Inversion of impurity photoconductivity type in a doped semiconductor

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Light in the fundamental absorption band erases that component of the impurity photoconductivity which is due to the predominant dopant in p-type doped silicon and intensifies the component due to small amounts of residual donor impurities.

The illumination of a semiconductor with light in its fundamental absorption band at a low temperature leads to an optical charge exchange of impurities and to the onset of an impurity photoconductivity which is caused by not only the predominant dopant but also compensating dopants.[1] In pure and slightly doped silicon and germanium crystals, the ratio of the photoconductivity component corresponding to the compensating dopants ($\Delta\sigma_{\text{comp}}$) to that corresponding to the predominant dopant ($\Delta\sigma_{\text{pre}}$) increases with increasing intensity of the illumination and reaches saturation at a level[1-3] $\Delta\sigma_{\text{comp}}/\Delta\sigma_{\text{pre}} < 1$ (this ratio is usually determined from the measured ratio of the amplitudes of a selected pair of lines in the line parts of the photoconductivity spectrum associated with a photothermal ionization of impurities). In other words, in all known experiments in a semiconductor which has undergone charge exchange the impurity photoconductivity due to the dopant present in the greatest quantity in the crystal remains the predominant component of the photoconductivity. In the present letter we report experiments with exactly the opposite result: In a crystal doped to a high impurity concentration, the photoconductivity corresponding to this impurity disappears entirely when the exposure to light begins, and a photoconductivity, due exclusively to a compensating impurity present in the sample in an extremely small amount, arises.

The test samples are made of silicon doped with gallium or boron to a concentration of $(2\text{–}5)\times 10^{16}$ cm^{-3}. The concentration of the compensating dopants, determined from the temperature dependence of the Hall coefficient, lies in the range 5×10^{-3}–5×10^{-5} of the concentration of the predominant dopant. The measurements are carried out on a Fourier spectrometer either by the standard method or by a contactless method.[4] The light in the fundamental absorption region, from an illuminator with an incandescent lamp with a maximum power of 20 W and an angular aperture of 35°, is transmitted to the sample through a KRS-6 filter and a hollow lightguide consisting of a 1-m-long stainless-steel tube. Figure 1 shows the photoconductivity in the spectra of one of the Si:Ga samples ($N_{\text{Ga}} = 2.5\times 10^{16}$ cm^{-3}, $N_{\text{comp}} = 1.4\times 10^{12}$ cm^{-3}) measured (a) without and (b) with illumination in the fundamental absorption band. We see that in the absence of the illumination, the spectrum of the impurity photoconductivity has the shape characteristic of a Ga

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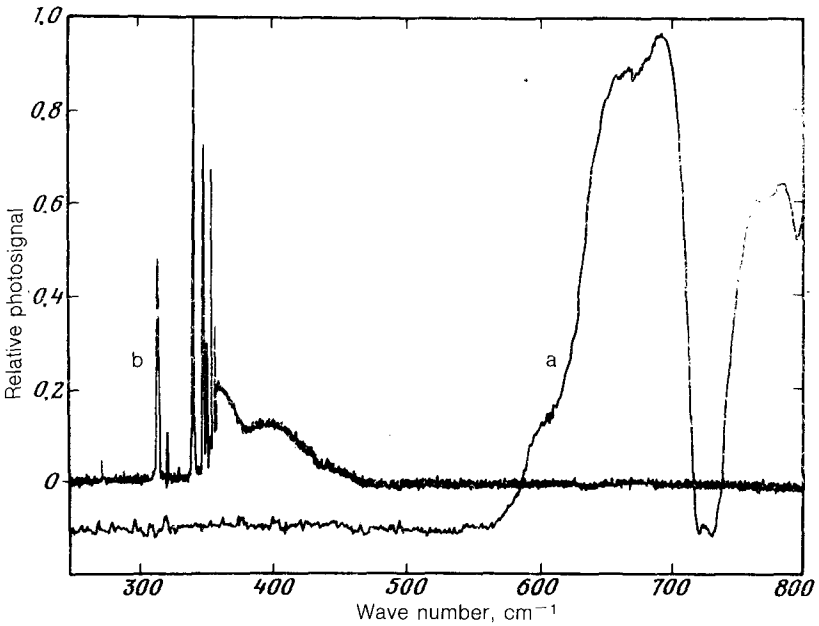

FIG. 1.

dopant in Si (the dip at 725 cm^{-1} in spectrum a and that at 380 cm^{-1} in spectrum b reflect the absence and decrease, respectively, of the energy in the exit beam of the spectrometer at these frequencies). Lines corresponding to the photothermal ionization of Ga can be clearly seen by increasing the scale of the part of the spectrum near the edge. When the illumination is turned on, and when its intensity is increased, we observe a progressive intensification of the impurity photoconductivity in the region $\sim$280–480 cm^{-1}, with intense, narrow lines of photothermic ionization which correspond to the phosphorus impurity (in some cases, it also corresponds to antimony and arsenic). The spectrum of the photoconductivity component due to the main dopant (which is many times stronger!) gradually decreases with respect to the spectrum of the compensating dopant, disappearing entirely at the maximum illumination (curve b). The shape of the spectrum of the compensating impurity and the position, height, and width of the lines in it are the same as in pure samples.

We attribute the observed effect to the appearance during the illumination of a sharp asymmetry in the lifetimes of the holes and electrons. When the illumination is turned on, at the temperature in these experiments (14–17 K), the overwhelming majority of the electrons and holes form excitons (with a carrier binding energy of 14 meV). These excitons attach to neutral atoms of the main dopant (of which there are many) and recombine there in an Auger process. As a result, free holes and negatively charged acceptors N_a^- form, so that the concentration $N_a^+ - N_a^-$ does not decrease during the illumination; in fact, it may increase. The holes ultimately recombine with vacant acceptors, either directly or through a capture by neutral impurity atoms (through the formation of A^+ centers), a migration along them to the acceptors N_a^-, and a recombination in $N_a^+ - N_a^-$ pairs. Under our conditions

the latter process is extremely effective and can lead to a highly pronounced decrease in the lifetime of the holes.[5,6] At an acceptor concentration of $(2–5)\times 10^{16}$ cm^{-3}, the binding energy of a hole at a neutral acceptor, ϵ_a^+, should be large (~ 10 meV; Ref. 7). For the sample whose spectrum is shown in Fig. 1, we determine this binding energy directly from the photoionization spectrum of the A^+ centers, measured at 6 K; it turned out to be $\epsilon_a^+ = 8.2$ meV. On the other hand, the number of charged donors (not neutralized by the illumination) is extremely small (a small fraction of a small concentration), especially since the coefficient for the capture of excitons by neutral donors is substantially smaller than the corresponding coefficient for acceptors.[8,9] The degree of charge exchange of the donors during illumination is thus close to unity, and the electron lifetime is long.

In summary, illumination with light in the fundamental absorption region leads, in the samples of these experiments, to an essentially complete neutralization of the compensating dopants (donors) and to a sharp increase in the lifetime of the minority carriers. Correspondingly, it also leads to a large impurity donor photoconductivity. On the other hand, this illumination not only fails to reduce the number of N_a^- capture centers for holes but in fact increases this number. By virtue of the appearance of A^+ centers, the illumination creates an additional effective mechanism for the recombination of holes, sharply reducing the photoconductivity component due to the photoionization of acceptors.

Calculations carried out on the basis of the kinetic equations for steady-state illumination, incorporating optical, thermal, and interimpurity transitions and using the published parameter values for these transitions, lead to a qualitative confirmation of the picture drawn above.

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