

Direct Observation of Intercenter Charge Transfer in Dominant Nonradiative Recombination Channels in Silicon

W. M. Chen, B. Monemar, and E. Janzén

Department of Physics and Measurement Technology, Linköping University, S-581 83 Linköping, Sweden

J. L. Lindström

Swedish Defense Research Establishment, Box 1165, S-581 11 Linköping, Sweden

(Received 7 May 1991)

We present direct observations on the alternating roles of a defect level in trapping and recombination processes of nonequilibrium charge carriers in silicon, by combined photoluminescence and magnetic-resonance techniques, where the microscopic signature of the defect can be monitored unambiguously. Intercenter charge-transfer processes are shown to be efficient and important in the trapping and recombination processes of the carriers, beyond the framework of the established Shockley-Read-Hall model.

PACS numbers: 72.20.Jv, 71.55.Hi

Trapping and recombination (denoted below as TR) of nonequilibrium charge carriers at defect levels are among the most important processes in semiconductor physics and technology. These processes have been widely described in the past decades by the Shockley-Read-Hall (SRH) model [1], where electrons and holes can be successively captured by a single defect level in the forbidden energy gap and recombine. Within this model, various physical mechanisms responsible for the carrier capture and recombination via the defect level have been discussed, including Auger [2], optical [3], multiphonon [4], and cascade [5] processes.

One of the limitations in the treatment by these existing models is obviously that they only describe recombination processes involving *independent* defect centers. The only link which has been considered so far between the centers is indirect, i.e., the excess carriers thermally emitted from one center to the bands can be subsequently captured by other centers [1], as shown in Fig. 1(a). The role of *direct intercenter* interactions in carrier TR as shown in Fig. 1(b) has been largely ignored, due to a lack of experimental evidence. Distant donor-acceptor pair

recombination is generally believed to be inefficient in silicon [6].

In this Letter, we shall present a direct observation of the alternating roles of a defect level in TR processes of nonequilibrium charge carriers in silicon by a novel approach of combined photoluminescence (PL) and magnetic-resonance techniques. Efficient intercenter charge transfer is observed and shown to represent an important shunt for the carrier recombination beyond the SRH model. In this way the total recombination rate can be enhanced, since efficient electron capture of one center can be combined with efficient hole capture of another center. Typical examples are given by the shallow phosphorus substitutional donors [with a (0/+) energy level at $E_c - 0.045$ eV [7]] and the deep-vacancy-oxygen (V-O) complex [with a (-/0) energy level at $E_c - 0.17$ eV [8]]. Both of them are among the most common defects in silicon. Data about the samples used in this work are given in Table I.

The methods we employed in this work are electron spin resonance (ESR) and optically detected magnetic resonance (ODMR). The advantage of such an approach is that a direct correlation to a defect center is unambiguous, since the microscopic signature of the defect is monitored directly in both cases. If a defect level acts as an efficient carrier trap, i.e., the lifetime of the carriers trapped at the defect is sufficiently long at low temperature, an appreciable steady-state carrier occupation on

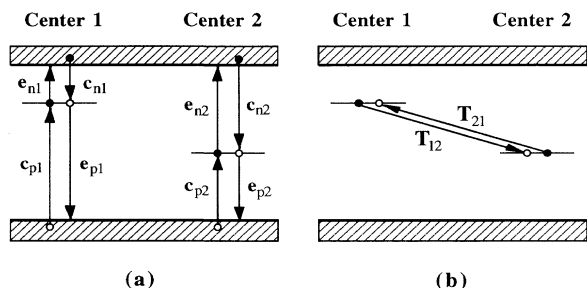


FIG. 1. (a) Schematic picture for the trapping and recombination processes of nonequilibrium carriers at independent defects, considered in the SRH model. (b) The intercenter charge-transfer process considered in this work, in addition to the processes shown in (a).

TABLE I. Properties of the *n*-type Czochralski-grown Si samples studied in this work.

Sample	Shallow P dopant (10^{16} cm^{-3})	Dose of e^- irradiation (10^{17} cm^{-2})	Annealing
1	~ 0.5	~ 4	250°C/20 min
2	~ 8	~ 4	
3	~ 8	~ 8	

this level can be established during excitation or injection. The ESR technique is then highly appropriate [9]. If a defect level on the other hand acts as an efficient recombination channel for the charged carriers, i.e., the carriers trapped at the defect are short lived, the opposite situation is relevant. The ODMR technique is then highly appropriate, since any spin-resonant transitions between the magnetic sublevels of the defect may result in an enhanced (nonradiative) carrier recombination via the defect level, and consequently to some extent quench the PL emissions from other defects, which is detected as a negative signal in the ODMR [10,11]. The technique is thus only sensitive to dominant recombination channels.

In Fig. 2(a) we show energy-level schemes of the P donor and the V-O complex, for the three samples taken as examples in this work. In Figs. 2(b) and 2(c) photo-ESR and ODMR spectra are shown, respectively, for each sample.

In the ODMR spectrum from sample 1 shown in Fig. 2(c), besides the central doublet ODMR lines which will be discussed below as arising from the P donors, another set of ODMR lines appear to be strong. They originate from the spin-triplet excited state of the V-O center in its neutral charge state [12]. The corresponding photo-ESR signal is very weak. This strong negative ODMR signal shows that the neutral excited state of the V-O complex

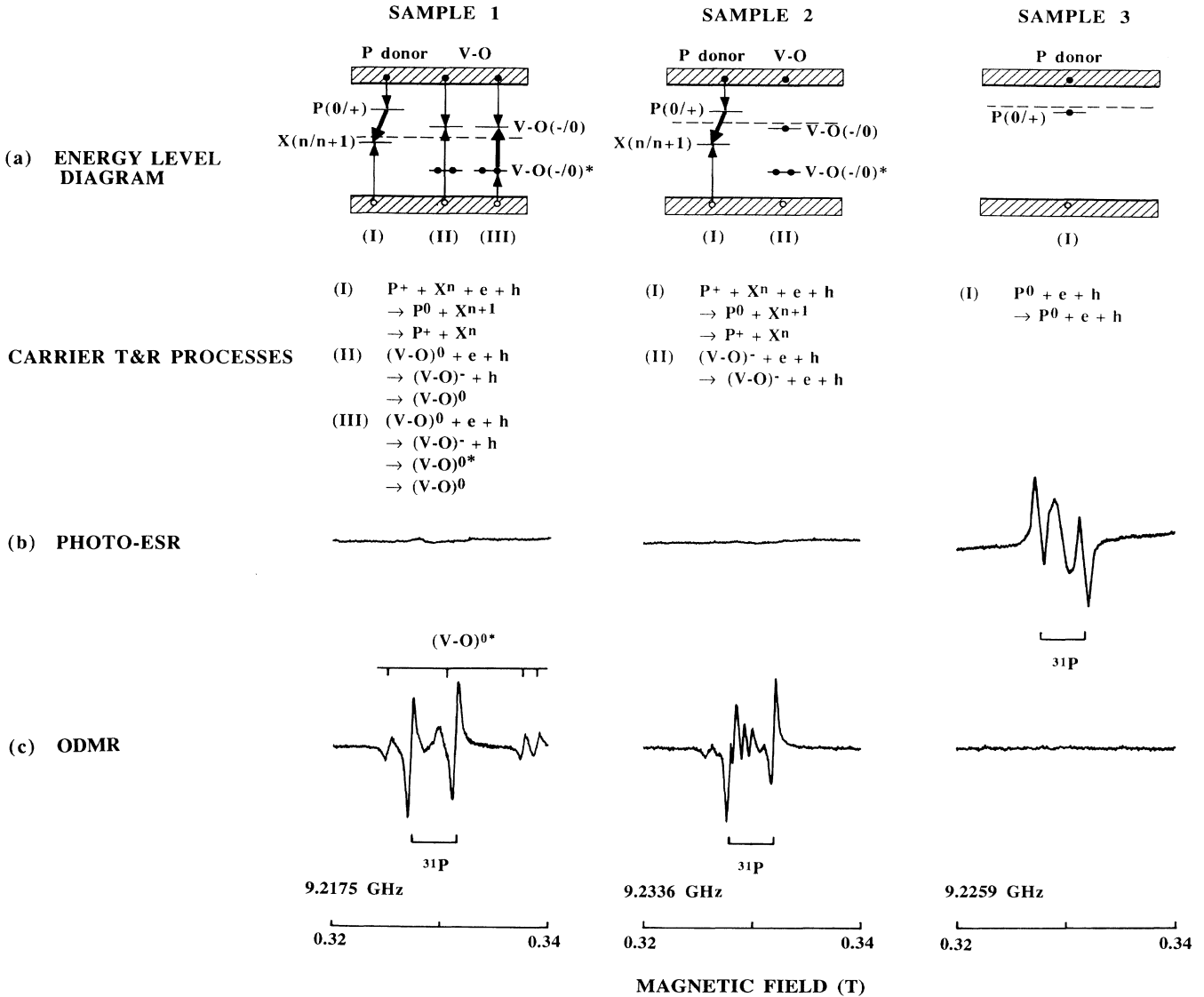


FIG. 2. (a) Schematic picture for the energy-level diagrams and the TR processes of nonequilibrium charge carriers, where the dashed lines represent the quasi Fermi level. The thicker full lines mark the spin-dependent processes detected in the ODMR. (b) The photo-ESR spectra at 10 K with a calibrated scale. (c) The ODMR spectra at 10 K. Additional lines around the P doublet in the photo-ESR spectrum from sample 3 and in the ODMR spectrum from sample 2 arise from other centers, not discussed in this paper.

serves effectively as a recombination channel for the photoexcited charge carriers. The recombination processes involved can be explained with the aid of Fig. 2(a). First the excess conduction electron is captured by the neutral $V-O$ complex, either directly via its own (-0) level or indirectly via the $(0/+)$ level of the P donors followed by the charge transfer to the $V-O$ complex, as will be discussed below in detail. Then the photocreated hole is successively captured, either via the (-0) level directly leading to the neutral ground state or via the $(-0)^*$ level leading to the neutral spin-triplet excited state of the $V-O$ center.

In sample 2, having a higher P concentration but similar $V-O$ concentration, very little of the spin-triplet ODMR signal from the $V-O$ center can be seen. The $V-O$ (-0) level is thus no longer part of an important recombination channel but behaves now mainly like an electron trap, which is supported by the experimental observation of a weak photo-ESR signal related to the negative ground state of the $V-O$ complex [13] if one increases the ESR detection sensitivity by at least one order.

We have shown above that the deep-level defects such as the $V-O$ complex can act alternatively either as a carrier trap or as a carrier recombination center. This has been observed before by other techniques [14]. We shall show that the same situation occurs for a shallow-level defect such as the P donor, which is in general believed to behave only as a carrier trap.

In sample 3 a strong ESR signal from the P donor in its neutral-charge ground state is observed, where the characteristic doublet hyperfine (HF) structure of the P donors (corresponding to the nuclear spin $I = \frac{1}{2}$ of the ^{31}P atom with 100% natural abundance [15]) can be clearly seen. No ODMR signal related to such an ESR transition could be detected. In this case, the electrons are readily captured by the P donors at low temperature (10 K). Because of the much smaller capture cross section of the valence-band holes by the neutral P donors ($\sigma_p \sim 10^{-20} - 10^{-21} \text{ cm}^2$ as compared to $\sigma_n \sim 10^{-10} - 10^{-11} \text{ cm}^2$) [16] and very few deep defect levels present, the lifetime of the trapped electrons is very long [6]. Consequently a nearly complete electron filling at this level is achieved. Recombination process between the electrons and the holes can be neglected.

On the contrary, the P donors in samples 1 and 2 act as a very strong recombination channel for the free carriers, as can be seen by the strong negative ODMR signal related to the neutral P donors (Fig. 2). Very little can be seen in a photo-ESR spectrum from these samples, though the concentration of the P donors is well above the detection limit, which indicates that the P level is nearly empty. The level will still capture electrons strongly, as in sample 3, but the carrier recombination via this level is more efficient, leading to a very short lifetime of the trapped electrons. This efficient recombination is not due to a successive capture of holes at the neutral P donors (electron already trapped) directly from the valence band

[16]. The electron-hole recombination process can in this case be understood in the following way: The electrons are first captured by the P donors and are transferred to deep centers, where they recombine with the holes captured by the deep centers. This is symbolically shown in Fig. 2(a), where X^n represents the deep center X in the n charge state (n for the net excess charges). Examples of such deep centers include the $V-O$ complex and the phosphorus-vacancy complex, which are known to be among the dominant products of the electron irradiation in our samples.

Such a charge transfer can be very efficient, as partly indicated by the very short time scale in the photo-ESR data for a higher frequency modulation, where the P-donor ESR signal starts to be apparent only at frequencies higher than 50 kHz when the spin flips start to feel the kinetic charge-transfer process. In fact, there are two main processes occurring while the P donor is in the neutral ground state after the capture of the electron: charge (electron) transfer to other deeper centers, or binding an exciton. Since the bound-exciton formation at the neutral P donors is quite efficient [17] (estimated to be in the sub- μs range in our experimental conditions), the inter-center electron-transfer process must be even faster. It is even more efficient than the filling of the level by cascade capture of the conduction electrons or the excitonic Auger capture of electrons [18] by the positively charged P donor, since the fraction of the electron occupation on the donor level is very low. The transfer process is largely facilitated by a rather extended wave function of the P-donor electrons. This may be one of the reasons why the recombination of the bound excitons at the neutral P donors vanishes after irradiation by high energetic particles. Such a strong electron-transfer process, however, has been ignored in the past in the existing treatment of the TR processes of the nonequilibrium carriers in semiconductors.

In order to have a more general and complete description of the carrier TR processes, a term such as $-T_{ij}n_{Ti}p_{Tj} + T_{ji}n_{Tj}p_{Ti}$ should therefore be added to the rate equations to describe the evolution of the filling of the i th center due to its charge transfer to the j th center. Here n_{Ti} and p_{Ti} denote the filled and empty level for the i th center. The parameter T_{ij} is the charge-transfer coefficient from the i th center to the j th center.

As an example we consider a simple case of two interacting defect centers with only one level each, as shown in Fig. 1. The rate equations can be written as

$$\begin{aligned} dn/dt &= -c_{n1}np_{T1} + e_{n1}n_{T1} - c_{n2}np_{T2} + e_{n2}n_{T2}, \\ dp/dt &= -c_{p1}pn_{T1} + e_{p1}p_{T1} - c_{p2}pn_{T2} + e_{p2}p_{T2}, \\ dn_{T1}/dt &= c_{n1}np_{T1} - e_{n1}n_{T1} - c_{p1}pn_{T1} + e_{p1}p_{T1} \\ &\quad - T_{12}n_{T1}p_{T2} + T_{21}n_{T2}p_{T1}, \\ dn_{T2}/dt &= c_{n2}np_{T2} - e_{n2}n_{T2} - c_{p2}pn_{T2} + e_{p2}p_{T2} \\ &\quad + T_{12}n_{T1}p_{T2} - T_{21}n_{T2}p_{T1}. \end{aligned}$$

To illustrate how the charge transfer affects the carrier TR, we take a simplified case assuming that the defect level 1 (or 2) is a strong electron (or hole) trap and the thermal emissions can be neglected. In the absence of the charge transfer, $n_{T1}=N_1$, $\tau_{n1} \rightarrow \infty$; $p_{T2}=N_2$, $\tau_{p2} \rightarrow \infty$; $\tau_n=1/c_{n1}p_{T1} \rightarrow \infty$; and $\tau_p=1/c_{p2}n_{T2} \rightarrow \infty$. (Here τ_{n1} and τ_{p2} denote the electron and hole lifetime at levels 1 and 2, respectively. τ_n and τ_p are the lifetime for the free electrons and holes.) This means that the levels act as strong carrier traps as they should. If the charge transfer is dominating, on the other hand, $n_{T1} \ll N_1$, $\tau_{n1} \rightarrow \tau_{n1,\min}=1/T_{12}N_2$; $p_{T2} \ll N_2$, $\tau_{p2} \rightarrow \tau_{p2,\min}=1/T_{12}N_1$; $\tau_n \rightarrow \tau_{n,\min}=1/c_{n1}N_1$; and $\tau_p \rightarrow \tau_{p,\min}=1/c_{p2}N_2$. In other words, the defect levels act as strong carrier recombination channels in this case. The levels are sparsely populated and the carrier lifetimes reach the minimum values due to the efficient carrier recombination bridged by the strong charge transfer. These predictions are in full agreement with our experimental observations. If we estimate that only a few percent of the P-donor levels are filled in samples 1 and 2, the electron-transfer process should be 2 orders of magnitude more efficient than the electron filling to the levels, i.e., in a range of 10 ns or less.

The efficient charge transfer discussed in this work cannot be explained by a radiative process, since it is generally believed to be less efficient [16]. This leaves cascade, multiphonon, and Auger processes, where the energy dissipation during the charge transfer is done by emitting phonons or Auger particles due to electron-phonon and electron-electron interactions. It is a subject of future work to reveal the mechanism responsible in each case.

To summarize, we have observed directly the alternating roles of both shallow and deep defect levels (represented by the shallow P donor level and the deep levels related to the V-O complex in silicon) in the TR processes of nonequilibrium charged carriers in a semiconductor, by photo-ESR and ODMR techniques where the identity of the defects and their charge states is unambiguous. The intercenter charge-transfer processes, especially when a shallow defect is involved, have been shown to be very efficient. These processes are often involved in the dominant recombination channels, which has not been realized previously. This leads to the rather surprising observation that even a shallow hydrogenic level such as the P-donor level can act as an efficient recombination channel for the excess electrons and holes in certain cir-

cumstances. In other words, carrier capture to a deep level can be either direct as has been discussed in the existing theory, or indirect via some intermediate shallow levels of other centers. This work therefore strongly indicates the need of a more complete consideration *beyond* the framework of the SRH statistics in the modeling of the TR processes of excess carriers in semiconductors, to include the intercenter charge transfer.

-
- [1] W. Shockley and W. T. Read, Phys. Rev. **87**, 835 (1952); R. N. Hall, Phys. Rev. **87**, 387 (1952).
 - [2] P. T. Landsberg, C. Rhys-Roberts, and P. Lal, Proc. Phys. Soc. **84**, 915 (1964); A. Haug, Phys. Status Solidi **B 97**, 481 (1982).
 - [3] J. I. Pankove, *Optical Processes in Semiconductors* (Dover, New York, 1971).
 - [4] T. N. Morgan, Phys. Rev. B **28**, 7141 (1983).
 - [5] M. Lax, Phys. Rev. **119**, 1502 (1960).
 - [6] V. S. Vavilov, O. G. Koshelev, Yu. P. Koval', and Ya. G. Klyava, Sov. Phys. Solid State **8**, 2770 (1967).
 - [7] R. L. Aggarwal, P. Fischer, V. Mourzine, and A. K. Ramdas, Phys. Rev. **138**, A882 (1965).
 - [8] A. J. R. deKock, J. Electrochem. Soc. **118**, 1851 (1971).
 - [9] The magnetic-field modulation frequency in the ESR experiments in this work, unless noted, is chosen in such a way that it is most sensitive to the steady-state carrier occupation at the defect levels, rather than to follow the fast kinetics in the carrier trapping and recombination processes.
 - [10] W. M. Chen, O. O. Awadelkarim, B. Monemar, J. L. Lindström, and G. S. Oehrlein, Phys. Rev. Lett. **64**, 3042 (1990).
 - [11] W. M. Chen, O. O. Awadelkarim, J. H. Svensson, B. Monemar, and F. P. Wang, in *Proceedings of the Twentieth International Conference on the Physics of Semiconductors*, edited by E. M. Anastassakis and J. D. Joannopoulos (World Scientific, Singapore, 1990), p. 601.
 - [12] K. L. Brower, Phys. Rev. B **4**, 1968 (1971).
 - [13] G. D. Watkins and J. W. Corbett, Phys. Rev. **121**, 1001 (1961).
 - [14] A. G. Milnes, *Deep Impurities in Semiconductors* (Wiley, New York, 1973).
 - [15] G. Feher, Phys. Rev. **114**, 1219 (1959).
 - [16] P. Norton, T. Braggins, and H. Levinstein, Phys. Rev. Lett. **30**, 488 (1973); V. L. Bonch-Bruевич and E. G. Landsberg, Phys. Status Solidi **29**, 9 (1969).
 - [17] R. B. Hammond and R. N. Silver, Appl. Phys. Lett. **36**, 68 (1980).
 - [18] A. Hangleiter, Phys. Rev. B **37**, 2594 (1988).