

OPTIMIZATION IN CONDITIONS FOR CdS-Cu₂S HETEROPHOTOCELL SHAPING

We carried out the investigation in photoelectric properties of photoconverter on conditions that shaped each level of its structure. Cadmium sulphide layers doped with zinc (Zn_xCd_{1-x}S, x ≤ 0,2) obtained by electrohydrodynamic spray procedure on glass substrates coated with tin dioxide by the practice described in [–] were used as the basic ones.

The thickness of these layers is 3...4 μm. The layer of CuCl was applied by thermal sputtering on surface of cadmium sulphide one being under room temperature. Then, Cu₂S layer is shaped under heating as the result of substitution reaction in solid phase



where γ and δ – the numbers described the deviation degree from stoichiometry for CdS and CuCl, correspondingly. The compound CdCl₂ obtained as reaction outcome can be wasted by washing in distilled water. The deposition of copper contact was the crown stage to form the converter.

The introduction of Zn into CdS layer to increase open-current voltage (U_{oc}) leads simultaneously to increase in base resistance and respectively to decay of short-circuit current (I_{sc}). So, the decrease of resistivity was the first stage to optimize the conditions for heterojunction shaping. Zn_xCd_{1-x}S newly-made layers were thermally treated on air and in vacuum with different time intervals and under various temperatures. The dependencies of U_{oc} and I_{sc} on vacuum annealing temperature within the range 470 K – 770 K are presented in Figure 1. The given curves show that the maximum values of U_{oc} and I_{sc} can be reached within the annealing range 710...740 K.

Such higher temperature value is connected with recrystallization processes in Zn_xCd_{1-x}S layer. The optimal annealing time is 25 minutes. One should take into account that the decrease of sulphur surface concentration and desorption

oxygen adsorbed under growth are the important processes in vacuum annealing because oxygen in Zn_xCd_{1-x}S base level increases its resistivity and hampers the reaction of Cu_xS shaping. As the annealing result cadmium sulphide surface became enriched in cadmium.

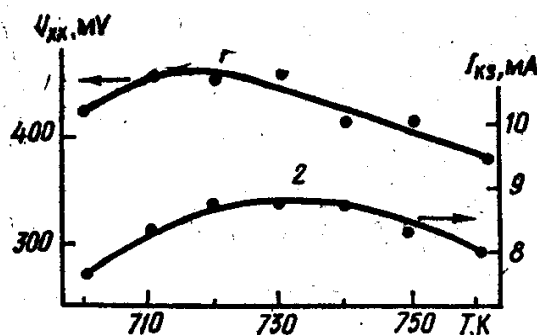


Figure 1. Photoconverter dependence of U_{oc} (1) and I_{sc} (2) on Zn_xCd_{1-x}S vacuum annealing temperature (AM- 1,5).

The base surface should be depleted with sulphur accordingly to chemical reaction to obtain Cu_xS of stoichiometric composition. The stoichiometric composition of Cu_xS is necessary to obtain photovoltaic effect observed only in chalcocite phase (Cu₂S). Vacuum annealing will improve the efficiency of elements when Zn_xCd_{1-x}S surface is enriched with sulphur that has been observed in our case.

The fact that vacuum annealing agrees with production technology of (ZnCd)S/Cu₂S photoconverters (by substitution process in solid

phase) should be referred to the positive aspects in thermal treatment of $Zn_xCd_{1-x}S$ layer. Such annealing is carried out before deposition of cuprum chloride and is one of the stages to shape heterostructure in the united technological process.

The annealing of base layers in air slightly improves photoconverter parameters. This can be explained as follows: oxygen and sulphur are not removed during such annealing, and surface parameters are not applicable to shape effective heterojunction.

The determination of optimal conditions to create cuprum sulphide layer that provides high efficiency of photoconverter is seemed to be important. The data [] showed that Cu_xS was grown by epitaxy on CdS and sulphur sublattice remain unchanged. Only cuprum and cadmium atoms diffuse during the reaction. The deviation in CuCl and CdS stoichiometry will be represented in cuprum sulphide stoichiometry. So, we have paid our particular attention to grow CuCl layer of stoichiometric composition. One knows that CuCl is not stable composition and can pass into $CuCl_2 \cdot 2H_2O$ crystalline hydrate phase. When this material is applied in deposited layer of cuprum chloride the impurity in the form of $CuCl_2$ or $CuCl_2 \cdot 2H_2O$ will be present and the composition Cu_xS that differs significantly from Cu_2S is determined. So, CuCl powder (newly-prepared or cleaned) was used for deposition of cuprum chloride layer, and evaporator was covered by copper chip to saturate chlorine ions with it fully. This resulted in cuprum chloride layer that the nearest to stoichiometric one.

When temperature of substrate with $Zn_xCd_{1-x}S$ and CuCl increases higher that 370 K copper began to diffuse from CuCl to the growing surface of cuprum sulphide, and at the same time cadmium diffuses from cadmium sulphide to the growing surface of $CdCl_2$. As the rates of copper and cadmium diffusion depend on vacancy concentration, there will be the dynamic equilibrium between diffusant concentrations. During the most period of reaction the diffusion of Cu and Cd will take place through the mixtures of cuprum chloride and cadmium chloride, on the one side, and through the mixtures of cuprum sul-

phide and cadmium sulphide, from the other side. At the start of reaction vacancy concentrations will be significant and diffusion through thin areas of mixtures will be easy. As reaction follows the areas of mixtures become thicker and thicker and diffusion through the whole width becomes hampered. So, when thickness (d) of $CdCl_2$ layer increases, diffusion of cooper from CuCl will decrease sharply. It follows that thickness of cuprum chloride layer influences considerably on kinetics of Cu_xS formation.

To determine the optimal thickness (d) of CuCl layer we studied the dependence of photocell parameters on the mentioned value. The thickness of cuprum chloride layer was varied by changes in amount of powder charged into evaporator.

Curves 1 and 2 (Fig. 2) demonstrate the changes in open-current voltage and short-circuit current of the samples from thickness (d) of CuCl layer. The given curves were measured under light intensity that corresponded to atmospheric mass AM 1,5. Figure 3 shows that maximum values of parameters and I_{K3} can be reached at values $d \sim 0,4 \dots 0,6 \mu m$. When thickness d decreases, the thickness of growing Cu_xS layer is not sufficient to absorb completely the incident radiation, so short-circuit current decreases, but at its increase the diffusion of cooper ions is blocked by the growing layer of cadmium chloride and the reaction results in formation of cuprum sulphide layer with higher deviation from stroichiometry.

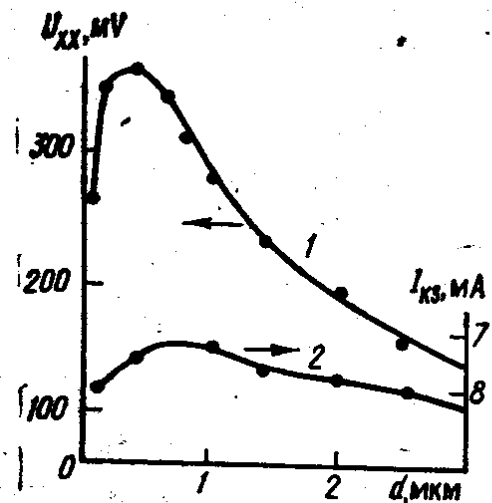


Figure 2. Photoconverter dependence of U_{oc} (1) и I_{sc} (2) on thickness (d) of CuCl layer (AM1,5).

Temperature of substitution process is rather significant to obtain Cu_xS being similar to the stoichiometric composition. The substrates with $\text{Zn}_x\text{Cd}_{1-x}\text{S}$ and CuCl layers were placed over the heater that increased temperature up to 440...460 K and withstand it during $t \sim (5...35)$ min.

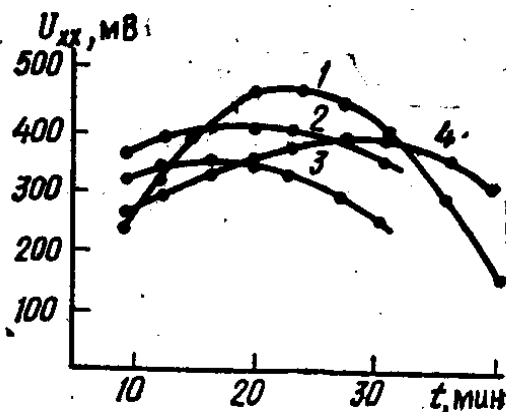


Figure 3. U_{oc} dependence of photoconverter on formation time of Cu_xS layer at temperatures: 1 — 440; 2 — 460; 3 — 480; 4 — 500 K

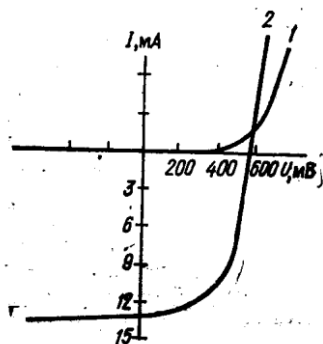


Figure 4. CVC of $\text{Zn}_x\text{Cd}_{1-x}\text{S} - \text{Cu}_2\text{S}$ heterojunction at AM1,5

The results for U_{oc} measurements on heating time are presented in Figure 3. All curves have the maximum, and the higher T , the maximum value U_{xx} reaches early. But the highest photovoltage value is reached at $T = 440$ K. At higher and lower temperatures these values decrease.

The optimal conditions of layer formation are $T \sim 440$ K and $t = 20$ min.

Experimental current-voltage characteristics (CVC) for $\text{Zn}_x\text{Cd}_{1-x}\text{S} - \text{Cu}_2\text{S}$ photoconverter made according to the optimized procedure are presented in Figure 4.

Under AM 1,5 the efficiency of photoconverter with square 1 cm^2 is 6,0% under open-circuit voltage $U_{oc} = 510$ mV and short-circuit current $I_{sc} = 15 \text{ mA/cm}^2$, CVC occupation coefficient is equal to $\approx 0,61$.

The described investigation determined the optimal conditions shape $\text{Zn}_x\text{Cd}_{1-x}\text{S} - \text{Cu}_2\text{S}$ heterojunction for high-effective converters of solar energy into electric one.

REFERENCES:

1. Ю. Н. Каракис, М. И. Куталова, Н. П. Затовская, В. В. Зотов, «Особенности релаксации фототока в кристаллах сульфида кадмия с запирающими контактами» 1-а Українська наукова конференція з фізики напівпровідників. Одеса, 10-14 вересня 2002 р. Тези доповідей. Т.2. С.138.
2. A. A. Dragoev, A. V. Muntjanu, Yu. N. Karakis, M. I. Kutalova «Calculation for migration-dependent changes in near-contact space-charge regions of sensitized crystals». «Photoelectronics», v. 19. Odessa «Astroprint» 2010. P. 74-78.
3. M. A. Novikova, Yu. N. Karakis, M. I. Kutalova «Particularities of current transfer in the crystals with two types of Recombination centers». «Photoelectronics», 2005, v.14, P. 58-61.
4. Melnik A. S., Karakis Y. N. Kutalova M. I., Cheme-resjuk G. G. «Features of thermo-optical transitions from the recombination centers excited states». «Photoelectronics», v. 20. Odessa «Astroprint» 2011. P. 23-28.

UDC 539.125.5

Karakis Yu. N., Kutalova M. I., Zatovskaya N. P.

OPTIMYZATION IN CONDITIONS FOR CdS-Cu₂S HETEROPHOTOCELL SHAPING

Abstract

CdS-Cu₂S thin film structures are prospective to be the base for high-efficient converters of solar energy to electric one. The theoretical efficiency of these elements is 27 %. But the complexity to obtain all components of the system with optimal parameters confines to reach such higher efficiency in practice.

Key words: optimization, geterophotocell, thin film structures.

УДК 539.125.5

Караис Ю. Н., Куталова М. И., Затовская Н. П.

ОПТИМИЗАЦИЯ УСЛОВИЙ ФОРМИРОВАНИЯ ГЕТЕРОФОТОЭЛЕМЕНТА CdS-Cu₂S

Резюме

Тонкопленочные структуры CdS-Cu₂S – являются перспективными для создания на их основе высокоэффективных преобразователей солнечной энергии в электрическую. Теоретический к.п.д. этих элементов составляет 27 %. Однако практическое достижение такого высокого коэффициента полезного действия ограничивается сложностью получения всех компонент системы с оптимальными параметрами.

Ключевые слова: оптимизация, гетерофотоэлемент, тонкопленочные структуры.