

The pulsed - laser annealing effect on the structural and electrical characteristic of the CdS layers

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The effect of the pulsed – laser annealing on the parameters of CdS thin layers in the medium of oxygen was studied. The CdS thin layers were deposited by spray pyrolysis and surface treatment by nanosecond pulses of XeCl-laser. The changes in the layers were characterized by SEM, XRD and XPS. The results showed that a change in the morphology of the surface occurred; a by-surface layer consisted of CdO with high transparency and conductivity is formed in consequence of oxidation of CdS. These results are discussed in the context of window layers in solar cells.

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1. Introduction

Metal chalcogenide semiconductors of II–VI compounds have hexagonal type structure and wide energy gaps. Hence, there is great interest in the application of these compounds to various optoelectronic devices such as light detector, photoconductor, display panel, LED and recently with the development of thin-layer photocells - as optical windows for them. As an example, CdS commonly has a direct band gap of width: 2.42 eV at room temperature. CdS can be doped with Cl, Li, Cu when carrying out activation and recrystallization in mixture of suitable compounds. There are several preparation methods for CdS films such as vacuum evaporation [1, 2], screen – printing [3, 4], close – spaced sublimation [5], spray pyrolysis [6 - 9], chemical vapor deposition, electrodeposition, sol – gel, MOCVD and pulsed laser deposition [10 -14].

The spray pyrolysis deposition of CdS is a technique giving possibilities of covering large areas at low cost price and suitable for thin-layer solar cells. Forming a front contact to CdS layers with high transparency and conductivity is a target of many researches. Suitable materials are: In, ZnO, SnO₂, as well as CdO. Forming a by-layer of CdO with high conductivity is carried out in [15] by oxidation CdS at 370 ÷ 500 °C. Our preceding work [16] showed the possibilities of forming contacts by laser treatment on sintered layers of CdS and in [17] - on vacuum deposited layers.

In the present work it is shown the possibility to form local areas on the surface of the pulverization layers, which consist of CdO of high conductivity. The characteristic of the layers were studied by SEM, XRD, XPS and by four point probe conduction measurements.

2. Experimental procedure

CdS thin films were prepared at concentration of solutions 0.375 M of cadmium chloride and thiourea aqueous solution. The CdS films were deposited at the

temperature 300 °C and subsequently annealed at temperatures 450 °C for 30 min. The activation and recrystallization of the layers was carried out in air with composition of the powder matrix 89.28 mass% CdS, 8.93 mass% CdCl₂, 19 mass% CuCl and 0.6 mass% LiCl according to [18]. The films are about 1.0 – 1.1 µm in thickness.

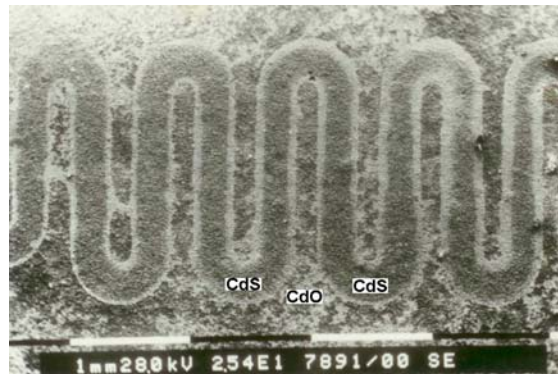


Fig. 1 Morphology of the surface. a. without surface destruction; b. with surface destruction.

A laser system was used with the aim to change the properties. It is an excimer laser EMG. Lambda Physik – 10L with parameters: $\lambda = 308$ nm (XeCl); $E_i = 150$ mJ; $P_i = 9$ MW; $f = 0 \div 100$ Hz; $\tau = 20$ ns.

Energy density and repetition frequency are chosen so that the CdS layers do not destroy or evaporate.

3. Results and discussion

A contact mask was used when processing the surface. Photos of the surface, processed by pulsed-laser radiation are given on Fig.1: a – without and b – with surface destruction.

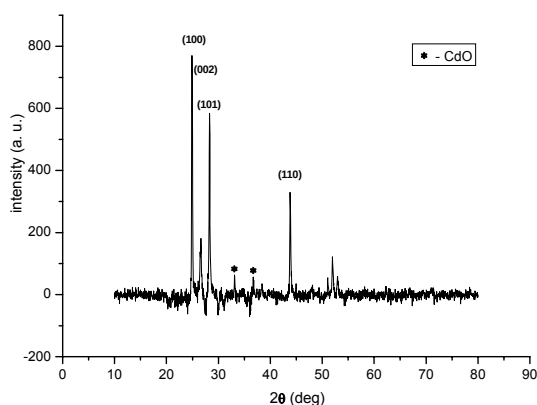


Fig. 2. XRD analysis of the CdS – CdO layer.

Fig. 2 shows XRD analysis of the CdS surface, and Fig. 3 – the XPS spectra of the CdS surface before and after pulsed-laser annealing. The XRD analysis shows the cubic CdO phase on the surface with predominant orientation (111). The measurements carried out by means of a four point probe show that the specific conductivity is $2 \times 10^{-5} \Omega^{-1} \text{cm}^{-1}$.

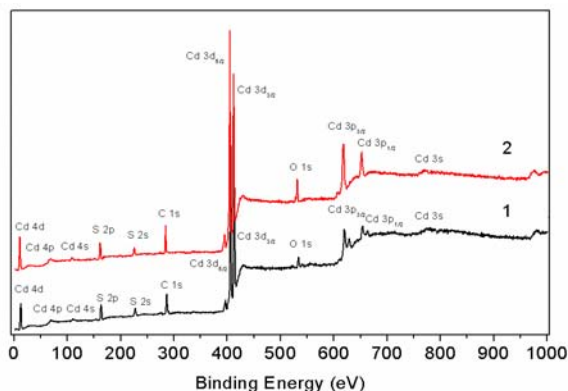


Fig. 3a. XPS spectra of CdS before 1. and after 2. laser treatment.

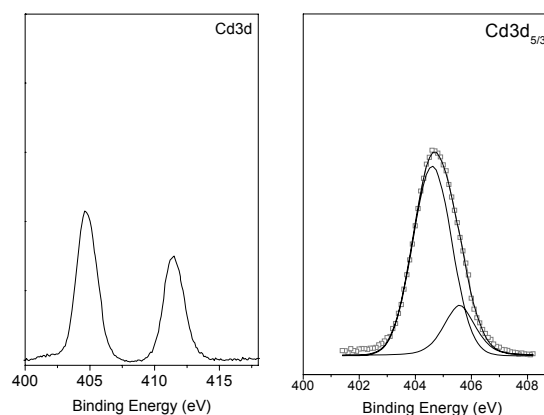


Fig. 3b. Cd 3d and Cd 3d_{5/2} XPS spectra after pulsed-laser annealing.

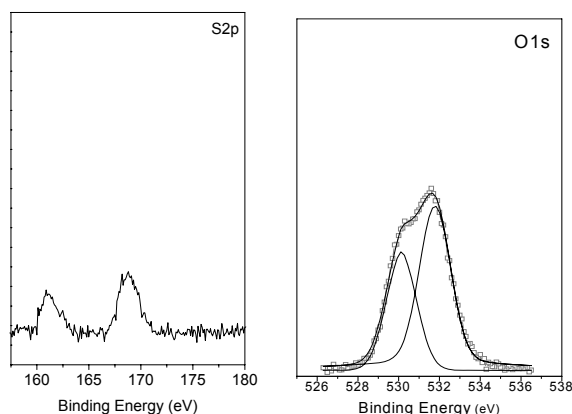


Fig. 3c. S 2p and O 1s XPS spectra after pulsed-laser annealing.

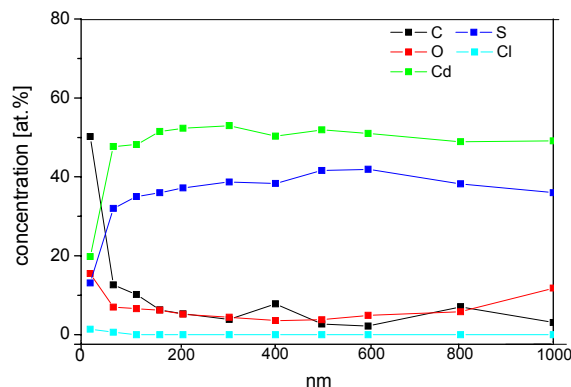


Fig. 4. Distribution of the elements in depth.

XPS spectra of sample 2 show a transformation of CdS in CdO. This is a consequence of the S2p spectrum of sulfur in which the peak characteristic of a sulfide decreases highly at 161.1 eV in intensity. Besides the Cd3d peak is displaced to lower binding energy and becomes wider. The peak splits into two parts when making deconvolution of the Cd3d_{5/2}: one of them with

maximum at 404.6 eV, which is determined by CdO and another of weak intensity at 405.6 eV corresponding to CdS. The deconvolution of the O1s peak also gives two peaks, attributed respectively to oxygen in oxide phase and connected to sulfate and carbonate groups.

An in-depth profile of CdS layers obtained by pulverization with following pyrolysis was made, shown on Fig. 4, after pulsed-laser treatment when using Ar⁺ ions with energy of 3 keV and current of 16 μ A.

An occurrence of oxygen in-depth in the layers was observed after pulsed-laser annealing with concentration of 8 – 9 % on the surface which decreases in depth up to 3–4 % and increases again when coming to the interface. The S and Cd concentration differ from the stoichiometric ratio which is due to less cadmium in the layers.

The following succession was found in-depth after a pulsed-laser treatment: CdS – Cd – CdO. The X-ray analysis shows that the composition on the surface is CdO. The CdO layer's thickness is about 80 nm, determined by selective etching with acetic acid. The XPS spectrum of a CdS layer after etching is analogous of that shown on Fig. 3 – 1, i.e. after CdO removing. The basic phase is CdS. This is shown by the binding energy of the Cd3d peak at 405.1 eV and the S 2p peak at 168.8 eV. The oxygen peak observed in O1s spectrum was determined by sulfate and carbonate groups, which were removed from the surface after ion bombardment. The presence of such groups is probably due to remnants of the interface CdO – CdS.

The formation of local areas of CdO gives possibilities of building contacts which retain the plainness of the structure and don't demand deposition of additional metal layer. These areas can be used in producing photo cells - CdS/CuInSe₂. A similar technique was used in [19], where the surface of Si is cut through by laser treatment in order to achieve effectiveness of the photo cells.

4. Conclusions

The effect of laser pulses on CdS layers has been investigated.

The formed CdO areas on CdS have high conductivity, retain the plainness of the CdS layer and are suitable for contact net of the thin-layer photo cells. Their size depends of the technological possibilities on the laser system.

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