Thermal-Donor–Related Isoelectronic Center in Silicon Which Can Bind up to Four Excitons

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A group of photoluminescence lines recently observed in thermally treated Si was studied in detail by transient spectroscopy, excitation spectroscopy, and temperature– and excitation-density–dependent measurements. An earlier interpretation in terms of free-to-bound transitions cannot explain these results. Instead, the lines are found to be due to an inhomogeneously broadened distribution of isoelectronic centers which can bind from one to four excitons.

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The wide range of complex defects produced by extended heat treatments of oxygen-rich Czochralski-grown Si have been the subject of extensive studies over the past thirty years. A major impetus to these studies has been the need to understand the properties of the electrically active "thermal donor" (TD) complexes, which can have deleterious effects on device performance.[1,2] Considerable progress has been made in the understanding of the TD, but much uncertainty remains as to their microscopic nature.

In this Letter we report the results of photoluminescence (PL) and photoluminescence-excitation (PLE) spectroscopy on a recently reported[3] set of lines which is produced in high-O_i, low-C Si after extended heat treatments at 450 °C–500 °C. Our results cannot be reconciled with the proposed[3] model explaining these lines in terms of the recombination of free holes with several neutral TD. Instead, we find that the main line is an inhomogeneously broadened isoelectronic-bound-exciton (IBE) transition. This binding center is unique in that it can bind up to four electron-hole (e-h) pairs, thus explaining the multiplicity of the lines. The only other isoelectronic center capable of binding more than one e-h pair is N_p in GaP, which binds at most two.[4] Our model predicts a long lifetime for the IBE line, but very shoft lifetimes for the bound-multiexciton-complex (BMEC)[5] lines, due to Auger processes. We have verified that these otherwise very similar lines do have vastly different lifetimes, ranging from 85 μs for the IBE to 8 ns for the four-exciton BMEC. We have also resolved a ground-state splitting of the IBE line which leads to a strong dependence of IBE lifetime on temperature, an effect already well known for other IBE systems.[6]

After heat treatment and etching in CP4, PL was measured with samples immersed in liquid He at 1.6–4.2 K, with 514.5-nm excitation. The PL was dispersed by a $\frac{3}{4}$-m double spectrometer and detected with a Varian model VPM159A3 photomultiplier tube operated in the photon-counting mode. PLE spectra were recorded with a pulsed, tunable, dye-laser–pumped optical parametric oscillator as an excitation source. For some of the PLE spectra, a 2-kHz mechanical chopper synchronized with the optical parametric oscillator pulses was interposed between the sample and spectrometer so as to block the excitation pulses but pass the long-lived IBE luminescence. This enabled us to observe the PLE spectrum of the IBE ground state as well as the excited states. Transient PL measurements were obtained by use of a number of pulsed excitation sources, including the optical parametric oscillator, a GaAs laser-diode array, and a mode-locked cavity-dumped rhodamine-6 G dye laser.

In agreement with Weber and Queisser[3] (WQ), we found that the maximum intensity of the lines correlated only with high O_i and low C concentrations in the starting material, but not with the presence of group-III or -V dopants or with initial conductivity type. Also in agreement with them, we found the new luminescence lines to have a long incubation period—in one set of samples the new lines could barely be observed after 48 h at 500 °C, but reached a maximum and totally dominated the spectrum at 96 h, thereafter slowly decreasing in intensity with increasing heat treatment as other luminescence systems appeared. This behavior does *not* parallel the time-dependent TD concentration as measured by ir absorption, but instead correlates with the *decrease* of the TD concentrations after very long heat treatment.

The PL system under study here was also briefly mentioned in an earlier paper by Tajima *et al.* (Y_1–Y_3 lines.[7] Some representative PL spectra are shown in Fig. 1. We have retained the O label used by WQ,[3]

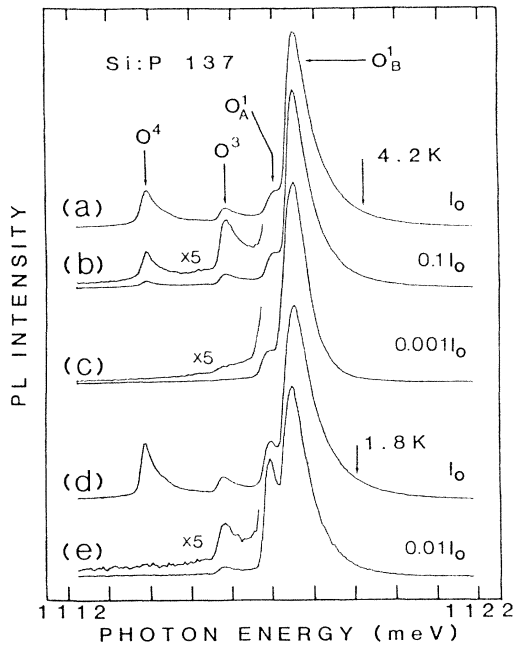

FIG. 1. (a)–(c) PL spectra at 4.2 K at three excitation levels; $I_0 \simeq 12$ W/cm^2. (d),(e) PL spectra at a bath temperature of 1.8 K at two excitation levels. O^1_A is lower in (d) than in (e) as a result of sample heating. All spectra normalized to equal O^1_B height.

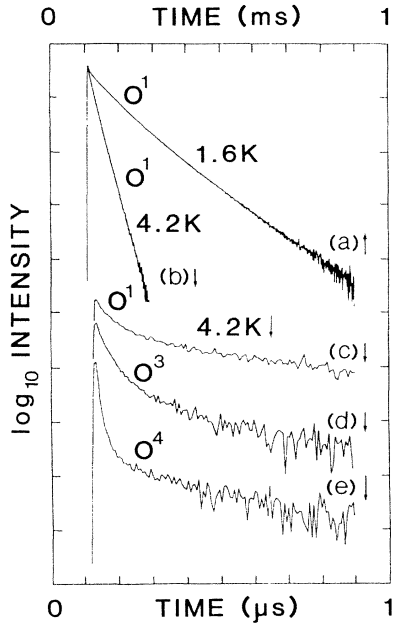

FIG. 2. PL transient decay curves. Note that the time scale used for (a) and (b) is 10^3 times longer than that used for (c)–(e). The horizontal markers are decades. (a) and (b) have been arbitrarily shifted from (c)–(e). (a),(b) Decay of the O^1 IBE line at 1.6 and 4.2 K under low excitation conditions, with decay times of 85 and 17 μs, respectively. (c)–(e) Fast transient decays measured at the peak of O^1_B, O^3, and O^4 under higher excitation conditions. (e) has been shifted down one decade for clarity. Exponential fits to the initial decay transients of (c), (d), and (e) yield lifetimes of 45, 33, and 8 ns, respectively.

since the lines are certainly associated with O, but we have changed the details of the labels to correspond to our model. Their O_1, O_2, and O_3 lines become our O^1_B, O^3, and O^4 lines, where the superscript denotes the number of electron-hole pairs in the initial state. WQ also refer to a fourth line, O_4, but it does not appear in their spectra and we have never observed it.

We have observed a new, sample-independent splitting of the O^1 line into two components labeled O^1_A and O^1_B in Fig. 1, and separated by ~ 0.45 meV. The two components are found to thermalize, indicating an initial-state splitting. The low oscillator strength of the O^1_A transition causes a strongly temperature-dependent lifetime for the O^1 line, as shown in Fig. 2. O^1_A and O^1_B have identical transient behavior at all temperatures. The lifetime of 85 μs at 1.6 K does not represent the low-temperature limit, since even at this temperature O^1_A and O^1_B are of roughly equal intensity. This splitting, and the resultant temperature dependence of the PL lifetime, are typical of IBE.[6] They would be difficult to reconcile with the model of free-to-bound transitions proposed by WQ.

The IBE interpretation is confirmed by our PLE results, some of which are shown in Fig. 3. In Fig. 3(a) the PLE spectrum is shown with the PL being detected over the entire, broadened O^1_B line. The PLE excitation spectrum of O^1_B itself is seen to have the same shape as the O^1_B PL line, but to be considerably broader. O^1_A is not observed in PLE because of its low oscillator strength. A number of excited states are also observed, labeled O^1_C–O^1_F, having the same asymmetric shape as O^1_B. This excited-state series is reminiscent of those previously observed for other IBE.[6] It appears to have an ionization limit at about 30 meV above O^1_A, which would thus be the predicted thermal quenching energy of the O^1 luminescence. This did not agree with the previously given value of 55 ± 3 meV, which supported the free-to-bound model.[3] We have consequently remeasured the intensity of O^1 versus temperature for very low, moderate, and very high excitation levels. When $\log[T^{3/2}(\times O^1 \text{ intensity})]$ was plotted versus $1/T$, straight lines of slope 30, 33, and 32 meV were obtained in the high-temperature limit. These values are in excellent agreement with the IBE thermal-dissociation energy predicted on the basis of the excited states detected in PLE spectra shown in Fig. 3, but cannot be reconciled with the free-to-bound model.

The PLE spectra also reveal that the broadening mechanism which produces the unusual O^1 lineshape

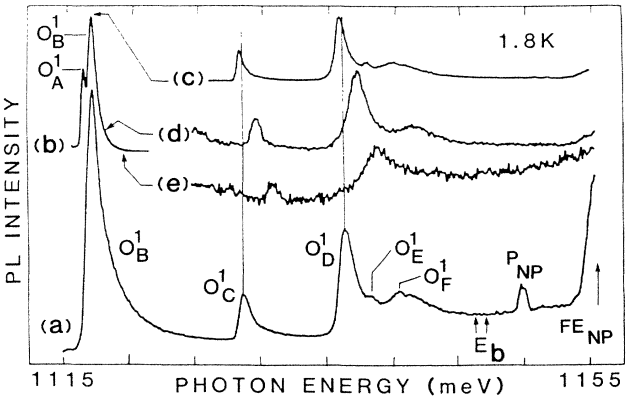

FIG. 3. (a) PLE spectrum of all O^1 states, including the O^1 ground state, with the PL signal detected from the entire, broadened O_B^1 line. A mechanical chopper synchronized to the laser pulses prevented the direct detection of scattered excitation photons, but passed most of the long-lived luminescence signal. A number of excited states with the same asymmetric shape as the PL lines are observed. A signal is also observed due to excitation transfer from the P BE line in the sample, which contains 5×10^{15} cm^{-3} P. FE_{NP} marks the beginning of no-phonon free-exciton absorption. The arrows labeled E_b indicate the range of thermally determined binding energies for O^1, which are in good agreement with the apparent ionization limit of the excited-state spectrum. (c)–(e) Three PLE spectra taken with PL pickup in narrow bands centered (c) at the peak of O_B^1, (d) 1.3 meV above the peak, and (e) 2.5 meV above the peak, as indicated on the PL spectrum (b). The PLE lines shift upwards in energy from (c) to (e), the signature of an inhomogeneously broadened distribution. The P_{NP} line is not observed in this undoped sample.

has nothing to do with the kinetic energy of a free particle. As shown in Figs. 3(c)–3(e), the PLE spectra change considerably when the PL signal is collected from different positions on the O^1 line. The results show that the broadening results from an inhomogeneous distribution of binding centers having very similar shifts of ground-state and excited binding energies. It is also clear that IBE created in the higher-energy tail of the distribution have a considerable probability of tunneling to lower energy before recombining. This explains the extra width of O_B^1 in PLE as compared to PL. The inhomogeneously broadened distribution could result either from random strains or from a distribution of very similar centers having slightly different total IBE binding energies. Since PL from other bound excitons (BE) in these samples, such as the P donor BE, is not broadened, the latter possibility seems most likely.

We will now consider the origin of the lines labeled O^4 and O^3 in Fig. 1 (O_3 and O_2 of Ref. 3). It was previously argued that since the relative intensities of O^1, O^3, and O^4 were somewhat sample dependent, they must originate from different centers.[3] We instead find that the modest sample dependence of the relative intensities is exactly what one expects for a BE-BMEC system associated with a single center.[5] In *all* samples one can observe $O^1 > O^4 > O^3$ at high excitation levels, $O^1 > O^3 > O^4$ at intermediate levels, followed by the disappearance of first O^4 and then O^3 at lower excitation.

This behavior, which is outlined in Fig. 1, is consistent with O^1 being a BE transition, while O^3 and O^4 are BMEC transitions, with O^4 having more bound e-h pairs than O^3.[5] The BMEC explanation of O^3 and O^4 is also supported by the fact that these lines, unlike O^1, cannot be created by resonant, sub-band-gap excitation.

Further support is provided by measurements of the PL lifetimes of O^3 and O^4. Typical decay curves are shown in Figs. 2(d) and 2(e)—note that the time scale is 10^3 times shorter than that used to display the O^1 PL decay in Figs. 2(a) and 2(b). These results were carefully checked for background effects by recording of complete spectra at various times after excitation. The O^3 and O^4 PL lifetimes, as determined by fitting of an exponential to the initial part of the decay curves, were 33 ns for O^3 and 8 ns for O^4. Longer decay times were observed at high excitation levels. This and the slower, weaker tails on both the O^3 and O^4 decays are evidence for the saturation of free-exciton (FE) decay channels and the generation of new FE during the decay process itself, from the Auger dissociation of BMEC.

The surprising observation that O^3 and O^4 had lifetimes up to 10^4 times shorter than O^1, even though all the lines are clearly related, is readily explained in our BE-BMEC model. The BE (O^1) initial state contains only one electron and one hole, and hence has the long lifetime typical of an IBE. The BMEC, on the other hand, have more than one bound e-h pair, and can decay by the nonradiative Auger process, which will be very rapid for these relatively tightly bound excitonic systems.

Although there is no direct evidence that O^3 and O^4 are transitions of BMEC's containing specifically three and four excitons, this seems the most likely scheme. Both the excitation intensity dependences outlined in Fig. 1, and the lifetimes shown in Fig. 2, are consistent with O^4 having more bound e-h pairs in its initial state than O^3. Detailed measurements of line intensity versus excitation density showed O^1 to vary as the 0.9 power of the excitation in the low-excitation limit, typical of a BE, while O^3 and O^4 varied as the 1.04 and 1.65 power of the excitation density, typical of BMEC. The relative intensities of BMEC lines, and their binding energies, are very dependent on the filling of electron or hole shells, as described in Kirczenow's shell model.[8] Since at least three lines are observed, it is

clear that the fourfold-degenerate valence-band edge has not been significantly split by any strain field associated with the defect.

PL transient measurements provide an answer as to the location of the missing fourth line. At low excitation levels, or with resonant excitation, the O_B^1 line decays with its many-microseconds-long time constant right from $t=0$. However, at higher levels an initial rapid decay process, with a typical lifetime of ~ 45 ns, is observed to be superimposed over the much slower O^1 decay. It thus appears that a third BMEC line occurs at almost the same energy as O_B^1. Since the lifetime of this line is greater than that of O^3 and O^4, while its binding energy is less, it seems most probable that the hidden line is O^2, the two-exciton BMEC transition.

We will now consider the possible origin of this unique isoelectronic binding center. The requirement of high O_i and low C concentrations in the starting material, along with heat treatment at 450 °C–500 °C, are identical to those needed for TD generation. On the other hand, the very long incubation period needed to produce this system shows that it does not grow in parallel with the TD population, but rather grows as the TD population *decreases* at long treatment times. We therefore propose that the new isoelectronic binding centers are the remnant cores of the TD after these lose their electrical activity through some reaction, the details of which are at present unknown. The inhomogeneous linewidth may result from the unresolved superposition of many similar centers having slightly different binding energies, similar to the TD themselves.[2]

These results demonstrate conclusively that the new PL lines are associated with a BE-BMEC system localized on a broadened distribution of a single binding center. The agreement[3] of the PL line energies with those predicted for free-to-bound transitions involving three known TD species must be regarded as a coincidence. Stress- and Zeeman-splitting studies on the ground and excited states of the IBE would be most useful, with resonant excitation being used to eliminate the inhomogeneous broadening. The nature of the binding mechanism which produces this unique isoelectronic BE-BMEC system also needs further study. Since the binding energies of all of the species are almost identical, a rather extended isotropic "strain well" seems a more likely possibility than the usual short-range central-cell binding mechanism.

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