THE OPTICAL PROPERTIES OF CuInSe₂ THIN FILMS

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(Received March 26, 1992; in final form July 7, 1992)

The optical constants of vacuum deposited CuInSe₂ thin films of different thicknesses (60-135 nm) were determined in the photon energy from 1.03 to 3.1 eV. It was found that both the refractive index n and the absorption index k are independent of the film thickness. The analysis of the experimental points of the refractive index revealed the existence of normal dispersion and fits Sellmeier dispersion formula for single oscillator model. Using the previous model the optical dielectric constant as well as the oscillator energy and dispersion parameter have been calculated. CuInSe₂ is found to be a direct gap semiconductor with a gap energy of 1.03 eV. At energies well above the absorption edge, the absorption behaviour can be explained by the existence of a forbidden direct transition with the same direct energy gap and an indirect one with energy gap of 0.85 eV.

PACS numbers: 78.65.-s, 81.40.Tv

1. Introduction

In recent years the Cu-III-VI₂ semiconductors have attracted great attention because of their wide applications in nonlinear optics and solar cell devices [1]. At present, it seems to be well established [2-4] that CuInSe₂ is a direct gap semiconductor with a gap energy of about 1 eV. This point of view is supported by luminescence measurements [5]. However, Parkes [6] concluded from photovoltage measurements that the absorption behaviour immediately above the fundamental edge is more complicated, and can be described by at least two independent optical transitions, one of them being an indirect transition.

In the present work an attempt was made to determine the shape of the absorption edge by determining the optical constants from measured transmittance and reflectance at normal incidence in the wavelength range from 400 to 1200 nm for thin CuInSe₂ films.

2. Experimental work

Thin CuInSe₂ films with thicknesses in the range of 68-135 nm were prepared by thermal evaporation of the ingot of the CuInSe₂ compound. The ingot was prepared by vacuum fusion of stoichiometric elements [7], in evacuated and sealed silica tube at 1050°C. A measured pressure of about 10^{-5} torr was maintained during deposition process on quartz slides held at room temperature. The film thickness was controlled using thickness monitor and was measured by applying Tolansky's method [8]. Figure 1 illustrates the X-ray diffraction of CuInSe₂ films annealed for one hour at 200°C in vacuum better than 10^{-4} torr. It is clear



Fig. 1. X-ray diffraction pattern of CuInSe₂ thin films after being annealed for one hour at 200°C under vacuum.

from Fig. 1 that CuInSe₂ films have a single phase polycrystalline with sphalerite structure. Therefore, all films used in the present work were annealed for one hour at 200°C in vacuum. The transmittance and reflectance of the annealed CuInSe₂ films were measured at normal incidence in the spectral range from 400 to 1200 nm using a Carey 2390 spectrophotometer. Figure 2 illustrates the transmittance and reflectance of three different thicknesses as a function of wavelength λ .

3. Results and discussion

In order to determine the optical constants (n, k) from the measured transmittance T and reflectance R, knowing the film thickness t, a computational program suggested in Refs. [9, 10] was used to solve Murmann's exact formula [11]. Figure 3 shows the spectral distribution of both n and k for CuInSe₂ in the spectral range 400-1200 nm. Each curve represents the mean values of either n or kfor a set of three films of different thicknesses. The spectral distribution of the refractive index $n(\lambda)$ of CuInSe₂ films shows normal dispersion and fits Sellmeier



Fig. 2. The spectral behaviour of the transmittance T and reflectance R for CuInSe₂ films at different thicknesses (X) 68 nm, (\odot) 110 nm, (\Box) 135 nm.



Fig. 3. The spectral behaviour of the refractive index $n (-\odot -)$ experimental points [11] and n(---) calculated points [12] and absorption index k for CuInSe₂ films.

dispersion formula. An approximation, which retains the physical significance of the oscillator parameters, is due to the single-term Sellmeier relation [12]:

$$n^{2}(\lambda) - 1 = \frac{S^{2}\lambda_{0}^{2}}{\left[1 - (\lambda_{0}/\lambda^{2})^{2}\right]},$$
(1)

where λ_0 is an average oscillator position and S_0 is an average oscillator strength. For further analysis of the refractive index data of CuInSe₂ films, the quantity $(n^2-1)^{-1}$ versus λ^{-2} was plotted as shown in Fig. 4. In the range 0.85-2.75 μ m⁻²



Fig. 4. Plot of $(n^2 - 1)^{-1}$ versus λ^{-2} for CuInSe₂ films.

the data yield a straight line, the slope of which gives $1/S_0$, and the infinite wavelength intercept gives $1/(S_0\lambda_0^2)$. Accordingly, S_0 and λ_0 were determined and were found to be equal to $61.1246 \ \mu m^{-2}$ and $0.3254 \ \mu m$, respectively. Substituting the values of S_0 and λ_0 in Eq. (1), the calculated refractive index as a function of wavelength is plotted and shown in Fig. 3 by a dashed line together with the experimental points. The agreement between the experimental and theoretical values confirms that the single oscillator model adequately describes the refractive index dispersion curve of CuInSe₂ films in the considered spectral region. Following this assumption, the refractive index according to the simple classical dispersion relation [13], varies as

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

where n_{∞} is the refractive index of an empty lattice at an infinite wavelength. Extrapolating the $(n^2-1)^{-1}$ versus λ^{-2} yields $n_{\infty}^2 = \varepsilon_{\infty}$ which is found to be equal 7.4724, while the oscillator energy $E_0 = 3.8106$ eV and the dispersion parameter $E_0/S_0 = 6.234 \times 10^{14}$ eV m². The values of *n* are found to be in good agreement with the previous published data [14-16].



Fig. 5. The spectral behaviour of absorption coefficient (α) of CuInSe₂ films ($-\odot$ -) experimental points and ($-\bullet$ --) calculated points using A_d and E_g values.

The absorption coefficient (α) was calculated as a function of the wavelength λ using the well-known formula $\alpha = 4\pi k/\lambda$ and is represented in Fig. 5. The analysis of α shows that for $h\nu \leq 1.15$ eV the rise of α is due to an allowed direct transition described by [17]

$$\alpha = \frac{A_{\rm d}}{h\nu} (h\nu - E_{\rm g})^{1/2} \tag{3}$$

with the gap energy $E_{\rm g}$ being equal to 1.03 ± 0.01 eV, (see Fig. 6). The value



Fig. 6. A plot of $(\alpha h\nu)^2$ versus $h\nu$ [eV] for CuInSe₂ films.

of $E_{\rm g}$ is in good agreement with the earliest published data [18, 19]. However, if we calculated $\alpha_{\rm d}$, where $\alpha_{\rm d}$ is the value of α for direct transition obtained from

the relation $(\alpha h\nu)^2$ as a function of $h\nu$ for energies above 1.15 eV and plot it as a function of λ (dashed line in Fig. 5), using A_d , where A_d is a parameter that depends on the transition probability and E_g calculated from Fig. 6, it is clear that α_d is considerably smaller than α measured experimentally. This can be explained only by the existence of an additional absorption transition. An analysis of the additional absorption coefficient $\alpha' = \alpha - \alpha_d$ showed that this additional absorption may be due to either:

i) a forbidden direct transition characterized by [17]

$$\alpha' = \frac{A_{\rm f}}{h\nu} (h\nu - E_{\rm gf})^{3/2} \tag{4}$$

or ii) an indirect transition described by [17]

$$\alpha' = \frac{A_{\rm i}}{h\nu} (h\nu - E_{\rm gi})^2. \tag{5}$$

Following these two assumptions, the dependence of $(\alpha' h\nu)^{2/3}$ and $(\alpha' h\nu)^{1/2}$ on $h\nu$ is partially linear (Fig. 7), the corresponding gap energies were found to be $E_{gf} = (1.03 \pm 0.03)$ and $E_{gi} = 0.85$ eV, respectively. Thus our results confirm the conclusion of Parkes [6] and W. Hörig et al. [18] that the absorption behaviour immediately above the fundamental edge is more complicated and can be described by the existence of two optical transitions, one of them being an indirect transition with a characteristic energy below the direct gap energy.



Fig. 7. Plot of $(\alpha' h\nu)^{2/3}$ and $(\alpha' h\nu)^{1/2}$ vesus $h\nu$ for CuInSe₂ films.

According to the energy band structure [2, 4, 19] of CuInSe₂ the simultaneous existence of an allowed and forbidden direct transitions with the same gap energy can be caused by the transition between the copper *d*-states to the upper most valence band [20], or by the polarization dependent selection rules between the valence and conduction band state [21]. We assume that the first mechanism is the most important under our experimental conditions (polycrystalline samples and unpolarized light).

References

- [1] J.L. Shay, J.H. Wernick, Ternary Chalcopyrite Semiconductors: Growth, Electronic Properties and Applications, Pergamon Press, New York 1975.
- [2] J.L. Shay, H.M. Kasper, Phys. Rev. Lett. 29, 1162 (1972).
- [3] J.L. Shay, B. Tell, H.M. Kasper, L.M. Schiavone, Phys. Rev. B 7, 4485 (1973).
- [4] J.L. Shay, B. Tell, Surf. Sci. 37, 748 (1973).
- [5] P. Migliorato, J.L. Shay, H.M. Kasper, S. Wagner, J. Appl. Phys. 46, 1777 (1975).
- [6] J. Parkes, R.D. Tomlinson, M.J. Hampshire, Solid-State Electron 16, 773 (1973).
- [7] L.S. Lerner, J. Phys. Chem. Solids 27, 1 (1966).
- [8] S. Tolansky, Multiple Beam Interferometry of Surface and Films, Oxford University, London, New York 1948, p. 147.
- [9] F. Abeles, M.L. Theye, Surf. Sci. 5, 325 (1966).
- [10] M.M. El-Nahass H.S. Soliman, N. El-Kadry, A.Y. Morsy, S. Yaghmour, J. Mater. Sci. Lett. 7, 1050 (1988).
- [11] H. Murmann, Z. Phys. 80, 161 (1933); ibid. 101, 643 (1936).
- [12] M. DiDomenico, Jr., S.H. Wemple, J. Appl. Phys. 40, 720 (1969).
- [13] T.S. Moss, G.J. Burell, B. Ellis, Semiconductor Opto-Electronics, Butterworths, London 1973, p. 23.
- [14] J.N. Gan, J. Tauc, V.G. Lambrecht, Jr., M. Robbins, Phys. Rev. B 12, 5797 (1975).
- [15] J.N. Gan, J. Tauc, V.G. Lambrecht, Jr., M. Robbins, Phys. Rev. B 13, 3610 (1976).
- [16] V. Riede, H. Sobotta, H. Neumann, Hoang Xuang Nguyen, W. Möller, G. Kühn, Solid State Commun. 28, 449 (1978).
- [17] E.J. Johnson, Semicond. Semimetals 3, 153 (1967).
- [18] W. Hörig, H. Neumann, H. Sobotta, B. Schumann, G. Kühn, Thin Solid Films 48, 67 (1978).
- [19] A.S. Poplavnoi, Yu.I. Polygalov, Izv. Akad. Nauk SSSR. Neorg. Mater. 7, 1711 (1971).
- [20] J.L. Shay, B. Tell, H.M. Kasper, L.M. Schiavone, Phys. Rev. B 5, 5003 (1972).
- [21] J.E. Rowe, J.L. Shay, Phys. Rev. B 3, 451 (1971).