Effect of heat treatment on the structural and optical properties of CuInTe$_2$ thin films

A. M. ABO EL SOUD, T. A. HENDIA, L. I. SOLIMAN
Solid State Physics Laboratory, National Research Centre, Dokki, Cairo, Egypt

H. A. ZAYED, M. A. KENAWY
University College for Women, Ain shams University, Cairo, Egypt

The CuInTe$_2$ thin films were prepared by thermal vacuum evaporation of the bulk compound. The structural and optical properties in the temperature range 300–473 K of thin films grown on glass substrates and annealed in vacuum were studied. The films were investigated by X-ray diffraction and electron microscope techniques. The calculated lattice constants for CuInTe$_2$ powder were found to be $a = 0.619$ nm and $c = 1.234$ nm. From the reflection and transmission data, the optical constants, refractive index n, absorption index, k, and the absorption coefficient, α, were computed. The optical energy gap was determined for CuInTe$_2$ thin films heat treated at different temperatures for different periods of time. It was found that E_g increases with both increasing temperature and time of annealing.

1. Introduction

The ternary I–III–VI$_2$ chalcopyrite (I = Cu and Ag, III = Al, Ga and In, and VI$_2$ = S, Se and Te) form a large group of semiconducting materials [1–3]. These materials are valence analogues of the II–VI binary compounds. Joffe and Alexzunger [4] proposed a theory for the band gap anomaly, structural deformation and the relationship between them for the ternary chalcopyrite. A considerable amount of effort has been invested to gain a better and deeper understanding of electronic [5] as well as optical properties of these compounds. I–III–VI$_2$ ternary compounds in general and CuInSe$_2$, CuInS$_2$ and CuInTe$_2$ in particular have aroused much interest in recent years due to their important technological application [6–9] in visible and infrared light–emitting diodes, infrared detectors, optical parametric oscillators and solar energy converters. CuInTe$_2$ ternary compound is a direct band gap semiconductor, and can be prepared as both p- and n-type. Therefore, their potential for application in optical and photovoltaic devices is most suitable [10, 11]. Solar cells based on CuInTe$_2$ have shown some promise for energy conversion application [12]. Because these ternary compounds have a wide range of device applications, it is necessary to produce them in thin-film form for economical and large-scale utilization. Many investigations of the structural properties of thin films of these materials have been reported [13–15].

Knowledge of the optical properties of CuInTe$_2$ is incomplete so far. The optical constant data for the photon energy range below the fundamental edge were found to be about 1 eV calculated from reflectivity and transmission measurements on bulk crystals [16]. The refractive index, n, and the absorption index, k, were also determined at photon energies above the fundamental edge using multiple angle of incidence ellipsometry [17–19].

The purpose of the present work was to determine the optical constants and to study the structural property variations of CuInTe$_2$ thin films produced by the effects of heat treatment, annealing temperature and time, on both optical and structural properties of the CuInTe$_2$ thin films.

2. Experimental procedure

CuInTe$_2$ was prepared by direct fusion of spec. pure copper, indium and tellurium in a sealed evacuated silica tube. The mixture was heated at 850 °C for 20 h. The tube was shaken throughout the melting operation to ensure mixing of the elements. The temperature was then reduced to 300 °C over a period of 6 h.

Thin films were prepared by thermal evaporation of the fine-grained powder from a tantalum boat on to clean glass substrates under a vacuum of 10^{-5} torr (1 torr = 133.322 Pa) at a deposition rate of 10 nm s^{-1} using a Leybold Univex 300 coating unit.

The X-ray diffraction (XRD) patterns were obtained for samples in the powder form and thin films by X-ray diffractometry (Philips, P. W. 1373) with a nickel filter and copper target. Films of about 150 nm thick were used for the XRD investigations.

To study some morphological features of the thin films under test, transmission and diffraction electron microscopic examinations were carried out using a Siemens instrument.

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An image analysis system Model IBAS I and II (Kontron, Germany) was used as a new technique for measuring the particle size and its distribution using the computer programs available with the possibility of constructing the Gaussian as well as the cumulative curves of the measured particle dimensions. By using the available programs the minimum particle size (min), the maximum particle size (max), the arithmetical means size "mean", the particle size of 90% of particles, "median", the high-frequency particle size, "mode", and the standard deviation "s.d" were obtained directly.

The transmittance, T, and the reflectance, R, at normal incidence for $CuInTe_2$ films were recorded using a PMQ III Carl Zeiss spectrophotometer in the spectral range 500–2000 nm. The optical absorption coefficient, α, of $CuInTe_2$ films heat treated in vacuum (10^{-5} torr) at 373, 423 and 473 K for different periods of time from 0.5 h and up to 2 h, were measured.

3. Results and discussion
3.1. Structural properties
X-ray diffraction studies of the $CuInTe_2$ samples were performed. No evidence for the existence of more than

(a)

2θ (deg)

(b)

2θ (deg)
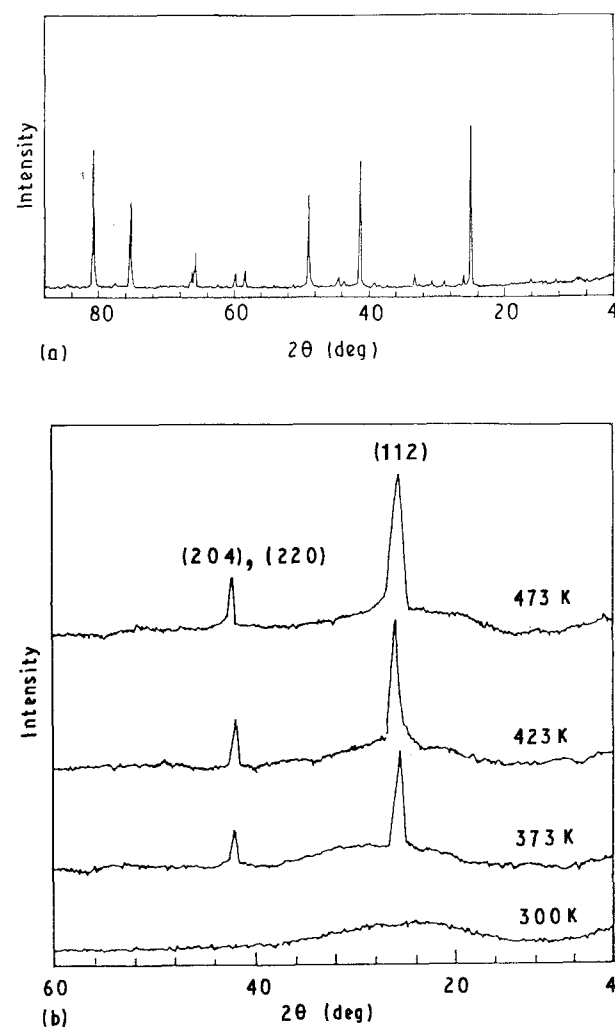
Figure 1 X-ray diffraction pattern of $CuInTe_2$: (a) powdered sample, (b) annealed in vacuum at different temperatures.

one phase [20, 21] in the prepared bulk materials was observed in the X-ray diffraction patterns obtained.

Typical diffraction patterns of powder and the as-deposited films annealed in vacuum at different temperatures are shown in Fig. 1a and b. The peak heights and positions are in good agreement with the data reported for the bulk material [22]. The calculated lattice constants of $CuInTe_2$ powder were found to be $a = 0.6195$ nm and $c = 1.239$ nm with the ratio $c/a = 2$. It was also observed from this figure that the as-deposited and the low-temperature (323 K) heat-treated films deposited on glass substrates were amorphous in nature, whilst those heat-treated at moderate temperature (373–473 K) were polycrystalline. The peak intensity, and the half amplitude-peak width, increased appreciably with increasing annealing temperature which gave information about the degree of preferred orientation and the degree of crystallinity, for the crystalline planes (1 1 2), (2 0 4) and (2 2 0).

Electron diffraction studies of $CuInTe_2$ films (thickness 80 nm) annealed in vacuum at different temperatures were performed to check their crystalline nature. Fig. 2 represents the selected area of electron diffraction patterns of the as-deposited film (Fig. 2a) as well as the annealed samples at 373 and 473 K for an annealing time of 1 h (Fig. 2b and c). It was found that the diffraction patterns of the as-deposited films (Fig. 2a) consisted of holes which may be due to the presence of a number of phases or to the amorphous nature of the thin film [23]. Improvements in the crystallinity of the films were observed after annealing (Fig. 2b and c). The sharp rings obtained indicated the polycrystalline nature of the films.

The transmission electron microscope results of the same annealed films were introduced to the Bild analysis system and the computerized particle size data obtained are shown in Fig. 3a–d. These results were taken as selected ones representing the sample, and which confirm the variation of the particle size in relation to the annealing temperature. From the obtained Bild analysis results it can be concluded that the particle size of the material was increased by increasing the annealing temperature. These results are in harmony with those obtained throughout the analysis of X-ray diffraction patterns carried out for samples of higher thickness.

3.2. Optical properties
The most accurate method for determining the energy band structure of semiconductors is one based on investigating the spectral distribution of both the refractive index, n, the absorption index, k, and hence the absorption coefficient, α.

To investigate the effect of the annealing temperature on the energy gap of $CuInTe_2$, the transmission, T, and the reflection, R, at normal incidence in the spectral range 500–2000 nm were measured for a thin film of thickness 264 nm, subjected to different annealing temperatures.

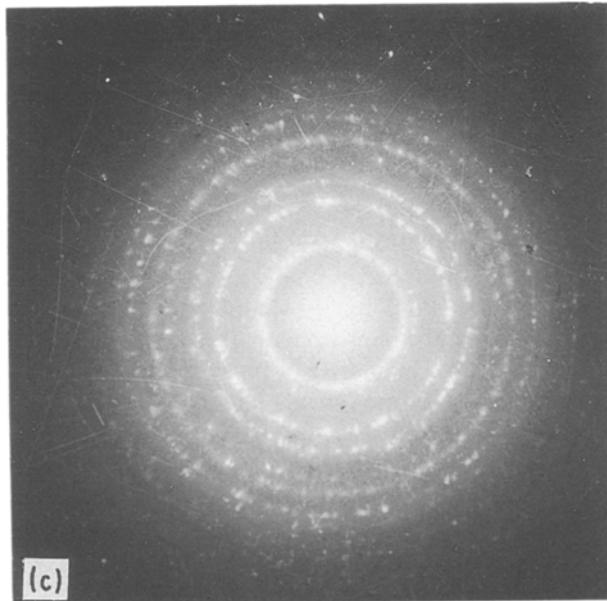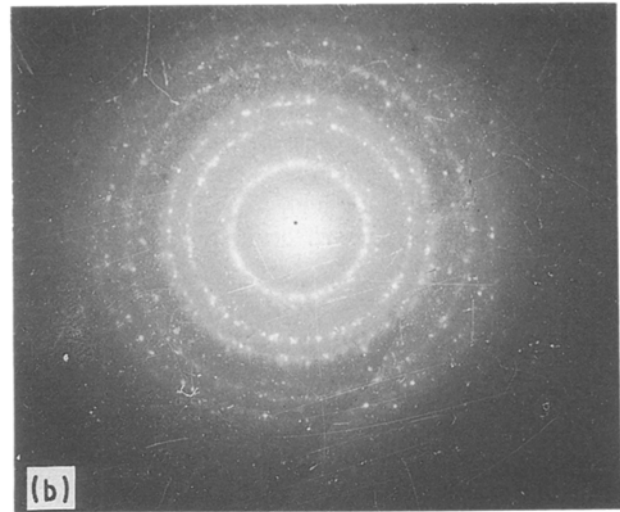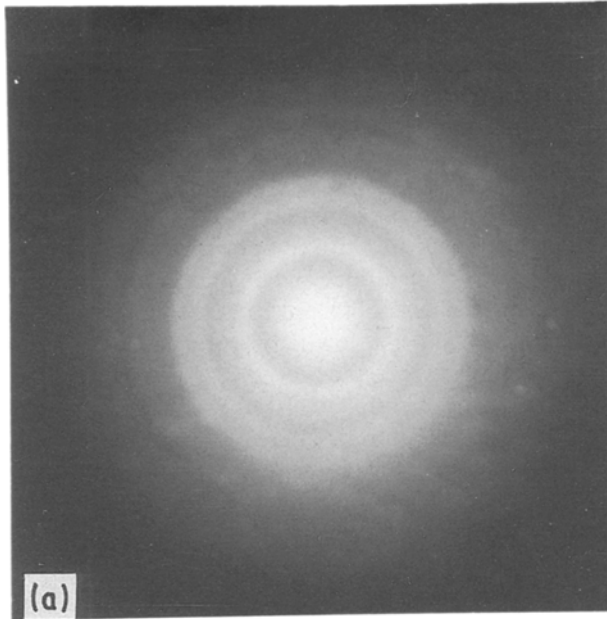The optical absorption coefficients, α, for the as-deposited and heat-treated film were calculated using

Figure 2 Electron diffraction patterns of the as-deposited $CuInTe_2$ and that annealed in vacuum at 373 and 423 K, respectively.

the following equation

$$T = (1 - R^2)\exp(-\alpha t)/(1 - R^2)\exp(-2\alpha t) \quad (1)$$

The optical absorption coefficient for these films can be described by the relation $(\alpha h v)$ $(h v - E_g)^{1/2}$, indicating a direct energy gap [24]. The plot of $(\alpha h v)^2$ against photon energy for the tested thin films is shown in Fig. 4. The relations are found to be identical in character and indicate tailing of the absorption coefficient towards low photon energies. The exponential form of the tail may be due to the amorphous state of the material or to the broadening of the impurity band which extend into the forbidden gap [24].

The observed values of the optical energy gap, E_g, are found to increase from 0.97 eV to 1.0 eV with increasing temperature of heat treatment from 300–473 K. This change in E_g value may be attributed to slight changes in the lattice constants [25].
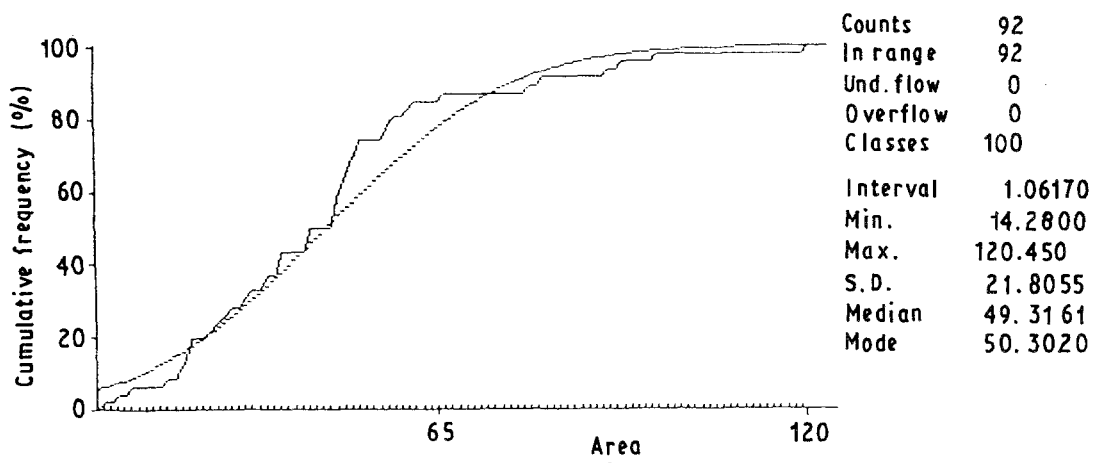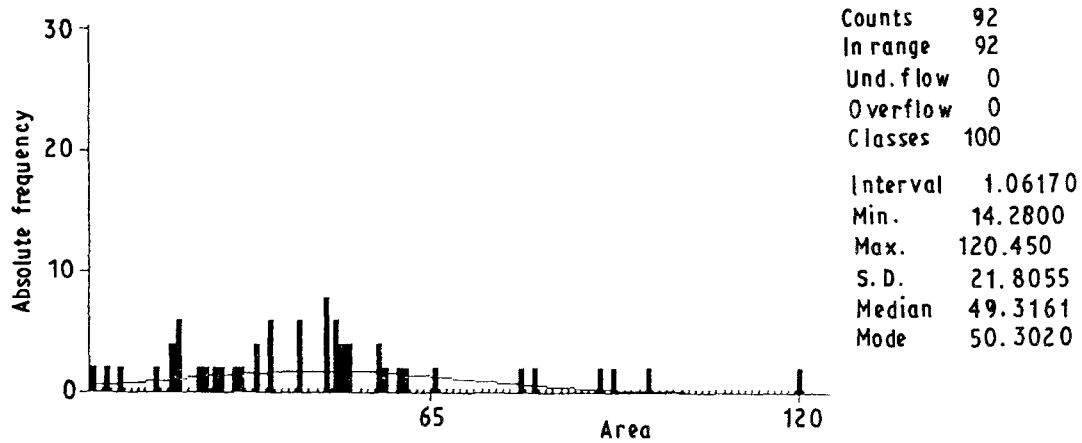
Samples of amorphous $CuInTe_2$ thin films of thickness 264 nm were heat-treated in vacuum at 373, 423, 473 K for different periods of time. Fig. 5 shows the variation of the absorption coefficient $(\alpha h v)^2$ as a function of photon energy $(h v)$ for the tested films. The deduced energy gap values for such heat-treated films at different temperatures and different periods of time are illustrated in Fig. 6.

The refractive index, n, and the absorption index, k, for these thin films were calculated from transmission and reflection measurements of photon energy in the range from 0.619–1.032 eV and are shown in Fig. 7a and b. It is clear from the figures that n and k at a given wavelength decrease with increasing annealing temperature.
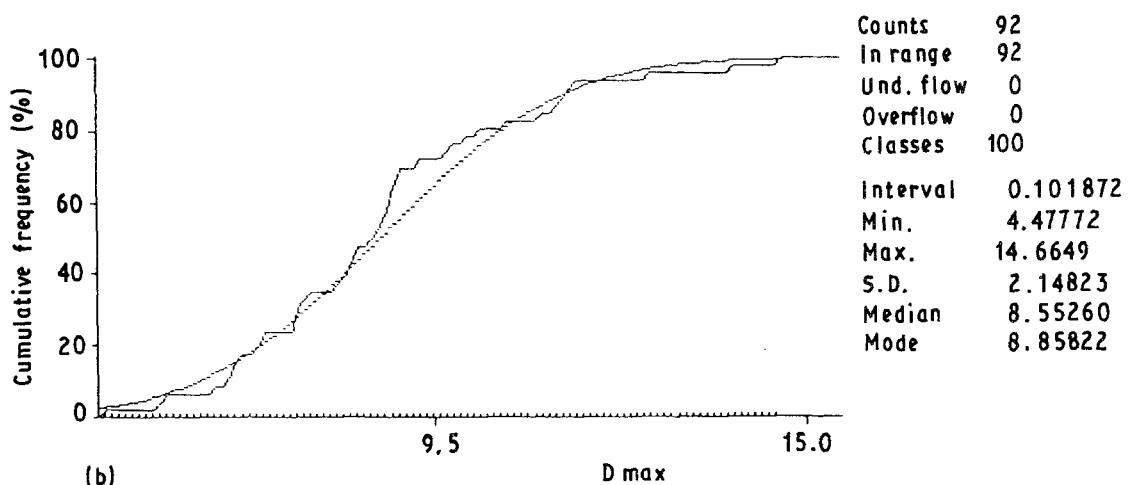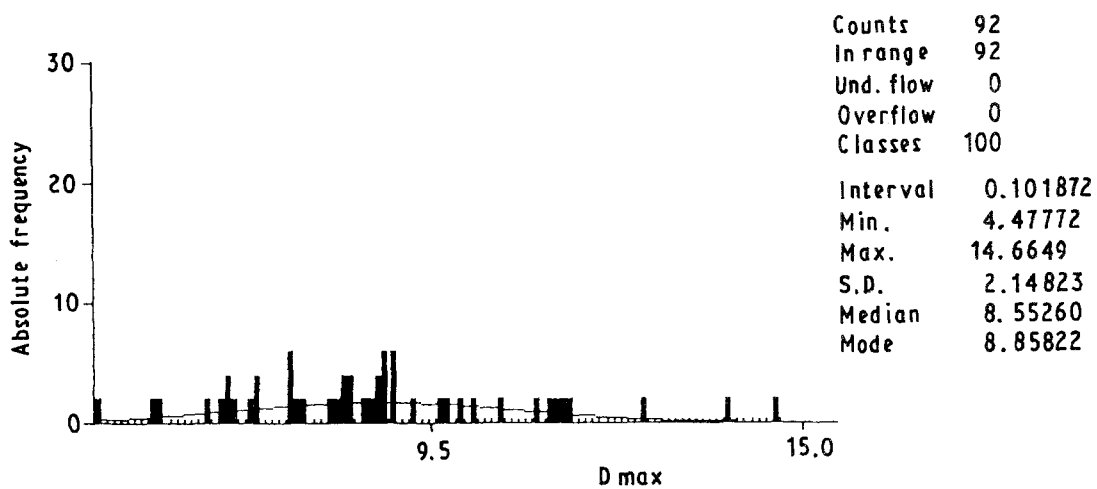
The variation of the refractive index with annealing temperature is related to the change in the lattice parameters [26]. So it can be suggested that the lattice parameter may decrease as a result of increasing the temperature of annealing, which may be the reason for the observed increase in the values obtained for the energy gap, E_g, by increasing the annealing temperature. This, in turn, would require more detailed study for the change of the lattice parameters with annealing temperature to be determined.

4. Conclusion

The as-deposited thin films of $CuInTe_2$ are amorphous in character, whilst those heat-treated at moderate temperatures are polycrystalline. The grain size of the particles increases as a result of increasing the annealing temperature. It can also be concluded that $CuInTe_2$ is a direct gap semiconductor, whose E_g value increases with increasing annealing temperature as well as the annealing time.
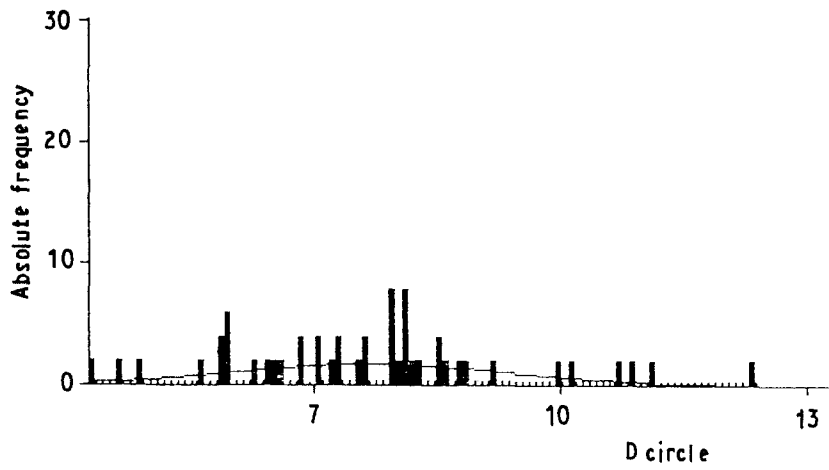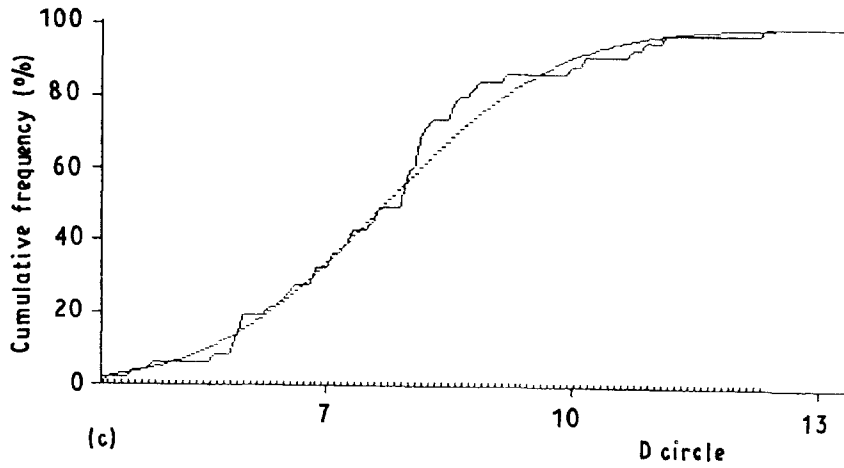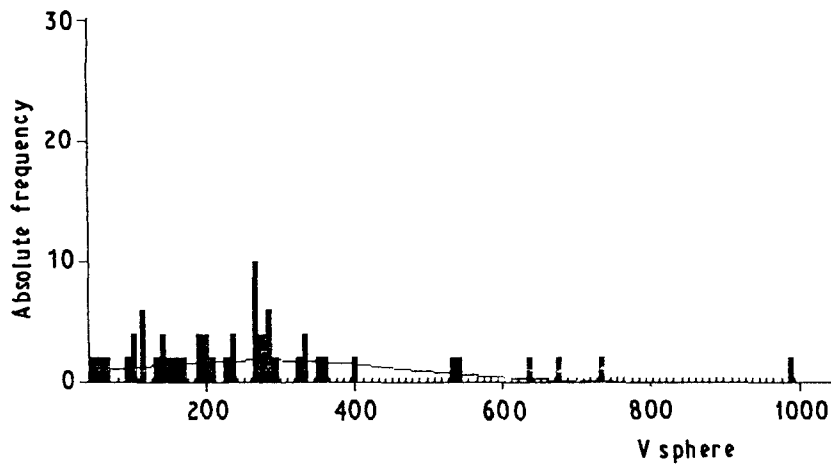
Counts 92
In range 92
Und. flow 0
Overflow 0
Classes 100

Interval 1.06170
Min. 14.2800
Max. 120.450
S. D. 21.8055
Median 49.3161
Mode 50.3020

Counts 92
In range 92
Und. flow 0
Overflow 0
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Interval 1.06170
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Max. 120.450
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Median 49.3161
Mode 50.3020

(a)

Counts 92
In range 92
Und. flow 0
Overflow 0
Classes 100

Interval 0.101872
Min. 4.47772
Max. 14.6649
S.D. 2.14823
Median 8.55260
Mode 8.85822

Counts 92
In range 92
Und. flow 0
Overflow 0
Classes 100

Interval 0.101872
Min. 4.47772
Max. 14.6649
S.D. 2.14823
Median 8.55260
Mode 8.85822

(b)

Figure 3 Selected transmission electron microscope Bild analysis results of the particle size.

Top chart (Absolute frequency vs D circle):

Counts	92
In range	92
Und. flow	0
Overflow	0
Classes	100
Interval	0.811991 E−01
Min.	4.26402
Max.	12.3839
Mean	7.68623
S.D.	1.69834
Median	7.91798
Mode	8.12098

(c) Cumulative frequency (%) vs D circle:

Counts	92
In range	92
Und. flow	0
Overflow	0
Classes	100
Interval	0.811991 E−01
Min.	4.26402
Max.	12.3839
Mean	7.68623
S.D.	1.69834
Median	7.91798
Mode	8.12098

Absolute frequency vs V sphere:

Counts	92
In range	92
Und. flow	0
Overflow	0
Classes	100
Interval	9.53856
Min.	40.5934
Max.	994.429
Mean	273.383
S.D.	190.131
Median	259.976
Mode	267.470

(d) Cumulative frequency (%) vs V sphere:

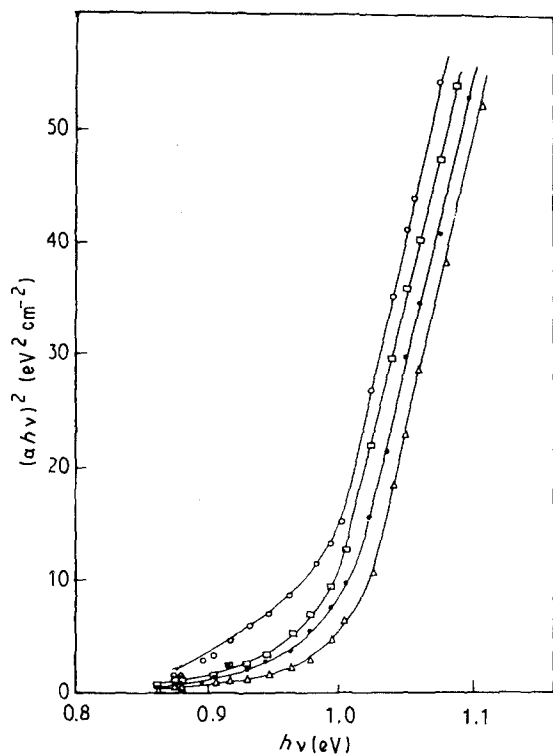|	
Counts	92
In range	92
Und. flow	0
Overflow	0
Classes	100
Interval	9.53856
Min.	40.5934
Max.	994.429
Mean	273.383
S.D.	190.131
Median	259.976
Mode	267 470

Figure 3 continued

Figure 4 $(\alpha h\nu)^2$ as a function of $h\nu$ for the as-deposited CuInTe$_2$ thin films and that annealed in vacuum at (○) room temperature, (□) 373 K, (●) 423 K and (△) 473 K.
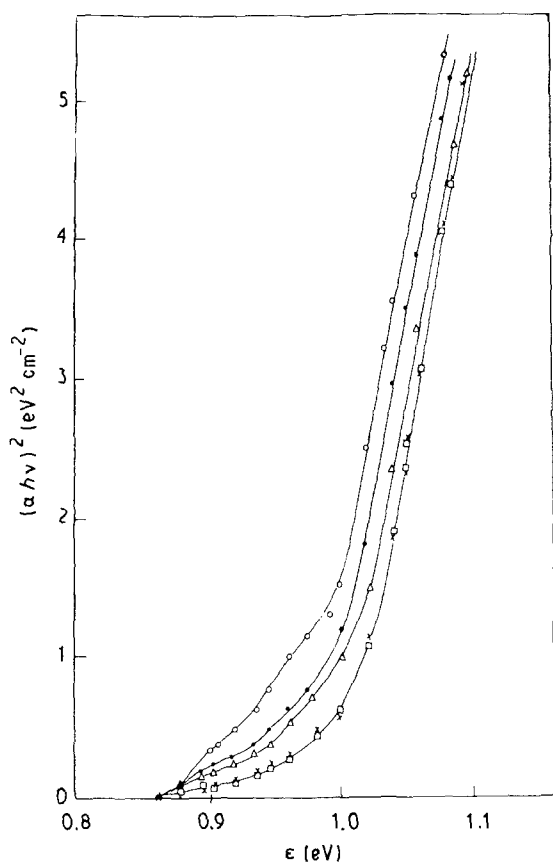

Figure 5 $(\alpha h\nu)^2$ as a function of $h\nu$ for CuInTe$_2$ films heat-treated at 473 K for (○) 0 min, (●) 30 min, (△) 45 min, (×) 60 min, (□) 90 min.

Figure 6 Variation of E_g of CuInTe$_2$ thin films 264 nm thick heat-treated at (△) 373 K, (○) 423 K, and (×) 473 K, as a function of the time of heat-treatment.

Figure 7 Dispersion curves of (a) n and (b) k for CuInTe$_2$ thin films heat-treated at (a) (△) room temperature, (○) 373 K, (●) 423 K and (□) 473 K, (b) (○) room temperature, (□) 373 K, (△) 423 K and (×) 473 K.

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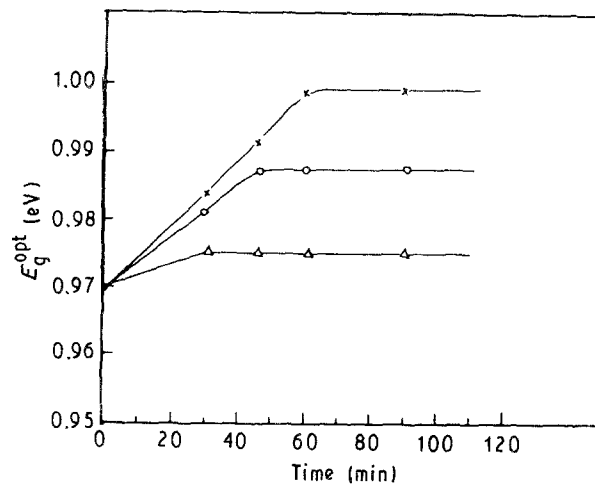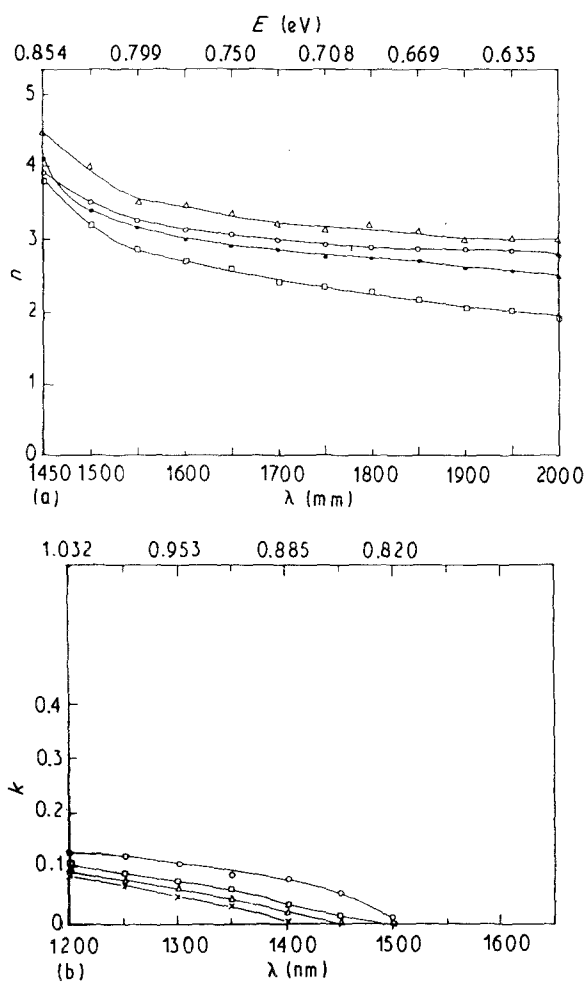
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