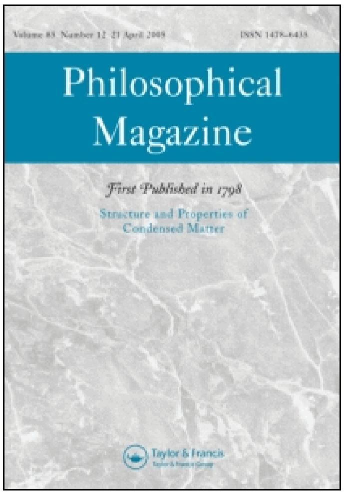

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Refractive index of inhomogeneous films

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Refractive Index of Inhomogeneous Films

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Abstract

A suggested form for the inhomogeneity found in certain thin films is a bilayer structure with a boundary layer of different refractive index from that of the main film. This boundary layer lies between the main film and the substrate. A simple formula is deduced to allow calculation of the index of this layer. For zinc sulphide the calculated results agree well with the possibility of the boundary layer being zinc oxide.

§ 1. Introduction

Studies have been made of the optical properties of dielectric films by Koppelmann and Krebs (1961) and Jacobsson (1964). Although inhomogeneity in thin films may take one of several forms, they attributed the effects that were found to an inhomogeneity in the form of a bilayer structure. Their results were applied by Koppelmann, Krebs and Leyendecker (1961) to the structure of cryolite films, produced by evaporation in the vacuum chamber. Bakos, Nagy and Szigeti (1966) investigated zinc sulphide and magnesium fluoride films deposited either as single or alternate layers on glass substrates. They concluded that the bilayer structure was not the explanation. Bispinck (1967) also studied zinc sulphide deposited on glass and on metals and found evidence for non-homogeneity on glass. Monaco (1961 a, b) derived an exact formula using the matrix-theory approach for reflectance of a non-absorbing inhomogeneous thin film at normal incidence. He assumed that the refractive index changed exponentially with film thickness. He also treated the case for a bilayer structure of a homogeneous film and an inhomogeneous film, with the refractive index varying exponentially.

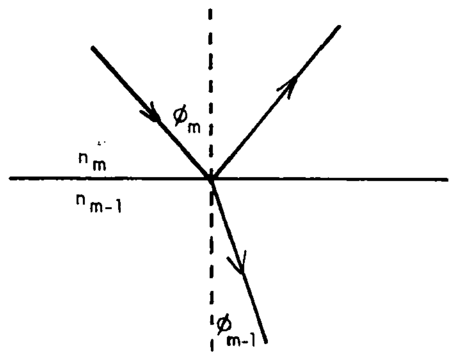
The present article analyses the bilayer structure for a thin inhomogeneous film by considering it to consist of two homogeneous layers and, in particular, the result is applied to zinc sulphide films.

§ 2. Theoretical Analysis for the Case of a Boundary Layer Lying Against the Substrate

When a thin homogeneous, transparent film on a clean glass substrate is illuminated by a collimated beam of monochromatic light, plane polarized with the electric vector in the plane of incidence and such that the angle of incidence equals the Brewster angle for the film, the reflection factor R_P is the same as that for the substrate alone at this particular angle of incidence. The occurrence of a transitional layer causes a systematic shift in the Brewster angle.

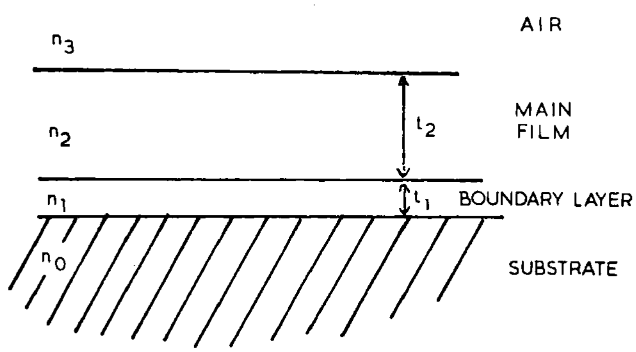
The effect of an underlying layer on the reflected intensity when the film is illuminated at its Brewster angle is studied. The notation outlined by Heavens (1960) and shown in figs. 1 and 2 is used.

Fig. 1



Notation used (Heavens 1960).

Fig. 2



Notation used (Heavens 1960).

Define matrices $[M_1]$ and $[M_2]$ as follows:

$$[M_1]=\begin{bmatrix}(u_2+u_1)\exp(i\theta_1)(u_2-u_1)\exp(-i\theta_1)\\(u_2-u_1)\exp(i\theta_1)(u_2+u_1)\exp(-i\theta_1)\end{bmatrix}, \quad . \quad . \quad . \quad (1)$$

$$[M_2]=\begin{bmatrix}(u_3+u_2)\exp(i\theta_2)(u_3-u_2)\exp(-i\theta_2)\\(u_3-u_2)\exp(i\theta_2)(u_3+u_2)\exp(-i\theta_2)\end{bmatrix}, \quad . \quad . \quad . \quad (2)$$

where

$$u_m=n_m\sec\phi_m \quad \text{and} \quad \theta_m=\frac{2\pi}{\lambda}n_m\cos\phi_m t_m.$$

The complex amplitudes of the incident and reflected waves in the incident medium (air, $m=3$) are respectively E_3^+ and E_3^-. They are given by:

$$\begin{bmatrix} E_3^+ \\ E_3^- \end{bmatrix} = \frac{1\cos\phi_0}{2^3 u_3 u_2 u_1 \cos\phi_3} [M_2][M_1] \begin{bmatrix} (u_1+u_0)E_0^+ \\ (u_1-u_0)E_0^+ \end{bmatrix}. \quad . \quad . \quad (3)$$

The reflection factor R_P is given by:

$$R_\text{P} = \left| \frac{E_3^-}{E_3^+} \right|^2. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

The fact that incidence is at the Brewster angle gives the simplification that

$$u_3 = u_2. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Evaluating the matrix product in eqn. (3) yields, for the reflectance:

$$R_\text{P} = \frac{(u_3 u_1 - u_1 u_0)^2 \cos^2 v_1 t_1 + (u_3 u_0 - u_1^2)^2 \sin^2 v_1 t_1}{(u_3 u_1 + u_1 u_0)^2 \cos^2 v_1 t_1 + (u_3 u_0 + u_1^2)^2 \sin^2 v_1 t_1}, \quad . \quad . \quad . \quad (6)$$

where

$$v_1 = \frac{2\pi}{\lambda} n_1 \cos\phi_1.$$

Equation (6) shows that the reflectance is independent of the main film thickness t_2.

On differentiating eqn. (6) with respect to u_1 and treating $v_1 t_1$ as a constant then, since u_3 and u_0 are constants at the Brewster angle, $dR_\text{P}/du_1 = 0$ will give the conditions for maxima and minima of the reflection factor with the index of the boundary layer.

Further reduction gives:

$$\underline{u_1^2 = u_3 u_0}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

A knowledge of the Brewster angle for the material (67° 06′) gives $u_3 = \sec 67°\,06' = 2{\cdot}57$, $u_0 = 1{\cdot}52 \sec\phi_0$, where $1{\cdot}52 \sin\phi_0 = \sin 67°\,06'$ and so $u_0 = 1{\cdot}91$. $u_1 = n_1 \sec\phi_1$ can now be determined and since $n_1 \sin\phi_1 = \sin$ 67° 06′, then n_1 can be estimated. As already noted, any inhomogeneity in the film will cause a shift in the Brewster angle from its theoretical value. This calculated boundary layer index is the value which will give the maximum shift.

It has been noted that $(\partial R_\text{P}/\partial\theta_1)_{u_1} = 0$ also gives a maximum of R_P but on examination this gives either that $u_1 = u_0$ or $u_1 = u_3$. At the Brewster angle of incidence this means that either the boundary layer has the same index as that of the substrate ($u_1 = u_0$) or that it has the same index as the main film ($u_1 = u_3$). In other words no transitional layer exists.

§ 3. Results

The following results are obtained by calculation from the above theory.

Material	Main film index	Boundary layer index
ZnS	2·37	1·95
CdS	2·53	2·03
HgS	3·03	2·26
MgF_2	1·39	1·47
CaF_2	1·24	1·39
Cryolite	1·36	1·46

In the case of ZnS and CdS, the main film index was determined by the author using Abelès' (1950) method with an accuracy of $\pm 0{\cdot}01$. The value for HgS was obtained by the author with an accuracy of $\pm 0{\cdot}05$. Values for the main film index of the other materials are given by Heavens (1960). Films of zinc oxide and cadmium oxide were also deposited. Their refractive indices were found to be 1·98 and 2·05 respectively for films approximately 100 Å thick. The boundary layer indices are calculated from eqn. (7).

A set of five films deposited during the same evaporation but exposed to the beam for different times was prepared. Measurements of the refractive indices of the various films by Abelès' method as described by Holland (1964) showed them to be notably dependent on film thickness. Equation (6) was solved at a Brewster angle incidence and half a degree either side to give $dR_{\mathrm{P}}/d\phi_3$ for chosen values of n_1 and t_1. This was also done for the bare substrate. The difference between the reflection factors for the main film and the bare substrate at the Brewster angle for the main film index is calculated. The shift in angle needed to give equality of reflection is then found. Graphs of apparent index as a function of film thickness are then drawn and the experimental results are fitted to one of them (Oliver 1969). This curve is for a particular boundary layer index and thickness.

§ 4. Discussion

The reflection factors for the film R_{P} and for the substrate R_{S} are equal at the Brewster angle if the film is homogeneous. If the film is inhomogeneous this is no longer true (Jacobsson 1966). Since R_{S} is independent of the film the error is due to R_{P}. It is likely that a maximum in R_{P} due to a transitional layer will coincide with the maximum shift in the incident angle required to give equal reflection factors. The calculated value of n_1 is such as to make R_{P} a maximum. It does not follow from this that the error in the index determination will be greatest for a boundary layer of this index since the rate of change of reflection factor with angle of incidence is not constant for all boundary layer indices. This variation in the rate of change of reflection factor is quite small, however, and maximum error in the index determination should occur for a boundary layer having an index of approximately the value given by eqn. (7).

The sulphide compounds are known to decompose on heating. Zinc sulphide forms hydrogen sulphide and zinc oxide on being heated in the presence of water vapour (Mellor 1923). The residual atmosphere in a kinetically pumped vacuum system is mainly water vapour liberated from the walls of the vacuum chamber (Holland 1956). Thus there could be a zinc oxide layer lying next to the substrate. Pulker (1969) has reported that excess zinc and zinc oxide occur in the initial stages of condensation. From mass spectrometric results he noted that all of the oxygen present had disappeared. Bond (1965) gives the refractive indices of single crystals of zinc sulphide and zinc oxide as 2·37 and 2·00 respectively. This agrees well with the values obtained in § 3 and indicates that a zinc oxide boundary layer is indeed possible.

The author has obtained experimental data using Abelès' (1950) method, which indicates that a transitional layer with a refractive index 2·0 and thickness 100 Å does exist in zinc sulphide films deposited at a pressure of 2×10^{-5} torr. These results were obtained for several films deposited under similar conditions. Thin films of zinc oxide prepared under identical conditions, were found to have a refractive index 1·98. Hacskaylo and Feldman (1962), who also used Abelès' method, obtained refractive index values similar to those of the present author. They found that zinc sulphide films less than 700 Å thick had a refractive index which decreased with decreasing thickness becoming 2·17 at a thickness of 550 Å.

Bakos *et al.* (1966) studied the deposition of thin layers of zinc sulphide and magnesium fluoride, on each other and on glass. Evaporation of magnesium fluoride onto a $\lambda/4$ thickness of zinc sulphide on glass and onto bare glass, simultaneously, did not give simultaneous reflectivity minima. Similar results were obtained on depositing zinc sulphide simultaneously onto magnesium fluoride and onto bare glass. They estimated the thickness deviation between the two minima and found that they were in the same sense for both films. They assumed that the transitional layer would have the same value of refractive index for both materials and so would produce thickness deviations which would have opposite directions for the two materials. This caused them to reject the transitional layer explanation. The calculated results in § 3 show that the refractive index of the boundary layer is greater than that of glass for zinc sulphide and less than that of glass for magnesium fluoride. This means that the thickness deviation would in fact be in the same sense for the two materials.

Describing their work on cadmium sulphide films Shalimova, Travina and Golik (1961) reported that cadmium sulphide decomposed and that a boundary layer composed of cadmium oxide and excess cadmium was formed between the substrate and the main film. Again, cadmium oxide has a refractive index less than that of cadmium sulphide, although the single crystal value is higher than the calculated value. From the measured values of refractive indices for cadmium sulphide and cadmium oxide a transitional oxide layer seems possible.

Very little has been reported on thin films of mercury sulphide but again dissociation would be expected with a boundary layer of mercury oxide.

The fluorides do not readily dissociate on heating, but inhomogeneities are known to exist. Pulker (1969) reported a slight F and HF evolution, depending on the amount of water vapour present, as also did Hacman (1969). Weaver (1962) assumes, from evidence of progressive crystallization during ageing, that magnesium fluoride films contain a large number of lattice vacancies giving a highly disordered lattice. The diffusion of vacancies during ageing produces a more crystalline structure which is accompanied by an increase in both density and refractive index.

Thin films of calcium fluoride have been extensively studied by Bousquet (1956) and Bousquet and Delcourt (1957) who suggested that the measured index could be explained by the existence of a very thin boundary layer at the main film–substrate interface and a thicker layer at the main film–air interface. The layer next to the substrate has the highest refractive index, and that at the air film surface has the lowest index. Heavens and Smith (1957) decided that a better interpretation would be a graded index with the high value next to the substrate. A bilayer structure with a high index layer next to the substrate is thus another possible explanation.

Cryolite dissociates into NaF and AlF_3 and, due to the higher vapour pressure of NaF, fractionation occurs. Cryolite films are also known to be inhomogeneous (Hass and Ritter 1966) and a similar explanation to that for calcium fluoride seems possible.

Compositional changes caused by differences in vapour pressure of the alloy or compound components will only be critical if the evaporation rates of the components are widely different. Selective loss of the more volatile component produces a layered film structure. Dissociation may also occur at the substrate due to large differences in the sticking coefficients for the constituent elements or to actual loss of the more volatile ingredients at high substrate temperatures. The results will be an inhomogeneous film.

§ 5. Conclusion

An attempt has been made to show that the known inhomogeneities in thin films can be explained by the existence of a boundary layer lying next to the substrate. A simple formula has been developed to allow an estimate of the refractive index of this layer to be made. For the sulphide compounds where the corresponding oxide forms the boundary layer, the calculated result for refractive index agrees reasonably well with the accepted value for the oxide.

It is worth noting that eqn. (6) shows that the presence of a boundary layer next to the substrate will not affect measurement at the Brewster angle provided that the optical path difference in the direction of the beam in the layer is an integral number of half-wavelengths. This throws some doubt on the Brewster angle method for inhomogeneous films as already observed by Heavens and Smith (1957) and others.

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References

Abelès, F., 1950, *J. Phys. Radium, Paris*, **11,** 310.
Bakos, J., Nagy, Gy, and Szigeti, J., 1966, *J. appl. Phys.*, **37,** 4433.
Bispinck, H., 1967, *Optik*, **25,** 235.
Bond, W. L., 1965, *J. appl. Phys.*, **36,** 1674.
Bousquet, P., 1956, *Optica Acta*, **3,** 153.
Bousquet, P., and Delcourt, Y., 1957, *J. Phys. Radium, Paris*, **18,** 447.
Hacman, D., 1969, Paper read at Thin Films Conference, University of York.
Hacskaylo, M., and Feldman, C., 1962, *J. appl. Phys.*, **33,** 3042.
Hass, G., and Ritter, E., 1966, *J. Vac. Sci. Tech.*, **4,** 71.
Heavens, O. S., 1960, *Rep. Prog. Phys.*, **23,** 1.
Heavens, O. S., and Smith, S. D., 1957, *J. opt. Soc. Am.*, **47,** 469.
Holland, L., 1956, *Vacuum Deposition of Thin Films* (Chapman & Hall); 1964, *The Properties of Glass Surfaces* (Chapman & Hall), p. 88.
Jacobsson, R., 1964, *J. Phys., Paris*, **25,** 46 ; 1966, *Progress in Optics*, Vol. V, p. 249.
Koppelmann, G., and Krebs, K., 1961, *Z. Phys.*, **163,** 539.
Koppelmann, G., Krebs, K., and Leyendecker, H., 1961, *Z. Phys.*, **163,** 557.
Mellor, J. W., 1923, *A Comprehensive Treatise on Inorganic and Theoretical Chemistry* (Longmans).
Monaco, S. F., 1961 a, *J. opt. Soc. Am.*, **51,** 280; 1961 b, *Ibid.*, **51,** 855.
Oliver, W. R., 1969, Paper read at Thin Films Conference, University of York.
Pulker, H. K., 1969, Paper read at Thin Films Conference, University of York.
Shalimova, K. V., Travina, T. S., and Golik, L. L., 1961, *Soviet Phys. Dokl.*, **6,** 396.
Weaver, C., 1962, *Adv. Phys.*, **11,** 83.