Photoconductivity anomalies in semiconductors doped with magnetic impurities

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An anomalous photoconductivity was dectected in silicon doped with rare-earth elements. It is shown that the appearance and disappearance of an impurity photoconductivity in semiconductors can be controlled by varying the concentrations of a shallow donor impurity in rare-earth element (REE) impurities.

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This paper presents the experimental results of an investigation of the photoconductivity of silicon doped with phosphorus and rare-earth element impurities (gadolinium and praseodymium).

Silicon single crystals containing phosphorus as the base impurity were doped with the REE during their growth from the melt by using Czochralski method. The concentration of the REE impurity in the crystals which was determined by neutron-activation analysis. was varied: 1) from 10^{13} cm^{-3} in the upper part of the ingot to 10^{19} cm^{-3} in the lower part in the gadolinium-doped silicon [phosphorus concentration $[N(P) \approx 2 \times 10^{13}$ cm$^{-3}]$; 2) from 10^{13} cm^{-3} in the upper part of the ingot to 10^{20} cm^{-3} in the lower part in the praseodymium-doped silicon $[N(P) \approx 5 \times 10^{13}$ cm$^{-3}]$.

The photoconductivity spectra were recorded at $T = 77$ K by means of an IKS-21 monochromator with an NaCl prism. We used 100% modulation of the light intensity at a frequency of 30 Hz. The Dewar flask had leucosapphire windows. The measured photoresponse amplitudes were normalized to the number of quanta striking the sample.

The experimental photoconductivity spectra obtained are shown in Fig. 1. We can see that the impurity photoconductivity behaves anomalously in the silicon crystals doped with REE impurities. At low REE concentrations (10^{13}–10^{16} cm^{-3}) the impurity photoconductivity is missing. Only the intrinsic photoconductivity of silicon can be observed at these concentrations (see curves 1 in Figs. 1a and 1b). The impurity photoconductivity appears in a nearly "jump-like" fashion at REE impurity concentration $N > 10^{16}$ cm^{-3} (see Figs. 1a and 1b). With a further increase in the REE impurity concentration, the impurity photoconductivity disappears suddenly $[N > (3\text{–}5) \times 10^{18}$ cm$^{-3}]$ (see curves 5 in Figs. 1a and 1b). At high REE concentrations, just as at low concentration $N \lesssim 10^{16}$ cm^{-3}), only the photoconductivity due to band-to-band transitions is present.

Such photoconductivity in semiconductors can be explained in the following manner. The energy of the impurity exchange level in the forbidden band of semicon-

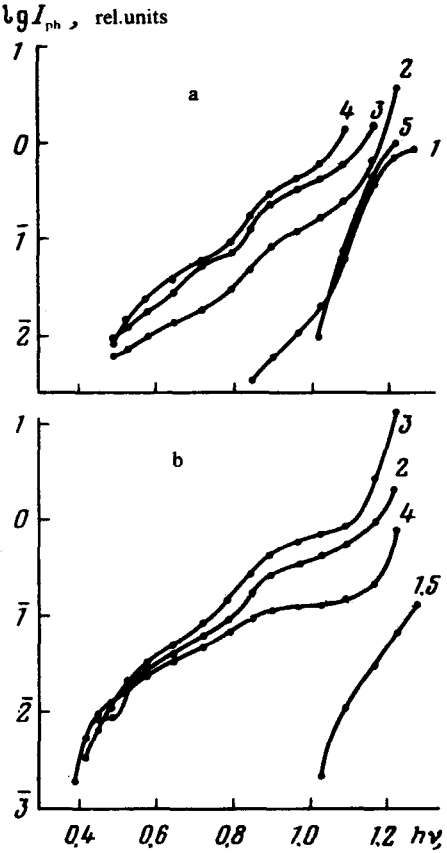

FIG. 1. Dependence of the photocurrent of the quantum energy of light for silicon samples doped with REE impurities. (a) Silicon doped with gadolinium: 1, N(Gd) from 10^{13} cm^{-3} to 10^{16} cm^{-3}; 2, 5×10^{16} cm^{-3}; 3, 3×10^{17} cm^{-3}; 4, 5×10^{17} cm^{-3}; 5, 3×10^{18} cm^{-3}. The phosphorus concentration was 2×10^{13} cm^{-3} in all the samples. (b) Silicon doped with praseodymium: 1, N(Pr) from 10^{13} cm^{-3} to 10^{16} cm^{-3}; 2, 10^{17} cm^{-3} 3, 10^{18} cm^{-3}; 4, 5×10^{18} cm^{-3}; 5, 5×10^{19} cm^{-3}. The phosphorus concentration was 5×10^{13} cm^{-3} in all the samples.

ductors is of the order of the exchange interaction constant of an electron in the conduction band with a magnetic impurity (the energy operator of this interaction has the form $\hat{\mathscr{H}} = a(\hat{\mathbf{S}}\hat{\mathbf{L}})\delta(\mathbf{r}-\mathbf{R})$, where $\hat{\mathbf{S}}$ and $\mathbf{r}$ are the spin and radius vector of an electron in the conduction band, $\hat{\mathbf{L}}$ and $\mathbf{R}$ are the spin and radius vector of a rare-earth impurity, a is the exchange interaction constant of an electron in the conduction band with the f-electrons of the REE impurity.[1] Because of the narrowness of the potential well, the capture cross section from the conduction band in the REE impurity is very small. Therefore the capture of a conduction-band electron in the exchange level is possible only with the participation of a shallow donor impurity (phosphorus) when the electron is initially captured in the shallow donor impurity and then goes to the REE (the capture cross section of a conduction-band electron at the phosphorus center is large[2] $\sigma_{capt} = 2.6\times10^{-13}$ cm^2). Thus, only the + REE phosphorus centers exhibit

photoelectric activity.

Assuming that the probability of an electron transition from phosphorus to REE is proportional $|\psi(r)|^2 \sim \exp(-2r/r_B)$, we have for the characteristic capture time τ of a conduction-band electron via phosphorus in the exchange level

$$\frac{1}{\tau} \approx N(P)\,\sigma_{\text{capt}}\; v \exp\left(-\frac{2r}{r_B}\right), \tag{1}$$

where r is the distance between the phosphorus and the REE, and r_B is the Bohr radius of an electron localized in the shallow donor center (phosphorus in silicon $r_B = 17$ Å, $v = 1.03 \times 10^7$ cm/sec is the average velocity of electrons in the conduction band).

Since only the centers for which $r \lesssim T$ (where T is the modulation period $T = 1/\nu_0$, $\nu_0 = 30$ Hz is the modulation frequency) appear in the photoconductivity, only those REE atoms are photoelectrically active which are at a distance $r < r_{\text{cr}}$ from the shallow donor center. Here r_{cr} is determined from the condition $\tau(r_{\text{cr}}) = T$:

$$r_{\text{cr}} = \frac{r_B}{2} \ln\left[N(P)\sigma_{\text{capt}}\, vT\right]. \tag{2}$$

It is easy to determine the concentration of active REE center N_a, i.e., the centers located at a distance $r < r_{\text{cr}}$ from the phosphorus centers if we assume that the REE is randomly distributed in the sample:

$$N_a = N(P)\left[1 - \exp(-NV)\right] \tag{3}$$

N is the REE impurity concentration, $V = \frac{4}{3}\pi r_{\text{cr}}^3$.

If the impurity photocurrent is proportional to the number of photoelectrically active impurity centers, we can see that the impurity photoconductivity appears at an REE concentration $N_{\text{cr}} \sim V^{-1}$ (see Fig. 1). The calculated dependence of the impurity

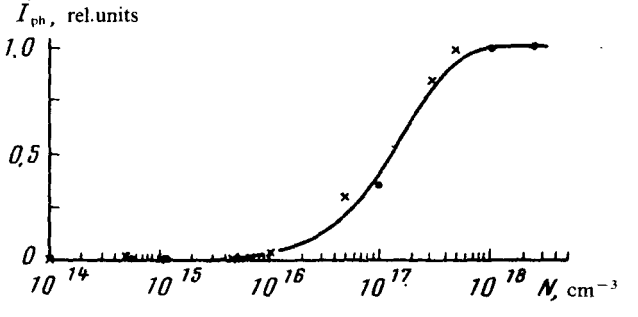

FIG. 2. Dependence of the impurity photocurrent on the REE concentration. x represents gadolinium-doped silicon and denotes praseodymium-doped silicon. The solid curve represents the calculated dependence.

photocurrent on the concentration N of the REE impurity is shown in Fig. 2. Also shown in this figure are the experimental values of the impurity photocurrent $\bar{I}_{ph}$ in the samples with different REE concentrations obtained from the data of Figs. 1a and 1b. The value of $\bar{I}_{ph}$ is obtained by integrating the photoconductivity spectra in the impurity region. We assume that $I_{ph}(\mathrm{Pr}) = 2.5 I_{ph}(\mathrm{Gd})$, since in the first case $N(P) = 5\times 10^{13}\ \mathrm{cm}^{-3}$ is 2.5 times greater than in the silicon containing gadolinium.

As shown in Fig. 2, the probability for the appearance of photoactive centers N_a at low REE concentrations ($< 10^{16}\ \mathrm{cm}^{-3}$) is very low and the impurity photocurrent is equal to zero, as indicated in Figs. 1 and 2. As the REE concentration ($N > 10^{16}\ \mathrm{cm}^{-3}$) increases, the number of photo-electrically active centers N_a increases, leading to a rapid increase of $\bar{I}_{ph} \sim N_a$. With a further increase in N the concentration N_a reaches the value of $N(P)$, which leads to saturation of the impurity photocurrent (see Figs. 1 and 2).

We shall now determine the cause for the disappearance of impurity photoconductivity at higher REE concentrations. The impurity photoconductivity disappears at concentrations that give rise to precipitation of the second phase. Since the second-phase regions, which are formed at high REE concentrations, have large linear dimension $R > 0.1\ \mu\mathrm{m}$,[3] the electrons will be captured rapidly by these regions, where energy is reduced relative to the bottom of the conduction band as a result of s-f exchange interaction. (Note that a similar problem was considered in Ref. 4.)

The cross section for capture of conduction electrons by the second-phase regions is $\sigma_1 \sim R^2$ and the concentration of the second-phase regions $\mathcal{N}$ greatly exceeds the capture cross section and the number of donor centers $N(P)$, *i.e.*,

$$\mathcal{N} \sim \frac{N}{N_2 \frac{4}{3}\pi R^3} > N(P); \qquad \sigma_1 \sim R^2 > \sigma_{capt} \sim 10^{13}\ \mathrm{cm}^2$$

(here N_2 is the REE concentration in the second-phase region, $N_2 \sim 10^{20}\ \mathrm{cm}^{-3}$, for gadolinium centers in silicon and N is the REE concentration in the crystal.) Therefore, all the electrons are captured by the second-phase regions, and the population of the deep exchange centers associated with phosphorus (phosphorus + REE) approaches zero. This, of course, leads to disappearance of the impurity photoconductivity observed in the experiment (see curves 5 in Figs. 1a and 1b). This is confirmed by the results of a measurement of the resistivity at $T = 77$ K in samples containing a second phase. The second phase abruptly increases the resistivity.

Thus, the impurity photoconductivity in semiconductors can be controlled by varying the concentrations of the shallow donor impurity and the REE impurities.

We have obtained similar results in silicon doped with other REE impurities and with different elements.

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[1]S. V. Vonsovskiĭ, Magnetizm (Magnetism, Nauka, Moscow, 1971, p. 553.
[2]N. T. Bagraev, L. S. Vlasenko, and R. A. Zhitnikov, Pis'ma Zh. Tekh. Fiz. 3, 269 (1977) [Sov. Tech. Phys.

Lett. **3**, 107 (1977)].
[3]A. R. Salmanov, G. I. Aleksandrova, G. I. Voronkova, M. A. Il'in, V. P. Grishin, and Yu. A. Karpov, Izv. Akad. Nauk SSSR Ser. Neorg. Mater. **12**, 85 (1978).
[4]E. L. Nagaev, Fizika magnitnykh poluprovodnikov (Physics of Magnetic Semiconductors), Nauka, Moscow, 1979, p. 225.