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Determination of the optical constants of zinc sulphide

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ABSTRACT A method to calculate the optical constants in the transparent region of e-beam sputtered zinc suphide thin film having a direct interband energy gap is reported.

ABSTRAK Satu kaedah untuk mengira pemalar optik dalam kawasan lutsinar dari filem nipis znk slfida tersedia secara percikan elektron dengan jurang tenaga antara jalur langsung dilaporkan.

(optical constants, zinc sulphide)

INTRODUCTION

A knowledge on the optical constants of semiconductors is crucial in the design of electro-optical devices such as light emitting devices [1,2] and heterojunction solar cells [3], and several attempts have been made to determine the optical constants of semiconducting thin films deposited on transparent substrates [4-8]. However, these attempts require a large number of interference fringes in the transmission and/or reflection spectrum. A new method is described in this paper to calculate the thickness and the optical constants of thin film in the transparent region of transmission spectrum at normal incidence. This methods does not require the presence of the interference fringes, and a minimum of two interference fringes is sufficient to estimate the thickness of the film. The method is then used to investigate the optical characteristics of e-beam sputtered zinc sulphide thin film that has a direct interband energy gap.

EXPERIMENTAL

Zinc sulphide pellets of 99.99% purity (diameter = 8 mm, thickness = 3 mm) were prepared by pressing ZnS powder. The pellets were used as the source for depositing of thin films of ZnS on transparent glass substrates by using the electron beam (e-beam) sputtering technique. The source was placed in a ceramic crucible in an Edward Auto 306 evaporator and was vaporized by an electron beam gun operated at 3 kV and 1.5 mA. The substrate was fixed horizontally 15 cm above the source and was kept at temperature of about 255 °C. The initial base pressure inside the chamber was less than 2×10^{-5} Torr, increasing to 10^{-4} Torr during the deposition. The optical transmission spectrum was recorded in the wavelength range of 190-3200 nm at normal incidence using a Shimadzu UV-3101 PC spectrophotometer. The X-ray diffractogram was recorded on a Philips PW 1840 diffractometer system equipped Cu K_α radiation ($\lambda_{\alpha1}$=1.54060 Å and $\lambda_{\alpha2}$=1.54438 Å).

RESULTS AND DISCUSSION

Method of calculating optical constants

Fig. 1 represents a thin film (thickness *t* and complex refractive index $n^*=n-ik$) bounded by two transparent media (vacuum or air and glass) with refractive indices n_0 and n_1; *k* is the extinction coefficient. The transmission *T* of weakly absorbing films ($n>>k$) can be expressed as [4,5,8]:

$$T=\frac{16n_0n_1n^2A}{C_1^2+C_2^2A^2+2C_1C_2A\cos\left(\frac{4\pi nt}{\lambda}\right)} \tag{1}$$

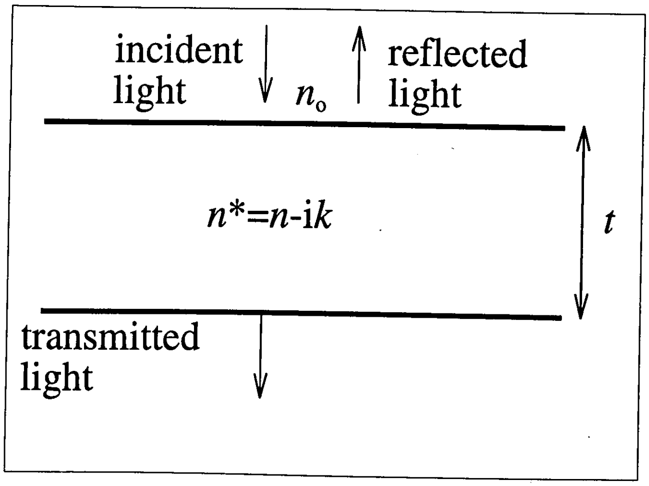

Figure 1. Reflection and transmission of light by a single film.

where $C_1 = (n+n_0)(n+n_1)$, $C_2 = (n-n_0)(n_1-n)$, $A = e^{-4\pi k t/\lambda} = e^{-\alpha t}$, α is the absorption coefficient of the film, and λ is the wavelength of photon in vacuum. In the transparent region of the material, Eq. (1) can be used to calculate the thickness of the film from the interference fringes. Under these conditions, k is very small and n is a slowly varying function of wavelength. Since $T \equiv T(n, k, \lambda)$, to a good approximation the slope of the interference peaks arises from the variation of transmission with respect to wavelength, i.e. $dT/d\lambda \cong \partial T/\partial\lambda$. For such a case, a relation between t and n can be deduced from Eq. (1) such that

$$t = \frac{\lambda}{4\pi n}\left\{\cos^{-1}\left[\frac{16n_o n_1 n^2 - T\left(C_1^2 + C_2^2\right)}{2C_1C_2T}\right] - 2m\pi\right\} \tag{2}$$

where m is an integer. We have

$$t = \frac{-2\lambda^2 n_o n_1 n \dfrac{dT}{d\lambda}}{T^2 \pi C_1 C_2}\left[1 - \left(\frac{16n_o n_1 n^2 - T\left(C_1^2 + C_2^2\right)}{2C_1C_2T}\right)^2\right]^{-\frac{1}{2}} \tag{3}$$

Eqs. (2) and (3) can be solved to determine n and t for any point at any interference edge. For a particular wavelength with known value of T, Eqs. (2) and (3) give multiple solutions for each value of m, the correct value of which may be obtained from another interference edge with the same value of T, if the difference between the values of m for two consecutive edges is unity. The correct solution must be guided by the fact that t is independent of wavelength. Furthermore, the value of t can be used to calculate the values of n and k in the transparent region by using Eq. (1). Eq. (1) can be rewritten as

$$\left(C_2^2 T\right)A^2 + \left(2C_1C_2T\cos\left(\frac{4\pi n t}{\lambda}\right) - 16n_1 n_o n^2\right)A + C_1^2 T = 0 \tag{4}$$

The roots of this equation are

$$A = \frac{-\left[2C_1C_2T\cos\left(\frac{4\pi n t}{\lambda}\right) - 16n_1 n_o n^2\right] \pm \left[\left(2C_1C_2T\cos\left(\frac{4\pi n t}{\lambda}\right) - 16n_1 n_o n^2\right)^2 - \left(2C_1C_2T\right)^2\right]^{\frac{1}{2}}}{2C_2^2 T} \tag{5}$$

Thus the values of n and k for a particular wavelength can be estimated and should satisfy equation 4 with $0 < A \leq 1$.

Optical characteristics of zinc sulphide

Fig. 2 shows the X-ray diffraction patterns of polycrystalline ZnS film grown by e-beam sputtering on glass substrates at about 255 °C. The diffraction patternd show a pronounced peak corresponding to the <111> orientation perpendicular to the glass substrate. The associated lattice parameter a_0 of cubic ZnS is calculated to be 5.4007 Å. Fig. 3 illustrates a typical optical transmission curve in the range of 0.3 - 2.0 µm for the ZnS film. Well-defined interference fringes are observed, the positions and the number of fringes as well as the separation between them being dependent on the thickness of the film. An average transmittance of 73% is found below the fundamental absorption edge for the ZnS film, suggesting that the film can be considered as being essentially transparent in this wavelength range. The onset of absorption is at approximately 290 nm.

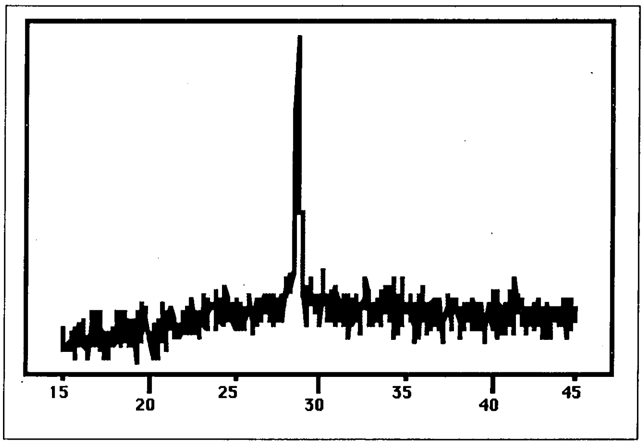

Figure 2. X-ray diffraction pattern of ZnS polycrystalline thin film.

The transmittance values were then used to calculate t of the films by solving Eqs. (2) and (3). The value of t (Table I) was used to solve Eq. (1) for n and k at each wavelength in the range of 190 - 3200 nm. Fig. 4 shows the dispersion relation of n for the ZnS film. The refractive index satisfies the Cauchy relation

$$n^2 = a_1 + \frac{a_2}{\lambda^2} + \frac{a_3}{\lambda^4} \tag{6}$$

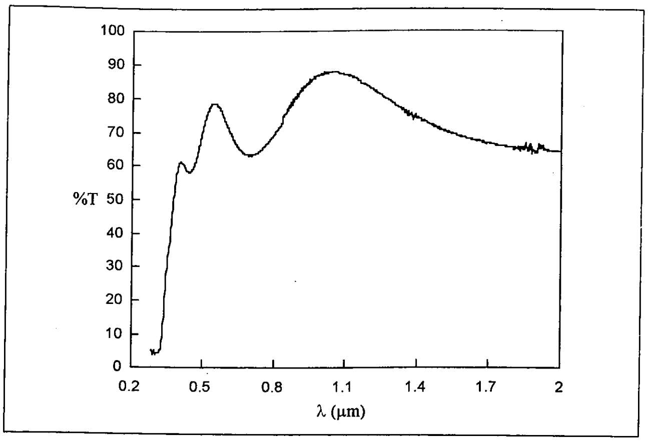

Figure 3. Optical transmission of ZnS film prepared by e-beam sputtering at 255 °C.

Table 1. Thickness and optical energy gap for ZnS thin film.

Sample	Thickness (nm)	Energy gap (eV)	reference
ZnS	185	3.6	this work
ZnS	*	3.82	ref. 13

*1 x 1.5 x 3 mm cubic ZnS.

where a_1, a_2, and a_3 are constants with a static refractive index (at the long wavelength limit) of 2.29 for this material. As ZnS is a direct band gap semiconductor [2,3,9,10], the fundamental absorption edge will satisfy the condition for direct interband transitions [3] :

$$\alpha E = C(E - E_g)^{1/2} \tag{7}$$

where C is a constant, E is the incident photon energy and E_g is the optical energy gap of the polycrystalline film. Fig. 5 shows a plot of $(\alpha E)^2$ vs. E; the values of E_g (evaluated from the intercept of this plot) are tabulated in Table I, which compares values obtained by other workers. In a semiconductor such as ZnS, the conduction band is principally composed of an S-type orbital of zinc whereas the valence band is composed of P-type functions of the sulphur atoms [11]. Figs. 6 and 7 show the variations of the real $\varepsilon'=n^2-k^2$ and imaginary $\varepsilon''=2nk$ parts of the complex dielectric function $\varepsilon^*=\varepsilon'+i\varepsilon''$. The magnitude of ε' in semiconductors is related to the rate of change of ε'' described by the Kramers-Kronig relationship. In our calculations, there

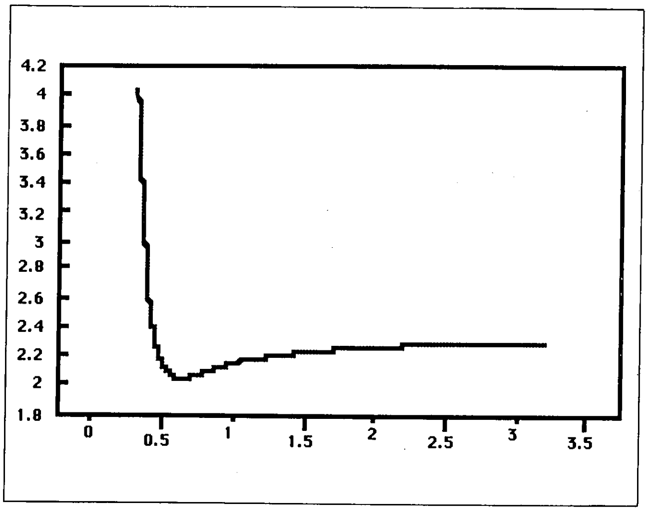

Figure 4. The variation of the refractive index n with wavelength for e-beam sputtered ZnS thin film.

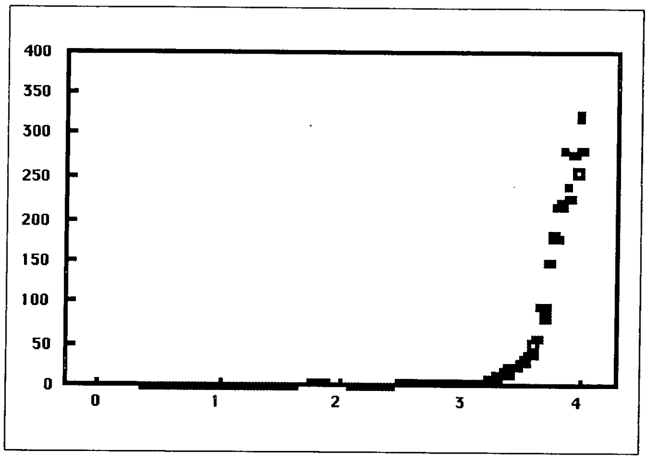

Figure 5. Plot of (aE) ^{2} vs. E for ZnS film.

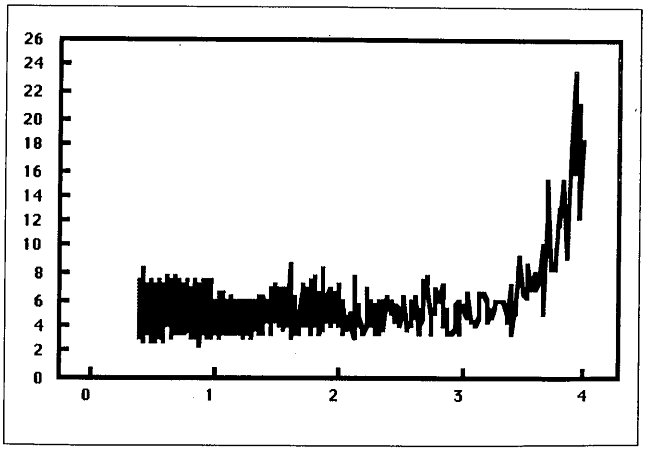

Figure 6. Variation of the real part of the dielectric function with photon energy for ZnS thin film.

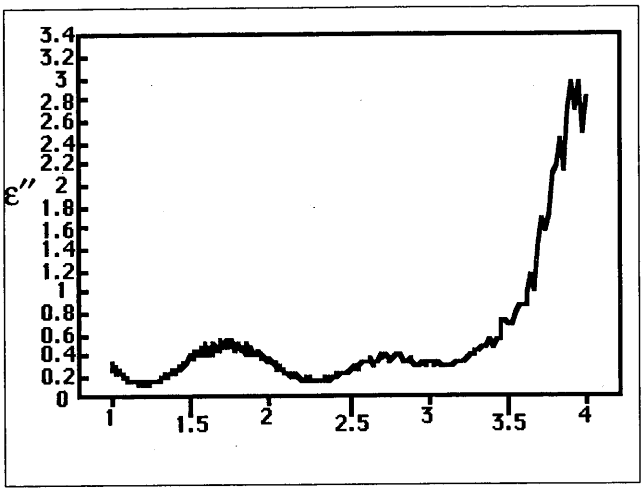

Figure 7. Variation of the imaginary part of the dielectric function with photon energy for ZnS thin film.

will be an associated peak in ε' and n for a sharp increase in ε'' (Fig. 7). This effect commonly occurs, for example, at the fundamental absorption edge [12], as shown in Fig. 6 (for ε') and in Fig. 4 (for n).

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REFERENCES

1 Fan and Woods J. (1981) *IEEE Trans. Elec. Dev.* **28**: 428.
2 Yokogawa T., Taguchi T., Fujita S. and Satoh M. (1983) *IEEE Trans. Elec. Dev.* **30**: 271.
3 Pawlikowski M. *(1985) Thin Solid Films* **127**: 9.
4 Lyashenko S. P. and Miloslavskii V. K. (1964) *Opt. Spectrosc.* **16**: 80.
5 Manifacier J. C., Gasiot J. and Fillard J. P. (1976) *J. Phys. E.* **9**: 1002.
6 Cisneros J. I., Rego G. B., Tomyiama M., Bilac S., Goncalves J. M., Rodriguez A. E. and Argüell Z. P. (1983) *Thin Solid Films* **100**: 155.
7 Davis E. A., Piggins N. and Bayliss S. C. (1987) *J. Phys. C.* **20**: 4415.
8 Ying X., Feldman A. and Farabaugh E. N. (1990) *J. Appl. Phys.* **67** : 2056.
9 Kuroyanagi A. (1990) *J. Appl. Phys.* **68** : 5567.
10 Adachi S. and Taguchi T. (1991) *Phys. Rev.* **B43**: 9569.
11 Chestnoy N., Hull R. and Brus L. E. (1986) *J. Chem. Phys.* **85**: 2237.
12 Cook R. K. and Christy R. W. (1980) *J. Appl. Phys.* **41**: 668, and references therein.
13 Bir G. L., Pikus G. E., Suslina L. G. and Fedorov D. L. (1970) *Phys.Solid State* **12**: 962.
14 Larach S., Shrader R. E. and Stocker C. F. (1957) *Phys. Rev.* **108**: 587.