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SOME FEATURES OF ELECTROCHEMICALLY DEPOSITED CdS NANOWIRES

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The crystallographic structure and elemental composition of cadmium sulfide (CdS) nanowires (NW) with diameters ranging between 30-40 nm were prepared by means of electrodepositing CdS from non-aqueous solution containing cadmium chloride (0.2 M $CdCl_2$), sulfur(0.02 M S_8), and ammonium chloride (0.1 M NH_4Cl) dissolved in ethylene glycol at T = 120-130^0 C and deposited at 90-100^0 C into pores of anodic aluminum oxide. CdS-deposited nanowires were examined by means of energy dispersion X-ray spectrometry (EDX), X-ray diffractometry (XRD), Raman scattering and photoluminescence (PL)spectra. It was determined that the selected electrolyte composition and electro-deposition conditions make it possible to form the CdS nanowire with a predominantly hexagonal modification while the stoichiometric composition is suitable for the use in solar energy converters.

Keywords: *nanowire, cadmium sulfide, electrochemical deposition, non-aqueous solution, ethylene glycol, XRD, EDX, Raman scattering, photoluminescence spectra*

INTRODUCTION

Currently, CdS is widely used in solar photovoltaic (PV) converters as a transparent conductive barrier layer. Cadmium sulfide (CdS) is a commonly used n-type semiconductor as a window layer for hetero-junction solar cell application. By selecting proper p-type semiconductor as an absorber layer, researchers have developed many kinds of hetero-junction solar cells, among which CdS/Cu_2S, CdS/CdTe, and CdS/ CdS/$CuInGaSe_2$ combinations are the most promising solar cells [1].

The deposition of CdS films and nanowires (NW) was explored using different techniques: magnetron sputtering [2,3], sol-gel process [4], chemical bath deposition and electrodeposition [5-7]. The electrochemical deposition is widely used in the manufacture of solar cells due to low costs, relative simplicity in the production of NW and possibility to obtain high-quality polycrystalline NW of stoichiometric composition on substrates with a large surface area [4-6]. This feature of electrochemical deposition is especially important for mass production of solar cells. In addition, by controlling the potential of the working electrode in this deposition technology, it becomes possible to produce semiconductor layers with predetermined composition and properties. The growth of NW in the course of electrochemical deposition occurs under equilibrium conditions, which makes it possible to reduce the concentration of defects. This method is effective in obtaining NW as compared with other deposition methods. Despite the availability of a great number of publications devoted to the synthesis of CdS NW, the structure and phase composition of the synthesized NW remains insufficiently studied.

We have chosen method from non-aqueous solution to deposition route to deposit CdS thin film over glass sample because it offers deposition over a large area. It also

provides other advantages, such as low temperature operation and economic feasibility. Many authors succeeded in gaining the highest efficiency due to this method and growing transparent optic window for CdTe and CIGS solar cells [4-6]. In this work, we report CdSNW grown in pores of AAO templates at 90 ± 2º C by electrochemical deposition from containing 0.2 M $CdCl_2$, 0.02 M S_8, 0.1 M NH_4Cl dissolved in ethylene glycol (non-aqueous solvent) and its characterization by various techniques like XRD, SEM, Raman spectroscopy and PL spectroscopy.

EXPERIMENTAL DETAILS

The indium-tin oxide (ITO) and aluminum layers were deposited on glass substrates by reactive high-frequency magnetron sputtering method onZ-550 Leybold-Heraeus unit in a mixture of argon and oxygen inside the chamber [7,8]. Then nanoporous anodic aluminum oxide (AAO) templates were prepared through the two – step anodisation process in a 0.1Moxalic acid solution, as described in detail in [7-9]. The electrodeposition of CdS nanowire into the AAO pores was carried out by potentiostatic method in a homemade two-electrode electrochemical cell equipped with a temperature sensor, an electric heater and an electric mixer from the non-aqueous solution containing 0.2 M $CdCl_2$, 0.02 M S_8, 0.1 M NH_4Cl dissolved in ethylene glycol at T=130^{0}C. Electrochemical deposition was carried out in potentiostatic conditions at 90 ± 2º C.The electrolyte was constantly mixed, the deposition time was 10-100 sec, and the current density was 15mA / cm^2. Then the samples were washed in acetone to remove residual sulfur and finally dried in nitrogen and annealed in air at 400^{0}C for 20-30 minutes.

The structural analysis of the grown NW was carried out on a Rigaku X-ray diffractometer of the Miniflex 500 model with CuKα radiation (λ = 1.5418Å). Note that Energy Dispersion X-ray analysis (EDAX) was also carried out through the use of Bruker Nano GmbH, b Berlin, Germany, whereas Raman and Photoluminescence spectra - by means of confocal laser spectroscopy (model "Tokyo Instruments"). XRD patterns have been recorded over the range of 20°-75° at the scan rate of 2°/min.

RESULTS AND DISCUSSION

The resulting CdSNW electrodeposited in Al_2O_3 pores were optically transparent over a wide spectral range. The diameter of the grown CdS NW ranged between 20-40 nm depending on the duration of deposition process. The EDAX spectrum (Fig.1) of CdS NW exhibits peaks of Cd, S, O, Na, K, Si, and In series with Cd:S=36,73:35,60 indicating the films to be Cd-stoichiometric, perhaps, due to the greater reactivity of Cd ions than S ions.

Comparing the intensities of the Cd (36.73% at) and S (35.6% at) peaks, it may be inferred that the composition of CdS is close to stoichiometry. The presence of In and oxygen with ITO layer is observed.

In addition to Cd and S peaks, Si and O signals are also observed. The Si signal is from glass substrate. The presence of oxygen is, perhaps, associated, first of all, with substrate, as well as oxides of In_2O_3 and SnO_2, constituting ITO. Besides, as shown below, the X-ray diffraction of the structure shows the presence of an impurity phase of CdO which follows from the CdS oxidation in air. Therefore, the presence of oxygen in the system is a result of the same factor.

X-ray diffraction pattern of the Al_2O_3/ITO/glass and CdS NW grown in Al_2O_3/ITO/glass substrates is shown in Fig.2a, and 2b respectively. It contains more than 18 peaks of varying intensity and blur. In Fig.2ITO

the peak at 2θ=22,020 is solely available while the broad peak resulting from the Al_2O_3 indicated that AAO is amorphous.

The observed values of inter planar spacing (d), miller indices (hkl) as well as basic and impurity phases of CdS NW are presented in the Table.

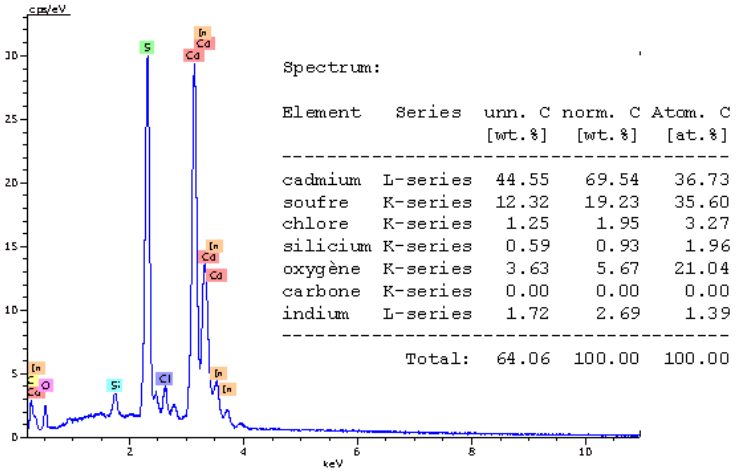

Fig.1. EDAX spectrum (a) and elemental composition of CdS

Table . The observed values of lattice spacing (d), miller indices (hkl) and basic phase of CdS.

peaks No	2θ	d, Å	Muller Index (hkl)	Basic phase of CdS	Impurity phases
1	22.020	4.12212	_	_	(ITO*)
2	24.874	3.57668	100	Hexagonal	_
3	26.527	3.3660	002 or (111) (**)	Hexagonal or cubic (**)	**(**)**
4	28.247	3.1568	101	Hexagonal	_
5	31.458	2.916	-	_	(ITO*)
6	34.145	2.704	-	_	(ITO*)
7	36.682	2.44793	102	Hexagonal	-
8	38.657	2.2704	-	_	CdO
9	43.805	2.06499	110	Hexagonal	-
10	43.889	2.06121	220	_	Cubic
11	47.905	1.89741	103	Hexagonal	_
12	51.028	1.78834	200	Hexagonal	_
13	51.944	1.75894	112	Hexagonal	_
14	51.98	1.75781	311	_	Cubic
15	52.943	1.7281	201	Hexagonal	-
16	54.478	1.68297	222	_	Cubic

17	54.626	1.67875	004	Hexagonal	_
18	58.422	1.5784	202	Hexagonal	_

Notes: (*)Peaks number 1, 5 and 6 are related to ITO.
(**)It is known that high quality as-deposited CdS NW have just one preferred orientation corresponding to either cubic (111) or hexagonal (002), but it is difficult to distinguish these two phases based on the XRD peak position [10].

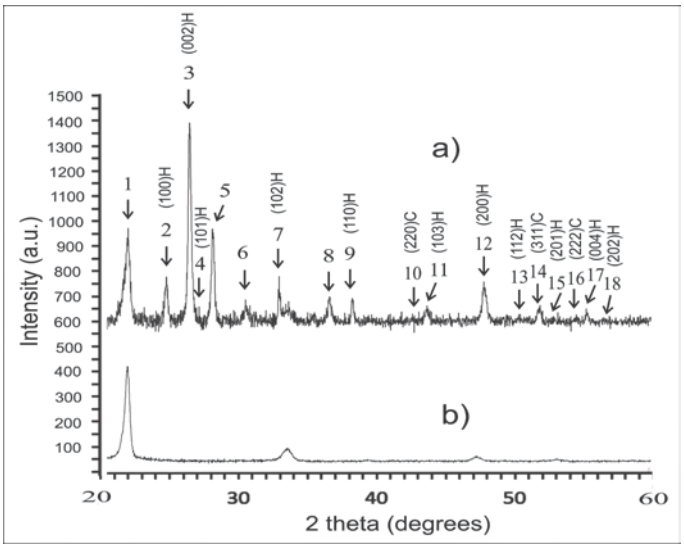

Fig. 2. XRD pattern of CdS/Al_2O_3/ITO/Glass (**a**) and Al_2O_3 /ITO/Glass (**b**) system.

As shown in Table, the observed diffraction peaks are formed mainly by the CdS planes of the hexagonal modification (belonging to the space group P-63mc (186)) by responses from the ITO layer (peaks Nos.1,5 and 6), planes (220), (311) and (222) CdS of the cubic modification (space group F-43m (216)), as well as response from the CdO phase (peak No. 8). Taking into account the relatively low intensities of the response from the cubic phase and CdO, we regard it as the impurity phase, and the hexagonal phase as the main phase. As has been noted in [11], the blurriness of some peaks with a width of some 1° reveals the nanocrystalline structure of the material. The narrowest and most intense reflex (peak No.3) and, correspondingly, the structure with greater crystallinity, is observed for the (002) plane of the hexagonal modification of CdS. Therefore, crystal growth occurs mainly in the plane corresponding to this reflex, which is very typical for thin-film CdS [10]. The presence of an impurity phase of CdO is apparently due to the oxidation of CdS in air. The average size d(Å) of CdS crystallites was deduced to be~ 35nm from the peak No. 3 ofthe experimental XRD pattern using the Debye-Scherer formula $d = k\lambda/\beta\cos\theta$, where $\theta(13.25°)$- is the maximum scattering Bragg angle, $\beta(0.23°)$- is the full width half maxima (FWHM) of the diffraction peak, $k\approx0.89$ is Scherer factor for spherical nanoparticles, λ- implies the wavelength of the X-ray used.

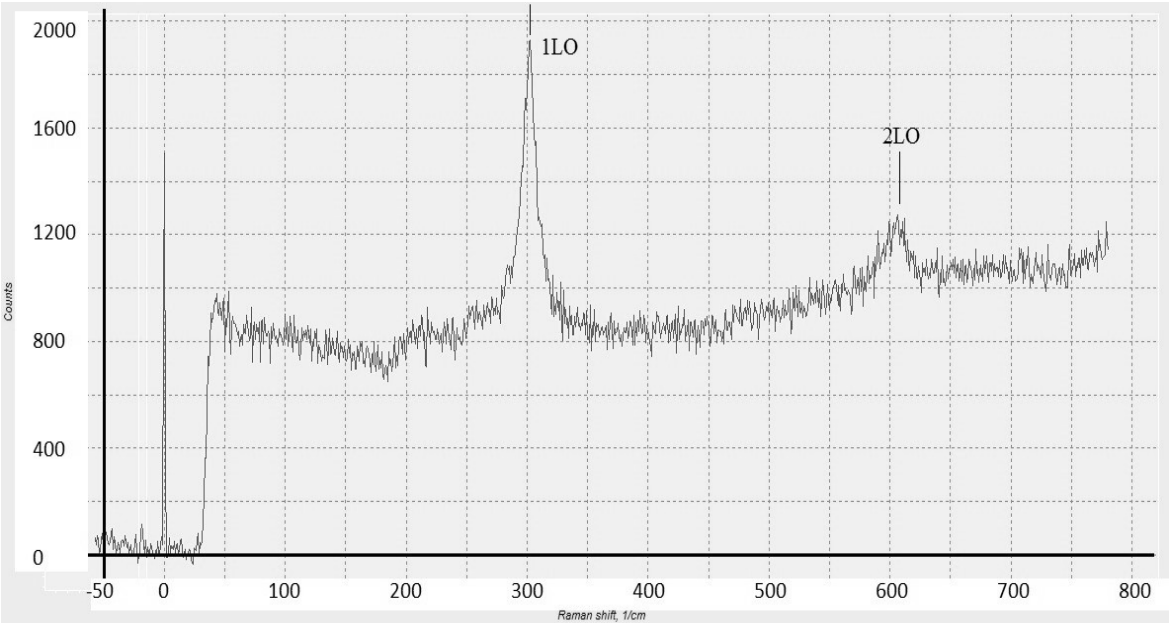

Fig.3. The Raman spectrum of CdS NW/ITO/glass system.

Figure 3 shows the spectrum of Raman scattering of CdS NW taken in the backscattering configuration and analyzed by using the model of "Tokyo Instruments" spectrometer at room temperature. As an excitation source we used the 532 nm line of an Ar – iron laser. The dominant structure in these spectra is longitudinal mode at 305 cm^{-1} and its first overtone at 611 cm^{-1}, which is consistent with the fact that the one of the striking features of the Raman spectra CdS is the remarkable overtones series of the longitudinal optical phonons [12].The peak corresponding to the optical background mode (1LO) of the first order is inherent in the hexagonal (wurtzite) modification of CdS, as well as the peak at 605 cm^{-1} corresponding to the optical background mode CdS (2LO) of the second order and corresponding to the cubic (sphalerite) modification of CdS. The presence of these peaks is confirmed by the data obtained on the basis of the difractogram.

The room-temperature photoluminescence (PL) measurement results of the CdSNW in their AAO matrix are shown in Figure 4. The excited wavelength made up 532 nm (which was apparently weaker than the edge of CdS' own absorption), and no filter was used. Although some short wavelengths had been used as excitation light in PL measurements, only one emission band with a maximum at about 760 nm could be observed and its intensity was relatively weak.

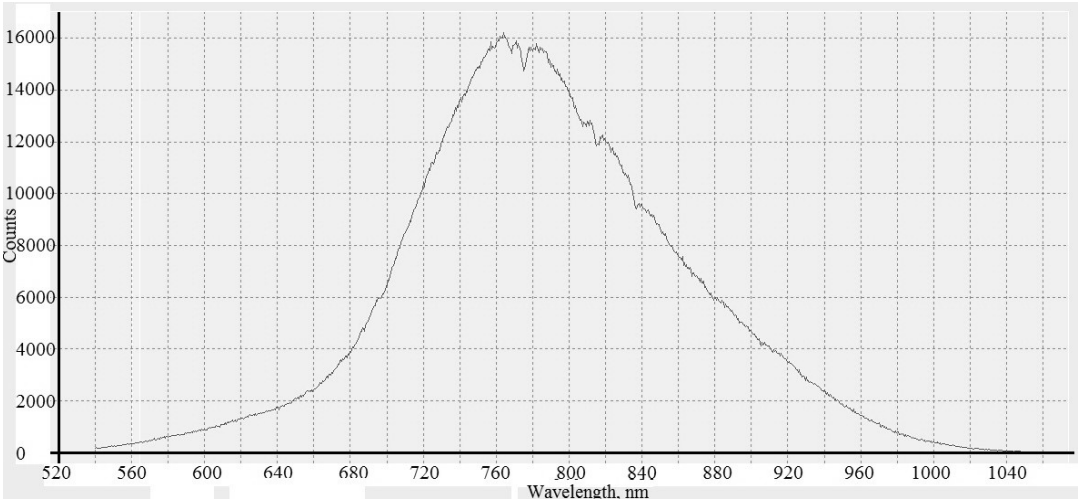

Fig.4. The PL spectra of CdSNW

The luminescence mechanisms of CdS have been studied over a few decades [13,14]. Usually, two emissions are observed from semiconductor nano particles excitonic and trapped luminescence [15,16]. The first one is observed at 380- 475 nm around the band edge and is attributed to higher-level transition while the other at 690 nm is due to trap or surface states. It is believed that the trap emission is mainly due to the excess of sulfur at the interface which is well-known to quench radiative band gap recombination, and not to the low crystalline of the particles.

In addition, the diameters of our synthesized CdSNW (35nm) are significantly larger than the exciton Bohr diameter in CdS. Therefore, the luminescence from the synthesized CdSNW observed by us at 750 nm is the trapped emission.

CONCLUSION

The structural-morphological properties of CdS thin films electrodeposited on ITO glass/AAO substrate from non-aqueous solution are analyzed. XRD patterns indicated that the structure of CdS thin film is cristallinity and hexagonal, the Raman scattering, the elemental composition and morphology SEM micrographs as well as the photoluminescence (PL) spectra indicates that the selected composition of anhydrous electrolyte (0.2M $CdCl_2$, 0.02M S_8, 0.1M NH_4Cl) dissolved in ethylene glycol and the electrodeposition film mode, allow to form layers of nano-crystalline CdS thin films with stoichiometric composition and predominately hexagonal characteristics suitable for the use as a window layer in CdS/Cu_2S, CdS/CdTe , CdS/ CdS/$CuInGaSe_2$, etc. hetero junction solar cells.

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ELEKTROKİMYƏVİ ÜSULLA ÇÖKDÜRÜLMÜŞ CdS NANOTELLƏRİNİN BƏZİ XÜSUSİYYƏTLƏRİ

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Elektrokimyəvi üsulla tərkibində kadmium-xlorid (0.2 M $CdCl_2$), kükürd (0.02 M S_8), ammonium xlorid (0.1 M NH_4Cl) saxlayan, T = 120-130^{0}C-də etilenqlikolda həll olan susuz məhluldan, 90-100^{0}C-də məsaməli alüminium-oksid (anodda oksidləşmiş alüminium) üzərinə çökdürülmüş 30-40 nm diametrə malik kadmium sulfid (CdS) nanotellərinin kristaloqrafik strukturu və element tərkibi öyrənilmişdir. Çökdürülən CdS nanotelləri enerji dispersiya X-ray spektrometriyası (EDX), rentgen diffraktometriyası (XRD), Raman səpilmə və fotolüminesens (PL) spektrləri ilə xarakterizə edilmişdir. Müəyyən edilmişdir ki, seçilən elektrolitin tərkibi və elektroçökmə şərtləri günəş çeviricilərində istifadə üçün yararlı olan, stexiometrik tərkibə uyğun altıbucaqlı modifikasiyaya malik CdS nanotellərinin formalaşmasına imkan verir.

Açar sözlər: *nanotellər, kadmium-sulfid, elektrokimyəvi çökmə, susuz məhlul, etilen qlikol, XRD, EDX, kombinasion səpələnmə, fotolüminessensiya spektrləri.*

НЕКОТОРЫЕ ОСОБЕННОСТИ ЭЛЕКТРОХИМИЧЕСКИ ОСАЖДЕННЫХ НАНОПРОВОДОВ CdS

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Изучены кристаллографическая структура и элементный состав нанопроводов CdS с диаметром в диапазоне 30-40 нм, изготовленных путем электроосаждения при 90-100^{0}C в поры анодного оксида алюминия из неводного раствора, содержащего хлорид кадмия (0.2 M $CdCl_2$), серу (0.02 M S_8) и хлорид аммония (0.1 M NH_4Cl), растворенных в этиленгликоле при T = 120-130^{0}C. Осажденные нанопровода CdS исследованы методами энергодисперсионной рентгеновской спектроскопии (EDX), рентгеновской дифрактометрии (XRD), комбинационного рассеяния и фотолюминесценции (PL). Было обнаружено, что выбранная композиция электролита и условия электроосаждения позволяют сформировать CdS нанопровода с преимущественно гексагональной модификацией, а стехиометрический состав подходит для использования в солнечных преобразователях энергии.

Ключевые слова: *нанопроволока, сульфид кадмия, электрохимическое осаждение, неводный раствор, этиленгликоль, XRD, EDX, комбинационное рассеяние, спектры фотолюминесценции.*