New shallow donors in silicon

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Five new shallow donor centers were observed in *p*-type silicon grown by the Czochralski method. The ionization energy of these centers is in the range 35.2–37.14 MeV, and the energy spectra are similar to the donor spectra for the V group in silicon.

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We observed a group of shallow donors with "hydrogen-like" spectra in the investigation of *n*-type silicon, by using the photoelectric spectroscopy method.[1] Five such donors were found (D_1–D_5). These donors have been observed in different combina-

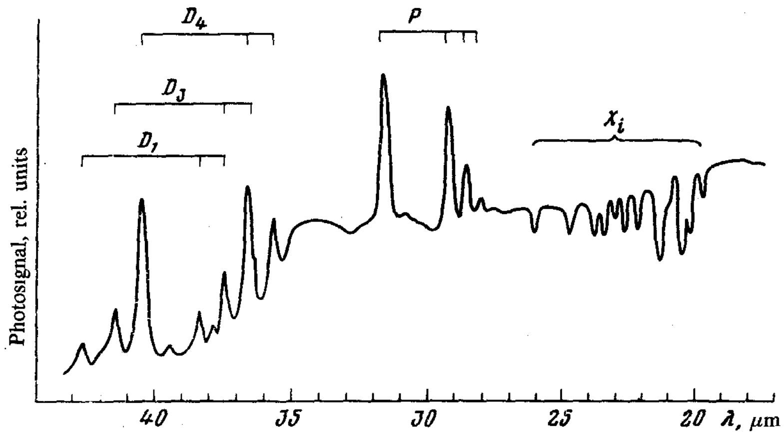

FIG. 1.

combinations in different samples. Their ground states lie in the ionization energy interval $\vec{\epsilon}_i$ from 35.2 to 37.14 MeV and, thus, the ionization energy $\vec{\epsilon}_i$ for these donors is less than that for the elements of group V in silicon.

The samples were grown by the Czochralski method. In addition to the D_i donors, they contain phosphorus and oxygen in a concentration of $(1-2)\times 10^{18}/\text{cm}^3$. The total concentration of the noncompensated donors in these samples is $N_D - N_A \sim 10^{14}/\text{cm}^3$. Figure 1 shows the spectrum of the impurity photoconductivity of one of these samples obtained at $T = 20$ K. In addition to the series of lines due to photothermal ionization of phosphorus and the D_1, D_3, and D_4 donors, the usual impurity photoconductivity associated with photoionization of the indicated donors is clearly evident. Table I gives the observed optical transition energies and the ground state energies of the D_i donors in the photothermal ionization spectra. For comparison, Table I gives the energies of the ground-state and of the corresponding transitions, which were calculated in the effective-mass approximation.[2]

TABLE I

Donor	Optical transition energies, MeV			
	$1s \rightarrow 2p_\pm$	$1s \rightarrow 3p_\pm$	$1s \rightarrow 4p_\pm$	$\vec{\epsilon}_i$
Effective mass approximation	24.87	28,15	29.08	31,27
D_1	29,03	32,26	33. 19	35,20
D_2	29.78	33,00	33,96	35,95
D_3	29,96	33.19	—	36.13
D_4	30,58	33.90	34.8	36,75
D_5	30.97	34.24	35,2	37,14

In addition to the photothermal ionization peaks in the short wavelength region of the photoconductivity spectrum, we can also see deep valleys due to nonphotoelectric absorption of radiation by deeper centers. These centers were observed earlier[3,4] in optical absorption spectra, and were interpreted as thermal donors that originate in silicon as a result of processing.

To determine whether there exists a correlation between the observed D_i donors and the known thermal donors responsible for the absorption lines X_i, we subjected several samples to thermal processing that is usually used for the production of thermal donors (430°C, 5–10 hr) and for their destruction (600°C, 15–30 min). It turned out that the D_i donors, which are present in the initial material, remain after the thermal processing at 430, 600, and even 1250 °C. Thus, sometimes one kind of donors (D_i) as a result of thermal processing change into other kinds of donors (D_k) of the same group. The amplitudes of the peaks of photothermal ionization of the D_i donors relative to the corresponding amplitudes of the phosphorus peaks for such heat processing remain almost constant. At the same time, after heating the samples at $T = 430$ °C, the absorption lines X_i remain unchanged or are produced if there were none in the original material, and then disappear after heat processing at a higher temperature, which is characteristic for thermal donors. Thus we can say, that the five donor centers D_1–D_5 in silicon are not related to the known thermal donors, and that the latter appear in the impurity photoconductivity spectra of silicon in the region of phosphorus photoionization as centers that have nonphotoelectric absorption in this energy region.

It should be noted that the D_i donors are present in crystals grown under conditions where the diameter of the growing crystal is almost equal to the inside diameter of the quartz crucible containing the melt, so that there is no free surface for the melt, and evaporation of oxygen and other impurities is difficult. The D_i donors have not been observed in crystals whose diameters are much smaller than that of the crucible in which they were grown. At present, we are not able to determine which impurities are responsible for the D_i donors. Since the difference in energies of the ground states of the D_i donors are small (fractions of a millielectron volt between the neighboring centers), and since these donors merge as a result of heat treatment, we can assume that these donors are complexes of the same nature that differ only in the relative location of the components in the silicon lattice or in number.

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