrared absorption spectroscopy and used the analysis on defect dynamics from 2006 [3] (we called this method “infrared defect dynamics” [4]). Here, the behavior of  $C_iO_i$  with emphasis on that of related complexes such as VO and in various crystals was examined in detail. These results are compared with those arising from PL and CL measurements.

**2 Experimental** We examined various middle [C] MCZ (magnetic CZ) [4] and low [C] CZ [5] silicon, FZ silicon [6] and NCZ (nitrogen doped) silicon [6]. Sample size was about 1 cm square and 2 mm thick with both sides mirror polished. Impurity concentrations, [C] and [O] (oxygen) and conductivity type and dopant are summarized in Table 1. [C] and [O] were obtained from the absorption coefficient ( $\alpha$ ) by using the conversion coefficients 0.82 and  $3.14 \times 10^{17}$  atoms/cm<sup>2</sup> given in SEMI MF1391 and MF1188, respectively.

The samples were irradiated by electrons accelerated at 4.6, 2 or 1 MeV (in the last case from both sides) at room temperature. He irradiation was done on middle [C] MCZ crystal at an acceleration voltage of 5 MeV [7]. After irradiation, the samples were annealed at from 100 to 800 °C (temperature range was different for different sample sets) separately for each temperature for 10 min.

Differential infrared absorption measurement of the irradiated and annealed samples was done using non-irradiated sample as the reference at room temperature. The wavenumber resolution was 2 cm<sup>-1</sup> or 4 cm<sup>-1</sup> (the latter was used for ultra low concentration complexes). The noise level was about  $10^{-7}$  absorbance at best and the complex absorption lines with  $10^{-6}$  peak height were successfully detected and evaluated [7]. To improve the reliability, a few absorption lines from the same complex were measured and compared (complexes and absorption lines are listed in the Appendix).

**Table 1** [C], [O] (cm<sup>-3</sup>),  $\alpha_{CiOi}$  (862 cm<sup>-1</sup>),  $\alpha_{VO}$  (830 cm<sup>-1</sup>) and residual ratio (RR) in various crystals.

	[C]	[O]	$A_{As\ ir.}$		$\alpha_{400^\circ C}$		RR <sub>(400RT)</sub>		type
	E15	E17	CiOi	VO	CiOi	VO	CiOi	VO	
C-rich	9	2.5	0.0197	0.0273	0.0025	0	0.15	0	N(As)
C-med	1.5	9	0.0028	0.1035	0.0014	0.0023	0.50	0.02	P(B)
FZ	0.4	0.2	0.0059	0.0434	0	0	0	0	P(B)
NCZ	1	7	0.0013	0.1150	0.00049	0.00024	0.39	0.002	P(B)

### 3 Results and discussion

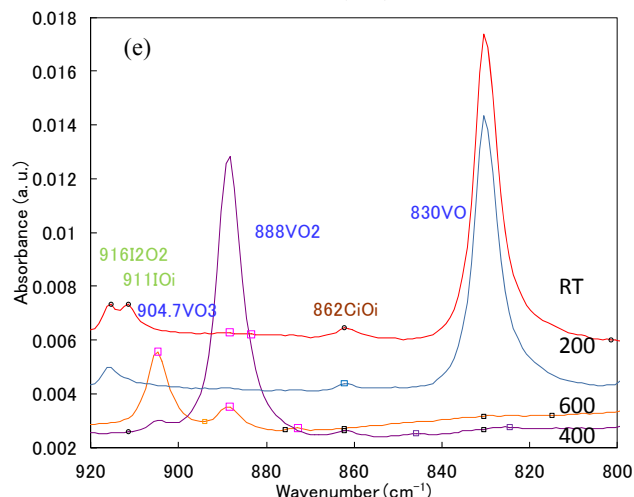
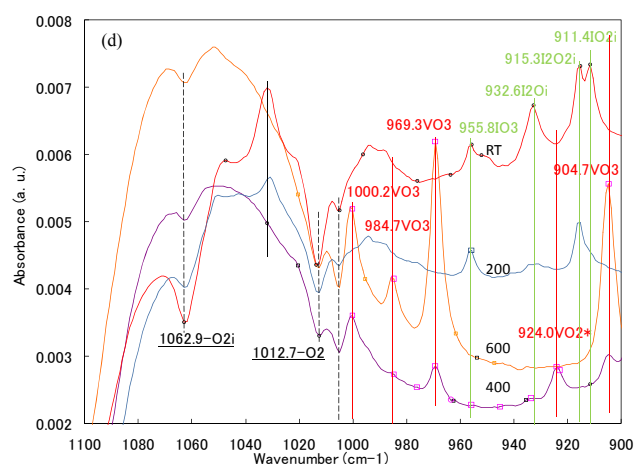
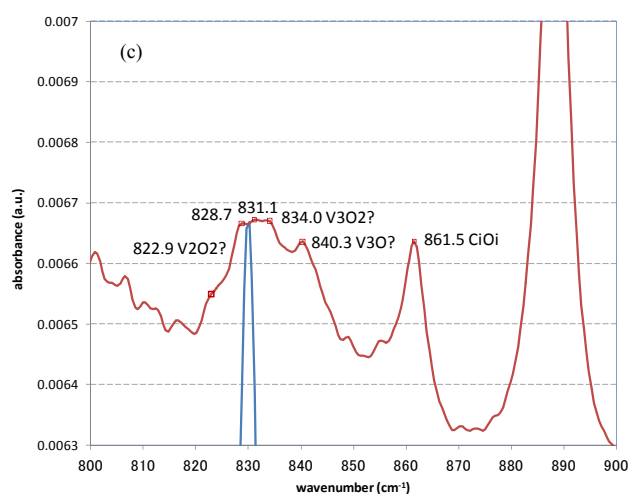
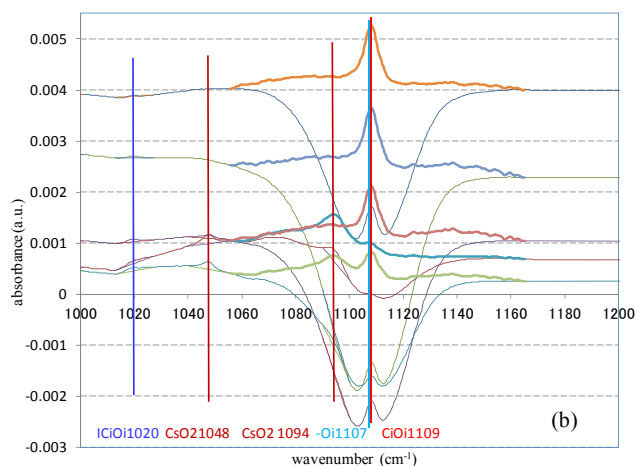
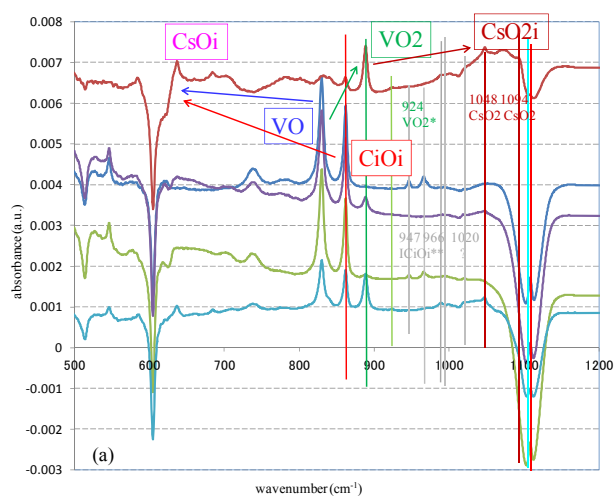
**3.1 Middle [C] MCZ crystal** In this case, [C] =  $9 \times 10^{15}$  and [O] =  $2.5 \times 10^{17}$  cm<sup>-3</sup>. Figure 1(a) shows the differential absorption spectra of so called C-rich [2] case. The spectra for the annealing temperature between 300 and 400 °C are shown here and those for as irradiated and annealing at 100 and 200 °C had been shown in Ref. [8], Fig.

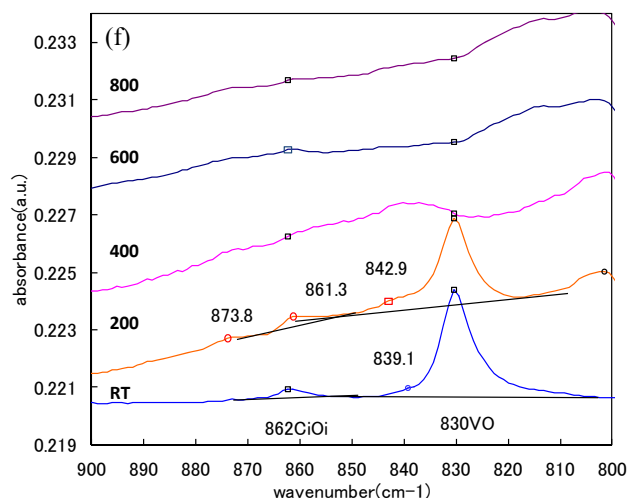
5. There are more than 10 complexes and more than 20 absorption lines:  $-C_s$  (605 cm<sup>-1</sup>),  $-O_i$  (515, 1107),  $C_iO_i$  (545, 738, 862, 1109),  $IC_i$  (956, 962),  $IC_iO_i$  (936, 1020),  $IC_iO_i^{**}$  (947, 966),  $I_2C_iO_i$  (994),  $I_3C_iO_i$  (990),  $C_sO$  (585, 635, 685, 1096, 1104),  $C_sO_2$  (1048, 1094), VO (830), VO<sub>2</sub> (888), VO<sub>2</sub>\* (923), V<sub>2</sub>O (833), V<sub>3</sub>O (839) and #1020 (unidentified yet, at 1020 cm<sup>-1</sup>). Assignment mostly followed that by Murin et al. and Lindstroem et al. The bold wavenumber lines are mainly used for quantitative discussion. The reactions including  $C_iO_i$  and its counterpart VO at above 350 °C were suggested to be simple. They are expressed by the following three equations and indicated by arrows in Fig. 1(a) [2]:



In detail, (1) includes pre-reactions  $C_iO_i \rightarrow C_i + O_i$  or  $VO \rightarrow V + O$ , both emit excess O, before meet with each other. The last one (3) was usually observed only in the irradiation at elevated temperature [9, 10]. In this case, however, both  $C_sO$  and  $C_sO_2$  were observed by irradiation at RT as marked in Fig. 1(a) and shown in more detail in Fig. 1(b) ( $CsO_2$  at 1048 and 1094 cm<sup>-1</sup>). VO has two parallel reactions competing with each other, as shown in Eqs. (1) and (2). Product VO<sub>2</sub> of reaction (2) was removed by the reaction (3). As already reported, the other complexes, minor ones, were much less and did not react with the major complexes described here, need not to be taken care of [4]. Figure 2(a) shows the annealing temperature dependence of the peak absorbance of major complexes. Both  $[C_iO_i]$  and  $[VO]$  started to reduce at 350 °C and most of them disappeared at 400 °C. Instead,  $C_sO$ ,  $C_sO_2$  and VO<sub>2</sub> monotonously increased from 350 to 400 °C. The presence of  $C_iO_i$  upto 400 °C was confirmed by the 1109 cm<sup>-1</sup> line shown in Fig. 1(b). Different signals from the same origin improved the reliability. Figure 2(b) shows the various signals from  $C_iO_i$ . Good agreement between the temperature dependence of 862 and 1109 cm<sup>-1</sup> lines was confirmed. Unfortunately weaker signals of 545 and 738 cm<sup>-1</sup> lines and CL intensities were not reliable quantitatively. At 400 °C, the absorption at around 830 cm<sup>-1</sup> had not a sharp line. The magnified picture is shown in Fig. 1(c). There were five apparent peaks at about 823, 829, 831, 834 and 840 cm<sup>-1</sup>. They were similar to the 826 (VO<sub>2</sub>), 834, 839 (V<sub>3</sub>O) cm<sup>-1</sup> bands [11], 833.4 cm<sup>-1</sup> (V<sub>2</sub>O) bands (LT) [12] and 825 (V<sub>2</sub>O<sub>2</sub>), 834 (V<sub>3</sub>O<sub>2</sub>) and 840 (V<sub>2</sub>O) cm<sup>-1</sup> (1 cm<sup>-1</sup> shifted upward from the original paper according to that VO=829 (830 is correct) and VO<sub>2</sub>=887 cm<sup>-1</sup> (888 is correct) in the paper) bands [13]. Among them, the 829 and 840 cm<sup>-1</sup> bands were strong here, but the VO 830 cm<sup>-1</sup> line was hardly observed. Unfortunately there was the interference fringe which prevented us to get correct peak wavenumber. Quantitatively, the absorption coefficients ( $\alpha$ ) are summarized in Table 1. Because the conversion coefficient ( $k$ ) to concentrations

was  $k_{VO} = 3 k_{CiOi}$  (see the dipoles in the table of the Appendix),  $[VO]$  was more than 4 times higher than  $[CiOi]$ . As a result, both were enough to react with and most were consumed. Only about 15% (residual ratio,  $RR = \alpha_{400\text{ °C}}/\alpha_{RT}$ ) of  $CiOi$  left after the annealing at 400 °C. Loss of VO was much higher, transformed into  $VO_2$ ,  $V_2O$ ,  $V_3O$  and so on. The peak height of  $C_5O$  and  $C_5O_2$  of the sample annealed at 400 °C was much lower than that of initial  $CiOi$ . This suggested that the dipole of  $C_5O$  and  $C_5O_2$  (assumed to be almost equal with each other) was much smaller than that of  $CiOi$ . There is the discussion on  $CiOi_2$  or P-line [14, 15]. We have not enough information to discuss this now. The annealing time was 10 min. in this case and the P-line had been shown to develop up to 100 min.

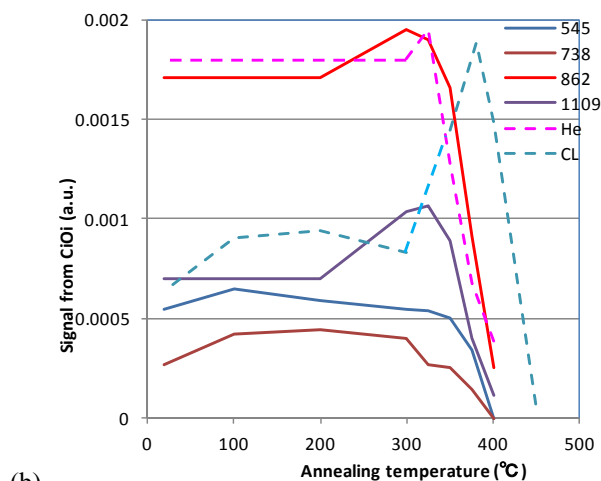
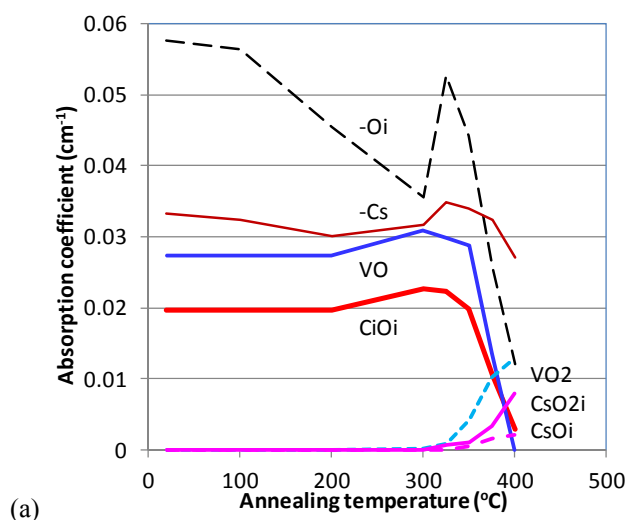




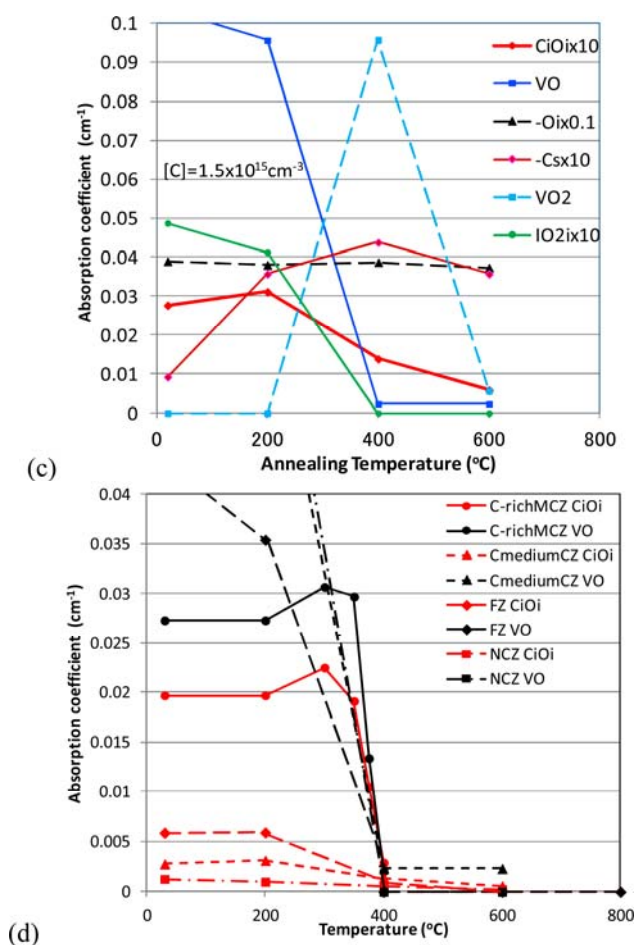
**Figure 1** Annealing temperature dependence of differential absorption spectra of irradiated and annealed silicon. (a) C-rich MCZ, after annealing at 300, 325, 350, 375 and 400 °C. Absorption lines are labelled and the dominant reactions are indicated. (b) Ibid,  $\text{C}_5\text{O}_2$  absorption at 1048 and 1094  $\text{cm}^{-1}$  and  $\text{C}_i\text{O}_i$  absorption (delineated by cancelling the  $\text{O}_i$  loss) at 1109  $\text{cm}^{-1}$ . (c) Ibid, magnified spectra at around 830  $\text{cm}^{-1}$  for 400 °C. (d) Low [C] CZ, between 900 and 1100  $\text{cm}^{-1}$ . (e) Ibid, magnified spectra between 800 and 920  $\text{cm}^{-1}$ . (f) FZ, magnified spectra between 800 and 900  $\text{cm}^{-1}$ . Vertical unit is absorbance  $A$ . Absorption coefficient is  $\alpha = A \times 11.3$  ( $= (\log_{10}/\log_e) \times (1 \text{ cm}/2 \text{ mm})$ ).

**3.2 low [C] CZ silicon** Carbon concentration in commercial silicon has been decreasing recently. Low [C] samples were examined here. The most examined sample contained  $[\text{C}] = 1.5 \times 10^{15}$  and  $[\text{O}] = 8.6 \times 10^{17} \text{ cm}^{-3}$  [6]. Previously, low [C] samples have been categorized C-clean type in the irradiation studies [10]. In the C-clean case, C-rich type complexes listed above including  $\text{C}_i\text{O}_i$  have not been observed but C-clean type  $\text{IO}_{2i}$  group was observed,  $\text{IO}_{2i}$  (911  $\text{cm}^{-1}$ ),  $\text{I}_2\text{O}_{2i}$  (916, 1031),  $\text{IO}_{3i}$  (956),  $\text{O}_{2i}$  (1013, 1062) and TDD (thermal double donor, 976, 989, 999, 1006  $\text{cm}^{-1}$ ) [8]. Here, however,  $\text{C}_i\text{O}_i$  group was observed in addition to  $\text{IO}_{2i}$  group, owing to the ultra high sensitivity. Therefore we call this case “C-medium.” An example of the spectra between 800 and 1100  $\text{cm}^{-1}$  (as irradiated and after annealing at 200, 400 and 600 °C) is shown in Figs. 1(d) and (e). 862  $\text{cm}^{-1}$  absorption line due to  $\text{C}_i\text{O}_i$  was much weaker than the 830  $\text{cm}^{-1}$  VO line due to low [C].  $\text{C}_i\text{O}_i$  absorption was clearly observed after annealing at 200 and 400 °C, in contrast to the C-rich case described above. VO absorption at 830  $\text{cm}^{-1}$  was almost disappeared at 400 °C as in the C-rich case. Figure 2(c) shows the annealing temperature dependence of the peak absorbance.  $\alpha_{\text{C}_i\text{O}_i}$  was 15% and  $\alpha_{\text{VO}}$  was 1/4 of the above C-rich case, respectively. After annealing at 400 °C,  $\alpha_{\text{C}_i\text{O}_i}$  was 1/2 (=RR) of that after irradiation. The reaction was basically same as that in the C-rich case. It is considered, however that, as  $[\text{C}_i\text{O}_i]$  was very low, less than 15% of C-rich case and 3% of [VO], the reaction probability with VO was much re-

duced, resulting in more part of  $\text{C}_i\text{O}_i$  left after annealing at 400 °C (RR=1/2). On the other hand, almost all VO changed into  $\text{VO}_2$ , due to rich [O] and that the reaction (2) of VO with O was superior to that (1) with  $\text{C}_i\text{O}_i$ . At above 400 °C,  $\text{VO}_n$  ( $n > 2$ ) were formed. We do not discuss  $\text{VO}_n$  ( $n \geq 3$ ) here (they had been discussed in detail in [16]). The effect of presence of  $\text{IO}_{2i}$  group will be examined in the future.







**Figure 2** Annealing temperature dependence of peak absorbance of dominant complexes including  $C_iO_i$  and VO. (a) C-rich MCZ case. (b) Ibid, various signals from  $C_iO_i$ , (c) C-medium CZ case. Someones are magnified or reduced. (d) Summary of  $C_iO_i$  and VO including FZ and NCZ cases.

**3.3 FZ silicon crystal** FZ crystals, not using crucible, contain more than 1 order of magnitude less [O] than CZ crystals which use  $SiO_2$  crucible. Dependence of the spectra on sample and annealing temperature had been shown in [6] Figs. 1 and 2. One example of behavior is discussed in detail here. [C] was about  $1 \times 10^{15} \text{ cm}^{-3}$  and [O] about  $2 \times 10^{16} \text{ cm}^{-3}$ . As shown already in [6] Fig. 1, C-rich type  $C_iO_i$  absorption lines, at 545, 862 and 1109  $\text{cm}^{-1}$ ,  $IC_iO_i$  at 936 and 1020  $\text{cm}^{-1}$ ,  $I_2C_iO_i$  and  $I_3C_iO_i$  at 994 and 989  $\text{cm}^{-1}$ , and VO line at 830  $\text{cm}^{-1}$  were observed though [O] was low, but C-lean type complexes were not observed after irradiation. This was similar to the C-rich MCZ case described above. Annealing temperature dependence of the spectra between 800 and 900  $\text{cm}^{-1}$  is shown in Fig. 1(f).  $C_iO_i$  and VO were observed after irradiation and annealing at 200 °C, but not after annealing at 400 °C. This resembled to middle [C] CZ case. The difference was that  $C_iO_i$  and VO decreased a little after annealing at 200 °C. Also,  $VO_n$  ( $n \geq 2$ ) was not formed by annealing at above 400 °C

These were not observed in CZ silicon. At 400 °C  $C_5O_2$  (1048 and 1094  $\text{cm}^{-1}$  lines) was not confirmed. Figure 2(d) shows the temperature dependence of the absorbance. After irradiation  $\alpha_{C_iO_i}$  was 2 times larger and  $\alpha_{VO}$  was less than 1/2 of C-medium crystal but 7 times higher than  $\alpha_{C_iO_i}$ .  $C_iO_i$  content and thermal behavior was similar to that in C-medium CZ crystal. Here, VO content reduced rapidly with temperature by  $VO \rightarrow V+O$  due to low [O]. As  $[C_iO_i]$  was low and VO was rapidly broken, they did not meet easily with each other.  $C_iO_i$  was considered to be broken.

**3.4 Nitrogen doped crystal** Nitrogen doping in silicon crystal is widely used to suppress grown-in micro-defects [17]. The interaction between N and intrinsic point defects of both I and V plays an important role in the defect formation. It also should affect the  $C_iO_i$  behavior in power devices using N-doped silicon crystal. Both CZ and FZ crystals were examined. Nitrogen concentration ranged  $2 \times 10^{14}$ – $6 \times 10^{15} \text{ cm}^{-3}$ . The result of an example of NCZ case is shown in Table 1 and Fig. 2(d). [C] and  $[C_iO_i]$  were about 1/10 of C-rich MCZ case and 1/2 of C-medium CZ case. The behaviour was similar to C-medium CZ case and the residual ratio (RR) was also high, 0.39. This will be examined in more detail in the future.

$N_2$  absorption line apparently weakened by the irradiation of FZ crystal. On the other hand, the reduction was not observed in CZ crystal. New peaks appeared at 778, 725, and 551 (NV)  $\text{cm}^{-1}$  in FZ Si as shown in Fig. 3(a). NV band at 551  $\text{cm}^{-1}$  had been observed only in laser annealed and quenched sample [18]. The linear relation of loss of 766 and gain of 778  $\text{cm}^{-1}$  lines suggested that the latter's origin was some transform from  $N_2$ . By the post-annealing,  $N_2$  absorption lines recovered and several new absorption lines appeared as shown in Fig. 3. Among them, those at 689 and 725  $\text{cm}^{-1}$  were prominent. The intensity of the lines at 778 and 725  $\text{cm}^{-1}$  reduced monotonously as the annealing temperature increased. The loss of  $N_2$  absorption lines increased a little with higher annealing temperature and steeply increased by the annealing at 600 °C but almost disappeared at 800 °C. The absorption lines at 778, 725 and 551 (not shown here)  $\text{cm}^{-1}$  weakened monotonously upto 400 °C and disappeared at 800 °C. The absorption line at 689  $\text{cm}^{-1}$  appeared by the annealing at 400 °C and with smaller intensity at 600 °C, but not appeared at 800 °C.

From the behavior of the 766 and 778  $\text{cm}^{-1}$  lines, it is plausible that  $N_2$  was not completely destroyed but something was added by the irradiation. The accompanying complexes were C-rich type only and C-lean (I-rich) types were not found. This suggested the V-rich condition and the added material was thought to be V rather than I. Jones [19] calculated and examined the  $N_iN_s$  ( $VN_2$ ) to be at 774  $\text{cm}^{-1}$  and related it to the 782 and 790  $\text{cm}^{-1}$  lines from unknown structure observed by Goss [20]. Here, we tentatively assigned 778 (and 726)  $\text{cm}^{-1}$  lines to  $VN_2$ . Karoui [21] calculated  $VN_2$  also and obtained 781 and 585  $\text{cm}^{-1}$

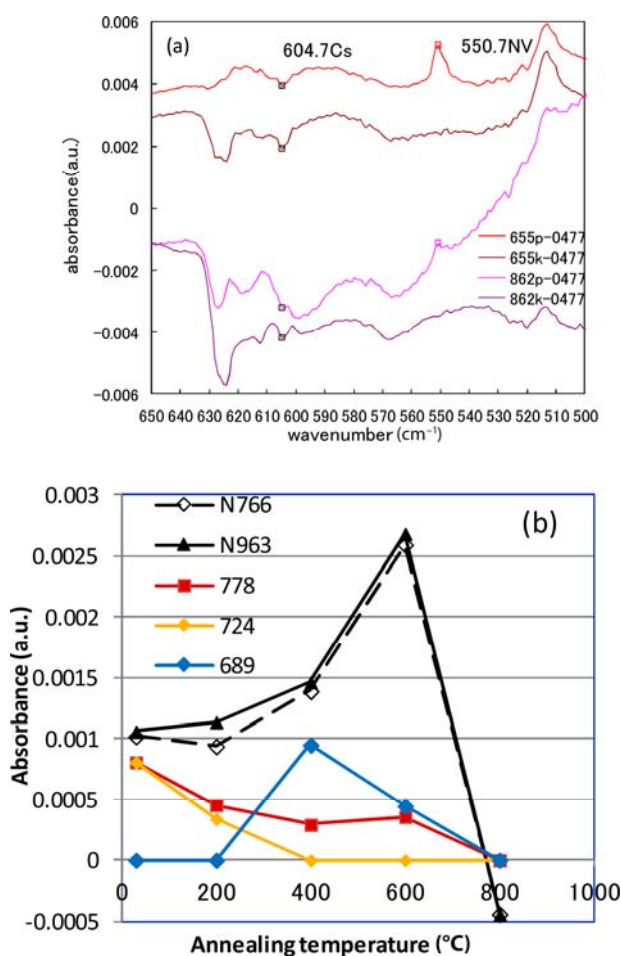
lines, and related  $585\text{ cm}^{-1}$  to observed  $551\text{ cm}^{-1}$  and assigned to  $N_s$  by Stein.

On annealing at  $400^\circ\text{C}$ ,  $689$  and  $724\text{ cm}^{-1}$  lines appeared instead of  $778$  and  $725\text{ cm}^{-1}$  lines. Simple explanation was further attachment of V resulting in the formation of  $V_2N_2$ . VO disappeared on annealing at  $400^\circ\text{C}$ . In contrast, in CZ silicon VO transformed into  $VO_2$ . These suggested that VO released both V and O in FZ silicon here as described above. Karoui [21] calculated  $V_2N_2$  absorption, to be at  $615$ ,  $625$  and  $637\text{ cm}^{-1}$ , and related to the observed  $653\text{ cm}^{-1}$  line by Stein ( $N_s$ ). We tentatively assigned  $689$  (and  $714$ )  $\text{cm}^{-1}$  lines to be from  $V_2N_2$ . The stability of  $VN_2$  and  $V_2N_2$  had been theoretically examined in relation to the effect of nitrogen on the grown-in defect formation in Si. The above results made it possible to estimate the dipole of  $VN_2$  ( $2/3$  of  $N_2$ ) and  $V_2N_2$ . N changes both [V] and [I]. These N-V interactions might affect the  $C_iO_i$  behavior in NFZ silicon.

**3.5 He irradiation** He irradiation is used to introduce  $C_iO_i$  to the power devices for the hybrid cars [1]. It was examined here on the samples from the same C-rich MCZ crystal as that used in the electron irradiation described in Section 3.1 [7]. Absorption lines were mostly similar to those shown in Section 3.1. Not only C-rich type complexes such as  $C_iO_i$  and  $IC_iO_i$ , however, but also C-lean type complexes such as  $I_2O_{2i}$  and  $IO_{3i}$  shown in Section 3.2 (C-medium CZ case) were observed, in contrast to the electron case. Peak absorbance for He case is about half that of electron irradiation. He dose was  $5 \times 10^{13}\text{ cm}^{-2}$ ,  $1/200$  of the electron dose of  $10^{16}\text{ cm}^{-2}$ . Peak absorbance A corresponds to the total amount of complexes in the sample. In this case  $A_{He} = 1/2A_{El}$ . As for the dose  $F_{He} = 1/200A_{El}$ . Production rate ( $P$ ) =  $A/F$ .  $P_{He}/P_{El} = (1/2/1/200)/1/1 = 100$ . Thus, the complex production rate per particle was about 100 times as large as that of electron. The production range in He case was restricted to  $20\text{ }\mu\text{m}$  from the surface,  $1/100$  thickness of the electron case in which complexes had been formed uniformly throughout the  $2\text{ mm}$  thick sample. Therefore, the complex concentration in the layer was about 100 times as high as that in the electron case. Annealing behavior of  $C_iO_i$  and others was similar to that in the electron case, but there was some difference in the detail. The annealing temperature dependence of  $C_iO_i$  peak intensity is compared to the electron case in Figs. 2(b) and (d). Electronic property of  $IO_{2i}$  was examined [22]. This must be taken into account for low [C] crystals.

**3.6 Comparison to PL studies** These studies were mainly addressed at the analysis of the dependence of  $C_iO_i$  on the crystal type by photoluminescence (PL) for power device application [23, 24]. The temperature dependence of normalized luminescence (C-line) from  $C_iO_i$  was examined. In case of FZ crystals, annealing out temperature was about  $350$ ,  $375$  and  $450^\circ\text{C}$  for the specimen with [C]  $9$ ,  $8$ ,  $3 \times 10^{14}$  and [O]  $1$ ,  $2 \times 10^{15}$  and  $1 \times 10^{17}$  (CZ-FZ)  $\text{cm}^{-3}$ , re-

spectively. The authors of the papers suggest that the high [O] kept the anneal temperature high. In their other study including CZ crystal,  $C_iO_i$  anneal temperature was  $350$  for gas-dope FZ,  $375$  for poly-FZ,  $400$  for CZ-FZ and  $450^\circ\text{C}$  for MCZ (carbon ND and [O] highest). They considered that the unbalance of [C]/[O] reduced the bonding probability with each other. In the other DLTS study, deep level due to VO had been observed differently in the different FZ crystals and had been suggested to be responsible for diode characteristic difference [25]. In our study, however, Goto et al. observed VO also in the He irradiated diodes, but did not find correlation to the device characteristic difference [26]. Sugiyama et al. did cathodoluminescence (CL) study after He irradiation. As shown already in Ref. [7] and in Fig. 2(d), the luminescence intensity was modified from the  $[CiOi]$  and restricted usually only to  $C_iO_i$ . IR gives a quantitative information of all related complexes as shown here. A difference of VO behavior in FZ from that in low [C] CZ, for example, was found. Thus, “infrared defect dynamics” will help to clarify the behavior and mechanism.



**Figure 3** (a) NV band at  $551\text{ cm}^{-1}$  observed in as-grown NFZ silicon. (b) Annealing temperature dependence of loss of absorption from  $N_2$  and new absorption in irradiated NFZ silicon.

**4 Summary** In summary, behavior of radiation induced  $C_iO_i$  (and VO) during post annealing in crystals grown by various techniques was examined by highly sensitive and systematic infrared absorption spectroscopy. Not only dominant complexes but also minor groups were analyzed for the first time. Carbon concentration ( $[C]$ ) ranged  $5 \times 10^{14}$ – $1 \times 10^{16}$  and oxygen concentration ( $[O]$ ) between  $1 \times 10^{16}$  and  $5 \times 10^{17} \text{ cm}^{-3}$ . In the most well established C-rich type middle  $[C]$  MCZ silicon,  $C_iO_i$  and VO were dominant and almost disappeared by the annealing at 400 °C. At above 300 °C they reacted with each other as  $C_iO_i + VO = C_sO + O$ . They steadily decreased with annealing temperature up to 400 °C where most  $C_iO_i$  and all VO were consumed.  $VO + O = VO_2$  also took place and competed with the above reaction. From  $VO_2$ ,  $C_i + VO_2 = C_sO_2$  also took place. It is to be noted that the complexes in  $C_iO_i$ -VO- $C_sO$  system react only within this system. In the other crystals, low  $[C]$  CZ and FZ silicon,  $C_iO_i$  was minor. In a new “C-medium” type,  $[C_iO_i]$  was comparable to  $[IO_{2i}]$  group which are known to be dominant in C-lean type crystals. For low  $[C]$  CZ silicon, higher ratio of  $C_iO_i$  was reserved. It was probably due to that low content  $C_iO_i$  after irradiation could not easily react with VO. In low  $[O]$  FZ silicon, such residual  $C_iO_i$  was not confirmed yet, probably due to that they were rapidly broken. In the luminescence studies  $C_iO_i$  residual ratio by C-line intensity at 400 °C had been reported to be higher in MCZ and FZ silicon than in CZ silicon. It was difficult whether  $[C_iO_i]$  was high or nonradiative center concentration was low. Moreover it could not reveal the behaviour of source and product of  $C_iO_i$ . Highly sensitive and quantitative IR study will reveal the behaviour. In nitrogen-doped FZ silicon,  $N_2$  was modified by irradiation and complicated reaction took place with V or I. This would affect the  $C_iO_i$  behavior. The case of He irradiation was similar to that of electron irradiation.

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## Appendix

Tentative list of infrared absorption lines from radiation induced light element impurities (C, O, N) - intrinsic point defects (vacancy V and self interstitial I) complexes. Complex, wavenumber of absorption line both at RT and at LT, normalized dipole (estimated conversion coefficient from absorption coefficient to concentration, that of carbon (SEMI MF1391:  $0.82 \times 10^{17} \text{ cm}^{-2}$ ) as 1. Complexes are grouped. The references were listed in references [3–7] here. The assignment follows mainly those by Murin and Lindstroem. For hydrogen see Ref. [27, 28].

common type:							dipole
Cs	605	1206					1
LT	607						
Oi	514	560	1107	1226			3.9
	515	1136					
VO	531	830	876				3.4
LT	534	835.8	885.5	1370			
VO–	877.1						
LT	545	885	1430.1				
formed by annealing:							
VO2	889						1.7
LT	895.5						
VO2*	923						
LT	928.4	1003.8					
V2O	826						
LT	833.4	1003.8					
V2O2	824						
LT	829	923	1000				
V3O2	833						
LT							
V3O	839						
LT	842.4						
VO3	905	969	1000	(985)			
LT							
LT	910	975.9	1005.3	1105	(991)		
VO3C	902	956	1025				
LT	985	1009					
VO4	985	1009					
LT	992	1011	1024	1041	1043	1056	1062
VO5,6L	991	1011	1024	1040.6	1042.7	1056	1062
T		1097	1099	1108			
	1097						
LT	842.4						
C-rich type:							
Ci	922	932					

LT							
CiOi	527	537	545	583	738	862	1109
LT	529.6	542	549.8	588	742.8	866	1116.3
ICiOi	936	1020					1.2
LT	939.8	1024.2					
ICi	954	962					1.3
LT	960.1	966.7					
I2CiOi	994						3.4
LT	998						
I3CiOi	988						3.4
LT							
formed by annealing:							
CsO	585	635	685	1096	1104		
LT	589			1104	1104		2.4
CsO2	1048	1094					2.4
LT		1099.5					
ICiOi*	724.5	952.1	973.1				
ICiOi**	947	966					1
LT	951.3	969.3	977.8				
#1020	1020						1.2
C-lean type:							
I Oi							
LT	944.3	956.2					
IO2i	545	922	1042				
LT		922	1037				
I2O2i	916	933	1031				
LT	545	917	1034				
IO3i							
LT	956	1054					
I2Oi							
LT	936						
O2i	552	686	1013	1062			
LT	555.9	690.1	1012.4	1059.8	1105.3		
O3i							
LT		1006.8					
O-lean type:							
CiCs(G)							
LT	540.4	543.3	579.8	640.6	730.4		
CsCs							
LT	527.4	(748.7)					
TDD	578	730	975	988	999	1006	1013
LT	580	730			1000		
Intrinsic point defect cluster:							
V2	1.8um						



LT	2767							
3 (W)	62.7meV							
LT	565							
4 (X)	66.2meV	67.9meV	69.0meV					
LT	534	548	557					
Nitrogen:								
N2	766	963						0.9
Ns(VN)	551	653						
VN2	725	778						0.9
V2N2	689	713						
Hydrogen:								
H LT								
VH	2067.5							
VH2	2122.4	2145.2						
VH3	2167	2191.8						
VH4	2222.9							
V2H2	2072.5							
IH2	1987.2	1990.1	743.1	748				
I2H2	1870.2							
H2*	1838.7	2062.1	817.6					
H2	3618.9							