OSCILLATIONS IN THE IMPURITY PHOTOCONDUCTIVITY SPECTRA OF GERMANIUM

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A study was made of the relationships governing the oscillation effect in the impurity photoconductivity spectra of p-type germanium. The experiments were carried out at temperatures of 8–14°K on samples with partly compensated levels of copper at 0.041 eV, of gold at 0.041 eV, of zinc at 0.03 eV, and of cadmium at 0.05 eV. It was found that the depth of oscillations was different for different samples and that in some cases the oscillations were completely absent. The oscillation effect was not observed in the absorption spectra. The oscillation depth of the photoconductivity spectra was compared with the photoelectric properties of the samples. In the groups of samples containing copper, gold, and zinc, which were investigated in greatest detail, the relative depth of the oscillations was correlated with the recombination center concentration. The "cold" hole lifetimes, for which oscillations were observed in the photoconductivity spectra, were determined using the values of the cross sections for the capture of holes by impurity levels, taken from the published data and also found in the present work (from the noise spectrum).

INTRODUCTION

RECENTLY, there have been several reports of the observation of oscillations in the impurity and intrinsic photoconductivity spectra of InSb and GaSb[1-4] and in the impurity photoconductivity spectra of p-type germanium.[5-7] A characteristic feature of this effect is the separation of the neighboring minima of the photoconductivity signal, which is equal to the energy of the optical phonons in these substances. However, because of the absence of systematic experimental data, the interpretation of the effect cannot be regarded as convincing, at least in the case of germanium.

The earlier studies[5,6] and our preliminary experiments have already shown that the oscillations are observed only at sufficiently low temperatures, that their depth is different in different samples, and that in some cases the oscillations are completely absent. We may assume that the existence and intensity of the oscillations are associated with definite photoelectric properties of the investigated samples.

The purpose of the present study was to investigate in greater detail the oscillation effect in the impurity photoconductivity spectra of p-type germanium. The study included: a) comparison of the photoconductivity and absorption spectra; b) comparison of the photoconductivity spectra of samples having different concentrations of impurity centers, recombination centers, and scattering centers; c) investigation of the effect in crystals containing different impurities.

EXPERIMENT AND RESULTS

We investigated p-type germanium samples with partly compensated acceptor levels of copper ($E_V + 0.04$ eV), zinc ($E_V + 0.03$ eV), and cadmium ($E_V + 0.05$ eV), and at a donor level of gold ($E_V + 0.04$ eV) (in the designations of the samples the first two letters represent these impurities). Phosphorus, gallium and antimony (the second set of letters in the designations) were used for counter-alloying. Some of the samples containing copper were doubly compensated with phosphorus and gallium (CuPGa-2 and CuPGa-5) for the purpose of altering the number of charged scattering centers without changing the concentration of recombination centers.

The total concentration of the main impurity, the number of recombination and scattering centers, and the carrier mobility and its temperature dependence were determined from the measurements of the Hall coefficient and the electrical resistivity in the temperature range 300–6°K; in this determination, we used the data of Ostroborodova[8] on the degeneracy factors of impurity centers and the degree of ionization of these centers at room temperature. The properties of the

Properties of investigated samples

Impurities and sample No	Concentrations × 10^{14}, cm^{-3}			K_2, %
	N	N_r	N_s	
AuGa-1	1.8	1.0	1.6	0
AuGa-2	13.0	6.4	13.0	16
AuGa-3	14.6	12.0	6.0	28
CuSb-1	13	0.6	1.2	0
CuPGa-2	82	0.8	20.0	9
CuSb-3	150	1.0	5.0	23
CuSb-4	80	0.7	3.0	7
CuPGa-5	60	10.0	30.0	41
CuSb-6	80	0.4	2.0	0
ZnSb-1	92	10.0	20.0	69
ZnSb-2	26	0.06	0.4	7
ZnSb-3	50	1.7	4.0	52
CdSb-1	5.5	1.0	4.0	26

samples are given in the table.

The measurements of the electrical resistivity and the Hall coefficient at low temperatures showed that below 15°K the hole mobility of all the samples was governed by the scattering by charged centers. Samples CuPGa-2, CuPGa-5, ZnSb-1, CdSb-1, contained, apart from the main impurity, a shallow-acceptor impurity. The latter was deliberately introduced into the samples containing copper, but in those containing cadmium and zinc it was introduced unintentionally during the process of growth. This impurity clearly affected the electrical properties of the crystals which did not contain the compensating donor impurity of antimony. In these samples, the temperature dependence, at low temperatures, of the electrical resistivity and the Hall coefficient deviated from the usual exponential dependence in the same way as is usually observed in the phenomena of the "impurity" conductivity.[9,10] However, the photoconductivity spectra were investigated under conditions of considerable background and the steady-state "dark" conductivity of the samples was governed by the background hole density in the valence band.

To investigate their photoconductivity and absorption spectra, the samples were placed in a metal helium cryostat with potassium bromide and germanium windows. The temperature of a sample in the cryostat could be varied, by means of a heater, from 8 to 35°K and was measured with a carbon resistance thermometer. The IKS-21 instrument was used as a monochromator with NaCl and KBr prisms, covering the photon energy range 0.6—0.05 eV. However, here we give the spectra only to the photon energy of 0.09 eV, since at lower energies the spectra were distorted by the lattice absorption in the germanium, which made it difficult to obtain a quantitative estimate of the oscillation depth.

Thus, we were able to record reliably the oscillations in the spectra, beginning with the second minimum. We shall use the concept of the relative depth of oscillations, which has the following meaning. If we draw an envelope along the photoresponse maxima and take the ratio of the difference of the photoresponse amplitudes on the envelope (at the wavelength of a minimum) and at the minimum to the amplitude on the envelope $(A_{env} - A_{min})/A_{env} = K$, then the resultant quantity expressed in per cent represents the relative oscillation depth.

A. Comparison of Absorption and Photoconductivity Spectra

Two samples were used in this investigation: ZnSb-1 with a large oscillation depth, and CuSb-1, in which no oscillations were observed (Fig. 1). The sample containing zinc was 2 mm thick, which was sufficient for it to be used as a filter. The radiation was passed through this sample before reaching the sample containing copper, which served as a detector. The cryostat was fitted with two windows, so that in the same experiment we could record the photoconductivity spectrum of the detector under direct illumination and under illumination through the filter. According to a theoretical estimate, made using the effective photoionization cross section of zinc $\sigma_{ph} \approx 1.5 \times 10^{-15}$ cm^2,[11] the transmission of the filter should have amounted to ≈ 2%, which allowed us to record very accurately even small oscillations. The reduction in the photoconductivity signal of the detector after the beam had passed

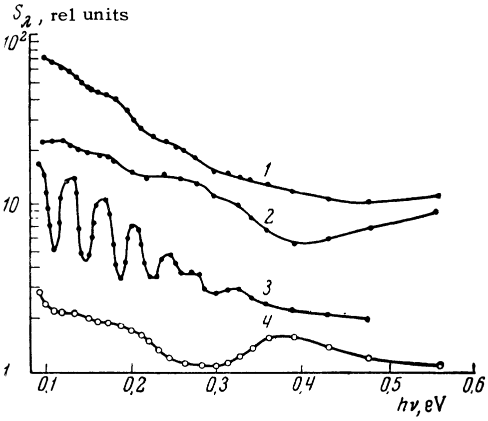

FIG. 1. Comparison of the absorption and photoconductivity spectra of sample ZnSb-1 (14°K): 1), 3) spectra of the relative photoresponse (Sλ) of samples CuSb-1 and ZnSb-1; 2) photoresponse of sample CuSb-1 in the presence of a ZnSb-1 filter; 4) the ratio of the photoresponses of sample CuSb-1 with and without a filter, which represents the absorption by ZnSb-1.

through the filter was in agreement with this estimate. However, as shown by the appropriate curves in Fig. 1, no oscillations were found in the absorption spectrum of the sample ZnSb-1.

B. Photoconductivity Spectra

Figures 2 and 3 show the impurity photoconductivity spectra of germanium containing copper and zinc. It is evident that the oscillation depth is different for different samples. Moreover, it can be seen that the depth decreases as the order of the minima increases. It is possible that this is due to an increase in the scatter of the excited carrier energy when the incident light energy is increased. In view of this, the most characteristic quantity should be the depth of the first minimum. However, analysis of the curves having a pronounced oscillation structure shows that the difference between the depths of the second (K_2) and the first (K_1) minima should not exceed 10–15%. The table gives the oscillation depth K_2 for all the samples, in addition to the concentration of the main impurity N, and the concentration of the recombination centers N_r (in the case of gold, these centers are neutral atoms, while in other cases they are negatively charged ions) and of the scattering centers N_s (all charged centers in the crystal). We can draw the following conclusions from a consideration of the data for the first three groups of samples.

1. The existence and the depth of oscillations are not related to the presence of the main impurity. Thus, the samples AuGa-1 with $N = 1.8 \times 10^{14}$ cm^{-3} and CuSb-6 with $N = 8 \times 10^{15}$ cm^{-3} exhibit no oscillations, while the sample CuPGa-5 with $N = 6 \times 10^{15}$ cm^{-3} exhibits pronounced oscillations ($K_2 \approx 40\%$).

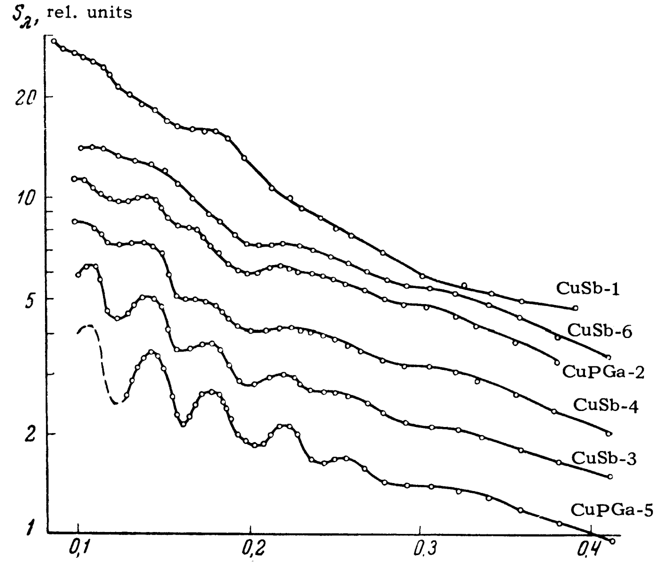

FIG. 2. Photoconductivity spectra of germanium samples containing copper (8°K).

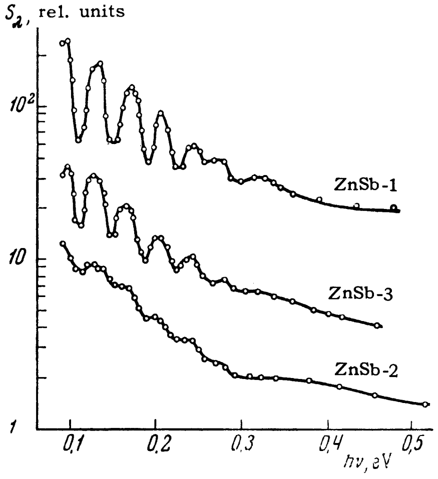

FIG. 3. Photoconductivity spectra of germanium samples containing zinc (8°K).

2. The samples with low values of N_s exhibit no oscillation (AuGa-1, CuSb-1, CuSb-6), but there is no correlation between K_2 and N_s in the presence of oscillations.

3. In each group of samples, the oscillation depth increases with N_r.

4. The concentration N_r at which the oscillations "begin" is lowest in the samples containing zinc and increases gradually with the transition from copper to gold.

5. The depth of oscillations observed for $N_r \approx 10^{15}$ cm^{-3} (the samples ZnGa-3, CuPGa-5, ZnSb-1) increases with the transition from gold to copper and zinc.

DISCUSSION OF RESULTS

The results of the investigation of the absorption spectrum of the sample ZnSb-1 allow us to reject the mechanism proposed by Benoit à la Guillaume et al,[5] according to which the oscillations in the impurity photoconductivity spectra of p-type germanium are due to the corresponding oscillations in its absorption spectra. The experimentally observed correlation of K_2 with the concentration of recombination centers indicates that the observed effect is related to the hole lifetime in the band.

Therefore, it seems to us that the most probable mechanism is that related to the difference between the effective lifetimes of holes excited by photons of different energies.[3] When the lifetimes of "cold" holes (τ_0) become comparable with the energy relaxation times (τ_a) of "hot" holes in the band representing the interaction with acoustical phonons, where $\tau_a \gg \tau_{op}$ (τ_{op} is the energy relaxation time due to the interaction with optical phonons), the effective lifetimes of excited holes are found to be different when their energy in the band (1) is, or (2) is not, a multiple of the optical phonon energy.

In the first case, a hole is rapidly cooled, emitting n optical phonons, and is captured from the band edge by an impurity center with a lifetime τ_0. In the second case, the hole is below the band edge due to the emission of n optical phonons and its residence time in the band is governed by τ_a, τ_0 and $\tau(E)$, where the latter is the lifetime in the "hot" state (which corresponds to the capture from a state with an energy E by an impurity center). Since, in this case, the photoexcited holes remain "hot" for a longer time than in the first case, their effective mobility in the presence of impurity scattering is higher.[2]

Thus the photoconductivity signal in the second case becomes greater compared with the signal in the first case, both due to the increase in the effective lifetime and due to the increase in the effective hole mobility. We could separate these two effects in an investigation of the oscillations under such conditions that the mobility be independent of the carrier energy. Then the oscillations would be governed only by the change in the effective lifetime. It seemed to us that it would be difficult to separate the oscillations associated only with the mobility since for these oscillations to appear the same condition $\tau_a \sim \tau_0$ would have to be satisfied. Our experimental data do not allow us to make such an analysis, since we did not investigate in detail the temperature dependence of the mobility of holes in the presence of background.

The magnitude and the temperature dependence of the capture cross sections for copper σ_p^- and gold σ_p^0 in the temperature range 20–29°K were determined in [13,14] from the noise spectra. Extrapolating these values to 8°K, we obtained $\sigma_p^- = 1 \times 10^{-12}$ cm^2 and $\sigma_p^0 = 1 \times 10^{-13}$ cm^2. Assuming that the number of recombination centers under background conditions remains equal to N_r, we could estimate the value of τ_0 in the investigated samples.

Figure 4 (curve 1) shows the dependence of K_2 on τ_0 for samples containing copper and gold. It is evident that there is some "threshold" value $\tau_0 = \tau_t$; in samples with $\tau_0 > \tau_t$, there are no oscillations, while in samples with $\tau_0 < \tau_t$, there are oscillations and their depth increases as τ_0 decreases. Thus, the difference between the oscillation depths for samples with copper and gold having the same N_r may be associated with the difference between the capture cross sections and, consequently, with the difference between the values of τ_0.

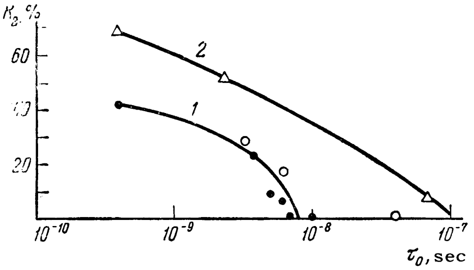

FIG. 4. Dependence of the relative depth of oscillations K_2 on the lifetime τ_0 for samples containing copper (●), gold (o), and zinc (△).

From this point of view, it was natural to assume that the large values of the depth of oscillation and the considerably lower "threshold" number of recombination centers in samples containing zinc were related to the large hole capture cross section of the zinc level $E_V + 0.03$ eV. However, an investigation of the noise spectra in the temperature range 14–18°K showed that the values of σ_p^- for zinc did not exceed the corresponding capture cross sections for copper. This was responsible for the dependence of K_2 on τ_0 in the case of zinc (curve 2) being different from the corresponding dependence for copper and gold. The occurrence of such a difference forced us to two alternative conclusions: 1) the hole lifetimes under background conditions differ from τ_0 by different amounts in different groups of samples; 2) in the case of samples containing copper and gold, there are additional factors which either weaken the oscillations (and give rise to the "saturation" of the effect, as indicated by curve 1), or, in the case of zinc, intensify them. Further investigations are proposed to obtain information on these questions.

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