SOME OPTICAL PROPERTIES OF Zn_3P_2*

By L. Żdanowicz, W. Żdanowicz, D. Petelenz and K. Kloc

Institute of Solid State Physics, Polish Academy of Sciences, Zabrze**

(Received February 12, 1979)

Optical transition energy values for bulk and thin films of Zn_3P_2 have been determined from transmission and reflectivity data in the spectral range 0.45–2.7 μm and at 300 K. The investigated samples were Zn_3P_2 single crystals obtained from the vapour phase and vacuum deposited thin Zn_3P_2 polycrystalline films. The refractive index n calculated from the interference data changed from 3.2 in the infrared region up to 4 in the visible region. The calculated absorption coefficient α was in the range 3–300 cm^{-1} for single crystal samples and $4 \cdot 10^3$–$4 \cdot 10^4$ cm^{-1} for thin films. From the analysis of spectral dependence of absorption coefficient α the following energy values for direct optical transitions have been obtained: 1.42 eV; 1.52 eV; 1.66 eV and 1.82 eV. The smallest energy $E_0 = 1.35$ eV has been described to indirect optical transitions at 300 K. The obtained results have been discussed in comparison with the literature data.

1. Introduction

During the past several years increasing interest has been given to zinc phosphide Zn_3P_2 — a semiconductor compound of the II–V group, because of its promising photovoltaic properties. Only a few works about the preparation technique and electrical and optical properties of this material in bulk crystalline form have been published up to now [1–3, 6, 7, 11–14]. The properties of thin Zn_3P_2-films have been reported in only four publications [4, 8–10]. Zn_3P_2 is always a p-type semiconductor with a tetragonal unit cell and resistivity of 1.0–10^4 ohm · m and a very low Hall mobility of $(1–4) \times 10^{-3}$ m^2/Vs at 300 K [1–4, 9]. The energy gap value of Zn_3P_2, estimated by various authors from dc conductivity measurements, is 1.15–1.3 eV [1–4], and from optical absorption and photoconductivity measurements it is about 1.28–1.4 eV [4, 6, 7, 11, 12] for bulk material. The first data for Zn_3P_2-films have been reported by Lagrenaudie who obtained from electrical data the big dispersion of activation energy values in the range 1.16–1.36 eV. The value of ΔE_g obtained in our laboratory from dc resistivity measurements was 1.2 eV [9]. From optical absorption measurements, performed for thin films, it was impossible to obtain

* This work was sponsored by the Institute of Physics, Polish Academy of Sciences under contract MR-I-4-9.

** Address: Instytut Fizyki Ciała Stałego PAN, Kawalca 3, 41-800 Zabrze, Poland.

the smallest energy gap because of a long absorption "tail" for energies below 1.5 eV, depending on deposition conditions [4]. From the theoretical model for band structure of Zn_3P_2 proposed by Lin Chung [5] the existence of an energy gap of 1.9 eV, corresponding to direct transitions at the Γ point has been expected. However, in this model the calculations for pseudo-cubic hypothetical fluorite-like structure have been performed, but the spin-orbit coupling and tetragonal symmetry of the crystalline field were not taken into account. For this reason the value of the smallest energy gap obtained from these calculations can be too high and triply degenerate. This value has not been confirmed by the experimental data. On the basis of absorption, reflectivity and photoconductivity results, Sobolev et al. [6] proposed the band structure diagram for Zn_3P_2 with the valence band predicted as triply split at the Γ point by spin-orbit and tetragonal field interaction, and direct energy gap of 1.3 eV at 293 K. The existence of a three-fold split valence band and the energy gap value in the range 1.3–1.4 eV were also confirmed by the results of photoelectric effect measurements on the Au-Zn_3P_2 junction by [7] and also by [4, 10–13] from optical absorption data. However, the results obtained by various authors from optical and electrical data cover a wide range of values and some controversy is, whether the smallest energy gap in Zn_3P_2 is a direct [4, 6] or indirect one [10, 11]. The aim of this work was to determine the optical transition energy values for bulk and thin films of Zn_3P_2 from transmission and reflectivity data.

2. Experimental details

The investigated samples were Zn_3P_2 single crystals obtained by vapour-phase growing in a closed system and vacuum deposited thin Zn_3P_2 polycrystalline films.

The starting material for the single crystal growing and preparation of thin films was a Zn_3P_2 ingot synthesized from the elements and purified by vacuum sublimation [2, 3, 12, 14]. Single crystals of Zn_3P_2 were obtained by vacuum sublimation of the polycrystalline material under a small temperature gradient from 1010 to 1050 K. For optical investigations samples were oriented, cut and polished with a diamond paste and then etched. The final sample thicknesses were in the range 0.18–0.30 mm. Thin Zn_3P_3-films have been prepared by thermal deposition in a vacuum better than 10^{-5} Torr from a ceramic crucible. Deposition was carried out on BK-7 glass substrates heated to a temperature in the range $T_s \sim 300$–720 K [9]. The structure and microstructure of obtained films were investigated by means of a Jeol JEM-120 electron microscope. On the base of these investigations the optimal conditions for preparation of polycrystalline Zn_3P_2-films have been established as follows: source temperature 950–990 K, substrate temperature 540–560 K and source–to–substrate distance 12 cm. The films deposited with the substrate temperature below 520 K were usually amorphous. The thicknesses of obtained films measured by the interference method were in the range 0.7–6 μm. These conditions resulted in an average film growth rate 40–50 Å/sec with background pressures of the order of 10^{-5} Torr during deposition. The electron probe X-ray microanalysis of chemical composition of films prepared in this manner showed their very good homogeneity and the only impurity revealed was silicon, which probably originated from the synthesis process of bulk Zn_3P_2 [14].

Optical measurements of transmission and reflectivity have been performed in the spectral range 0.45–2.7 μm by use of a Beckman Acta M-IV spectrophotometer. Typical transmission and reflection spectra obtained for thin Zn_3P_2 films are presented in Fig. 1a. From the sets of interference maxima and minima of transmittivity and reflectivity data

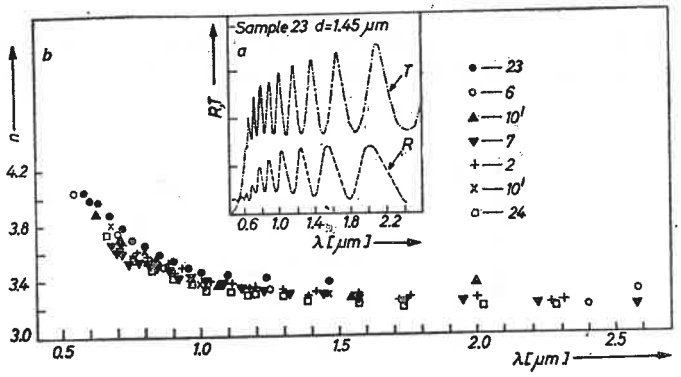

Fig. 1. a) Typical transmission and reflectivity spectra for Zn_3P_2 films, b) Spectral dependence of the refractive index for Zn_3P_2 films

it was possible to calculate the refractive index n_1 for this material in a wide spectral range according to the well known relation $4n_1d = m\lambda$, where m is an integer and d — thickness of the film.

The absorption coefficient α for thin films has been calculated on the basis of transmission data using the relations [15]

$$T_{av} = \frac{A \exp(-\alpha d)}{1+r_1^2 r_2^2 \exp(-2\alpha d)},$$

where

$$A = \frac{16 n_1^2 n_2}{(1+n_1)^2(n_1+n_2)^2}, \quad r_1 = \frac{n_1-1}{n_1+1}, \quad r_2 = \frac{n_1-n_2}{n_1+n_2},$$

n_1 and n_2 — refractive indices for the investigated film and substrate respectively, and

$$T = \frac{A \exp(-\alpha d)}{1-2r_1 r_2 \exp(-\alpha d)+r_1^2 r_2^2 \exp(-2\alpha d)}$$

for maxima sets in the region where the interference fringes appeared. For the calculations for each sample suitable experimentally obtained values of the refractive index n_1 were used. For bulk samples, the well-known formula

$$T = (1-R)^2 \exp(-\alpha d)$$

was used where the values of reflectivity R were measured experimentally.

3. Results and discussion

The spectral dependence of the refractive index n_1 calculated from the interference data is shown in Fig. 1b. The average values of n_1 in the infrared region are 3.2–3.4, while in the visible region the values 3.5–4 have been obtained. The small scattering of results for different films can be noticed.

The spectral dependence of the absorption coefficient α for several measured bulk samples and also for thin polycrystalline films is presented in Fig. 2. The calculated absorp-

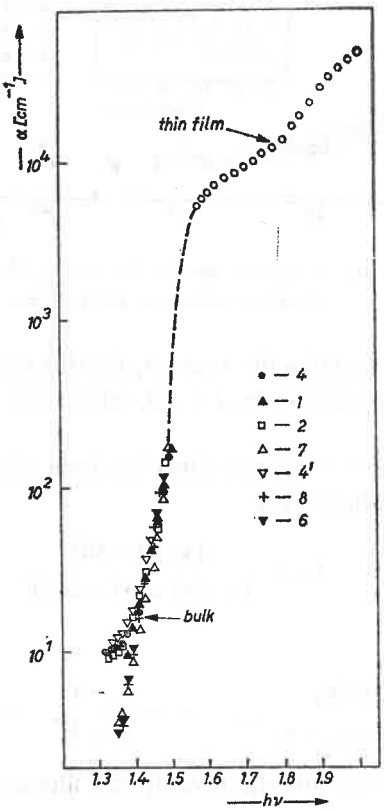

Fig. 2. Spectral dependence of the absorption coefficient for several bulk samples and thin films of Zn_3P_2 in the interband absorption edge region

tion coefficient was in the range 3–300 cm^{-1} for measured bulk samples and 4.10^3–4.10^4 cm^{-1} for thin films. The long absorption "tails" below about 1.5 eV, similar to those reported by Catalano et al. [4], make it impossible to interpret the data for thin films in this region. It seems, that these "tails" will be substantially reduced for thicker films with better crystal structure. The especially good agreement among the values of calculated α for all investigated films in the energy range 1.55–2.05 eV should be emphasized. Fig. 3 shows the linear

dependences of $(\alpha h\nu)^2$ vs $h\nu$ for several investigated Zn_3P_2-films in the spectral range 1.55–2.0 eV. As it can be seen, the experimental points fit very well the three straight lines with slopes giving three energy values for direct optical transitions

$$E_2 = 1.52\ \text{eV}, \quad E_3 = 1.66\ \text{eV}, \quad E_4 = 1.82\ \text{eV}.$$

The same relation for the best bulk samples No 6 and 8 (see Fig. 2) presented in Fig. 4a gives, for the narrow spectral region 1.43–1.47 eV, the direct transition with energy

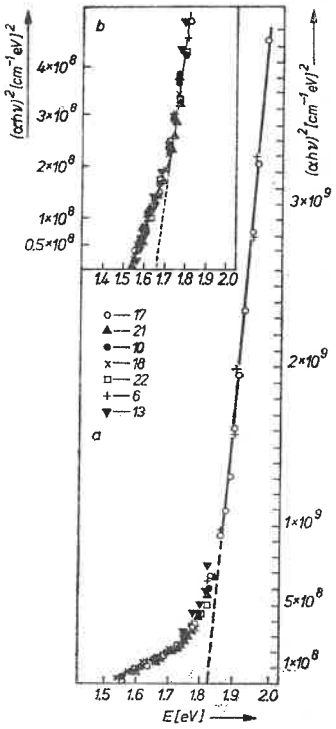

Fig. 3

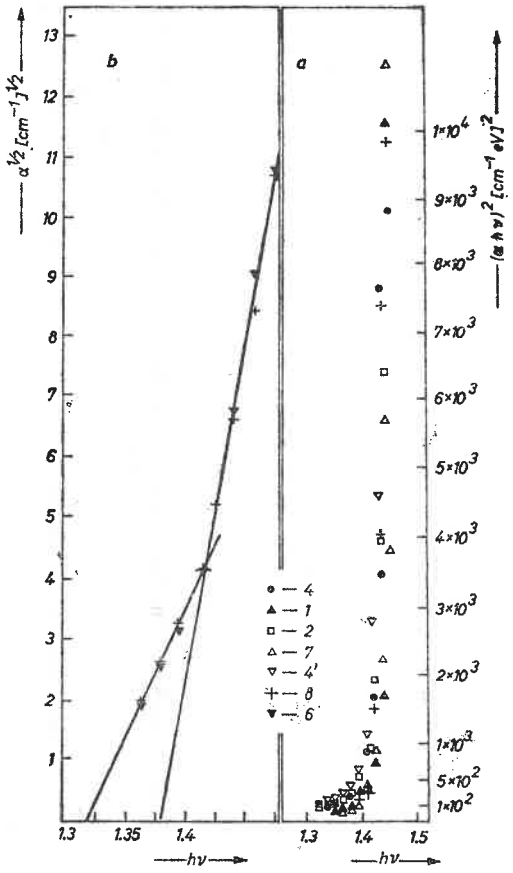

Fig. 4

Fig. 3. Dependence $(\alpha h\nu)^2$ vs energy for several thin films of Zn_3P_2 (a) and lower part of curve *a* in enlarged scale (b)

Fig. 4. Energy dependence $(\alpha h\nu)^2$ (a) and $\alpha^{1/2}$ (b) for several bulk Zn_3P_2 samples presented in Fig. 2

$E_1 = 1.42$ eV at room temperature. The obtained value E_1 is in good agreement with the results of Catalano et al. [4] and also with [10, 11]. It confirms also the reported luminescence and photoconductivity data [7, 12, 13] and may be accepted as the smallest direct energy gap for Zn_3P_2. The only problem is with the values of the energy gap $\Delta E \simeq 1.15$–

TABLE I

Energy gap and energies of optical transitions (in eV) for Zn_3P_2 obtained by different authors for bulk and thin films in the spectral region 1.0–2.0 eV at 293 K

Theory	Electrical measurements		Absorption measurements				Photoconductivity		Reflection	Type of transition
[5]	[3]	[9]	[6]	[4]	[11]	this work	[6]	[7]	[6]	
1.9	1.15	1.2	1.3		1.28	$E_0 = 1.35$		$e_1 = 1.25$		indirect
				1.4	1.365	$E_1 = 1.42$	$A_1 = 1.44$	$E_1 = 1.40$		direct at Γ
					1.47	$E_2 = 1.52$		$E_2 = 1.58$		direct at Γ
						$E_3 = 1.66$	$A_2 = 1.61$	$E_2 = 1.68$	E_1	direct at Γ
						$E_4 = 1.82$	$A_3 = 1.84$	$E_3 \simeq 2$	$E_2 = 1.85$	direct

–1.2 eV obtained from electrical measurements for bulk [3] and for thin films [9]. However, when we have tested the absorption data from the absorption "tail" in the spectral region below about 1.45 eV for bulk Zn_3P_2 samples (and for very low values of α) (see Fig. 2), we have obtained a good approximation of the relation $\alpha^{1/2}$ vs energy by the two straight lines presented in Fig. 4b. From this plot we have got an energy value $E_0 = 1.35$ eV for indirect phonon-assisted transitions with a phonon energy of about $k\theta \simeq 0.031$ eV corresponding to $\theta \simeq 363$ K.

For this reason it seems to be reasonable to accept the smallest indirect energy gap connected with transitions between the centre of the Brillouin zone to the extremum off the Γ point. This type of transition explains the absorption data for the lowest values of α and also confirms the low values of the energy gap obtained from electrical measurements. The energy values $E_1 = 1.42$ eV, $E_2 = 1.52$ eV and $E_3 = 1.66$ eV obtained in this work can be ascribed to direct optical transitions at the Γ point connected with the three-fold coupling of the valence band owing to spin-orbit and tetragonal-field interactions. The estimated energy E_4 may be related to optical transitions off the centre of the Brillouin zone.

The obtained values are in agreement with previously published reference data [11]. The observed dispersion of energy values may be explained by probable small deviations from chemical stoichiometry of Zn_3P_2 for samples obtained by different authors.

The results obtained in this work are compared with reference data in Table I.

One of us (W. Ż.) would like to express his appreciation to prof. dr L. Huldt for the possibility of preparing good single crystals of Zn_3P_2 during his stay at the Physics III of the Royal Institute of Technology in Stockholm.

REFERENCES

[1] W. Żdanowicz, L. Żdanowicz, *Ann. Rev. Mat. Science*, Ed. R. Huggins, Palo Alto, Calif., **5** (1975) p. 301.
[2] W. Żdanowicz, Z. Henkie, *Bull. Acad. Pol. Sci., Ser. Sci. Chim.* **12**, 729 (1964).
[3] W. Żdanowicz, F. Królicki, P. Plenkiewicz, *Acta Phys. Pol.* **A41**, 27 (1972).
[4] A. Catalano et al., Proc. Intern. Photovoltaic Solar Energy Conf., Luxemburg 1977, D. Reidel, Dordrecht 1977, p. 644.
[5] P. J. Lin Chung, *Phys. Status Solidi* (b) **47**, 33 (1971).
[6] V. V. Sobolev, N. N. Syrbu, *Phys. Status Solidi* (b) **64**, 423 (1974).
[7] S. J. Radautsan, N. N. Syrbu, V. J. Volodina, V. K. Kiosev, *Sov. Phys. Dokl.* **21**, 193 (1976).
[8] J. Lagrenaudie, *J. Phys. Radium* **16**, 234 (1955); *J. Chem. Phys.* **150**, 545 (1953).
[9] M. Kwaśniewski, L. Żdanowicz, Proc. 6th Czechosl. Confer. on Electronics and Vacuum Physics, Bratislava, Aug. 23–26, 1976, p. 169.
[10] A. Möller, C. Clemen, U. Elrod, P. Munz, J. Hönigschmid, E. Bucher, 14th Intern. Conf. on Semicond. Physics, Edinburgh, 1978, publ. by the Institute of Phys., London 1978, p. 825.
[11] J. M. Pawlikowski et al., *Phys. Status Solidi* (b) **88**, K153 (1978).
[12] L. Huldt, N. G. Nilsson, B. O. Sundström, W. Żdanowicz, *Phys. Status Solidi* (in press).
[13] L. N. Kurbatov et al., *Sov. J. Quantum Electron.* **6**, 166 (1976).
[14] W. Żdanowicz, K. Kloc, A. Kalińska, E. Cisowska, A. Burian, *J. Crys. Growth* **31**, 56 (1975).
[15] L. Żdanowicz, *Phys. Status Solidi* **20**, 473 (1967).