Inversion of the sign of the "linear" photovoltaic effect in semiconductors

A. V. Andrianov, P. M. Valov, and I. D. Yaroshetskiĭ
A.F. Ioffe Physicotechnical Institue, USSR Academy of Sciences

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A temperature and concentration inversion of the sign of the photovoltaic effect (PVE) in semiconductors was observed. The temperature inversion is due to a change of the PVE mechanism from an intraband to an impurity mechanism. The concentration inversion is caused by a delocalization of the impurity states.

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The PVE, which is caused by asymmetry in the momentum distribution of photoexcited charge carriers,[1–8] can be observed in uniformly stimulated, homogeneous crystals without an inversion center. The magnitude and character of the PVE should be strongly dependent on the optical transitions that produce it. At present, however, the theory cannot determine unambiguously the properties of the photovoltaic tensor D_{ike} for different mechanisms for formation of the PVE. The experimental situation is also extremely complicated, since in one class of crystals where the PVE is observed—ferroelectrics—the mechanism of its formation is still not adequately understood, and explanations of the "linear" PVE in semiconductors.[1,3,4] based on an analogy of the dc effect, are not correct. Under these conditions, the experiments, which make it possible to observe new PVE effects and to identify with certainty the mechanisms for formation of PVE in semiconductors, assume special importance. In this paper we report the first observation of temperature and concentration inversion of the sign of the "linear" PVE in semiconductors, in particular, in Zn-doped ($E_v + 30$ meV), p – type GaAs. A pulsed CO_2 laser ($\lambda = 10.6\ \mu$m and $\lambda = 9.5\ \mu$m) with a power of ~ 6 kW and a pulse duration of $\sim 1.5 \times 10^{-7}$ sec was used in the experiments. The radiation was incident on the sample along the [110] direction, and the PVE field E was observed in the [1$\bar{1}$0] direction. In this case $E = ID \sin 2\theta$, where I is the light intensity, D is the value of the D_{ike} tensor in the GaAs crystal, and θ is the angle between the polarization vector of the light wave and the [001] direction. The measured photo-emf is linearly dependent on the light intensity, completely duplicates the shape of the laser pulse and depends

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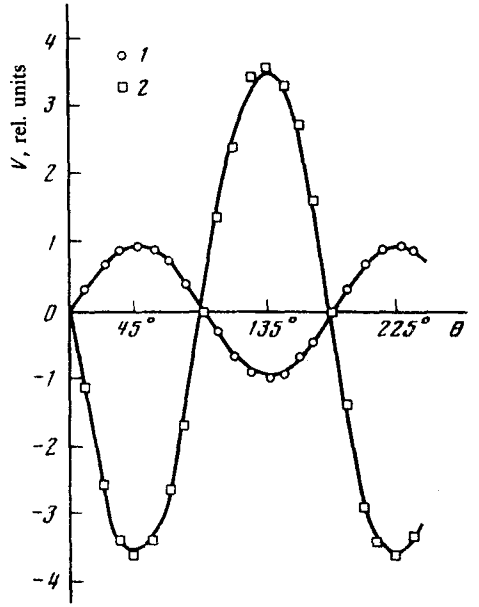

FIG. 1. Dependence of the EMF of PVE on the angle θ: $\lambda = 10.6\ \mu m$, $p = 2.3 \times 10^{16}\ cm^{-3}$: 1 – $T = 300$ K, 2 – $T = 77.3$ K.

on the polarization (Fig. 1), consistent with the equation given above. The PVE was investigated for other orientations, in both a longitudinal and transverse geometry, and the results of measurements of the constant D agreed.

It was found that a temperature inversion of the sign of the "linear" PVE occurs in p-GaAs (Zn) with a hole density of $5.2 \times 10^{15}\ cm^{-3}$– $4.3 \times 10^{17}\ cm^{-3}$, and it increases in magnitude as the temperature varies from 300 to 77.3 K (Fig. 1). At hole

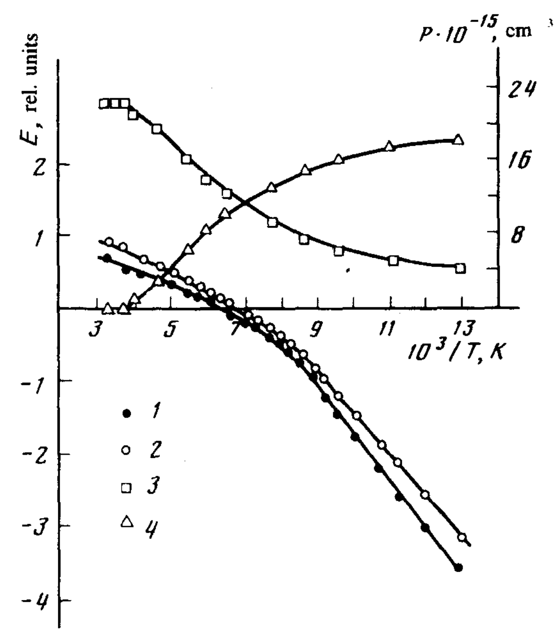

FIG. 2. Temperature dependence of the PVE field and of the charge carrier density. 2, 1—PVE field for $\lambda = 10.6\ \mu m$ and $\lambda = 9.5\ \mu m$, respectively; 3, 4—carrier density in the band and in the impurities, respectively.

densities $p \geqslant 4 \times 10^{18}$ cm $^{-3}$ the sign of the PVE does not change with changing temperature. A simultaneous measurement of the temperature dependence of the Hall coefficient, of the conductivity and of the photovoltaic effect showed that the PVE changes sign only in those samples in which a freezing of the carriers in the zinc impurity level occurs with cooling (Fig. 2). At room temperature the constant D is almost independent of the charge carrier density (Fig. 3), whereas the constant $D^* = D\sigma$, where σ is the sample conductivity, determining the magnitude of the photovoltaic current, depends linearly on the carrier density. This fact indicates that at 300 K the PVE mechanism cannot be attributed to asymmetrical scattering of the photoexcited free carriers by the impurities. In fact, if this mechanism were to occur, then the photovoltaic current would depend quadratically on the carrier density. The cause of the PVE in the case under consideration, allowing for the observed temperature behavior at high temperatures, is the direct optical transition between the subbands of heavy and light holes with asymmetrical scattering by lattice vibrations. The change in the PVE sign as the temperature decreases is attributable to a change in the mechanism of the effect. At low temperatures the PVE is produced as a result of photoionization of the local impurity states. The correlation of the sign of the effect with the change in carrier density one going from 300 to 77.3 K, as well as the positive photoconductivity $(1/I)(\Delta\sigma/\sigma) \sim 10^{-3}$ cm ^{2}/kW at 77.3 K, favors this explanation. The constant D remains constant at 77.3 K within a wide interval of densities (Fig. 3), after which it decreases comparatively sharply and then—and this is especially interesting—it changes sign. The sign change is attributable to disappearance of the PVE due to optical transitions from localized impurity state to the valence band. This occurs due to delocalization of the impurity states at a high impurity concentration.[9] This is indicated by the results of an investigation of the temperature dependence of the conductivity and Hall coefficient, showing that the metal-insulator transition in p-GaAs (Zn) begins at concentrations $p \sim 10^{18}$ cm $^{-3}$, i.e., in the region of drastic decrease of the PVE. According to theory,[10] for $p \geqslant 6 \times 10^{18}$ cm $^{-3}$ the impurity and valence bands overlap in p-GaAs (Zn), which apparently causes a slight change in the PVE on going from 300 to 77.3 K in this range of concentrations. The results presented above allow us to conclude that the impurity PVE is due not only to a distortion of

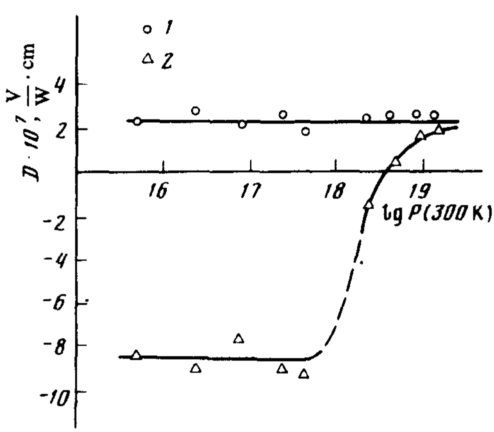

FIG. 3. Concentration dependence of the constant D: 1—T = 300 K; 2—77.3 K.

the wave function of the final state by the field of the impurity center,[5,6,8] but is also determined to a large extent by the anisotropy of the wave function of the initial state.

In conclusion, we note that we observed the PVE in n-GaAs. At 300 K and an electron density of $\sim 2.5 \times 10^{17}$ cm^{-3} the constant D is $\sim 5 \times 10^{-9}$ V cm/W. As the temperature decreases to 77.3 K, the effect changes sign and decreases by a factor of two.

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