ESR and spin relaxation of deep centers in semiconductors in the presence of photoelectrons (Si:Fe^0)

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An investigation was made of the influence of photoelectrons on the ESR and spin relaxation of deep centers in semiconductors in the specific case of Si:Fe^0. It was established that the appearance of conduction electrons generated by optical illumination reduced the ESR signal intensity and gave rise to photoelectron-stimulated spectral diffusion in an inhomogeneously broadened ESR line of Fe^0. Heating photoelectrons by an electric field resulted in a further reduction in the ESR signal of Fe^0 because of an increase in the effective temperature of the photoelectrons. The observed behavior was explained by exchange scattering of photoelectrons on Fe^0 centers. Allowance for photoelectron recombination processes made it possible to explain the reduction in the ESR signal which occurred as a result of optical illumination. A new mechanism of spectral diffusion in inhomogeneously broadened ESR lines was suggested: this diffusion was due to double exchange scattering of carriers by paramagnetic centers. A comparison of the theory with experiment yielded the cross section for the exchange scattering of electrons by Fe^0 impurities and the dependence of the spin-lattice relaxation time of hot photoelectrons on their effective temperature.

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1. INTRODUCTION

Studies of the influence of carriers on the ESR and spin relaxation of deep impurity centers in semiconductors are of considerable interest because they can provide information on various characteristics of carriers in a crystal and on the mechanism of the interaction between carriers and local centers.

The influence of photoelectrons on the spin relaxation of shallow phosphorus donors in silicon was discovered by Feher and Gere.[1] They established that the reduction in the relaxation time of Si : P could be explained satisfactorily by the exchange scattering of electrons on phosphorus impurity centers.[2] However, some experimental observations, particularly the fall of the ESR signal due to illumination of the sample, were not explained.

Deep impurity centers in semiconductors are more complex and have been investigated much less than shallow donors. In particular, in the case of deep centers, we have not only the exchange mechanism of the spin-electron coupling but also the electric dipole mechanisms of the interaction between paramagnetic centers and an electric field generated by high-frequency plasma oscillations of electrons[3] and individual carriers.[4]

The present paper reports the first investigation of the interaction of photoelectrons with deep centers in the specific case of Si : Fe^0. We found that the exchange scattering of electrons was the predominant mechanism in this system.

We developed a consistent theory of the interaction between photoelectrons and paramagnetic centers, making allowance for the homogeneous broadening of the ESR lines and for photoelectron recombination processes. The results obtained by Pines et al.[2] were found to be the special case of this theory. In contrast to[1], in which case the appearance of photoelectrons altered the rate of the spin-lattice relaxation of phosphorus impurities and of the cross relaxation between the components of the hyperfine structure in the ESR spectrum, in our case, the influence of photoelectrons, was manifested by the appearance of spectral diffusion along the ESR line of Fe^0.

We established that the experimentally observed fall in the ESR signal due to illumination of a sample was essentially associated with the rate of photoelectron recombination. We also studied experimentally and theoretically the interaction of deep centers with hot photoelectrons. We found that experiments of this kind could be used to determine the dependence of the spin-lattice relaxation rate of hot electrons on their effective temperature, and we found this dependence.

2. EXPERIMENTS

Electron spin resonance and spin relaxation of interstitial Fe^0 centers in silicon were observed at $T = 4.2°K$ at 9.2 GHz using a superheterodyne ESR spectrometer (relaxometer). The ESR spectrum of Fe^0 was a single line ($g \approx 2.07$) with an anisotropic width.[5] All the measurements were carried out in a field $\mathbf{H} \parallel [100]$, in which the line width was minimal.

Since the Fe^0 line was inhomogeneously broadened because of the superhyperfine interaction between paramagnetic centers and the Si^{29} nuclei and because of the interaction with local stresses in a crystal (the latter were responsible for the width anisotropy), the relaxation time could be measured by the "hole burning" method by analogy with[6] or by the pulse saturation of the whole ESR line. Both methods were used to determine the magnetization recovery time in the absence of optical illumination and they gave the same value $\tau_1 \approx 1.2 \times 10^{-2}$ sec. This indicated that the value of τ_1 was the spin-lattice relaxation time and the processes of spectral diffusion along the ESR line of Fe^0 were ineffective.

We investigated silicon samples of KÉF-15 grade (phosphorus concentration $\sim 2.5 \times 10^{14}$ cm^{-3}) doped with iron ($N \approx 10^{16}$ cm^{-3}). At $T = 4.2°K$, the resistivity ρ

was $5 \times 10^9\ \Omega$.cm. Conduction electrons were created by illumination through a quartz light guide using an incandescent lamp of 220 W power. The effective photon flux was $\sim 4 \times 10^{15}$ photons/sec. Illumination reduced ρ by about three orders of magnitude. Using the electron mobility $\mu \approx 1200\ cm^2 \cdot V^{-1} \cdot sec^{-1}$, typical of iron-doped silicon,[7] we determined the average photoelectron density $n_0 \approx 2 \times 10^9\ cm^{-3}$. These results were used to find the photoelectron recombination time $\tau \approx 3 \times 10^{-8}$ sec. This value of τ was in good agreement with the measured[8] electron-capture cross section of Si : Fe^0.

Illumination produced the following two effects.

1. The intensity of the ESR signal of Fe^0 decreased to $A^* \approx 0.75A_0$ (A_0 was the signal intensity in the absence of illumination).

2. The filling time of a "hole" decreased to $\tau_f \approx 4 \times 10^{-3}$ sec. Various clear signs of spectral diffusion along the ESR line were also observed: these were the broadening of a "hole" compared with the width in the absence of illumination and a reduction in the total ESR line intensity under "hole burning" conditions. Direct proof that the filling of a "hole" was accelerated by the spectral diffusion along the ESR line was the observation that, after pulse saturation of the whole line, the magnetization recovery time (spin-lattice relaxation time) was not affected by illumination.

Moreover, we observed the influence of photoelectron heating in an electric field on the ESR signal intensity. Figure 1 shows the current-voltage characteristic of a sample together with the dependence of the relative intensity of the ESR signal A/A* on E. We found that $j \propto E$ in a wide range of electric fields and this was followed by a steep rise of the current right up to the breakdown value, identified by an arrow in Fig. 1. Beginning from a certain value of E, we observed a reduction in the ESR signal intensity. This indicated that an increase in the effective temperature of conduction electrons during their heating raised the spin temperature of the investigated paramagnetic centers.[1)]

3. THEORY

We shall consider the interaction of photoelectrons with paramagnetic centers in the case of inhomogeneous broadening of the ESR lines of these centers and we shall allow for photoelectron recombination. The need to make this allowance arises from the fact that a reduction in the ESR signal intensity due to illumination

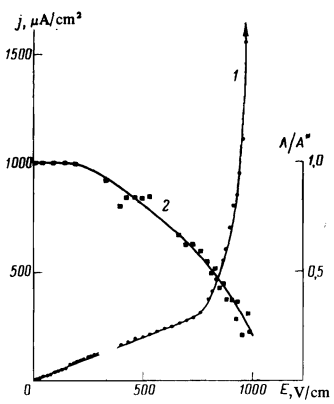

FIG. 1. Current-voltage characteristic (1) and dependence of the ESR signal intensity on the electric field (2) applied to Si : Fe^0.

is evidence of direct thermal contact between the spin systems of the photoelectrons and paramagnetic centers. In fact, the difference between the populations of the photoelectron levels does not generally correspond to the Boltzman value at the lattice temperature and it differs from this value by an amount which increases with reduction in the photoelectron recombination time compared with the spin relaxation time.[9] The spin temperatures of the photoelectrons and the paramagnetic centers interacting with them are then higher than the lattice temperature, and this reduces the ESR signal intensity.

If the paramagnetic centers are in thermal contact with the kinetic degrees of freedom of the electrons, which is particularly true in the case of the electric dipole mechanism of the spin-electron coupling,[3,4] the spin temperature of the centers corresponds to the temperature of the kinetic degrees of freedom, which—in the absence of carrier heating—is practically identical with the lattice temperature.[2)]

The processes of energy exchange between the spin systems, lattice, and kinetic degrees of freedom of electrons are shown schematically in Fig. 2. When the exchange scattering predominates, these processes can be described by the following kinetic equations:

$$\frac{\partial \beta(\omega)}{\partial t} = -nU[\beta(\omega) - \beta_e] - \frac{\beta(\omega) - \beta_L}{\tau_1}, \tag{1}$$

$$\frac{\partial \beta_e}{\partial t} = -NU[\beta_e - \beta] - \frac{\beta_e - \beta_k}{\tau_e} - \frac{\beta_e}{\tau},$$

$$\beta = \int d\omega \rho(\omega) \beta(\omega), \tag{2}$$

which must be supplemented by the equation governing the photoelectron density n in the conduction band

$$\frac{\partial n}{\partial t} = -\frac{n}{\tau} + S. \tag{3}$$

Here, $\beta(\omega)$ is the reciprocal temperature characterizing an inhomogeneously broadened ESR line with a form factor $\rho(\omega)$: β_S, β_k, and β_L are the reciprocal temperatures of the photoelectron spin system, kinetic degrees of freedom of photoelectrons, and the lattice, respectively; U is the probability of exchange scattering; S is the number of photoelectrons created per second in a unit volume of the sample; τ_S is the spin-lattice relaxation time of the conduction electrons.

The spin-relaxation time of paramagnetic centers is usually considerably longer than the photoelectron recombination time. This makes it possible to simplify the system (1)—(3) because, in the $t \gg \tau$ case, the number of photoelectrons in a band is steady ($n_0 = S$) and their spin temperature follows adiabatically the value of $\bar{\beta}(t)$ [in Eq. (2), we may assume that $\partial \beta_S / \partial t = 0$]. In this case, the evolution $\beta(\omega, t)$ is described by just one equation

$$\frac{\partial \beta(\omega)}{\partial t} = -n_0 U \left[\beta(\omega) - \frac{NU\bar{\beta} - \tau_e^{-1}\beta_k}{NU + \tau_e^{-1} + \tau^{-1}} \right] - \frac{\beta(\omega) - \beta_L}{\tau_1}. \tag{4}$$

The solution of Eq. (4) is

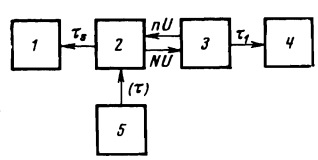

FIG. 2. Processes involving energy exchange in Si : Fe^0 in the presence of photoelectrons: 1) kinetic degrees of freedom of photoelectrons; 2) photoelectron spins; 3) Fe^0 centers; 4) lattice; 5) photoelectron source.

$$\beta(\omega, t)-\beta_0=\exp(-t/\tau_1)\{[\beta(\omega, 0)-\beta(0)] \times\exp(-n_0Ut)+[\beta(0)-\beta_0]\exp(-t/\tau_1^*)\}, \quad (5)$$

$$\beta_0=\frac{n_0U\tau_s^{-1}\beta_k+\tau_1^{-1}(NU+\tau_s^{-1}+\tau^{-1})\beta_L}{n_0U(\tau_s^{-1}+\tau^{-1})+\tau_1^{-1}(NU+\tau_s^{-1}+\tau^{-1})}, \quad (6)$$

$$\frac{1}{\tau_1^*}=\frac{n_0U(\tau_s^{-1}+\tau^{-1})}{NU+\tau_s^{-1}+\tau^{-1}}. \quad (7)$$

The expressions (5) and (6) determine the nature of the spin relaxation and the steady-state value of the spin temperature of paramagnetic centers in the presence of photoelectrons.

In the case of homogeneous broadening of ESR lines, we have $\beta(\omega, 0) = \bar{\beta}(0)$ and the results obtained by Pines et al.[2] follow from the general expression (5).

4. DISCUSSION OF EXPERIMENTAL RESULTS

Pulse Saturation

It follows readily from Eq. (5) that the recovery of the total magnetization, proportional to $\bar{\beta}(t)$, is described by a simple exponential law with a rate $\tau_1^{-1} + (\tau_1^*)^{-1}$. The quantity τ_1^* governs the degree of influence of the carriers on the spin-lattice relaxation of paramagnetic centers. Since there is no reduction in the spin-lattice relaxation time of Fe^0 due to the appearance of photoelectrons, we may assume that $\tau_1^* > \tau_1$. It is clear from Eq. (5) that, in the presence of electrons, we must allow not only for the spin-lattice relaxation but also for the equalization of the spin temperature along the ESR line at a rate n_0U without energy transfer to the lattice. This process represents the photoelectron-stimulated spectral diffusion resulting from the double exchange scattering of carriers by paramagnetic centers. In each exchange scattering event, an electron receives energy from a center corresponding to the saturation part of the EPR line and, in the next exchange event, this energy is given up to an unsaturated paramagnetic center.

In our experiments, we have $\bar{\beta}(0) \approx 0.9\beta_0$ because of saturation of a small part of the ESR line of the order of $0.1\Delta H$. Then, at moments defined by

$$t<(n_0U)^{-1}\ln[\beta(0)/[\beta_0-\beta(0)]]\approx 2(n_0U)^{-1} \quad (a)$$

the second term in the brackets of Eq. (5) can be ignored. In this case, the filling of a "hole" is described by a single exponential function with the time constant

$$\tau_f^{-1}=n_0U+\tau_1^{-1}. \quad (8)$$

Substituting in Eq. (8) the experimental values of τ_f, τ_1, and n_0, we find the exchange scattering probability U and the exchange scattering cross section σ, bearing in mind that $U = 2\sigma V$ (V is the average velocity of electrons at $T = 4.2°K$). It is found that $\sigma \approx 1.7 \times 10^{-14}$ cm^2. It should be noted that a value of σ of similar order of magnitude can be obtained by using the estimate $\sigma = 144\pi a^2$[2] (which is only a very rough approximation in the case of deep centers) and assuming that the radius a of the impurity state is the radius of the Fe shell with the $3d^8$ configuration ($a \approx 0.4$ Å[10]).

Steady-State Conditions

The relative change in the steady-state magnetization of paramagnetic centers in the presence of photoelectrons but in the absence of heating ($\beta_k = \beta_L$) is described, in accordance with Eq. (6), by the relationship

$$\frac{A^*}{A_0}\equiv\frac{\beta_0}{\beta_L}=\frac{1}{1+n_0\tau_1/(N\tau)} \quad (9)$$

obtained on the assumption of the above inequalities $\tau_1^* > (n_0U)^{-1}$, $\tau_1^* > \tau_1$. For the values of τ_1 and τ found above, we obtain $A^*/A_0 \approx 0.9$. The agreement with the experimental value of $A^*/A^0 \approx 0.75$ can be regarded as satisfactory in view of the errors made in the measurements of the parameters occurring in Eq. (9).

It should be noted that, if $\tau_1^* \gg (n_0U)^{-1}$, it follows from Eq. (7) that $NU \gg (\tau_S^{-1} + \tau^{-1})$, and Eq. (2) yields $\beta_S = \beta_0$. This means that the spin relaxation of electrons involves paramagnetic centers and not the kinetic degrees of freedom. These degrees of freedom are involved in the $NU \ll (\tau_S^{-1} + \tau^{-1})$, case, which gives $\beta_S = \beta_L(1 + \tau_S/\tau)^{-1}$.

Hot Photoelectrons[3)]

The explanation of the fall of the ESR signal as a result of electron heating follows directly from Eqs. (5)–(7). According to Eq. (6), the fall due to the electric-field heating of carriers is given by

$$\frac{A}{A^*}\equiv\frac{\beta_0(T_c)}{\beta_0(T_0)}\approx\frac{1+n_0\tau_1/(N\tau)+(T_0/T_c)x(T_c)}{1+n_0\tau_1/(N\tau)+x(T_c)}, \quad (10)$$

The dependence $\tau_S(T_c)$ can be found by comparing Eq. (10) with the experimental results provided we know the relationship between E and T_c. This relationship depends on the actual carrier scattering mechanisms and can be found from the equation describing the balance between the energy acquired by an electron from the electric field and lost by inelastic scattering[13]

$$\left\langle\frac{\partial\varepsilon}{\partial t}\right\rangle_s=e\mu E^2. \quad (11)$$

It follows from the current-voltage characteristic (Fig. 1) that the conduction is governed by the elastic scattering of carriers on neutral impurities (μ is independent of E). If we consider the inelastic scattering of carriers by zero-point vibrations of the lattice, which are important at low temperatures,[13] we find from Eq. (11) that

$$T_c=CE^{4/3}, \quad C=2.5\cdot10^{-2}\ [\mathrm{K\ (cm/V)^{4/3}}]. \quad (12)$$

Figure 3 shows the dependence $x(T_c/T_0)$ deduced from curve 2 in Fig. 1 by applying the relationship (12). It is clear that in the range $10 < (T_c/T_0) \lesssim 50$ the quantity x and, consequently, τ_S^{-1} are both proportional to T_c^2 (the scale of values of τ_S^{-1} is given on the right of Fig. 3). In the range $T_c/T_0 > 50$, the dependence of x on T_c/T_0 becomes steeper. This range corresponds to the part of the current-voltage characteristic (Fig. 1) where the shallow phosphorus donors are clearly impact-ionized by hot electrons and, consequently, the change in x is mainly due to an increase in the carrier density.

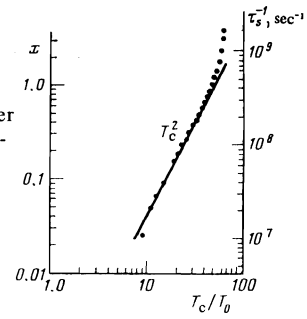

FIG. 3. Dependence of the parameter $x = n\tau_1/(N\tau_S)$ on the effective temperature of hot electrons.

It follows from Fig. 1 and Eq. (12) that the impact ionization of the phosphorus donors becomes important starting with $kT_c \approx 0.4\epsilon_i$ (ϵ_i is the donor ionization energy), which is typical of the impurity breakdown in semiconductors at low temperatures.[14] It is not possible to determine the nature of the temperature dependence of τ_s^{-1} in the range $T_c/T_0 < 10$ and to estimate τ_s^{-1} at a temperature $T_s = T_0$ because, firstly, the experimental accuracy is insufficient to determine (in this temperature range) the value of x by comparing Eq. (10) with the experimental results and, secondly, the relationship (12) is valid only if $T_c/T_0 \gg 1$.

CONCLUSIONS

The above discussion shows that the ESR and spin-relaxation measurements are effective methods for investigating the interaction between carriers (photoelectrons) and deep impurity centers in semiconductors. Important information can be obtained both on electrons (spin scattering mechanisms and spin relaxation times of hot electrons) and on deep centers (mechanisms of interaction with carriers and exchange scattering cross sections).

[1)]Control experiments established that there was no significant heating of the sample because of the dissipated Joule heat.

[2)]This occurs because the time usually needed to establish an equilibrium distribution of the electron energies is $\tau_\epsilon \ll \tau$.

[3)]The influence of hot electrons on the ESR of shallow phosphorus donors in silicon was observed in [11,12].

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