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COMMUNICATIONS

PULSED–LASER ANNEALING EFFECT ON STRUCTURAL AND ELECTRICAL CHARACTERISTICS OF CdS LAYERS

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The effect of 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 a 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 consisting of CdO with high transparency and conductivity is formed as a consequence of oxidation of CdS. These results are discussed in the context of window layers in solar cells.

K e y w o r d s: CdS, spray pyrolysis, laser annealing, CdO, SEM, XRD, XPS

1 INTRODUCTION

Metal halogenide semiconductors of II–VI compounds have a hexagonal structure and wide energy gaps. Hence, there is a great interest in the application of these compounds in 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 of 2.42 eV at room temperature. CdS can be doped with Cl, Li, Cu when carrying out activation and recrystallization in a 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 vapour deposition, electrodeposition, sol-gel, MOCVD and pulsed laser deposition [10–14].

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, SnO_2, as well as CdO. Forming a by-layer of CdO with high conductivity is carried out in [15] by oxidation CdS at 370 to 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 a possibility of forming local areas on the surface of the pulverization layers is shown which consists of CdO with high conductivity. Characteristics of the layers were studied by SEM, XRD, XPS and by a four-point probe.

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 300 °C and subsequently annealed at 450 °C for 30 minutes. Activation and recrystallization of the layers was carried out

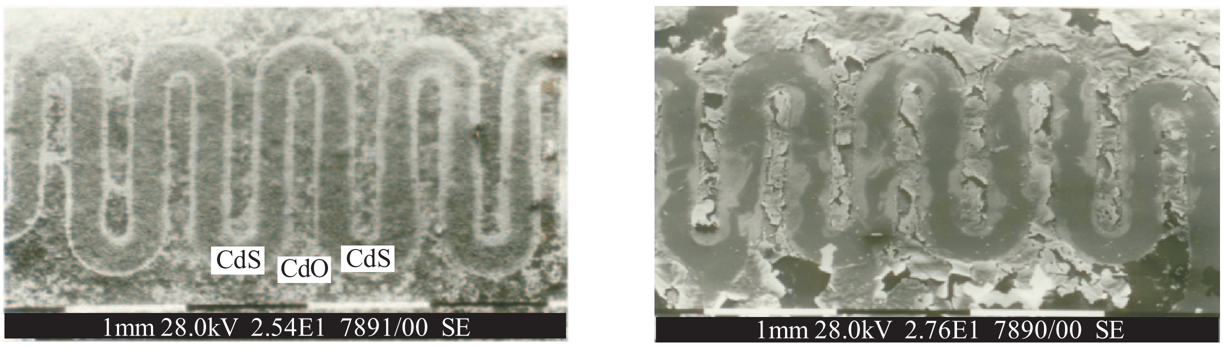

Fig. 1. Morphology of the surface: a) without surface destruction, b) with surface destruction

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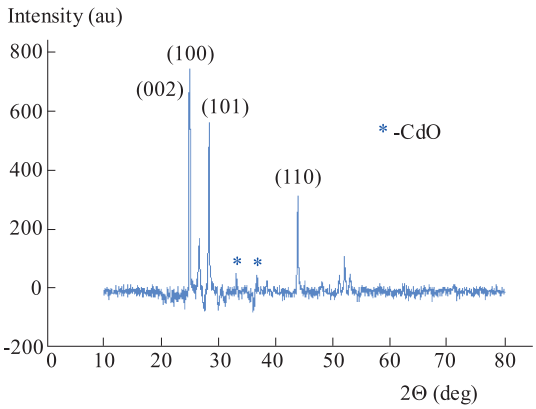

Fig. 2. XRD analysis of the CdS–CdO layer

in an air medium with composition of the powder matrix 89.28 mass% CdS, 8.93 mass% $CdCl_2$, 19 mass% CuCl and 0.6 mass% LiCl according to [18]. The films are about 1.0–1.1 μm in thickness.

A laser system was used for purposefully changing the properties with the following parameters: Excimer laser EMG. Lambda Physik — 10L with parameters: $\lambda = 308$ nm (XeCl), $E_i = 150$ mJ, $P_i = 9$ MW, $f = 0$ to 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. Micrographs of the surface processed by pulsed-laser radiation are given in Fig. 1: a – without, and b – with surface destruction.

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

XPS spectra of sample 2 show a transformation of CdS in CdO. This is a consequence of the S 2p spectrum of sulphur in which the peak characteristic of sulphide decreases highly at 161.1 eV in intensity. Besides, the Cd 3d peak is shifted to a lower binding energy and becomes wider. The peak splits into two parts when making deconvolution of the Cd $3d5_{/2}$: one of them with maximum at 404.6 eV, which is determined by CdO, and another poorly intensive at 405.6 eV corresponding to CdS. Deconvolution of the O1s peak also gives two peaks, attributed respectively to oxygen in oxide phase and connected in sulphate and carbonate groups.

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

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

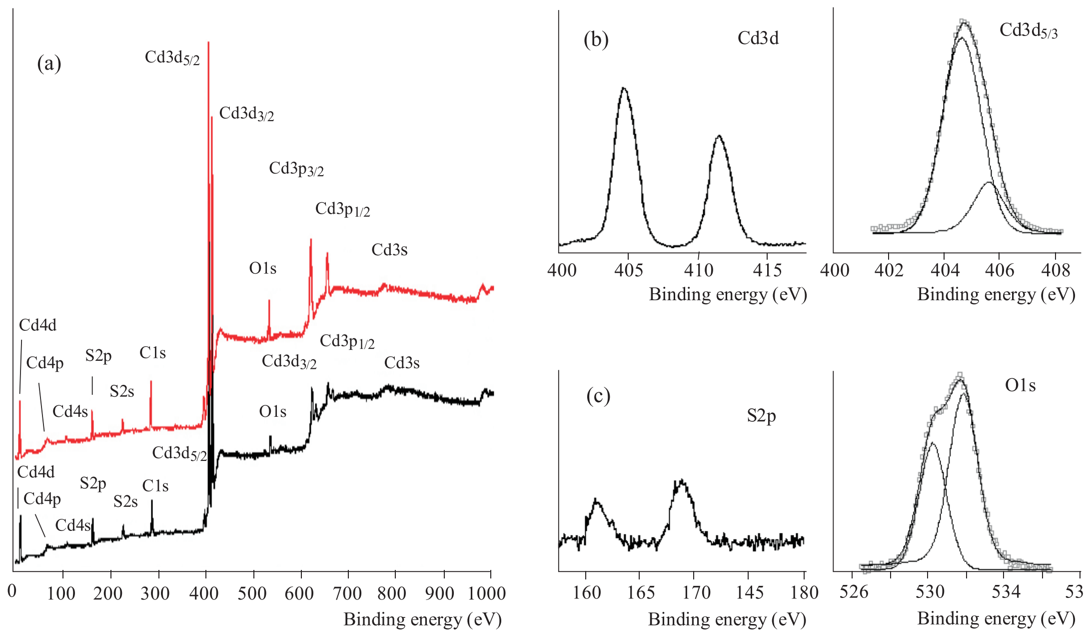

Fig. 3. (a) XPS spectra of CdS before (1) and after (2) laser treatment, (b) Cd 3d and Cd $3d_{5/2}$ XPS spectra after pulsed-laser annealing, (c) Sulphur 2p and Oxygen 1s XPS spectra after pulsed-laser annealing

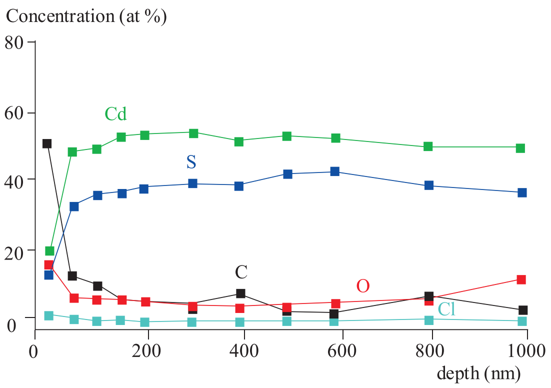

Fig. 4. In-depth distribution of elements

The following succession was found in-depth after pulsed-laser treatment: CdS–Cd–CdO. X-ray analysis shows that the composition on the surface is CdO. The CdO layer thickness is about 80 nm, determined by selective etching with acetic acid. The XPS spectrum of a CdS layer after etching is analogous to that shown in Fig. 3, *ie* after CdO removing. The basic phase is CdS. This is shown by the binding energy of the Cd3d peak 405.1 eV and the S 2p peak at 168.8 eV. The oxygen peak observed in O 1s spectrum was determined by sulphate 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.

Formation of local areas of CdO gives possibilities of building contacts which retain the plainness of the structure and do not demand deposition of an additional metal layer. These areas can be used in producing photo cells — $CdS/CuInSe_2$. 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 formed CdO areas have high conductivity, retain the plainness of the CdS layer and are suitable for a contact net of thin-layer photo cells. Their size depends on the technological possibilities of the laser system.

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