Optica Applicata VIII/3, 1978

Jan Misiewicz, Nella Mirowska*. Franciszek Królicki***

Photoconductivity and diffuse reflectivity of Zn_3P_2 in 0.70—1.10 μm waverange***

Photoconductivity and diffuse reflectance spectra of Zn_3P_2 were measured near fundamental absorption edge at 300 and 77 K The values of energy gap have been determined as 1.33 and 1.38 eV at 300 and 77 K, respectively.

1. Introduction

Zinc-phosphide (Zn_3P_2) compound is a semiconductor of the $A_3^{II}B_2^V$ type having a tetragonal-type lattice of the D_{4h}^{15} space group [1]. Fundamental electrical properties are presented in papers [1–6]. Zn_3P_2 is a *p*-type semiconductor with resistivity in the range 10^4–10^5 Ωm [3–5]. The holes concentration *p* and mobility μ are equal to $p = 3.56\times10^{20}m^{-3}$ and $\mu = 10^{-3}$ m²/Vs at 300 K and $p = 3.69\times10^{19}$ m^{-3} and $\mu = 5\times10^{-3}$ m²/Vs at 77 K, respectively [6]. Optical and photoelectric properties of Zn_3P_2 were investigated in the work [7].

LIN-CHUNG performed a theoretical band structure calculation of Zn_3P_2 basing, however, on the simplified hypothetical crystal lattice [8].

The values of the Zn_3P_2 energy gap obtained from electrical and optical measurements as well as theoretical calculations are presented in table. It has been noticed that these values differ remarkable from one another. The precise method to estimate the energy gap is based on the fundamental absorption edge measurements. In the case of Zn_3P_2, however, it is very difficult, because of the great value of the absorption coefficient. On the other hand, another methods can be useful; among others the photoconductivity or diffusion reflectivity measurements are often performed.

This paper just presents the photoconductivity and diffuse reflectivity spectra and also the estimation of the Zn_3P_2 energy gap.

The values of Zn_3P_2 energy gap

$E_g(eV)$	Methods	References
1.15	conductivity measurements	[3]
1.20	conductivity and Hall-coeff. measurements	[5]
1.30 (300 K) 1.32 (77 K) 1.44 (300 K) 1.46 (77 K)	absorption edge photoconductivity (peak)	[7]
1.886	pseudopotential calculation	[8]
1.33±0.02 (300 K) 1.39±0.02 (77 K) 1.33±0.03 (300 K) 1.38±0.03 (77 K)	long-wave edge of photoconductivity diffuse reflectivity	this work

2. Experimental part

Zn_3P_2 crystals were grown by the method described in [9]. In the photoconductivity measurements the monocrystals of Zn_3P_2 with an area of 6×2 mm² and a thickness about 0.2–0.5 mm have been used. Electrical contacts were made by vacuum ($p = 10^{-5}$ Torr) thermal evaporation of pure indium.

Photoconductivity spectra in the range 0.70–1.1 μm at 300 and 77 K have been measured using the SPM-2 (Carl Zeiss Jena) monochromator with quartz prizm. Zn_3P_2-powder with average grain sizes about a few μm has been used in diffuse reflectance measurements. The spectra of MgO as a standard substance [10] have been measured under the same conditions. Low temperature measurements have been made in a steel cryostat with quartz windows (photoconductivity) and spatial quartz cryostat (diffuse reflectance).

* Institute of Physics, Technical University of Wrocław, Wrocław, Poland.

** Institute of Inorganic Chemistry and Metallurgy of Rare Elements, Technical University of Wrocław, Wrocław, Poland.

*** This work was supported by Wrocław Technical University under contract 7/77 (IM-116).

3. Discussion of results

Spectral dependences of photoconductivity are presented in fig. 1. Both the maximum and sharp cut-off in photoconductivity spectrum were observed in the investigated waverange. The values of energy

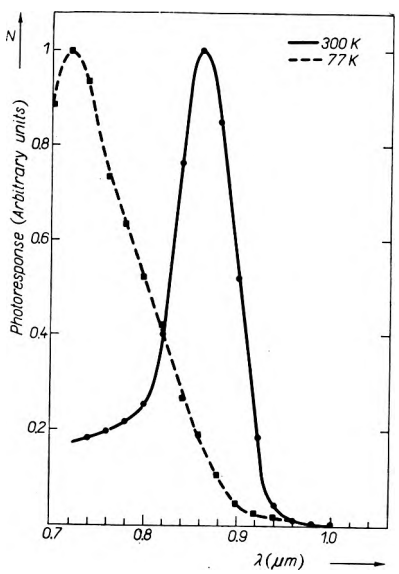

Fig. 1. Spectral dependence of photoconductivity of Zn_3P_2 at 77 K and 300 K

gap from the edge position* by linear approximation to zero [11] are 1.33±0.02 eV at 300 K, and 1.39±0.02 eV at 77 K. These values are in a relatively good agreement with the results of the absorption measurements presented in the paper [7], but they differ considerably from the values obtained from the photoconductivity measurements made by the same authors. It should be mentioned that in this paper the energy of the optical transitions of electrons was defined from the position of the maximum photoresponse[7].

Exponential increase of the observed longwave edge of photoconductivity (it is close, with a good approximation, to the fundamental absorption edge [12]) refers to the Urbach-type plots [13]. They are presented in the fig. 2. Such behaviour of the absorption (or photoconductivity) edge is connected with the presence of the density-of-states tails. Their origin in Zn_3P_2 is not known yet.

Diffuse reflectivity measurement was used as an additional method to estimate the energy gap of Zn_3P_2. This method is the best for powder semiconductors investigation, it can be, however, successfully used for other semiconductors, especially when the absorption measurements are difficult [14, 15]. In this work the diffuse reflectance spectra of Zn_3P_2 were obtained at 77 and 300 K as examplary shown in fig. 3.

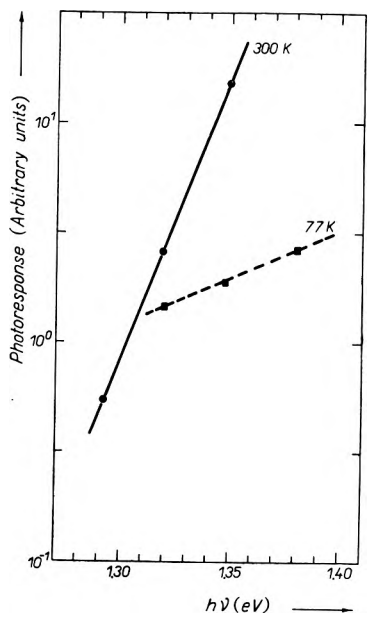

Fig. 2. Low-energy part of photoconductivity edge of Zn_3P_2 at 300 K and 77 K

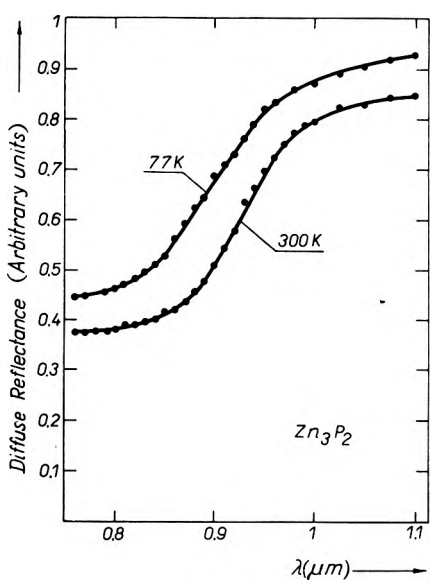

Fig. 3. Diffuse reflectance spectra of Zn_3P_2 powder at 77 K and 300 K

The KUBELKA-MUNK method [14–16] was used to estimate the values of the energy gap. This method applies spectral dependence of the remission function F:

$$F = \frac{(1-R)^2}{2R},$$

* The other values (ranged between 1.30–1.45 eV) have been observed. The presented spectrum shows the typical result in this series of measurements.

where R is the diffuse reflectance. The onset of the linear increase of the F-function (with the increase of the photon energy) determines the energy gap value, as it is seen in fig 4. The values of the energy

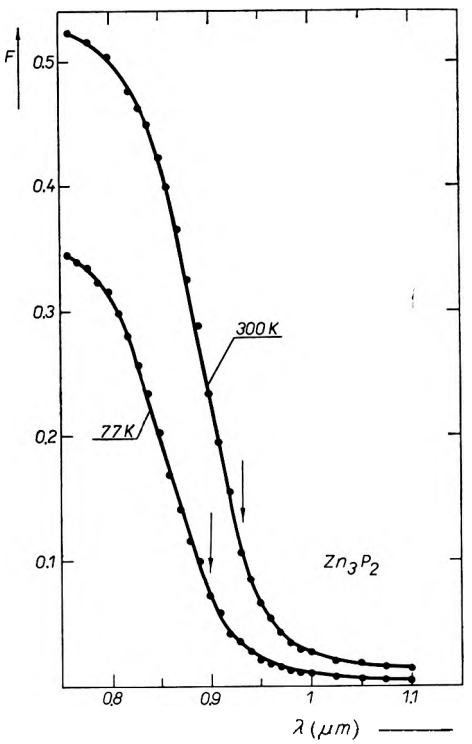

Fig. 4. Spectral dependence of Kubelka–Munk remision function F (see the text) of Zn_3P_2 at 77 K and 300 K

gap were estimated as 1.33 ± 0.03 eV at 300 K, and 1.38 ± 0.03 eV at 77 K. The values of the energy gap obtained from both the photoconductivity and diffuse reflectivity measurements are in relatively good agreement (see also table).

By assuming the linear dependence of E_g on temperature in 77–300 K range, the thermal coefficient of Zn_3P_2 energy gap has been obtained $dE_g/dT = -2.2\times10^{-4}$ eV/K.

Acknowledgments

The authors are very grateful to Dr. J. M. Pawlikowski for his valuable remarks. Special thanks are due to P. Plenkiewicz, for his help in the investigations and discussion of results.

Фотопроводимость и диффузионное рассеяние Zn_3P_2 в диапазоне волны 0,7-1,1 мкм

Измерены спектральные характеристики фотопроводимости и диффузионного рассеяния Zn_3P_2 вблизи грани поглощения, при температурах 77 и 300 К. Дается оценочное определение значения запрещенной зоны, а именно: при 77 К 1,38, а при 300 К — 1,33 электрон-вольта.

References

[1] Żdanowicz W., [in:] *Fizykochemia ciała stałego*, Part III, PWN, Warszawa 1967.
[2] Lagrenaudie J., J. Chim. Phys. **150**, 545 (1953).
[3] Lagrenaudie J., J. Phys. Radium **16**, 234 (1955).
[4] Juza R., Bar K., Z. Anorg. Allg. Chem. **283**, 230 (1956).
[5] Żdanowicz W., Henkie Z., Bull. Acad. Polon. Sci., ser. sci. Chem. **12**, 729 (1964).
[6] Shevchenko V. Ya. Babarina L. R., Kozlov S. E., Lazarev U. B., Izv. AS USSR, Neorg. Mater. **11**, 1719 (1976).
[7] Sobolev V. V., Syrbu N. N., Phys. Stat. Sol. (b) **64**, 423 (1974).
[8] Lin-Chung P. J., Phys. Stat. Sol. (b) **47**, 33 (1971).
[9] Żdanowicz W., Królicki F., Plenkiewicz P., Acta Phys. Pol. A **44**, 447 (1973).
[10] Shapiro J. P., Optica i Spektroskopiya **4**, 256 (1958).
[11] Kowtoniuk N. F. Koncewoj J. A., *Pomiary parametrów materialów półprzewodnikowych*, PWN, Warszawa 1973 (in Polish).
[12] Kasprzak J. F., Pawlikowski J. M., private communication (1977).
[13] Urbach F., Phys. Rev. **92**, 1324 (1953).
[14] Tandon S. P., Gupta J. P., Phys. Stat. Sol. **37**, 43 (1969).
[15] Tandon S. P., Gupta J. P., Phys. Stat. Sol. **38**, 363 (1970).
[16] Kubelka P., Munk F., Zh. Tekh. Fiz. **12**, 593 (1931).

Received, November 3, 1977