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PHYSICOCHEMICAL FEATURES OF DIELECTRICAL NANO-BARRIER LAYERS IN $CdSe_xS_{1-x}$ FILMS FORMED BY SCREEN PRINTING METHOD

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The thermal activation process of $CdSe_xS_{1-x}$ films, formed by screen printing, was investigated. We mostly focused on the influence of thermal treatment conditions on oxidised film formation on the crystalline grain surface with nano-barrier "dielectric-semiconductor" layer generation. The composition and thickness of nano-barrier layers were determined by X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) methods. The thickness of nano-barrier layers was found to be 2–5 monolayers. It was shown that photoelectric properties of $CdSe_xS_{1-x}$ films were determined by the doping level and nano-barrier layer characteristics. By the use of XRD and SEM methods we experimentally investigated and justified that better microstructure and photoelectric properties (R_D / $R_L \geq 10^7$) of $CdSe_xS_{1-x}$ films are achieved by photosensitivity activation during 15–30 min thermal treatment in quasi-closed air atmosphere at 550 °C or during 5–15 min at 600 °C with low speed cooling (3 °C/min). The manufacturing method for obtaining $CdSe_xS_{1-x}$ films with assigned characteristics determined by paste composition and properties, thermal treatment regime and medium optimisation was developed.

Keywords: nano-barrier layer, thermal activation, screen printing, $CdSe_xS_{1-x}$ solid solution

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1. Introduction

It is well known that $CdSe_xS_{1-x}$ can be screen printed and sintered to form films that display photosensitivity. Such films are used to produce large-area photosensitive devices, commutating elements and more recently for photovoltaic cells [1, 2].

Under development of $CdSe_xS_{1-x}$ film formation by using screen printing, the most important question is the investigation of nano-barrier "dielectric-semiconductor" layer generation [3] which is responsible for the photosensitivity of these materials. The parameters of this barrier can be manipulated by the processing temperature range, gas medium composition and paste formulation.

2. Experiment

The $CdSe_xS_{1-x}$ solid solution film formation was carried out in two ways. The first method consisted in preliminary synthesis of solid solution by means of original powders (CdS, CdSe), flux ($CdCl_2 \cdot H_2O$), and dopant (CuOCl) mixture sintering. Then the ingot was crushed to particle size of <2 μm, the prepared paste was screen printed onto glass-ceramic substrates, and finally the photosensitivity thermal activation was carried out. The second method included the direct synthesis of $CdSe_xS_{1-x}$ films on substrate from the paste consisting of original powders. In detail the process of screen printed film formation is described in [4-6]. The photosensitivity thermal activation was carried out in a diffusion furnace SDO 125/4 at the temperature of 525–600 °C during 5–60 min in nitrogen and air atmosphere as well as in the regime of quasi-closed air atmosphere.

X-ray diffractograms of films were recorded using a diffractometer D8 (*Bruker*) with $CuK_{\alpha 1}$ – emission to perform the structural analysis of obtained films. XRD data was analysed by a standard procedure,

using the X-Pawer program and PDF-2 File. The surface morphology of the studied films was investigated with the scanning electron microscope LEO SUPRA 50 VP and Jeol JSM 6490LV. Atomic force microscopy (AFM) studies of grain boundaries were carried out with a scanning probe microscope (R47 Smena). XPS patterns were collected on the ESCALAB MK-II spectrometer equipped with a dual Al/Mg anode as a source of X-ray radiation. The anode was operated at 240 W (12 kV, 20 mA).

On the base of these films photoresistors with indium contact metallisation were manufactured. The resistance of photoresistors was measured at 200 lux illumination of a tungsten incandenscent lamp (light resistance R_L) and without illumination (dark resistance R_D). When the resistance change factor $K_R = R_D / R_L$, the ratio of dark resistance to light resistance was estimated.

3. Results and discussion

Thermal activation is the key process in photosensitive $CdSe_xS_{1-x}$ film producing. At this stage it is possible to achieve the necessary degree of photosensitivity and regulate many photoelectric properties and film structure. In the thermal activation process along with recrystallisation, the oxidation of film crystallites with the formation of the "dielectric-semiconductor" barrier takes place.

Cadmium sulphide and/or selenide oxidation proceeds as follows:

$$CdS + 2O_2 = CdSO_4\ (550–650\ °C), \quad (1)$$

$$2CdSe + 3O_2 = 2CdSeO_3\ (410–650\ °C). \quad (2)$$

Cadmium sulphate and/or selenite decomposition is carried out as follows:

$$2CdSO_4 = 2CdO + 2SO_2\uparrow + O_2\uparrow\ (650–880\ °C), \quad (3)$$

$$CdSeO_3 = CdO + SeO_2\uparrow\ (650–720\ °C). \quad (4)$$

The investigation of photosensitivity thermal activation atmosphere influence on phase composition, microstructure and photoelectric properties of films was carried out. The thermal treatment of films in air atmosphere resulted in full oxidation of film surface since the oxidation processes proceeded strongly at temperatures ≥500 °C (Fig. 1, curve 1).

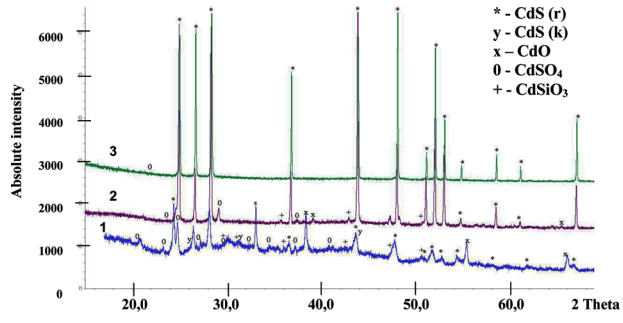

Fig. 1. X-ray diffractograms of CdS films thermally treated at different regimes: (1) in air; (2) and (3) in quasi-closed air atmosphere.

The thermal treatment in nitrogen atmosphere allows producing films with good microstructure and without impurity phases still not having photoconductivity.

Under thermal treatment in quasi-closed air atmosphere the sintered samples were laid in a stack with 0.5 mm gaps between them at the angle of 60° in a closed titanium container. In this case the growth of grain took much more time which provided the formation of large grains with the size up to 10 μm (or even more). The reason of this was the control of $CdCl_2$ evaporation rate, which defined the effective period of the eutectic melt steady-state. This enabled to decrease film imperfection due to better grain packaging (Fig.2). The dosed air oxygen exposure facilitates grain binding and enlargement with simultaneous film structural improvement. In case of quasi-closed volume during photosensitivity thermal activation the equilibrium between cadmium sulphite, cadmium oxide and

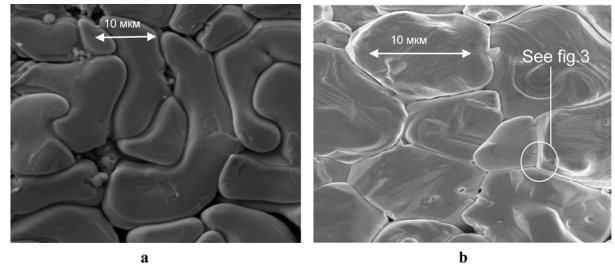

Fig. 2. SEM micrographs showing the surface morphology of films thermally treated in quasi-closed air atmosphere with low speed cooling (3 °C/min): (a) $CdS_{0.2}Se_{0.8}$: 30 min/550 °C, (b) $CdS_{0.8}Se_{0.2}$: 15 min/600 °C.

sulphur oxide was established; therefore, cadmium sulphite was oxidised to cadmium sulphate, which is more stable at temperatures of photosensitivity thermal activation. This is confirmed by XRD (Fig. 1, curves 2 and 3).

Figure 3 shows AFM images of the grain boundaries structure in $CdS_{0.8}Se_{0.2}$ film (Fig. 2b) in greater detail. It is obvious that the depth of boundaries is not more than 150 nm. Thus at thermal activation in quasi-closed volume single-phase $CdS_{0.8}Se_{0.2}$ films with the close-packed grain structure and well-formed grain boundaries were obtained.

XPS data indicates the presence of the oxidised phase on grain surface. Cd 3d spectra are not informative, because Cd $3d_{5/2}$ line positions are slightly distinguished for different possible oxidation products containing Cd^{2+} ($CdSO_4$, $CdSeO_3$, $CdCO_3$, CdS, CdSe and others). Therefore in this work the conclusions about $CdS_{1-x}Se_x$ film surface oxidation products are drawn on the base of S and Se spectra. In S 2p spectra two components with chemical shifts corresponding to typical cadmium sulphate and sulfide values are found (Fig. 4a). Moreover, in Se 3d spectra two components with chemical shifts corresponding to typical cadmium selenide and selenite values are found (Fig. 4b).

To estimate the thickness of the oxidised layer on CdS film surface S 2p spectra with different excitation energies (1030, 485 and 205 eV) were recorded.

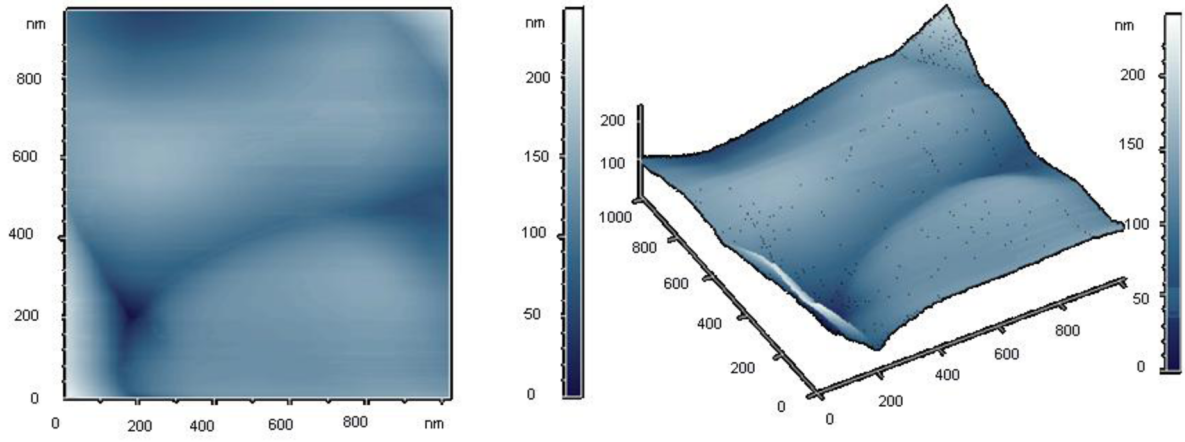

Fig. 3. AFM images of the grain boundaries structure in $CdS_{0.8}Se_{0.2}$.

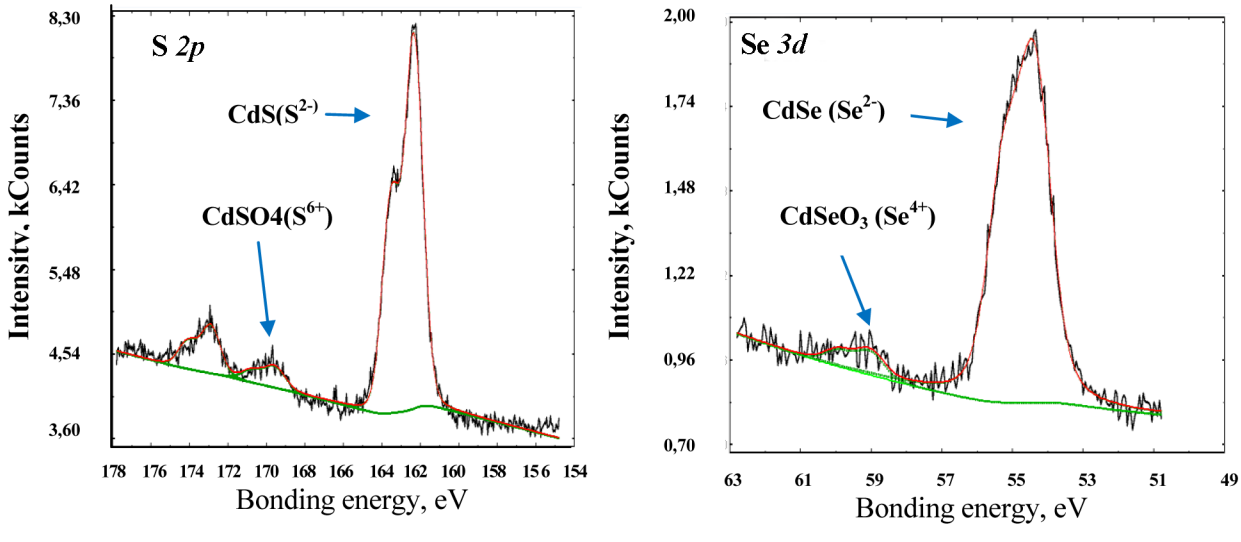

Fig. 4. S *2p* and Se *3d* XPS spectra of $CdS_{0.2}Se_{0.8}$ film.

As it is seen from Fig. 5, relative intensity of S II (S_2^{2-}), S III (S^0) and S IV(SO_4^{2-}) components in S 2p spectra is decreased with excitation energy increasing, i. e. surface atom contribution to the registered signal is decreased. The dependence of excitation energy on the escape depth of electrons is given in Table 1 (data are calculated using TTP-2m program [7]).

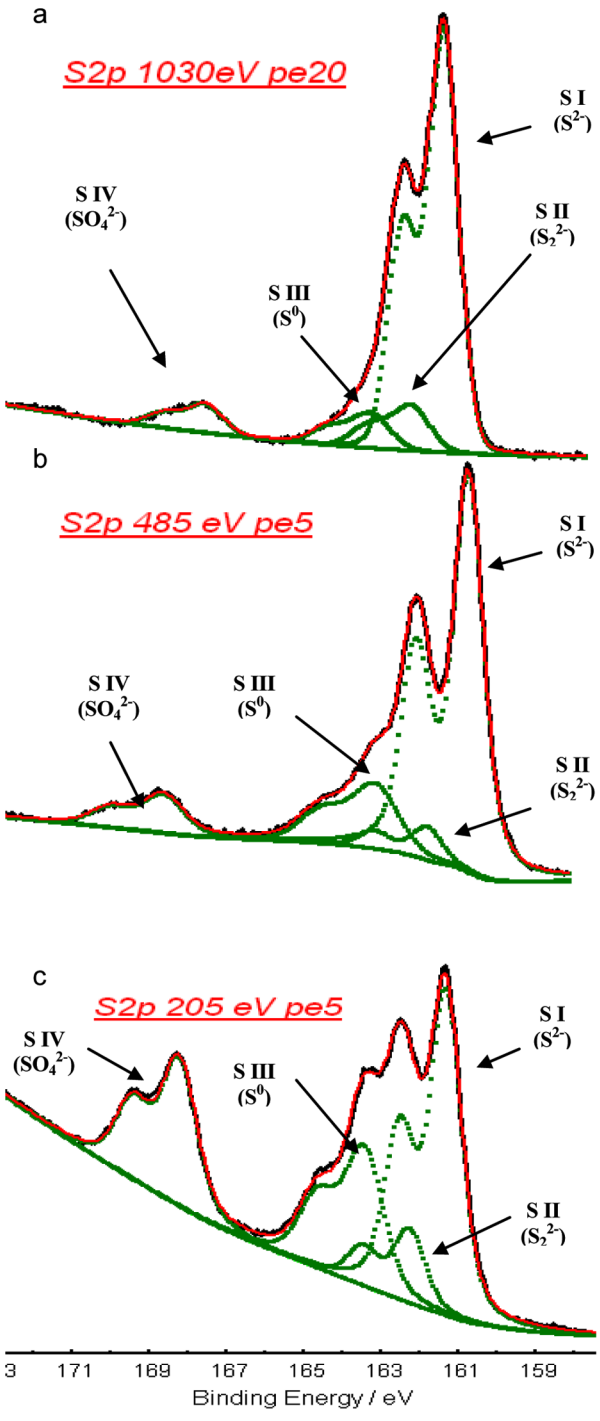

Fig. 5. S 2p spectra of CdS film with different excitation energies: (a) 1030 eV; (b) 484 eV; (c) 205 eV.

Table 1. The escape depth of S 2p electrons for different excitation energies.

No.	Excitation energy (E), eV	Escape depth (λ), Å
1	205	4.51
2	485	9.89
3	1030	18.23

These results mean that all listed components are related to the CdS surface layer. The thickness of this layer is estimated to be ~5–10 Å. Hence, only 2–5 monolayers are formed on the CdS surface during thermal treatment of $CdSe_xS_{1-x}$ films in the regime of quasi-closed air atmosphere.

Thus $CdSO_4$, $CdSeO_3$ and CdO are basic oxidation products. With the film photosensitivity thermal activation continuation the amount of oxidised components corresponding to SO_4^{2-} SeO_3^{2-} is increasing.

The better photoelectric properties ($R_D/R_L \geq 10^7$) of photoresistors, based on $CdSe_xS_{1-x}$ films, are achieved by photosensitivity activation during 15–30 min thermal treatment in quasi-closed air atmosphere at 550 °C or during 5–15 min at 600 °C with low speed cooling (3 °C/min).

4. Conclusion

The physico-technological aspects of controllable nano-barrier "dielectric-semiconductor" layer formation are developed. This enables to produce well crystallised films with high uniformity of photoelectric properties on the whole substrate. The thickness of this nano-barrier consisting of $CdSeO_3$, $CdSO_4$ and CdO amounts to 2–5 monolayers.

On the base of these films we produced photoresistors with low light resistivity (R_L < 50 Ohm) and high R_D/R_L ratio ($\geq 10^7$).

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STORASLUOKSNE TECHNOLOGIJA PAGAMINTŲ $CdSe_xS_{1-x}$ SLUOKSNIŲ FIZINĖS IR CHEMINĖS DIELEKTRINIŲ NANOBARJERŲ SAVYBĖS

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Santrauka

Ištirta $CdSe_xS_{1-x}$ sluoksnių, pagamintų storasluoksne technologija, termoaktyvacinio proceso eiga. Pagrindinis dėmesys skirtas terminių sąlygų įtakai formuotis oksiduotiems ploniesiems sluoksniams kristalo paviršiuje vykstant nanobarjero sluoksnio „dielektrikas–puslaidininkis“ generavimui. Nanobarjero sudėtis ir storis (2–5 monosluoksniai) nustatyti Rentgeno difrakcijos ir Rentgeno fotoelektronų spektroskopijos (XPS) metodais. Parodyta, kad fotoelektrines plonųjų $CdSe_xS_{1-x}$ sluoksnių savybes lemia priemaišų įtaka ir nanobarjero sluoksnio parametrai. XRD ir skenuojančios elektroninės mikroskopijos metodais eksperimentiškai nustatyta, kad geriausia mikrosandara ir fotoelektrinės savybės ($R_D/R_L \geq 10^7$) gaunamos fotojautrio aktyvacijos metu termiškai veikiant 15–30 min kvazi-uždaroje oro atmosferoje 550 °C temperatūroje arba lėtai šaldant (3 °C/min) 5–15 min 600 °C temperatūroje. Sukurtas plonųjų $CdSe_xS_{1-x}$ sluoksnių, pasižyminčių tam tikromis savybėmis, gamybos metodas. Šias sluoksnių savybes lemia pastos sudėtis ir savybės, terminė proceso eiga bei aplinkos sąlygų optimizavimas.