

Distribution of electronic states in amorphous Zn-P thin films on the basis of optical measurements

BOŻENA JARZĄBEK^{1*}, JAN WESZKA¹, JAN CISOWSKI^{1,2}

¹Centre of Polymer Chemistry, Polish Academy of Sciences, P.O. Box 20, 41-819 Zabrze, Poland

²Institute of Physics, Cracow University of Technology, ul. Podchorążych 1, 30-084 Cracow, Poland

*Corresponding author: jarzabek@cchp-pan.zabrze.pl

Transmission and fundamental reflectivity studies, completed on amorphous Zn-P thin films, allowed us to obtain parameters describing the fundamental absorption edge, *i.e.*, the optical pseudogap E_G , Urbach energy E_U and exponential edge parameter E_T . All these data, together with the results of earlier transport measurements, have been utilized in developing simple models of electronic structure (distribution of electronic states) for amorphous Zn-P thin films of two compositions, *i.e.*, $Zn_{57}P_{43}$ (near stoichiometry of Zn_3P_2) and $Zn_{32}P_{68}$ (near stoichiometry of ZnP_2).

Keywords: amorphous semiconductors, thin films, absorption coefficient, model of electronic structure.

1. Introduction

Amorphous films of the Zn-P system are of interest due to their potential applications in solar cells [1], similarly to the Zn_3P_2 crystalline counterpart [2]. Stoichiometric Zn_3P_2 thin films have been prepared by various techniques, including electron beam evaporation [3, 4], thermal vacuum evaporation [5–8], and reactive r.f. sputtering of zinc in a PH_3 -containing argon atmosphere [9, 10]. All these films have been prepared in both the crystalline and amorphous forms near the stoichiometric Zn_3P_2 ratio. The optical properties of thermally evaporated amorphous films belonging to the Zn-P system within a broader Zn to P ratio have been presented in [11].

Optical measurements are one of the simplest and most direct experimental methods used to investigate the electronic structure of semiconductors, also in amorphous phase [12]. In the case of crystals, the band structure models can be obtained by theoretical methods and verified by experimental results, while the optical investigations allow one to deduce the energy, character and direction of the optical transitions, the width and type of the forbidden gap E_G , as well as existence of

the excitons or impurity levels. For amorphous semiconductors, the electronic structure appears to be a very complicated problem because the long-range order (LRO) is absent in their atomic structure and the forbidden gap is not clearly defined. In spite of that, the optical investigations carried out on amorphous semiconductors revealed the presence of a characteristic energy value, called the pseudogap E_G^{opt} , which may be connected with the short-range order (SRO) [13], *i.e.*, atomic order on a length of a few inter-atomic distances (1–2 nm).

Based on the experimental results and the theoretical works of ANDERSON [14] and MOTT [15], some phenomenological models of the electronic structure have been proposed for amorphous semiconductors [16–19] and these schematic density of states diagrams are well known as Cohen–Fritsche–Ovshinsky [16], Mott–Davis [17] and Marshall–Owen [18] or “real” glass with defect states models [19]. All these models and parameters such as: the optical pseudogap E_G^{opt} , mobility gap E_G^{m} , Fermi level E_F , Urbach energy E_U , exponential edge parameter E_T and E_{04} energy are shortly described in [12].

The aim of this paper is to present the simple models of electronic states distribution in amorphous Zn-P (a-ZnP) thin films, based on our optical data and the phenomenological models mentioned above. The fundamental absorption edges along with the optical parameters obtained by us for the a-ZnP thin films system have been discussed and compared with the optical parameters presented by other authors [3, 6–10]. Moreover, the earlier transport data of the a-ZnP films [9, 10], are also utilized to create these models.

2. Experimental

Amorphous Zn-P thin films were prepared by thermal vacuum evaporation of bulk polycrystalline material of either Zn_3P_2 or ZnP_2 compositions from one source onto borosilicate glass substrates held at 300 K. During the deposition process, the vacuum was maintained at a level of 10^{-3} Pa and the film deposition rate v_s was 10 nm/s. The thickness of the films, determined with an interference microscope, was in the range 0.5–3.5 μm (± 0.05 μm). The compositions of evaporated films (determined by photometric analysis, with accuracy ± 2 at%) were $\text{Zn}_{57}\text{P}_{43}$ and $\text{Zn}_{32}\text{P}_{68}$ and have appeared to be dependent on the source material.

The optical properties were studied at room temperature, using both transmission and fundamental reflectivity measurements within the 0.4–2.0 eV photon energy interval.

3. Results and discussion

3.1. Optical absorption

The recorded transmission and reflectivity spectra of as-prepared a-ZnP thin films were used to calculate the absorption coefficient α according to the formulae given elsewhere [11]. The resulting fundamental absorption edges α vs. the photon energy

E for all investigated a-films deposited from bulk Zn_3P_2 and ZnP_2 are presented in Fig. 1, while the method used to obtain optical gaps for these films is shown in Fig. 2. The spectral dependences for these two types of a-ZnP films are presented together because of the similarity of the values of their optical pseudogaps. Figures 1a and 2a show the spectra recorded on thinner films ($d = 0.5 \mu\text{m}$), while Figs. 1b and 2b illustrate the spectra taken on the $3.5 \mu\text{m}$ thick films.

The spectra presented reveal quite a high absorption level, being of the order of 10^4 cm^{-1} (Fig. 1b) and even reaching 10^5 cm^{-1} for thinner films (see Fig. 1a). Such a high level of absorption coefficient is typical of amorphous thin films, especially of very thin ones, where various defects such as voids and dangling bonds in the interfacial film-substrate and film-surface areas play an important role in the absorption

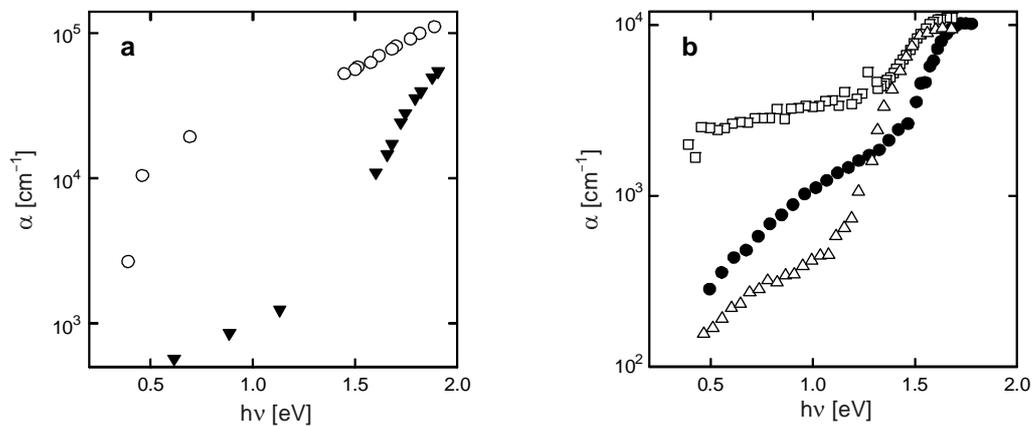


Fig. 1. Absorption coefficient α vs. photon energy for a-ZnP thin films (\circ , \square , \triangle – $\text{Zn}_{57}\text{P}_{43}$ films; \blacktriangledown , \bullet – $\text{Zn}_{32}\text{P}_{68}$ films): $d = 0.5 \mu\text{m}$ (a), $d = 3.5 \mu\text{m}$ (b).

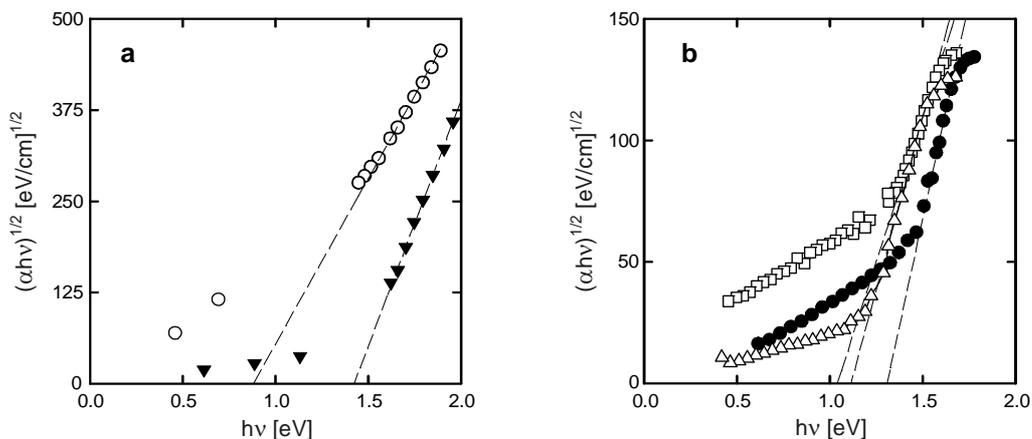


Fig. 2. Absorption edges, obtained from the Tauc dependence, for a-ZnP thin films (\circ , \square , \triangle – $\text{Zn}_{57}\text{P}_{43}$ films; \blacktriangledown , \bullet – $\text{Zn}_{32}\text{P}_{68}$ films): $d = 0.5 \mu\text{m}$ (a), $d = 3.5 \mu\text{m}$ (b).

process. The defect related localized states connected with interfacial areas have considerably stronger impact on the bulk properties of thinner films than thicker ones. The values of the standard deviation of thickness of the a-ZnP thin films (σ_w), obtained by the interference spectroscopy from the optical transmittance and reflectance interferences, as well as the average surface roughness (R_a) evaluated from the atomic force microscopy (AFM) studies were comparable, *i.e.*, $\cong 20$ nm [20, 21] and appeared to be independent of the film thickness. This means that the localized states, due to defects on the surface play a considerably greater role for thinner films than for thicker ones. Additionally, such defects as voids and dangling bonds on the surface cause disorder in the tetrahedral coordination and weak molecular bonds or bipolarons are formed [22]. The higher the density of defects, the larger the wave function overlap, which in turn leads to an increase in matrix element of optical transitions in the vicinity of the mobility gap. Therefore, the increasing level of the absorption coefficient observed in the range of the absorption edge for thinner Zn-P films may be explained by an increase in the density of localized defect states and also by higher matrix elements for these films. This seems to show that the f-sum rule may give different results when applied to films with different thickness.

The shapes of nearly all absorption edges presented in Fig. 1 are at the first sight, similar to those suggested by Tauc for an idealized amorphous semiconductor [23–25]; two exponential parts with different slopes are seen for almost all $\alpha(E)$ curves in this figure. The low energy exponential absorption edges follow the $\alpha \propto \exp(E/E_T)$ dependence, with parameter E_T obtained for nearly all absorption curves, as seen in Fig. 1. The fast increasing linear part of absorption in the higher energy region following the Urbach relation: $\alpha \propto \exp(E/E_U)$ [26] and the Urbach energy E_U have been found for all a-ZnP films under investigation.

Figure 2 shows, typical of amorphous semiconductors, dependence $(\alpha E)^{1/2} \propto (E - E_G^{\text{opt}})$ proposed by Tauc to obtain the optical gap. The linear approximation of $(\alpha E)^{1/2}$ vs. E (in the high absorption region, where $E > E_G^{\text{opt}}$) allows us to find the values of pseudogaps E_G^{opt} for all the films investigated. For thicker films, the parameter E_{04} (corresponding to the energy when the absorption coefficient $\alpha = 10^4 \text{ cm}^{-1}$ and the level of absorption is almost constant) has also been found (see Fig. 1b). All the optical parameters of a-ZnP films investigated are gathered in the Table.

At low energy region, a nearly exponential behavior of absorption is attributed to the optical transitions between the defect states, localized inside the optical gap. These states are mainly due to the voids, which provide additional boundary surfaces for dangling bonds. These defects play a significant role in the structure of films prepared by the vapor deposition technique. The absorption curves, presented in Fig. 1, indicate that the defect states are distributed over a large part of the gap, similar as in III–V compounds [22], and the dangling bonds at the void surface form bonding states at P atoms and anti-bonding states at Zn atoms. It would be interesting to compare the influence of interatomic bonding of a-ZnP films of both compositions on their defect states. These films reveal tetrahedral coordination but there are differences between the atomic structures, as found in structural investigations [27, 28].

Table. Optical parameters of a-ZnP films under investigation.

Material	d [μm]	E_T [meV] (± 5 meV)	E_U [meV] (± 2 meV)	E_G^{opt} [eV] (± 0.01 eV)	E_{04} [eV] (± 0.01 eV)
a-Zn ₃₂ P ₆₈	0.56	660	171	1.45	—
	3.50	455	142	1.30	1.75
a-Zn ₅₇ P ₄₃	0.56	—	572	0.90	—
	3.50	575	145	1.15	1.55
	3.50	1265	313	1.05	1.55

The structure of amorphous P-rich films (near ZnP₂ composition) resembles the tetragonal ZnP₂ crystal, where the hybridization is realized through the promotion of p electron from two different P atoms to one Zn atom. Thus, each Zn atom is coordinated to four P atoms, while each P atom is linked by two different P atoms and two Zn atoms. The Zn and P atoms are binding more through sp^3 -type bonds while p -type P–P bonds are mostly covalent with the P spiral chains characteristic of both amorphous and crystalline ZnP₂ films [27]. A different situation is in the case of a-Zn₃P₂ films with homopolar bonds (between Zn atoms and between P atoms) since their atomic structure is clearly different from the Zn₃P₂ crystal structure and similar to the deformed CdAs mixed rhomb and regular Si III structures [28]. A higher structural disorder of Zn₃P₂ amorphous films causes a decrease of the slope of the linear part of absorption edge in the low energy region (Fig. 1) and values of E_T are higher than for the amorphous films of near ZnP₂ composition.

Structural disorder influences also the defect states in the band tails and the Urbach edge slope. Thus, instead of an abrupt absorption edge, we can observe the edges with smaller slopes, as seen in the case of a-ZnP films (Fig. 1). It is thought that lower values of the Urbach energies for a-ZnP₂ films are the result of lesser structural disorder than for a-Zn₃P₂ and the existence of P chains like in the ZnP₂ crystalline structure.

Comparing the values of E_T and E_U for films with different thickness, one can see that these parameters are higher for thinner films independently of composition, indicating a greater number of localized defect states inside the gap and localized states in the Urbach tails for very thin films.

The pseudogaps E_G^{opt} of the a-ZnP films investigated cover the range 0.9–1.1 eV for a-Zn₃P₂ films and 1.3–1.45 eV for a-ZnP₂ films. The absorption edges, following the Tauc power law, are due to the interband transitions between the extended states beyond the mobility gap as well as to transitions between localized states in the vicinity of the mobility edge in one band and the delocalized states at the mobility edge in the other band [22–25]. Therefore, for amorphous semiconductors, the optical gap is always smaller than mobility gap. In most cases, the value of mobility gap can be approximately represented by the E_{04} . From Fig. 1b, we have the values $E_{04} \cong 1.55$ eV for Zn₅₇P₄₃ films and 1.75 eV for Zn₃₂P₆₈ film. The limiting value of the mobility gap for amorphous semiconductors seems to be the energy gaps for their crystal counterparts [29], *i.e.*, 1.5 and 2.0 eV for Zn₃P₂ and ZnP₂, respectively. These two

compounds are wide-gap semiconductors, so for their amorphous counterparts, the energy gap is smaller than for crystalline phase, according to Vorlíček's rule [29].

3.2. Models of electronic structure

The results of optical measurements presented above and gathered in the Table, together with earlier transport parameters [9, 10], have been used to create models of distribution of electronic states for the a-ZnP films of compositions near Zn_3P_2 and ZnP_2 . We have utilized the phenomenological models, mainly the “real” glass and the Mott–Davis models, as a basis of our proposition. The models proposed are shown in Figs. 3 and 4, for a- Zn_3P_2 and a- ZnP_2 , respectively; the localized states are marked by dashed lines and the optical transitions which suit the optical gap are shown as arrows.

3.2.1. Amorphous Zn-P films evaporated from Zn_3P_2

In developing the model of distribution of electronic states for the a- Zn_3P_2 films (Fig. 3) we have used the mobility gap $E_G^m = 1.6$ eV and the activation energy $E_a = 0.69$ eV obtained by WEBER *et al.* [9, 10]. The Fermi level is located ~ 0.1 eV below the middle of the mobility gap [9, 10], making these films *p*-type semiconductors. This value of the mobility gap obtained from transport measurements is comparable to $E_{04} = 1.55$ eV, determined by us from the absorption spectra. A distinct difference between the mobility gap $E_G^m = 1.6$ eV and the optical gap $E_G^{\text{opt}} \cong 1.1$ eV, and relatively great value of the Urbach energy, indicate that localized states in the band tails play important role in optical transitions which are responsible for the existence of optical gap. The optical transitions within the optical gap in a- Zn_3P_2 can occur not only between the extended states but also from the localized states below the Fermi level and above the mobility edge of the valence band to the extended states near the mobility edge of the conduction band (see the arrow with $E_G^{\text{opt}} \cong 1.1$ eV, in Fig. 3).

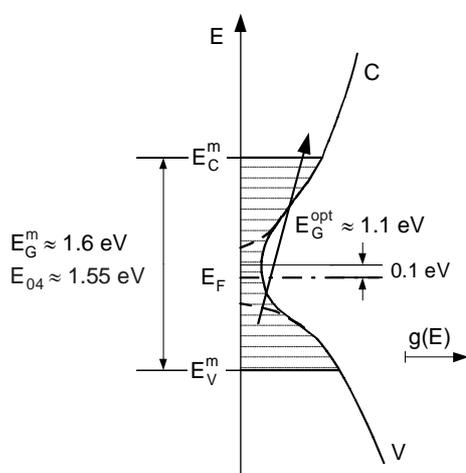


Fig. 3. Model of the electronic structure for a- Zn_3P_2 thin films.

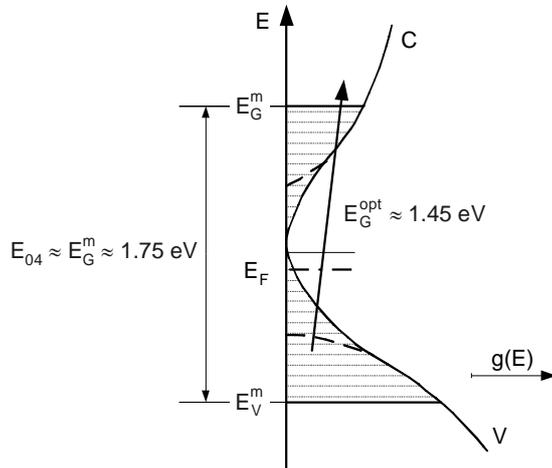


Fig. 4. Model of the electronic structure for a-ZnP₂ thin films.

Greater values of the optical gap (1.25–1.6 eV) for a-Zn₃P₂ thin films reported in works [6–9] may be due to the differences in technology, but $E_G^{\text{opt}} \cong 1.95$ eV in [3] indicate rather a-ZnP₂ films because this value is near to the crystalline ZnP₂, *i.e.*, $E_G^{\text{opt}} \cong 2.0$ eV.

The relatively large values of energies E_U and E_T for the a-Zn₃P₂ thin films indicate the existence of the localized states in the band tails and inside the gap and the overlapping band tails, as seen in Fig. 3. Transitions between the localized states inside the gap may occur between states lying under the Fermi level and above the mobility edge of the valence band. These localized states are due to defects created during the evaporation process, and result in a smaller slope of the low energy absorption edges of a-Zn₃P₂ than that of a-ZnP₂ films (see Fig. 1).

3.2.2. Amorphous Zn-P films evaporated from ZnP₂

In the case of a-ZnP₂, we have not found any information about the transport parameters, so the proposed model of distribution of the electronic states (shown in Fig. 4) is based on our optical measurements. As a mobility gap, we have taken the value of energy $E_{04} \cong 1.75$ eV and situated the Fermi level a little below the middle of the mobility gap (*p*-type semiconductor). A lower value of the Urbach energy for a-ZnP₂ than for a-Zn₃P₂ indicates a lesser number of the localized states in the band tails and a smaller overlapping of these tails, as compared to the a-Zn₃P₂ (see Fig. 3). Additionally, a lower energy E_T for a-ZnP₂ than for a-Zn₃P₂ indicates a lesser number of the localized states inside the gap. This is a consequence of a lesser structural disorder in a-ZnP₂ than in a-Zn₃P₂ and the existence of a part of P chains in the former films, as confirmed by structural investigations [27]. Optical transitions responsible for the existence of the optical gap $E_G^{\text{opt}} \cong 1.45$ eV in a-ZnP₂, take place from the localized states in the valence band tail under the Fermi level up to the extended states near the mobility edge of the conduction band (as shown by the arrow in Fig. 4).

4. Conclusions

Analysis of the optical data obtained for amorphous Zn-P films has yielded the values of optical parameters, such as energy E_{04} , pseudogap E_G^{opt} , Urbach energy E_U and parameter E_T , which together with accessible transport data providing the mobility edge E_G^{m} and the activation energy E_{act} , have allowed us to create the simple models of distribution of extended and localized states and the optical transitions for these materials. The greater values of both E_T and E_U energies for amorphous films evaporated from Zn_3P_2 than for a- ZnP_2 films indicate a greater number of the localized states inside the gap and in the band tails and more distinct overlapping of these tails in the case of a- Zn_3P_2 films. Also, a greater difference between the values of E_G^{opt} and E_G^{m} confirms the role of the localized states of a- Zn_3P_2 films. Transitions between the localized states in the valence band tail under the Fermi level and the extended states near the mobility edge of conduction band energy are responsible for the pseudogap in the films studied (*p*-type semiconductors). These considerations confirm once more the important role of the optical measurements in creating models of the electronic structure for amorphous semiconductors.

References

- [1] LOUSA E., BERTRAN E., VARELA M., MORENZA J.L., *Deposition of Zn_3P_2 thin films by coevaporation*, Solar Energy Materials **12**(1), 1985, pp. 51–6.
- [2] MISIEWICZ J., SZATKOWSKI J., MIROWSKA N., GUMIENNY Z., PŁACZEK-POPKO E., *Zn_3P_2 – a new material for optoelectronic devices*, Materials Science and Engineering: B **9**(1–3), 1991, pp. 259–62.
- [3] RAO V.J., SALVI M.V., SAMUEL V., SINHA A.P.B., *Structural and optical properties of Zn_3P_2 thin films*, Journal of Materials Science **20**(9), 1985, pp. 3277–82.
- [4] NAYAK A., RAO D.R., BANERJEE H.D., *Optical studies on electron-beam-deposited Zn_3P_2 thin films*, Journal of Materials Science Letters **10**(7), 1991, pp. 403–5.
- [5] BRYJA L., JEZERSKI K., MISIEWICZ J., *Optical properties of Zn_3P_2 thin films*, Thin Solid Films **229**(1), 1993, pp. 11–3.
- [6] DEISS J.L., ELIDRISSI B., ROBINO M., WEIL R., *Amorphous thin films of Zn_3P_2 : preparation and characterization*, Applied Physics Letters **49**(15), 1986, pp. 969–70.
- [7] DEISS J.L., ELIDRISSI B., ROBINO M., TAPIRO M., ZIELINGER J.P., WEIL R., *Amorphous thin films of Zn_3P_2* , Physica Scripta **37**(4), 1988, pp. 587–92.
- [8] ARSENAULT C.J., BRODIE D.E., *Crystallization of Zn-rich and P-rich amorphous Zn_3P_2 thin films*, Canadian Journal of Physics **66**(5), 1988, pp. 373–5.
- [9] WEBER A., Thesis, Zurich 1993.
- [10] WEBER A., SUTTER P., VON KAENEL H., *Optical, electrical, and photoelectrical properties of sputtered thin amorphous Zn_3P_2 films*, Journal of Applied Physics **75**(11), 1994, pp. 7448–55.
- [11] JARZĄBEK B., WESZKA J., BURIAN A., POCZTOWSKI G., *Optical properties of amorphous thin films of the Zn-P system*, Thin Solid Films **279**(1–2), 1996, pp. 204–8.
- [12] JARZĄBEK B., WESZKA J., CISOWSKI J., *Distribution of electronic states in amorphous Cd-As thin films on the basis of optical measurements*, Journal of Non-Crystalline Solids **333**(2), 2004, pp. 206–11.
- [13] WEAIRE D., THORPE M.F., *Electronic properties of an amorphous solid. I. A simple tight-binding theory*, Physical Review B: Solid State **4**(8), 1971, pp. 2508–20.
- [14] ANDERSON P.W., *Absence of diffusion in certain random lattices*, Physical Review **109**(5), 1958, pp. 1492–505.

- [15] MOTT N.F., *Conduction in non-crystalline systems. IV. Anderson localization in a disordered lattice*, Philosophical Magazine **22**(175), 1970, pp. 7–29.
- [16] COHEN M.H., FRITSCHÉ H., OVSHINSKY S.R., *Simple band model for amorphous semiconducting alloys*, Physical Review Letters **22**(20), 1969, pp. 1065–8.
- [17] DAVIS E.A., MOTT N.F., *Conduction in non-crystalline systems. V. Conductivity, optical absorption and photoconductivity in amorphous semiconductors*, Philosophical Magazine **22**(179), 1970, pp. 903–22.
- [18] MARSHALL J.M., OWEN A.E., *Drift mobility studies in vitreous arsenic triselenide*, Philosophical Magazine **24**(192), 1971, pp. 1281–305.
- [19] OWEN A.E., SPEAR W.E., *Electronic properties and localised states in amorphous semiconductors*, Physics and Chemistry of Glasses **17**(5), 1976, pp. 174–92.
- [20] JARZĄBEK B., JURUSIK J., CISOWSKI J., NOWAK M., *Roughness of amorphous Zn-P thin films*, Optica Applicata **31**(1), 2001, pp. 93–101.
- [21] JARZĄBEK B., Thesis, Zabrze 1997.
- [22] CONNELL G.A., [In] *Amorphous Semiconductors*, [Ed.] M.H. Brodsky, Springer, Berlin 1979, p. 79.
- [23] TAUC J., MENTH A., *States in the gap [of chalcogenide glasses]*, Journal of Non-Crystalline Solids **8–10**, 1972, pp. 569–85.
- [24] MOTT N.F., DAVIS E.A., *Electronic Processes in Non-Crystalline Materials*, 2nd Ed., Clarendon, Oxford 1978.
- [25] Cody D., [In] *Semiconductors and Semimetals*, [Ed.] J.I. Pankove, Vol. 21, Part B, Academic Press, New York 1984, p. 11.
- [26] URBACH F., *The long-wavelength edge of photographic sensitivity and of the electronic absorption of solids*, Physical Review **92**(5), 1953, p. 1324.
- [27] LECANTE P., MOSSET A., GALY J., BURIAN A., *Structural studies of amorphous Zn-P films*, Journal of Materials Science **27**(12), 1992, pp. 3286–92.
- [28] BURIAN A., LECANTE P., MOSSET A., GALY J., *Extended X-ray absorption fine-structure studies of short-range order in amorphous Zn-P films*, Philosophical Magazine B: Physics of Condensed Matter, Electronic, Optical and Magnetic Properties **66**(6), 1992, pp. 727–36.
- [29] VORLICEK V., *Optical absorption edge of CdAs₂-based glasses*, Physica Status Solidi B **67**(2), 1975, pp. 731–42.

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