Observation of Rapid Direct Charge Transfer between Deep Defects in Silicon

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Direct electron transfer is observed between two deep defects in silicon upon selective laser excitation with an energy lower than the band gap. This transfer is shown to be very efficient when one of the defects is a pseudodonor and the other is a dominant recombination center. It is argued that such processes must in general be considered when modeling capture and recombination processes of charge carriers in semiconductors.

In the description of recombination processes of nonequilibrium charge carriers involving different defect centers in semiconductors it is commonly assumed that the connection between the centers is indirect; i.e., the charge carriers are thermally excited from a center to one of the bands and subsequently captured by another center [1,2]. The role of direct intercenter transfer has usually been discarded and, for instance, shallow donor-acceptor pair recombination in silicon is found to be an inefficient process with a typical decay time of 100 μs [3]. Recently, however, Chen et al. [4] have demonstrated that efficient intercenter charge transfer in silicon can occur, when a shallow defect is involved (such as a P donor), which can connect to a dominant recombination channel. The recombination process in this case cannot be described by the conventional Shockley-Read-Hall (SRH) model [1,2].

In this Letter we report the observation of fast, direct charge transfer between two *deep* defects in silicon. We show that this process is very efficient and that in general it must be considered when modeling capture and recombination processes of charge carriers. As examples serve the $(C_i\text{-}O_i)$ and deep-vacancy-oxygen $(V\text{-}O)$ complexes, two of the major defects present in electron irradiated Czochralski (CZ) silicon. In the experiment the $(C_i\text{-}O_i)^0$ pseudodonor complex, which is also known as the 0.79 eV or C-line defect, is excited into its first excited singlet state S_1 with a pulsed tunable laser. The proof that an electron is directly transferred from the excited $(C_i\text{-}O_i)^0$ to the $(V\text{-}O)^0$ complex is provided by the presence of the electron spin echo (ESE) detected EPR spectrum of the excited triplet state of $(V\text{-}O)^0$, of $(V\text{-}O)^-$, and of $(C_i\text{-}O_i)^+$ immediately after the resonant laser excitation of $(C_i\text{-}O_i)^0$.

The experiments were performed on n-type CZ-grown silicon material. Sample I was irradiated with 2 MeV electrons ($10^{16}e^-$ cm^{-2}) and contains O and C contaminants in concentrations of 1×10^{18} cm^{-3} and 2×10^{17} cm^{-3}, respectively. Sample II was irradiated with $3 \times 10^{18}e^-$ cm^{-2} and contains carbon at a much lower concentration ($< 10^{16}$ cm^{-3}). The oxygen concentration, however, is relatively high (6.4×10^{17} cm^{-3}). From infrared (ir) absorption measurements, detecting the local vibrational modes (LVM) of defects, it is seen that the $(V\text{-}O)^0$ complex is one of the dominant ir-active impurities in both samples. The $(C_i\text{-}O_i)$ complex, however, is only abundant in sample I as shown by photoluminescence (PL) experiments.

The pulsed laser excitation was at a variable wavelength and was provided by a laser system consisting of a Nd:YAG pumped dye laser followed by a Raman shifter (RS). By varying the wavelength of the dye laser and by selecting either the first or second Stokes-shifted output of the RS, tunability is achieved between 1 and 3 μm with typical pulse energies of a few mJ in 5-8 ns. The sample was placed in a liquid helium bath cryostat with optical access in which the temperature could be varied between 1.2 and 4.2 K. For temperatures above 4.2 K the sample was kept in the same cryostat which was slowly warming up after the liquid helium had evaporated.

In the three types of EPR experiments to be discussed here the ESE signal is used as a measure of the population of the paramagnetic species induced by the optical excitation. The ESE signal is generated by two intense microwave pulses with pulse lengths of 50 and 100 ns. The first $\pi/2$ pulse creates a quickly decaying magnetic moment oscillating at the Larmor frequency. This free induction decay is restored by the second π pulse at time τ to form the echo at time 2τ. In the first type of experiment we detect the echo signal of the excited triplet state of $(V\text{-}O)^0$ as a function of the wavelength of the laser pulse preceding the microwave pulse sequence. The wavelength is varied over the excitation spectral range of $(C_i\text{-}O_i)^0$, to search for a direct communication between $(C_i\text{-}O_i)$ and $(V\text{-}O)$. In the second experiment we measure the intensity of the echo signal of the excited triplet state of $(V\text{-}O)^0$ as a function of the delay time t_d between the laser flash and the first $\pi/2$ pulse to provide for a real-time measure of such communication. In the third experiment we registrate the echo signal as a function of

the strength of the magnetic field and obtain the ESE-detected EPR spectrum so as to positively identify the individual defects and to show that a charge transfer process is responsible for the intercenter communication. For a more detailed description of the ESE phenomenon the reader is referred to [5,6].

The relevant energy levels of the $(C_i\text{-}O_i)$ and $(V\text{-}O)$ defects are presented in Fig. 1. The $(C_i\text{-}O_i)$ defect has been identified as an interstitial carbon atom trapped near an interstitial oxygen atom [7]. Its optical emission spectrum is characterized by a strong no-phonon line at 0.79 eV. The excited states are interpreted as effective-mass (EMT) states of a pseudodonor. The lowest excited state has an ionization energy $E_i = 38.3$ meV [8]. The singly positively charged state $(C_i\text{-}O_i)^+$ (Si-G 15) has been studied by EPR and was identified as the core of the pseudodonor excited neutral state involved in the 0.79 eV emission. The neutral $(V\text{-}O)^0$ complex has been identified by EPR measurements on its excited triplet state [9,10] and the negatively charged $(V\text{-}O)^-$ complex on its doublet ground state [11]. In both states the center was found to be of C_{2v} symmetry. The position of the $(-/0)$ level of $(V\text{-}O)$ is located at $E_c - 0.17$ eV [12,13]. The position of the $(+/0)$ level of $(V\text{-}O)$ was not known before. In this work we shall argue that it is located at $E_c - 0.76$ eV (see below). The position of the lowest triplet state T_0 of $(V\text{-}O)^0$ is about 0.2 eV above the singlet ground state as estimated from *ab initio* cluster calculations by van Oosten [14].

The first indication of the presence of a transfer process between the $(C_i\text{-}O_i)^0$ and $(V\text{-}O)^0$ defects is provided by
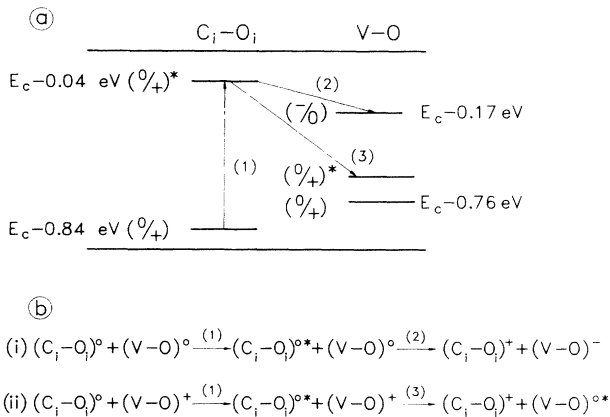
the excitation spectrum of sample I presented in Fig. 2(a). It is obtained by detecting the ESE signal of the 964.3 MHz $T_x - T_y$ zero-field transition of the excited triplet state of the $(V\text{-}O)^0$ complex [15] as a function of the wavelength of the laser pulse preceding the microwave pulses. The interesting feature is a sharp line spectrum superimposed on a steady increase when going to higher photon energy. We shall argue that the background signal represents the onset of the excitation from the ground state of the $(V\text{-}O)^0$ defect to the conduction band (see below). In Fig. 2(b) we show a similar ESE-detected excitation spectrum of sample II. Here only the steady increase is observed. The line spectrum in Fig. 2(a) is assigned to the $(C_i\text{-}O_i)^0$ defect because it is identical to the excitation spectrum detected via the C-line luminescence; see Fig. 2(c) [16]. Our observations indicate the presence of an efficient communication between the $(C_i\text{-}O_i)^0$ defect in its excited state and $(V\text{-}O)^0$. The absence of this spectrum in sample II is in agreement with the fact that the concentration of $(C_i\text{-}O_i)$ is much lower in this sample due to a very low carbon concentration.

To measure the rate of transfer we excited $(C_i\text{-}O_i)^0$ resonantly at 0.79 eV and recorded the ingrowth of the ESE signal of T_0 of $(V\text{-}O)^0$ as a function of t_d. This experiment was performed in a magnetic field of 0.34 T at a microwave frequency of 9.3 GHz since in zero-magnetic field, owing to the equal initial populations of the triplet sublevels [15,17], the ESE signal at short t_d is zero. The ingrowth of the ESE signal is instantaneous, indicating that the transfer process is faster than the time resolution of our ESE spectrometer which is 50 ns.

Direct communication between different defects in semiconductors is commonly discussed in terms of charge transfer or energy transfer. In the former case, one of the

FIG. 1. (a) A schematic drawing of the energy levels of the $(C_i\text{-}O_i)^0$, $(V\text{-}O)^-$, and $(V\text{-}O)^0$ defects. The pathway for the selective optical excitation of $(C_i\text{-}O_i)$ into its first excited pseudodonor state is indicated by (1). The subsequent electron transfer from $(C_i\text{-}O_i)^{0*}$ to $(V\text{-}O)^0$ is indicated by (2). The electron transfer process from $(C_i\text{-}O_i)^{0*}$ to $(V\text{-}O)^+$, leading to the excited triplet state of $(V\text{-}O)^0$, is indicated by (3). (b) The two routes for producing $(C_i\text{-}O_i)^+$, $(V\text{-}O)^-$, $(C_i\text{-}O_i)^+$, and $(V\text{-}O)^{0*}$. The initial concentration of $(V\text{-}O)^+$ in process (ii) is induced by the photoionization.
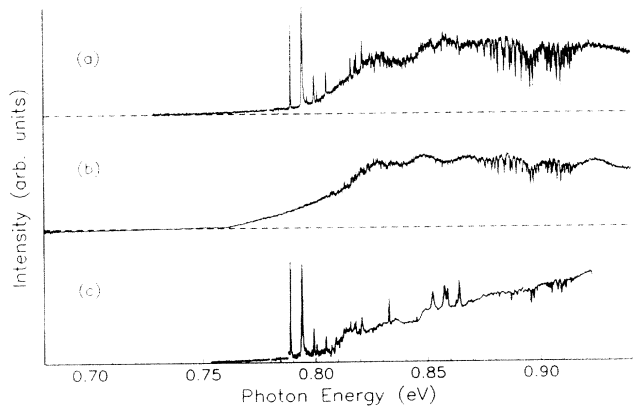

FIG. 2. (a) The ESE-detected excitation spectrum of sample I. (b) The same spectrum for sample II. (c) The PL-detected excitation spectrum of sample I. The peaks in the 0.87 to 0.92 eV region are caused by absorptions in the windows of the Raman shifter. The spectra are not corrected for the nonlinearity of the microwave detector. $T = 1.2$ K.

charged particles of the electronic excitation (i.e., an electron-hole pair) at one defect is transferred to the other defect before the electron-hole pair can recombine. In the latter case the energy of the electron-hole pair as an entity at one defect is transferred to the other defect. The major feature distinguishing between the two processes is that the centers change their charge states by one unit after the charge transfer while they retain the same charge during the energy transfer.

To establish whether direct, interdefect charge transfer takes place upon selective excitation into the 0.79 eV transition of $(C_i$-$O_i)^0$ we performed an ESE experiment at 95 GHz. Here both the identity of the defects and the change in their charge states could be monitored during the transfer process. First we established that sample I, when cooled in the dark to 1.2 K, did not show any signal of $(C_i$-$O_i)^+$, $(V$-$O)^-$, or of the excited triplet state of $(V$-$O)^0$. This indicates that in thermal equilibrium $(C_i$-$O_i)$ and $(V$-$O)$ both are in their diamagnetic, neutral charge state. Then we excited the sample at 0.79 eV and measured the ESE-detected EPR spectrum (Fig. 3). In addition to the transitions of the excited triplet state T_0 of the $(V$-$O)^0$ complex, signals of the paramagnetic ground states $(S = \frac{1}{2})$ of three different defects can be discerned. The analysis of the orientational dependence of these spectra shows that they belong to $(V$-$O)^-$ (Si-$B1$, [111]), $(C_i$-$O_i)^+$ (Si-$G15$, [18]), and C_i^- (Si-$L6$, [19]). At 1.2 K the signal of C_i^- grows in with a time constant of about 1 s after the laser flash and subsequently decays with a characteristic time of about 1 s. The signals of $(V$-$O)^-$ and $(C_i$-$O_i)^+$ persist as long as the temperature is kept below 4.2 K and disappear only when the temperature is raised to approximately 100 K. It should be stressed that the EPR signals of $(V$-$O)^-$ and $(C_i$-
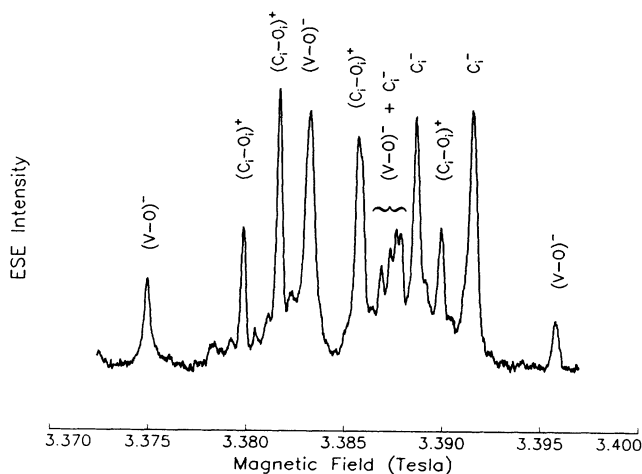

FIG. 3. The ESE-detected EPR spectrum at 95 GHz of sample I after resonant laser excitation of $(C_i$-$O_i)^0$. B_0 is parallel to $\langle 110 \rangle$. $T = 1.2$ K. The lines of $(V$-$O)^-$ and $(C_i$-$O_i)^+$ persist at low temperature. The spectrum is not observed after cooling the sample in the dark.

$O_i)^+$ could be observed only after resonantly exciting $(C_i$-$O_i)^0$ at 0.79 eV into the first, pseudodonor, excited singlet state S_1. With the laser slightly tuned away from this transition it proved impossible to detect signals of these two charged defects. This gives evidence that a direct charge transfer, as shown in Fig. 1, indeed occurs between the two deep defects. Unfortunately the ESE experiments did not allow us to measure the rate of ingrowth of the spectra of $(V$-$O)^-$ and $(C_i$-$O_i)^+$ because of the long spin-lattice relaxation times T_1 (4 s in the presence of laser light and 45 s in the dark).

The fact that $(C_i$-$O_i)^+$ and $(V$-$O)^-$ are produced at 1.2 K by selective excitation at 0.79 eV proves that the loosely bound EMT electron of the pseudodonor $(C_i$-$O_i)^0$ in its first excited singlet state S_1 is lost to $(V$-$O)^0$ without the intermediate of the conduction band. This is in close resemblance to the charge transfer from a true shallow donor to another defect [4]. Such a process is strongly facilitated by the extended wave function of the transferred charged particle. Two-photon processes are excluded because the concentration of photoinduced paramagnetic species is always found to be proportional to the laser intensity. Moreover we exclude that at 1.2 K thermal excitation from S_1 to the conduction band produces an appreciable amount of free carriers, in agreement with the photoconductivity experiments of Kleverman et al. [20]. After the transfer the electron is tightly bound at $(V$-$O)^-$. The resulting localized wave function prohibits the transfer of the electron back to $(C_i$-$O_i)^+$ to annihilate the localized hole. This explains the persistent character of $(V$-$O)^-$ and $(C_i$-$O_i)^+$ after the electron transfer.

As mentioned above the energy position of the ground state S_0 of $(V$-$O)^0$ is inferred from the excitation spectra presented in Figs. 2(a) and 2(b). Here the steady increase of the background has the characteristic spectral dependence of a transition from a localized state to a continuum band. We conclude that it corresponds to an ionization process of $(V$-$O)^0$. The recapture of the carrier by $(V$-$O)^+$ leads partially to the excited triplet T_0 which is detected by ESE. We estimate the ionization energy of $(V$-$O)^0$ to be 0.76 eV by fitting the excitation spectra to the expression for the cross section $\sigma \propto (h\nu - E_i)^{3/2}$ for an excitation from a deep level to a continuum band. This would imply that the $(+/0)$ level of $(V$-$O)$ is at $E_c - 0.76$ eV since the $(-/0)$ level is well known to be at $E_c - 0.17$ eV. It should be pointed out that the $(0/+)$ level of $(V$-$O)$ has never been positively identified before, despite numerous studies on this major defect produced in electron-irradiated oxygen-containing silicon. Previous studies by deep-level transient spectroscopy (DLTS) in electron-irradiated oxygen-containing p-type silicon revealed many defect levels in the same energy range [21]. However, none has been positively assigned to the $(0/+)$ level of $(V$-$O)$ owing to the lack of corresponding microscopic identification. The failure of conventional EPR to detect the paramagnetic $(V$-$O)^+$ is still not fully under-

stood. Presumably this is related to the difficulties to create $(V\text{-}O)$ in sufficiently high concentration by electron irradiation (to meet the EPR detection limit) and at the same time to keep the Fermi level below the $(0/+)$ level. While the $(V\text{-}O)$ defect is known from our ir-absorption studies to be quite abundant in the samples studied in this work, the nonequilibrium population of $(V\text{-}O)^+$ (induced by photoionization) can still be very low. This can be explained by a very efficient capture of electrons (either free or loosely bound, e.g., at pseudo-donors) when $(V\text{-}O)$ becomes positively charged. The fast ingrowth (less than 50 ns) of the excited triplet state of $(V\text{-}O)^0$ due to the transfer from the excited $(C_i\text{-}O_i)^{0*}$ complex already indicates the likelihood of this possibility. This also explains why no $(V\text{-}O)^+$ EPR signal was observed within the time resolution of the ESE experiments after the laser flash. Since we have demonstrated that the electron transfer from $(C_i\text{-}O_i)^{0*}$ to $(V\text{-}O)^0$ can occur it is natural that the electron transfer from $(C_i\text{-}O_i)^{0*}$ to $(V\text{-}O)^+$ is even more efficient owing to the presence of the additional long-range Coulomb potential. An energy transfer process is believed to be unimportant in this case because of the lack of spectral overlap between the emission of the transfer sensitizer [i.e., $(C_i\text{-}O_i)^0$] and the absorption of the energy acceptor [i.e., $(V\text{-}O)^0$] [22,23]. This is based on the experimental observation that no absorption of $(V\text{-}O)^0$ to its excited states can be detected within the range of the $(C_i\text{-}O_i)^{0*}$ emission.

In conclusion, our experiments demonstrate that direct and efficient charge transfer between two deep centers in silicon can occur when one of them behaves as a pseudo-donor (or pseudoacceptor) and therefore possesses an extended wave function in its excited state. From the observation that $(C_i\text{-}O_i)^+$, $(V\text{-}O)^-$, and $(V\text{-}O)^{0*}$ are created upon selective optical excitation into the first excited singlet state of $(C_i\text{-}O_i)^0$ we conclude that an electron bound to this neutral center is directly transferred to the $(V\text{-}O)^0$ complex. From the time-resolved EPR studies the electron transfer is shown to be very efficient, faster than 50 ns. While only the $(C_i\text{-}O_i)$ and $(V\text{-}O)$ defects are discussed here the charge transfer concept applies to such defects in general. Our result supports the idea that the direct charge transfer in silicon is an important mechanism which has to be considered when modeling electron transfer and recombination processes.

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