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Electrodeposition, characterization and photo electrochemical properties of CdSe and CdTe

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KEYWORDS

Group II–VI; Electrodeposition; Photo electrochemical properties

Abstract CdSe and CdTe are electrodeposited using 0.1 M Cd^{2+} and different ion concentrations of Se and Te. The effect of the temperature on the electrodeposition process is also studied. The crystal structure of the deposited CdSe and CdTe is investigated by X-ray diffraction (XRD). Scanning electron microscopy (SEM) of samples deposited at optimized parameters reveals that CdSe has spongy spherical grains while CdTe has coralloid morphology. Optical absorption shows the presence of direct transition with band gap energy 1.96 and 1.51 eV for CdSe and CdTe, respectively. The highest photo-conversion efficiencies of electrodeposited CdSe and CdTe films per unit area are 6% and 9.6%, respectively that achieved under simple laboratory conditions. © 2014 Production and hosting by Elsevier B.V. on behalf of Ain Shams University.

1. Introduction

The interest in the use of photo-electrochemical (PEC) solar cells for low-cost energy conversion has led to an extensive research in the development of thin film polycrystalline materials for the chief electrode component. Among the non-silicon polycrystalline materials, CdSe and CdTe (Group II–VI) are regarded as two of the most promising binary compounds semiconductor material of low cost, exhibiting stable performance and high efficiency toward solar cell application due to its direct band gap of 1.5–2 eV that nearly matches the solar

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energy spectrum. Moreover due to their high optical absorption coefficient, these compounds are attractive material for optoelectronics, gamma ray detector, and infrared detector besides its PEC application [\[1–5\]](#page-5-0).

The growth of high quality cadmium selenide and telluride fine crystalline powder is important because of its potential applications in semiconducting devices, photovoltaic optoelectronic devices, radiation detectors, laser materials, thermoelectric devices, solar energy converters, Videocon devices, sensors and nano devices [\[6,7\]](#page-5-0).

A variety of deposition techniques such as electrodeposition [\[8,9\],](#page-5-0) vacuum evaporation [\[10–12\]](#page-5-0), liquid phase deposition [\[13\]](#page-5-0), molecular beam epitaxy [\[14\]](#page-5-0), closed space sublimation [\[15\]](#page-5-0) vacuum deposition [\[16,17\]](#page-5-0) and chemical bath deposition [\[18–20\]](#page-5-0) have been used to deposit CdSe and CdTe thin films. It is known that the opto-electronic and other properties of II–VI class of compound thin films are highly structure sensitive, which in turn can severely influence the device performance. The structure parameters such as the crystallinity, crystal phase, lattice constant (a) , average stress (S) and strain

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(e), grain size (D) , orientation $(1111/1220)$ are strongly dependent on deposition parameters.

Among these methods electrodeposition is an attractive method, which has successfully been employed for the preparation of elemental, binary, intermetallic and ternary compounds [\[21,22\].](#page-5-0) It is an isothermal process, mainly controlled by electrical parameters, which are easily adjusted to control film thickness, morphology, composition, etc.

The structure of electrodeposited CdSe thin films is governed by the pH of the bath solution, temperature, composition and film thickness. Abundant literature is available on preparation and characterization of CdSe using CdSO4, cadmium acetate and CdCl₂ as source materials for Cd²⁺ ion and SeO₂ one for Se⁴⁺ ion [\[21–25\]](#page-5-0).

The XRD pattern of the deposited CdSe thin films on the different substrates exhibits two polycrystalline phases with hexagonal and cubic crystal structures [\[9,26–29\].](#page-5-0) The XRD of the electrodeposited CdTe revealed cubic structure [\[30,31\].](#page-5-0)

CdTe is considered as the reference material for the fundamental studies of compound semiconductor electrodeposition and most of the research papers in this area of research have been devoted to CdTe [\[32\].](#page-5-0) They mainly focused on the deposition of nanocrystalline CdTe because the nano-structured semiconductor materials have attracted much attention due to their unique electrical, magnetic and optical properties. CdTe is one of the most promising photovoltaic materials for the thin film solar cells due to its direct band gap matching to the solar energy spectrum and high absorption coefficient [\[33\].](#page-5-0)

Since the seminal work of Kroger on the theory of CdTe compounds deposition [\[34,35\]](#page-5-0), the main studies have been focused on the electrodeposition of CdTe from acidic aqueous solution containing Te^{4+} species (HTeO₂⁺) in the presence of Cd^{2+} ions. Most often, experimental work has been done with low concentrations of telluric ions (typically in the order of a few 10^{-4} M or 10^{-3} M) at pH around 2. Under these conditions, the cadmium ions are also present in large excess, and give the best quality of deposited CdTe films as demonstrated by the possibility of the epitaxial growth [\[36\].](#page-5-0) Furthermore, the solubility of Te^{4+} in the form of $HTeO₂⁺$ was severely limited in the pH range 2–6 [\[37\].](#page-5-0)

CdTe cyclic voltammetry was studied at various scanning potentials and temperatures [\[38\]](#page-5-0).

Excellent-quality CdTe thin films can be obtained after annealed at 350 °C for 1 h, although better electronic properties can be obtained by annealing at 450 °C.

The aim of this work is the study of CdSe and CdTe electrodeposition in different conditions and parameters such as: concentrations of Se^{4+} and Te^{4+} ions and temperature of the bath deposition in order to achieve the optimum conditions.

2. Experimental

Potentiodynamic measurements were carried between 0 and -1.2 V. The scan rate was 1 mV s⁻¹. This measurement was carried out at different temperatures from 25 to 90 °C. Potentiodynamic measurements were carried out using VoltaLab P.G. 201 Multistat. The working electrode was platinum rotating disk electrode (RDE, EG and G Electro-instrument) with 3 mm diameter. The reference electrode was $Hg/Hg_2SO_4/$ $H₂SO₄$ (mercury sulfate electrode, MSE), 615 mV vs. $H₂$

electrode. All potentials were recorded against this reference. The counter electrode was graphite rod (5 mm diameter).

The Potentiostatic cathodic depositions of CdSe and CdTe were run at -550 mV vs. MSE on Ti substrate for XRD, SEM investigations and photo electrochemical (PEC) measurements. The exposed area of deposition was $2 \text{ cm} \times 2.5 \text{ cm}$. The bath pH was 2.5 and the temperature of the deposition bath was about 50 °C. The solution contained $0.1 M$ $Cd^{2+} + 0.005 M Te^{4+}$ or 0.002 M Se⁴⁺ ions. The indium tin oxide (ITO) coating borosilicate glass substrate has dimensions of 2.5 cm \times 7 cm \times 1.1 mm. It was used for electrodeposition of CdSe and CdTe that used for optical spectra. The resistivity of the conducting ITO coating borosilicate glass (one face only) was $12.5 \Omega/cm^2$.

The crystal structure was studied using Siemens Powder diffractometer with Cu K α radiation. Scanning electron microscopy (SEM) was conducted with a JEOL SEM Model 5040. The absorption spectra were achieved by a spectrometer model V-570 by JASCO Corp.

The electrodeposited CdSe or CdTe on Ti substrate was used as the working electrode for photo electrochemical cell. Counter electrode was platinum. The cell configuration was Ti:CdSe or CdTe/0.5 M $Na_2S + 0.5 M S + 0.5 M NaOH/Pt$. It was fabricated and characterized through current–voltage $(I-V)$ measurements [\[39\]](#page-5-0). The cell was put in a beaker containing water for cooling of the electrolyte cell. Xenon arc lamp 150 W is used as a light source with solar simulator Sciencetech SS150W-AAA. The cell was exposed to light intensity 1 Sun (100 mW/cm^2) using Air Mass 1.5 Global Filter. IV tester is 2400 Keithley Source Meter SSIVT-60WC. The calibrated reference cell consists of a 20×20 mm monocrystalline silicon (model SC-LT) photovoltaic cell encased in a $92 \times 70 \times 16$ mm metal enclosure with a protective quartz window. The reference detector (SSIVT-refl) is effective in sensing wavelengths between 190 nm and 1100 nm and is calibrated with the sun. Parameters measured by IV Software were $V_{\rm oc}$, $I_{\rm sc}$, $P_{\rm max}$ and FF.

3. Results and discussions

3.1. Electrochemical behavior

The electrochemical behavior effect of Se^{4+} ion concentration on the Cd^{2+} ion in the bath mixture was studied through the Potentiodynamic measurements. Cyclic voltammograms (CVs) of 0.1 M $Cd^{2+} + 0.001 - 0.004$ M Se^{4+} ions are shown in [Fig. 1a](#page-2-0). The anodic dissolution of electrodeposited CdSe is occurred around – 650 mV vs. MSE. The highest anodic dissolution was achieved with 0.1 M $Cd^{2+} + 0.002$ M Se^{4+} . The study of the electrochemical deposition of II–VI compound semiconductors is complicated due to the presence of side cathode reactions of hydrogen and hydrogen selenide H_2 Se reduction as well as by the influence of the surface condition [\[40\]](#page-5-0). These factors may limit a theoretical range of the deposition potential of compounds. Lower bound of the CdSe deposition potential range by the reaction:

$$
Cd^{2+} + Se^0 + 2e^- \rightarrow CdSe
$$

is limited by the cadmium reduction potential in accordance with the reaction

Figure 1 CV of (a) CdSe from 0.1 M Cd²⁺ + 0.001–0.004 M Se⁴⁺ and (b) CdTe from 0.1 M Cd²⁺ + 0.001–0.006 M Te⁴⁺, $v = 1$ mV s⁻¹ pH = 2.5 at 25 °C.

$$
Cd^{2+} + 2e^- \rightarrow Cd^0(E = -1040 \text{ mV vs.} Hg/Hg_2SO_4/H_2SO_4)
$$

Gibbs free energy for the binary CdSe compound is equal to $\Delta G_{\text{CdSe}} = -100 \text{ kJ/mole}$ and a shift of the deposition potential of the metal Cd component is equal to 0.52 V. So, a theoretical range of the CdSe deposition potentials are within -1.05 and -0.505 V.

The effect of Te ion concentration was studied by CV as shown in Fig. 1b. It is observed that maximum anodic dissolution was achieved with $0.1 M \text{ Cd}^{2+} + 0.005 M \text{ Te}^{4+}$, $pH = 2.5$. It was reported that electrodeposition of CdTe took place at potentials positive to the Nernst potential for bulk Cd deposition [\[41\].](#page-5-0) The mechanism of CdTe deposition is considered to be: (i) cathodic electrodeposition of surface Te atoms [Te $(IV) + 4e + Te(ads)$], followed by (ii) intermediate adsorption of Cd(II) ions to form CdTe $[Cd(II) + Te(ad$ s) + 2e \rightarrow CdTe]. Most studies assume an overall process under diffusion control by Te(IV) ions [\[42\]](#page-5-0). Therefore, the mass transport of the $HTeO_2^+$ limiting species at the cathode is a key parameter governing the overall electrodeposition rate, despite kinetic limitations [\[42,43\].](#page-5-0)

The effect of the bath temperature on the CdSe deposition was studied using 0.1 M Cd²⁺ + 0.002 M Se⁴⁺ with pH 2.5 at 25, 50, 60, 70 and 80 °C. The CVs are recorded in Fig. 2a. It was found that 50 °C enhances the anodic dissolution of the electrodeposited CdSe rather than the other temperatures. The effect of the temperature for the electrodeposition CdTe

Figure 2 Effect of temperature on CV of (a) CdSe from 0.1 M $Cd^{2+} + 0.002 \text{ MSe}^{4+}$ and (b) CdTe from 0.1 M Cd²⁺ + 0.005 M Te^{4+} , $v = 1$ mV s⁻¹ pH = 2.5.

from 0.1 M Cd²⁺ + 0.005 M Te⁴⁺, pH = 2.5 was observed as shown in Fig. 2b. The suitable temperature is also 50 °C. The electrodeposited CdSe or CdTe on Ti substrate had thickness in the range of $0.7-4.0 \mu m$. It was affected by deposition time period.

3.2. XRD and SEM investigations

XRD of electrodeposited CdSe on Ti substrate is illustrated in [Fig. 3](#page-3-0)a. The pattern displays three main diffraction peaks at 2θ values of 25.44° , 42.08° , and 50.08° . It is observed that the peaks are well defined and sharp. The lattice parameter 'a' for cubic samples was calculated using the relation: $a = d$ $(h^2 + k^2 + l^2)^{0.5}$, where h, k, l are the lattice planes and 'd' is the interplanar spacing, measured using Bragg's equation. According to literature survey and JCPDS data (19-0191), the peaks can be classified to (111) , (220) and (311) planes of the cubic CdSe planes, respectively [\[29\].](#page-5-0) The XRD pattern of the electrodeposited CdTe powder is shown in [Fig. 3](#page-3-0)b. The pattern displays six diffraction peaks at 2θ values of 23.73°, 39.5°, 47.2°, 63.1°, 72° and 77.5°, which correspond to the diffraction lines produced by the (111) , (220) , (311) , (331) , (422) and (511) crystalline planes of cubic CdTe, respectively. The XRD data are in agreement with the reported literature (JCPDS Data file 75-2086) [\[43\]](#page-5-0). The crystallite size of the electrodeposited CdSe and CdTe was determined using

Figure 3 XRD of CdSe from 0.1 M Cd²⁺ + 0.002 M Se⁴⁺ (b) CdTe from 0.1 M Cd²⁺ + 0.005 M Te⁴⁺, $T = 50$ °C, pH = 2.5, at -800 mV vs. $\text{Hg/Hg}_2\text{SO}_4$.

different diffraction peaks based on Debye–Scherrer equation [\[43,44\].](#page-5-0) The calculation shows that the average crystallite size is 12 and 20 nm for CdSe and CdTe, respectively.

The morphology of the electrodeposited CdSe on Ti substrate was shown in Fig. 4a. The particles of electrodeposited CdSe crystals have spherical morphological shape with average of 3 lm. SEM investigation of CdTe electrodeposited powder using solution 0.1 M Cd^{2+} + 0.005 M Te⁴⁺ ions is recorded in Fig. 4b. The crystal microstructure is similar to the coral reefs.

3.3. Transmission spectra and energy band gap (E_{φ})

The optical transmission spectra of CdSe and CdTe prepared on ITO conducting glass were studied using a spectrophotometer in the range 300–1000 nm. They are recorded in Fig. 5. The peak of the transmission spectrum of the prepared CdSe is observed at 630 nm. On the other hand, the peak of the transmission spectrum of the CdTe film is observed at 830 nm. This means that the transition of electrons between the valence band and conduction one occurs at lower energy for electrochemically deposited CdTe rather than CdSe one.

The energy band gap of a direct band gap material can be obtained through the plot of $(\alpha h v)^2$ vs. the energy hv as shown in [Fig. 6](#page-4-0). The absorption coefficient " α " is give by the following relations [\[26\]](#page-5-0):

(a) CdSe

(b) CdTe

Figure 4 SEM of CdSe from 0.1 M Cd²⁺ + 0.002 MSe⁴⁺ (b) CdTe from 0.1 M Cd²⁺ + 0.005 M Te⁴⁺, $T = 50$ °C, pH = 2.5, at -800 mV vs. Hg/Hg_2SO_4 .

Figure 5 Transmission spectra of (a) CdSe and (b) CdTe.

 $Log(1/T) = \alpha t$ (1)

The absorbance $A = \text{Log}(I/I^c) = \alpha t$ (2)

$$
Transmittance \% T = 100(I/I°)
$$
\n(3)

Figure 6 Dependence of $(\alpha h v)^2$ photon energy on hv, from which the direct allowed band gap for electrodeposited CdSe and CdTe.

Figure 7 Power output plot of the Photo electrochemical of CdSe and CdTe cells.

where T is transmittance of the spectra, t is the film thickness, I° and I are the intensities of the incident and transmitted light through the sample.

The absorption coefficient (α) for direct band semiconductors transition is given by:

$$
\alpha h v = B(hv - Eg)^{0.5} \tag{4}
$$

The energy gap (E_g) value is given by extrapolation. *B* is a constant. It is observed that the E_g value obtained for CdSe is 1.96 eV, while E_g for CdTe is 1.51 eV. It was reported that the band energy gap of electrodeposited CdSe using cadmium acetate and SeO_2 solutions at different pH (2.5–3) varied between 1.72 and 2.50 eV as reported by different researchers [\[9,45,46\]](#page-5-0). On the other hand, the reported band gap energy

of CdTe electrodeposited from the sulfate and $TeO₂$ solutions was achieved between 1.50 and 1.58 eV [\[47,48\].](#page-5-0)

Furthermore, the obtained energy gap value of CdSe has a blue shift of 0.26 eV from the reported bulk microcrystalline CdSe (1.7 eV) [\[49\].](#page-5-0) The blue shift is due to the three dimensional quantum size effects, i.e. the CdSe crystals behave as quantum dots. These results prove the existence of CdSe nanoparticles as revealed from the calculation of the crystallite size in Section 3.2. While, the bulk energy band gap of CdTe is 1.475 eV [\[50–52\].](#page-5-0) The blue shift in the energy gap of CdTe from the bulk one is very small, 0.035 eV in comparison with CdSe, i.e. the CdTe has little quantum dots behavior.

3.3.1. I–V Characteristics

To obtain the power output characteristics of the PEC cells, the open circuit potential (V_{oc}) and the short circuit currents (I_{sc}) were recorded for the deposited films.

The $I-V$ curves as shown in Fig. 7 were further analyzed to evaluate power conversion efficiency $(\eta\%)$ and fill factor $(FF\%).$

$$
FF = (V_{\text{max}}I_{\text{max}}/V_{\text{oc}}I_{\text{sc}}) \times 100 \tag{5}
$$

$$
\eta = \left(V_{\text{max}}I_{\text{max}}/P_{\text{in}}^*A\right) \times 100\tag{6}
$$

where V_{oc} : open circuit potential for CdTe electrode, I_{sc} : short circuit current measured at zero voltage, V_{max} and I_{max} : are the optimum maximum voltage and current at the tangent point to the I–V characteristic relation.

It is observed that the $I_{\rm sc}$ of the electrodeposited CdTe is more than CdSe one. The highest photo-conversion efficiency of 9.6% was achieved under simple laboratory conditions with the electrodeposited CdTe films as shown in Table 1.

4. Conclusion

The electrodeposited CdSe was achieved from an electrolytic bath contained 0.1 M Cd²⁺ + 0.002 M Se⁴⁺ with pH = 2 at 50 °C. The anodic dissolution of electrodeposited CdSe was occurred at -650 mV vs. MSE. The crystal structure of electrodeposited CdSe was cubic. The energy band gap was 1.96 eV. Also, the electrodeposited CdTe was achieved from an electrolytic bath at -800 mV vs. MSE for solution containing 0.1 M Cd^{2+} + 0.005 M Te^{4+} ions for half-hour at $pH = 2.5$ and 50 °C on ITO glass substrate electrode. The transmission of the electrodeposited CdSe material took place at about 630 nm. However, the transmission spectrum of electrodeposited CdTe is observed at 830 nm. It is observed that the energy band gap " E_g " was 1.96 and 1.51 eV for CdSe and CdTe, respectively. Therefore, the electrodeposited CdTe has lower energy gap than CdSe. The highest photo-conversion efficiency of 9.6% was achieved under simple laboratory conditions with the electrodeposited CdTe films while CdSe had one of 6.03% .

Table 1 Photo electrochemical cell (PEC) parameters for CdSe and CdTe.

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Type of sample	$_{\rm oc}$	$I_{\rm sc}$ (mA)	max	I_{max} (mA)	FF(%)	η (%)
CdTe	0.608	10.27	0.502	95.7	71.65	9.60
CdSe	0.48	88.54	0.4	75.48	71.04	6.03

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