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Carbon- and oxygen-related point defects created by annealing the dicarbon radiation-damage center in crystalline silicon

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Thermal annealing can destroy the dicarbon center with its zero-phonon line at 969 meV (7818 cm^{-1}). After the destruction of the dicarbon center, we observed many previously unreported photoluminescence lines. The point defects providing these lines consist of carbon and oxygen atoms. Finally, the annealing of the dicarbon centers is not completely understood. The breakup process is not the only way to destroy the dicarbon centers and the presence of other defects in the crystal may also affect the annealing process.

INTRODUCTION

2-MeV electron bombardment of a silicon crystal can produce different kinds of point defects.[1] The 2-MeV electron will knock out the substitutional silicon atoms into interstitial sites forming the self-interstitial atoms (I) and the remaining vacancies (V) and divacancies (V_2).[1] At room temperature, the self-interstitial atoms (I) and vacancies (V) are mobile. In a silicon crystal that contains substitutional carbon atoms (C_s) and interstitial oxygen atoms (O_i), the following reactions will occur. The self-interstitial atoms I will displace the C_s, forming interstitial carbon atoms C_i: $I + \text{C}_s \rightarrow \text{C}_i$. The C_i atoms are mobile at room temperature as well, and will react with other impurities. One C_i can react with another C_s atom, forming the dicarbon G center. An interstitial oxygen O_i may also capture the C_i atom, forming the carbon-oxygen C center: $\text{C}_i + \text{O}_i \rightarrow \text{CO}$.[1]

The dicarbon center will produce the familiar vibronic G band in silicon under photoluminescence and photoabsorption experiments with its zero-phonon line at 969 meV or 7818 cm^{-1}.[2] We have identified its local-mode sidebands at 7239, 7275 cm^{-1}, etc.[2] Local-mode sidebands are produced either by unusually strong bonds or by a small effective mass of the vibrating system. They have a phonon energy which is greater than the lattice cutoff, i.e., in silicon 65 meV.[2] The electronic transition of the local-mode sideband is different from the zero-phonon line. The zero-phonon line is a pure transition between the excited state and ground state of the center, while in the local-mode sideband the transition involves a phonon[3] (i.e., in absorption the center jumps from the ground state to the excited state plus a phonon, and in luminescence the center drops from the excited state to the ground state minus a phonon). Since the photon energy of the local-mode sideband is different between luminescence and absorption, they do not have the problem of self-absorption when taking photoluminescence (PL) measurement like the zero-phonon line (i.e., the release luminescence photon is reabsorbed by the center). Therefore, the intensities of the local-mode sidebands of different centers can indicate their concentrations more realistically than their zero-phonon lines.

The dicarbon center has been studied extensively by photoluminescence, photoabsorption, uniaxial stress, carbon 13 isotope doping, optically detected magnetic resonance (ODMR), and electron paramagnetic resonance (EPR). Its structure, its metastability, and the properties of its different charge states are well known.[4–7] In addition, four satellite sublines at 951.16 (7671), 952.98 (7686), 953.96 (7694), and 956.91 meV (7717 cm^{-1}) are related to the dicarbon center.[8] The literature suggests that these four sublines are formed when a radiation defect is trapped near (but not at) the G center when the defects in question may be self-interstitial or vacancy.[8] Isochronal annealing shows that the sublines have the same thermal stability as the G line, except for the subline at 953 meV (7686 cm^{-1}) which is destroyed at a higher temperature (325°C).[9] Some report that the subline at 953 meV (7686 cm^{-1}) grows as the G line anneals.[8]

The thermal destruction of the G centers (as monitored by the absorption in the 969-meV G zero-phonon line) in irradiated float-zone silicon (FZ) was previously reported. Four processes occur during the annealing: (a) an intrinsic breakup of the dicarbon center, in which an interstitial carbon atom is emitted; (b) multiple recapture of the interstitial carbon content; (c) motion of a diffusing species to the dicarbon centers which destroys them at a rate proportional to the radiation dose; and (d) a growth process superimposed on the destruction.[10] In Czochralski silicon (Cz) with higher oxygen concentration, the decaying rate of the dicarbon center is generally faster than in float-zone silicon.[10]

In this paper, we show that, after decaying the dicarbon center, different kinds of carbon- and oxygen-related point defects are created depending on the ratio between carbon and oxygen atoms in the silicon samples. These point defects are identified by their photoluminescence lines. It seems that different, yet undetermined, processes occur between float-zone and Czochralski silicon as the dicarbon centers anneal, which result in different decay rates.

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EXPERIMENTS

Two groups of samples were used in the experiment. The first group contained five Cz and three FZ silicon samples. The thicknesses of the samples were within 2 mm, while the areas were within 1 cm^2. The FZ samples contained 2×10^{17}-cm^{-3} carbon concentration and less than 10^{16}-cm^{-3} oxygen concentration. Cz samples, however, contained more oxygen atoms: the concentration was equal to 9×10^{17} cm^{-3}. The carbon concentration was also equal to 2×10^{17} cm^{-3}. Two of the Cz silicon samples were doped with carbon-13 isotope atoms. The carbon concentration was equal to 1×10^{17} cm^{-3} and the ratio between ^{13}C and ^{12}C was 9:1. The oxygen concentration was equal to 8×10^{17} cm^{-3}. The 2-MeV electron radiation doses given to the sample were either 1 or 2×10^{17} e^- cm^{-2}. The samples were annealed in a vertical cylindrical furnace at 300°C. After annealing, they were vertically dropped into liquid nitrogen placed under the furnace. Finally, they were cooled down to 4.2 K in a bath cryostat filled with liquid helium for the photoluminescence measurement. The final anneal times given to the samples were within 4 min.

The second group contained five FZ and two Cz silicon samples that were used for an isothermal annealing experiment. The method applied to detect the dicarbon center was photoabsorption. The results have been published elsewhere.[10] However, for this paper, the samples were remeasured by photoluminescence. Their photoluminescence spectra are reported for the first time, to our knowledge. The 2-MeV electron radiation doses given to the samples ranged from 0.5 to 3.13×10^{17} e^- cm^{-2}. They contained different carbon and oxygen concentrations. The anneal temperature was 200°C. The maximum and minima anneal times given to the samples were 70 and 6 h.

All samples were polished and etched by a mixture of acid with 10% HF and 90% HNO_3. An Ar-ion laser beam of wavelength at 514.5 nm was used to generate the luminescence spectra. The power of the beam was 0.2 W. A Nicolet fast Fourier transform spectrometer (FTIR) was applied to analyze the luminescence spectra, and the detector was a North Coast Ge detector.

RESULTS

A typical photoluminescence spectrum that contained the dicarbon center is shown in Fig. 1. The sample is of FZ type with a carbon concentration equal to 2×10^{17} cm^{-3} and an oxygen concentration less than 10^{16} cm^{-3}. The 2-MeV electron radiation dose given to the sample was equal to 1×10^{17} e^- cm^{-2}. The zero-phonon *G* line at 7818 cm^{-1} and its local-mode sidebands at 7239 and 7275 cm^{-1} are clearly seen. However, we only observed three satellite sublines of the dicarbon center, and the subline at 953.96 meV or 7694 cm^{-1} was absent. The line at 7523 cm^{-1} was previously unreported.

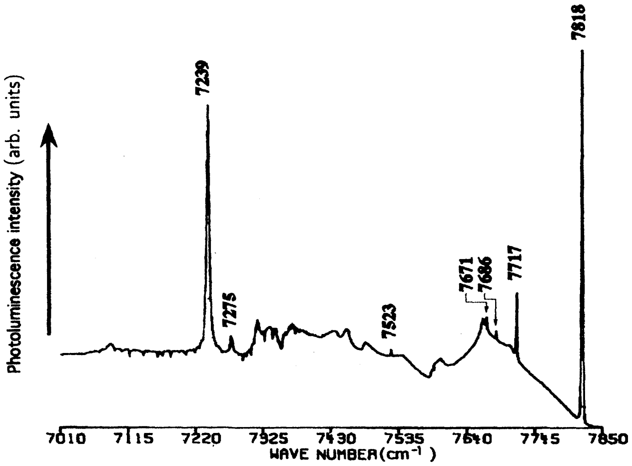

FIG. 1. The photoluminescence spectrum obtained from the irradiated carbon-doped FZ sample measured at 4.2 K before anneal.

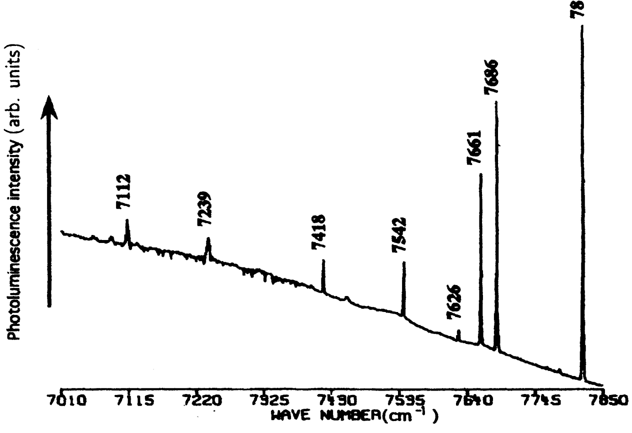

FIG. 2. The photoluminescence spectrum measured at 4.2 K obtained from the same FZ sample of Fig. 1 after 3-min 30-s anneal at 300°C.

After destroying the *G* centers by annealing, different unreported photoluminescence lines were detected among the FZ and Cz silicon samples. As shown in Fig. 2, unreported lines at 7661, 7626, 7542, and 7418 cm^{-1} were observed, after annealing the same FZ sample of Fig. 1 for 3 min 40 s at 300°C. The intensity of the *G* line local-mode sideband at 7239 cm^{-1} was greatly reduced. The tiny peak at 7112 cm^{-1} was the local-mode sideband of the subline at 7686 cm^{-1}. In addition, the line at 7523 cm^{-1} was destroyed after the anneal. However, as shown in Fig. 3, the spectrum measured from the Cz sample after annealing for 2 min at 300°C was different from the spectra measured from FZ samples. Unreported lines at 7661 and 7418 cm^{-1} were observed, so were lines at 7453 and 7281 cm^{-1}. Note that none of the satellite sublines of the dicarbon center were detected. The carbon concentration of the sample was equal to 2×10^{17} cm^{-3}, while the oxygen concentration was equal to 9×10^{17} cm^{-3}. The 2-MeV electron radiation dose given was equal to 1×10^{17} e^- cm^{-2}. The tiny peaks at 7129, 7087,

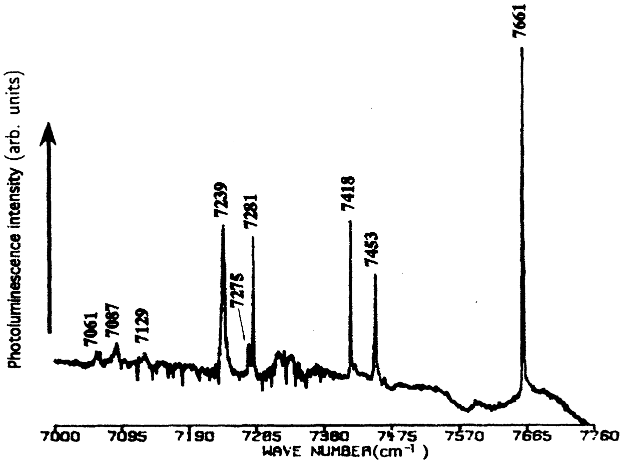

FIG. 3. The photoluminescence spectrum obtained from the irradiated Cz sample measured at 4.2 K after 2-min anneal at 300°C. The *G* line at 7818 cm^{-1} was not shown in the spectrum, since there was a very strong self-absorption effect at the line.

TABLE I. (a) The linewidth and the shift in cm^{-1} with the ^{13}C isotope effect for different PL lines are shown. (b) The linewidth and shift in cm^{-1} with the ^{13}C isotope effect, and the ratio of shift in energy of different local mode peaks were shown.

(a)

PL lines (cm^{-1})	Linewidth (cm^{-1})	Shift in cm^{-1}
7281	1.7±0.5	+1.2±0.1
7418	2.0±0.5	+1.2±0.1
7453	2.2±0.5	+1.1±0.1
7542	1.4±0.5	
7661	2.2±0.5	+1.0±0.1

(b)

PL lines (cm^{-1})	Linewidth (cm^{-1})	Shift in cm^{-1}	Ratio of shift in energy (^{12}C/^{13}C)
7129[a]	4.0±1.0		
7087[a]	4.0±1.0	+10.0±1.0	1.016± 0.003
7061[a]	4.0±1.0	+11.0±1.0	1.017± 0.003
6969[a]	3.0±1.0	+22.0±1.0	1.031± 0.003
6894[b]	5.0±1.0		
6859[c]	3.0±1.0	+5.0±1.0	1.005± 0.003 (1) 1.007± 0.003 (2)

[a] The peaks shown are the local-mode sidebands of the line at 7661 cm^{-1}.

[b] The peak shown is the local-mode sideband of the line at 7453 cm^{-1}.

[c] The peak shown is the local-mode sideband of the lines either at 7661 or 7418 cm^{-1}. A calculation of the ratio of shift from both lines is made , i.e., (1) for 7661 and (2) for 7418.

and 7061 cm^{-1} were the local-mode sidebands of the unreported line at 7661 cm^{-1}. Their phonon energies measured from the line at 7661 cm^{-1} exceeded 65 meV (524 cm^{-1}), i.e., the lattice cutoff of the silicon crystal. Note that any local-mode sideband should have phonon energies greater than the lattice cutoff frequency.[2]

Unreported photoluminescence lines were also probed to see if the defects producing them were composed of carbon and oxygen atoms. Spectra measured at 4.2 K obtained from Cz samples doped with ^{13}C and ^{18}O isotope atoms were compared with other normal Cz and FZ samples. Four photoluminescence lines gave unambiguous shifts in cm^{-1} in the samples doped with ^{13}C atoms. The shifts of these lines and their local-mode sidebands are summarized in Tables I(a) and I(b). Note that in Table I(b), the ratio of shift in energy refers to the shift in the quantum of the vibrational energy, i.e., the energy difference of the local-mode sideband with respect to its zero-phonon line. The results confirmed that the defects producing these four photoluminescence lines contained carbon atoms.

We did not detect any shift in cm^{-1} of the photoluminescence lines obtained from the Cz sample doped with ^{18}O atoms. However, this does not establish that all unreported photoluminescence lines do not involve oxygen atom. The photoluminescence line may not affect different isotopes of the element contained in the center by doping. It depends on how strongly the element can vibrate at the photoluminescence center. For example, when we dope 50% ^{6}Li and ^{7}Li atoms into the silicon sample, the photoluminescence line of the 4-Li-V *Q* center at 1045 meV will split into multiple peaks according to the number of ways of randomly choosing ^{6}Li and ^{7}Li atoms.[2] However, when we dope 50% ^{12}C and ^{13}C atoms into silicon samples, the photoluminescence line of the dicarbon *G* center at 969 meV only splits into two peaks because only one C atom is involved in the vibration, with the second C atom producing a small effect.[2]

As shown in Fig. 4, the spectrum measured from the

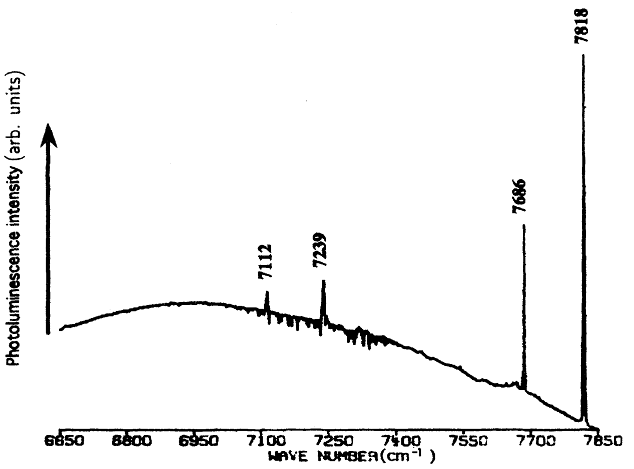

FIG. 4. The photoluminescence spectrum obtained from the irradiated FZ sample measured at 4.2 K after 70-h anneal at 200 °C. The oxygen concentration of the sample was less than 1.5×10^{15} cm^{-3}.

FZ sample with $3.13\times10^{-17}\ e^{-}\,\mathrm{cm}^{-2}$ radiation dose, none of these lines were observed. The oxygen concentration of that sample was less than $1.5\times10^{15}\ \mathrm{cm}^{-3}$, and the carbon concentration was equal to $2\times10^{17}\ \mathrm{cm}^{-3}$. The sample had been annealed for 70 h at 200°C. Therefore, we can conclude that the optical centers producing these five lines contain one or more oxygen atoms.

DISCUSSIONS

In summary, seven sharp unreported lines at 7661, 7626, 7542, 7523, 7453, 7418, and 7281 cm^{-1} were detected from the photoluminescence spectra of group-1 and -2 samples. Therefore, we can confirm that the unreported point defects providing these lines are not caused by special short-time heat treatment. The other tiny peaks at 7129, 7087, 7061, 6962, 6859, and 6894 cm^{-1}, etc. were the local-mode sidebands of these sharp lines. The line at 7523 cm^{-1} only existed in FZ samples, and was easily destroyed by heat treatment. The line at 7626 cm^{-1} existed after annealing at higher temperature. It was not observed in other samples annealed at 200°C. No further comments can be made on these two lines. The other remaining lines consisted of carbon and oxygen atoms, except for the line at 7532 cm^{-1}. The line at 7542 cm^{-1} did not exist in the Cz samples with ^{13}C isotope doping. Therefore the dependence on carbon cannot be verified.

The lines at 7661 and 7418 cm^{-1} were observed in FZ and Cz samples after annealing. For the other three lines at 7542, 7453, and 7281 cm^{-1}, however, their existence seemed to depend on the ratio between carbon and oxygen concentrations among the samples as shown in Table II. The higher the proportion of oxygen against carbon, the greater the chance that we can detect the lines at 7453 and 7281 cm^{-1} after annealing. The centers producing these lines are possibly created by capturing a released interstitial carbon atom at the oxygen atoms.

Another interesting phenomenon was that the strength of the subline at 7686 cm^{-1} or 953 meV with higher thermal stability increased as the *G* center decayed. The local-mode sideband at 7112 cm^{-1} became clear when a certain amount of heat treatment was given to the FZ sample as shown in Fig. 2. Therefore, we can conclude that the subline at 7686 cm^{-1} grew as the *G* center decayed.

TABLE II. The carbon and oxygen concentrations and the ratio between them are related to the observation of different unreported PL lines.

C conc. (cm^{-3})	O conc. (cm^{-3})	C:O	PL lines (cm^{-1})
2.0×10^{17}	$<1.5\times10^{15}$	133:1	none
2.0×10^{17}	$<10^{16}$	20:1	7542
1.1×10^{16}	2.7×10^{15}	4.1:1	7542
1.6×10^{17}			7542 and 7281
3.3×10^{16}	1.5×10^{16}	2.2:1	7453 and 7281
$1.25-1.35\times10^{18}$	0.9×10^{18}	1.4–1.5:1	7281
1.65×10^{17}	2.0×10^{17}	1:1.2	7453 and 7281
2.0×10^{17}	9.0×10^{17}	1:4.5	7453 and 7281
1.0×10^{17}	8.0×10^{17}	1:8	7453 and 7281

CONCLUSION

Although the dicarbon *G* center has been well investigated previously, we are still missing one piece of information; that is, how the dicarbon center is destroyed by heat treatment. In the literature, four processes have been suggested to carry out the annealing of the dicarbon center, as mentioned above. However, we are missing at least two other possible reactions; i.e., the dicarbon centers capture a mobile atom forming the 7686-cm^{-1}, line and the released interstitial carbon atom complex with oxygen atoms forming the photoluminescence lines at 7661 and 7418 cm^{-1}, etc. The second reaction has explained why the decay rate of the dicarbon center is different in FZ and Cz silicon. Since the interstitial carbon atoms released are more difficult to recapture by the substitutional carbon atoms in the presence of oxygen atoms, therefore, in Cz silicon with a high concentration of oxygen atoms, the decay rate of the dicarbon center is much faster. A full picture of reactions between different defects cannot be given until the atomic structure of the reported photoluminescence lines are discovered. Future discussion of the decay mechanism of the dicarbon center should include oxygen, as well as carbon concentrations, the irradiation dose, and the anneal temperature. Finally, photoluminescence measurements are again demonstrated to be a powerful tool in investigating the decay mechanism of the dicarbon center.

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