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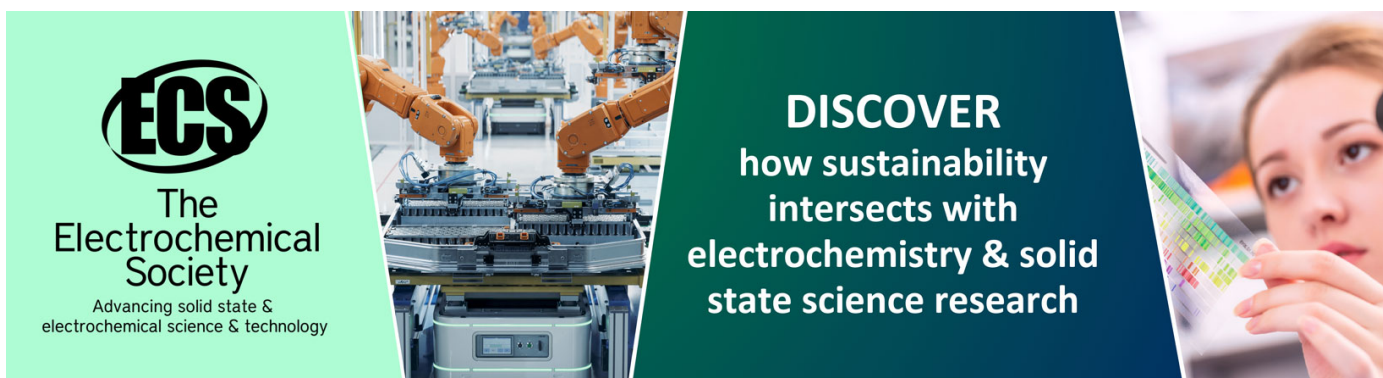
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The optical constants of thin evaporated films of cadmium and zinc sulphides

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Abstract. The optical constants n and k of thin evaporated films of CdS and ZnS have been determined over the wavelength range from 2000–250 nm by measurements of reflectance and transmittance at normal incidence and treating these data by the method of Denton *et al* (1972). The effects of surface roughness have been taken into account. Analysis of the dependence of absorption on photon energy have shown that the experimental results may be explained by the occurrence of direct transitions from 2.42 eV to 2.82 eV, in the case of CdS, followed by combined direct and indirect transitions beyond 2.82 eV assuming the energy bands to be parabolic, or equally well by assuming only direct transitions between nonparabolic bands, the forms of which may be deduced from the optical absorption curves. The results for ZnS films are similar and may be treated in the same way. It is concluded that these materials both show absorption by direct transitions just beyond the absorption edge, and that at higher energies the form of the absorption curve is probably due to the combined effects of indirect transitions together with direct transitions between nonparabolic bands. It has not been possible, on the basis of these optical measurements alone, to separate these two effects.

1. Introduction

The method devised by Denton *et al* (1972) of determining the optical constants of thin films from measurements of reflectance and transmittance at normal incidence has been applied to a study of evaporated layers of CdS and ZnS. This is part of a systematic investigation of the optical properties of the II–VI compounds attempting to eliminate discrepancies apparent in reported results by using a method which avoids the use of approximate formulae relating reflectance R and transmittance T to n and k , the refractive and absorption indices respectively. It will appear that the surface roughness of these films is an important factor in the interpretation of the measurements of R and T , particularly at the shorter wavelengths. These effects may be most effectively dealt with by using Schopper's (1951) theory to derive an equivalent uniform thin surface layer of about 10 nm thickness, in the case of CdS, and then treating the film as a double film on a substrate using the formulae of Tomlin (1972) and the criterion of completion of the dispersion curve as discussed by Denton *et al* (1972). This procedure leads to an unambiguous and accurate determination of the optical constants as far into the ultra-violet as it is possible to measure the transmittance, ie to about 250 nm for these two materials.

The resulting absorption curves can be satisfactorily analysed in two possible ways:

either in terms of direct transitions at lower energies and combined direct and indirect transitions at higher energies, or in terms of direct transitions between nonparabolic energy bands.

2. Experimental details

The films of CdS and ZnS of thickness 50–300 nm were prepared on quartz substrates in the form of wedges of 3° angle, by evaporation from an alumina crucible heated by an external tungsten wire coil, in a vacuum of 10^{-5} Torr. Rates of evaporation ranged from 20 to 60 nm min⁻¹. The substrates were cleaned in hot chromic acid, washed in doubly distilled water, dried in a stream of dry nitrogen, and then ion-bombarded in a low-pressure gas discharge. During deposition of the film the substrates were rotated to improve the uniformity of the films, and could be maintained at any desired temperature up to 500 °C.

The normal incidence, reflectance and transmittance were measured in air using a reflector based on the design of Strong (Kuhn and Wilson 1950). The use of a wedge substrate ensured that reflections from the back of the substrate were deflected out of the optical path of the instrument so that multiple reflections in the substrate do not affect the measurements. However, the wedge angle was small enough for transmission across the back face to be given accurately enough by the transmittance formulae for

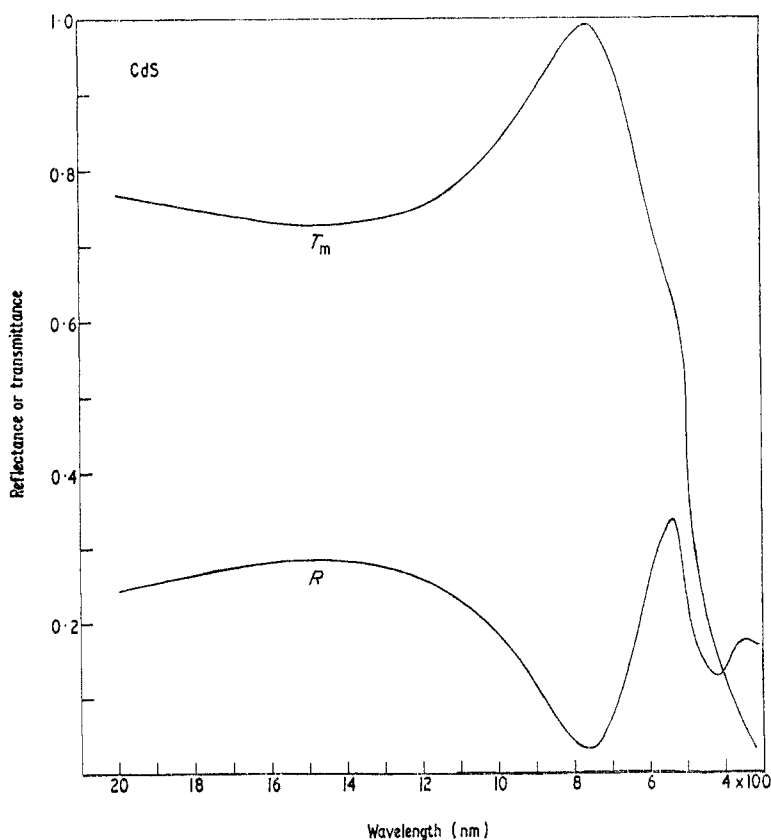


Figure 1. Measured reflectance and transmittance curves for a CdS film deposited on a quartz substrate at 140 °C.

normal incidence. A Carl Leiss double-prism monochromator was used to select the incident light. The detectors used were a PbS cell, a silicon diode detector, and a photomultiplier.

Figure 1 is an example of the reflectance and transmittance curves for a CdS film of 170 nm thickness deposited at 140 °C. It should be noted that the transmittance T required for computation of the optical constants is the transmittance into the substrate. The measured transmittance $T_m = T/T_s$, where T_s is the transmittance across the back face of the substrate and is $4n_0n_2/(n_0 + n_2)^2$, where n_0 is the refractive index of air and n_2 that of the substrate.

From the values of R and T so obtained the optical constants were derived by the methods described in the next section.

3. Derivation of the optical constants

At first the optical constants were calculated from measured R and T using the formulae for $(1 \pm R)/T$ for a single film on a substrate (Tomlin 1968) beginning with an approximate film thickness obtained from the position of the minimum of the reflectance curve (figure 1) and then adjusting this value in an attempt to obtain a closed dispersion curve (Denton *et al* 1972). Figure 2 shows the result of such a calculation based on the data of figure 1, and is typical of the results for some 50 different films of CdS deposited at different rates, at different substrate temperatures, and of different thicknesses. It shows that no choice of thickness was possible for which closure of the dispersion curve over the whole range of wavelengths could be achieved. In the light of the discussion of Denton *et al* (1972) it shows that the chosen thickness was too large for closure at A (figure 2) and too small for closure at B. No variation of film thickness improved this situation.

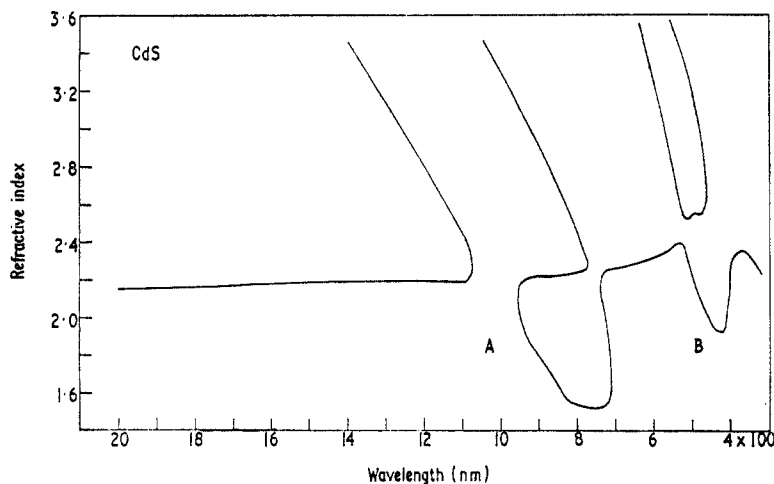


Figure 2. Typical unclosed dispersion curve for CdS from the results of figure 1.

It was concluded that the measured values of R and T were not those appropriate to a perfectly plane-parallel uniform thin film such as is assumed for the derivation of the formulae used. This view was supported by comparing the reflectance curves in the UV region, where the film is strongly absorbing so that multiple reflections are ineffective,

with corresponding results for single crystals (Cardona and Harbeke 1965). The reflectances of a 140 nm film, for example, were about 10 to 20% less than for the, presumably, smooth crystalline surfaces. This effect could be attributed to a roughness of the film surfaces such as has been demonstrated by Simov (1973) and Shallcross (1967) by electron microscopy, and considered by Coogan (1957) and Bujatti and Marcelja (1972) in optical studies of ZnS and CdS respectively. Such surface roughness would have a greater effect on reflectance values as the wavelength decreases, a point to which attention has been called by Tauc *et al* (1964) and Daude *et al* (1972).

We have examined our own CdS films by electron microscopy of Pd-shadowed carbon replicas of the surfaces and find that the surfaces are indeed rough (ie have a pebbly appearance) with a roughness dimension of about 10–20 nm. There are two methods for allowing for this roughness effect which we have considered.

The first of these makes use of the following relation due to Davies (1954):

$$R = R_0 \exp(-4\pi\sigma/\lambda)^2$$

where R_0 is the reflectance at normal incidence of a perfectly smooth surface, and R is that for a rough surface such that σ is the RMS roughness, and λ is the wavelength.

Since this result applies to a single reflection it can be used for thin films only when the absorption is great enough for multiple reflection effects to be negligible. For CdS films thicker than 150 nm this is in the wavelength range below 400 nm. In this region the measured reflectances from a rough surface would be less than for the ideal surface and need correcting before substituting into the single film equations to be solved for n and k . To check the adequacy of Davies's formula for this purpose we assumed that the measurements of Cardona and Harbeke (1965) on single crystals gave correct values for R_0 in the absorbing region, and then found calculated values of R in good agreement with our measurements on CdS films with values of the parameter σ which were in agreement with the roughnesses estimated from electron micrographs, and with the thicknesses of surface layers determined by the second method given below. Then using the results of Cardona and Harbeke (1965) as corrected thin film values in the uv region we found it possible, using single film formulae, to close the dispersion curves and eliminate the gaps at both A and B in figure 2.

Tauc *et al* (1964) have proposed the formula

$$(R_0 - R)/R_0 \propto \lambda^{-4}$$

to correct for surface roughness. Although it differs in form from the Davies formula, it is subject to the same limitations, and neither is entirely satisfactory for our purpose because of the need to cover a wide range of wavelengths and to include the effects of multiple reflections.

A more satisfactory procedure, we believe, is to make use of Schopper's (1951) theory of the optical constants of a discontinuous layer represented by an assembly of ellipsoidal particles. This allows the replacement of the rough surface layer of a film by an equivalent smooth surface layer, resting on an ideal film of the evaporated material. It is then necessary to use the formulae for $(1 \pm R)/T$ for a double layer on a substrate (Tomlin 1972) for the calculation of the optical constants of the film.

According to Schopper (1951) if $N = n + ik$ is the complex refractive index of the bulk material and N_1 is that of the ideal equivalent film by which the particulate layer may be replaced,

$$\gamma(N_1^2 - 1) = \frac{N^2 - 1}{(N^2 - 1)f + 1}$$

where γ is the ratio of the average film thickness to that deduced from the mass per unit area of the particulate film and the bulk density, and f is a function of the axial ratio of the ellipsoids known as David's function (Heavens 1955).

The explicit forms for n_1 and k_1 are readily obtained and from them, using values of γ and f estimated from electron micrographs of film surfaces, the constants n_1 and k_1 of the equivalent surface layer may be calculated if n and k for the bulk material are known. If these are not directly available from studies of the reflectance of bulk specimens, they may be estimated with what appears to be sufficient accuracy by treating the film as a single layer and completing the dispersion curve by eye where it does not close properly. This will give a fairly good estimate of n and the values of k are known to be not much affected by errors in film thickness. Then by using double-layer formulae a better closure of the dispersion curve will lead to a better estimate of n and k and one or two iterations should be sufficient to obtain the required closure of the dispersion curve.

Alternatively one may find values of absorption index k from the experimental thin film data regardless of whether or not the dispersion curve closes properly, since it is known that the absorption curve is not very dependent upon precise closure. These approximate values of k may then be used together with experimental results for reflectance from a bulk specimen to find n .

The error in n is considerably less than that in k as is clear from plots of n against R , for different k , shown by Coogan (1957).

In practice it is found that for a thin surface layer the values of n_1 and k_1 are not critical and changes in these values only modify the thickness of the surface layer for which closure occurs, without appreciable effect on the calculated values of n_2 and k_2 for the film itself. However, an accurate result for the thickness of the surface layer can be found only if n_1 and k_1 are known accurately.

This method has been applied in the study of evaporated films of Ge (Denton and Tomlin 1972) and more details of procedures for dealing with the double layer equations were given by Denton *et al* (1972). With these Ge films the surface layers were found to be only a few nm thick, and satisfactory closure of dispersion curves could be obtained without taking into account absorption in the layer. But the CdS and ZnS films had relatively rough surfaces, with surface layers of about 15 nm in thickness, and in these cases it was necessary to allow for absorption in the surface layers. This required use of the full double-layer equations (Tomlin 1972), and then it was found possible to obtain satisfactory closure of dispersion curves and consequently unambiguous values for the optical constants of the films.

4. Results for CdS films

The CdS films studied were deposited on quartz substrates at room temperature, at 140 °C or at 180 °C, and are referred to as films of types I, II and III respectively. X-ray diffraction patterns of the powdered material scraped from substrates showed a predominantly hexagonal structure with a small proportion of cubic crystallites. The patterns from type I films were less sharp than those of the type III patterns, indicating an increase in crystallite size as the substrate temperature during evaporation was raised.

All of the optical results discussed here were obtained by the double-layer method outlined above. A comparison of a set of results obtained in this way with those derived by correcting measured intensities by means of Davies's (1954) formula is shown in table 1. The agreement is good, in the limited region to which the latter procedure is

Table 1. The optical constants of a type II CdS film obtained by using the two methods of allowing for surface roughness.

Wavelength (nm)	Davies correction method		Double-layer method	
	<i>n</i>	<i>k</i>	<i>n</i>	<i>k</i>
400	2.49	0.356	2.47	0.370
380	2.50	0.377	2.49	0.391
360	2.51	0.405	2.51	0.420
340	2.55	0.444	2.55	0.460
320	2.64	0.496	2.62	0.516

applicable, for films of types II and III but less good for type I. The double-film method gave consistently higher values for *k* and lower values for *n*. However, this method has been preferred, since it is valid over the whole wavelength range and the choice of parameters for the very thin surface layer is not at all critical in its effect on the final values of the optical constants of the film (Denton *et al* 1972).

Table 2. Thicknesses of films and surface layers

Film type	Film thickness (nm)	Surface layer thickness (nm)
CdS type I	50	4
CdS type I	70	6
CdS type I	150	15
CdS type I	300	18
CdS type II	150	12
CdS type II	200	14
CdS type III	150	10
CdS type III	200	12
ZnS type I	40	1
ZnS type I	150	10
ZnS type I	200	12
ZnS type II	150	8
ZnS type II	200	10

Table 2 gives the thicknesses of films and surface layers as estimated from the criterion of closure of the dispersion curves. For each type of film it was found that increasing the film thickness resulted in a rougher surface and consequently a thicker equivalent surface layer. But for a given film thickness the equivalent surface layer decreased as the substrate temperature during deposition was increased. For a given temperature and film thickness the rate of deposition (in the range 20–60 nm min⁻¹) had little or no effect upon the surface layer thickness.

Figure 3 is a typical dispersion curve for a type II film showing multiple solutions and proper closure of the curve. Where the error bars are large they probably grossly overestimate the error for reasons discussed by Denton *et al* (1972). Uncertainties in the absorption index varied from 2% at low values to 5% at the highest values when the transmittance was very small.

Figure 4 shows typical results for *n* and *k* for each of the three types of CdS films. The results for different specimens of a given type of film were reproducible to within 1%.

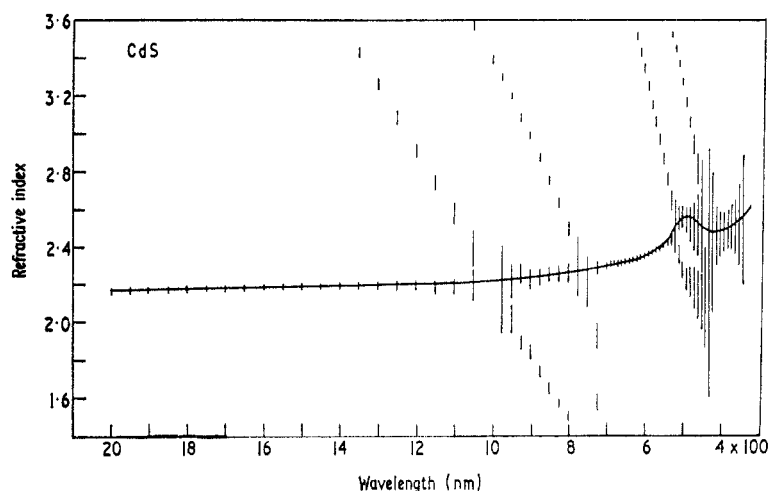


Figure 3. Typical closed dispersion curve for a type II CdS film.

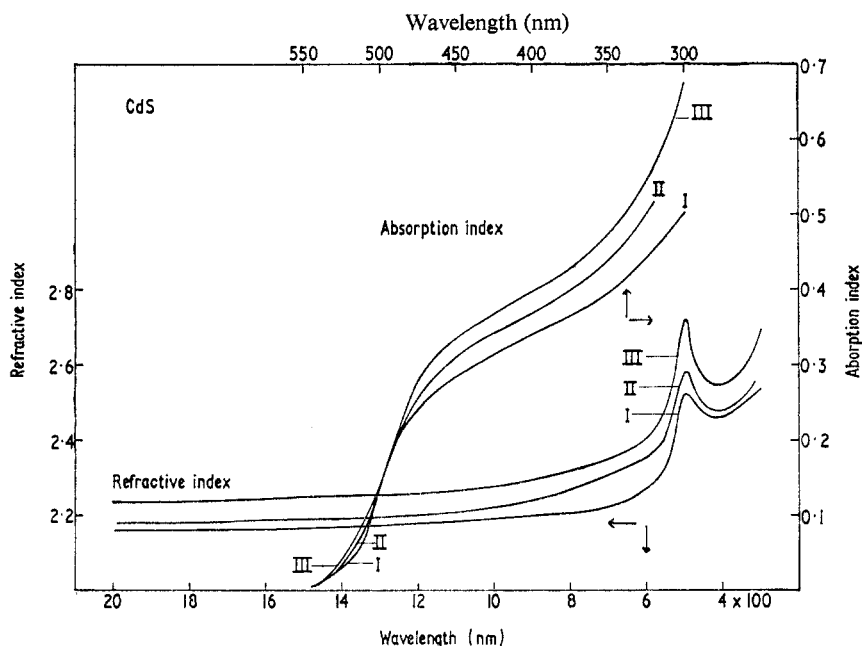


Figure 4. n and k curves for CdS films of type I (deposited at room temperature), type II (deposited at 140 °C) and type III (deposited at 180 °C). Arrows indicate appropriate scales.

in the values of n , and within 3% in the values of k . At the highest substrate temperature the refractive index approaches that for single-crystal material.

5. Results for ZnS films

ZnS films of type I were deposited on substrates at room temperature, and of type II on substrates at 180 °C. X-ray powder diffraction patterns showed that the films were predominantly of cubic crystallites, the type I films having diffuse patterns in agreement

with Vlasenko (1959). The patterns of the type II films had sharp lines corresponding to the cubic phase together with a broad diffuse line which could be attributed to the (100) reflection from hexagonal crystallites, indicating the presence of a small proportion of the hexagonal phase.

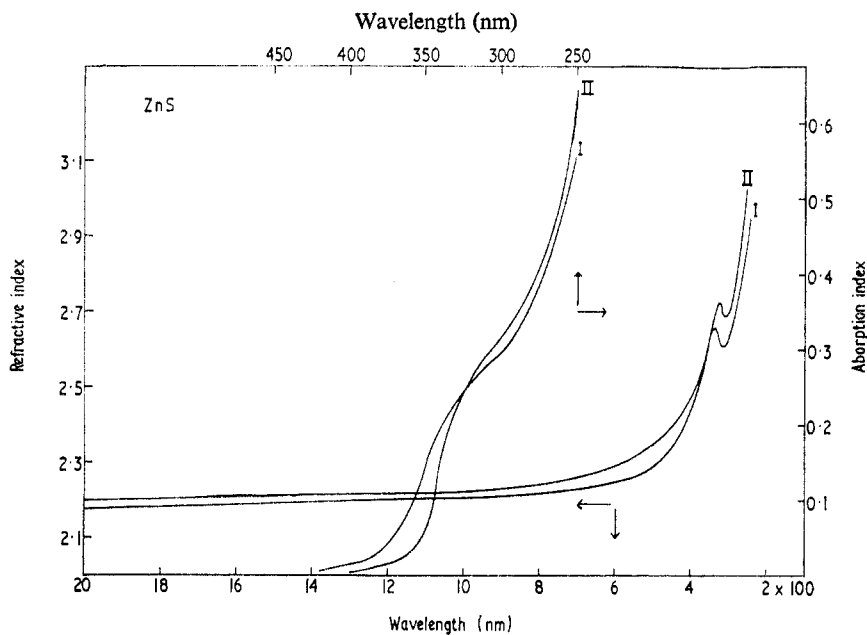


Figure 5. n and k curves for ZnS films of type I (deposited at room temperature) and type II (deposited at 180 °C). Arrows indicate appropriate scales.

Typical results for the optical constants of both kinds of film are shown in figure 5. The refractive index of the type II film in the transparent region is about 3–4% smaller than that of single crystals of ZnS determined by Czyzak *et al* (1957), while that of type I films is in good agreement with the results of Coogan (1957), except in the wavelength range below 350 nm where our values are slightly higher. This latter difference is a consequence of our taking into account the effects of surface roughness which would be more significant at the shorter wavelengths.

Our results show no evidence of a dependence of refractive index on film thickness as suggested by Kuwabara and Isiguro (1952), and in this respect agree with those of Coogan (1957).

6. Absorption and optical transitions

A first analysis of the absorption curves was made on the assumption that absorption results from direct or indirect transitions between parabolic energy bands for which the following relations hold respectively (see eg Smith 1961)

$$(EnK_1)^2 = C_1(E - E_{g1})$$

$$(EnK_2)^{1/2} = C_2(E - E_{g2})$$

where E is the photon energy, E_{g1} and E_{g2} are band-gap energies, n is the refractive index, $K_1 = 4\pi k_1/\lambda$ is the absorption coefficient for a direct transition, and $K_2 = 4\pi k_2/\lambda$ is that

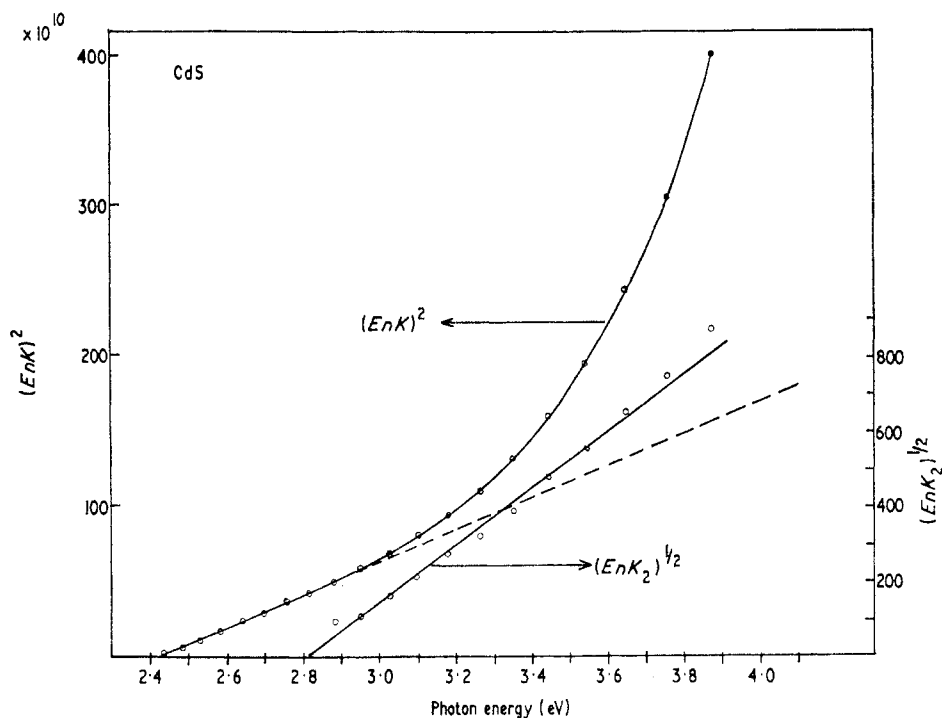


Figure 6. A plot of experimental values of $(EnK)^2$ against E for a type II CdS film, showing that at lower energies the absorption is due to direct transitions. On extrapolating this direct transition curve and subtracting the direct from the total absorption to find EnK_2 then, as shown, $(EnK_2)^{1/2} \propto E$ suggesting indirect transitions above 2.82 eV.

for an indirect transition; C_1 and C_2 are constants. In the relation for the indirect transition the phonon energy has been neglected.

Figure 6 shows a plot of $(EnK)^2$ against E for a type II CdS film. It suggests that the absorption follows the law for direct transitions up to an energy of 2.82 eV at which point a second absorption process begins to operate. The band-gap for the direct transition is 2.42 eV.

Beyond 2.82 eV the absorption coefficient is assumed to be the sum of two parts: K_1 due to the first process, and K_2 due to the second. K_2 may be found by extrapolating the straight line of figure 6 and subtracting the resulting values of K_1 from the total absorption coefficient K . For both CdS and ZnS films this second absorption process appears to be due to indirect transitions as is shown by the plot of $(EnK_2)^{1/2}$ against E for CdS, also in figure 6.

In figure 7 the experimental value of EnK for CdS is plotted together with that obtained from the above theoretical formulae assuming a direct transition from 2.42 to 2.82 eV and both direct and indirect transitions beyond 2.82 eV, the constants C_1 , C_2 , E_{g1} and E_{g2} being found from plots like those of figure 6. The band-gaps for each type of CdS film were $E_{g1}=2.42$ eV and $E_{g2}=2.82$ eV, and the other constants were as follows:

CdS film type	$C_1(10^{14} \text{ eV m}^{-2})$	$C_2(\text{eV}^{-1/2}\text{m}^{-1/2})$
I	89	7300
II	107	7900
III	130	8500

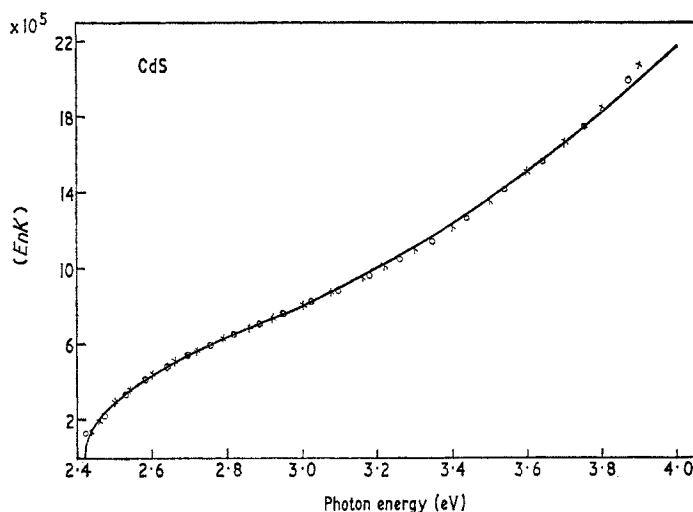


Figure 7. Plots of EnK against E for a type II CdS film. The continuous curve is the theoretical one for direct and indirect transitions between parabolic bands. The points $\circ$ are experimental results, and the points $\times$ were calculated from the expression given for direct transitions between nonparabolic bands.

The agreement between these theoretical curves and the experimental points for each film type is similar to that shown in figure 7 and is remarkably good.

The absorption curves for both types of ZnS films could also be analysed in the same way. The band-gaps for the type I films were 3.45 and 3.98 eV, and for type II films 3.57 and 4.10 eV. Between the band-gaps absorption could be attributed to direct transitions, and at higher energies to combined direct and indirect transitions:

ZnS film type	C_1 (10^{14} eV m $^{-2}$)	C_2 (10^3 eV $^{-1/2}$ m $^{-1/2}$)
I	244	15.1
II	381	16.9

These conclusions about the nature of the absorption processes are consistent with the theoretical band structures which have been calculated for hexagonal CdS and cubic ZnS, for example those of Bergstresser and Cohen (1967), Cohen (1967), Herman *et al* (1967) and Treusch *et al* (1967), if it is assumed that indirect transitions such as $L_3 \rightarrow \Gamma_1$ in cubic crystals, and $A_{56} \rightarrow \Gamma_1$ or $H_3 \rightarrow \Gamma_1$ in hexagonal crystals, can occur. However, the magnitude of the indirect absorption is comparable with the direct absorption, whereas it might be expected to be an order of magnitude smaller. For this reason we have considered the effect of nonparabolic energy bands on the absorption process as it is unlikely that a parabolic form could hold over the energy range of our measurements.

Following Smith (1961, p 408) we modify his calculation by writing the E, κ relation (using κ for the wave vector to avoid confusion with the k used for absorption index) in the form

$$\kappa^3 = (E - E_g)^{3/2} \sum_{n=0} A_n (E - E_g)^{n/2} \quad (1)$$

instead of

$$E = E_g + \frac{\hbar^2}{2m_r} \kappa^2$$

where $E = \hbar\omega$ is the energy difference between valence and conduction bands for a given κ , E_g is the direct band-gap, m_r is the reduced effective mass of the electron-hole pair, and the A_n are constants. The first term in equation (1) then gives a quadratic relation between $E - E_g$ and κ , and the remaining terms of the series, or polynomial, express deviation from such behaviour.

Using this expression, together with the assumption that the matrix element $\overline{p_{mo}^2}$ of the momentum operator is a constant, one finds

$$EnK = A \sum_{n=0} \frac{n+3}{2} A_n (E - E_g)^{(n+1)/2} \quad (2)$$

where

$$A = \frac{\hbar e^2 \overline{p_{mo}^2}}{3\pi\epsilon_0 c m^2}$$

in which m is the free-electron mass (Smith 1961).

Figure 7 shows also the accuracy with which the experimental data for CdS can be fitted using the first four terms of the above expression and matching the curves at four chosen points to determine the constants A , A_n . It should be noted that the values of the constants depend significantly on the points chosen, but the resulting curve is little affected (Ralston 1965 p 394). A least-squares method also gave similar accuracy of fit although the constants differed from those obtained by a four-point matching procedure.

Clearly the experimental results can be accounted for equally well by assuming the existence of direct and indirect transitions with parabolic bands, or by assuming only direct transitions between nonparabolic bands.

Taking an arbitrary value for A we may use the derived coefficients to plot the

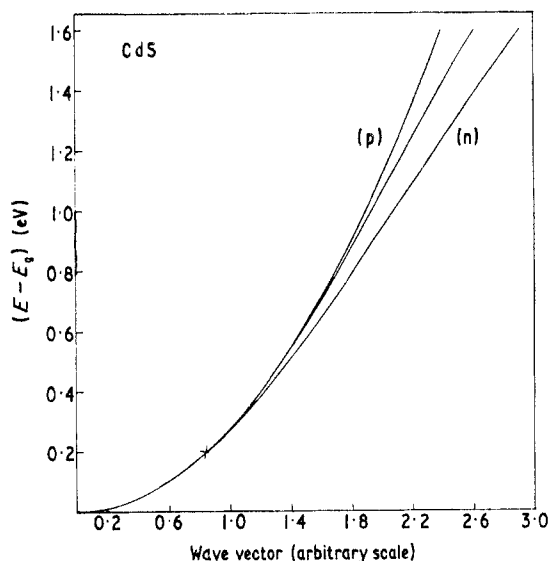


Figure 8. The curve of E against κ given by the coefficients obtained for calculating the points $\times$ in figure 7 together with a parabolic curve (p) chosen to pass through the point $+$, and a nonparabolic curve (n) modified by the assumed decreasing matrix element with parameter $\alpha = 0.2$.

relation between $E-E_g$ and κ with an arbitrary κ scale. This is shown in figure 8 together with the parabolic curve through the point marked X. It appears that relatively little departure from the quadratic form is needed to account for the form of the experimental absorption curve. The assumption of a constant matrix element is not really valid, and in the case of InSb it decreases with increasing $E-E_g$ (Johnson 1967). To assess, roughly, the effect of this, we assume that $\overline{p_{m0}^2}$ can be expressed in terms of a series in powers of $(E-E_g)$ of which we will take only the first two terms and write

$$\overline{p_{m0}^2} = P[1 - \alpha(E-E_g)].$$

Then in place of (2), retaining only the first four terms we have

$$EnK = A \left[\frac{3}{2}A_0(E-E_g)^{1/2} + 2A_1(E-E_g) + \left(\frac{5}{2}A_2 - \frac{3}{2}A_0\alpha\right)(E-E_g)^{3/2} + (3A_3 - 2A_1\alpha)(E-E_g)^2 \right]$$

and in the expression for A , $\overline{p_{m0}^2}$ is replaced by P .

Fitting the experimental curve of EnK against E with an arbitrary choice of α modifies the values of AA_0 , AA_1 , AA_2 , AA_3 and consequently the shape of the curve of E against κ . Figure 8 shows the effect for a choice of $\alpha=0.2$, and a range of $(E-E_g)$ such that $\alpha(E-E_g)$ remains small compared to unity. Such a decreasing matrix element broadens the curve of E against κ , making the deviation from the parabolic form more than that for a constant matrix element. However, the conclusion still stands that, over the energy range of our measurements, a relatively small departure from a quadratic relation between $E-E_g$ and κ is sufficient to explain the form of the absorption curves in terms of direct transitions only.

The theoretical band structures for CdS suggest that direct transitions $\Gamma_6 \rightarrow \Gamma_1$ between nonparabolic bands may occur together with indirect transitions such as $A_{56} \rightarrow \Gamma_1$ or $H_3 \rightarrow \Gamma_1$. For a limited range of photon energies above 2.82 eV the indirect absorption would be expected to follow the $EnK_2 \propto (E-E_g)^2$ relation, but for higher

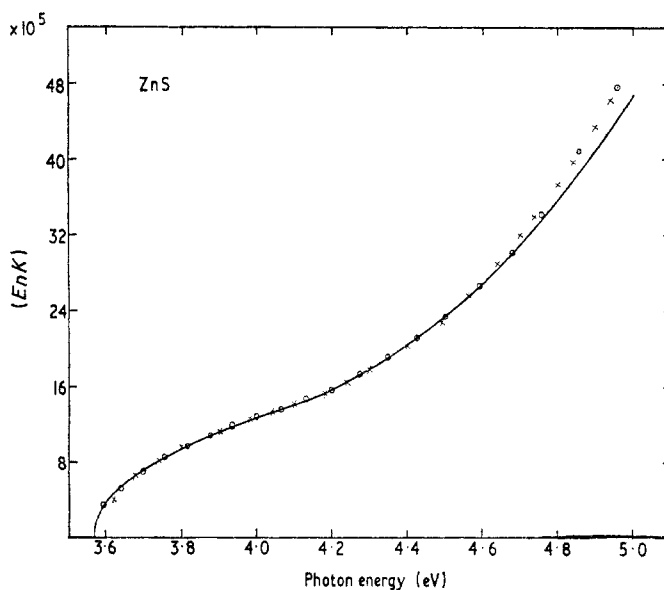


Figure 9. Plots of EnK against E for type II ZnS film. The continuous curve is the theoretical one for direct and indirect transitions between parabolic bands. The points $\circ$ are experimental results, and the points $\times$ were calculated from the expression given for direct transitions between nonparabolic bands.

energies this would be modified for nonparabolic bands in a way which is not easily determined. In fact the experimental results can be fitted just as well as in figure 7 by combining direct absorption between nonparabolic bands, as given by equation (2), with any fraction of the amount of indirect absorption required for strictly parabolic bands. Obviously the larger the amount of indirect absorption included, the smaller are the coefficients of the higher terms in (2) and the more nearly do the bands become parabolic. The optical measurements alone are not sufficient to separate the two contributions to the absorption process, and it is not possible to assert that the figure of 2.82 eV is a precise measurement of the indirect band-gap, although it is consistent with the theoretical band-gap calculations.

The above discussion has been restricted to consideration of CdS films, but the results for ZnS can be interpreted in terms of the same absorption processes, except that, the films having cubic crystallites, the direct transitions are $\Gamma_{15} \rightarrow \Gamma_1$ and the possible indirect transitions are $L_3 \rightarrow \Gamma_1$. Figure 9 shows how well the experimental data for ZnS may be fitted with the theoretical expression for combined direct and indirect transitions between parabolic bands, or by means of equation (2) for direct transitions between nonparabolic bands. The first procedure gives band-gaps which are consistent with the calculated energy band results, but again one cannot assert that the values for the indirect gap of 3.98 or 4.1 eV for two different types of film are unequivocal.

7. Conclusions

This study has shown that the method described for making the optical measurements and deriving the optical constants of thin films is successful. It reveals the effects of surface modifications and provides a means of dealing with them so that reliable values of n and k may be found.

The analysis of the resulting absorption curves for CdS and ZnS allows a precise determination of the direct band-gap for the material in thin film form, but the absorption at higher energies cannot be certainly ascribed to the onset of an indirect absorption process because the energy bands may not be precisely parabolic. It seems likely that there is some indirect absorption which may be enhanced by the effect of band shape on the direct transitions. As a result of this the values given for the indirect band gaps on the assumption of parabolic bands may be uncertain, although close to the results of theoretical band calculations.

These measurements showed no evidence of spin-orbital splitting of the valence bands of either CdS or ZnS, but this is known to be small (Dimmock 1967) for these compounds. A similar study of the selenides and tellurides, not yet complete, shows this effect quite clearly.

Acknowledgments

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