Investigation the structures CdSe/CdS, CdS/CdSe for production of solar cells

Ruslana Guminilovych[1], Pavlo Shapoval[1], Yosyp Yatchyshyn[1], Viktor Kusnezh[2], Martyn Sozanskiy[1], Hryhoriy Il'chuk[2]

1. Analytical Chemistry Department, Lviv Polytechnic National University, UKRAINE, Lviv, S. Bandera Street 12, E-mail: guminilovych@gmail.com

2. Physics Department, Lviv Polytechnic National University, UKRAINE, Lviv, S. Bandera Street 12, E-mail: w_kusnierz@polynet.lviv.ua

Abstract – The process of obtaining CdS and CdSe thin films by a chemical surface deposition method (CSD) has been investigated. The optical transmission, absorption spectra, surface morphology of films and degree of phase uniformity, crystallinity of structures based on CdS and CdSe films have been studied.

Key words – semiconductor films, chemical surface deposition, structure and morphology of thin films, solar cells.

I. Introduction

At the present stage of development of photosensitive thin film heterostructures based on cadmium chalcogenides Cd(S, Se, Te), the demands for specific surface properties of the semiconductors, e.g. surface roughness, purity, homogeneous distribution of surface macrodefects over large areas, have sharply increased. This is due to the fact that the surface morphology of the films determines the electrophysical properties of the interface.

Due to their semiconducting properties such as a large band gap, photoconductivity, photovoltaic, photochemical and fluorescent properties, the ability to reflect the visible area of the spectrum of radiation and to absorb in the ultraviolet region, as well as small coefficient of linear expansion CdS and CdSe films are widely used in the production of highly efficient solar cells, semiconductor lasers, photoresists, X-ray detectors, phosphors.

Combining CdSe and CdS in a single nanostructure creates a material with heterogeneous carrier confinement or "mixed dimensionality" where holes are confined to CdSe while electrons can move freely between CdSe and CdS phases, spreading over the entire structure [1]. The CdS can behave as an efficient antenna, absorbing light and funneling the excited carriers into the CdSe core where they recombine [1]. In addition, CdSe/CdS structures exhibit novel properties originating from the concept of "mixed dimensionality": universal correlation between the spectral linewidth and the position of the excitonic transition in the single particle spectral jitter [2], giant Stark effect, the possibility of manipulating lifetimes by applying an external electric field (exciton storage) [3].

Development of CdSe/CdS heterostructures with different morphologies will provide new possibilities for wave function engineering and in tailoring optical and optoelectronic properties of semiconductor structures. A CdSe-based system exhibiting a different band alignment is the CdSe/CdS structure. Because of the high surface to volume ratio of films, the surface properties have significant effects on their structural and optical properties.

II. Experimental

The obtaining of CdS and CdSe semiconductor films is carried out by many methods. Technologically convenient way to their obtaining is the method of chemical surface deposition (CSD) [4]. Compared with the other it allows to pursue the deposition at temperatures below 100 ^{0}C on the large-sized substrates of different nature and use different combinations of starting substances.

The deposition of thin films of cadmium sulfide (CdS) was conducted with the initial working solution which consisted of cadmium chloride $CdCl_2$, thiourea $CS(NH_2)_2$ and 14.28 M solution of the ammonium hydroxide NH_4OH. The working solution which consisted of cadmium chloride $CdCl_2$ and sodium selenosulphate Na_2SeSO_3 was used for the deposition of cadmium selenide thin films (CdSe). Only freshly prepared reagents entered the working solutions for CSD of CdS and CdSe thin films.

Cadmium chloride has been the source of Cd^{2+} ions, thiourea – S^{2-} ions and sodium selenosulphate – Se^{2-} ions. Sodium selenosulphate was prepared by dissolving selenium powder in the aqueous solution of sodium sulfite (Na_2SO_3) at 60 ^{0}C under constant stirring for 3 h. After the end of the reaction the solution was cooled and filtered. The concentration of the solution cadmium chloride was equal to 0.01 M; thiourea – 1 M; sodium selenosulphate – 0.1 M. The deposition time varied from 3 to 24 min. The temperature CSD was 70 ^{0}C.

The deposition has carried out on pre-prepared and thermostated glass substrates area of 3.96 cm^2 by the method [4]. The dosed causing of the working solution has ensured the uniform heating of the surface substrate and, therefore, uniform deposition of films. The substrate was eliminated after heating the surface was washed with a jet of distilled water and was dried in air.

The investigation of surface morphology of the films was carried out using a scanning electron microscope EVO-40XVP (Carl Zeiss, Germany) with a system of microanalysis INCA Energy 350 (Oxford Instruments, England) and atomic force scanning probe microscope Solver P47 PRO (NT-MDT, Russia).

Absorption-transmittance optical spectra of CdSe and CdS films were obtained with a spectrophotometer AvaSpec-ULS2048 (Avantes, Netherlands). A comparative signal was passed through a substrate identical to the substrates used for the investigated films.

Crystallinity of CdSe and CdS films was investigated by the automatic X-ray diffractometer HZG-4A, using data on the reflection of the X-ray beam. Experimental arrays of small-angle X-ray diffraction intensities of CuK_α radiation were obtained by sequential scanning method (range of angles 10-100^0, step 0.0500). Optimum exposure for each of the samples was selected.

III. Results and discussion

The structural analysis of CdSe and CdS films on glass substrates has been held. Peaks that corresponded to the cubic phase of CdS (Fig. 1) and CdSe (Fig. 2) on all diffractograms can be identified, but the highest intensity have peaks of 26.45^0 and 25.59^0, accordingly. The diffractograms of cubic and hexagonal phases are shown for comparison. Except maximum peaks, significant number of peaks that corresponded to a mixture of two structural phases (cubic and hexagonal) is present.

The optical transmission spectra of the obtained structures were investigated. The spectral dependences of optical transmittance, which indicate the existence of CdS and CdSe compounds, are shown on Fig. 3.

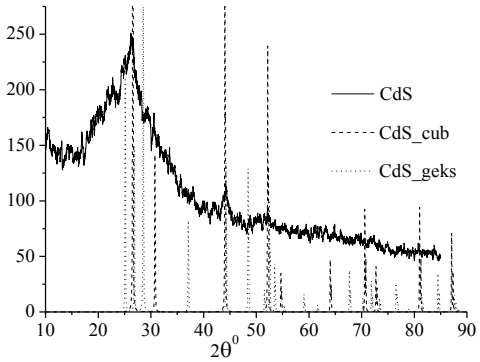

Fig. 1. X-ray diffractograms of structure CdS/CdSe

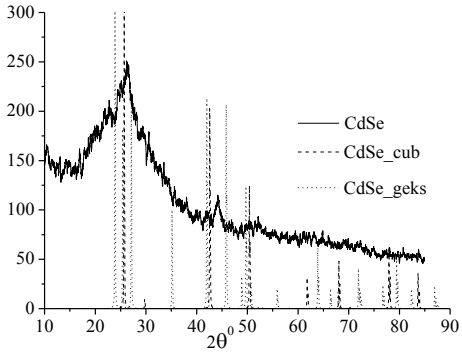

Fig. 2. X-ray diffractograms of structure CdSe/CdS

Deposited films are polycrystalline as seen from Fig. 1 and Fig. 2. Structures having the same properties were obtained regardless of the sequence of deposition (cadmium sulphide film on the cadmium selenide film or conversely). It can be concluded that the films are mutually insoluble and each next layer does not destroy preceding layer and does not change their structure.

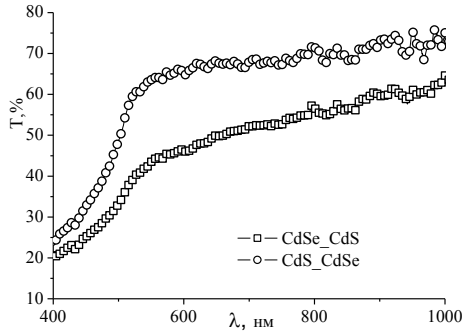

Fig. 3. The spectral dependences of optical transmission of CdS and CdSe films in the CdSe/CdS and CdS/CdSe structures

An increase in transmittance was observing for all samples in the transition from short-wavelength region to long-wavelength, similarly, as for CdS films or for CdSe films. Maximum values of the absorption were observed for the structures of CdSe/CdS (i.e. during deposition of cadmium selenide on cadmium sulfide). Absorption reaches 67% and 76% in the short-wavelength and long-wavelength regions, accordingly.

Investigation of structures surface morphology (Fig. 4 and Fig. 5) showed that the substrate is completely covered by the films. As seen from micrographs, macrodefects of two types: in the form of pores and in the form of conglomerates particles, are on the surfaces of substrates. Moreover, the nature of defectiveness is the same for both structures. The surface macrodefects are formed on the final stages of growth, when conditions for hetero epitaxial growth of films already has not fulfilled.

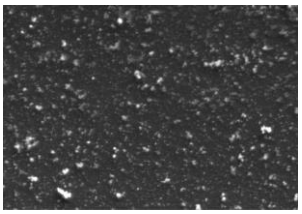

Fig. 4. Surface morphology of the CdSe/CdS structure

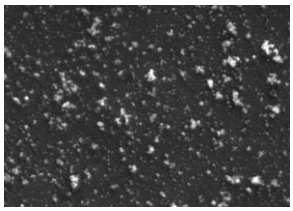

Fig. 5. Surface morphology of the CdS/CdSe structure

Macrodefects in the form of particles on the surface, are the particles of CdS and CdSe with stoichiometry other than in the film, was set.

Conclusion

Thus, the opportunity of using the CSD method for the synthesis of not only double structures, but and perspective modification of method for creating ternary, quaternary heterostructures etc. were shown. Benefits of chemical surface deposition, which allows significantly to reduce and to simplify the process of creating solar cells that can be the basis for the mass production of solar cells and solar modules, were proven.

References

[1] Talapin D. V. «Highly emissive colloidal CdSe/CdS heterostructures of mixed dimensionality» / D. V. Talapin, R. Koeppe, S. Götzinger et. all // Nano Letters, 3 (12), pp 1677–1681, 2003.

[2] Muller J. «Signatures of surface charge migration in the spectral diffusion of single elongated CdSe/CdS nanocrystals» / J. Müller, J. M. Lupton, A. Rogach et. all // Physical Review B 72, pp. 205339, 2005.

[3] Becker K. «Electrical control of Förster energy transfer» / K. Becker, J. M. Lupton, J. Müller et. all // Nature Materials 5, pp. 777 – 781, 2006.

[4] Il'chuk H. «Chemical surface deposition of CdS ultra thin films from aqueous solutions» / H. Il'chuk, P. Shapoval and V. Kusnezh // Solar Cells – Thin-Film Technologies, edited by Leonid Kosyachenko ISBN: 978-953-307-570-9, pp. 381-404, 2011.