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# SOME PROPERTIES OF AMORPHOUS THIN FILMS OF $Zn_3P_2$

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Zinc phosphide ($Zn_3P_2$) was synthesized by applying two different methods. Polycrystalline $Zn_3P_2$ obtained was used as a source for vacuum thermal evaporation. Structural analysis of thin films revealed that they are amorphous. Both refractive index and optical absorption coefficient of amorphous $Zn_3P_2$ thin films as a function of incident photon energy have been calculated by computer fitting of measured optical data to the theoretical expressions. The optical gap of the amorphous $Zn_3P_2$ films is determined to be equal to 1.45 eV.

## *1. Introduction*

Amongst the II—V compounds, zinc phosphide ($Zn_3P_2$) has attracted considerable attention because of its promising properties for photovoltaic applications[1], as well as for application to infrared detectors[2] and lasers[3]. Intensive research work on $Zn_3P_2$ was initiated at the University of Delaware, Newark, Delaware, U. S. A., where the potential application in the solar cell production has been determined[4-6]. They reported a maximum conversion efficiency of 6.1% for Schottky barrier single crystal[5]. Beside Schottky barrier, some heterojunctions[7] and $p-n$ homojunction have also been made[8]. That was the first report on $n$-type $Zn_3P_2$ obtained by heating $Mg/Zn_3P_2$ Schottky diode in the air at 100 °C[8]. All previous attempts to prepare the $n$-$Zn_3P_2$ by incorporating In, Ga, Sn or Al as substitutional donors have yielded only high-resistivity $p$-type material[1]. It has been found that the electrical conductivity of the undoped $Zn_3P_2$ is controlled by native phosphorus interstitial atoms[1] and the effect of self-compensation seems to prevent preparation of $n$-type material by high-temperature methods.

## 2. *Synthesis of* $Zn_3P_2$ *and formation of thin films*

In order to obtain a source material for thin film formation by vacuum evaporation, it was necessary to synthesize polycrystalline $Zn_3P_2$. Two different methods were applied: the first one proposed by Catalano[9], and the second one by Wang[10].

In the first method, $Zn_3P_2$ was synthesized by a direct recombination of zinc and phosphorus of high purity (6N Zn, 5N8 P). Stoichiometric quantities of the elements were mixed and sealed in an evacuated silica ampoule with 2 mm inner diameter and 3 mm thick walls at a nominal pressure of $10^{-5}$ mb. The 40 cm long ampoule was heated to a maximum of 760 °C, the temperature of the hot end, while the opposite end reached only 520 °C, and reaction was complete in 24 hours.

*X*-ray diffraction analysis of the synthesized material confirmed the existence of the $Zn_3P_2$ compound. However, near the colder end, 5—10% of $ZnP_2$ and a small amount ($\ll 1\%$) of Zn were found, too. The middle portion of the ampoule contained the pure $Zn_3P_2$, but near the hot end, $ZnP_2$ in a small percentage ($\lesssim 1\%$) was found again. As a source for thin film formation by vacuum evaporation, the pure $Zn_3P_2$ from the middle sections of ampoules has been used.

The crystal phases were identified according to the powder data contained in the JCPDS Powder Diffraction File (Card No 22—1021 for $Zn_3P_2$, 24—1463 for $ZnP_2$ and 4—831 for Zn). All of the specimens studied have given one and the same diffraction pattern of $Zn_3P_2$ (reproducible values of interplanar spacings and relative intensities with well-resolved spectral doublets $Ka_1a_2$ at medium and ihgh Bragg angles) which could be interpreted in terms of a cubic primitive unit cell with the dimension of $a_c = 1.1450$ nm. If tetragonal symmetry is accepted for $Zn_3P_2$ (the space group $P4_2/nmc$), as it is stated in literature, the corresponding unit-cell dimensions are $a_t = a_c/\sqrt{2} = 0.8096$ nm, $c_t = a_c = 1.1450$ nm. However, the powder data found in the card No. 22—1021 have not agreed satisfactorily with ours, neither in interplanar spacings nor in relative intensities. The data listed in that card deviate at random from ours. However, our data are in a very good agreement with thouse published by Catalano[9]. On the other side, our powder data for $ZnP_2$ agreed excellently with those contained in the card No. 24—1463.

In the second, vapour phase synthesis method with the constant phosphorus pressure, $Zn_3P_2$ was synthesized in an evacuated quartz ampoule 45 cm long and 20 mm diameter. Red phosphorus was placed near one end of the ampoule at 350 °C, and zinc near the opposite end at 850 °C. The synthesis occured in the intermediate portion of the ampoule within the 600—750 °C range; it lasted for 45 hours and the polycrystalline material with a relatively large (several mm in diameter) single crystal grains was obtained. *X*-ray diffraction analysis confirmed that the crystals obtained had only one phase, $Zn_3P_2$.

Thin films have been prepared by direct thermal vacuum evaporation of pure $Zn_3P_2$ from the molybdenum boat onto the duran glass substrates held at 260—290 °C at a pressure of $1.33 \times 10^{-4}$ Pa. The deposition rate was 10 nm/s. The thickness of thin films was $\sim 1.5$ μm.

## 3. *Properties of thin films of* $Zn_3P_2$

The deposited thin films have been found to be amorphous by the *X*-ray diffraction technique, although the temperature of the substrates was well above 200 °C, the limiting value for the growth of the polycrystalline films[11]. It seems that a relatively high deposition rate of 10 nm/s, compared to the usual one (about 3 nm/s) has been responsible for the amorphous state.

The electrical measurements have shown that the electrical resistivity of these films was of the order of $10^5$ Ωcm.

Emission spectroscopy indicated the presence of Si, Mg and Fe as impurities in the evaporated $Zn_3P_2$ films.

Several optical measurements were done on the amorphous $Zn_3P_2$ films such as: the direct determination of the real index of refraction, $n$, and the extinction coefficient, $k$, by Gaertner ellipsometer with He-Ne laser as a light source (for $\lambda = 632.8$ nm, $n = 3.667$, $k = -0.260$); measurements of optical transmittance by Carry 17 spectrophotometer between 700 and 1200 nm and reflectance measured in the same wavelength region by a system consisting of Zeiss SPM2 monochromator and a photomultiplier. Fig. 1 shows representative curves of optical transmittance and reflectance vs. wavelength, $\lambda$, with normaly incident radiation (at 300 K).

The general equations for the transmittance $T$ and reflectance $R$ of normally incident radiation impinging upon an absorbing parallel plane film separating two non-absorbing semi-infinite media[12] are quite complicated containing the Fres-

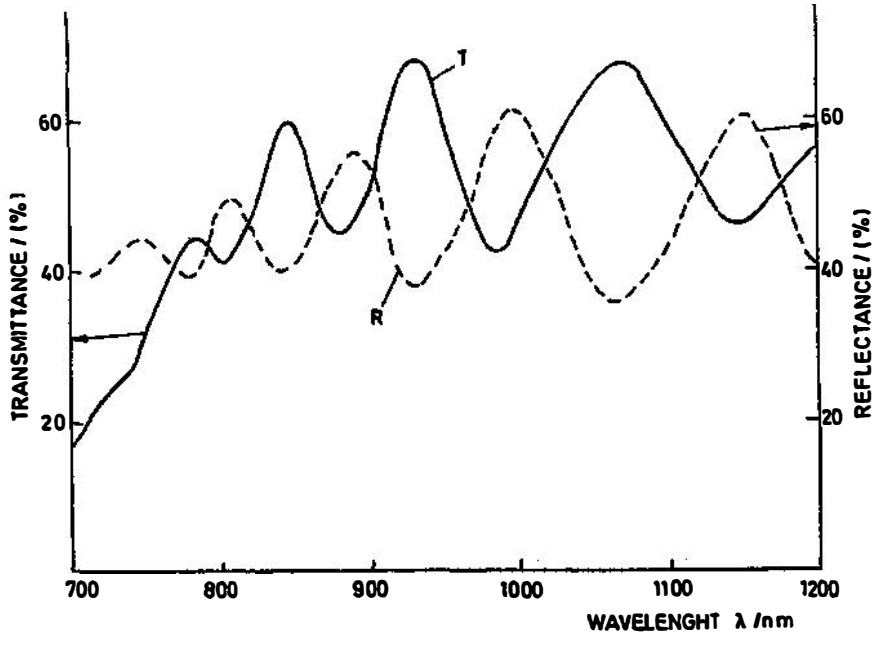


Fig. 1. Typical transmittance ($T$) and reflectance ($R$) spectra of amorphous (1.52 μm thick) $Zn_3P_2$ film.

nel coefficients for the air-film and film-substrate interfaces, the absorption coefficient, $\alpha$, and refractive index, $n$, of the film, extinction coefficient, $k$, of the film, $n_1$ — refractive index of the substrate, $t$ — film thickness, $\lambda$ — the wavelength of incident radiation, and phase angles due to reflection at the interfaces. However, in the region of very strong absorption of the film, the general equations reduce to

$$T = \frac{16\,(n^2 + k^2)\,\mathrm{e}^{-\alpha t}}{[(n+1)^2 + k^2]^2} \tag{1}$$

$$R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2} \tag{2}$$

which reduce further for $k \ll n$ to

$$T = (1 - R)^2\,\mathrm{e}^{-\alpha t} \tag{3}$$

$$R = \left(\frac{n-1}{n+1}\right)^2 \tag{4}$$

where

$$\alpha = \frac{4\pi k}{\lambda}. \tag{5}$$

In the other extreme case, when absorption of the film is small, multiple reflections occur in the film, and reflectance and transmittance show oscillatory variation with the wavelength. Hall and Ferguson[13] have shown that at the transmission maxima (where $nt$ is an even multiple of $\lambda/4$), the extinction coefficient is given by (provided $n > n_1$ and $\frac{\alpha t}{2} < 0.05$),

$$k = \frac{\lambda}{2\pi t}\,\frac{n\,(n_1 + 1)}{n^2 + n_1}\,(T^{*1/2} - 1), \tag{6}$$

where

$$T^* = \frac{4n_1}{T\,(n_1 + 1)^2}. \tag{7}$$

For reflectance maxima ($nt$ is odd multiple of $\lambda/4$), the refractive index of the film is given by (provided $n > n_1$ and $\frac{\alpha t}{2} < 0.05$),

$$n = \left[n_1 \cdot \left(\frac{1 + \sqrt{R}}{1 - \sqrt{R}}\right)\right]^{1/2}. \tag{8}$$

Figs. 2 and 3 show the absorption coefficient $\alpha$ vs. photon energy $h\nu$ and refractive index $n$ vs. wavelength $\lambda$, which have been calculated by computer fitting of measured optical data ($R$ and $T$) to the theoretical expressions (Eqs. (1) to (8)).

In the long-wavelength region of the absorption edge amorphous semiconductor films show usually an exponential decrease in the absorption coefficient (»tail«) with decreasing photon energy. Such a tail is absent in our samples, and $\alpha$ is almost constant in energy interval from 1.00 to 1.35 eV (Fig. 2). The apparent discrepancy may be explained by additional diffuse scattering at the film-air interface which gives rise to large spurious absorption similar to the observed earlier in the case of polycrystalline thin films of $Zn_3P_2$[4].

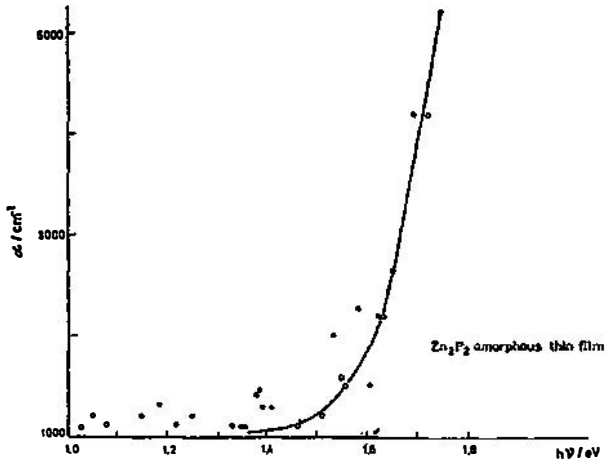


Fig. 2. Absorption coefficient ($\alpha$) vs. photon energy ($h\nu$) for amorphous $Zn_3P_2$ thin film.

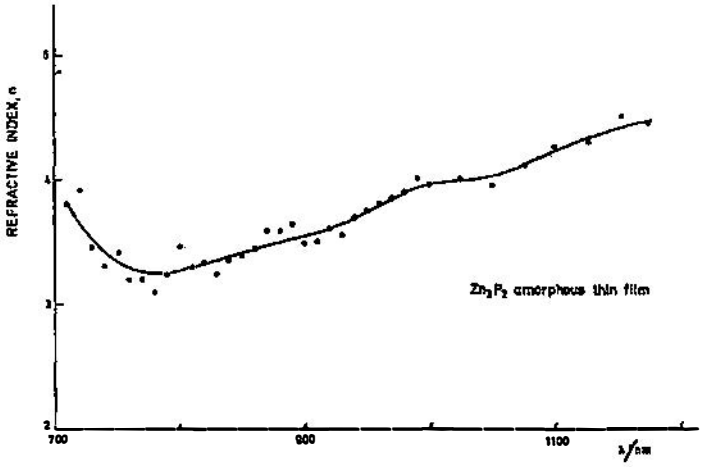


Fig. 3. Wavelength dependence of the refractive index ($n$) at 300 K of amorphous $Zn_3P_2$ film.

If we replot the results of Fig. 2 (the high-energy region of the absorption edge) as $(h\nu\alpha)^{1/2}$ against $h\nu$, a straight line is obtained in the spectral region 1.6—1.8 eV, which indicates that the following relation holds, namely

$$(h\nu\alpha)^{1/2} = const.\,(h\nu - E_g^0). \tag{9}$$

This relation which is similar to the variation for an indirect transition in a crystalline semiconductor, defines the *optical energy gap*, $E_g^0$, of amorphous semiconductor[14]. Making the linear extrapolation of $(h\nu\alpha)^{1/2}$ to the intercept (see Fig. 4),

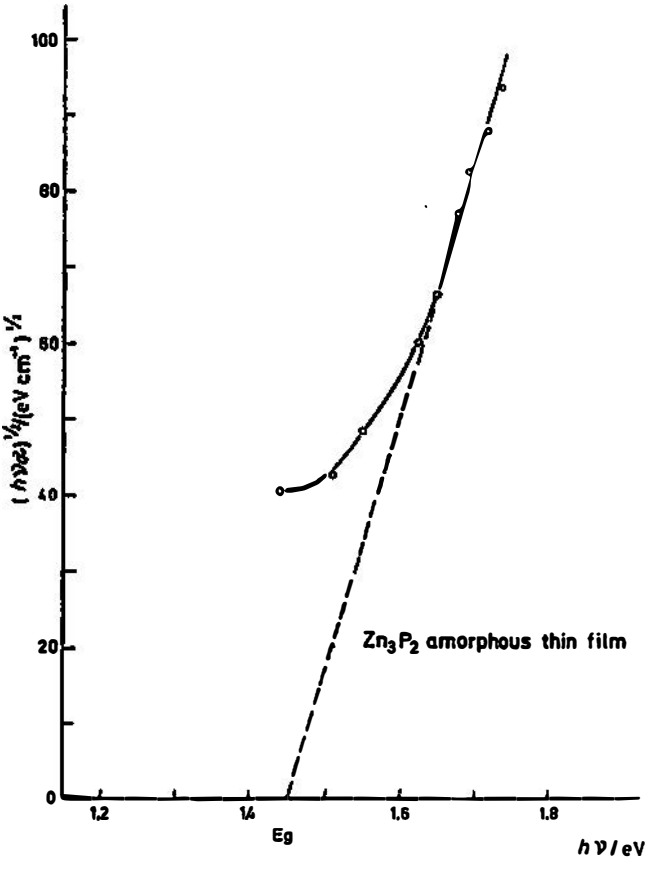


Fig. 4. A replot of Fig. 2 in the form $(h\nu\alpha)^{1/2}$ vs. photon energy.

$E_g^0$ of amorphous thin film of $Zn_3P_2$ is found to be 1.45 eV at room temperature, the value, to our knowledge, reported for the first time in the literature. The absorption described by Eq. (9) is considered to be related to transitions from the top of the extended states in the valence band to the extended states in the conduction band[14]. The value obtained for $E_g^0$ is somewhat lower than the direct band gap (1.52 eV) of the single crystal of $Zn_3P_2$, but larger than the value reported for the indirect transitions (1.32 eV) of the single crystal $Zn_3P_2$ at 300 K[15].

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## NEKA SVOJSTVA AMORFNIH TANKIH SLOJEVA $Zn_3P_2$


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Cink fosfid ($Zn_3P_2$) sintetizirao se na dva načina. Dobiveni polikristalinični spoj $Zn_3P_2$ koristio se kao izvorni materijal za vakuumsko termičko naparavanje. Strukturna analiza ovih slojeva pokazala je da su oni amorfni. Indeks loma i koeficijent optičke apsorpcije u ovisnosti o energiji upadnih fotona određivao se pomoću kompjuterskog fitovanja izmjerenih optičkih podataka sa teorijskim izrazima. Određen je optički zabranjeni pojas koji iznosi 1,45 eV.