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Donor-acceptor transitions in Zn_3P_2*

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Photoluminescence within 1.15–1.7 eV energy range and absorption derivative spectrum within 1.38–1.62 eV energy range of Zn_3P_2 crystal at liquid helium temperature are presented. Features observed at the energies of 1.31, 1.41, 1.51, 1.53, 1.56, 1.59 and 1.66 eV are interpreted in terms of transitions involving acceptor and donor levels. Energies of residual donors are proposed as 10–20 meV and 110 meV.

1. Introduction

Zn_3P_2 – p-type semiconductor [1] – has recently become one of the most promising materials for low cost solar cells due to the following properties:

i) Location of the optical absorption edge at 1.5–1.6 eV which is in the optimum range for solar energy conversion [2], [3].

ii) Minority carrier diffusion length of ≈ 10 μm [4] which permits high current collection.

iii) Both constituent elements are aboundant and inexpensive.

The review of Zn_3P_2-based solar cell studies was made by Pawlikowski [5]. Ultraviolet detectors were made on the base of thin Zn_3P_2 films in [6]. A distinct photodichroism observed on metal-Zn_3P_2 (oriented single crystal) junctions was applied in light polarization step indicator [7].

The konwledge of the levels located within the energy gap is the important indicator of the potential applicability of the material and its quality. Several works on this field were published until now. Electrical transport measurements were studied in the papers [8]–[14]. DLTS measurements of the Mg-Zn_3P_2 diodes were performed and analysed in papers [15], [16]. Photoluminescence investigations were made within 0.4–1.2 eV energy range [17], 0.9–1.7 eV [18], 1.25–1.4 eV [19], [20] and 1.5–1.7 eV [21]. Optical absorption of the deep levels within the 0.1–1.4 eV energy range was measured and discussed in papers [22], [23]. Photoelectrical spectra on metal-Zn_3P_2 contacts were presented in papers [7], [24]–[29].

This paper brings results of photoluminescence measurements within 1.15–1.7 eV energy range and absorption derivative spectrum within 1.38–1.62 eV at liquid helium temperature.

Based on these data, a set of optical transitions was determined. The observed features are discussed in terms of donor-acceptor and acceptor-donor transitions.

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2. Experimental

Zn_3P_2 was synthesized by a direct reaction of stoichiometric proportions of high purity zinc and red phosphorous. The load was sealed in clean quartz ampoule at a nominal pressure of 5×10^{-6} Torrs. The ampoule temperature was maintained at about 670 K for 4 hours, and for the next 8 hours it was increased up to 720 K. Then the temperature was stabilized for 24 hours at 1100 K in the hot end and at 650 K in the cold end. Zn_3P_2 was formed in the cooler part of the ampoule. Multiple sublimation processes were applied to purify the obtained material. Chemical analysis showed that the zinc and phosphorous content was that one expected for the stoichiometric compound, with only some trace of foreign elements.

Single crystal growth was performed by using chemical transport method with iodine as an active carrier and directed vapour transport method (for details, see [30], [31]). The first technique gave single crystals with dimensions of approx. $5 \times 3 \times 1$ mm^3, while the second one – single crystals of approx. 0.9 cm in diameter and 1–2 cm long. The samples were cut out from the boule to the appropriate thickness, mechanically polished using alumina powder of 1, 0.3 and 0.05 μm grain sizes. After polishing the samples were decreased in acetone and methanol and then etched in 1.5–2% bromine methanol solution. To obtain samples ≈ 20 μm thick, appropriate for absorption measurements, they were polished up to 100 μm and then subjected to additional etching in bromine methanol solution.

The measuring set-up for absorption derivative spectra based on the GDM–1000 as well as SPM–2 Zeiss monochromators and a plane parallel vibration plate technique was described previously [32].

To perform photoluminescence measurements, two different equipments were used. In the 1.15–1.48 eV the set-up consisted of ILA–120 argon ion laser at 488 nm line, grid SPM–2 monochromator a cooled MIO–FD29 photomultiplier, lock-in and a multichannel analyser (for details, see [33]). To measure photoluminescence within 1.48–1.70 eV energy range, the samples were excited by krypton ion laser at 676 nm line. A double-grating SPEX spectrophotometer, cooled GaAs photomultiplier at photon counting system were used.

3. Results and discussion

Representative plot of the absorption derivative within 1.38–1.62 eV energy range measured at 10 K is presented in Fig. 1. In this region, the absorption coefficient rises from a few cm^{-1} in the low energy part to a few thousand cm^{-1} (see, e.g., [2]). The main maximum on the absorption derivative curve is located at 1.51 eV. This transition well corresponds with distinct change in absorption curve as well as in photoresponse plots at low temperatures also [2], [7], [23]. Besides this peak, there are two small bumps in the low energy part of the spectrum at 1.41 eV and 1.44 eV. On the high energy part, there are transitions visible at 1.53, 1.55 and 1.59 eV.

In Figure 2, a typical plot of photoluminescence within 1.15–1.48 eV energy range

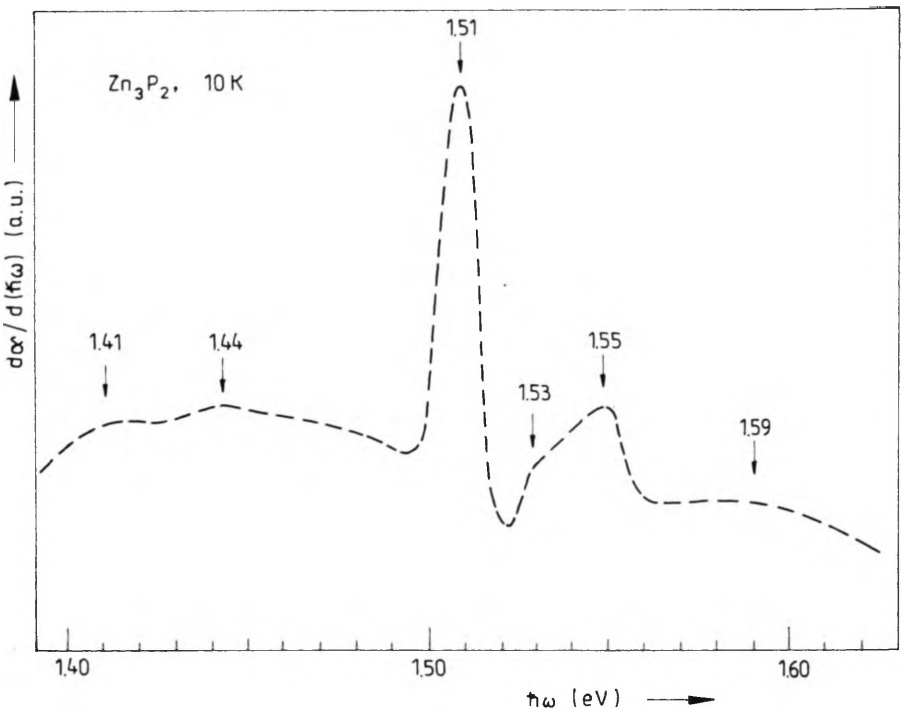

Fig. 1. Absorption derivative spectrum of Zn_3P_2 at low temperature. Characteristic energies are marked

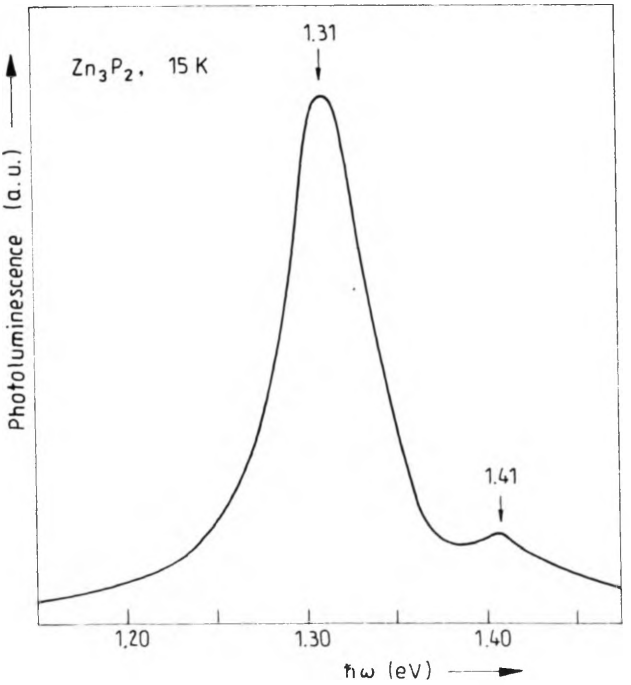

Fig. 2. Photoluminescence spectrum of Zn_3P_2 at low temperature in 1.15–1.48 eV energy range. Characteristic energies are marked

at 15 K is presented. The main band possesses a maximum at 1.31 eV. The second much weaker peak is located at 1.41 eV. Figure 3 presents exemplary photoluminescence plots for two different samples for the 1.48–1.7 eV energy region at 4.2 K. In these spectra, several relatively weak transitions are visible. Energies of the denoted

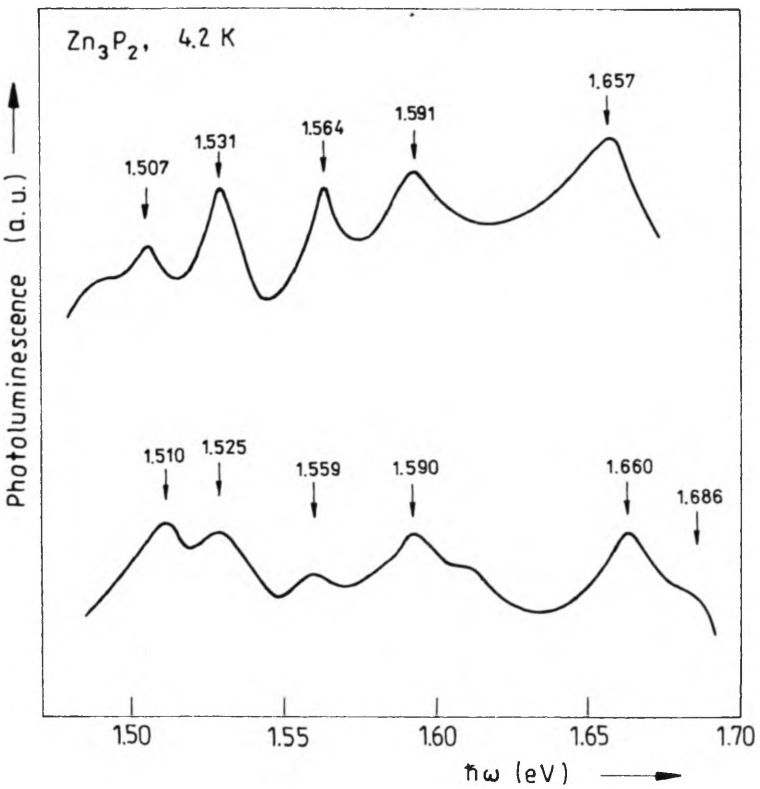

Fig. 3. Photoluminescence spectra of Zn_3P_2 samples at low temperature in the 1.48–1.69 eV energy range. Characteristic energies are marked

peaks for both samples are in good coincidence. Table 1 collects the energies of transitions observed in photoluminescence and absorption derivative spectra. Data from the literature are also included.

The agreement between photoluminescence peak position within 1.5–1.7 eV energy range in [21] and this paper may arise from the fact that measured samples were cut from the same Zn_3P_2 single crystal.

To explain the results obtained, as a first step we should take the direct energy gap value at liquid helium temperature equal to 1.69 eV [2]. Thus, a small feature observed in photoluminescence at 1.68 eV may be connected with band-to-band recombination. The most probable explanation of the other transitions in the measured PL spectra is based on the assumption of the predominant role of donor-acceptor pair (DAP) recombination.

Table 1. Energies of the transitions observed in photoluminescence and absorption derivative spectra at liquid helium temperature (in eV)

$d\alpha/dE$	Photoluminescence				
	this work	[18]	[19]	[20]	[21]
	1.31		1.32	1.33	
			1.36	1.37	
1.41	1.41				
1.44					
1.51	1.51	1.51			1.51
1.53	1.53				1.53
1.55	1.56				1.56
1.59	1.59				1.59
	1.66	1.665			1.66

Until now, by using electrical and optical methods, the following acceptor levels were found in Zn_3P_2 (main values are presented): 0.03 eV [9]–[11], [13], [14], [22], [23]; 0.16 eV [10], [11], [13], [15], [16], [22], [23]; 0.275 eV [11], [14]–[16], [22], [23], and 0.42 eV [10], [11], [15], [16], [22], [23]. All available data are collected in Table 2.

Table 2. Energies of acceptor levels in Zn_3P_2 (in eV)

[23]	0.015, 0.04	0.14–0.19	0.25–0.30	0.36–0.42
[11]	0.02, 0.034	0.14	0.25	0.47
[9]	0.034			
[13]	0.04–0.045	0.14		
[14]	0.034		0.27	
[10]		0.18		0.44
[15], [16]		0.13	0.20	0.36, 0.48
[22]	0.05	0.17	0.27	0.36

Features attributed to the DAP recombination have energies given by

$$h\nu = E_g - (E_A + E_D) + \frac{e^2}{\varepsilon r} \tag{1}$$

where E_A and E_D are acceptor and donor ionization energies, respectively, and $r \sim (\pi N_A)^{1/2}$ is the main pair separation distance. For N_A close to 10^{17} cm^{-3} [23] we obtain $e^2/\varepsilon r \approx 10$ meV ($\varepsilon \approx 11$ for Zn_3P_2 [2]). This value is within the energy uncertainty of the peaks.

By using the main values of acceptor levels listed above and relation (1) we may correlate the observed transitions with some unknown donor levels. Thus, peaks denoted at energies 1.31 eV and 1.41 eV may be connected with acceptors at 0.36 eV and 0.27 eV, respectively, assuming donor in the range of 10–20 meV. Transitions visible at energies of 1.51 eV, 1.53 eV and 1.66 eV may be correlated with acceptors

at 0.17 eV, 0.15 eV and 0.03 eV, respectively, taking into account donor level at 10–20 meV. To explain the feature at 1.56 eV as a transition to acceptor at 0.03 eV we should assume the existence of deeper donor level like ≈ 110 meV below conduction band.

A very good agreement between transitions observed in photoluminescence and absorption derivative spectrum is visible.

It is possible that the transitions observed in absorption plot and those observed in photoluminescence measurements make pairs of absorption-luminescence transitions between the acceptor levels and residual donor levels. Such an interpretation needs the assumption of small electron-lattice coupling effect to be involved, because the differences between the energies of absorption and emission processes are small. The existence of residual donor levels seem to be comprehensible in the light of acceptor compension mechanism clearly indicated in [23].

Unfortunately, the existence of the donor levels proposed in this paper to explain photoluminescence and absorption derivative spectra has not been confirmed directly, as yet.

4. Conclusions

Photoluminescence spectra of Zn_3P_2 within 1.15–1.7 eV energy range are presented together with the absorption derivative plot within 1.38–1.62 eV energy range. All results were obtained at liquid helium temperature. The observed transitions are interpreted in terms of donor-acceptor transitions in photoluminescence spectra and acceptor-donor ones in absorption plot. This explanations are based on known acceptor level energies and lead to suggestion that donor energies participate in the observed transitions.

References

[1] ŻDANOWICZ W., ŻDANOWICZ L., Ann. Rev. Mater. Sci. **5** (1975), 301.
[2] PAWLIKOWSKI J. M., MISIEWICZ J., MIROWSKA N., J. Phys. Chem. Solids **40** (1987), 1027.
[3] PAWLIKOWSKI J. M., Phys. Rev. B. **26** (1982), 4711.
[4] NAUKA K., MISIEWICZ J., Phys. Status Solidi A **64** (1982), K95.
[5] PAWLIKOWSKI J. M., Rev. Solid State Sci. **2** (1988), 581.
[6] BENDETT M. P., HUNGSPERGER R. G., J. Electron. Mater. **10** (1981), 559.
[7] MISIEWICZ J., MIROWSKA N., GUMIENNY Z., Phys. Status Solidi A **83** (1984), K51.
[8] ŻDANOWICZ W., HENKIE Z., Bull. Acad. Polon. Sci., Ser. Sci. Chim. **12** (1964), 729.
[9] SHEVCHENKO V. Ya., BABARINA L. R., KOZLOV S. E., LAZAREV V. B., Izv. Akad. Nauk SSSR, Neorgan. Mater. **11** (1975), 1719.
[10] MÖLLER A., ELROD U., MUNZ P., HÖNIGSCHMID J., CLEMEN C., BUCHER E., Inst. Phys. Conf. Ser. **43** (1979), 825.
[11] WANG F. C., FAHRENBUCH A. L., BUBE R. H., J. Electron. Mater. **11** (1982), 75.
[12] CATALANO A., HALL R. B., J. Phys. Chem. Solids **41** (1980), 635.
[13] SIERAŃSKI K., SZATKOWSKI J., Phys. Status Solidi A **94** (1986), K133.
[14] SZATKOWSKI J., SIERAŃSKI K., Acta Phys. Pol. Ser. A **71** (1987), 297.
[15] SUDA T., BUBE R. H., Appl. Phys. Lett. **45** (1984), 775.

[16] SUDA T., KUROYANAGI A., Jpn J. Appl. Phys. **25** (1986), L993.
[17] SUNDSTRÖM B. O., NILSSON N. G., HULDT L., ŻDANOWICZ W., [In] *Proc. Ist. Int. Symp. Phys. Chem. II–C Compounds*, Mogilany 1980, [Eds.] M. J. Gelten, L. Żdanowicz, Eindhoven, Netherlands, p. 175.
[18] HULDT L., NILSSON N. G., SUNDSTRÖM B. O., ŻDANOWICZ W., Phys. Status Solidi A **53** (1979), K15.
[19] BRIONES F., WANG F. C., BUBE R. H., Appl. Phys. Lett. **39** (1981), 805.
[20] KURBATOV L. N., DIROCHKA A. I., SINITSYN E. V., LAZAREV V. B., SHEVCHENKO V. Ya., KOZLOV S. E., Sov. J. Quantum Electron. **6** (1976), 166.
[21] MISIEWICZ J., Phys. Status Solidi A **107** (1988), K65.
[22] MISIEWICZ J., SUJAK CYRUL B., BARTCZAK A., Solid State Commun. **58** (1986), 677.
[23] MISIEWICZ J., J. Phys. Chem. Solids (1989), to be published.
[24] RADAUTSAN S. J., SYRBU N. N., VOLODINA V. J., KIOSSEV V. K., Sov. Phys. Dokl. **21** (1976), 193.
[25] VOLODINA V. J., RADAUTSAN S. J., KADYGROB V. J., SYRBU N. N., Sov. Phys. Semicond. **11** (1977), 354.
[26] PAWLIKOWSKI J. M., MIROWSKA N., KRÓLICKI F., Infrared Phys. **18** (1978), 343.
[27] SYRBU N. N., STAMOV I. G., MOROZOVA V. I., KIOSSEV V. K., PEEV L. G., [In] *Proc. Ist Int. Symp. Phys. Chem. II–V Compounds*, Mogilany 1980, [Eds.] M. J. Gelten and L. Żdanowicz, Eindhoven, Netherlands, p. 237.
[28] WANG F. C., BUBE R. H., J. Appl. Phys. **53** (1982), 3335.
[29] MISIEWICZ J., Infrared Phys. **28** (1988), 215.
[30] MISIEWICZ J., KRÓLICKI F., Mater. Sci. **11** (1985), 39.
[31] MISIEWICZ J., KRÓLICKI F., LEWICKI F., KASPRZAK J. F., Acta Phys. Pol. Ser. A **69** (1986), 1127.
[32] GUMIENNY Z., MISIEWICZ J., Opt. Appl. **16** (1986), 175.
[33] MISIEWICZ J., GUMIENNY Z., CYWIŃSKI R., MUGEŃSKI E., Phys. Status Solidi A **111** (1989), K249.

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Переходы донор-акцептор в фосфиде цинка (Zn_3P_2)

Спектры фотолюминесценции Zn_3P_2 измерены в пределах энергии от 1,15 до 1,70 эв а спектры производной коэффициента абсорбции – в пределах от 1,38 до 1,62 эв. Измерения были выполнены в температурах 4,2 и 15 К. Особенности, наблюдаемые для энергий 1,31; 1,41; 1,51; 1,53; 1,56; 1,59 и 1,66 эв интерпретировались как переходы между акцепторными и донорными уровнями. Энергии донорных уровней, участвующих в переходах, определены на 10–20 мэв и 110 мэв.