Structure and Optical Properties of CdS Thin Films after Hard Ultraviolet Irradiation

Andrii Dobrozhan, Andrii Meriuts
Department of Materials for Electronics and Solar Cells
National Technical University "Kharkiv Polytechnic Institute"
Kharkiv, Ukraine
dobr.abs@gmail.com

Galina Kopach
Department of Physics
National Technical University "Kharkiv Polytechnic Institute"
Kharkiv, Ukraine
gkopach@ukr.net

Ruslan Mygushchenkoб Olha Kropachek
Department of Theoretical Foundations of Electrical Engineering
National Technical University "Kharkiv Polytechnic Institute"
Kharkiv, Ukraine

***Abstract* — The influence of hard ultraviolet radiation on the crystalline structure and optical properties of thin-film semiconductor cadmium sulfide layers obtained by the method of non-pulsed direct current magnetron sputtering was investigated. It was established that for hexagonal modification cadmium sulfide films after hard UV irradiation with a quantum energy of 10.5 eV for 10 hours the lattice parameter *c* changes from 6.77(01) Å to 6.78(88) Å. The results of the study of the optical properties of cadmium sulfide films before and after hard ultraviolet irradiation indicate that the transmission coefficient, reflection coefficient, refraction coefficient and band gap do not change.**

Keywords — cadmium sulfide, non-pulsed direct current magnetron sputtering, hard ultraviolet, thin films.

I. Introduction

The CdTe/CdS thin film layers heterosystem is promising for the creation of economical high-performance thin film solar cells for terrestrial and space application [1-4]. At present, the value of the efficiency of the real photovoltaic converters obtained on the basis of this heterojunction is lower than the theoretically possible [5]. This is due to the high specific resistance of the base layer of cadmium telluride, the low lifetime of minority carriers in CdTe, the low quality of separation barrier and inappropriate usage of new physical principles for the solar cells design. For example, the creation of varieussed structures in the area of the separation barrier allows us to improve the parameters of the photoelectric converters [6]. Direct current magnetron sputtering (DC magnetron sputtering) is one of the most economical and high-tech methods for obtaining thin films and is used in various microelectronic devices. Technological problems caused by low conductivity of pulsed pressed semiconductor targets and relatively low emissivity of materials for sulfide and cadmium tellurides were solved in [7].

Sunlight in space at the top of Earth's atmosphere, which is named as extraterrestrial solar irradiance, contains of about 10% of ultraviolet light (UV) with a wide range of wavelengths (λ), mostly 100-399 nm, having total UV intensity about 140 W/m^2. A short-wave (100-279 nm) hard ultraviolet is completely absorbed by the ozone layer and atmosphere, and this ultraviolet part of the solar spectrum drives the photochemistry of a number of considerable atmospheric trace gases such as ozone, nitrogen dioxide and hydroxyl radicals. When using solar cells based on the CdTe/CdS heterosystem in outer space, the radiation of hard ultraviolet may result a degradation of the output parameters of solar cells.

The crystalline structure and optical properties of the CdS window layer in solar cells based on the CdS/CdTe film heterosystems significantly affect the quality of the separation barrier and the initial parameters of the solar cell. Therefore, the study of the influence of hard ultraviolet radiation on the structure and optical properties of CdS films obtained by direct current magnetron sputtering for space solar cells is relevant.

II. Experiments

In laboratory technology of condensation CdS thin films by DC magnetron sputtering the design of VUP-5m magnetron was used. Its feature is that the cooling circuit covers only the magnetic system and as the result there are no forced cooling of sputtered semiconductor pressed powder target. The targets were made by cold pressing from cadmium sulfide powder and with diameter 74 mm and thickness 2 mm. Target cold pressing pressure was 100 MPa. The dwell time of the target at this pressure was 15 hours. After pressing the targets its vacuum annealing has been performed at a residual pressure of at least 10^{-4} mm Hg and a temperature of 80°C. For the implementation of the process of thermionic emission of electrons from the pressed powder target for plasma discharge ignition the target was preheated for 10-15 minutes.

CdS thin films were condensed on a soda-lime glass substrates at following physical and technological mode: substrate temperature T_{sub}=130^{0}C, pressure of inert gas Ar P_{Ar}=0,9-1 Pa, magnetron discharge current density J=1,1 mA/cm^2, the voltage on magnetron V=470-500 V, deposition time 10 min.

The crystalline structure was studied by X-ray diffractometry. Taking of X-ray diffractograms (XRD) for the cadmium sulphide was carried out by θ-2θ scanning method with Bragg-Brentano focusing procedure using X-ray diffractometer DRON-4 with a step 0.01-0.02 degrees in K_α-radiation of a Mo-anode.

In accordance with [8, 9], to evaluate the crystallite size D and lattice microstrains induced mainly by point defects Δd/d (where d is the crystal interplanar spacing according to JCPDS, and Δd is the difference between the corresponding experimental and reference interplanar spacings) we applied the X-ray line broadening method using the Scherrer equation.

Under these conditions, the diffraction pattern has been formed by the grains with reflecting planes parallel to the surface of samples (hkl) [10, 11]. Identification of the phase composition of the samples was carried out by comparing the angles 2θ of clearly defined peaks obtained when shooting, with filed reference data from JCPDS, which has obtained by means of an electronic database "PCPDFWIN" for the respective phases.

Optical studies of CdS layers were conducted using the spectrometer SF-2000. The transmission spectrum of studied films was used to determine the thickness of the layers according to [8]. The thickness of the layers was calculated using the formula:

$$\tau = M \lambda_1 \lambda_2 / (2 (\eta_{\lambda 1} \lambda_2 - \eta_{\lambda 2} \lambda_1)) \quad (1)$$

where λ_1, λ_2 – the wavelengths of two adjacent extremums (interferential maxima or minima of transmission spectrum) in nm; $\eta_{\lambda 1}$, $\eta_{\lambda 2}$ – refractive index, depending on the wavelength λ_1, λ_2.

The bandgap of thin films were determined by calculating the dependence of absorption coefficient on the wavelength α(λ) using [12]:

$$T = (1 - R) \exp(-\alpha \tau) \quad (2)$$

where T is the transmission coefficient; R is the reflection coefficient; τ is the film thickness.

The CdS polycrystalline films bandgaps were determined by extrapolation of the linear portion of the $(\alpha \cdot h\nu)^2 = f(h\nu)$ curves (where h is the Planck constant, ν is the frequency) to the intersection with the hν energy axis.

Irradiation by the hard ultraviolet of the CdS film samples was carried out using a barrier discharge lamp with argon filling having maximum energy illumination in the plane of the lamp window ~ 10^{20}-10^{21} quantum/m^2 with a maximum energy 10.5 eV ($\lambda \geq 118$ nm). The irradiated samples were densely pressed to the lamp window. The hard ultraviolet irradiation was carried out in air at $T = 300$ K for 10 hours.

III. Results and discussion

Cadmium sulfide layers were exposed to hard UV radiation in the air. The calculated accumulated dose of radiation is $1.7 \cdot 10^9$ Gy, which is 10^4 times more than accumulated dose of ionizing radiation of the satellite mission [13]. In order to study the influence of hard ultraviolet radiation on the properties of cadmium sulfide layers obtained under the same physical and technological condensation modes, the crystalline structure and optical properties of CdS semiconductor layers before and after irradiation were compared.

The XRD of CdS films in the initial state and after hard UV irradiation (CdS+UV) are shown in Fig. 1.

The results of the XRD analysis performed for a CdS sTable hexagonal phase are shown in Table 1. The reflection of the peak (002) on the angle $12{,}03^0$ was found. The calculated constant crystal lattice c for the sample in the initial state is $c = 6.77(01)$ Å, which is 0.74% different from the tabulated value for hexagonal cadmium sulfide (PCPDFWIN # 41-1049, $a = 4.14092$ Å, $c = 6.7198$ Å).

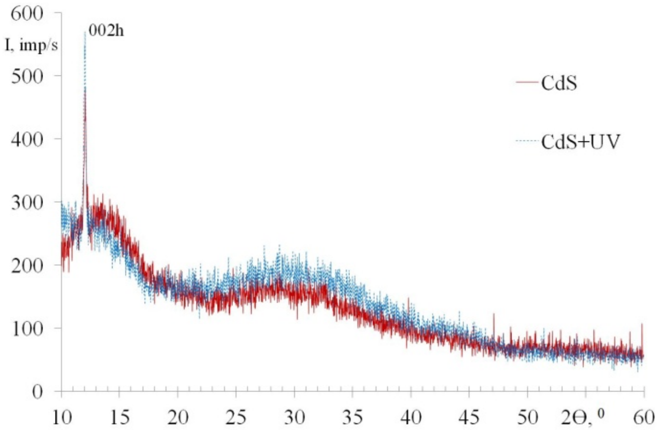

Fig. 1. XRD of CdS film after obtaining (CdS) and after hard ultraviolet irradiation (CdS+UV).

TABLE I. THE PROCESSING RESULTS OF XRD OF CDS FILMS AFTER OBTAINING AND AFTER HARD UV IRRADIATION (CDS+UV)

	hkl	Peak position, degrees	Inter-planar spacing, Å	Inten-sity, imp/s	FWHM, degrees	D, nm	Δd/d *10^{-3}, a.u.
CdS	002	12,03	3,385	145	0,24	15	7,5
CdS +UV	002	11,99	3,394	208	0,20	18	10

a.

After hard UV irradiation of the cadmium sulfide thin-film layer the peak reflection of the sTable hexagonal phase - (002) on the 11.99^0, respectively (tab. 1), was detected. Calculated crystal lattice constant $c = 6.78(88)$ Å, which is 1.03% different from the Table value. The values of crystallite size are 15 nm for the initial state of cadmium sulfide films and 18 nm after irradiation. The values of Δd/d lattice microstrains in CdS films are $7.5 \cdot 10^{-3}$ a. u. and $10 \cdot 10^{-3}$ a. u. in the CdS layers after UV irradiation. These values are greater both for tabular value and for the value that was in the initial state, which indicates increased pressure of the crystal lattice in the direction of the axis c. For the reflection (002) the diffraction reflection curve was received (Fig. 2). The FWHM of the captured peak for the initial state was 7.2 degrees, and after UV irradiation was 4.5 degrees.

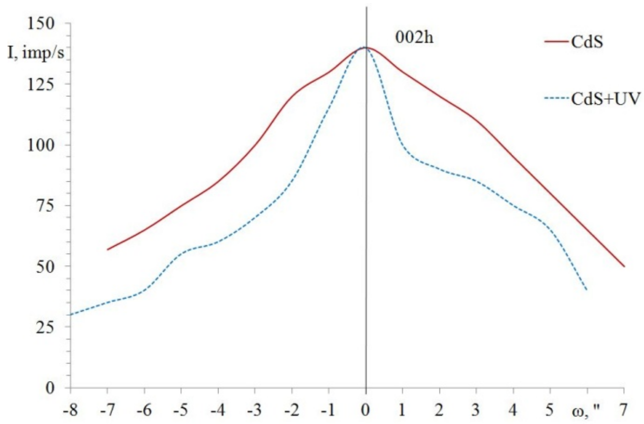

Fig. 2. The diffraction reflection curve of (002) reflection.

Thus, it can be concluded that under the action of hard UV irradiation in a thin film CdS, on the one hand, there are recrystallization processes that increase the values of crystallite size and change their orientation. On the other hand, there is the formation of antisite defects, as evidenced by the increase of permanent crystalline lattice.

The spectral dependences of transmission coefficient and reflection coefficient of typical CdS layers in the initial state are shown in Fig. 3. In the range of wavelengths of 400-500 nm, there is a strong absorption of radiation, while in the visible and infrared region of the spectrum, the average transparency of CdS films is 85%. The average reflection coefficient in the wavelength range of 400-1100 nm is 10%.

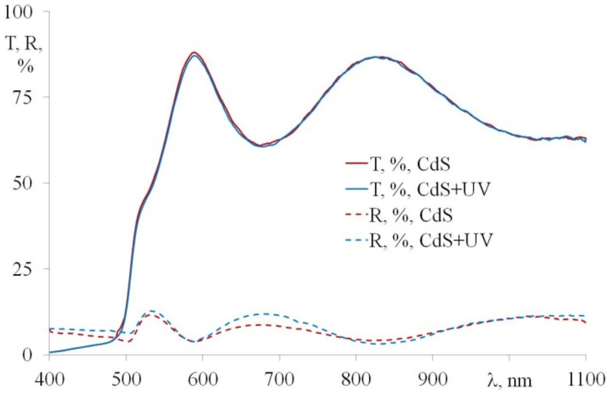

Fig. 3. Spectral dependences of transmission coefficient (*T*) and reflection coefficient (*R*) of CdS films in the initial state and after hard UV irradiation (CdS + UV).

The calculated refractive index is 2.34-2.51, the thickness of the investigated layers of cadmium sulfide is 360 nm. The bandgap of the CdS films in the initial state is 2.42 eV.

As it is shown in Fig. 3, the spectral dependence of the transmission coefficient and reflection coefficient of cadmium sulfide layers after hard UV irradiation remain unchanged within the measurement error. The average refractive index also does not change. The bandgap of cadmium sulfide after hard UV irradiation is 2.44 eV (Fig. 4).

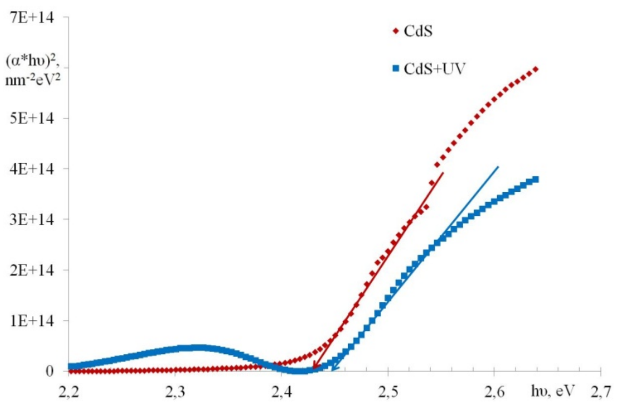

Fig. 4. Dependence of the $(\alpha \cdot h\nu)^2 = f(h\nu)$ curves of CdS films in the initial state and after hard UV irradiation (CdS + UV).

IV. Conclusions

The influence of hard ultraviolet radiation on the crystalline structure and optical properties of thin-film semiconductor cadmium sulfide layers obtained by the method of non-pulsed direct current magnetron sputtering was investigated.

It was established that for cadmium sulfide films of hexagonal modification after hard UV irradiation with a quantum energy of 10.5 eV for 10 hours the parameter *c* changes from 6.77(01) Å to 6.78(88) Å. The increase of the lattice microstrains after irradiation varied from $7.5 \cdot 10^{-3}$ a. u. up to $10 \cdot 10^{-3}$ a. u. These indicate an increase in the micropressure of the crystal lattice in the direction of the axis *c*.

The results of the study of the optical properties of cadmium sulfide films before and after hard ultraviolet irradiation indicate that the transmission, reflection, refraction and band gap do not change.

Thus, hard ultraviolet radiation with a accumulated dose of $1.7 \cdot 10^{9}$ Gy does not affect the crystalline structure and optical properties of CdS films obtained by non-pulsed direct current magnetron sputtering.

References

[1] A. Bosio, N. Romeo, S. Mazzamuto, and V Canevari, "Polycrystalline CdTe thin films for photovoltaic applications," Prog. Cryst. Growth Charact. Mater, vol. 52, no. 4, pp. 247-279, 2006.

[2] X. Wu et al., "16.5%-efficient CdS/CdTe polycrystalline thin-filmsolar cell," Proceedings of the 17th European Photovoltaic Solar Energy Conference, Dover, pp. 995, 2001.

[3] G. S. Khrypunov, G. I. Kopach, R. V. Zaitsev, A. I. Dobrozhan, and M. M. Harchenko, "Flexible Solar Cells are Based on Underlying Layers of CdTe Obtained by Magnetron Sputtering," J. Nano-Electron. Phys., vol. 9, p. 02008, 2017.

[4] D. A. Kudii, M. G. Khrypunov, R. V. Zaitsev, and A. L. Khrypunova, "Physical and Technological Foundations of the «Chloride» Treatment of Cadmium Telluride Layers for Thin-film Photoelectric Converters," J. Nano- Electron. Phys., vol. 10, no 3, p. 03007, 2018.

[5] A. Polman, M. Knight, E. C. Garnett, B. Ehrler, and W. C. Sinke, "Photovoltaic materials:present efficiencies and future challenges," Science, vol. 352, p. 6283, 2016.

[6] B. T. Boiko, G. I. Kopach, V. R. Kopach, ands G. S. Khrypunov, "Photovoltaic properties and structures of multilayer heterojunction systems based on cadmium telluride," Sol. Energy, vol. 21, pp. 123-126, 1991.

[7] M. V. Kirichenko, R. V. Zaitsev, A. I. Dobrozhan, G. S. Khrypunov, and M. M. Kharchenko, "Adopting of DC Magnetron Sputtering Method for Preparing Semiconductor," IEEE International Young Scientists Forum on Applied Physics and Engineering (YSF-2017), October 17-20, Lviv, pp.108-111, 2017.

[8] A. K. Zak, W. H. A. Majid, M. E. Abrishami, and R. Yousefi, "X-ray analysis of ZnO nanoparticles by Williamson–Hall and size–strain plot methods," Solid State Sci., vol. 13, pp. 251-256, 2011.

[9] N. P. Klochko et al., "Influence of UV Light of Extraterrestrial Solar Irradiance on Structure and Properties of ZnO Films Prepared Through Pulsed Electrochemical Deposition and via SILAR Method," J. Nano- Electron. Phys., vol. 10, pp. 06038, 2018.

[10] D. M. Vasilyev, Diffraction methods for structural studies. Moscow: Metallurgy, 1977.

[11] P. A.Panchekha, O. G. Alaverdova, and V. I.Gnidash, "Heterophase state and polytexture of CdTe films deposited from the ion-molecular beam," Ukr. J. Phys., vol. 45, no. 1, pp.75-80, 2000.

[12] A. M. Salem and M. E. El-Ghazzawi, "Structural and optical properties of chemically deposited CdCr2S4 thin films," Semicond. Sci. Technol., vol. 19, pp. 236–241, 2004.

[13] S. Krishnan, G. Sanjeev, M. Pattab, and X.Mathew, "Effect of electron irradiation on the properties of CdTe/CdS solar cells," Sol. Energy Mater. Sol. Cells, vol. 93, pp. 2–5, 2009.