

Photoelectrical properties of $\text{Zn}_3\text{InGaS}_6$ single crystals

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The results of a study of photoconductivity (PC) spectra, and optical and thermal PC quenching in $\text{Zn}_3\text{InGaS}_6$ single crystals are presented. A scheme for localized states is proposed which contains quasi-continuously distributed electron traps below the bottom of the conduction band as well as two acceptor r- and s-levels.

1. Introduction

The complex $\text{A}^{\text{II}}\text{B}_{1-x}^{\text{III}}\text{C}_x^{\text{III}}\text{D}^{\text{VI}}$ phases are of interest due to their potential application in solar cells and optoelectronics [1]. The $\text{Zn}_3\text{InGaS}_6$ layer compound belongs to the above mentioned phases and has a band-gap energy $E_g = 3.26$ eV ($T = 300$ K). Data on the structure of edge absorption and photoluminescence of this compound have been published [2,3]. The $\text{Zn}_3\text{InGaS}_6$ photoluminescent characteristics proved to be determined by the presence of quasi-continuously distributed electron traps below the bottom of the conduction band as well as by the presence of a compensated acceptor level not far from the top of the valence band [3]. The photoelectric properties have not been studied yet. The goal of the present work is to investigate the stationary photoconductivity spectra, and optical and thermal PC quenching. Besides the current-power characteristics of $\text{Zn}_3\text{InGaS}_6$ single crystals, the photosensitivity (PS) spectrum of Pt- $\text{Zn}_3\text{InGaS}_6$ Schottky barriers is also presented.

2. Experimental technique

$\text{Zn}_3\text{InGaS}_6$ single crystals with $10 \times 10 \times 1$ mm³ dimensions have been prepared by the iodine transport technique. The crystals possess n-type conductivity with a resistivity of 10^{11} Ω cm. Electrical contacts were made for PC measurements. Ohmic indium contacts were soldered onto the (0001)-oriented faces of the samples. Another contact was a thin semitransparent platinum rectifying contact prepared by vacuum deposition. When PC optical quenching was investigated, the samples were illuminated by primary ($\lambda_1 = 366$ nm and $\lambda_2 = 436$ nm) and sec-

ondary ($\lambda_s = 500\text{--}1300$ nm) light simultaneously. Note that the absorption of light with $\lambda_1 = 366$ nm resulted in surface excitation of the crystals, while absorption of light at $\lambda_2 = 436$ nm occurred in the bulk. The investigated photoelectrical spectra were normalized to the unit quantum flux of the original beam. The accuracy of the energy position of the spectral response was determined to be within 0.02 eV.

3. Results

Fig. 1 presents the PC spectra of $\text{Zn}_3\text{InGaS}_6$ crystals as well as the PS spectrum of Pt- $\text{Zn}_3\text{InGaS}_6$ Schottky barriers. The PC spectrum at 300 K shows two peaks (curve 1) at 2.73 and 3.25 eV, the intensity of the long wavelength feature being considerably smaller than that of the short wavelength one. When the temperature is lowered, the low-energy feature amplitude drops until it disappears at 80 K. The energy position of both features turns out to depend on the intensity of the electric field applied to the sample. When the electric field ε diminishes, a shift of both features to the short wavelength region of the spectra occurs while their shape remains unchanged.

The PS spectrum of Pt- $\text{Zn}_3\text{InGaS}_6$ Schottky barriers shows a broad smooth band with the maximum at 3.55 eV ($T = 300$ K). It can be seen that the sensitivity field of the barriers involved corresponds to the visible violet region. The value of the barrier sensitivity is about 10^2 mA/W at 300 K.

Fig. 2 illustrates the current-flux characteristics of two $\text{Zn}_3\text{InGaS}_6$ single crystals. At room temperature the characteristic consists of two parts with different slopes. When the fluxes of excitation radiation (L) are in the range $3 \times 10^{-4}\text{--}5 \times 10^{-3}$ W/cm² a superlinear part with a slope coefficient α , equal to 1.3, is observed. At $L > 5 \times 10^{-3}$ W/cm² a sublinear part is distinguished with $\alpha = 0.6$. The inflection point (between the superlinear and sublinear parts of the current-power characteristics) is shifted toward smaller excitation fluxes when the temperature decreases. As a result the sublinear part of the characteristic is considerably broader at 80 K than at 300 K.

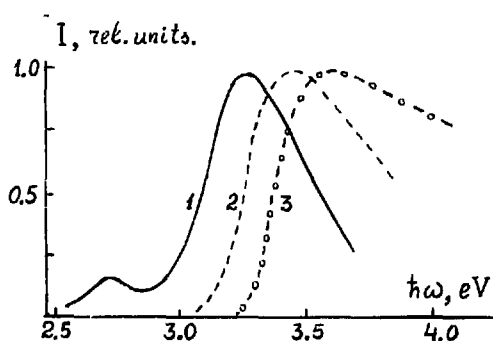


Fig. 1. PC spectra of $\text{Zn}_3\text{InGaS}_6$ crystals (1, 2) and PS spectrum of Pt- $\text{Zn}_3\text{InGaS}_6$ Schottky barriers (3) (1, 3) $T = 300$ K; (2) $T = 80$ K.

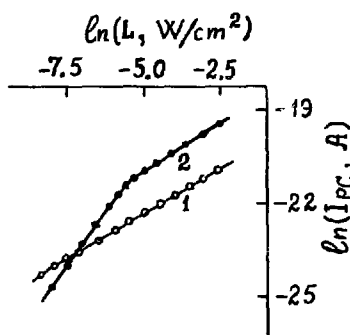


Fig. 2 Current-flux characteristics of $\text{Zn}_3\text{InGaS}_6$ crystals at 80 (1) and 300 K (2).

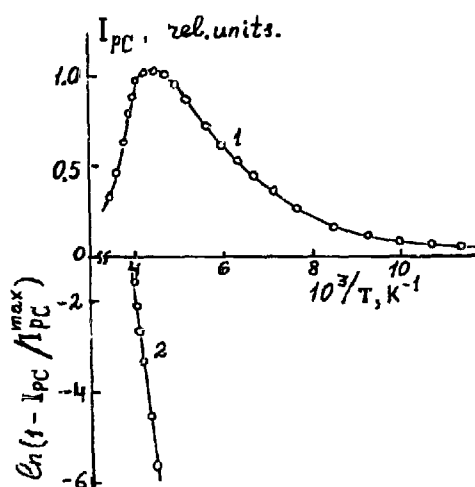


Fig. 3 The temperature dependence of $\text{Zn}_3\text{InGaS}_6$ photocurrent for flux $L = 5 \times 10^2 \text{ W/cm}^2$.

Fig. 3 shows the temperature dependence of $\text{Zn}_3\text{InGaS}_6$ photocurrent at flux $L = 5 \times 10^2 \text{ W/cm}^2$ (curve 1). The higher the temperature in the interval 80–220 K the greater the photocurrent, while at $T > 220 \text{ K}$ a sharp drop of the I_{PC} occurs. The semilogarithmic dependence of photocurrent on T^{-1} shows a straight line (curve 2), the analysis of which allows one to estimate the depth of the sensitizing s-level. The value of 0.9 eV has been obtained.

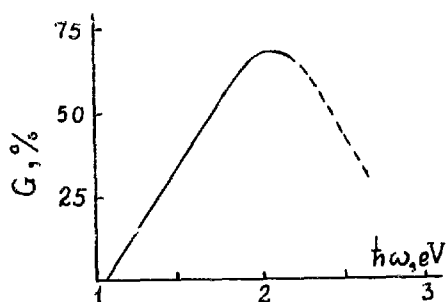


Fig. 4 The spectral dependence of the $\text{Zn}_3\text{InGaS}_6$ PC quenching. $T = 300 \text{ K}$

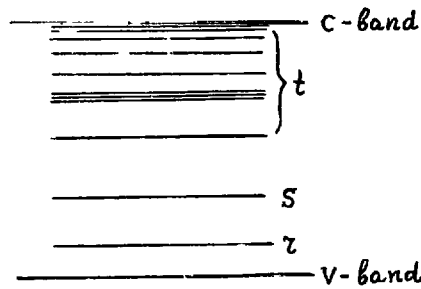


Fig. 5. Proposed scheme for the localized states in $\text{Zn}_3\text{InGaS}_6$ crystals

Fig. 4 presents the spectral dependence of the PC quenching $G(\omega)$ determined according to the relation

$$G(\omega) = \frac{I_{\text{PC}} - I'_{\text{PC}}}{I_{\text{PC}}},$$

where I_{PC} is the photocurrent caused by the primary radiation and I'_{PC} is the one induced by both the primary and the secondary radiation. The threshold of the quenching band is situated at the secondary radiation quantum energy, equal to 1.1 eV, which correlates well with the depth of the s-level determined above.

4. Discussion

The decrease in amplitude with temperature of the peak at 2.73 eV seems to be caused by electron transitions from the compensated acceptor r-level to the quasi-continuously distributed t-traps (fig. 5), from where the electrons are thermally generated to the conduction band. As the temperature decreases the probability of radiative recombination of the electrons from the above mentioned t-states with holes from r-levels increases. As a consequence, the probability of electron thermal generation to the c-band drops. This results in a monotonous decrease of the PC peak intensity as the temperature is lowered, until it vanishes. Taking into consideration the data concerning the optical edge absorption in $\text{Zn}_3\text{InGaS}_6$ single crystals [2] the PC peak at 3.25 eV can be attributed to direct band-to-band transitions.

The shifting of the Pt- $\text{Zn}_3\text{InGaS}_6$ Schottky barrier photoresponse band towards the ultra-violet region (relative to the intrinsic PC peak) can be connected with the bending of the conduction and valence bands in the near-junction region.

The appearance of the superlinear part in the current-power characteristic at 300 K may be explained by the so-called electron doping [4], e.g. by the shift of electron and hole Fermi quasi-levels toward the band-gap edges. The superlinear part appears when the acceptor r-level is crossed by the hole Fermi quasi-level, which at 80 K proves to be situated between the r-level and the valence band top. Because of this the sublinear part of the current-power characteristics becomes predominating with flux diminution.

The increase of PC intensity with temperature in the range 80–220 K is caused by the thermal release of electrons from the t-levels. When $T > 220$ K the thermal jumping of electrons from the valence-band to the r-level takes place. As the generated holes are being captured by s-levels, an intensive recombination of free electrons upon these levels occurs. This leads to an abrupt drop of the free electron life time and consequently to the presence of thermal quenching of PC. This mechanism explains also the optical quenching of $\text{Zn}_3\text{InGaS}_6$ PC.

5. Conclusion

The investigation carried out has shown that the properties of $\text{Zn}_3\text{InGaS}_6$ crystals are determined by the existence of the exponentially distributed electron traps below the conduction band bottom, as well as by that of the acceptor r- and s-levels. Those localized states appear to be caused by native defects. For instance in the ternary $\text{A}^{\text{II}}\text{B}_2^{\text{III}}\text{C}_4^{\text{VI}}$ semiconductors the quasi-continuously distributed electron traps are accounted for by the antistructural disorder in the cation sublattice of the crystals [5]. The investigation of the order–disorder effects in $\text{A}^{\text{II}}\text{B}_{j-x}^{\text{III}}\text{C}_x^{\text{III}}\text{D}^{\text{VI}}$ phases is in progress in our laboratory [6].

References

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