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Optical and Electrical Transport Properties of the ZnO:CdO Composite Film

In this work, zinc oxide films and composite ZnO:CdO films with cadmium oxide concentrations of 3 μl, 5 μl, 7 μl, 10 μl, and 12 μl were obtained by spin-coating on FTO. The films were annealed in the atmosphere under the same temperature conditions of 450°C. The morphology of ZnO:CdO composite films was studied by the SEM method and an electron-dispersion analysis of the concentration of the studied substance was carried out. The influence of the surface morphology of the composite film with an increase in the CdO concentration from 3 μl to 12 μl on the optical and electrotransport properties of the ZnO:CdO composite film was studied. The optical absorption spectra of composite films of zinc oxide and cadmium were measured. A Tauc plot is presented to determine the band gap of a ZnO:CdO composite film. It has been established that an increase in the CdO concentration on the ZnO surface leads to a decrease in the optical band gap. The observed decrease in the optical band gap of the film with increasing CdO is due to the small band gap of CdO. The method of impedance spectroscopy was used to study the main electrophysical characteristics, in particular, the dynamics of charge carrier transfer in nanocomposite films based on ZnO:CdO. It has been established that the CdO layer on the ZnO surface contributes to a decrease in the resistance value of the composite film R_w, an increase in the charge recombination resistance parameter R_{rec} at the interface, and an increase in the efficiency of electron injection.

Keywords: ZnO, CdO, composite, morphology, electron transport layer, absorption, structural layer, impedance spectroscopy.

Introduction

The transformation of the demand for electricity is one of the possible cases, which in the short term may take place in the case of a rapidly growing value on true energy. Among the various photovoltaic converters that currently exist, organic solar cells are of great interest among various international scientific groups. The efficiency level of organic solar cells (OSC) already exceeds 14% due to the search for new materials, the improvement of existing materials and the optimization of the active layer morphology [1–6]. The inverted structure is widely used in organic photoconverters due to its good stability and efficient phase separation [7–9]. The electron transport layer (ETL) in the inverted structure plays an important role in the performance of organic solar cells. The ETL layer can not only enhance electron extraction and reduce charge recombination, but also affect the morphology of the photoactive layer.

ETL layers based on metal oxides have attracted great attention because of their high transparency in the visible region of the spectrum, as well as their ability to change energy levels and electrical properties by doping or chemical modification [10]. Among the known metal oxides used in OSC is ZnO [11–14] and TiO_2 [15]. However, ETL layers based on ZnO and TiO_2 have relatively low charge carrier mobility and photoactivity in the visible spectral range. One way to increase the photoactivity of oxide semiconductors is to dope them with another semiconductor with a narrow band gap. This will increase the sensitivity of the composite system in the visible range of the spectrum and reduce the efficiency of charge recombination. As such a semiconductor, CdO, which is an n-type oxide semiconductor with a narrow band gap, can be used (2.16-2.6 eV). The purpose of this work is to increase the photoactivity of oxide semiconductors.

In this regard, in this work, ZnO:CdO composite structures are obtained and the optical and electrical transport properties of composite films are studied.

Experimental

To obtain composite films, initial research solutions were preliminarily prepared. For this purpose, $Zn_5(OH)_8Cl_2$ (pure 99.9%, Sigma Aldrich) powder with m=48.9 mg was dissolved in V=0.5 ml of isopropanol. After 20 min, monoethanolamine was added to the resulting solution in an amount of V=36 μl. After the solution was stirred at a temperature of T=60°C for 2 hours, and then kept for 24 hours at room temperature. To obtain CdO films, $Cd(CH_3COO)_2$ (pure 99.9%, Borun New Material Technology Co., Ltd) crystallites weighed m=34.5 mg were dissolved in V=0.5 ml of isopropanol. After the solution was kept for 20 minutes, then V = 0.5 μl of monoethanolamine was added to the resulting mixture. After the solution was stirred at a temperature of T=80°C for 2 hours.

Preparation of substrates for composite films was carried out according to the procedure [16]. The preparation of composite films was carried out as follows: the initial solution for ZnO films (V=30 μl) was applied to FTO surfaces by centrifugation (model SPIN150i, Semiconductor Production System) at a rotation speed of 4000 rpm/min. After the films were annealed in an air atmosphere at a temperature of 200°C for 10 min, then a solution for CdO films (V = 3 μl, 5 μl, 7 μl, 10 μl, and 12 μl) was applied to the surface of the resulting film at a rotation speed of 4000 rpm/min, after which the resulting films were annealed at a temperature of 450°C for 50 min [17].

To carry out electrophysical measurements, the surface of the ZnO and ZnO:CdO films were deposited on an aluminum electrode 120 nm thick by thermal deposition on a CY-1700X-SPC-2 (Zhengzhou CY Scientific Instruments Co., Ltd) setup.

The film morphology was studied on a MIRA 3 LMU (TESCAN) scanning electron microscope. Elemental analysis (EDX analysis) of the samples was carried out using an INCAPentaFET-x3 (Oxford Instruments, England) energy dispersive analyzer. A Co (9905-17, Micro-Analysis Consultants Ltd Unit 19, Edison Road, St Ives Cambridgeshire PE27 3LF U.K) sample was used as a standard. The absorption spectra of the studied samples were measured on an AvaSpec-ULS2048CL-EVO spectrometer (Avantes). The impedance spectra were measured using a P45X potentiostat-galvanostat (Elins) in the impedance mode.

Results and Discussion

Figure 1 shows SEM images of ZnO and ZnO:CdO films. The surface of the ZnO film has a granular structure with an average grain size of d~12 nm. For the ZnO:CdO composite film, the film surface does not change.

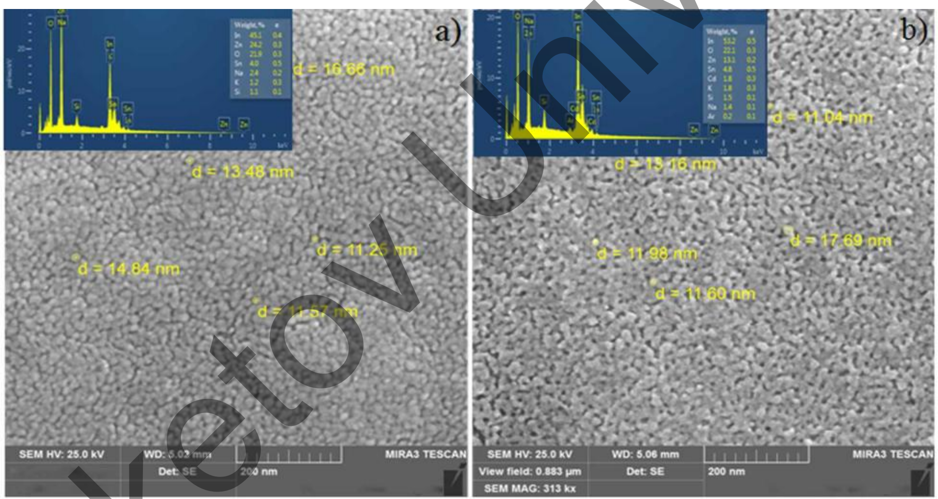

Figure 1. SEM images and EDX spectra of the films
a) morphology of the ZnO film, b) morphology of the ZnO:CdO composite film

The inset in Fig. 1 shows the EDX spectra of the studied composite films. When a CdO layer is deposited on a ZnO layer, a change in the redistribution of elements in the quantitative ratio at the surface layer is observed. According to Table 1, the initial film is enriched with zinc and oxygen; after the deposition of the CdO layer, an increase in the proportion of cadmium is observed, the amount of oxygen does not change.

Table 1

Elemental composition of ZnO and ZnO:CdO films

No.	Films	Zn, weight %	Cd, weight %	O, weight %	Zn/Cd ratio
1	ZnO	14.1	-	22.6	-
2	CdO (3 μl)	19.7	1	22.9	19.7
3	CdO (5 μl)	14.1	1.2	22.6	11.7
4	CdO (7 μl)	13.7	1.4	21.9	9.7
5	CdO (10 μl)	13.1	1.5	22.2	8.7
6	CdO (12 μl)	13.1	1.8	22.1	7.2

Figure 2 represents the absorption spectra of the films. The absorption spectrum is typical of the absorption spectrum of wide-gap semiconductors. The edge of the fundamental absorption band falls in the near ultraviolet region, which corresponds to the optical transition of the band gap of oxide semiconductors. It can be seen from the figure that an increase in the CdO concentration on the surface of the ZnO layer leads to a threefold increase in the absorption of the composite film.

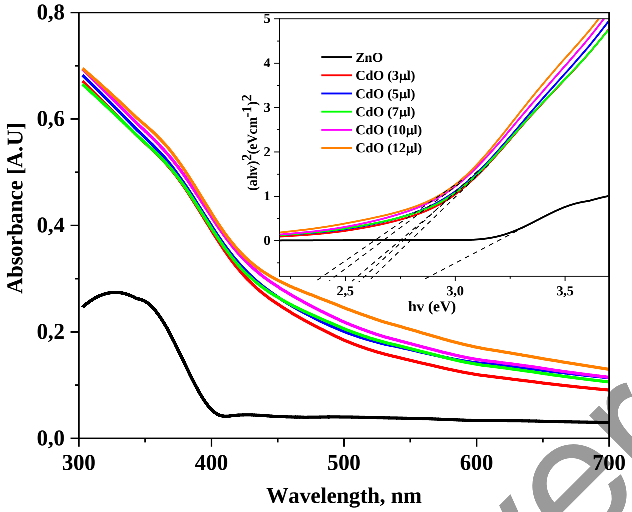

Figure 2. Absorption spectra of ZnO and ZnO:CdO films

The inset in Figure 2 shows the Tauc plot for determining the band gap (Eg) of the composite films. Table 2 lists the values of the film band gap depending on the CdO concentration. It can be seen that an increase in the CdO concentration on the surface leads to a decrease in the optical band gap (Eg) from 2.9 eV to 2.37 eV. The decrease in the optical band gap of the composite film is due to the fact that CdO is a semiconductor with a small band gap.

Table 2

Maximum absorption value of ZnO and ZnO:CdO films

No.	Films	D, (λ= 360 nm)	Optical band gap (eV)
1	ZnO	0.25	2.9
2	CdO (3 μl)	0.51	2.62
3	CdO (5 μl)	0.52	2.58
4	CdO (7 μl)	0.54	2.54
5	CdO (10 μl)	0.57	2.4
6	CdO (12 μl)	0.59	2.37

Figures 3b and 3c demonstrate the structural layer of a ZnO film and a ZnO:CdO composite, respectively. To determine the mechanisms of transport and recombination of charge carriers, the impedance spectra of composite films consisting of several layers were measured: a glass substrate coated with a transparent conducting FTO electrode (anode); ZnO:CdO layer; aluminum electrode in Figure 3c. Figure 3d shows the equivalent electrical circuit that was used to interpret the impedance spectra. The fitting of the impedance spectra was calculated using the EIS-analyzer software package.

Figure 3a designates the following parameters for obtaining the film hodograph: R_1 and R_2 – R_h and R_{ext} – resistances corresponding; where R_w is the resistance of the ZnO:CdO nanocomposite layer, R_{rec} is the charge carrier recombination resistance at the ZnO:CdO/electrode interface associated with the extraction of charge carriers from ZnO:CdO, CPE_1 is the constant phase element, which is the equivalent component of the electrical circuit that models the behavior double layer but is an imperfect capacitor.

After fitting, the values of the hodograph parameters were determined, characterizing the kinetics of transport and recombination of charge carriers based on ZnO and ZnO:CdO films. These parameters are given in Table 3, where τ_{eff} is the effective lifetime of charge carriers, k_{eff} is the recombination index characterizing the recombination rate.

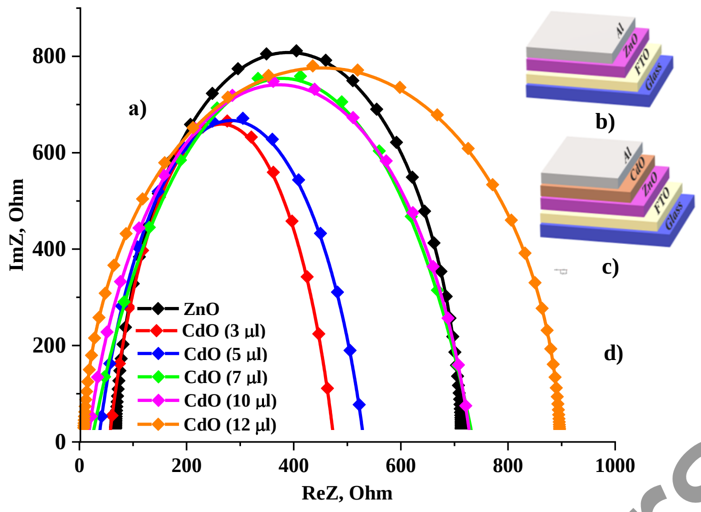

Figure 3. a) impedance spectra of ZnO and ZnO:CdO, b) structural layer of ZnO, c) structural layer of ZnO:CdO, d) equivalent electrical circuit

Table 3

The value of the electrophysical parameters of the films

No.	Films	R_w, (Ohm)	R_{rec}, (Ohm)	R_{rec}/R_w	τ_{eff}, (msec)	k_{eff}, (sec^{-1})
1	ZnO	73.6	642.4	8.7	0.13	7309
2	CdO (3 μl)	60.2	412	6.8	0.12	8176
3	CdO (5 μl)	38.9	489.4	12.9	0.11	9054
4	CdO (7 μl)	27.3	702.4	25.7	0.08	12882
5	CdO (10 μl)	21.4	706.3	33	0.08	12589
6	CdO (12 μl)	11.9	880.1	73.9	0.06	15848

Table 3 presents the obtained values of R_w, R_{rec}, etc. It can be seen that the R_w value has the highest value for the ZnO film. With an increase in the concentration of CdO in ZnO, the resistance R_w of the film decreases, which should improve the transport of injected electrons to FTO. R_{rec}, the resistance characterizing the recombination of electrons at the ZnO:CdO/electrode interface, varies depending on the CdO concentration. A slight decrease in the film recombination resistance is compensated by a decrease in the resistance R_w. The effective lifetime of charge carriers τ_{eff} decreases, which indicates an increase in the rate of charge injection onto the current-collecting electrode. Also, an increase in k_{eff} is observed, which characterizes the rate of charge recombination after a complete cycle in the circuit; this indicates a decrease in electron recombination at the ZnO:CdO/electrode interface. Thus, the conducted studies show that the CdO layer on the ZnO surface contributes to a decrease in the resistance of the composite film, an increase in the resistance of charge recombination at the interface, and an increase in the efficiency of electron injection.

Conclusions

In this work, ZnO films and a ZnO:CdO composite were obtained by spin-coating on the FTO surface. The concentration of cadmium in the solution to obtain a layer on the surface of zinc oxide ranged from 3 to 12 μl. The influence of the CdO layer on the ZnO surface on the morphology, optical and electrical properties of composite films has been studied. Analysis of SEM images showed a change in the redistribution of elements in a quantitative ratio with the surface layer of the composite film. According to the absorption spectrum of ZnO:CdO composite films, an increase in the CdO concentration leads to an increase in the optical absorption of the composite film and a decrease in the optical band gap. The study of impedance spectroscopy showed that the CdO layer on the ZnO surface contributes to a decrease in the resistance of the composite film, an increase in the resistance of charge recombination at the interface, and an increase in the efficiency of electron injection.

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ZnO:CdO композитті қабықшаның оптикалық және электротасымалдау қасиеттері

Мақалада мырыш оксидінің қабықшалары мен кадмий оксидінің концентрациясы 3 мл, 5 мл, 7 мл, 10 мл және 12 мл композиттік ZnO:CdO қабықшалары FTO-да spin-coating әдісі арқылы алынды. Қабықшалар атмосферада бірдей температура жағдайында 450°С қыздырылды. SEM әдісімен ZnO:CdO композиттік қабықшаларының морфологиясы зерттеліп, зерттелетін заттың концентрациясына электронды-дисперстік талдау жүргізілді. CdO концентрациясы 3 мл-ден 12 мл-ге дейін артқан кезде ZnO:CdO композиттік қабықшаларында оптикалық және электротасымалдау қасиеттерінің композиттік қабықшасының беткі морфологиясына әсері зерттелді. Мырыш және кадмий оксидінің композит қабықшаларының оптикалық жұтылу спектрлері өлшенді. ZnO:CdO композиттік қабықшасының тыйым салынған аймағын анықтау үшін Таук графигі (Tauc plot) көрсетілген. ZnO бетіндегі CdO концентрациясының артуы тыйым салынған аймақтың оптикалық енінің төмендеуіне әкелетіні анықталды. CdO артқан сайын қабықшаларда бақыланып отырған тыйым салынған аймақтық оптикалық енінің төмендеуі CdO-ның шағын тыйым салынған аймағымен байланысты. Импеданс спектроскопия әдісі арқылы негізгі электрофизикалық сипаттамаларды, атап айтқанда ZnO:CdO негізіндегі нанокомпозиттік қабықшалардағы заряд тасушының динамикасын зерттеу үшін қолданылды. ZnO бетіндегі CdO қабаты композиттік қабықшаның Rw кедергісінің төмендеуіне, бөлу шекарасындағы зарядтардың Rw рекомбинация кедергісінің жоғарылауына және электронды инжекция тиімділігінің артуына ықпал етеді.

Кілт сөздер: ZnO, CdO, композит, морфология, электрондық тасымалдау қабаты, жұтылу, құрылымдық қабат, импеданс спектроскопия.

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Оптические и электротранспортные свойства композитной пленки ZnO:CdO

В статье методом *spin-coating* на FTO были получены пленки оксида цинка и композитные пленки ZnO:CdO с концентрацией оксида кадмия 3 мл, 5, 7, 10 и 12 мл. Пленки отжигались на атмосфере при одинаковых температурных условиях 450°С. Методом СЭМ исследована морфология композитных пленок ZnO:CdO, и проведен электронно-дисперсионный анализ концентрации исследуемого вещества. Изучено влияние морфологии поверхности композитной пленки при увеличении концентрации CdO с 3 мл до 12 мл на оптические и электротранспортные свойства композитной пленки ZnO:CdO. Проведены измерения спектров оптического поглощения композитных пленок оксида цинка и кадмия. Приведен график Таука (*Tauc plot*) для определения ширины запрещенной зоны композитной пленки ZnO:CdO. Установлено, что увеличение концентрации CdO на поверхности ZnO приводит к уменьшению оптической ширины запрещенной зоны. Наблюдаемое уменьшение оптической ширины запрещенной зоны пленки с увеличением CdO связано с малой запрещенной зоной CdO. Методом импедансной спектроскопии исследованы основные электрофизические характеристики, в частности, динамика переноса носителей заряда в нанокомпозитных пленках на основе ZnO:CdO. Доказано, что слой CdO на поверхности ZnO способствует уменьшению значения сопротивления композитной пленки Rw, увеличению параметра сопротивления рекомбинации зарядов *Rrec* на границе раздела и возрастанию эффективности инжекции электронов.

Ключевые слова: ZnO, CdO, композит, морфология, электронный транспортный слой, поглощение, структурный слой, импеданс-спектроскопия.