Anomalous photoelectric effect on bound excitons in gallium phosphide

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A photoelectric effect in the A_N, NN_3, NN_4, NN_5, and $A_{\rm Bi}$ lines of bound excitons was observed in GaP *p-n* junctions at temperatures of 40–80 K. The photoelectric response in the region of the A_N line exceeded the maximum value in the intrinsic region of the spectrum.

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It is generally assumed that a bound exciton, a localized excited state in crystal, cannot participate directly in the energy (charge)-transfer processes. The photoelectric response in the region of the A_N line of a nitrogen-bound exciton, which was observed earlier in gallium phosphide,[1,2] was not surprising, since the binding energy of the exciton E_i in the investigated temperature range was of the order of kT, and the photoelectric effect could be explained by the ordinary thermal "pre-excitation" of an exciton with a subsequent production of free charge carriers.

The experimental data obtained by us, which are inconsistent with the current ideas, show that the bound excitons can migrate effectively in the crystal.

Investigations were performed using diffusion and epitaxial GaP *p-n* junctions. The excitation was accomplished via the *p* or *n* region. The concentration of nitrogen, which was substituted for phosphorus in gallium phosphide and which was an effective isoelectronic trap (isoelectronic acceptor), varied from 2×10^{15} to 2×10^{18} cm^{-3}. The photocurrent characteristics of the diodes were linear at the investigated excitation densities.

Figure 1 shows the spectra of a short-circuit photocurrent in one of the samples obtained by double liquid epitaxy and doped with nitrogen to $N=1.1\times10^{18}$ cm^{-3}. The thickness of the *p* region, through which the excitation was achieved, amounted to 30 μm, and the width of the region of the space charge, according to the data for volt-farad measurements, was $w=0.3$ μm. Notice that the photoelectric response at low temperature in the region of the A_N line of the excitons that are bound on single

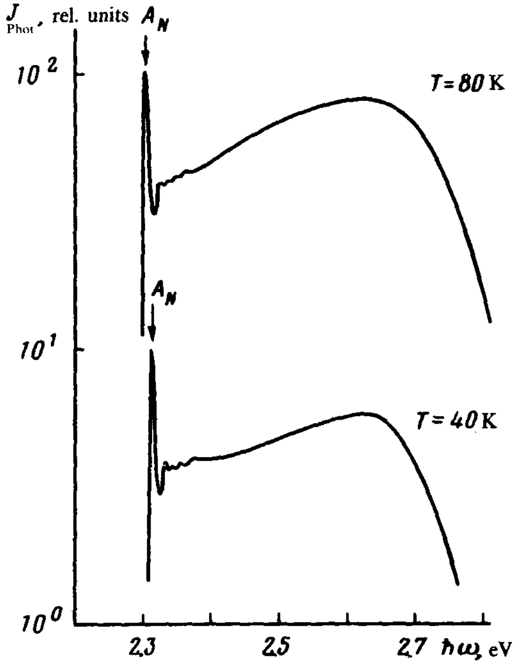

FIG. 1. Spectra of short-circuit photocurrent in an epitaxial GaP:N *p-n* junction.

nitrogen atoms is anomalously large and exceeds the maximum photoelectric response in the intrinsic region of the spectrum. The temperature measurements showed that the ratio of the photocurrent in the A_N line to the maximum photocurrent in the region of self-absorption increases monotonically with decreasing temperature from 300 to 40 K. This shows that the observed photoelectric effect in the A_N line of a bound exciton cannot be accounted for by the processes of thermal dissociation or the decay of excitons in the defects of the crystal.[1)] This is confirmed by the photoelectric effect observed by us in the NN_3, NN_4, and NN_5 lines of the excitons that are bound to the pairs of nitrogen atoms (Fig. 2). The location of the maxima in the spectrum of the photoelectric response and the line width coincide with an accuracy of 1 meV with the results of studies of the absorption and luminescence spectra,[3] and the binding energies, equal to 64, 39, and 31 meV, exceed kT by an order of magnitude.

We note that the absorption coefficient in the region of the NN_n lines did not exceed 1 cm^{-1}, and the concentration of the NN_n pairs in the sample, whose spectrum is shown in Fig. 2, was of the order of 5×10^{14} cm^{-3}. The A_N line in the spectra of photoelectric responses was displayed rather prominently in the samples with a 10^{15} cm^{-3} nitrogen concentration.

The photoelectric effect was observed in the excitons that were bound to the N and NN_n isoelectronic acceptors and to the isoelectronic donors, as indicated by the spectrum in Fig. 2 (curve 2) for the bismuth-doped gallium phosphide sample. A fine structure, whose analog was observed earlier only in the luminescence spectra, was evident in addition to the deepest A_{Bi} line with a binding energy of 117 meV. This

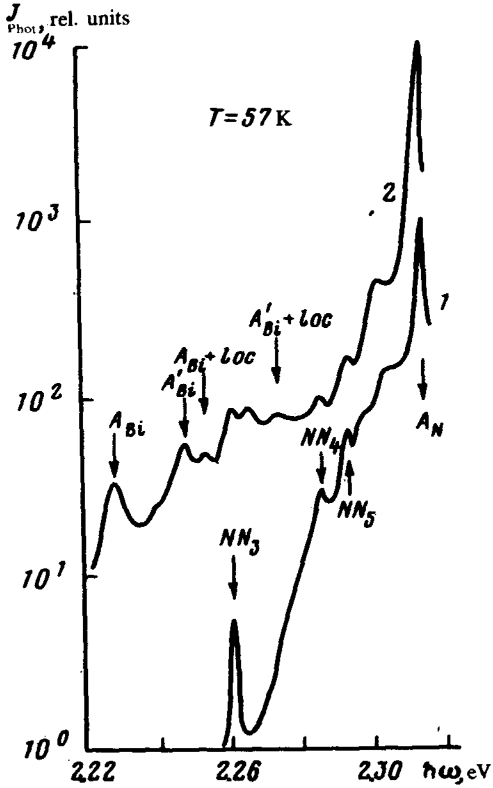

FIG. 2. Structure of the spectra of short-circuit photocurrent in the GaP *p-n* junctions doped with nitrogen (curve $1 - N = 1.1 \times 10^{18}$ cm^{-3}, $w = 0.3$ μm, $d = 30$ μm) and with nitrogen and bismuth (curve $2 - N = 9 \times 10^{17}$ cm^{-3}, $w = 0.5$ μm, $d = 7$ μm). The arrows indicate the evaluation of the exciton lines associated with the single nitrogen atoms (A_N) and bismuth atoms (A_{Bi}) and with pairs of nitrogen atoms (NN_n). The excited state of an exciton bound to bismuth is denoted by A'_{Bi}, and A_{Bi} + loc and A'_{Bi} + loc denote the phonon repetitions of the corresponding lines with a local phonon emission.

structure is evaluated in Fig. 2. Note that the ordinary and even the differential absorption spectra do not have such a structure, and the observed effects make it possible to investigate the weak optical absorption on bound excitons in the thin layers.

A possible mechanism for the photocurrent in the region of absorption lines on bound excitons at low temperatures, which is consistent with the experimental data obtained in this work, is the migration of bound excitons to the *p-n* junctions and their subsequent dissociation in the space-charge layer in which the field strength reaches a value of $\geqslant 10^5$ V/cm.[2] The data in Fig. 1 show that the transfer of excitation by the bound excitons can be very effective and the cooresponding "diffusion lengths," which can exceed L_n and L_p for the free carriers, amount to at least several microns.

The data,[5] in which the NN_1 luminescence on the NN_5 line was observed when the NN_5 line was selectively excited, show that the bound excitons can transfer the excitation.

[1)]The possible transfer of excitation energy by self-absorption and re-emission must also be excluded, since the relative values of the photo-current in the A line (I_A/I_{max}), as in the NN_n lines are independent of the quantum yield of the luminescence of the p and n regions. Moreover, in contrast with the excitons bound by neutral donors or acceptors, the electronic structure of the isoelectronic centers excludes the emission of an Auger electron (hole) almost entirely, an effect which was confirmed experimentally in Ref. 6 by using GaP:N and GaP:Bi.

[2)]The excitons bound by a single nitrogen atoms in GaP break up at a field intensity of about 10^5 V/cm.[4]

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