RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 31, NUMBER 8 15 APRIL 1985

Donorlike excited states of the thermally induced 0.767-eV (*P* line) defect in oxygen-rich silicon

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(Received 29 November 1984)

Photoluminescence-excitation spectroscopy with a KCl:Tl color-center laser is performed on the thermally induced defect in oxygen-rich silicon which emits the 0.767-eV (*P*) no-phonon line. We find two sets of excited states. One set 20–30 meV above the *P* transition is identified with effective-mass-like electron states of a pseudodonor. The ionization energy of the pseudodonor electron is 34.3 meV and the binding energy of the strongly localized hole amounts to 368.2 meV. The other set $\simeq 65$ meV above the *P* transition is due to anti-Stokes local modes of the excited defect, and one further line possibly originates from an excited state of the deeply bound hole.

Oxygen-rich pulled silicon that is heated to $\approx 450\,^{\circ}\mathrm{C}$ for several hours exhibits a prominent photoluminescence (PL) spectrum with a narrow no-phonon (NP) line at 0.7672 eV, generally labeled *P* line.[1,2] This spectrum is obviously associated with oxygen and has attracted much interest during the past years as the formation kinetics of the optical defect reveals features similar to the 450 °C thermal oxygen donors.[3–5] Recent PL measurements, however, have cast doubts on a simple relationship between the thermal donors and the *P*-line defect. These doubts are based, e.g., on different defect symmetries (the *P*-line defect has monoclinic I, C_{1h}, symmetry) and on different charge states of the defects (the *P* line is a singlet-to-singlet transition that does not split in a magnetic field up to 5.3 T).[5] Moreover, an asymmetric line broadening possibly indicating an unresolved splitting has been observed in ^{13}C-enriched silicon and has tentatively been ascribed to a carbon isotope effect, demonstrating the possible involvement of carbon in the optical defect as well.[6] Four low-lying excited states, *a*–*d*, at excess energies of ≤ 12.7 meV with respect to the upper *P*-line state, have been observed in temperature-controlled PL experiments,[5] but their generic character could not be explained.

In the present Communication, we report photoluminescence-excitation (PLE) measurements on the *P*-line center. We find two sets of excited states 20–30 and $\simeq 65$ meV above the *P* line. One of them can be ascribed to effective-mass-like states of a pseudodonor with 34.3-meV ionization energy. The other set contains two lines that we identify with anti-Stokes local modes of the excited defect. They correspond to two low-energy satellites of the *P* transition, which we observe in photoluminescence and identify with Stokes local modes.

The samples used in this study were floating zone or Czochralski-grown silicon samples obtained from various sources. Oxygen concentrations ranged from 10^{16} to 10^{18} cm^{-3} and carbon concentrations from below 10^{15} to $\approx 5\times 10^{16}$ cm^{-3}. A KCl:Tl color-center laser[7,8] tunable from 1.426 to 1.583 μm at a linewidth of 0.5 Å was the exciting light source in the PLE experiments. Output powers of typicaliy 100 mW were obtained, and a flat tuning curve over the broad tuning range was achieved by employing an output coupler of only 6% transparency. Conventional PL spectra were excited by the 647-nm line of a Kr ion laser and dispersed by a 1-m grating monochromator operated as a double-pass spectrometer for PLE. The signals were detected by a cooled Ge detector (PLE) or PbS detector (PL).

Figure 1 shows the PL and PLE spectra of the *P*-line defect. Line positions, half-widths, and related data are listed in Table I. The low-energy PL satellites 3, 5, and 6 (notation continued after Ref. 2) are due to the coupling of lattice phonons to the electronic *P* transition and reflect the maxima of the phonon density of states of the TA(*X*), LA, and TO phonon frequencies, respectively.[2] The lines 7 and 8 have also been reported earlier by Weber and Sauer;[2] it was not clear, however, whether they belong to the *P*-line spectrum or are independent features. In our present PL measurements, we examined the intensity ratios of line 7 to *P* and of line 8 to *P* in eight samples with largely varying carbon and oxygen concentrations. The two intensity ratios were found to be constant within 5% accuracy in all samples. The absolute value of the ratio 7 : *P* is 1 : 30 at 25 K. Considering also the small linewidth of *P* and the much larger widths of 7 and 8 (Table I), we identify these low-energy lines as being due to Stokes local modes of the optical defect with vibration quantum energies of 65.6 and 72.0 meV.

It is noteworthy that the local mode energies and the relative coupling strengths are very close to the local modes *L*1 (65.5 meV) and *L*2 (72.5 meV) of the 0.79 eV (*C* line) defect formed in irradiated and partially annealed silicon.[9] Moreover, the absolute energetic positions of the two different spectra are very similar, the *P* line occurring at 0.767 eV and the *C* line at 0.790 eV. Further similarities refer to the sensitivity of the *P* line to oxygen and the possible involvement of carbon: In fact, the *C*-line spectrum exhibits a carbon isotope splitting of the NP line and oxygen isotope shifts in the *L*1 and *L*2 local modes, directly demonstrating that oxygen and one carbon atom per optical center are in-

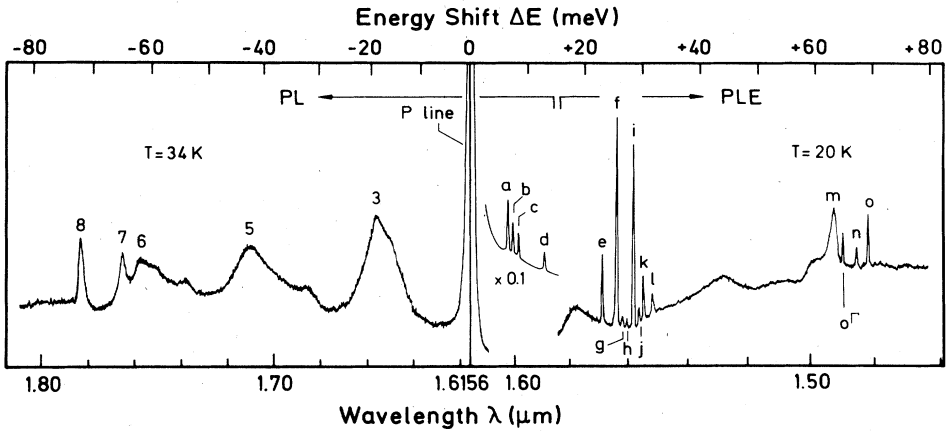

FIG. 1. Photoluminescence (PL) and photoluminescence excitation (PLE) spectrum of the 0.767-eV (P line) defect. The vibrational sidebands and local-mode replicas observed in emission are labeled 3, 5, 6, or 7, 8, respectively. The excited states are labeled a through o. O^{Γ} denotes the 64.7-meV Raman phonon line in silicon. (Note that the wavelength and energy scales are different for the left and right part of the figure.) The experimental resolution for the PL spectrum is 40 Å and for the PLE spectrum 0.5 Å.

volved.[6,10,11] Finally, the present 0.767-eV defect has monoclinic I (C_{1h}) symmetry[5] like the 0.790-eV defect.[12] All these features tend to suggest that the two optical defects may be highly similar in structure. Following this suspicion, one may expect weak extra-line components in satellites 7 and 8 due to oxygen- or silicon-isotope effects, as is the case with the 0.790-eV defect. We have looked for such extra structure in ^{18}O-enriched silicon without success, possibly since the absolute luminescence intensities are too weak and existing extra structure is obscured by the noise. Such work is being continued.

On the high-energy side of the P line, Fig. 1 shows the

TABLE I. Lines observed in PL and PLE. δE is the half-width of the lines; $\Delta E/P$ denotes the displacement energy of the lines from the P transition.

Line	λ (nm)	E (meV)	δE (meV)	$\Delta E/P$ (meV)	Interpretation
			Photoluminescence data		
8	1783.0	695.4	0.5	−72.0	Local mode
7	1766.6	701.6	0.8	−65.6	Local mode
6	1757	705	(Broad)	−62.2	TO sideband
5	1711	724	(Broad)	−43.2	LA sideband
3	1654	749	(Broad)	−18.2	TA sideband
P line	1615.6	767.2	0.17	0	
a	1602.0	773.7	Resolution limited	6.5	1s
b	1600.6	774.4	Resolution limited	7.2	
c	1598.3	775.5	Resolution limited	8.3	
d	1589.3	779.9	Resolution limited	12.7	
			Photoluminescence excitation data		
e	1568.7	790.1	0.17	22.9	2p_0
f	1564.0	792.5	0.17	25.3	2s
g	1562.3	793.4	≈0.4	26.2	
h	1560.8	794.1	≈0.15	26.9	
i	1558.3	795.4	0.18	28.2	2$p\pm$
j	1556.6	796.3	≈0.2	29.1	3p_0
k	1555.5	796.8	0.17	29.6	3s
l	1552.0	798.6	≈0.3	31.4	4s
m	1493.0	830.2	1.3	63.0	Local mode
n	1485.5	834.4	≈0.5	67.2	Excited hole state
o	1482.4	836.1	0.4	68.9	Local mode

components $a, \ldots, d$, which were recently observed in PL at elevated temperatures.[5] The spectrum is continued by the first PLE set of lines between $\simeq 20$ and $\simeq 30$ meV ($e, \ldots, l$) and the second set at approximately 65 meV (m,n,o). All PLE resonances are associated with the P-line defect, as we conclude from sample statistics and from PL spectra recorded with selective excitation into one of these excited states: Such spectra exclusively show the P line and its phonon sidebands.[13] The two broad PLE features at ≈ 18- and 43-meV displacement energy from the P line along with the shoulder on the low-energy side of line m at ≈ 60 meV are explained as anti-Stokes replicas of the P transition involving TA, LA, and TO lattice phonons. These PLE bands correspond to the Stokes replicas 3, 5, and 6 seen in emission.

The series of resonances $e, \ldots, l$ is shown in greater detail in Fig. 2. The spectral resolution in this PLE spectrum is determined by the linewidth (0.5 Å) of the exciting laser. Indicated is our interpretation of the excited defect states (which are reflected in the PLE spectrum) in terms of an effective-mass (EMT)-like pseudodonor.[14] Our slightly modified model assumes that the monoclinic defect strongly binds a hole by a short-range potential whose orbital momentum is quenched by the local strain field of the defect. The resulting spin-$\frac{1}{2}$-like hole represents the ionized pseudodonor that binds an electron in its long-range Coulomb potential. Spin pairing of these two localized particles leads to diamagnetic upper P-line states.

In Fig. 3 we compare the P-line states quantitatively with theoretical EMT[15] energies and experimental s- and p-like states of the Li donor,[16] and include in our interpretation the low-energy excited states $a, \ldots, d$ observed in photoluminescence. The entire experimental spectrum is shifted such that the line l coincides with the $4s$ EMT level. This arrangement yields good agreement with all p-like levels and with the $3s$ EMT level. In our model the higher s-like electron states have extended wave functions with a small probability density at the defect site, and all p-wave functions have nodes at the defect site. Therefore, these states remain virtually unchanged when the spherical symmetry of the effective-mass potential is reduced to monoclinic symmetry. This is different for the $2s$ state and, particularly, for the $1s$ ground state. In this case, we start from the A_1, E, and $T_1(=\Gamma_5)$ symmetric states arising from the s-like EMT envelope when the multivalley nature of the conduction electrons is taken into account: The sixfold degenerate superposition of valley functions is reduced in the true T_d symmetric potential of the isolated donor.[18] In the monoclinic potential of the P-line defect, the E state reduces further as $E \rightarrow A_1 + A_2$; the T_1 state reduces as $T_1 \rightarrow 2A_1 + A_2$ yielding six A_1 or A_2 states in total which are nondegenerate by symmetry. We associate the experimental states P, $a, \ldots, d$ with five of them in the $1s$ ground state manifold with the size of the splittings (12.7 meV) given by the quantitative strength of the monoclinic binding potential. Likewise, the lines f, g, and h are associated with $2s$-like levels with an overall splitting (1.6 meV), which is largely reduced in comparison with the $1s$ manifold as a consequence of the more extended EMT-$2s$ wave functions. Symmetry considerations show that PLE transitions from the defect ground state to all excited states can be caused by the dipole operator in monoclinic symmetry. (Selection rules are also the reason why we show in the comparison in Fig. 3 results from bound exciton spectra of the Li donor: This represents the only case where s- and p-like states can be observed[16] because of the *inverted* ground-state ordering of the donor electron.[17]) The larger half-width of line g

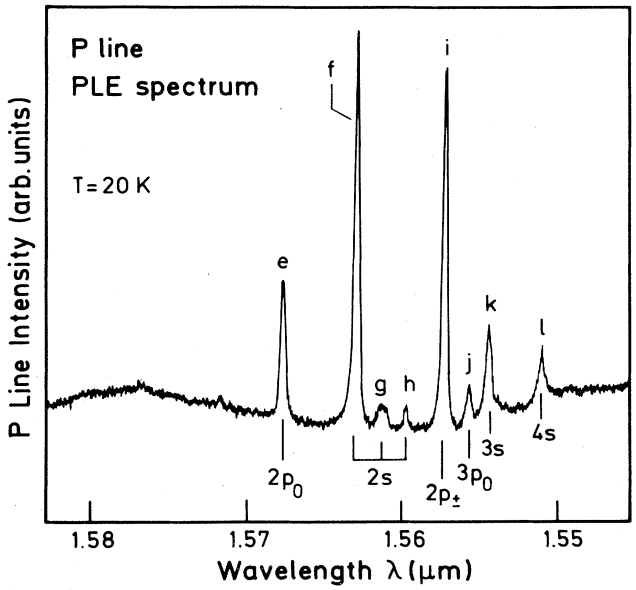

FIG. 2. PLE spectrum of the 0.767-eV defect showing the resonances $e, \ldots, l$ and our assignment in terms of effective-mass-like donor states.

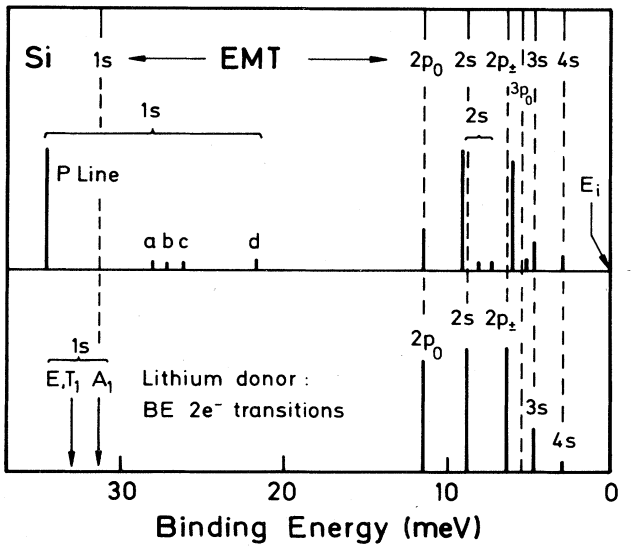

FIG. 3. Comparison of s- and p-like donor states with the excited 0.767-eV defect states. Top: theoretical effective-mass states of substitutional isolated donors in silicon after Faulkner (Ref. 15). Bottom: experimental s- and p-like states of the T_d interstitial Li donor from bound exciton (BE) two-electron transitions after Sauer (Ref. 16), $1s(E,T_1,A_1)$ ground-state structure after Aggarwal *et al.* (Ref. 17). The P-line spectrum has been shifted in such a way that line l coincides with the $4s$ EMT level. Experimental line intensities are indicated by the heights of the bars. The intensity of the $1s$ transitions is not to scale with the $2p_0, \ldots, 4s$ lines.

(Fig. 2) may be due to two or three unresolved line components, and a correspondence $P \leftrightarrow f$, $(a,b,c) \leftrightarrow g$, and $d \leftrightarrow h$ between the $1s$ and $2s$ substates is fully consistent with our model. Contrary to the pseudodonor model, a pseudo-acceptor model is not able to fit the experimental levels in a satisfactory way.

Our interpretation implies that the electron-binding energy is $E_e = 34.3$ meV, and from the total displacement (402.5 meV) of the P line from the band edge, the hole binding energy is $E_h = 368.2$ meV. The ratio $E_h : E_e \approx 10:1$ corresponds to a "classical" isoelectronic defect that binds the first particle much stronger than the second particle, which is localized in the Coulomb potential. As the electron and hole-binding energies are very different, the electron can be thermally released with ≈ 35-meV activation energy. Actually, Weber and Sauer[2] determined a thermal dissociation energy of ≈ 45 meV of the P line, which is consistent with the value of E_e, considering the accuracy limits of that particular temperature-controlled PL experiment.

Finally, we discuss the residual resonances *m*, *n*, and *o* in the PLE spectrum (Fig. 1). Line *o* reveals a displacement (68.9 meV) from the P transition which is similar to the PL local mode satellite 8 (72.0 meV) and has also comparably large linewidth (Table I). This suggests that it is an anti-Stokes local mode sideband of the P line corresponding to the Stokes line 8. Analogous arguments apply to line *m* in a comparison with the PL local mode satellite 7; particular attention has to be paid here to the half-widths: The *m* mode (quantum energy 63.0 meV) is energetically degenerate with lattice phonons (the O^{Γ} phonon energy is 64.7 meV), and damping of the local mode therefore broadens the line. On the other hand, its photoluminescence counterpart, satellite 7 (65.6-meV quantum energy), is outside the lattice mode regime, and therefore appears denotedly narrower than line *m*. The relative differences of the defect vibration energies in the electronic ground state and the upper radiative state are 4% (satellites 7,*m*) or 4.3% (satellites 8,*o*). These values are of comparable order to the 0.79-eV (C line) defect where the corresponding relative differences amount to 3.1% ($L1$ modes) or 3.9% ($L2$ modes),[9] and to the 0.97-eV (G line) defect where a relative difference of 2.4% (E,E^* modes) is found.[19] No corresponding local mode satellite exists in emission for the PLE resonance *n*. This line could be due either to a local mode that couples only to the excited state of the defect or to an (electronic) excited state of the tightly bound hole.

We thank G. D. Watkins (Lehigh University, Bethlehem, Pennsylvania) for many discussions and H. Hirt, M. Siemers, and P. Wurster for their technical assistance. We are grateful to B. Pajot (University of Paris) for communicating his recent absorption results prior to publication. The financial support of the Deutsche Forschungsgemeinschaft under Contract No. Sa 311/2 is gratefully acknowledged.

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