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Space-resolved photoeffect in Zn_3P_2*

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Experimental studies of photo-responses of metal-Zn_3P_2 structure have been made at 300 K in both the photovoltage and photocurrent mode. The effect of light-spot position upon the shape and value of the photo-response has been found. An explanation of this effect has been suggested by taking into account different electron transitions within the energy band gap of Zn_3P_2 as well as an influence of both the photostatic effect and the relatively high surface/interface carrier recombination.

1. Introduction

Recently, p-type zinc phosphide (Zn_3P_2) with a bandgap of 1.51 eV for direct transitions [1], [2] and a diffusion length of minority carriers of the order of 10 μm [3], [4] has been intensively investigated as one of the most promising semiconductors for applications as the infrared-to-ultraviolet photoconverter and, particularly, in low-cost and high-efficiency solar cells [5].

In our previous papers, we have studied experimentally the origin of photoeffects in Zn_3P_2 [6]–[9] and we have found the first indications of an effect of the light spot-versus-contact configuration upon the shape and value of the photoresponse of metal-Zn_3P_2 Schottky-type barrier structure [7], [9]. The goal of this paper is to present the recent experimental data and to discuss them comparatively.

2. Experimental

2.1. Sample preparation

The preparation of the Zn_3P_2 quasi-single crystals of Zn_3P_2 has been described elsewhere [10]. The slices have been cut out from the ingots and then polished mechanically and chemically. The 5% methanol solution of bromine has been used for final polishing. The p-type material with hole concentration of about 10^{21} m^{-3} and Hall mobility of holes equal to 2×10^{-3} m^2/V sec, approximately, has been obtained [11]. The metal contacts of gold have been made by PVD-thermal

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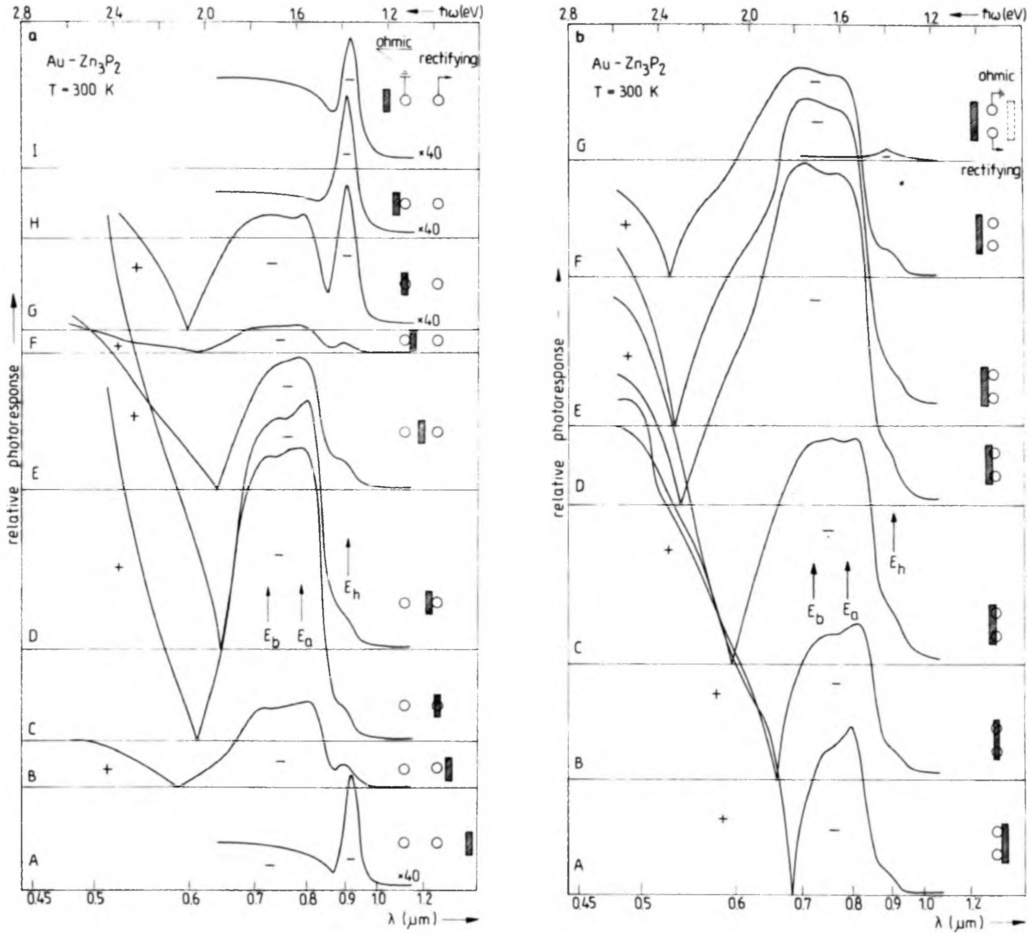

Fig. 1. Spectral characteristics of the photoresponse (in photovoltage mode) of Au-Zn_3P_2 rectifying contacts at the different LSP (explained in the insert) for the parallel (**a**), and perpendicular (**b**) light spot-versus-contact configuration

evaporation method under residual air pressure of $= 10^{-6}$ Torr on the fresh-prepared sample surface. Both circular (diameter $\simeq$ 1 mm) and rectangular (0.5 × 1 mm) shapes of contacts have been used.

2.2. Measurement procedure

Spectral measurements of the photoresponse of Au-Zn_3P_2 contacts were performed at room temperature by using a typical experimental arrangement with Zeiss SPM-2 monochromator equipped with 250 W halogen lamp and Vth-1 Zeiss thermocouple as a reference detector. The light beam was divided into two sub-beams and chopped with 12.7 Hz frequency. Each of the sub-beams were focused, respectively, on the reference thermocouple and the sample measured. Their intensity ratio was kept constant at the input. The output data from the measured sample and reference detector were then electronically divided. The recorded results of the sample photoresponse have been, in this sense, the relative ones.

To study the effect of lighting configuration on both the value and shape of the photoresponses of contacts, the measurements were made in two configurations of lighting spot versus contact position on the sample surface. The first light spot configuration called hereafter "parallel" was realised by moving the light spot along the line which crosses the two contacts (ohmic and rectifying, in the sense of the linear and nonlinear current-voltage characteristics, respectively). The light spot was placed either in between or outside the contacts (in several positions marked by capital letters A, B, C ..., I, also in second configuration). This configuration is shown schematically in Fig. 1**a** as an insert. The second configuration, called hereafter "perpendicular", was done by moving the light spot perpendicularly to direction in the parallel configuration; and that arrangement is shown schematically as an insert in Fig. 1**b**.

3. Results

Figure 1**a** shows typical shapes of wavelength-dependent photoresponses of Au-Zn_3P_2 structure at the different light spot position (LSP) in the parallel light-vs-contact configuration. Three distinguished peaks of the photovoltage spec-

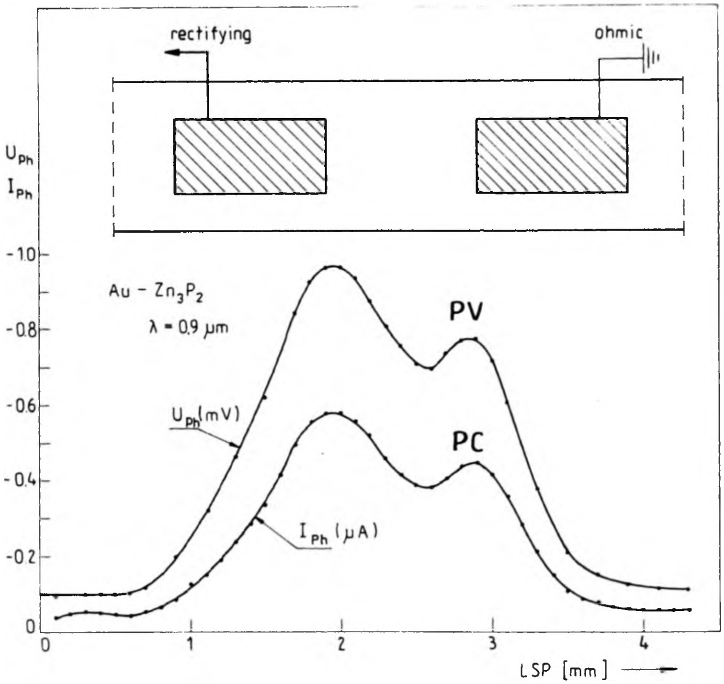

Fig. 2. Photoresponses in photovoltage (PV) and photocurrent (PC) modes versus LSP (for detailed explanation – see the text)

tra, namely E_a, E_b and E_h, can be found in this figure. Peak E_a is found to be within the energy range of 1.55–1.59 eV, peak E_b is found within the energy range of 1.70–1.74 eV whereas peak (or singularity) noted E_h is within the energy range of 1.36–1.38 eV. Fig. **1b** shows typical shapes of the photoresponses for the LSP in the perpendicular light-contact configuration. The measurements have been arranged on the same samples as above for comparison. The overall shape of curves in the same as for the LSP in the parallel configuration. Three peaks are also visible. Peak E_a is found within the energy range of 1.54–1.6 eV, peak E_b is within the range of 1.65–1.77 eV and peak/singularity E_h is within the range of 1.385–1.395 eV. These values correspond quite well with those in the parallel light-contact configuration, within the experimental error limit (estimated as not greater than 50 meV).

A comparison of the photoresponse spectra in photovoltage, PV, and photocurrent, PC, modes has also been done. The results of comparative measurements are shown in Fig. 2. These results were obtained for 0.9 μm light wavelength, by using the rectangular light beam having a width on the sample surface less than 0.5 mm (as

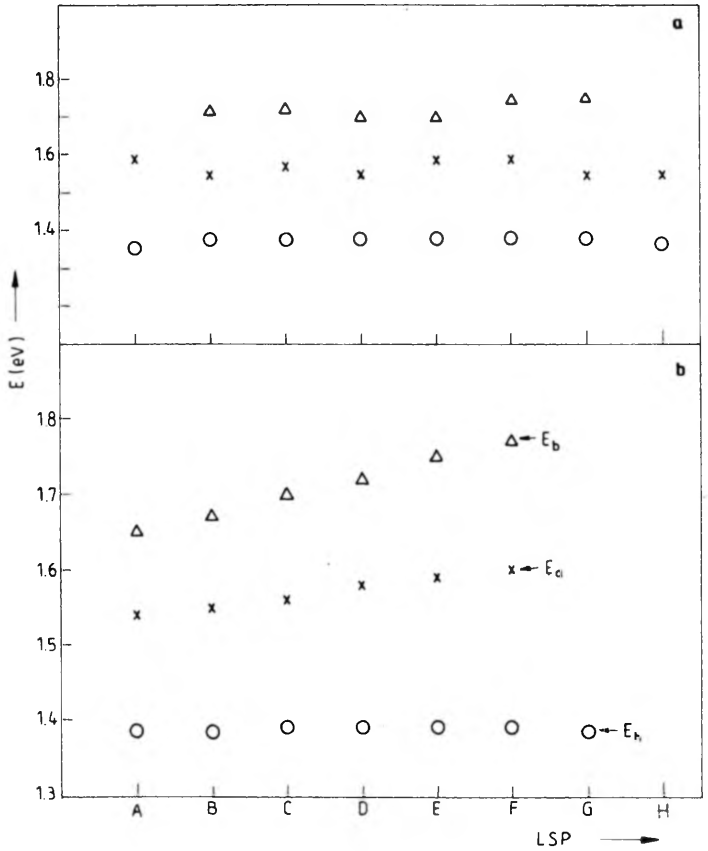

Fig. 3. Energy positions of the photoresponse peaks along the LSP for the parallel (**a**) and perpendicular (**b**) light spot-vs-contact configuration

above in Fig. 1). The contact geometry and dimensions are shown in this figure according to the scale of the LSP. The points represent the experimental results and the lines visualize the most probable shape of the measured photoresponse-versus-LSP dependence. The very good accordance of the shape of both the photoresponse modes is visible. This effect strongly suggests that the measured photoresponses in both configurations show actually how the number of photogenerated carriers depends upon the wavelength and the geometrical position of the lightbeam.

The relation between the average value of energy position of the photoresponse peaks and the LSP is shown in Fig. 3. From this figure we can conclude that the LSP does not have any essential effect on energy position of the photoresponse peak in the parallel light-contact configuration (Fig. 3**a**), while that effect is visible in the perpendicular configuration. In this configuration some quasi-linear trend for peaks E_a and E_b can be suggested, as shown in Fig. 3**b**.

Figures 1**a**, **b** reveal also that the relative values of peak intensities (i.e., photoresponse values) depend upon the LSP. Fig. 4**a** shows this dependence quite clearly and indicates that the maxima of the photoresponses for peaks E_a and E_b are at position marked C while that for peak E_h is found at position D, in the parallel light-contact configuration. The same results for the perpendicular configuration

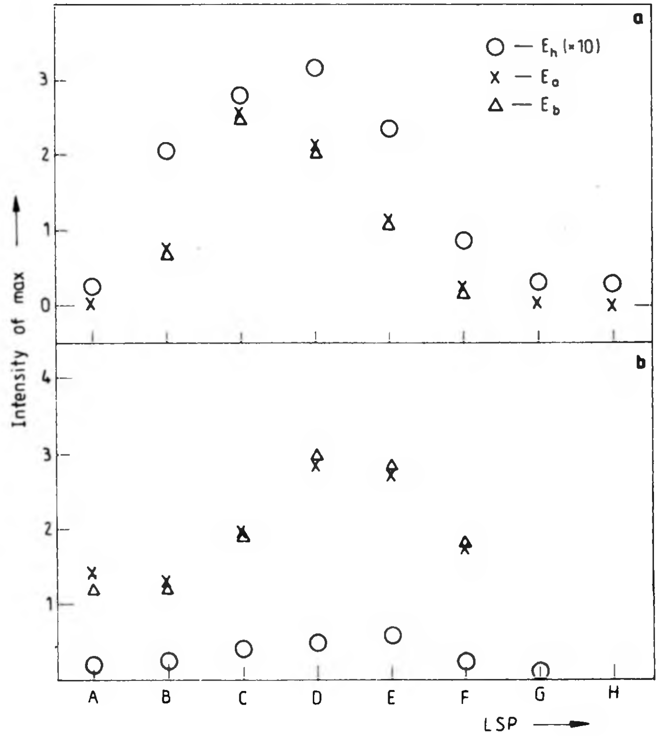

Fig. 4. Maximum value of the photoresponse peak versus the LSP for the parallel (**a**) and perpendicular (**b**) light spot-vs-contact configuration

shown in Fig. 4**b** indicate that peaks E_a and E_b have the highest intensities at the LSP denoted D while the maximal value for peak E_h is found at position marked E. In both the light-vs-contact configurations, these positions are the LSPs at which a light beam is very close to the rectifying contact and/or partially falls on it. Overall shape of the dependence of photoresponse value upon the LSP shown in Fig. 4**b** is very close to that in Fig. 4**a**. However, a mysterious observation, so far, is that the shapes and other singularities of spectral dependences for the positions A and E in the perpendicular configuration are not always the same (or very similar, at least) although these positions are quite symmetrical (see also discussion below). See here Fig. 1**b** as an example.

The intensity ratio for peaks E_a and E_b was found to be always more than one for the parallel light-contact configuration. For the perpendicular configuration, however, the intensity ratio changed its value and was found to be slightly higher and lower than one.

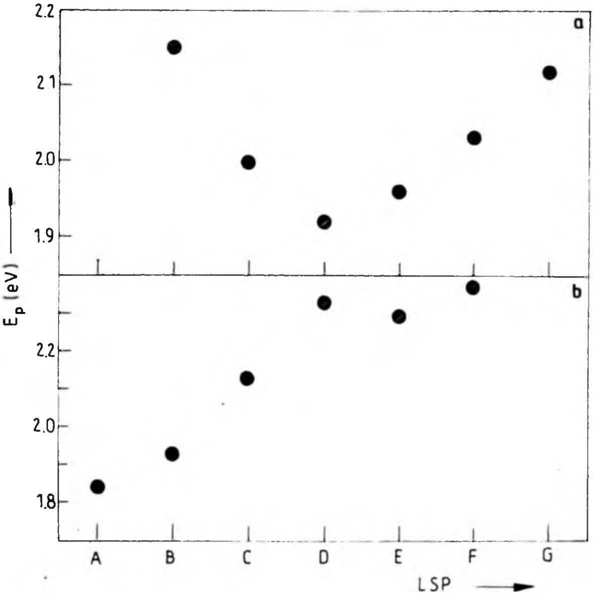

Fig. 5. Photon energy at which the polarity of the photovoltage response changes its sign in a function of the LSP, for the parallel (**a**), and perpendicular (**b**) configuration

Figures 5**a**, **b** show a relation between the value of energy at which the photoresponse changes its polarity (marked as E_p) and the LSP. Fig. 5**a** shows that the lowest value of E_p is at the LSP denoted by D, for the parallel light-contact configuration. This minimum corresponds roughly with the position of maxima of the LSP-dependent E_a and E_b peaks. Fig. 5**b** shows the E_p-versus-LSP dependence for the perpendicular configuration. The relation between E_p and LSP is here quite different than that for the perpendicular configuration.

4. Discussion

Overall shape of the measured photoresponses is similar to that observed previously [7], [9]. Also, there is no substantial difference (but one, see below) in the shape and singularities (peaks) of photoresponse for various metal contacts. Therefore, it strongly suggests that the photoresponse observed is the property of Zn_3P_2, i.e., the photoresponse is due to interband transitions (or those from acceptor levels to conduction band) and not due to the transitions over particular metal-Zn_3P_2 contact barrier.

Since Zn_3P_2 is a p-type semiconductor, and electrons are the photo-generated minority carriers, we should expect a negative polarity of the photovoltage measured on the potential barrier contact. Furthermore, Zn_3P_2 is an indirect-type material with the indirect band gap of 1.315 eV and the direct one of 1.505 eV, both values at room temperature [1], [2]. Therefore, two types of photo-generated electrons with different mobilities and then diffusion lengths are expected. We should also note the possibility of electron transitions from the impurity levels to conduction band with, however, no further difference in the properties of electrons generated from these levels and those from direct interband transitions.

Generally, one broad peak of photoresponse is observed having the negative polarity of photovoltage (with reference to the grounded contact) and the distinct hump with the threshold at the energy about 1.25–1.30 eV. This threshold can be ascribed to the transitions from impurity level at 0.25–0.27 eV above the valence band [12]–[14] and/or indirect band-to-band tansitions in the Zn_3P_2 energy band structure [15]. For some LSP (e.g., denoted as A, G, H and I in Fig. 1**a** and G in Fig. 1**b**) this peak exists separately (denoted as E_h) with the energy cut-off equal to 1.28–1.30 eV. The values are within the same range as above. Strong decrease (in some positions) of the photoresponse at energies higher than E_h is most probably associated with the surface recombination of minority photo-excited carriers.

The energy of the cut-off of the main photoresponse peak is estimated to be 1.41–1.45 eV, and the maximum slope of that cut-off (at the half-height of the peak) is around 1.5 eV which corresponds very well to either the direct bandgap of Zn_3P_2 [1] or to transitions from acceptor levels [16], [17]. Additionally, well marked maxima E_a and E_b (mentioned above) at the energies around 1.57 eV and around 1.72 eV, respectively, are also observed. These energy values may also be ascribed (to the first approximation) to direct band-to-band transitions at the gamma point from the levels splitted off from the top of the valence band due to spin-orbit and crystal field effects [15], [18], [19].

The energy positions of the E_a, E_b and E_h peaks for various LSP are shown in Fig. 3**a** and 3**b** for the parallel and the perpendicular light-contact configuration, respectively. For the parallel configuration these energy positions do not depend on the LSP significantly as shown in Fig. 3**a**; the results are scattered around the value of 1.37 eV ± 10 meV for E_h, and 1.57 eV and 1.72 eV (±20 meV) for E_a and E_b peaks, respectively; that is within the error limit at room temperature. For the perpendicular configuration there is rather linear dependence of the energy position of the

E_a and E_b peaks upon the LSP, whereas for the peak E_h we found almost constant value of the energy position, with the results scattered around 1.39 eV + 25 meV, as shown in Fig. 3**b**. This scatter of results is roughly equal to kT value at room temperature. The difference in the behaviour of the E_a and E_b peaks between the parallel and the perpendicular light-contact configuration could probably be ascribed to the effect of surface recombination combined with the different geometry of light spot with reference to the contact on which the photoresponse was measured. However, one should also observe that the weak linear growing-up dependence of the E_a and E_b versus the LSP falls within the relatively narrow range of the energy, equal to 60 meV for the E_a peak and equal to 120 meV for E_b peak (in Fig. 3**b**). The mean value for the energy position of the E_a peak is then 1.57 eV and 1.71 eV for the E_b peak. Therefore, the mean results of the energy positions of E_a, E_b and E_h peaks for both the light-contact configurations are practically the same.

The intensity of photoresponse (measured as the relative values for E_a, E_b and E_h peaks) versus the LSP is shown in Fig. 4**a** and 4**b** for the parallel and the perpendicular light-contact configuration, respectively. The highest intensity was found for the light spot positioned very close to an edge of the contact on which the photoresponse was measured. That was found for all the peaks and independently of the configuration. This effect was also found in the previous papers and was explained elsewhere [7]. In some cases, however (in the perpendicular configuration) the shape, intensity and the other singularities of photoresponses were not always the same for the same/symmetrical light beam-versus-contact positions. We suggest this effect to be due to some micro-nonhomogeneities of the sample.

Very strong drop of the photoresponse at short wavelengths side of the main peak is caused by two reasons, at least. The first is the surface recombination of photogenerated electrons. Photons with energies within this range (in contrast to low-energy photons) are absorbed effectively very close to the sample surface, where effectiveness of the surface recombination (within the distance shorter than the diffusion length, approximately) is very high. We should also add that intensity of illumination applied was rather weak. The second most probable reason of this very strong drop is a competitive photoeffect (competitive photo-generated carriers) which superposes over the first one (having negative polarity). This photoeffect is therefore responsible also for the change of the sign of the photovoltage polarity at energies denoted by E_p. The sign-reversal point E_p is found to be here at 1.85–2.35 eV and to slightly depend on the light spot position.

Actually, the most interesting singularity is therefore the change of photovoltage polarity and its dependence upon the light spot position. We should note that the effect of various polarity in photovoltage has also been observed in ZnS crystals [20], [21]. Here, for Zn_3P_2 crystals, we have found that there is a distinct relationship between the barrier height (the metal used to produce the barrier contact with Zn_3P_2) and the change of polarity of the photovoltage measured on the barrier. In this sense the metal used has some impact upon the photoresponse parameters.

For the Mg-Zn_3P_2 contacts with the highest barrier obtainable (see, e.g., [19], [22]) equal to 0.8 eV approximately we have found no change of the photovoltage

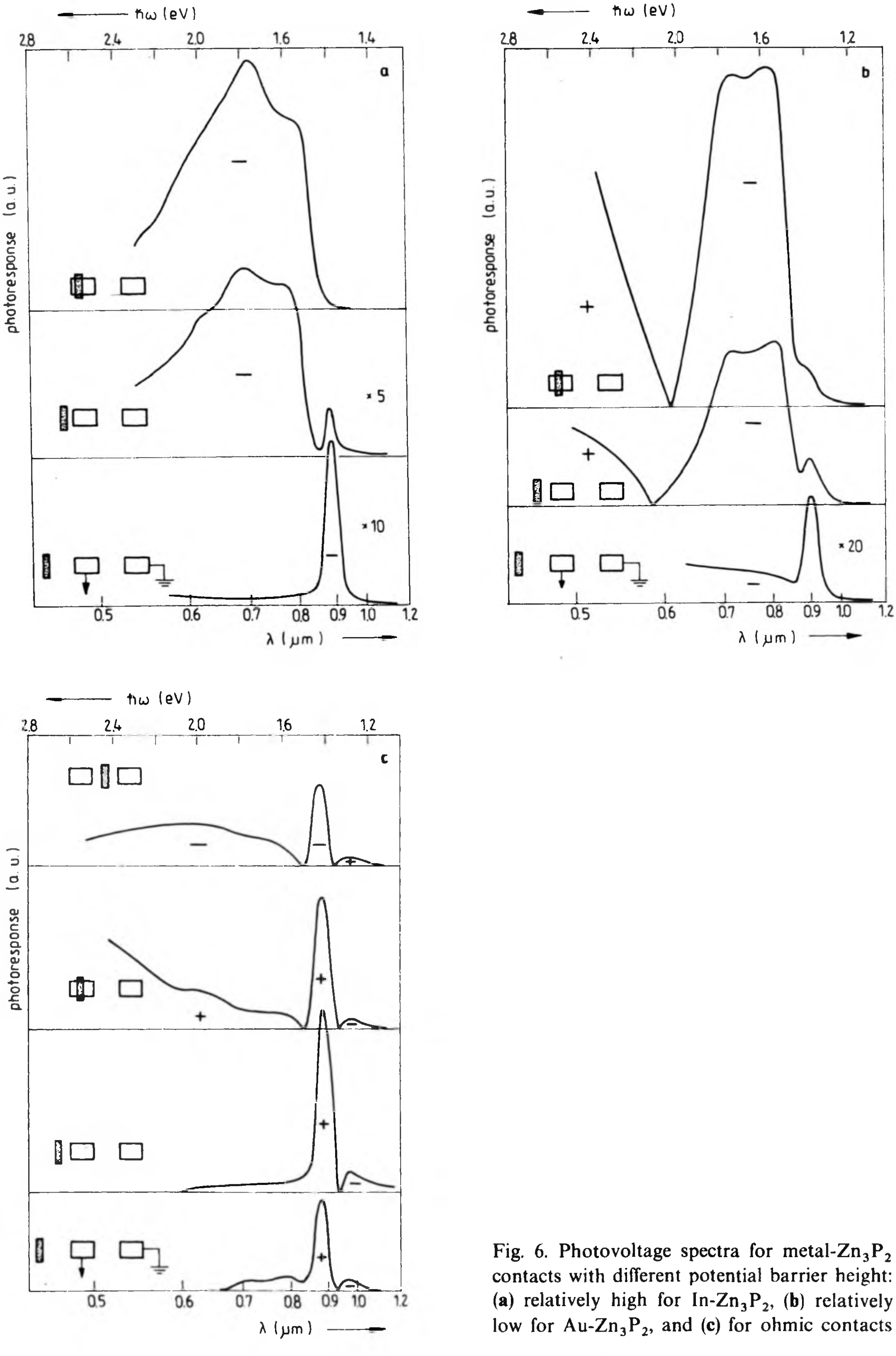

Fig. 6. Photovoltage spectra for metal-Zn_3P_2 contacts with different potential barrier height: (**a**) relatively high for In-Zn_3P_2, (**b**) relatively low for Au-Zn_3P_2, and (**c**) for ohmic contacts

polarity in this photon energy range and, simultaneously, the very strong photoresponse (high voltage/current photosensitivity). The results of this study are discussed, e.g., in [23]. The photovoltage spectra for relatively high a barrier (for In-Zn_3P_2 contacts) around 0.6 eV [19], for relatively weak a barrier (for Au-Zn_3P_2 contacts) averaging less than 0.5 eV [19] and for the ohmic contacts are compared in Fig. 6. The results are taken from [7] for In-Zn_3P_2 contacts and from this work for the last two. There is a visible transformation of the photoresponse behaviour when moving from the high-barrier contact to the ohmic one.

The dependence of the change of polarity of the photovoltage measured upon the contact barrier height is somehow (but certainly) related also to the high resistivity of Zn_3P_2 sample (photostatic effect) – see also discussion on the Dember effect published in [6]. Therefore, the change of polarity can be ascribed to the combination of i) the photostatic effec, and ii) the various height of the contact potential barrier;, and, therefore, is sensitive to both the surface recombination velocity and the light-spot position.

5. Conclusion

The study on photovoltage response of the metal-Zn_3P_2 contacts shows two important properties of the investigated structures:

1. Relatively high recombination on the surface/interface states.
2. Strong impact of the light spot position upon the sign and value of the photovoltage response. That effect is, to the first approximation, i) related to the two-type-carrier excitations (electrons from indirect interband transitions and these from the direct transitions); ii) influenced by the photostatic effect and presumably combined with iii) high recombination on the surface/interface states.

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Конфигурация зависимости фотоэффекта в Zn_3P_2

Исследовано влияние конфигурации освещения на форму и размер фотоответа в структуре металл-Zn_3P_2. Измерения были проведены в температуре 300 K в двух конфигурациях световой точки по отношению к металлическим контактам. Первую конфигурацию реализовали, перемещая световую точку параллельно к линии, соединяющей омический и выпрямляющий контакты. Во второй конфигурации светвую точку перемещали вертикально к линии, соединяющей два контакта. Выяснение полученных результатов базировало на присутствии различных электронных переходов в структуре Zn_3P_2, рекомбинации носителей тока и фотостатического эффекта.