THE INFLUENCE OF SAS ON CdSe THIN FILMS ELECTRODEPOSITION

Abstract: The nanostructured cadmium selenide films have been deposited from sulfuric acid electrolyte to [glass/FTO] substrates with a thin layer of fluorinedoped tin oxide applied to the electrodes as a conductive layer. Positive influence of additives in lignosulphonate electrolyte on the properties of deposited photosensitive CdSe films is shown. An increase in the temperature is found to affect positively the deposition rate and structure of CdSe deposits obtained. The established optimal parameters of CdSe electrodeposition process are as follows: 50°C temperature, maintaining permanent potential at -0.7 V (Ag/AgCl), and deposition within 20 minutes.

The composition and morphology of obtained surface films have been studied using the electronic scanning microscopy (JSM-6610, JEOL) with x-ray attachment and atomic electron spectroscopy (JSPM 5200, JEOL). The micrographs of surface confirm the improved uniformity of coating with no damage, and the grain size is 100-400 nm if the electrodeposition is conducted from the electrolyte in the presence of sodium lignosulphonate at 50°C temperature. Based on the elemental analysis, a conclusion has been made that the stoichiometric composition of deposited films is achieved, (Se:Cd = 49.6:50.4). Raman spectra have been recorded by Raman scattering spectroscopy to determine the phase composition of deposit. Characteristic peaks of CdSe compound have been obtained. The photoelectrochemical behavior of deposited CdSe films at which the anode photocurrent is recorded, has been investigated. It has been confirmed that the semiconductor exhibits n-type conductivity and can be used as a photoanode.

The studies show that the developed technique of CdSe film deposition makes it possible to obtain uniform nanocrystalline films with high photoelectrochemical activity and adjustable type of conductivity, promising for use in regenerative photoelectrochemical converters.

Key words: Solar energy materials, cadmium selenide, organic additives, sodium lignosulphonate.

Introduction

The synthesis of II-VI Group semiconductor particles has experienced tremendous development over the last two decades. Cadmium selenide (CdSe) has also been a subject of much basic research [1,2]. The importance of cadmium selenide as a photovoltaic material is due to its high coefficient of absorption and optimal width of forbidden zone (1.7eV) contributing to the efficient absorption and conversion of solar radiation. The semiconductor is of considerable interest as an active element of photovoltaic devices [2]. CdSe can be used as a promising semiconductor for converting solar energy and creation of optoelectronic devices.

The most remarkable characteristic of semiconductor nanocrystal is the possibility of adjustment of its optical and electronic properties by modifying the controllable particle size. If the size of semiconductor particles is reduced and its surface area to volume ratio increases, the optical and electronic properties of material become highly dependent on the structure of surface [1]. The method of
Electrochemical deposition with the specified potential allows one to perform monitoring of the surface condition and its optimization [3-17]. Electrodeposition is a simple and requiring no high energy cost method with a number of advantages. Due to the high accuracy of measurement of charge flowing in the electrochemical cell, the electrodeposition process provides the possibility of high reliability control of thickness and stoichiometric composition of films, which is very important in regulating characteristics such as the semiconductor conductivity type, degree of alloying, width of forbidden zone, etc. The electrochemical method provides also the possibility of obtaining semiconductor films and metals with a high degree of purity, even with the use of source materials not exposed to special treatment. This is because in the process of electrochemical formation of films in parallel there occurs a process of their electrochemical refining. The electrochemical method allows for the deposition on substrates of different shapes and sizes.

Electrodeposition of cadmium and selenium is widely used in the electrochemical synthesis of CdSe cadmium selenide [3-14]. Many studies have focused on the electrochemical synthesis of cadmium selenide in the form of thin films [15-18], 2D structures [19], nanostructures, including wires [19, 20] sticks [21] and points [22]. The possible impact of nanostructures on the behavior of CdSe anodes in photovoltaic cells has caused an interest in the study of its electrochemical deposition. The development of cheap and efficient way of obtaining cadmium selenide thin films, particularly with nanostructures on the surface is a pressing task.

Typically, the cathode co-deposition of cadmium and selenium is conducted from the aqueous solutions containing, as precursors, soluble salts of cadmium (sulfate, chloride, nitrate), selenious acid (H₂SeO₃), selenites (Na₂SeO₃), or selenosulphate (Na₂SeSO₃) [23-28].

In this work, sodium lignosulphonate is used as an organic additive to improve quality (uniformity and adhesion) of deposited films.

Lignosulphonates are anionic surface-active agents (surfactants) and represent water-soluble lignin sulpho-derivatives. This is a mixture of various salts (mostly sodium) of lignosulphonics acids with an abundant admixture of mineral substances. [29].

Using sodium lignosulphonate, in this paper we propose a new method of electrodeposition of CdSe to obtain nanostructured films with good adhesion to the glass/FTO/substrate.

**Research methods**

The electrodeposition of thin films of cadmium selenide is carried out in the potentiostatic mode using a thermostated quartz three-electrode cell, which is a sealed container with divided anode and cathode. The cathode is FTO/glass plates with fluorine doped thin layer of tin oxide applied as a thin layer with 2-cm² area. Platinum large-area spiral is used as a counter electrode. The working electrode potential is measured relative to the Ag/AgCl in a saturated solution of KCl. Electrodeposition is carried out in a sulfuric acid electrolyte containing salts of cadmium and selenium in the ratio of ions Cd : Se = 45 : 1, the concentration of sodium lignosulphonate (LSN) is 9 g/l. The experiment is conducted at 25°C or 50°C temperatures of solution to be adjusted by thermostat.

After electrodeposition, all samples are studied using SEM. The JEOL (Japan) electronic scanning microscope with JSM 6610 LV microanalysis possibilities is used for this purpose.

The atomic force microscope, JSPM-5200 (JEOL) is used to study the surface morphology.

The combined Solver Spectrum system is used to study the obtained samples by Raman Spectroscopy and Raman Spectra records. It represents an automated scanning probe and confocal Raman microscope designed for a broad range of studies (lattice 150/500, 600/600, 1800/500; lasers 473, 532 and 633 nm).

For all of the obtained films, photocurrents are recorded and the type of conductivity is defined. The study of photoelectrical properties is conducted using 0.3 M Na₂SO₃ solution MCS when illuminated with 50W polychromatic light and in the dark on the «Interface 1000» plant. Transmission spectra were obtained with two beam spectrophotometer СФ-256 УВИ (190-1200) nm (LOMO, Russia).

**Results and Discussion**

Figure 1 compares the results of electron microscopy and energy spectrum of distribution of elements for CdSe films deposited on glass/FTO, in three different environments: sulfuric acid electrolyte at 25°C (Fig. 1a), the same electrolyte with addition of 9 g/l sodium LSN (Fig. 1b) at 25°C, and electrolyte with addition of 9 g/l of sodium LSN at 50°C (Fig. 1c). The micrographs of sample surface show the films
obtained in the presence of sodium LSN at 50°C to be more homogeneous; the inter grain boundaries are well-pronounced, the particle shape is identical, and the grain size is 100-400 nm. The coating is uniform, with no change in the topography and no discontinuity.

Figure 1 - EDAX diagrams and SEM micrographs of the surface of deposited CdSe films a) without using sodium LSN, 25°C; b) in the presence of sodium LSN, 25°C; c) in the presence of sodium LSN, 50°C

Table 1 – Elemental composition of CdSe films electrodeposited from sulfuric acid electrolyte within 20 minutes

<table>
<thead>
<tr>
<th>Presence of organic additive (LSN) in electrolyte</th>
<th>No</th>
<th>9 g/l</th>
<th>9 g/l</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deposition temperature</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cd</td>
<td>43.6</td>
<td>37.9</td>
<td>50.4</td>
</tr>
<tr>
<td>Se</td>
<td>56.4</td>
<td>62.1</td>
<td>49.6</td>
</tr>
</tbody>
</table>

Based on the elemental analysis (table 1), it is concluded that the additives in sodium LSN electrolyte as surfactants and an increase in the deposition temperature up to 50°C make it possible to achieve the nearest stoichiometric composition (Se:Cd = 49.6:50.4). The deposition time for all experiments was equal to 20 minutes. Only at 50°C, the stoichiometric composition is achieved in the electrolyte under
these conditions with LSN additive. At a temperature of 25°C, in the electrolyte with sodium LSN and in the absence of this organic additive, a deviation from stoichiometry is substantial and is respectively ±12.14 at.% ±6.43 at.% and ± 6.43 at.%.

The electrodeposited samples of CdSe/FTO glass were studied by Raman scattering spectroscopy to determine the phase composition of deposit (Figure 2).

![Resonant Raman spectra of the CdSe thin films](image)

**Figure 2** - Resonant Raman spectra of the CdSe thin films a) without using sodium LSN, 25°C; b) in the presence of sodium LSN, 25°C; c) in the presence of sodium LSN, 50°C

Based on the analysis of Raman Spectra it has been found that the peak at 200 cm⁻¹ corresponds to the basic vibrational (longitudinal) LO mode of CdSe structure vibrations. The peak in ~ 400 cm⁻¹ region corresponds to the second order 2LO mode. The broad peak in 1600 cm⁻¹ region corresponds to amorphous carbon.

Based on these data, it is established that all three samples conform to CdSe phase.

In addition, it is noted that in the case of cadmium selenide sample deposited at 25°C in the presence of sodium LSN additive one observes weak luminescence in a high-frequency spectrum.

Figure 3 presents the results of the study of films by the atomic force microscope. In the case of sample deposited from the electrolyte containing sodium LSN at 50°C (Figure 3c), the surface of deposited CdSe film consists of identical rounded particles, whereas the coating of samples obtained under other conditions (Figure 3a, 3b) is non-uniform, and the grains have no clear boundaries.

By the SEM method in the "cross section" mode it has been determined that the thickness of samples ranges from 680 to 820 nm (Figure 3d). A difference in the thickness of coating of all deposits varies in the range of ± 75 nm.
Figure 3 – Micrograph of surface obtained on ASM for CdSe thin films prepared by electrodeposition a) without using sodium LSN, 25° C; b) in the presence of sodium LSN, 25° C; c) in the presence of sodium LSN, 50 °C d) height profile for CdSe thin films prepared by electrodeposition in the presence of sodium LSN, 50 °C

An important optical parameter for characterization of compound semiconductor is a band gap. This value for electrodeposited CdSe films has been determined based on the transmittance spectra obtained using the spectrometer СФ-256 УВИ (190-1200) nm (LOMO, Russia). (Figure 4).
Figure 4 - Transmittance spectrum of CdSe films/FSnO2/glass obtained at $E^\circ$=-0.7V within 20 min: a) without using sodium LSN, 25°C; b) in the presence of sodium LSN, 25°C; c) in the presence of sodium LSN, 50°C.

1 - under illumination
2 - in the dark

Figure 5 - Current density vs. electrochemical potential given by CdSe thin films prepared by electrodeposition a) without using sodium LSN, 25°C; b) in the presence of sodium LSN, 25°C; c) in the presence of sodium LSN, 50°C.

1 - under illumination
2 - in the dark
Photosensitivity of electrodeposited CdSe films has been investigated using the photoelectrochemistry method in 0.3M Na2SO3 with illumination by 50W polychromatic light. Figure 5 show the photocurrent curves for the samples of CdSe thin films obtained under various conditions of deposition (at 25°C and 50°C in the presence of surfactant (sodium LSN) and without it. One can see that under illumination, anode photocurrents are recorded for all samples. The photocurrents (curves 1) grow on potential sweep to the area of positive values and are much larger than the values (curves 2) obtained in the dark for the same samples.

The photoelectrochemical study of CdSe films deposited under illumination by polychromatic light has shown that the obtained semiconductor exhibits n-type conductivity.

The comparison of photocurrent values indicates that the photoelectrochemical activity of nanocrystalline films electrodeposited at 50°C in the presence of lignosulfonate appears 2 times higher than that of those deposited in the absence of LSN additives.

The developed technique of CdSe film deposition makes it possible to obtain deposits with high photosensitivity and adjustable type of conductivity.

Conclusion

A new composition of electrolyte for electrodeposition of CdSe FTO/glass thin films has been developed. Electrodeposition of nanocrystalline cadmium selenide films from sulfuric acid electrolyte to glass/FTO substrate has been carried out.

Positive effect of sodium LSN additives in the electrolyte on the properties of deposited CdSe photosensitive films is shown.

The optimum process parameters for the electrodeposition of CdSe are as follows: 50°C temperature, maintaining permanent potential at -0.7V (Ag/AgCl), and deposition within 20 minutes.

The composition and morphology of the surface of obtained films have been investigated by means of electronic scanning microscopy (JSM-6610, JEOL) with x-ray attachment and atomic electron spectroscopy (JSPM 5200, JEOL). Micrographs of the surface have confirmed the improved uniformity of coating with no discontinuity; the grain size is 100-400 nm if the electrodeposition of electrolyte is conducted in the presence of sodium LSN at 50°C temperature. Based on the elemental analysis, a conclusion is made that the stoichiometric composition of deposited films has been achieved (Se: Cd = 49.6:50.4).

The formation of CdSe phase has been confirmed by the Raman Spectroscopy method.

Based on the photovoltaic measurements, it is found that CdSe films deposited under optimal conditions show photoactivity 2 times higher than the samples obtained with conventional sulfuric acid electrolyte.

It has been confirmed that the semiconductor is characterized by n-type conductivity and can be used as a photoanode.

The developed new method of deposition of CdSe films makes it possible to obtain uniform nanocrystal films with high photoelectrochemical activity and adjustable type of conductivity, which are promising for use in photo-electrochemical converters of regenerative type.

Aknowlegement

The work was financially supported by the state program of scientific researches of the Republic of Kazakhstan, grant Committee of Science, MES RK GF4/217.

REFERENCES

М.Б. Дергачева¹, Г.М. Хусирова¹, Д.С. Пузикова¹, Р.Р. Немкаева², В.И. Яскевич¹, К.А. Мить³

1 Д. В Сокольский атындағы жаңақ және электролик денсаулық институту;
 Кызылорда 142, Алматы, 050010, Қазақстан;
 ²Ә-Фараби атындағы Қазақ Үлттық Үніверситет;
 «Ашық түрдәгі ұлттық науқадағы зертхана», Ә-Фараби, 71, Алматы 050040, Қазақстан;
 ³«Физика және Технология Институты», Ибрагимова,11, Алматы 050032, Қазақстан;

CdSe ЖУКА ҚАБЫҚТАРЫН ЭЛЕКТРОТУНДЫРУЫНА ПАВ-ТЫН ЭСЕРІ

Аннотация. Өткізіші кабат ретінде фторометдре дипирилененен қалайсы өскідіңің жұқа кабаты қазылған [шыны/FTO] электролық табашаларында құқыр қыышқылы электролиттегі қадим селенидін нанокрылымды қабатының электролық жасалған. Түздырлық фотоселімдідегі CdSe қабатының қасиетіне натрий линглсулығының электролиттік косу оң әсер ететіндігі көрсетілген. Температураға әсер ететін кішілік. CdSe электролық процесінің қасиетін басқаруға параметрлерді өңдеу үшін: температура 50°C, құралдың потенциалы ұстану -0,7В (Ag/AgCl), түздырға 20 минут ішінде.

Алынған кабаттардың құрылысы және бетінің морфологиясы реттіндік приставкасы бар электролық скиалюшілі микроскопия (JSM-6610, JEOL) және атом электролық спектроскопия (JSPM 5200,JEOL) адісімен зерттелген. Егер электролық ретінде натрий линглсулықтың электролиттегі 50°C температураға жасалса, онда беттің микрофотографиясы жабдықты біртектілігінің бұзымсыз қосуаны анықта алу және дүрістірілген дәлігер, 100-400 нм құрылғы. Элементтің анализын тапқа алға отырып тұрдырғының кабатының стехиометриялық құрылысы және сатып келген ерекшеліктер қосады (Sc/Cd = 49,6:50,4). Тұрдырғының фазалық құрылысы анықтау үшін комбинациялық шаңырақты адісемен Раман спектрологиялық және CdSe косылыстың тісті пиктер қолданылды. Тұрдырғының CdSe кабаттарындағы атомді фототекі тіркейтін фотолектрикалық қысықтыры зерттегіз және жаратылған кейініндерді қазынау үшін түрлі начылықтың біртектілігін сипаттайтін құрылыстың фазалық құрылысы ретінде қолдана болынып дәлелдейді.

Түйін сөздер: құрғақ энергиялық материалдары, қадим селениді, органикалық коспалар, натрийлі линглсулық.
ВЛИЯНИЕ ПАВ НА ЭЛЕКТРООСАЖДЕНИЕ ТОНКИХ ПЛЕНОК CdSe

Аннотация: Выполнено электроосаждение наноструктурированных пленок селенда кадмия из сернокислого электролита на подложки [стекло/FTO] электроды, на которых в качестве проводящего слоя нанесен дипольный фтором тонкий слой оксида олова. Показано положительное влияние добавок в электролит лизносульфанида натрия на свойства осаждаемых фоточувствительных пленок CdSe. Установлено, что повышение температуры положительно влияет на скорость осаждения и структуру получаемых осадков CdSe. Определены следующие оптимальные параметры процесса электроосаждения CdSe: температура 50°C, поддержание постоянного потенциала -0,7В (Ag/AgCl), осаждение в течение 20 минут.

Состав и морфология поверхности полученных пленок исследованы методом электронной сканирующей микроскопии (JSM-6610, JEOL) с рентгеновской приставкой и атомной электронной спектроскопии (JSPM 5200, JEOL). Микрофотографии поверхности подтверждают улучшение однородности покрытия без нарушения сплошности, размер зерна составляет 100-400 нм, если электроосаждение выполнено из электролита в присутствии лизносульфанида натрия при температуре 50°C. На основе элементного анализа сделан вывод, что достигнут стехиометрический состав осаждаемых пленок. (Se: Cd = 49,6:50,4). Методом спектроскопии комбинированного рассеяния были записаны Рамановские спектры для определения фазового состава осадка. Получены характерные пики соединения CdSe. Изучено фотоэлектрохимическое поведение осажденных пленок CdSe, при котором регистрируется анодный фототок, и подтверждено, что полупроводник характеризуется n-типом проводимости и может использоваться в виде фотоанода.

Исследования показали, что разработанная методика осаждения пленок CdSe позволяет получать равномерные нанокристаллические пленки с высокой фотоэлектрохимической активностью и регулируемым типом проводимости, перспективные для использования в фотоэлектрохимических преобразователях регенеративного типа.

Ключевые слова: материалы солнечной энергии, селенид кадмия, органические добавки, лизносульфанид натрия.