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II–VI thin-film polycrystalline multilayer converters for solar photovoltaics

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Abstract

Some new structures of thin-film solar converters (SC) based on heterojunctions (HJ) with intermediate semiconductor layers are suggested. Thin protective layers and a quasi-electric field incorporated into the space charge region (SCR) prevent cross-diffusion of HJ components and increase efficiency of charge carrier separation. They also decrease the diode dark current and provide high stability of the converter parameters. Thin ($\sim 0.1 \mu\text{m}$) $(\text{CdSe})_x(\text{ZnTe})_{1-x}$ or $\text{Zn}_x\text{Cd}_{1-x}\text{Se}$ layers were used as graded band-gap layers. They were placed between a photosensitive II–VI-compound (CdTe , CdSe , $\text{CdSe}_x\text{Te}_{1-x}$) base layer and the transparent $\text{Cu}_{1.8}\text{S}$ layer. The above structures were prepared by vacuum closed space sublimation. The properties of these compounds were studied by electron microscopy and X-ray photoelectron spectroscopy (XPS) with ion etching. The photoelectron properties of structures such as $\text{Cu}_{1.8}\text{S}/(\text{CdSe})_x(\text{ZnTe})_{1-x}/\text{CdSe}$ are presented in detail. The manufacturing technology for the integrated solar batteries based on CdTe , CdSe , and $\text{CdSe}_x\text{Te}_{1-x}$ compounds was developed. The solar cell parameters under low illumination intensities are comparable to those of solar batteries based on c-Si and a-Si. The competitiveness of the polycrystalline thin-film SC is due to ease and low cost of fabrication (as compared with c-Si and a-Si) and also to the extended photosensitivity range (as compared to a-Si).

1. Introduction

Strong absorption of light in thin-film polycrystalline materials, enhanced by multiple reflection and refraction at relief surfaces of films and at crystallite faces, provides the main mechanism of photocarrier loss, namely, the loss at the illumi-

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nated solar converters (SC) surface. Therefore, an optimum SC structure is characterized by the electric field localized just near the illuminated surface of the photosensitive component. Metal or a wide-band-gap semiconductor is used as a transparent component (optical “window”) of the SC.

Still another method may be employed in the structures under investigation. It includes using strongly degenerate (not necessarily wide-band-gap) semiconductors as a transparent component. Its transparency is achieved by an extreme reduction of layer thickness just as in the case of metals. Among these materials are copper chalcogenides ($\text{Cu}_{1.8}\text{S}$, $\text{Cu}_{1.75}\text{Se}$) that are strongly degenerate p-type semiconductors [1–3] having work function 5.3 to 5.5 eV. Their strong degeneracy is obtained without special doping.

Under illumination through the transparent SC component ($\text{Cu}_{1.8}\text{S}$), the photocurrent can be represented as

$$I_{\text{ph}} = e\phi\{Q_s[1 - e^{-kW/(1+kL_p)}] - \Delta Q\} = e\phi Q, \quad (1)$$

where k , L_p , and W are the light absorption coefficient, the diffusion length of minority carriers, and the SCR width, respectively. Q_s is the recombination losses at the interface, ΔQ_s is the losses due to the majority carriers transition, Q is the carrier collection coefficient, and ϕ is the light intensity in $\text{quant}/\text{cm}^2\text{s}$.

The carrier collection coefficient depends on photocarrier generation and recombination processes within the photosensitive base layer and also on the conditions of the carriers transition through the HJ interface.

It has been shown that the SCs of p- $\text{Cu}_{1.8}\text{S}/\text{n-A}_2\text{B}_6$ type with sufficiently wide SCR ($W \geq 1 \mu\text{m}$) are characterized by a sharp long-wavelength edge and by a high collection coefficient ($Q \approx 0.9$). This fact indicates that photocarrier losses are small in the long-wave spectral region, while in the short-wave one they have appeared to be substantial. One may suppose that in order to decrease the above losses it is necessary to increase an electric field near the HJ interface for example, by narrowing the SCR. The latter way, however, contradicts to the necessity of keeping a sufficiently wide photoactive region $W + L_p$ ($0.5 \div 1 \mu\text{m}$).

2. Experimental details

The II–VI base layers and the graded band gap intermediate layers made on the same basis were manufactured by quasi-closed space vacuum sublimation technique. In Ref. [4] the possibility has been demonstrated of obtaining graded band-gap structures in thin polycrystalline cells by the same method. Technological arrangement included two or three (depending on the number of components) sources attached to the bottom of the mixing chamber. The substrate was placed on the top of the chamber. Either of the sources had an autonomous heater. The vapour composition can be adjusted by a variation of the evaporation temperature of each component. The film composition and its change across the film were studied by XPS with ion etching.

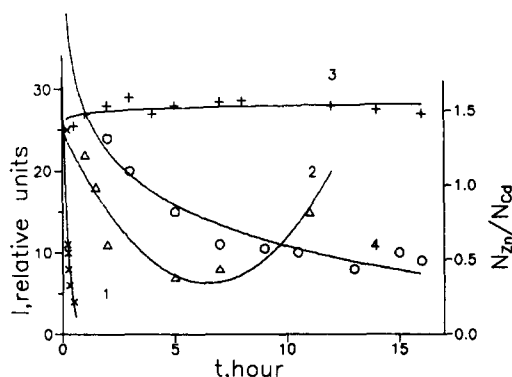


Fig. 1. The element concentration profiles in the $\text{Zn}_x\text{Cd}_{1-x}\text{Se}$ film subjected to Ar^+ etching (1–C, 2–O, 3–Se) and the ratio of the structure cationic component concentrations versus time [4]. Etching rate is 600 Å/h.

Fig. 1 shows the element concentration profiles in $\text{Zn}_x\text{Cd}_{1-x}\text{Se}$ film etched by Ar^+ ions. The ratio of the structure cationic components concentrations ($N_{\text{Zn}}/N_{\text{Cd}}$) versus etching time t is also given (etching rate was evaluated to be 600 Å/h) [4]. One can see that the latter dependence indicates the smooth transition from zinc-excess solid solutions to cadmium-excess ones.

Comparative investigations of the $\text{Cu}_{1.8}\text{S}/\text{CdSe}$ -type SC and the heterostructures containing $(\text{CdSe})_x(\text{ZnTe})_{1-x}$ illustrate the advantages of the use of graded band-gap layers.

CdSe base films and the variable composition layers were grown on metal-coated insulator substrates by the above mentioned method. The overall structure thickness was less than 7 μm , graded band-gap layer thickness was 0.1 μm , and that of the transparent component $\text{Cu}_{1.8}\text{S}$ was about 40 nm. The electron concentration in CdSe was $8 \times 10^{14} \text{ cm}^{-3}$, and the hole concentration in $\text{Cu}_{1.8}\text{S}$ was about $5 \times 10^{21} \text{ cm}^{-3}$.

3. Results and discussions

The results of the transmission investigations for 250 Å layers of copper chalcogenides are given in Fig. 2. Curve 1 corresponds to the stable $\text{Cu}_{1.8}\text{S}$ phase and curve 2 to $\text{Cu}_{1.75}\text{Se}$. The intermediate values of transmissibility could be obtained using $\text{Cu}_y\text{S}_x\text{Se}_{1-x}$ solid solutions.

Our transmission electron microscope studies of Cu_xS films produced in vacuum showed that increasing condensation temperature resulted in formation of local inclusions having higher than usual copper concentration. The latter fact causes the degradation of solar cells diode parameters due to formation of shunting channels. Understanding this phenomenon allowed us to correct the Cu_xS deposition conditions. However, any deposition technique has been found to

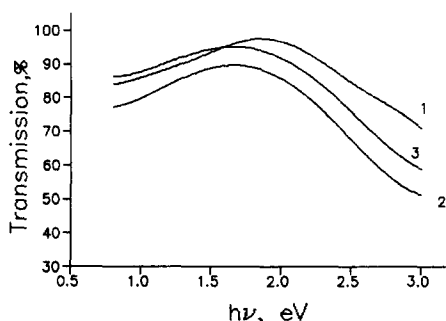


Fig. 2. Spectral dependence of the transmission of copper chalcogenides-based films for different compositions: (1) $\text{Cu}_{1.8}\text{S}$, (2) $\text{Cu}_{1.75}\text{Se}$, (3) $\text{Cu}_y\text{S}_x\text{Se}_{1-x}$.

produce deviations from the stable copper chalcogenide composition characterized by the excess of copper [4]. When the $\text{Cu}_{1.8}\text{S}$ composition restored after some time the excessive copper diffused and deposited onto the HJ interface [5]. Hence, there was a degradation of SC parameters due to both increased interface recombination and decreased electric field of the p-n HJ.

The above experimental facts allow one to make the following conclusions:

- (a) a need of both obtaining the optimum spectral distribution of photocurrent and minimizing diode dark currents leads to contradictory demands about the SCR width;
- (b) the degradation of solar cells operational characteristics is due to the excess copper deposited at the HJ interface and also to copper chalcogenide interaction with oxide layers existing, e.g., on the n-CdTe surface.

In this paper we presented the results of using thin semiconductor interlayers (including the graded band gap ones) to change the junction properties. Such a solution permits one to optimize the parameters of thin film polycrystalline solar cells and to stabilize their properties.

Application of the ultrathin intermediate layers, which in fact do not screen the contact potential difference and do not change the conditions for the minority carriers transport, enables one to look forward to:

- (a) Performing protective functions. The interlayers prevent undesirable chemical interaction of the HJ components and interdiffusion of the junction elements. The mechanisms of ageing and degradation of the SCs having $\text{Cu}_{1.8}\text{S}$ p-component are removed by using intermediate layers based on ZnS, ZnTe and some other materials;
- (b) Decreasing the photocurrent losses connected with the nonequilibrium majority carriers transport through the interface. The appropriate choice of semiconductor interlayer allows one to increase the potential barrier for the majority carriers.
- (c) Improving electrical and photoelectrical properties of the HJs owing to use of ultrathin graded band gap layers.

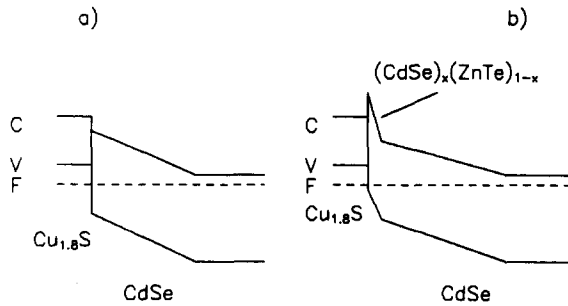
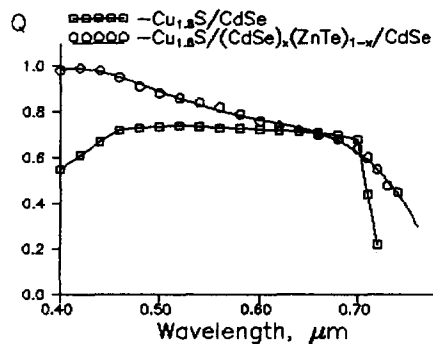


Fig. 3. Heterojunction energy band diagrams.

The method of application of the quasi-electric fields suggested and developed in this paper differs essentially from the known ones. For instance, in the known surface-energy barrier structures the width of the graded band gap region either exceeds the SCR width or coincides with it [6,7]. But in our case the quasi-electric field of ultrathin graded band gap interlayer is incorporated into the SCR. This leads to the increase of the electric field at the HJ interface and also preserves a sufficiently large photoactive region $W + L_p$. It should also be noted that an additional doping is not necessary if one uses II–VI based variable composition layers $(\text{Zn}_x\text{Cd}_{1-x}\text{Te})$, $(\text{CdSe})_x(\text{ZnTe})_{1-x}$ and others. This does not prevent obtaining maximum values of the quasi-electric field strength.

Figs. 3a and 3b show the energy band diagrams of the SCs under study. The cut-off voltage value 0.65 V of $C-V$ curves for the $\text{Cu}_{1.8}\text{S}/\text{CdS}$ -type HJ is in good agreement with known parameters of energy band diagram [2,5]. The SCR width for different samples was $0.8 \div 0.9 \mu\text{m}$. For the graded band-gap layer structure the $C^{-n}(U)$ dependence demonstrates a break corresponding to the non-uniform space charge distribution. The value of $U_d = 1.75 \text{ V}$ obtained by extrapolating the C^{-3} versus V dependence to the region of high positive bias voltages is consistent with the value of $eU_d = \Delta\chi + \Delta E_c$ (see Fig. 4b). Here $\Delta\chi$ is the work function

Fig. 4. Carrier collection coefficient (Q) spectral dependence.

difference between $\text{Cu}_{1.8}\text{S}$ and CdSe , and $\Delta E_c = 1.1$ eV is the electron affinity difference between CdSe and ZnTe .

The current–voltage (I – V) curves of the structures are well described by the expression $I = I_0 \exp(\alpha U)$ but their parameters show some distinct differences. At room temperature I_0 and α values fall within the range $I_0 = (2 \times 10^{-5} \div 8 \times 10^{-7})$ A/cm², $\alpha = 12 \div 8$ and $I_0 = (0.8 \times 10^{-8} \div 1.7 \times 10^{-8})$ A/cm², $\alpha = 16 \div 19$ for $\text{Cu}_{1.8}\text{S}/\text{CdSe}$ and $\text{Cu}_{1.8}\text{S}/(\text{CdSe})_x(\text{ZnTe})_{1-x}/\text{CdSe}$ samples, respectively. Both structures are characterized by a weak α temperature dependence. This is typical for the SC with copper chalcogenide p-component, where tunnel [2] or recombination-tunnel [3] current transmission mechanisms are realized.

Fig. 4 demonstrates the typical spectral dependencies of the carrier collection coefficient $Q(\alpha)$ for the structures studied. These curves were calculated from experimental spectral distributions of both the SC quantum efficiency and transmissibility of $\text{Cu}_{1.8}\text{S}$ films. The reliability of sufficiently high values of carrier collection coefficient obtained for the structures with graded band-gap interlayer is confirmed by the type of photocurrent versus external negative bias voltage dependence. Thus, when SC is illuminated by light having wavelength of $\lambda = 0.42$ μm , the photocurrent does not depend on bias voltage. This indicates the Q independence of the electric field. Hence $Q = 1$ is in agreement with the experimental curve $Q(\lambda)$ (see Fig. 4).

Comparing both $Q(\lambda)$ curves one can conclude that the dependencies for both structures are the same for low energy photons beginning from $\lambda = 0.6$ μm (but for the long-wave tail). This fact is evident because the above-mentioned spectral region is determined by carrier generation and recombination processes in CdSe , i.e., in the layers having the same properties for the SCs studied (due to the same SCR width).

Under the natural solar illumination the $\text{Cu}_{1.8}\text{S}/\text{CdSe}$ -type cells efficiency is about 4%, whereas for the $\text{Cu}_{1.8}\text{S}/(\text{CdSe})_x(\text{ZnTe})_{1-x}/\text{CdSe}$ -type cells the efficiency of about 8% is typical at the same conditions. It should be noted that for $\text{Cu}_{1.8}\text{S}/\text{CdTe}$ structure with an intermediate semiconductor layer we managed to reach the efficiency $\sim 11\%$.

The developed thin-film multilayer polycrystalline SCs were used as a basis for

Table 1
Comparison of the characteristics for various solar battery types

Solar battery type	85 lux Tungsten lamp		40 lux Tungsten lamp		100 lux Fluorescent lamp	
	V_{oc} (V) per one SC	I_{sc} $\mu\text{A}/\text{cm}^2$	V_{oc} (V) per one SC	I_{sc} $\mu\text{A}/\text{cm}^2$	V_{oc} (V) per one SC	I_{sc} $\mu\text{A}/\text{cm}^2$
k-Si	0.41	127	–	–	0.33	12
a-Si	0.6	10	0.58	5	0.6	11
n-CdS/p-CdTe	–	–	0.45	19.6	0.42	8.2
$\text{Cu}_{1.8}\text{S}/\text{CdSe}_x\text{Te}_{1-x}$	0.40	32	0.38	15	0.35	10
$\text{Cu}_{1.8}\text{S}/(\text{CdSe})_x(\text{ZnTe})_{1-x}$	0.45	14	0.41	8	0.42	10.6

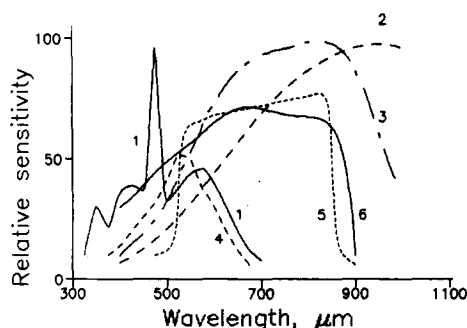


Fig. 5. Radiation spectra of a fluorescent lamp (1), of a tungsten lamp (2), and the spectral characteristics of photoelectric converters based on k-Si (3), a-Si (4), CdS/CdTe (5) (the curve is taken from [9]), and $\text{Cu}_{1.8}\text{S}/\text{CdSe}_x\text{Te}_{1-x}$ (6).

the production of integrated solar batteries. These SCs are useful at low illumination intensities. They demonstrate high stability of the basic physical parameters.

The photoelectric parameters of the SCs developed are given in Table 1. For comparison we give also the average reference data for the monocrystalline and amorphous silicon-based cells, as well as for the SCs of the CdS/CdTe type [9]. According to the Table 1 the II–VI compound cells are comparable with k-Si and a-Si SCs under illumination by fluorescent lamp. Moreover, when tungsten lamp is used our solar cells are better than those of a-Si. The latter fact is attributed to the wider spectral sensitivity region (as compared with a-Si, see Fig. 5).

4. Conclusions

The present paper demonstrates that the use of a quasi-electric field incorporated into the SCR allows to improve the efficiency of thin-film polycrystalline semiconductor-based SCs with gap width (E_g) near the optimum value: CdTe ($E_g = 1.45$ eV), $\text{CdSe}_x\text{Te}_{1-x}$ ($E_{g\text{min}} = 1.35$ eV), CdSe ($E_g = 1.7$ eV).

The possibility of the drastic increase of the efficiency for CdSe-based SCs containing the graded band gap interlayers makes these structures promising for using as upper photoconverter in cascade SCs, e.g., coupled with the cadmium telluride cells or with CdS/CuInSe₂-type cells. It should be pointed out that using CdTe or CdSeTe as lower SC would give an opportunity to product cascade SC based on II–VI compounds only, its advantages being determined by the common technology of component manufacturing.

The developed SCs can be used as a power supply for the electron devices of microWatt engineering. Such batteries can compete with those manufactured now due to ease and low cost of their fabrication (as compared with a-Si and k-Si), as well as to extended region of their spectral sensitivity (as compared with a-Si).

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