XRD, XPS AND SEM CHARACTERIZATION OF PHOTOCONDUCTIVE CDS – CDO LAYERS DEPOSITED BY VACUUM THERMAL EVAPORATION

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The photosensitivity of the CdS layers obtained by vacuum thermal evaporation depends of the carried out activation and recristalization. A method of activation and recristalization of the CdS layers is suggested where the diffusion of the impurities is carried out through a thin layer (10 - 30 nm) with composition CdO.

Keywords: CdO, CdS, XPS, Solar cells

1. INTRODUCTION

The polycrystalline layers from CdS, as a component of the thin-layer solar cells were put to thermal treatment in fixed medium independently from the method of their obtaining. The influence of the intercrystal barriers was reduced as a result of this technological operation, the phase CdO appeared with conductivity of the order of $10^{-5} \ \Omega^{-1}$ cm⁻¹. The heterojunction CdS – CdO is a target of variety of studies which aim is to determine the possibilities of its application in the thin layer solar cells. The manufacturing process optimization will widen the possibilities of using the CdO layer as a high conductive and transparent layer. When carrying out conventional thermal treating the whole CdS surface was covered with a CdO layer, and when carrying out impulse-laser treating – only the locations of the treatment.

2. EXPERIMENTAL PROCEDURE

A CdS layer, obtained by vacuum thermal evaporation is put to pulse rate laser treatment according to the methodic given in [1-3]. The so formed two-layer structure CdS – CdO is put to activation and recristalization in a powder matrix which is composed of CdCl₂, CuCl, LiCl, CdS and CdO, at temperature 450 - 500 °C, during 30 min in O_2 medium. The cooling velocity of the samples is 20 °C/15min. The layer with CdO composition is removed by a solution containing CH₃COOH. The technological sequence of activation and recristalization is repeated for a part of the first set of samples with the purpose of comparing of following change of their parameters.

XRD, XPS and SEM measurements

X-ray analysis was carried out with a DRON-2 X-ray diffractometer using a Co anode, K_{α} radiation and Ni filter for β radiation.

The XPS studies were carried out in an Escalab Mk II (VG Scientific) electron spectrometer with base pressures in the preparation and analysis chambers of 2.10^{-8} and 1.10^{-8} Pa, respectively. SEM micrographs of the samples were obtained by a Philips SEM 525M Scanning Electron Microscope with a spot size of 100 Å using a

secondary electron (SE) detector, a transmitted electron (TE) detector and signal differentiation.

3. RESULTS AND DISCUSSION

3.1. XRD study

Fig. 1 shows an X-ray diffraction (XRD) pattern of an as-deposited CdS layer (CdS N_{2} 1) obtained by vacuum thermal evaporation and an annealed CdS layer (CdS N_{2} 2). As a result of vacuum thermal evaporation of CdS on the cital substrate, columnar hexagonal phase crystallites with (002) orientation are deposited parallel to the surface. The evaporated CdS layers are highly faulted. The fault stacking is cubic while the planes above and below are hexagonal. Thermal treatment at 450 °C leads to recrystallization of cadmium sulfide and, whence, to a change in orientation of the CdS crystallites and prevalence of the hexagonal phase in the X-ray pattern of sample CdS N_{2} . The high intensity of the (002) peak may be due not only to the hexagonal CdS but also to the presence of a (111) peak of cubic CdS.

3.2. XPS study

XP spectra of CdS layers obtained by vacuum thermal evaporation on a cital substrate prior to (1) and after (2) thermal treatment in a powder are compared in Fig. 2 within the 5 – 1005 eV binding energy range. In contrast to the untreated CdS layer (1), the surface of the CdS treated (2) in the above layer displays additionally Cl 2p, Cl 2s and Cu 2p. The position of Cd 3d of the untreated CdS layer (1) is at 405.3 eV and corresponds to cadmium present as CdS. The halfwidth of Cd $3d_{5/2}$ after heat – treatment increases from 1.7 eV to 3.0 eV and the peak position is shifted to the high binding energies due to the formation of CdCl₂ on the surface of the CdS layer. The position of Cl 2p is at 199 eV and corresponds to chlorine in the from of CdCl₂. As a result of the thermal treatment, the cadmium chloride concentration on the CdS layer surface increases. It is known from the preparation of CdS/Cu₂S solar cells that the reaction

$$2CuCl + CdS \rightarrow Cu_2S + CdCl_2 \tag{1}$$

may proceed on the surface of the CdS layer in the presence of CuCl. The binding energy of S 2p at 161.7 3V corresponds to S present as CdS, formation of Cu₂S with a binding energy at 161.3 eV being also probable. The additional peak of S 2p at 169.7 eV corresponds to sulfur in the form of $SO_4^{2^-}$, the probable sulfates appearing on the surface being CuSO₄ at a binding energy of 169.3 eV and CdSO₄. This additional peak is due to oxidation of the sulfur on the CdS layer surface under the effect of oxygen from the air during the thermal treatment at 450 °C for 15 min. On the surface of as – deposited CdS, O 1s is positioned at a binding energy of 532 eV and corresponds to chemisorbed oxygen formed according to the reaction

$$O_2 + 4e^- = 2O^{2-}$$
 (2)

the electrons being supplied through photogeneration of charge carries. It should be noted that the intensity of O 1s increases after the thermal treatment and is shifted to the high binding energies. This is due to the binding of oxygen on the surface as sulfates. The position of Cu 2p at a binding energy of 932.5 eV corresponds to Cu⁺ in the form of Cu₂S. As a result of the thermal treatment of the CdS layer in a powder (CdS, CdCl₂ and CuCl), Cu⁺ with an ionic radius of 0.96 Å replaces Cd²⁺ (0.97 Å) in the CdS layer and diffuses into the depth. The calculated concentrations of the elements on the CdS layer surfaces in atomic percents are: Cd : S : Cl : O = 46.05 : 42.10 : 1.20 : 10.65 for as-deposited CdS and Cd : S : Cl : O : Cu = 25.75 : 21.50 : 17.37: 35.34 : 0.03 for annealed CdS. The stoichiometry of the as-deposited CdS layer is Cd : S = 1.09, while for the annealed CdS layer Cd : S = 1.20. As a result of the thermal treatment the cadmium amount on the layer surface increases due to oxidation of the sulfur in CdS to sulfates under the effect of the oxygen in the air. Thus, the amount of sulfur present as sulfides on the layer surface is 9.92 at % S, whereas the sulfur amounts to 11.58 at % S.



Fig. 1 X – ray diffraction pattern of CdS prepared by the vacuum thermal evaporation:CdS No1 as deposited, CdS No 2 - annealed in powder (CdS, CdSI, CuCL) at 450 $^{\circ}$ C.



Fig. 2 Cd 3d photoelectron spectra of CdS layers, dots - experimental spectrum, solid line FFT Filter smoothing spectrum of 2 pts: (1) asdepoisted by vacuum thermal evaporation : (2) annealed in powder (CdS, CdCl, CuCl) at 450°C.

3.3. SEM study

Fig. 3 shows the results from a SEM study of the CdS layers. Fig. 3 (1) presents a SEM picture of a cital substrate taken with 50 % SE and 50 % TE detectors. It should be noted that the substrate surface is uniform and the grains are small – sized. Fig. 3 (2) shows a picture of the cital substrate surface after deposition of a CdS layer by vacuum thermal evaporation. In this case, 25 % SE and 75 % TE detectors are used. In addition to large included particles, evaporated films can contain nodules. After exposure the head – treated CdS layers, the exposed part of the surface becomes quickly darker due to layer photosensitivity.

The used method of oxidation of the CdS until it is covered with a CdO - layer allows removal of layers of the CdS surface, while maintaining the photosensitivity which coincides with the results in [4].





Fig. 3 SEM photo of treated 2 and not treated 1 surface

4. Conclusion

Using of vacuum thermal evaporation layers of CdS on a cital substrate and thermal treatment of the layers in a powder of CdS, $CdCl_2$ and CuCl, the photosensitivity of the CdS layers has been improved by 6 orders of magnitude, which makes them suitable for photoresistrors.

1. As a result of thermal treatment of CdS layers obtained by vacuum thermal evaporation, doping with Cl^- and Cu^+ microimpurities occurs, followed by recrystallization of CdS, its hexagonal from prevailing. The presence of the elements Cd, S, Cl and Cu as CdS, CdCl₂, CdSO₄ and Cu⁺ incorporated in the CdS crystal lattice is established on the surface of photosensitive CdS layers.

2. The enhanced photosensitivity of the CdS layers has a complex character and is due to recrystallization of CdS accompanied by formation of a small – grain hexagonal structure. The stoichiometry of the main components is: Cd : S = 1.2, chlorine doped with 17 at % Cl, copper doped with 0.03 at % Cu, an enhanced oxygen concentration up to 35 at % O, and sulfur oxidation to $SO_4^{2^-}$.

3. The results of using a 10nm thick buffer layer of CdO show that heterojunction CdS - CdO is a suitable decision when carrying out activation and recristalization.

5. References

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