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An electron spin echo study of donor–acceptor recombination

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Abstract. It is shown that electron spin echo is a powerful tool to study the dynamics of D–A recombination in silicon, especially when one is interested in the 'long-term decay'. Moreover, this technique is used to study the influence of excitation light on the electron spin–lattice relaxation and polarisation of bound hole spins.

1. Introduction

Donor–acceptor (D–A) recombination has been studied in many semiconductors using optical methods. In some cases, like GaP, CdTe or ZnS, the photoluminescence spectra show many resolved peaks, which are attributed to the recombination of well defined donor–acceptor pairs. For a review article see the paper by Dean (1973). Though such resolved peaks have not been observed in the case of silicon, photoluminescence has been used to study the dynamics of the D–A recombination (Enck and Honig 1969).

Information on spin–lattice relaxation and spin polarisation of the bound photo-excited electrons and holes can often be obtained with optically detected magnetic resonance (ODMR). However, ODMR has proven to be very difficult to observe in silicon (Lee *et al* 1982), probably because of the lack of efficient photo detectors in the IR region.

In this paper we present a study of D–A recombination in silicon using electron spin echo (ESE) techniques, where we also obtain information about electron spin–lattice relaxation and electron spin polarisation. We note that on first sight, ESE techniques would appear to be less sensitive than optical techniques, because one observes the small quanta corresponding to microwave frequencies instead of optical quanta. Yet ESE can still compete in sensitivity with photoluminescence because the signal is directly proportional to the total number of electrons or holes N_S, and not to the rate $\partial N_S/\partial t$ at which photons are produced, which is especially low in silicon. This attractive aspect of ESE has been demonstrated for instance in the study of photo-excited triplet states of molecules (Bos *et al* 1985).

This study was undertaken to support microwave induced optical nuclear polarisation experiments in compensated silicon. In these experiments we use band gap light for optical creation of holes bound to acceptors. Then the polarisation $P_S = \langle S_z \rangle / S$ of the spin of these holes is transferred to the spins of the ^{29}Si nuclei by means of microwave irradiation. From the experiments it appears that the efficiency of this process depends strongly on the number, polarisation and spin–lattice relaxation rate of the bound holes.

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2. Experimental details

Our experiments are performed on a dislocation-free single crystal of silicon. It is doped with 5×10^{22} m^{-3} phosphorus donors and highly compensated with 4×10^{22} m^{-3} boron acceptors. The sample is rod-shaped with the longest dimension of 10 mm in the [111] direction and a cross section of 4 mm^2.

The ESE measurements are performed at 9.4 GHz (X band) and liquid helium temperature in a specially designed loop gap resonator (Dirksen 1989). Typical microwave pulse powers are 1 W and the pulse length for the $(\pi/2, \pi)$ pulse sequence are of the order of 100 ns and 200 ns. For optical excitation we use a CW Nd:YLaF laser emitting 1 W at 1.047 μm, which is close to the indirect band gap of silicon. At this wavelength and at low temperature the absorption coefficient is 10 m^{-1}, so the crystals are excited homogeneously. We use a mechanical shutter to shape pulses of variable length. The light intensity is varied using grey filters.

3. Results

The low temperature and the low concentration ensure that most electrons and holes are localised at the donor and acceptor sites respectively. The ESR spectrum of the bound electrons can easily be observed and shows two narrow lines with a width of 2×10^{-4} T and split by about 42×10^{-4} T by hyperfine interaction with the nuclear spin of the ^{31}P (Feher 1959). The g-value of these bound electron spins is $g_e = 2.00$. At X band and 1.2 K their electron spin–lattice relaxation time T_S is very long, of the order of 10^2 s (Feher 1959).

It is known that the ESR spectrum of the holes bound to boron acceptors is difficult to observe because of random stress broadening the ESR lines (Feher *et al* 1960). However, by applying uniaxial stress of 4 kbar along the [111] axis, the lines are strongly narrowed and reduced to a single line, with a width of about 14×10^{-4} T. The spectrum can be described as a Kramers doublet, with an effective (hole) spin $S = 1/2$. In our experiments we orient the static magnetic field perpendicular to the direction of the uniaxial stress. Then the g-value of these hole spins is $g_h = 2.48$. The relaxation time T_S of these hole spins is much shorter than that of the electron spins. It depends strongly on the applied uniaxial stress and the temperature and is typically 10 ms at 4 kbar, 9.4 GHz and 1.2 K. The advantage of the hole spins for studying the D–A recombination process is the short spin–lattice relaxation time T_S. This allows to follow the process at a much higher rate.

An example of our experiments is shown in figure 1. At $t = 0$ a laser pulse of intensity F and a length $\Delta t \simeq 0.1$ s is applied, creating bound electrons and holes. After a time $t' \simeq 1$ s we perform an ESE experiment on the spins of the bound holes. For this purpose we use a $(\pi/2, \pi)$ pulse sequence creating an electron spin echo with an amplitude proportional to the product $N_S P_S$. This ESE experiment takes about 1 μs.

Our first study concerns the decay of the number of bound holes due to D–A recombination after a laser flash. Before any laser flash is applied no ESE signal corresponding to bound holes is observed. This is in agreement with the fact that the crystal is n-type, so in equilibrium no holes should be present. Figure 2 shows the evolution of the amplitude $N_S P_S$ of the ESE signal after a laser flash of 0.1 s, using full laser power. The ESE signal is recorded after a delay $t' \geq 1$ s, which is much longer than the spin–lattice relaxation time T_S. So at all times the polarisation P_S of the hole

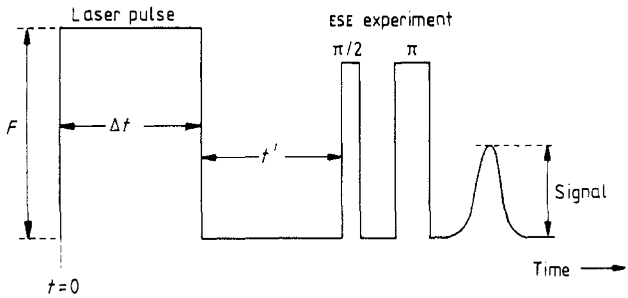

Figure 1. The timing sequence of the ESE experiments.

spins is equal to its thermal equilibrium value P_S^0 and the ESE signal directly yields $N_S(t')$. Figure 2 shows a strongly non-exponential decay of N_S. While at first the decay seems to take place with a time constant of about 30 s, after 500 s, N_S is still about 20% of its initial value. The time evolution will be discussed in the next section.

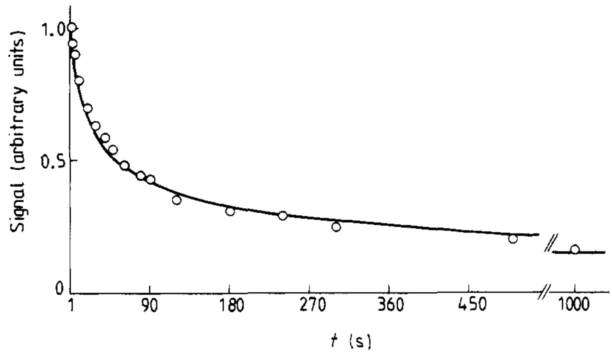

Figure 2. The decay of $N_S(\tau)$ after a laser flash. The full curve is calculated by the pair model.

Our next study concerns the number of bound holes N_S as a function of the intensity F and duration Δt of the laser flash creating them. We perform these measurements at a fixed delay time $t' = 0.3$ s $\gg T_S$, ensuring that the hole spins are in thermal equilibrium, and that the ESE signal is proportional to N_S only. The repetition time of this experiment is 10^3 s, so 85% of the bound holes have recombined before the laser flash at $t = 0$ is applied. As shown in figure 3(*a*), at all light intensities we observe an approximately exponential increase of the ESE signal strength as a function of Δt. Figure 3(*b*) shows the characteristic time constant τ_F as a function of the light intensity F. As can be seen, it is proportional to F^{-1}. At first sight it is surprising to find such a simple behaviour, since figure 2 clearly shows that the D–A recombination process is strongly non-exponential. Below we will discuss a simple model for D–A recombination and show that it provides a simple explanation.

In the pulsed experiments presented above, the conditions are such that the ESE signal is recorded when the polarisation P_S of the bound hole spins is equal to the thermal equilibrium value P_S^0. We will now discuss an experiment where this is not

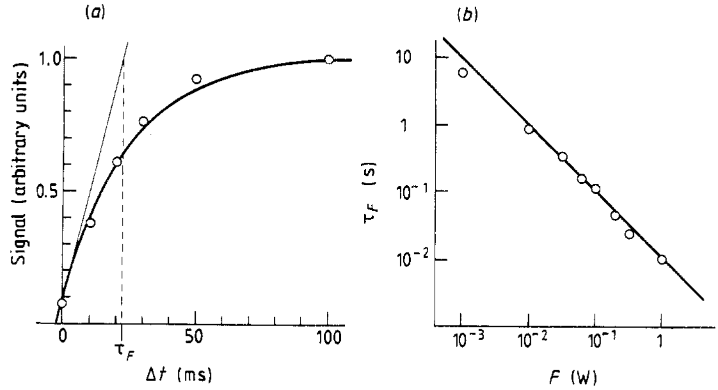

Figure 3. (*a*) The intensity of the ESE signal as a function of the length Δt of the laser flash at fixed delay t'. (*b*) The in-growth time τ_F of the ESE signal as a function of the light intensity F.

generally true. Figure 4 shows a measurement of the amplitude of the ESE signal of the bound holes as a function of the light intensity F, while the laser light is not pulsed but applied continuously. At low light intensities, $F < 10^{-3}$ W, we observe the ESE signal to increase with F, due to the increasing number of bound hole spins. At higher light intensities, one expects N_S to saturate to a constant value. The ESE signal however, is observed to *decrease*, indicating that the polarisation P_S of the bound hole spins decreases as well. We will discuss this decrease of P_S using extra spin–lattice relaxation processes due to photo-excited free carriers proposed by Feher and Gere (1959) below.

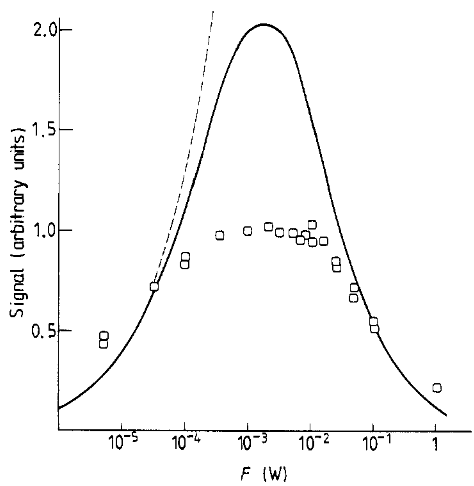

Figure 4. The ESE signal strength as a function of F in a steady-state experiment. The broken curve represents N_S as calculated by the pair model. The full curve takes interaction with free carriers into account.

4. Discussion

The kinetics of radiative recombination in a crystal containing randomly distributed donors and acceptors has been treated theoretically by Thomas *et al* (1965). They treat the problem exactly for the case of weak compensation, e.g. when the donor concentration greatly exceeds the acceptor concentration. Then each bound hole can be considered to be isolated from the other acceptor sites. Recombination takes place with an electron bound to one of the surrounding donors, because the donor and acceptor wave functions overlap. If we approximate their envelope by a hydrogen-like wave function, the time constant for this process depends very strongly on the distance r between donor and acceptor (Dean 1973, Thomas *et al* 1965) :

$$\tau(r) = \tau(0)\exp(2r/a_{\mathrm{H}}^{*}) \tag{1}$$

where a_{H}^{*} is the effective Bohr radius of either the donor or the acceptor, depending on which is larger. We apply uniaxial pressure to the sample. Then the smallest effective mass involved is the light hole mass $m^{*}/m = 0.153$ and $a_{\mathrm{H}}^{*} = 42$ Å. Hence, when hopping of the bound electron between donor sites is taken into account, the main channel for recombination will be between the acceptor and its nearest-neighbour donor.

Approximate solutions are obtained for the case of exact compensation by Thomas *et al* (1965). Their results for the initial time evolution of the number of bound holes are very similar to those for weak compensation. Comparing these two cases, the initial time evolution of the number of bound holes differs less than 10%. Only after 90% of the bound holes have recombined, the difference becomes larger.

In view of these results, we describe the present experiments that are obtained in a highly compensated sample, using a highly simplified 'pair model' (Dean 1973). We assume a completely compensated crystal, and divide it in N_a isolated pairs of donors and acceptors. Upon irradiating the crystal with band gap light all pairs are assumed to have equal probability of being occupied by a bound hole and a bound electron. Recombination is assumed to take place between this hole and this electron only and not with other bound carriers. All other recombination channels like band-to-band transitions are neglected. We furthermore assume the donor–acceptor (D–A) pairs to be completely characterised by their distance r, their density being

$$N_a P(r) = N_a^2 4\pi r^2 \exp(-\tfrac{4}{3}N_a \pi r^3) \tag{2}$$

where

$$\int_0^\infty P(r)\,\mathrm{d}r = 1.$$

This choice is made for the following reason. If we consider an acceptor in a real crystal containing N_a randomly distributed donors, then $P(r)$ is the probability of finding the nearest-neighbour donor at a distance r from that acceptor (Chandrasekhar 1943).

When we irradiate the sample continuously with band gap light with an intensity F so that W m^{-3} s^{-1} photons are absorbed, we may distinguish two types of pairs. Those whose r is so small that $W\tau(r)/N_a < 1$, and consequently are hardly occupied by bound electrons and holes. Those, where donor and acceptor are further apart, will be almost permanently occupied. Because $\tau(r)$ depends very strongly on r, there will be a sharp change from one regime to the other at a critical distance r_c, defined by $W\tau(r_c)/N_a = 1$.

First we calculate the number of occupied pairs $N_S(\Delta t, t')$ as a function of the time t' after a laser flash with a length Δt. In the experiment shown in figure 2, first a long saturating pulse is applied. Then, a stationary population $N_a P(r)$ is reached for those pairs where $r > r_c$ while the others are unoccupied. After the light pulse, first the occupied pairs with the smallest value of r will recombine. Hence, recombination mainly takes place for pairs with $r \approx r_c$ and the evolution of $N_S(\infty, t')$ as a function of t' simply corresponds to an increase of $r_c(t')$ in time. As a result,

$$N_S(\infty, t') = N_a \exp(-\tfrac{4}{3} N_a \pi r_c^3(t')) \tag{3}$$

where

$$r_c(t') = \begin{cases} r_c(0) & \text{if } t' < N_a/W \\ \tfrac{1}{2} a_H^* \ln(t'/\tau(0)) & \text{if } t' > N_a/W. \end{cases}$$

The full curve of figure 2 represents a fit of $N_S(\infty, t')$ as given by equation (3). We fitted the parameters a_H^* and $\tau(0)$ to obtain 38 Å and 10^{-3} s respectively. The value of the Bohr radius compares well with that of a light bound hole. For $\tau(0)$, Enck and Honig (1969) give a smaller experimental value of 5×10^{-5} s, which they obtained in a Si:P:B sample at 4.2 K and using optical methods. However, we note that they did not apply uniaxial stress to the sample, so the bound holes are heavy instead of light holes and a_H^* strongly differs from our case.

Next we consider the number of occupied pairs $N_S(\Delta t, t')$ at a fixed time t' after the flash, but now as a function of the duration of the laser flash Δt. Then

$$N_S(\Delta t, t') = N_S(\infty, t')(1 - \exp(-W/N_a \Delta t)) \tag{4}$$

where $t' > N_a/W$. Here $N_S(\infty, t')$ is given by equation (3). Hence we find an exponential growth as a function of Δt, which is in good agreement with the experimental results shown in figure 3(*a*). The time constant τ_F is found to be proportional to F^{-1} as shown in figure 3(*b*), proving that F is proportional to W. Consequently we can use τ_F for the calibration of the number of absorbed photons. For example, at full laser power of 1 W, we find $\tau_F = 10^{-2}$ s corresponding to $W = 4.10^{24}$ m^{-3} s^{-1}. This value is in reasonable agreement with an estimate of the number of photons falling on the sample. At 1.047 μm, the power of the laser is 1 Watt corresponding to 5.26×10^{18} emitted photons per second. The diameter of the laser beam is 2 mm, the distance from the laser to the sample is 1.5 m and the divergence of the laser beam is 4 mrad. Further at 1.047 μm and 4.2 K, for our crystal is 10% is absorpted (*Landolt–Börnstein* 1982), and thus one expects approximately 1×10^{24} m^{-3} s^{-1} photons to be absorbed.

Finally, we use the simple pair model to understand the dependence of the ESE signal on the laser power as shown in figure 4. For the number N_S of occupied pairs, it yields for CW irradiation:

$$N_S = N_a \exp(-\tfrac{4}{3} N_a \pi r_c^3) \tag{5}$$

where $r_c = \frac{1}{2} a_H^* \ln(N_a/W\tau(0))$. We note that this result holds only when the laser power is low enough to ensure that $r_c > a_H^*$, in order not to violate equation (1). The broken curve in figure 4 represents the dependence of N_S as given by equation (5) where a proportionallity constant has been used to fit it to the absolute intensity of the ESE signal. Furthermore, we use the values for a_H^*, $\tau(0)$ and W as obtained above. For low laser power a qualitative agreement is obtained.

The decrease of the ESE signal at high laser powers as demonstrated in figure 4 cannot be explained by the simple pair model. We think that this decrease can be understood using results of Feher and Gere (1959) who found that band gap light has a pronounced effect on the spin–lattice relaxation time T_S of electrons bound to phosphorus donors in silicon. They showed that T_S is shortened by optically produced free carriers. As we use unpolarised light, the optically created carriers are unpolarised. Hence, one expects the corresponding extra relaxation processes to lead to a lower spin polarisation of the bound holes than corresponding to the thermal equilibrium value P_S^0, which in turn leads to a lower ESE signal.

In order to check this explanation we also perform measurements of the spin–lattice relaxation time T_S of the bound holes as a function of the intensity of the continuously applied laser light. The experiments are performed at 1.2 K and 9.4 GHz, while the uniaxial stress is 4 kbar. The spin–lattice relaxation rate is observed by first saturating the spin polarisation by means of a $\pi/2$ pulse and subsequently investigating the return to equilibrium of this polarisation by observing the echo created with a $(\pi/2, \pi)$ pulse sequence. The results shown in figure 5 show a clear decrease of T_S upon increasing the intensity of the laser.

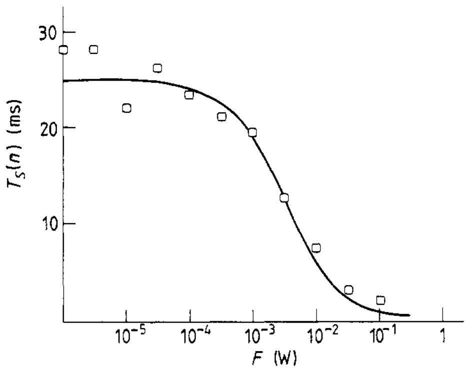

Figure 5. The observed relaxation time $T_S(n)$ as a function of the light intensity F. The full curve represents a fit assuming that the extra contribution to relaxation is proportional to F.

We will discuss the experimental results with a simple model, where the coupling between the spin of a bound hole and the free carriers produces spin flips with a probability nU, where n is the concentration of free carriers. We will not specify the type of coupling. It may be due to magnetic dipole or exchange interactions or to interaction of the bound spin with the field of the moving charge of a carrier (Pines *et al* 1957, Abrahams 1957).

Since we excite with unpolarised light, the free carriers are created with an initial spin polarisation equal to zero. Apparently their polarisation remains low, for they cause a significant decrease of the polarisation of the bound hole spins, as can be seen from figure 4. Then P_S evolves like

$$\partial P_S(t)/\partial t = -T_S^{-1}(0)(P_S(t) - P_S^0) - nUP_S(t) \tag{6}$$

where the first term represents the effect of normal spin–lattice relaxation, i.e. when the number of free carriers n is equal to zero. The second term is the extra relaxation due to the free carriers. Equation (6) can be rewritten as

$$dP_S(t)/dt = -T_S^{-1}(n)(P_S(t) - P_S(\infty)) \tag{7}$$

where

$$T_S^{-1}(n) = T_S^{-1}(0) + nU \qquad \text{and} \qquad P_S(\infty) = P_S^0 T_S(n)/T_S(0). \tag{8}$$

Equation (8) allows us to use the experimental results on $T_S(n)$ shown in figure 5 to explain the decrease of the polarisation at high laser power shown in figure 4. The full curve in figure 4 represents the calculated product $N_S P_S(\infty)$, where N_S is obtained from the broken curve, given by equation (3) and $P_S(\infty)$ is obtained from equation (8). It is clear that the simple models for D–A recombination and spin–lattice relaxation do not allow for a complete quantitative analysis of the experimental data. However, a qualitative picture of the increase and subsequent decrease of the ESE signal as a function of the laser power is clearly obtained.

5. Conclusion

This paper shows that ESE is a powerful tool to study the dynamics of D–A recombination. This technique is advantageous if the decay rate is slow, such as is the case in silicon and especially when one is interested in the 'long-term decay'. For instance, figure 5 shows that after 500 s the initial decay rate $\partial N_S/\partial t$ and hence the intensity of the luminescence is reduced by a factor $\sim 10^3$, while still 20% of the initial ESE signal is observed. Moreover, this technique can be used to study electron spin–lattice relaxation and the polarisation of the hole spins bound to the acceptor under influence of the excitation light.

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