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SPIN-DEPENDENT RECOMBINATION AT DISLOCATION DANGLING BONDS IN Si

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Abstract - Spin-dependent recombination of free carriers via dislocation dangling bonds (DDB) is investigated as a function of temperature and light intensity in magnetic fields of 0.04, 3.3 and 12.5 kOe. On the basis of an analysis of the data obtained, a model of the effect is proposed in which use is made of the concept of recombination via DDB with preliminary carrier capture at the intermediate shallow levels due, presumably, to the deformation potential of the dislocation.

Introduction

It is known that plastic deformation of Si-crystal at 650 - 700 °C creates special type of paramagnetic centers, so-called D-centers, which are Si-broken bonds in some defects [1,2]. Analysing the ESR signal of D-centers, their concentration is $N_D = 4 \times 10^{16}$ cm$^{-3}$ at 300 - 50 K for a dislocation density of about $2 \times 10^9$ cm$^{-2}$ and is proportional to the dislocation density. The energy spectrum suggested for D-centers using photo-ESR data obtained at 100 K [3] mainly consists of two narrow bands (fig. 1). Band 1 has been attributed to broken bonds, band 2 - to broken bonds (D-centers), occupied by additional electrons.

By investigating the ESR signal of neutral phosphorous atoms in plastically deformed crystals and comparing it with that from D-centers, it was shown that the number of electrons captured by D-centers did not exceed 0.2 $N_D$ [1]. Hall effect data suggest the same conclusion. The DLTS data [4] confirm this and shows that D-centers must be localized in dislocation cores (or very close to them) or in some clusters with high density so that the Coulomb barrier, caused by captured electrons or holes, restricts their occupation.

More than that, the data for temperature dependence of magnetic susceptibility shows deviation from curie law between 20 and 50 K, which corresponds to the diminishing effective number of spins at low temperatures [5]. The anisotropy of spectrum also slightly changes and at $T < 20$ K corresponds to broken bonds in dislocation cores [6]. Since D-centers are deep states (as deep as 0.4 eV) electron redistribution between them or other processes changing the effective number of spins (exchange interaction for example) can only occur through a direct overlap of the broken bonds wave functions. Since all these data fit well with what can be expected for the chain of dislocation dangling bonds (DDB) one can propose that D-centers corresponds to chains of DDB.
Since DDB can act as deep traps with a large capture cross section both for electrons and holes, they should be very effective as recombination centers. In order to obtain additional data about this recombination process and the nature of D-centers we have investigated in this work the influence of saturation the D-centers ESR on the recombination time (so-called spin dependent recombination (SDR)).

Such kind of effect has been found first by Lepine for the surface recombination in Si [7]. Then we found SDR for D-centers in Si at low temperature [8] and Wosinski and Figieliski found SDR in plastically deformed Si at room temperature [9]. More recently experiments of this kind have been reported for amorphous Si films (Solomon et al, [10]).

Experimental method and Results

Si crystals grown by a noncrucible zone melt in vacuum doped with $10^{13}$ cm$^{-3}$ boron were plastically deformed by 2% in compression along $<$110$>$ at 680 °C. From TEM data a dislocation density of $(1.5$ to $3)\times10^9$ cm$^{-2}$ was obtained.

HF magnetic field ($F = 110$ Mc/s, $9 \times 10^3$ Mc/s or $3.6 \times 10^4$ Mc/s) applied to the sample perpendicular to the d.c. magnetic field $H_0$ and a weak white light was used to produce photoconductivity. A Si filter with a thickness 1 mm was placed in front of sample to provide a homogeneous generation of free carriers. The photocconductivity $\delta(H_0)$ of the sample was measured as a function of applied d.c. magnetic field $H_0$ with and without HF-magnetic field and the difference $\Delta\delta(H_0)$ was accumulated by computer.

Fig. 2 shows a typical SDR-spectrum (that is $\Delta\delta(H_0)/\delta$) and ESR-spectrum for D-centers.

So far as D-centers ESR spectrum consists of individual spin packets [5], the ESR signal can be saturated only locally during the sweeping
The dependence of SDR-signal on HF-power

\[ \Delta \delta / \delta \]  

**Fig. 3:**

The dependence of SDR-signal on HF-power

\[ H_0 \]  

over. It means that the amplitude of SPR spectrum doesn't correspond to the total effect. In order to obtain the right magnitude for SPR, we applied additional magnetic field \( H_M \sin (2\pi f_M t) \) parallel to \( H_0 \) with amplitude \( H_M \) greater then the spectrum width and with frequency \( f_M \) greater then \( (2\pi \tau^*)^{-1} \), where \( \tau^* \) is some characteristic time for SDR (in simplest model \( \tau^* \) is \( \tau_1 \)-spin-lattice relaxation time). Indeed as one can see at fig. 3, it caused increasing the SPR signal by factor 2 to 4. The value of \( \tau^* \) was calculated from the experimentally measured curves \( \Delta \delta / \delta \) v.s. \( f_M \).

Our measurements show that the \( \tau^* \) and \( \tau_1 \) depend only on light intensity but not on temperature in range 1.3 to 10 K and light intensities used. Fig. 4 presents the dependence of \( \tau_1 \) and \( \tau^* \) on sample conductivity, measured at \( T = 1.4 \) K. At last, Fig. 5 presents dependences of \( \tau^* \) and \( \Delta \delta / \delta \) on temperature for \( F = 110, 9 \cdot 10^3 \) and \( 3.6 \cdot 10^4 \) Mc/s.

**Discussion and possible interpretation of data**

For D-centers we have found the SDR-signal which has the same shape as ESR-spectrum and the amplitude which is almost independent on d.c. magnetic field in the range from 40 to \( 1.2 \cdot 10^5 \) Oe. The characteristic time constant \( \tau^* \) of SDR is noticeably longer then spin-lattice relaxation time for D-centers.

Several theoretical models were moved to explain SDR. The simplest one consider the trapping free electrons to the paramagnetic centers with spin \( S = 1/2 \) providing the final state with \( S = 0 \). If the spin-orbit interaction is not large, recombination transition will conserve total spin. It means that the initial configuration must be also \( S = 0 \) for the transition to take place.

In d.c. magnetic field both electrons and centers have a polarization
SDR-time $\tau^*$ v.s. temperature. Solid line 1 is theory. Solid line 2 is extrapolation for $\tau^*_f$. Since the projection operator for singlet is $P_S = 1/4 - S_z \cdot S_y$, the average probability for recombination is $W_R = 1/4 W_{RS} (1 - p_{PD})$. Saturation of ESR means that $P_D = 0$ and should lead to increase in recombination rate.

This model, however, has almost nothing to do with data obtained for it predicts the $\Delta \delta/5 \propto (H_0/T)^2$ and $\tau^* = \tau_1$ and gives the maximal value of effect which is much lower then the experimental one. The assuming a spin larger than 1/2 due to direct $|11|$ or indirect $|12|$ ferromagnetic exchange interactions between D-centers can explain the larger value of effect, but it also predicts the dependence on $H_0$.

A model of resonant heating of the exchange reservoir of D-centers spin system and localised dislocation phonons were proposed in $|13,14|$. But these models also gives the dependence on $H_0$.

The only model which predicts (at the first approximation) no dependence on $H_0$ is one proposed by Kaplan, Solomon and Mott $|15|$ for SDR in amorphous Si.

It uses quite a universal idea of recombination via intermediate localised pair state to the final state with $S = 0$. Examples of such recombination involving pairs are exciton or donor-acceptor recombination.

Let's try now to use this idea and to change the original model $|15|$ taking into account what we know about D-centers.

Let us suppose that D-centers corresponds to one-dimensional chains of DDB N-spins long. Holes can be traped to band 1 (fig. 1) and electrons - to band 2.
Following the explanation proposed in \cite{16} for microwave conductivity observed at low temperatures in dislocated Si and Ge, we should suggest that trapped electron and hole can move along the chain and the final recombination would take place when they reach the same DDB.

But this last process is not interesting for us at the moment because states 1, 2 are very deep and thermal activation of captured carrier back to \(E_c\) or \(E_V\) is not possible at \(T < 100\) K. Let us suggest now that the electrons can be trapped to band 1 mainly from some shallow states \(E_{cd}\) (fig. 1) where they can be trapped to from conduction band \(E_c\). It is quite reasonable to assume that states \(E_{cd}\) are due to the deformation potential of the dislocation. The electron in \(E_{cd}\)-state can be excited back to \(E_c\) or be trapped to DDB (band 1). In the last case the final state is assumed to have spin \(S = 0\) and the total spin conservation rule assumed to be observed in this process.

Then the probability for transition \(E_{cd} \rightarrow E_1\) is \(W_C = W_o \cdot W_S\), where \(W_S\) is the probability for pair electron in \(E_{cd} \rightarrow \text{DDB}\) to be in singlet state \(S = 0\), averaged for all DDB in given chain. If \(H_o \neq 0\), the DDB spins rotates around \(H_o\) not with the same frequency as \(E_{cd}\) electron spin. If \(\gamma (g_{DDB} - g_e) H_o \gg (\tau^*)^{-1}\), we can use \(W_S = 1/4 (1 - P_{e, \text{DDB}})\), \(W_P(P_{\text{DDB}})\), where \(p = \cos \theta\), and \(\theta\) is angle between \(H_o\) and spin, \(W_P(P_{\text{DDB}})\) is probability to have chain with given average value \(P_{\text{DDB}}\). However, it is not very easy to calculate \(W_P\) exactly, but for estimations we used a simple formula:

\[
W_P(P) = \frac{(N!)^4}{(2N!)^2} (N-N_\uparrow) ! (N_\uparrow)! \quad \text{and} \\
P = \frac{(N_\uparrow - N_\downarrow)}{N}, \text{assuming } \mu H_o/kT \ll 1 \quad \text{and} \quad N \gg 1.
\]

If \(n(p_e, P_{\text{DDB}})\) is the number of \(E_{cd}\)-electrons with given \(p_e\), trapped to \(E_{cd}\) near DDB-chain with given \(P_{\text{DDB}}\), then, in equilibrium:

![Fig. 6: The dependence of SDR-signal on light intensity. \(T = 1.4\) K, \(H_o = 0.33\) T.](image)
where $G$ is generation rate, $W_D$ - probability of electron activation from $E_{cd}$ to $E_c$, $W_f$ - probability for PDDB to be changed by HF-field or by spin-lattice relaxation.

then the recombination rate is

$$ R = \frac{1}{4} W_o \sum_{-1}^{+1} \frac{dP}{dP_{DDB}} \left( 1 - P_{C,DDB} \right) dp_c dp_{DDB} \quad (1) $$

and

$$ \tau^* = 1/G \sum_{-1}^{+1} \frac{dP}{dP_{DDB}} \left( 1 - P_{C,DDB} \right) dp_c dp_{DDB} \quad (2) $$

So, SDR depends on parameters $b = W_D/W_o$, $A = (\tau_1, W_o)^{-1}$ and $N$ at $T < 4$ K we know parameters $\tau^*$ and $\tau_1$ and the only free are $N$ and $W_o$. Fig. 6 presents the experimental data, obtained at different light intensity and calculated theoretical dependence for $N = 8$ and $W_o = 63$ sec$^{-1}$.

As to the dependence on temperature, we don't know the exact dependence $W_o$ and $W_D$ on $T$. Experimental data for $\tau_1$ are available only for $T < 6$ K and $T > 20$ K but we can use some rough extrapolation within 6 K to 20 K range. Solid lines in fig. 5 shows result of computer's calculation for $\Delta \delta/6$ and $\tau^*$ obtained under the assumption that $N = 8$,

$$ W_o = 63 + 1.5 \cdot 10^5 \exp(-E^*/kT) \quad \text{and} $$

$$ W_D = 25 + 2 \cdot 10^5 \exp(-E^*/kT), \text{where } E^* = 0.01 \text{ eV}. $$

Several points should be made now.

1. We neglected all possible exchange interactions. For example, if some weak exchange interaction $H_{C,-DDB}$ between $E_{cd}$-electron and DDB exist and $H_{C-DDB} > h\gamma (g_{DDB} - g_C) H_o$, we will be able to use a direction of $E_{cd}$-electron spin as axis and therefore use only one integration in (1) and (2). The result will be qualitatively similar, but the value $\Delta \delta/6$ being larger we should take $N \approx 20$ instead of $N = 8$.

2. As the $\Delta \delta/6$ is almost inversely proportional to $N$, the obtained value $N = 8$ doesn't mean the average length of chains. If we, for example, have Gaussian distribution of DDB-chains lengths with dispersion $\Delta N/N = 0.6 - 3$, then $N$ will be 16 not 8.

3. Let's estimate the distance between DDB-chains. Assuming the distance between DDB within chain $a^*$ to be $4 - 10 \AA$, we can calculate the dipole-dipole interaction as $H_{dd} = \mu_B/(a^*)^3 < 10 - 100$ Oe. Since the real width of spin-packets from ESR data is 0.5 - 1 Oe, we should suggest the existence of exchange interaction $H_c$ and from $\Delta H = H_{dd}^2 H_c < 10$ Oe we have $H_c \geq 200 - 2000$ Oe. Since the effective interaction between chains $W_{C-C}$ must be weaker the experimental value for $W_f$, we can write:

$$ W_{C-C} \leq g \frac{\mu_B \gamma^3}{T_o^3} H_c \leq 10. $$
That means that the distance from chain to chain should be larger than $r_0 = 70 \, \AA$. The reason for existence such gaps without spins along the dislocation may be the same as for disappearance D-centers after annealing at $T > 700 \, ^\circ\text{C}$. As it was proposed in [17] it may be some kind of core reconstruction.

4. What is the reason for a strong influence of light on the D-centers spin-lattice relaxation time $\tau$, observed? The simplest mechanism to which one can attempt to attribute it is an exchange interaction between DDB and free carriers. Then:

$$
\frac{d(1/T_{\text{DDB}})}{dt} = -nU(1/T_{\text{DDB}} - 1/T_C) - \frac{1/T_{\text{DDB}} - 1/T_0}{\tau_{1\text{DDB}}}
$$

$$
\frac{d(1/T_C)}{dt} = -N_{\text{DDB}}U(1/T_C - 1/T_{\text{DDB}}) - \frac{1/T_{\text{DDB}} - 1/T}{\tau_{1C}} - (1/T_C) \cdot G/n,
$$

where $T_{\text{DDB}}$, $T_C$ are spin temperature for DDB and electrons, $n$, $N_{\text{DDB}}$ are concentrations of electrons and DDB, $\tau_{1\text{DDB}}$ and $\tau_{1C}$ are original spin-lattice relaxation times for DDB and electrons, $U$ is exchange probability. Therefore

$$
(\tau_{1\text{DDB}})^{-1} \geq \frac{nU (\tau_{1C}^0)^{-1} + G/n}{N_{\text{DDB}} u + (\tau_{1C}^0)^{-1} + G/n} + 1/\tau_{1\text{DDB}}^0
$$

The generation rate $G$ can be estimated from the light intensity used, and $\tau_{1C}^0 \approx 10^{-5} \, \text{sec}$ according to [18]. But to fit our data using this formula we need the $n$ value to be by several orders larger, than it can be estimated by conductivity. The possible way to remove this discrepancy is to take into account the deformation potential in the dislocation core vicinity, which can lead to the much higher local concentration of carriers.

References

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