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Excitation spectroscopy on the 0.79-eV (*C*) line defect in irradiated silicon

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We combine photoluminescence excitation measurements and conventional luminescence spectroscopy to show that the oxygen-related deep defect in irradiated silicon which emits the 0.79-eV (*C*) no-phonon line possesses local modes of 65.5-, 72.5-, 138.1-, and 145.3-meV quantum energy. These values are close to the vibration energies of interstitial oxygen (Si-O_i-Si), substitutional carbon, or oxygen-carbon complexes as observed in ir absorption. Two groups of electronic excited states centered at photon energies around 0.80 or 0.82 eV, respectively, are also identified.

Oxygen-rich, irradiated silicon emits a very common defect spectrum with a no-phonon (NP) transition at 790 meV (often labeled the *C* line) which has been studied extensively (see, for example, Refs. 1–9). The nature of the defect is not known although various identifications with EPR-active[3,5] and ir-active[6] centers have been suggested. Previous spectroscopic work associated several additional lines with optical transitions at the same defect. Two photoluminescence (PL) lines at 717 and 724 meV were ascribed to NP transitions from the upper ground state leaving the defect in electronic excited lower states.[4,5] Recent absorption spectroscopy revealed three upper electronic excited states responsible for absorption lines at 795, 800, and 800.3 meV.[8,9]

In the present study, we apply photoluminescence excitation (PLE) spectroscopy to the 790-meV optical defect in conjunction with high-resolution, sensitive PL measurements. We show that the low-energy lines at 717 and 724 meV are actually due to local vibrational modes of the defect. In addition, we identify up to nine electronic excited states of the center.

The samples used in our investigation were cut from different, *n*- or *p*-type starting materials and were irradiated either by 2-MeV electrons or thermal neutrons. A KCL:Tl color center laser constructed as described in literature[10,11] served as the light source in the PLE experiments. It could be tuned from 1426 to 1579 nm at a linewidth of 0.5 Å and yielded typically 50-mW output power. The luminescence was dispersed with a 1-m grating monochromator (operated as a double-pass spectrometer for PLE) and detected by cooled Ge or PbS detectors.

In Fig. 1 we compare a PL spectrum obtained for band-to-band excitation with a spectrum obtained for resonant excitation into the NP 790-meV transition. Line positions and related data are listed in Table I. Since for the resonant excitation we expect to see only such lines strongly which are associated with the same defect, we conclude that all lines belong to the oxygen-related defect except for the peak at $\simeq 1.613$ μm (unlabeled in Fig. 1). Evidently, the C_1 line is not seen in the resonantly excited spectrum as it originates in an electronic excited upper state of the defect.[4,5,9] The broad sidebands mirror the phonon density of states with maxima at the TA(*X*) energy (line C_0^{TA}), the LA and TO energies (lines C_0^{LA} and C_0^{TO}).[12] The two relatively sharp lines C_0^{L1} and C_0^{L2} (*A* and *B* in the notation of Refs. 3 and 5) were previously ascribed to NP transitions leaving the center in an electronic excited state.[4,5] We, in contrast, identify them as local mode satellites of the C_0 line since we observe in PLE the corresponding anti-Stokes sidebands (labeled C_0^{-L1} and C_0^{-L2}). Two additional sidebands, C_0^{L3} and C_0^{L4}, are detected in the conventional PL spectrum (Fig. 1) recorded with the PbS cell. These sidebands can be interpreted either as combination bands involving two *L*2 modes or a *L*1 plus a *L*2 mode, respectively, or alternatively, as independent modes of about twice the quantum energy of *L*1 and *L*2.

The anti-Stokes sidebands have been detected by monitoring the laser light absorption via the intensity of the NP C_0 luminescence transition (Fig. 2). The appearance of satellites obviously associated with both NP transitions, the

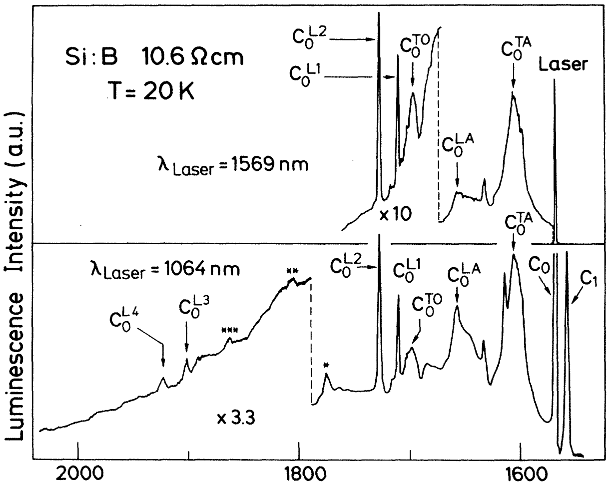

FIG. 1. Upper PL spectrum: Resonant excitation into the 790-meV C_0 line. The cutoff at $\lambda \gtrsim 1.75$ μm is due to spectral response of Ge detector. Lower PL spectrum: Nd-YAG laser band-to-band excitation; spectrum recorded with PbS cell. For notation and positions of lines, see Table I.

TABLE I. Lines observed in PLE and PL. Notation of lines: Upper labels refer to emitted (positive sign) or to absorbed (negative sign) vibrational modes; lower labels number the electronic excited states. δE is the half-width of the lines, $\Delta E/C_0$ denotes the displacement energy of the lines from the C_0 transition.

Line	λ (nm)	E (meV)	δE (meV)	$I_{\mathrm{rel.}}$[a]	$\Delta E/C_0$ (meV)
		Photoluminescence excitation data			
C_0	1569.0	790.0	0.15	100	0
C_1	1558.7	795.2	0.51	62	5.2
C_2	1548.5	800.4	0.36	15	10.4
C_3	1545.9	801.8	· · ·	5	11.8
C_4	1538.5	805.6	0.26	16	15.6
C_5	1517.4	816.8	0.27	17	26.8
C_6	1514.2	818.6	0.22	12	28.6
C_7	1513.0	819.2	0.32	13	29.2
C_8	1510.5	820.6	· · ·	3	30.6
C_9	1508.1	821.9	0.33	26	31.9
C_0^{-L1}	1452.4	853.4	$\simeq 0.9$	4	63.4
C_1^{-L1}	1443.5	858.7	$\simeq 0.9$	3	68.7
C_0^{-L2}	1441.5	859.8	$\simeq 0.3$	4	69.8
C_1^{-L2}	1433.2	864.8	$\simeq 1.0$	$\simeq 2$	74.8
		Photoluminescence data			
C_0^{TA}	1606.4	771.6	· · ·	3.7	−18.4
C_0^{LA}	1658.0	747.6	· · ·	2	−42.4
C_0^{TO}	1696.4	730.6	· · ·	1.2	−59.4
C_0^{L1}	1710.8	724.5	0.47	4	−65.5
C_0^{L2}	1727.6	717.5	0.33	8	−72.5
C_0^{L3}	1901.2	651.9	· · ·	$\simeq 0.8$	−138.1
C_0^{L4}	1922.6	644.7	· · ·	$\simeq 0.6$	−145.3
*	1774.6	698.6	· · ·	· · ·	−91.5
**	$\simeq 1804$	687.0	· · ·	· · ·	−103.0
***	1862.8	665.4	· · ·	· · ·	−124.6

[a] Intensities refer to peak heights.

ground-state–to–ground-state C_0 line and the excited-state–to–ground-state C_1 line confirms our identification of the lines C_0^{L1} and C_0^{L2} (cf. energies in Table I). In emission (Fig. 1, lower spectrum), local mode satellites of C_1 were not observed as the excited initial state of C_1 lies 5.2 meV higher than the upper ground state and is only weakly populated at 20 K. However, when the temperature was further increased we could also detect local modes associated with C_1 in the conventional PL spectrum again supporting our identification. The local modes have quantum energies of 65.5 meV ($L1$) or 72.5 meV ($L2$) in the defect ground state, and 63.4 meV ($L1$) or 69.8 meV ($L2$) in the excited defect state. The relative differences of these vibration energies in the upper and ground states are 3.1% ($L1$) or 3.9% ($L2$), and are of the same order as for the 0.97-eV (G) line defect[13] where the corresponding relative difference (of the E and E^* modes) amounts to 2.4%.

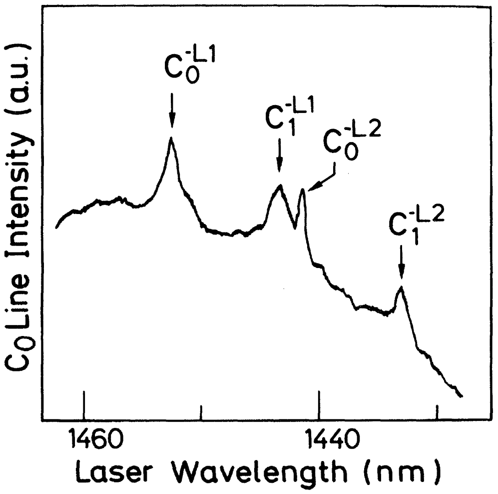

FIG. 2. PLE spectrum of anti-Stokes local mode bands associated with the C_0 and C_1 electronic transitions. The sample temperature was held at 20 K.

In a further PLE experiment we monitored the absorption of laser light by the luminescence emitted into the broad C_0^{TA} phonon sideband of the C_0 line at $\simeq 1606\ \mu$m. We observed the principal C_0 line and nine lines C_1 through C_9 (Fig. 3) which we ascribe to no-phonon transitions from upper excited states to the defect ground state based on their relative small half-widths and large intensities. Their spectral positions and their relative intensities were the same in all samples investigated. Resonant excitation into one of the lines exclusively enhances the C-line luminescence spectrum but no other defect luminescence observed in some of the samples. This gives evidence that the nine lines are really related to the 790-meV optical defect. The nature of the broad background band in Fig. 3 is not clear. The lines C_1 through C_3 are not principally new and their previous observation supports our interpretation of all C lines in terms of electronic excited states: The line C_1 (labeled D in Refs. 3 and 5 or a in Ref. 4) was observed in PL

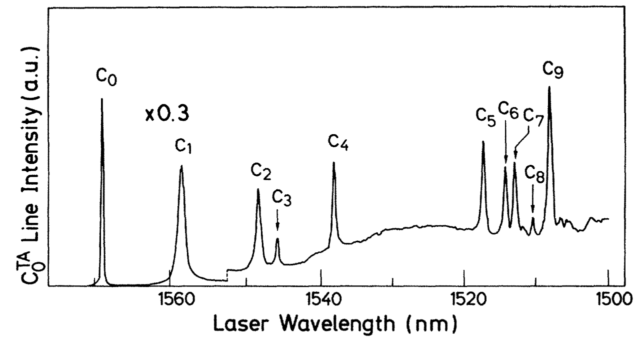

FIG. 3. PLE spectrum of phononless transitions from excited defect states to the ground state. The sample temperature was held at 20 K.

to thermalize with the ground-state–to–ground-state C_0 transition, and C_2 and C_3 were recently detected in absorption along with the C_1 line.[8,9] The absorption intensities of C_1 through C_3 are virtually the same as our PLE intensities. It is interesting that the excited states as reflected in the PLE spectrum in Fig. 3 seem to be arranged in two groups around 0.80 eV ($C_0, \ldots, C_4$) and 0.82 eV ($C_5, \ldots, C_9$) and that the overall spacing in the higher-energy group is about one-third of that in the lower-energy group. As too little is known about the nature of the defect we can no further interpret these excited states.

We return to the four sidebands C_0^{L1} through C_0^{L4} and their vibronic nature which we have now established. When all of them are identified with independent fundamental defect vibrations, their quantum energies are 65.5, 72.5, 138.1, and 145.3 meV. It is remarkable that these values are in the two energy ranges which roughly correspond to wavelengths around 18 and 9 μm and which are characteristic of vibrational absorption bands of interstitial oxygen (Si-O_i-Si), of substitutional carbon, and of carbon-oxyben complexes. To be more specific, one may refer to the absorption lines[14] at 64.1 meV (alternatively 517 cm^{-1}, 19.3 μm) and 140.8 meV (alternatively 1136 cm^{-1}, 8.8 μm) of the Si-O_i-Si defect and the fundamental vibrational mode at 75.3 meV (alternatively 607.5 cm^{-1}) of substitutional ^{12}C. Other vibrational modes at 72.7 meV (alternatively 586.2 cm^{-1}) (for ^{12}C), the so-called *X* line, and at 137 meV (alternatively 1103.9 cm^{-1}) have been ascribed to C-O complexes and a local mode at 138.3 meV (alternatively 1115.5 cm^{-1}) (for ^{12}C) to the $C(3)$ center, possibly a C_i-C_i complex.[14] We recall that the present optical defect is conclusively related to oxygen[1–8] but that Kirkpatrick, Myers, and Streetman[7] have also stated that the *C* line spectrum is stronger in samples doped with oxygen and carbon than in samples doped with oxygen alone. This is an important hint to the incorporation of O *and* C in the optical defect implying that these impurities could be mainly responsible for the vibronic sidebands observed in PL and PLE consistent with the energy range of the ir vibrational absorption lines.

Our identification of the local mode sidebands opens the possibility of looking for oxygen and carbon isotope shifts of these bands (isotope effects have partially been observed in the above mentioned vibrational absorption bands) and thus obtaining detailed information about the structure of the optical defect. Such work is in progress.

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