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SOME OPTICAL PROPERTIES OF THIN Zn_3As_2 FILMS EVAPORATED IN VACUUM

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The transmittivity in the 0.4 to 20 μm range and the reflectivity in the 0.4 to 1.1 μm range have been measured for thin Zn_3As_2 films deposited in vacuum on glass and NaCl substrates. The temperature of the substrates was variable between 20 and 270°C. The calculated value of the refractive index for the long wavelength region is $n = 3.85$; at $\lambda = 1.1$ μm the value $n_{max} = 4.6$ was found. The width of the energy gap for thin Zn_3As_2 films evaporated on substrates at temperatures between 200 and 270°C, calculated from the dependence of absorption coefficient on energy of incident radiation, is $\Delta E_{300°K} = (0.95 \pm 0.05)$ eV and is in good agreement with the value of ΔE for bulk Zn_3As_2.

1. Introduction

Zinc arsenide, α-Zn_3As_2, is a compound of the $A_3^{II}B_2^{V}$ group of relatively well known semiconductive properties [1–6]. At a temperature of 300°K the resistivity of Zn_3As_2 is $\varrho = 0.2$ ohm.cm, and the mobility of current carriers (holes) at a concentration of $p = 7.3 \times 10^{17}$ cm^{-3} is $\mu_H = 17$ cm^{2}V^{-1}sec^{-1} [1].

The width of the forbidden band, obtained from optical measurements at $T = 300$°K, is $\Delta E = 1.0$ eV according to Ref. [3] and $\Delta E = 0.93$ eV according to Refs [4, 5]. A measurement of the photoconductivity in thin Zn_3As_2 films deposited on a substrate at $T = 300$°K gave $\Delta E = 1.1$ eV [6].

Zinc arsenide is a compound which is isomorphic with respect to Cd_3As_2. The process of obtaining thin Cd_3As_2 films and their semiconductive properties have been described in papers [8, 9].

2. Experimental results

Thin Zn_3As_2 films were obtained by the vacuum evaporation technique applied in Refs [9, 10]. At a pressure of residual gases of the order of 10^{-5} torr films were deposited on optically polished BK-7 glass and NaCl single crystals. The successive temperatures of

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the substrate were 20, 110, 140, 160, 180, 190, 200, 210, 230, 250 and 270 Celsius degrees. The substrates were mounted in a clamp with an internally set heater which enabled the change of temperature of the clamp and substrate.

The transmittivity of the films deposited on the glass was measured with an SP 700 Unicam spectrophotome*er within a 0.4 to 2.5 μm range, whereas for the films deposited

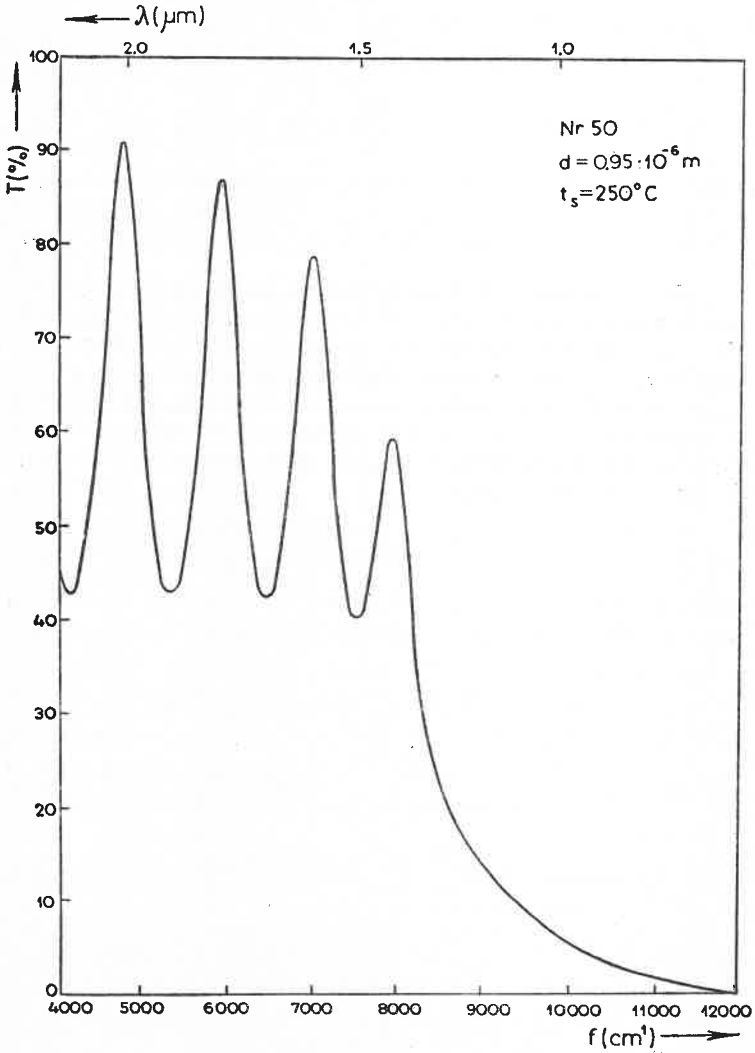

Fig. 1. Transmittivity T as a function of wavelengt λ in the 0.4 to 2.5 μm range Zn_3 As_2 layer evaporated on a glass substrate

on the NaCl crystals a UR-10 spectrophotometer in a 2 to 20 μm range was used. The transmittivity curve for the Zn_3As_2 film on the glass substrate at 250°C in the wavelength range from 0.4 to 2.5 μm is presented in Fig. 1.

The reflectivity of the Zn_3As_2 films was measured in the 0.4 to 1.1 μm wavelength range on a Zeiss spectrophotometer. The reflectivity of Zn_3As_2 films deposited on glass substrates were measured relative to an evaporated film of silver. Figure 2 shows the changes

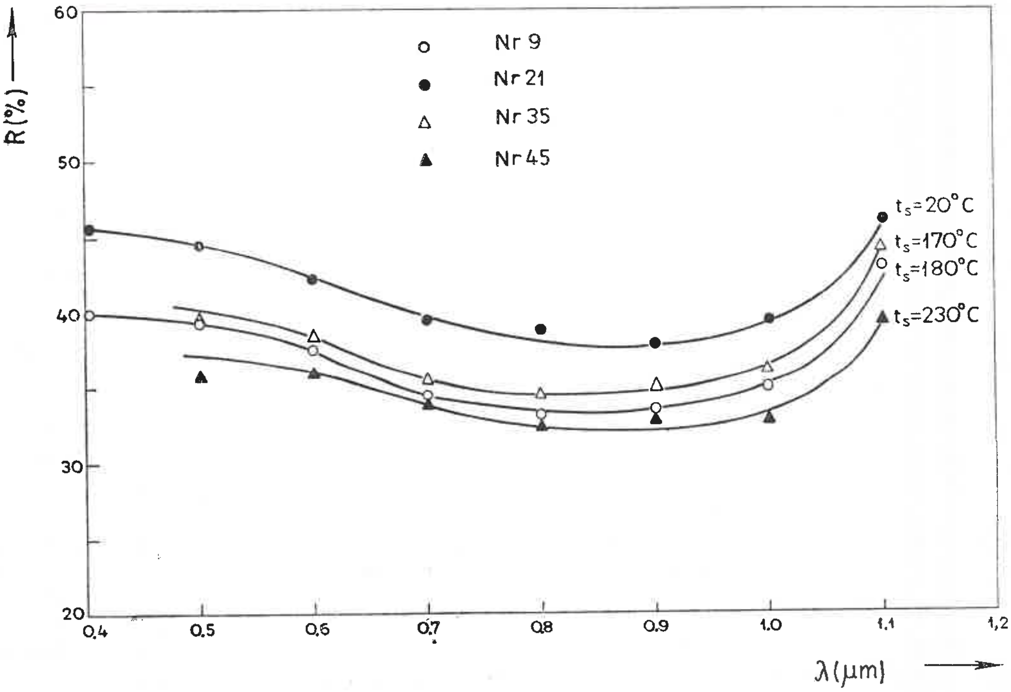

Fig. 2. Reflectivity as a function of λ in the 0.4 .o 1.1 μm range for Zn_3As_2 films deposited on glass

in reflectivity in the 0.4 to 1.1 μm range for several Zn_3As_2 films obtained at different substrate temperatures.

3. *Calculation of refractive index*

The refractive index n was determined on the basis of an analysis of the positions of interference maxima and minima in the long wavelength part of the transmittivity *versus* wavelength dependence. The order of the interference was determined analogously as in Ref. [8]. The value of refractive index n as a function of wavelength λ is presented in Fig. 3. This figure also shows the values of refractive index calculated from reflectivity measurements.

The values of refractive index n calculated from the reflectivity measurements supplement the $n = f(\lambda)$ dependence in the visible range where there is total absorption of radiation. The maximum value of refractive index $n_{max} = 4.6$ appears at $\lambda = 1.1$ μm. It is interesting that a similar $n = f(\lambda)$ dependence was earlier found by Żdanowicz [8] for thin Cd_3As_2 films.

The main source of error in the calculated values of n in the 0.4 to 12 μm range is the relatively low accuracy of film thickness (d) determinations, while in the 0.4 to 1.1 μm range the source of error was the state of the surface of the films for which reflectivity measurements were made.

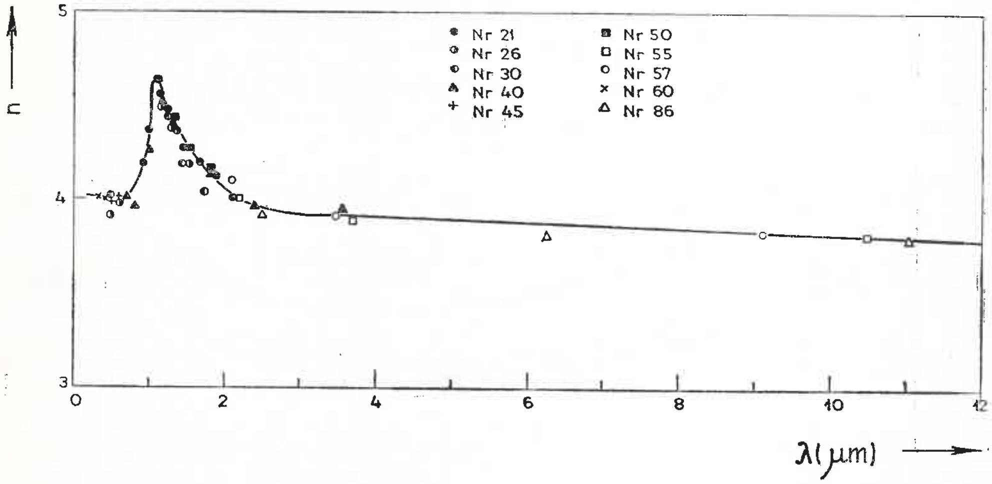

Fig. 3. Refractive index n for $Zn_3 As_2$ films as a function of wavelength. In the 0.4 to 1.1 μm range the result of reflectivity measurements were employed

With the $n = f(\lambda)$ dependence as a basis, the dispersion curve for thin Zn_3As_2 layers was plotted (Fig. 4). The graph is made for values of λ greater than 1.1 μm.

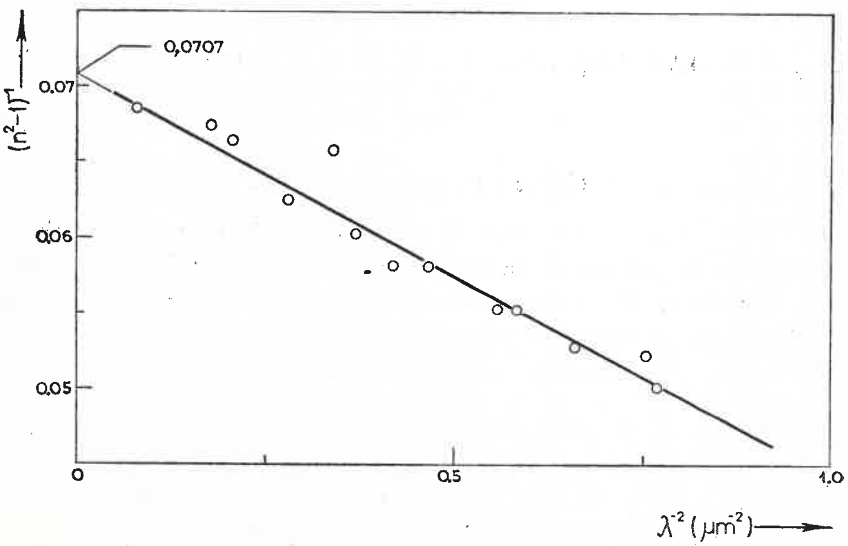

Fig. 4. Dispersion curve, $(n^2-1)^{-1} = f(\lambda^{-2})$, for thin $Zn_3 As_2$ films evaporated on glass

Walton and Moss [12], in their considerations on the model of a single harmonic oscillator, gave the equation

$$\frac{n_\infty^2-1}{n^2-1}=1-\frac{\lambda_0^2}{\lambda^2} \tag{1}$$

where $\lambda_0 = c/\nu_0$ is the wavelength corresponding to the natural frequency of the oscillator, and n_∞ is the value of refractive index for $\lambda \to \infty$. By approximating the curve in Fig. 4 with a straight line down to the value $\lambda^{-2} = 0$ the value $(n_\infty^2-1)^{-1} = 0.0707$ was obtained. Next, making use of Eq. (1), the values $\lambda_0 = 0.44$ μm and $n_\infty = 3.85$ were calculated.

4. Calculation of absorption coefficient

The absorption coefficient α_1 of thin Zn_3As_2 films were calculated by means of an "ODRA 1003" computer programmed according to the formula [7, 8]

$$\alpha_1 = \frac{1}{d} \ln \frac{A+2r_1r_2+[(A+2r_1r_2)^2-4T^2r_1^2r_2^2]^{1/2}}{2T} \tag{2}$$

where d is the thickness and T the transmittivity of the semiconductor film, and r_1, r_2 and A are the known functions of refractive indices of the film and surrounding media.

In the range of large absorption coefficients (or for a broad spectral beam) the coefficient α_1 assumes the form [8]

$$\alpha_1 = \frac{1}{d} \ln \frac{A+[A^2-4T^2-r_1r_2)^{1/2}}{2T} \tag{3}$$

The variables as a function of λ read into the computer were the percent value of transmittivity T and the refractive indices of the semiconductor film found from Fig. 3 and the substrate, *i.e.* glass or salt, from data in Ref. [11].

In the region of the principal absorption edge of the bulk material, *i.e.* from approx. 1 μm to approx. 1.5 μm, there is observed in the examined films a drop in the value of the coefficient α_1 from 10^5 cm^{-1} to 10^3 cm^{-1}.

In order to determine the width of the energy gap for the thin Zn_3As_2 films curves of absorption coefficient against energy of radiation quanta were plotted. Figures 5 and 6 depict the $\alpha_1(h\nu)$ dependence for several films deposited on substrates at temperatures from 20 to 170°C and substrates at high temperatures (from 190 to 270°C). From Figs 5 and 6 it is possible to estimate the width of the energy gap ΔE_0 for a thin Zn_3As_2 film. The values of ΔE_0 obtained in this manner and data from the literature are given in Table I. Attention is arrested by the difference in the values of ΔE_0 for layer evaporated on a substrate at ambient temperature (20°C) and the values of ΔE_0 for films evaporated on substrates heated to high temperatures. It may be presumed that this is affected by the structure of the obtained films. The films evaporated on the substrates at a temperature of 20°C were amorphous. The films evaporated on substrates heated to 200°C and more were observed to have a coarse-grain polycrystalline structure. Electron and X-ray diffraction patterns of

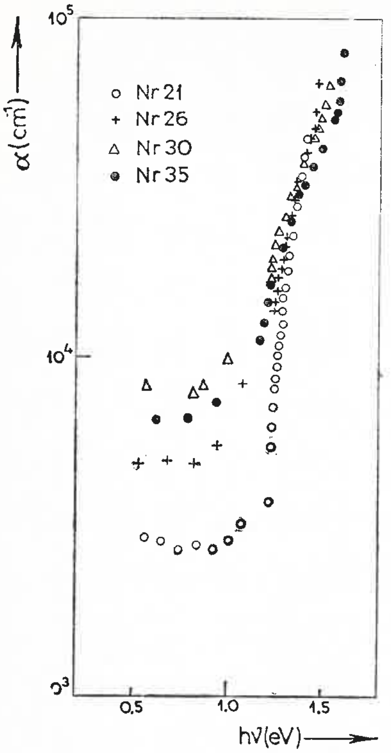

Fig. 5

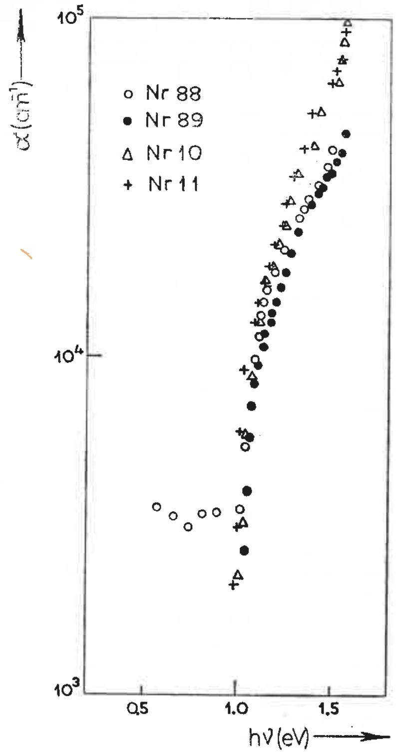

Fig. 6

Fig. 5. Dependence of absorption coefficient α_1 on energy for Zn_3As_2 films (substrate temperature 20° to 170°C)
Fig. 6. Dependence of absorption coefficient α_1 on energy for Zn_3As_2 films (substrate temperature 190° to 270°C)

TABLE I

Values of energy gap at bulk Zn_3As_2	Values of energy gap of thin Zn_3As_2 films
$\Delta E_{\text{therm.}} = (0.86-5.1\times10^{-4}\,T/eV$ [1]	$\Delta E_{\text{opt. }300^\circ K} = 1.1$ eV [6]
$\Delta E_{\text{therm.}} = 0.93$ eV [2]	$\Delta E_{\text{opt. }300^\circ K} = 1.14$ eV, $t_s = 20°C$
$\Delta E_{\text{opt. }300^\circ K} = 1.0$ eV [3]	$\Delta E_{\text{opt. }300^\circ K} = 1.00$ eV, $t_s = 110°C$
$\Delta E_{\text{opt. }300^\circ K} = 0.93$ eV [4, 5]	$\Delta E_{\text{opt. }300^\circ K} = 0.90$ eV, $t_s = 140°C$
	$\Delta E_{\text{opt. }300^\circ K} = 0.93$ eV, $t_s = 170°C$
	$\Delta E_{\text{opt. }300^\circ K} = 0.95$ eV, $t_s = 190°C$
	$\Delta E_{\text{opt. }300^\circ K} = 0.95$ eV, $t_s = 270°C$
	$\Delta E_{\text{opt. }300^\circ K} = 0.96$ eV, $t_s = 270°C$

the films evaporated on substrates heated to $t_p \geqslant 200°C$ were identical with those for bulk zinc arsenide [10].

Figure 7 gives the comparative changes of refractive index and absorption coefficient as a function of wavelength λ. As seen, the maximum of the refraction index is in the region of the pronounced drop in the absorption coefficient.

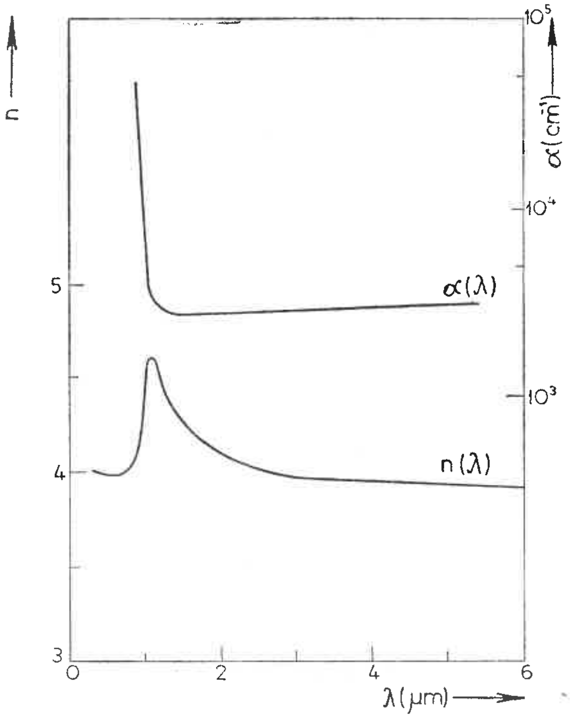

Fig. 7. Comparison of changes of absorption coefficient α_1 and refractive index n as a function of wavelength

This effect had also been observed for thin films of cadmium arsenide Cd_3As_2 [8]. It confirms the appearance of the principal absorption edge in this region.

The above results lead to the possible conclusion that Zn_3As_2 films of thickness 1 to 2 μm, obtained by evaporation in vacuum on substrates at temperatures between 200 and 270°C and having a polycrystalline structure, possess semiconductive properties very much like those of bulk Zn_3As_2. The estimated value of energy gap of zinc arsenide films, $\Delta E_0 = (0.95 \pm 0.05)$ eV, is very close to the values of ΔE_0 cited in the literature.

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