

PHOTOELECTRICAL PROPERTIES OF $\text{CuInSe}_2\text{-Cd}_{1-x}\text{Zn}_x\text{S}$ SOLAR CELLS

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Photoelectrical properties of $\text{CuInSe}_2\text{-Cd}_{1-x}\text{Zn}_x\text{S}$ thin film solar cells obtained by quasi-closed volume evaporation method were investigated. It was shown that using a $\text{Cd}_{1-x}\text{Zn}_x\text{S-CdS}$ bilayer substrates one can increase an efficiency of these cells to ~ 8%.

1. Introduction

$\text{CuInSe}_2\text{-CdS}$ structure is one of the most prospective structures on the base of which effective, economically cheap solar cells can be fabricated. This heterostructure possesses an efficiency of about 12 % and there is possibility to increase its parameters to obtain higher efficiencies [1-4].

It should be mentioned that at present time, these elements have an open circuit voltage not exceeding 0.5 volts, the reason is that the magnitude of the energy barrier at the junction is not relatively high [3-4]. One of methods to increase the value of the open circuit voltage is to use a base layer having a band gap greater than that of the CdS. Such a material is $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ solid solution which not only presents the structure and physical properties of CdS, but also possesses large gap depending on the Zn percentage in the solid solution.

In this work we present the preparation method and also photoelectrical properties of $\text{CuInSe}_2\text{-Cd}_{1-x}\text{Zn}_x\text{S}$ heterostructure along with the possibility of solar cell production on its basis.

2. Experimental methods

$\text{CuInSe}_2\text{-Cd}_{1-x}\text{Zn}_x\text{S}$ heterojunctions were fabricated by flash evaporation of CuInSe_2 polycrystalline powder onto $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ films. The $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ thin films were prepared by vacuum evaporation of CdS and ZnS powders mixture in required proportions using a quasi-closed volume system. As a substrate, a chemically cleaned glass with a conducting layer of SnO_2 was used. The CuInSe_2 homogenous films of stoichiometric composition were prepared at substrate temperature of $T_{\text{sub}}=500^\circ\text{C}$. X-ray analysis shows that, CuInSe_2 samples prepared under these conditions possess a single phase structure. After preparation, the heterostructures were annealed in vacuum for 10 minutes at 300°C .

Ohmic contact to the CuInSe_2 films was made by In-Ga eutectics. Active areas of samples were about 10 mm^2 .

The conductivity and transmission spectra of the samples were measured by standard method using SPM-2 monochromator and computerized complex KSVU-2 at room temperature.

The photoluminescence excited by a N_2 laser ($\lambda=337\text{ nm}$) was measured by DES-spectrometer and registered by a synchronized system at 77 K. The X-ray diffraction patterns of samples were taken using the K_α line of a Cu X-ray source.

3. Experimental results and discussion

a) Structure, electrical, photoelectrical, optical and luminescent properties of $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ thin films prepared by vacuum evaporation method using a quasi-closed volume system.

It has been found out that perfect $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ thin films can be successfully prepared using a quasi-closed volume system. The physical properties of thin films prepared by this method strongly depend on the deposition condition. Substrate temperature plays an important role during deposition process which can influence on the structural, electrical, photoelectrical, optical and luminescent properties of thin films. Therefore, finding an optimal regime for preparing perfect films is very important.

From the first let us consider the properties of CdS thin films prepared at different-substrate temperatures.

In Fig. 1 it is given the X-ray diffraction patterns of CdS films prepared at different substrate temperatures. As it is seen from the figure the increase of the substrate temperature does not change the reflection from (002) planes but changes the intensity of reflection which is due to the change of the orientation of the grains along [002] direction.

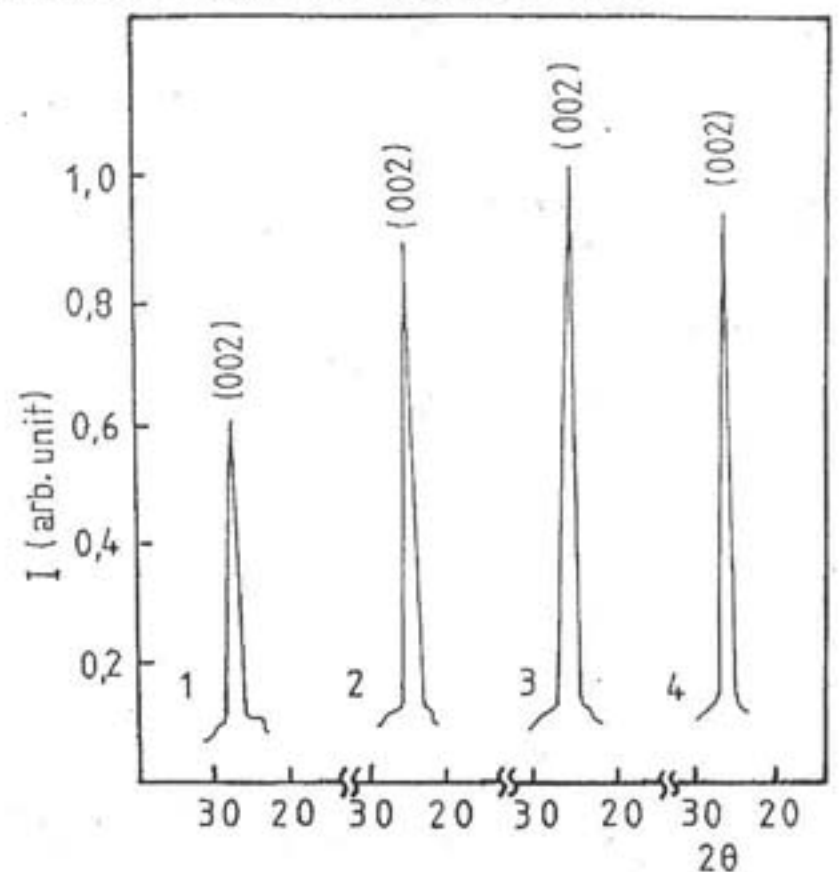


Fig. 1. X-ray diffractograms taken from CdS thin films prepared by vacuum evaporation using quasi-closed volume method at different substrate temperatures: 1 - 180°C ; 2 - 200°C ; 3 - 220°C ; 4 - 240°C .

Fig. 2 shows dependence of the resistivity on the substrate temperature. As it is clear from the figure the resistivity of CdS thin films increases linearly from 10^2 up to 10^6 Ω/cm by increasing substrate temperature from 150 to 250 $^{\circ}\text{C}$.

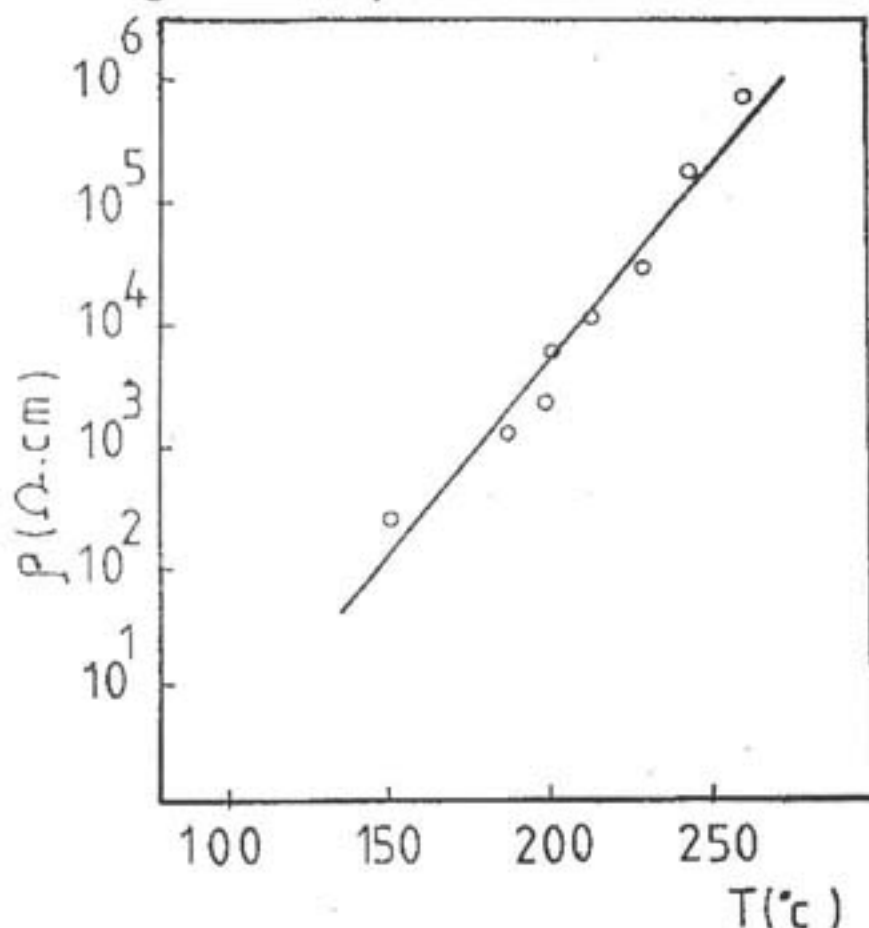


Fig. 2. Variation of the resistivity of CdS thin films prepared by the same method versus the substrate temperature ($T=300^{\circ}\text{C}$).

The change of the substrate temperature essentially changes the photoluminescence, photoconductivity and optical transmission spectra of CdS thin films. In Fig. 3 it is given the photoluminescence spectra of CdS thin films obtained at substrate temperatures in the range 180-240 $^{\circ}\text{C}$. It is clear that increase the substrate temperature increases the intensity of exciton luminescence (at $\lambda=490$ nm) and simultaneously a green band is also appeared at $\lambda=530$ nm. When the substrate temperature is equal to 220 $^{\circ}\text{C}$ the value of the exciton luminescence becomes maximum. The increase of the substrate temperature above 220 $^{\circ}\text{C}$ the exciton luminescence band essentially decreases.

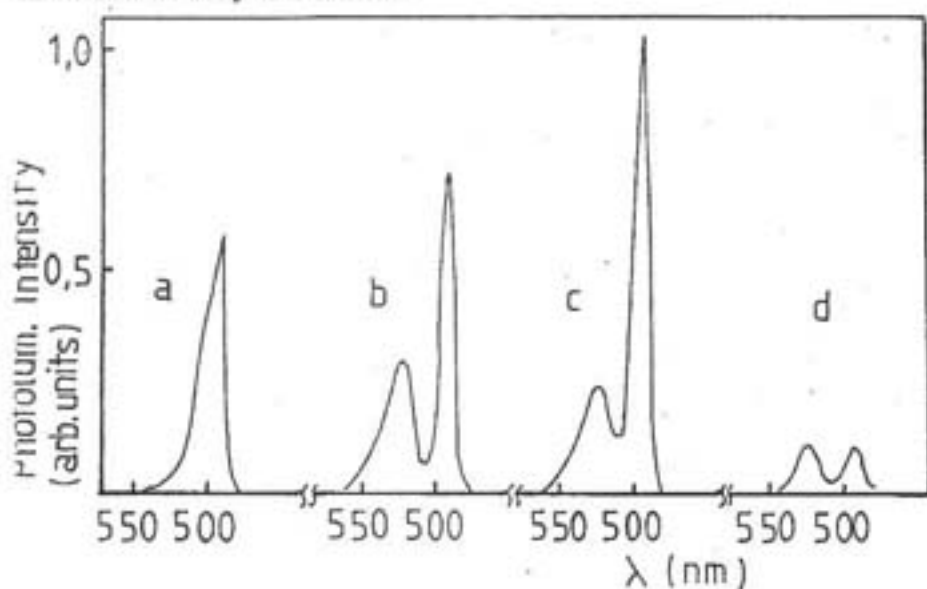


Fig. 3. Photoluminescence spectra of CdS films prepared by the same method at different substrate temperatures: a) 180 $^{\circ}\text{C}$, b) 200 $^{\circ}\text{C}$, c) 220 $^{\circ}\text{C}$, d) 240 $^{\circ}\text{C}$ (measurements are taken at $T=300$ K).

The photoconductivity of CdS films appears only in a small substrate temperature interval. In Fig. 4 the photocon-

ductivity spectra of CdS films prepared at substrate temperatures in the range 200-230 $^{\circ}\text{C}$ are given.

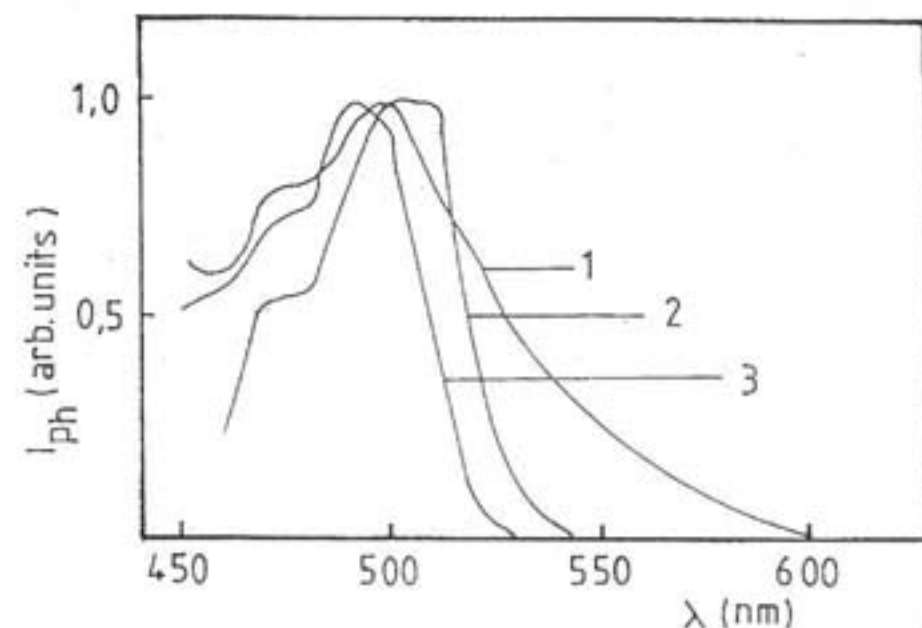


Fig. 4. Photoconductivity spectra of CdS thin films prepared by the same method at different substrate temperatures: 1) $T=200^{\circ}\text{C}$, 2) $T=220^{\circ}\text{C}$, 3) $T=240^{\circ}\text{C}$ (measurements are taken at $T=300$ K).

Fig. 5 depicts the optical transmission spectra of CdS films prepared at different substrate temperatures. As it is seen from the figure at the increase the substrate temperatures from 180 to 220 $^{\circ}\text{C}$ the transmission coefficient increases. The maximum transmission coefficient appears at substrate temperature above 230 $^{\circ}\text{C}$. At the increase the substrate temperature above 230 $^{\circ}\text{C}$ the transmission coefficient decreases.

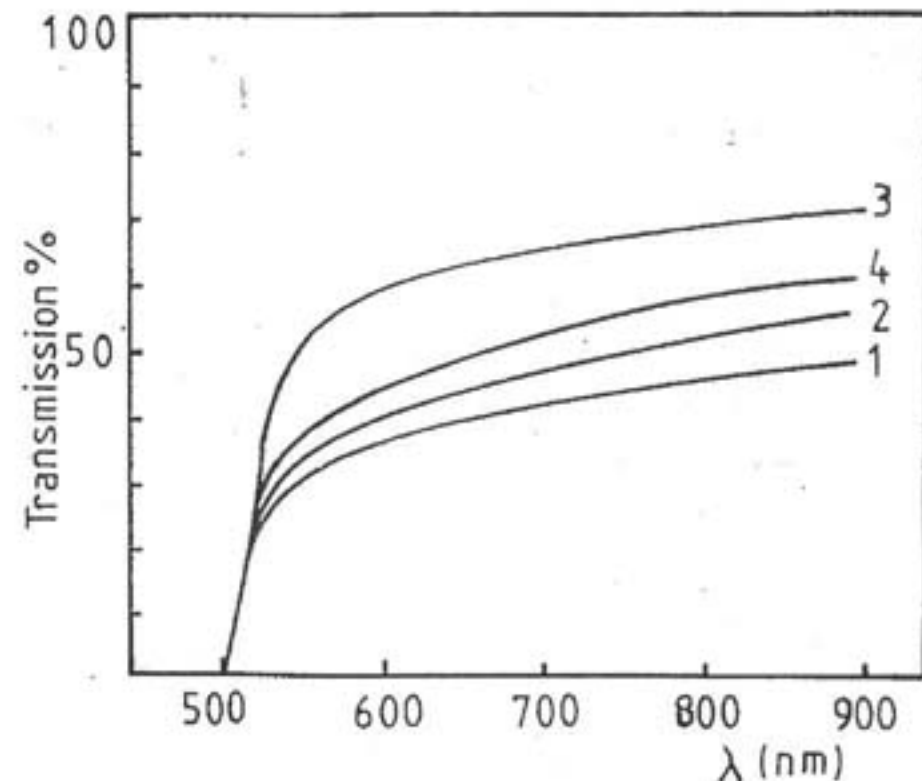


Fig. 5. Transmission spectra of CdS thin films prepared by the same method at different substrate temperatures: 1) $T=180^{\circ}\text{C}$, 2) $T=200^{\circ}\text{C}$, 3) $T=220^{\circ}\text{C}$, 4) $T=240^{\circ}\text{C}$ (measurements are taken at $T=300$ K).

Considering the above mentioned results it is concluded that the changes occurred in the physico-chemical properties of CdS films are due to the creation of defects at CdS films when the substrate temperature increases. Appearance of the green band at luminescence spectra of CdS films prepared at 200 $^{\circ}\text{C}$ is due to the creation of Cd vacancies [5]. Extinction of the green band at the luminescence spectra of CdS films

prepared at substrate temperatures in the range 200-240°C can be attributed to decrease of Cd vacancies in the films. The increase of the orientation of the grains at [002] direction shows that, when the substrate temperature is 220°C high quality CdS films from structural view point are created.

Appearance of photoconductivity at CdS films is due to the existence of photosensitive centers (i.e. Cd vacancies) which are responsible for the green luminescence. The reason for this conclusion is that the photoconductivity merely appears at those CdS films which also show green luminescence band. The intensity of photoconductivity is proportional to the intensity of the green band. When the intensity of the green band decreases at CdS films, the intensity of the photoconductivity also decreases. The increase of the transmission coefficient in CdS films by increase the substrate temperature from 180 to 220°C is due not only to decrease of the supplementary absorption centers but also to the increase of grain orientation. The decrease of the transmission coefficient in CdS films prepared at temperatures 240°C and above is probably due to the existence of a large number of defects created at high temperatures. This is also confirmed by the decrease of the orientation of the grains at [002] direction when the CdS films are prepared at substrate temperature of 240°C.

As mentioned before, when the substrate temperature increases from 150 to 200°C, the resistivity increases. This can be due to the increase of CdS vacancy concentration which act as acceptor centers.

Summarizing the results presented above we make the conclusion that the optimal temperature for preparation of ideal CdS films using the quasi-closed volume method is in the range 200-220°C, leading to sufficiently high photoconductivity, increased grain orientation and maximal transmission coefficient.

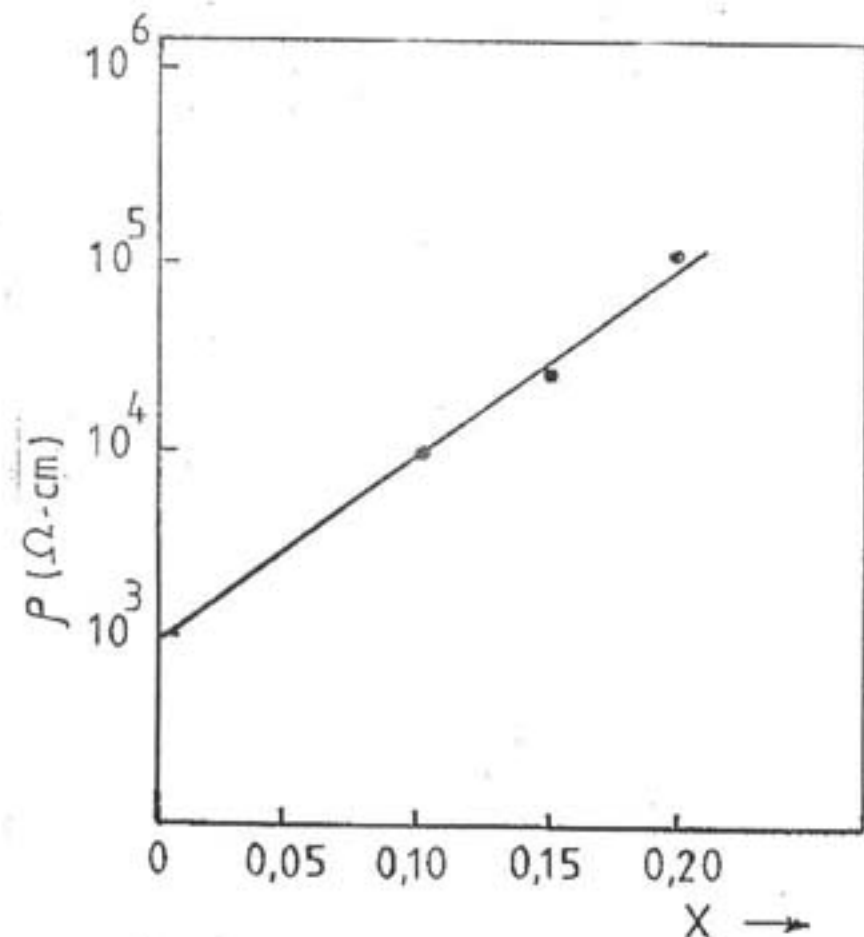


Fig. 6. Resistivity versus x values for $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ thin films prepared by the same method.

Now we consider electrical and optical properties of $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ thin films prepared at substrate temperatures in the range 200-220°C.

As it was expected, the electrical and optical properties of $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ thin films essentially depend on the percentage of ZnS in the $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ composition. In fig.6 the variation of the resistivity of $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ films with different values of x is given. As it is seen from this figure, by varying the value of x from 0 to 0.20, the resistivity increases from 10³ to 10⁵ Ω/cm.

Varying the value of x leads also to the variation of the transmission spectra (see Fig.7). As it is seen from this figure, the increase the value of x causes the transmission coefficient to rise and also to shift it towards short wavelengths. The obtained results may be explained by considering the fact that the increase of the percentage of ZnS in the solid solution results in an increase of the $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ band gap.

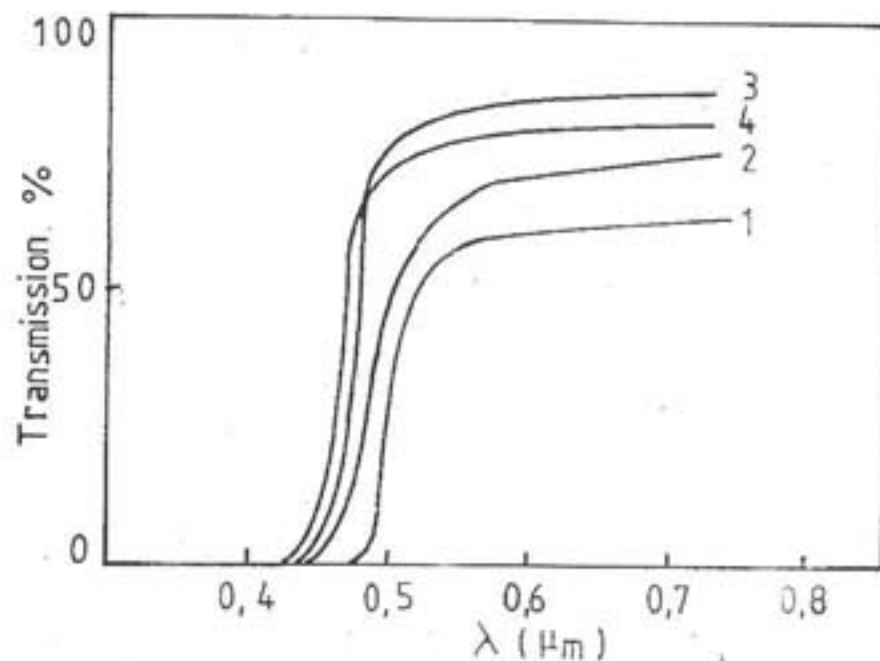


Fig. 7. Transmission spectra of $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ thin films prepared by the same method for different x values: 1) x=0, 2) x=0.10, 3) x=0.15, 4) x=0.2 (T=300 K).

b) photoelectrical properties of $\text{CuInSe}_2 - \text{Cd}_{1-x}\text{Zn}_x\text{S}$ heterostructure.

To prepare $\text{CuInSe}_2\text{-Cd}_{1-x}\text{Zn}_x\text{S}$ heterostructures, the value of x was varied between 0-0.20. Fig.8 shows the light I-V characteristics of a $\text{CuInSe}_2 - \text{Cd}_{1-x}\text{Zn}_x\text{S}$ heterostructure illuminated by a light source having a power of $W=100 \text{ mW/cm}^2$. As it is clear from this figure, the concentration of the Zn increases from 10 to 20%, the current density increases from 9 to 2.3 mA/cm² and open circuit voltage increases from 0.5 to 0.65 V, but the fill factor remains relatively unchanged (FF=0.4).

The increase of the value of x from 0 to 0.20 leads to an increase of current density, leading in turn to a decrease of the efficiency of the heterostructure from 4 to 0.6%.

The increase of the width of energy gap in the $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ layer by the increase of the value of x leads to an increase of the energy barrier of $\text{CuInSe}_2 - \text{Cd}_{1-x}\text{Zn}_x\text{S}$ heterostructure, leading ultimately to the increase of open circuit voltage up to 0.65 at x=0.2. But the increase of the value of $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ series resistance by the increase of the value of x leads to the decrease of short circuit current, leading in turn to a decrease of device efficiency.

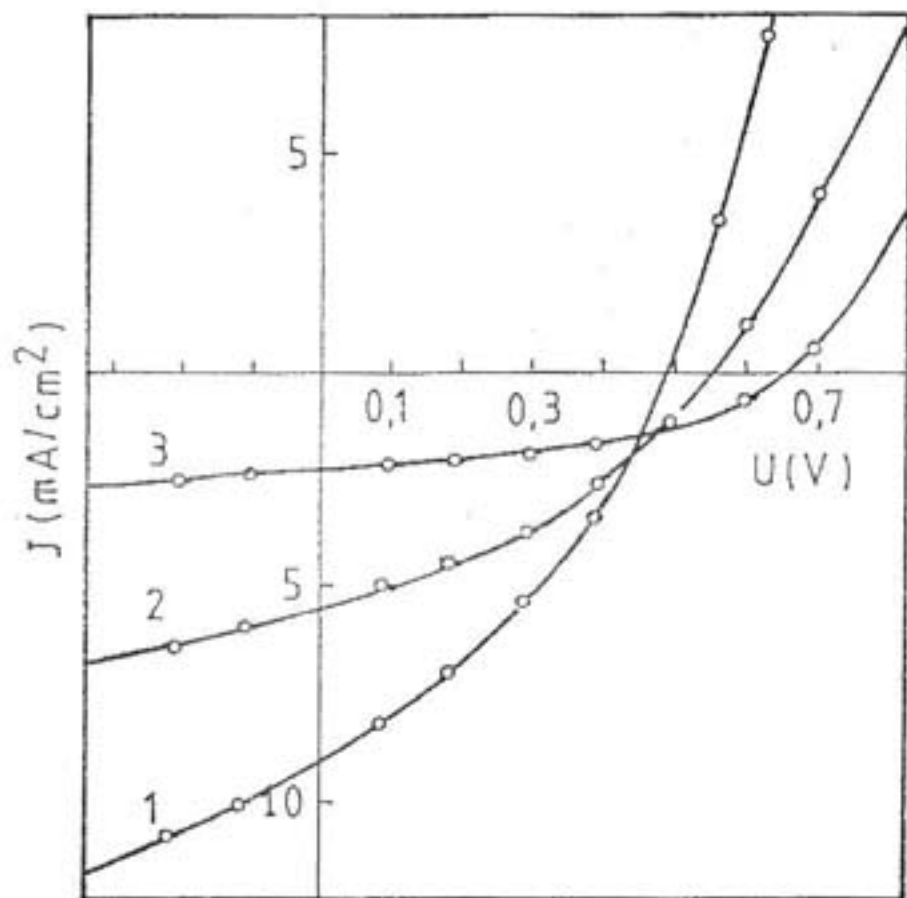


Fig. 8. Light I-V characteristics of $\text{CuInSe}_2\text{-Cd}_{1-x}\text{Zn}_x\text{S}$ heterostructure for different x values: 1) $x=0.10$, 2) $x=0.15$, 3) $x=0.20$, $W=100 \text{ mW/cm}^2$ ($T=300 \text{ K}$).

To decrease series resistance of the base layer, multilayer $\text{CuInSe}_2\text{-Cd}_{1-x}\text{Zn}_x\text{S}$ heterostructures were prepared. To obtain these multilayer systems, first a CdS layer with a thickness of about $8 \mu\text{m}$ and having a resistivity of $10^2 \Omega/\text{cm}$ was deposited on a glass substrate coated with SnO_2 by quasi-closed volume method at 150°C .

Then a $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ ($x=0.20$) layer of about $2 \mu\text{m}$ thick and resistivity of $10^5 \Omega/\text{cm}$ was coated on the CdS layer at 220°C using the same method. p-CuInSe₂ layer deposited by flash evaporation of CuInSe₂ polycrystalline powder on to the previously prepared $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ -CdS layer. The obtained structure was annealed in vacuum at 300°C for 10 minutes.

Fig. 9 depicts light I-V characteristics of the sample before (curve 1) and after (curve 2) annealing. As it is seen from the figure before annealing: $J_{sc}=8 \text{ mA/cm}^2$; $\text{FF}=0.62$ and the open circuit voltage negligibly decreases $U_{op}=0.60 \text{ V}$. Illuminating the sample with an illuminating power of 100 mW/cm^2 yields an efficiency of about 7.8%. Therefore using a $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ -CdS bilayer it is possible to decrease essentially series resistance of the heterojunction which in turn improves the output parameters of the structure.

Fig. 10 shows the photoresponse spectra of heterostructure before (curve 1) and after (curve 2) annealing in vacuum at 300°C for 10 minutes. As it is seen from this figure photoresponse maximum shifts towards long wavelengths of the spectrum after annealing. This can be explained if we

assume that annealing process causes the acceptor concentration to decrease in p-CuInSe₂ layer which results in the

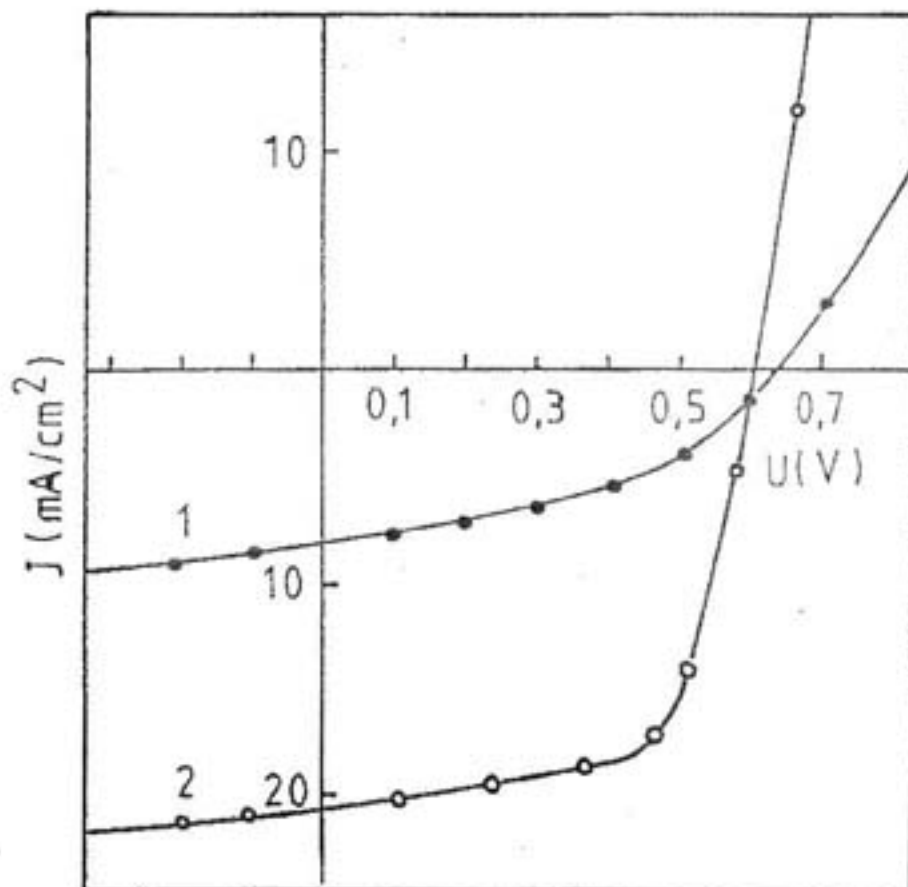


Fig. 9. Light I-V characteristics of $\text{CuInSe}_2\text{-Cd}_{1-x}\text{Zn}_x\text{S}$ heterostructure before (curve 1) and after (curve 2) annealing process.

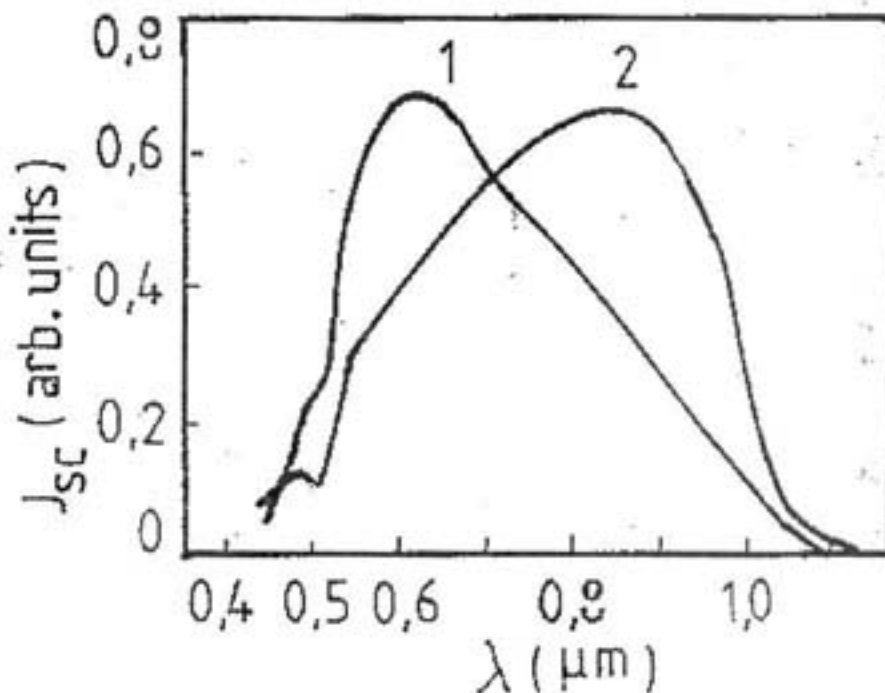


Fig. 10. Photoresponse spectra of $\text{CuInSe}_2\text{-Cd}_{1-x}\text{Zn}_x\text{S}$ heterostructure ($x=0.20$) before (curve 1) and after (curve 2) annealing in vacuum at 300 K for 10 min.

increase of the width of space charge region. Therefore separation of the photocarriers generated in CuInSe₂ occurs rapidly leading to the increase of photoconductivity of heterojunction at longer wavelengths of the spectrum.

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$\text{CuInSe}_2\text{-Cd}_{1-x}\text{Zn}_x\text{S}$ –GÜNƏŞ ELEMENTLƏRİNİN FOTOELEKTRİK XASSƏLƏRİ

Kvazi-qapalı həcmdə buxarlanma yolu ilə alınmış $\text{CuInSe}_2\text{-Cd}_{1-x}\text{Zn}_x\text{S}$ günəş elementlərinin fotoelektrik xassələri öyrənilmişdir. Göstərilmişdir ki, ikiqat $\text{Cd}_{1-x}\text{Zn}_x\text{S-CdS}$ altlıqların istifadə olunması bu elementlərin faydalı iş əmsalını ~ 8 % qədər artırır.

А.И. Байрамов

ФОТОЭЛЕКТРИЧЕСКИЕ СВОЙСТВА $\text{CuInSe}_2\text{-Cd}_{1-x}\text{Zn}_x\text{S}$ СОЛНЕЧНЫХ ЭЛЕМЕНТОВ

Исследованы фотоэлектрические свойства $\text{CuInSe}_2\text{-Cd}_{1-x}\text{Zn}_x\text{S}$ солнечных элементов, полученных методом испарения в квазизамкнутом объеме. Показано, что использование двухслойных $\text{Cd}_{1-x}\text{Zn}_x\text{S-CdS}$ подложек увеличивает КПД этих элементов до ~ 8%.

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