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Optical properties of $CuInSe_2$ thin films

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The optical constants of vacuum-deposited $CuInSe_2$ films were determined from the measured transmittance and reflectance at normal incidence of light in the wavelength range 500 to 2000 nm. The analysis of the experimental points of the absorption coefficient revealed the existence of two optical transition processes: an allowed direct transition with $E_g = 1.03 \pm 0.01$ eV and a forbidden direct transition with $E_f = 1.254 \pm 0.001$ eV. The optical constants of the films were independent of the substrate temperature.

1. Introduction

$CuInSe_2$ is a I–III–VI_2 semiconductor with good properties for solar cell application. The optical properties of $CuInSe_2$ thin films near and above the absorption edge have been studied [1–11] with particular attention to the spectral dependence of the absorption coefficient and the band gap energy values. It is a direct gap semiconductor with a gap energy of about 1.0 eV. However, Parkes *et al.* [12] concluded, from photovoltage measurements, that the absorption behaviour immediately above the fundamental edge is more complicated and can be described only by at least two independent optical transitions, one of them being an indirect transition with a characteristic energy below the direct gap energy. Such a possibility is not excluded by existing band structure calculations [13–14].

The aim of the present paper is to elucidate the structure of the fundamental absorption edge in thin films of $CuInSe_2$ by determining the optical constants from measured transmittance and reflectance at normal incidence in the range 500 to 2000 nm. The effect of the substrate temperature during the deposition process was also studied.

2. Experimental techniques

Polycrystalline ingots of $CuInSe_2$ were prepared by fusion of the constituent elements in the stoichiometric ratio in vacuum-sealed silica ampoules. The mixture was heated at 1100° C. The ingot was then ground, mixed with pure selenium in a vacuum-sealed silica ampoule and heated for 15 min at 600° C. The product was identified with X-ray diffraction to be $CuInSe_2$ of the chalcopyrite structure and to be p-type material as indicated by hot probing technique.

Thin films were prepared by a single source thermal evaporation method using the coating unit (Edwards 306). In the initial stage of deposition a shutter was used. The films were deposited on glass substrates kept at a temperature in the range 300 to 623 K. The vacuum pressure during deposition was 10^{-6} Pa. The film thickness was monitored by a quartz crystal thickness monitor and also determined interferometrically.

The transmittance, T, and reflectance, R, at normal incidence were determined using a spectrophotometer (Type VSU 2) with a special attachment [15–18]. If the intensity of the light passing through the film–glass system is I_0, and that passing through the glass is I_g, then

$$T = (1 - R_g)\, I_f/I_g \tag{1}$$

where R_g is the reflectance of glass. In addition, if the intensity of light reflected at normal incidence from the film–glass system is, I_f', and that reflected from the uncoated glass substrate is I_g', then

$$R = (I_f'/I_g')\, R_g[1 + (1 - R_g)^2(1 - A_g)^2] - T^2 R_g(1 - A_g)^2 \tag{2}$$

where A_g is the glass absorptance.

3. Results and discussion

The samples used in this investigation were single-phase polycrystalline $CuInSe_2$ of the chalcopyrite tetragonal structure (Fig. 1).

The spectral distribution of the transmittance and reflectance at normal incidence in the wavelength range 500 to 2000 nm are illustrated in Figs 2 and 3 for five samples of $CuInSe_2$ films. At long wavelengths below the absorption edge, $T + R = 1$, for each sample indicating transparency of the film and unscattered light.

The theoretical expressions for the transmittance, T, and reflectance, R, at normal incidence on plane-parallel surfaces absorping film on a non-absorbing

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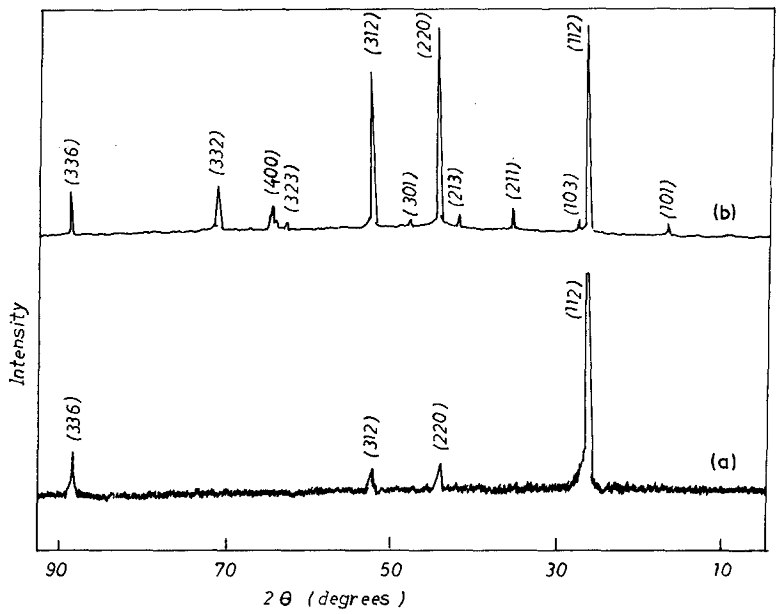

Figure 1 (a) X-ray diffraction pattern of $CuInSe_2$ thin film deposited on glass substrate at 300 K at a deposition rate of 3.5 nm sec^{-1} compared to the powder pattern (b).

substrate are given by [19, 20]

$$T = \frac{16 n_0 n_g (n^2 + k^2)}{E e^{\beta} + F e^{-\beta} + 2G \cos \alpha + 4H \sin \alpha}$$

$$R = \frac{A e^{\beta} + B e^{-\beta} + 2C \cos \alpha + 4D \sin \alpha}{E e^{\beta} + F e^{-\beta} + 2G \cos \alpha + 4H \sin \alpha}$$

where

$$A = [(n - n_0)^2 + k^2][(n + n_g)^2 + k^2]$$

$$B = [(n - n_g)^2 + k^2][(n + n_0)^2 + k^2]$$

$$C = (n^2 + k^2)(n_0^2 + n_g^2) - (n^2 + k^2)^2 - n_0^2 n_g^2 - 4 n_0 n_g k^2$$

$$D = k(n_g - n_0)(n^2 + k^2 + n_0 n_g)$$

$$E = [(n + n_0)^2 + k^2][n + n_g)^2 + k^2]$$

$$F = [(n - n_0)^2 + k^2][n - n_g)^2 + k^2]$$

$$G = (n^2 + k^2)(n_0^2 + n_g^2) - (n^2 + k^2)^2 - n_0^2 n_g^2 + 4 n_0 n_g k^2$$

$$H = k(n_g + n_0)(n^2 + k^2 - n_0 n_g)$$

$$\alpha = 4\pi t n/\lambda, \quad \beta = 4\pi t k/\lambda$$

Knowing the film thickness, t, the refractive index, n, and the absorption index, k, could be determined using Hadley's method which is summarized below [18, 21].

From Equations 1 and 2 sets of nomograms, representing $T = f(t/\lambda)$ and $R = f(t/\lambda)$ for incremental values of n corresponding to incremental values of k, were prepared using the Hewlett Packart 9836 computer attached to a Hewlett Packart 7475 A plotter

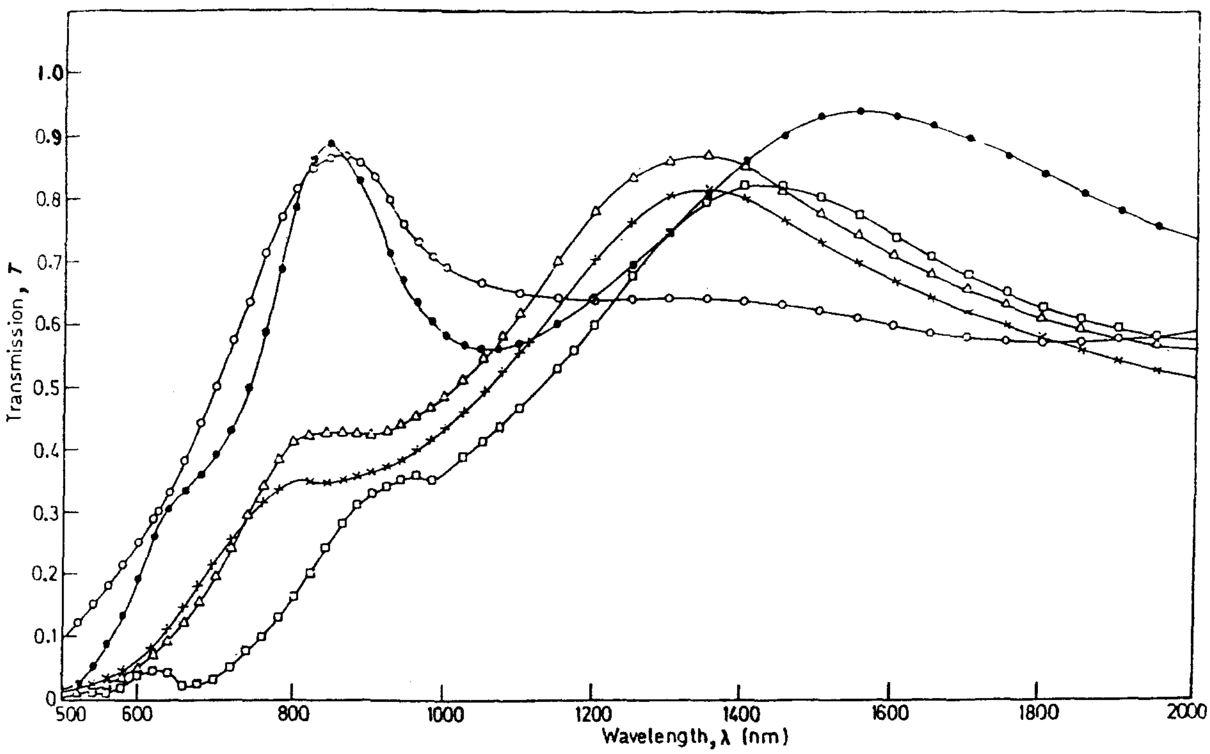

Figure 2 The spectral behaviour of the transmittance for $CuInSe_2$ films of different thickness, deposited at a rate of 3.5 nm sec^{-1}. (○) 119 nm, (△) 157 nm, (□) 162 nm, (●) 197 nm, (x) 200 nm.

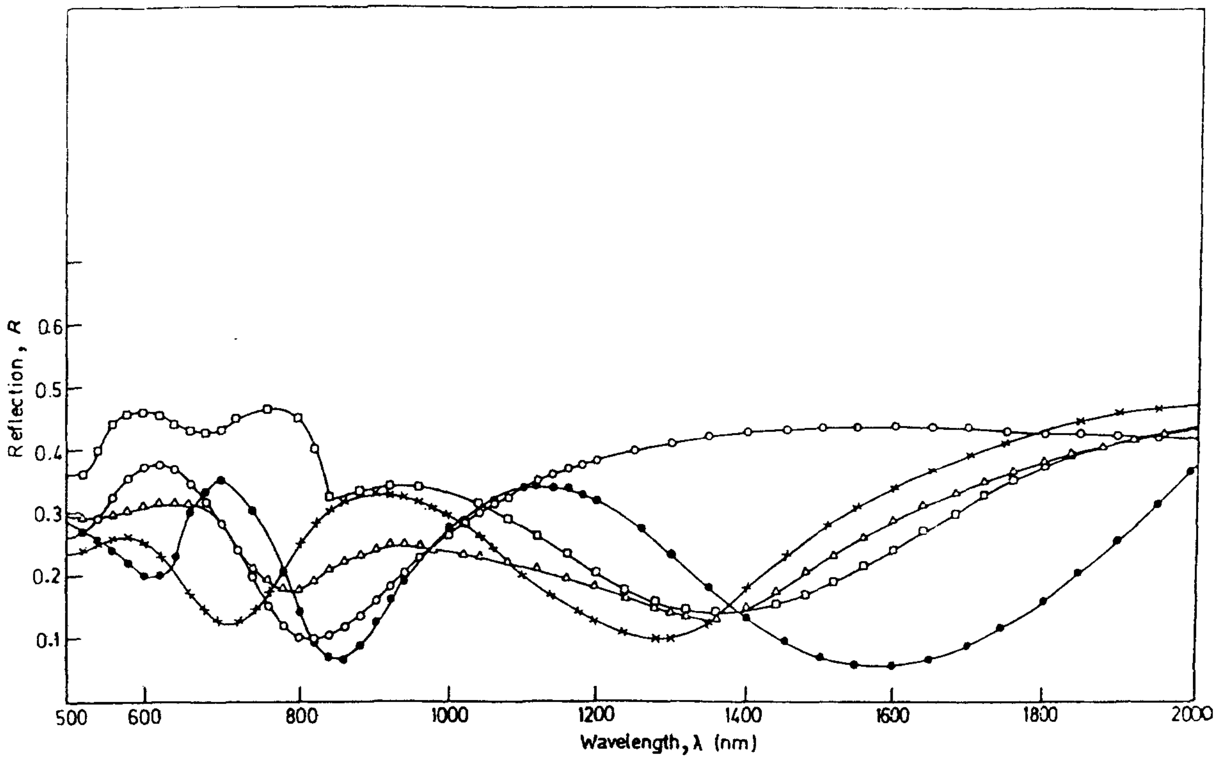

Figure 3 The spectral behaviour of the reflectance of $CuInSe_2$ films under the conditions and thicknesses shown in Fig. 2.

of King Abdulaziz University, Saudia Arabia. Using the experimental values T_{exp}, R_{exp} and $(t/\lambda)_{exp}$ the values of n corresponding to a given k can be found from the nomograms. Thus, two curves $n_T(k)$ and $n_R(k)$ can be plotted; the point of intersection determines n and k for the given λ.

The spectral distribution of both n and k for $CuInSe_2$ films is shown in Fig. 4. No variation either in n or in k with the film thickness could be observed within the limit of experimental error.

The absorption coefficient, $\alpha = 4\pi k/\lambda$, is represented in Fig. 5 as a function of photon energy. The α-values are small and practically constant for the lower energies. Beyond 0.92 eV, α increases by two orders of magnitude and reaches the 2 to 3 $\times$ $10^4\,cm^{-1}$ range.

Analysis of the experimental points of the absorption coefficient shows that for $h\nu > 0.95$ eV the absorption spectrum can be described by a relation of the form [22]

$$\alpha = (A_d/h\nu)(h\nu - E_g)^{1/2}$$

which indicates an allowed direct transition with a gap energy $E_g = 1.03 \pm 0.01$ eV (Fig. 6) in good agreement with the published data [8–10].

The absorption coefficient, α_d, calculated using A_d and E_g determined from Fig. 6, is considerably smaller than the absorption coefficient measured experimentally, indicating the existence of additional absorption processes. The additional absorption is characterized by an absorption coefficient, α', that is the difference between the experimental absorption coefficient, α, and the extrapolated one, α_d, calculated using values of A_d and E_g determined from the first absorption edge (Fig. 5).

The dependence of $(\alpha')^{2/3}$ on $h\nu$ is practically linear (Fig. 7) indicating a forbidden direct transition of the form [22]

$$\alpha' = (A_f/h\nu)(h\nu - E_f)^{3/2}$$

where E_f and A_f are the characteristic energy of the transition and a parameter that depends on the transition probability, respectively. The presence of such a forbidden direct transition in $CuInSe_2$ has also been detected in films grown by flash evaporation [9] and d.c. sputtering [23]. The values of E_f and A_f

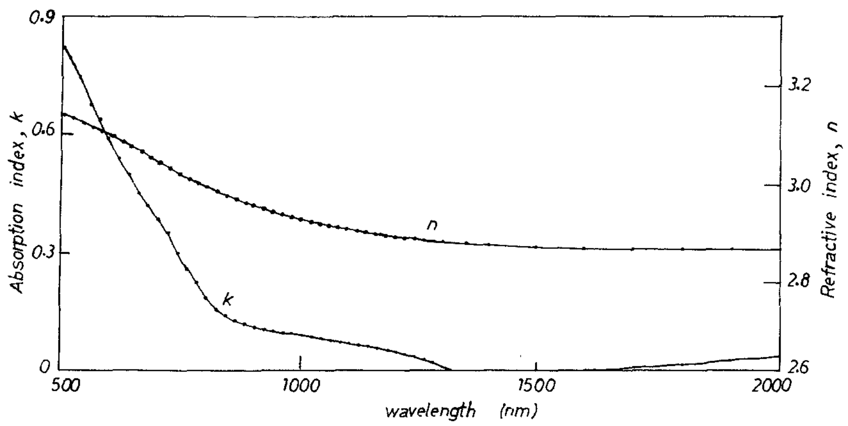

Figure 4 The spectral behaviour of the refractive index, n, and the absorption index, k, of $CuInSe_2$ films.

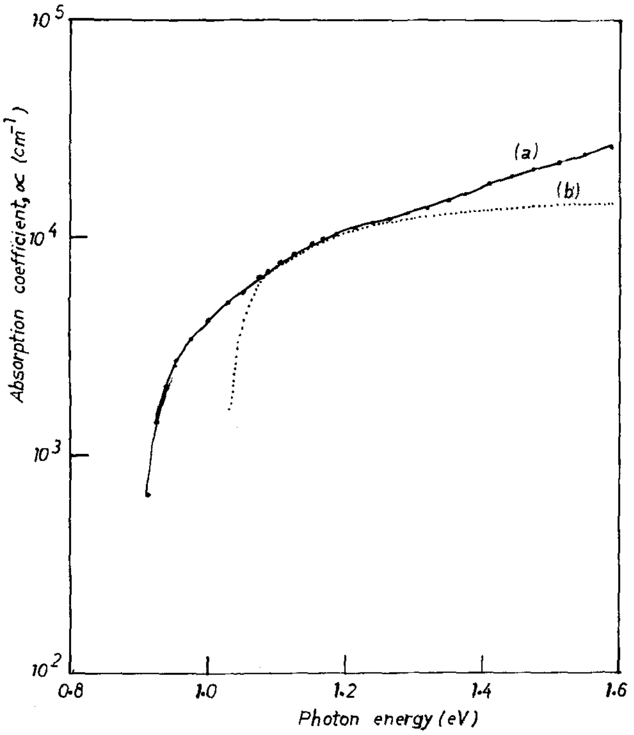

Figure 5 The spectral behaviour of the absorption coefficient of $CuInSe_2$ films: (a) experimental points, and (b) calculated using A_d and E_g values, determined from Fig. 6.

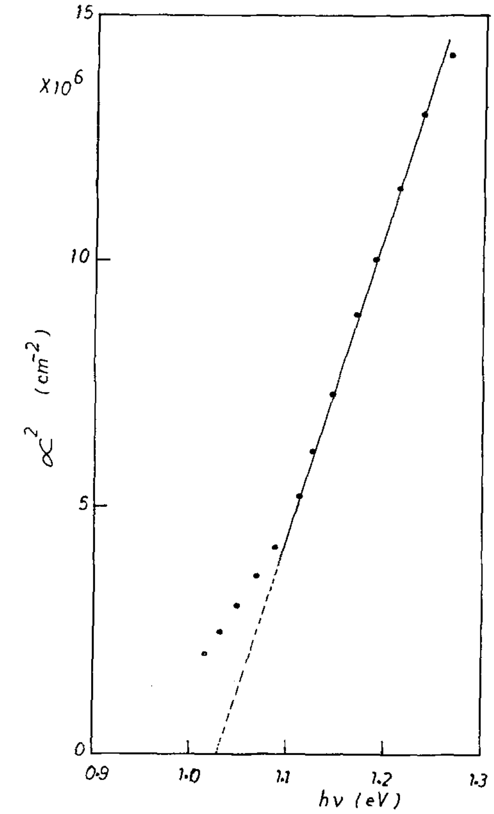

Figure 6 The square of the absorption coefficient, α^2 plotted against photon energy, $h\nu$.

obtained from the $(\alpha' h\nu)^{2/3}$ against $h\nu$ plot are 1.254 ± 0.001 eV and $4.8 \times 10^4\,cm^{-1}\,eV^{-1/2}$, respectively. The energy band structure of $CuInSe_2$ [24] predicts forbidden direct transition caused by transition between the copper d-states in the valence band and the s-type conduction band.

A comparative study of the optical properties of polycrystalline and epitaxial thin films of $CuInSe_2$ deposited on to CaF_2 substrates [25] showed that polycrystallinity gives rise to some increase in the constant A_d of Equation 1 and, therefore, in the absolute magnitude of the absorption coefficient above the edge, but no changes in the gap could be detected within the accuracy of the experiments. Further, on studying the optical properties of co-evaporated $CuInSe_2$ thin films [26] it was found that the value of A_d depends on the Cu–In percentages ratio and remains practically constant for values of the ratio lower than 1 : 1 and increase for the higher values. This decrease could be attributed to the defects which are present in films with an excess of copper, namely indium vacancies or copper at indium sites [27].

A set of samples of $CuInSe_2$ films of the same thickness (215 nm) was prepared at a deposition rate of $3.5\,nm\,sec^{-1}$ on glass substrates at different substrate temperatures ranging from room temperature to 623 K. Fig. 8 illustrates the spectral behaviour of the transmittance, T, and reflectance, R, respectively for such films. No significant variation is observed in both T and R with the substrate temperature. Hence, one

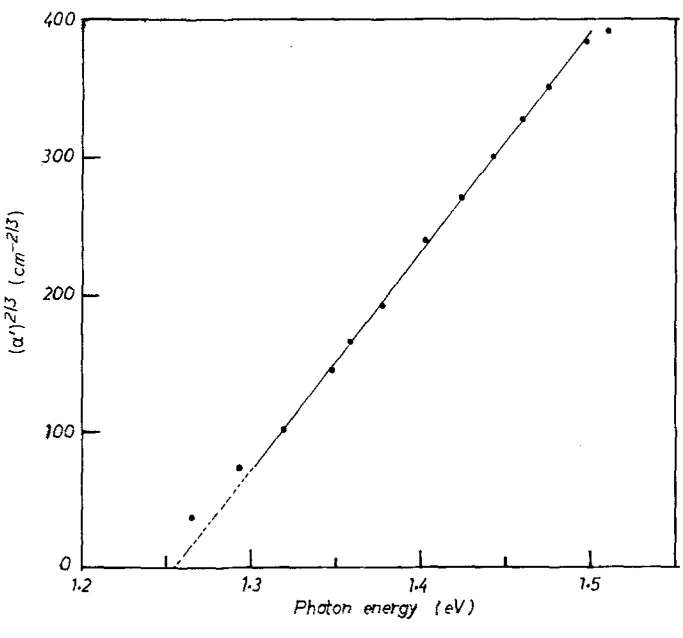

Figure 7 The dependence of $(\alpha')^{2/3}$ on photon energy, $h\nu$.

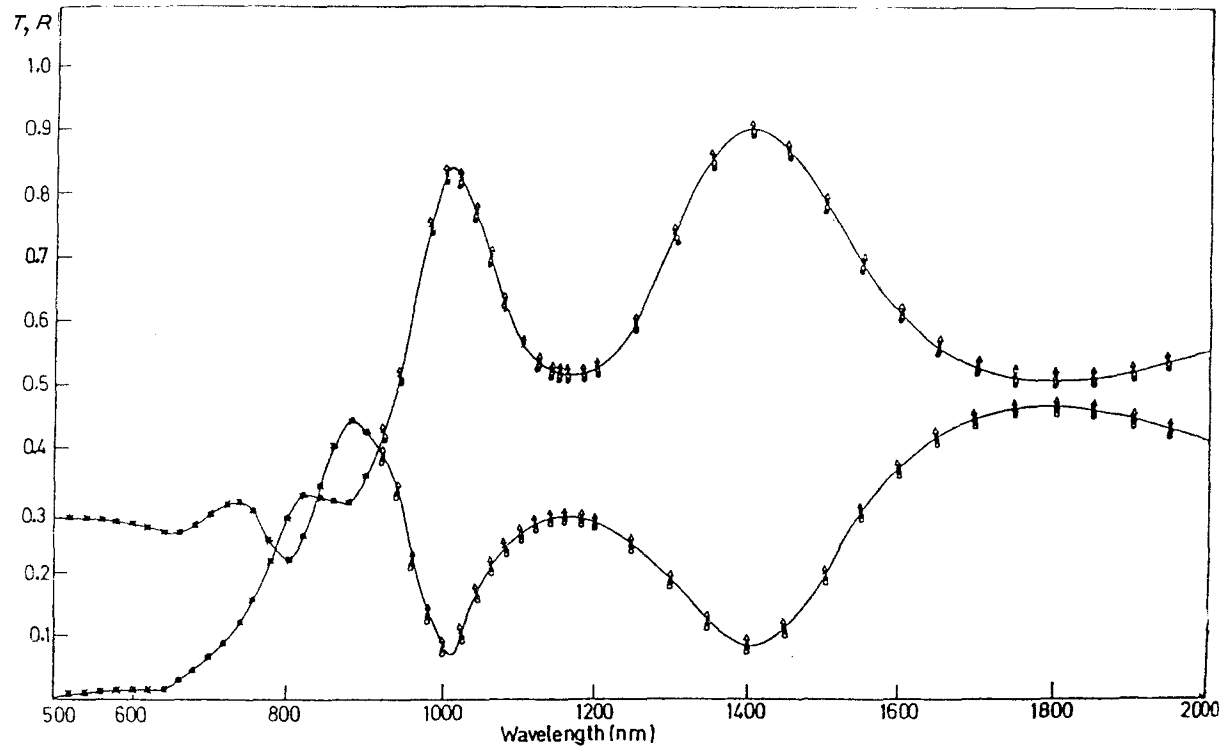

Figure 8 The spectral behaviour of T and R of $CuInSe_2$ films, of the same thickness deposited on glass substrate at a deposition rate of $3.5\,nm\,sec^{-1}$, at different substrate temperatures. (●) *RT*, (▲) 100° C, (x) 200° C, (■) 350° C.

may conclude that both n and k are independent of the substrate temperature for $CuInSe_2$ films under the stated conditions.

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