The interstitial carbon-oxygen center and its hydrogenation

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Previous stress alignment investigations have suggested a model for C_iO_i where the O-atom maintains its approximate bond-centered location. Local vibrational mode spectroscopy and *ab-initio* modeling are used to investigate this defect. We find new modes whose oxygen isotopic shifts give further evidence for a previously proposed over-coordination of oxygen. Complexes formed by adding both single (C_iO_iH) and a pair of H atoms ($C_iO_iH_2$), as well as the addition of a second oxygen atom, are considered theoretically. It is shown that the first is a negative-U defect, while the second is passive. The properties of C_iO_iH and $C_iO_{2i}H$ are strikingly similar to the first two members (D1 and D2) of a family of shallow thermal donors that contain hydrogen.

1. Introduction and motivation

The interstitial carbon-oxygen defect (C_iO_i) results from the interaction between O_i and mobile C_i defects, after e-irradiation or long-term annealing of Cz-Si crystals ($I_{Si} + C_s \rightarrow C_i$). It has been detected by the major characterization techniques:

- EPR — G15 signal from $C_iO_i^{(+)}$;
- PL — C-line at 0.7896 eV with several phonon-replicas;
- FTIR — 1116, 865, 742, 550 and 529.8 cm^{-1} bands;
- DLTS — Donor level at $E_v + 0.38$ eV;

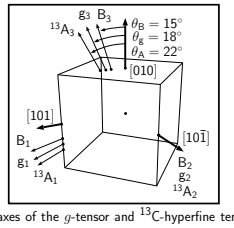

Fig. 1. Principal axes of the g-tensor and ^{13}C-hyperfine tensor from the G15 EPR signal ($C_iO_i^{(+)}$). Stress-energy B-tensor principal directions are also shown.

- Model shown in Fig. 2a was proposed after stress-alignment measurements.
- Theoretical modeling favor the tri-valent model (Fig. 2b), explaining the highest O-related LVM at 742 cm^{-1}.

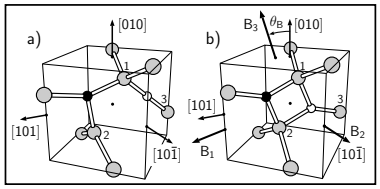

Fig. 2. Models for C_iO_i. (a) Di-valent oxygen model, (b) Tri-valent oxygen model. Gray, black and white atoms are Si, C, O. Crystallographic axes and principal directions of the B-tensor are also shown.

- **Hydrogenation of a prominent radiation-induced defect like VO or C_iO_i is thought to give rise to a precursor of the H-related shallow thermal donors [STD(H)N];**
- **Electron and hole traps E5($E_c - 0.36$ eV) and H4($E_v + 0.28$ eV) were assigned to C_iO_iH;**
- **Oxygen over-coordination is believed to play a key role on thermal donor electrical properties;**

Conclusions

1. FTIR measurements and calculations support the tri-valent C_iO_i in Fig. 2b (LVMs, B-tensor, E($+/0$), spin-density);
2. Two new bands (585 and 543 cm^{-1}) are assigned to C_iO_i;
3. C_iO_iH properties strikingly similar to D1 (Negative-U, E($0/+$), E($-/0$), E($-/+$), LVMs, spin-density);
4. $C_iO_{2i}H$ not bi-stable – consistent with assignment to D2;
5. This work supports a model of STD(H) containing an interstitial carbon.

2. The interstitial C_iO_i defect

Sample/Type		$[^{16}O_i]$	$[^{18}O_i]$	$[^{12}C_s]$	$[^{13}C_s]$
1	Cz-Si	1×10^{18}	—	3×10^{17}	—
2	Fz-Si	5×10^{16}	1.5×10^{18}	4×10^{17}	—
3	Fz-Si	1×10^{18}	—	2×10^{17}	1.5×10^{18}

Tab. 1. Concentration of O_i and C_s in samples (cm^{-3}).

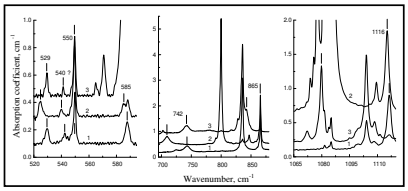

Fig. 3. Sections of the absorption spectra measured at 10 K for electron-irradiated and annealed Si samples (see Table 1).

^{16}O, ^{12}C		^{16}O, ^{13}C		^{18}O, ^{12}C	
Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
1116.3	1137.6	36.4	37.7	1.0	1.0
865.9	876.1	23.9	24.5	0.15	0.1
742.8	759.6	0.5	0.3	33.4	35.6
∼588	593.4	—	0.1	∼3	3.2
549.8	555.8	0.2	0.3	0.3	0.2
∼542	544.7	∼0.5	0.1	∼1.5	0.5
529.6	544.2	0.1	0.0	5.2	5.4

Tab. 2. Observed LVMs (cm^{-1}), for $C_iO_i^{(0)}$, along with calculations for the tri-valent model (Fig. 2b). First two columns report absolute frequencies, whereas remaining columns give downward isotopic shifts.

- Calculated donor level at $E_v + 0.36$ eV;
- Calculations indicate $B_1 = 8.5$, $B_2 = 2.3$ and $\theta_B = 22°$, compared with $B_1 = 8.6$, $B_2 = 0.2$ and $\theta_B = 15°$ from G15;
- p-orbital on C-atom with 25% of spin-density, compared with 28.6% for G15;

3. Hydrogenation of C_iO_i

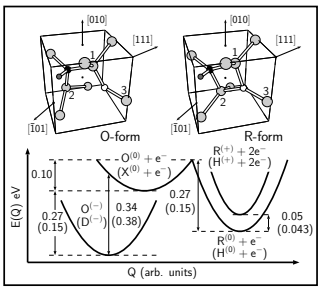

Fig. 4. Configuration coordinate diagram for C_iO_iH quoted with calculated energies for O and R forms. Experimental data relative to D1 (D and H forms) are shown in brackets.

	D1	C_iO_iH
$E_c - (-/0)$	0.11	0.10
$E_c - (0/+)$	0.043	0.05
$E_c - (-/+)$	0.076	0.08
LVM ($D^{(-)}/O^{(-)}$)	1025.5	1010
LVM ($H^{(+)}/R^{(+)}$)	—	720
D-shift ($D^{(-)}/O^{(-)}$)	2.4	2

Tab. 3. Thermodynamic gap levels (eV), oxygen LVMs and isotopic shifts (D-shift) in deuterated material (cm^{-1}), for D1 compared with those for C_iO_iH (see Fig. 4).

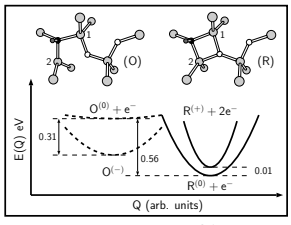

Fig. 5. Configuration coordinate diagram for $C_iO_{2i}H$ quoted with calculated energies for O and R-forms. Dashed lines are non-equilibrium states.

- Mulliken analysis indicate 0.5%, 0.1% and 0.0% of spin-density on C, H and O atoms;
- Donor electron lies in a strain-induced state, below any state overlapping the oxygen atom;
- C_iO_iH is a negative-U defect, which accounts well for D1;
- $C_iO_{2i}H$ has only a shallow donor level – D2 [STD(H)2]?;
- $C_iO_iH_2$ is electrically inert;

Grid (1 , 1)