

CdSe semiconducting layers produced by pulse electrolysis

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Thin films of CdSe semiconductors electrodeposited from acid aqueous electrolytes onto Ti substrates have been developed using periodically modified currents, such as pulse current. The products obtained were fully characterized and their photoelectric behavior was studied using a photoelectrochemical cell. All deposits obtained by pulse electrolysis exhibit some differences in their structure, surface morphology and photoelectric properties, depending on the imposed pulse current parameters such as pulse frequency and duty cycle. It was also found that increased photoelectrochemical efficiencies are observed to so higher pulse frequencies as more negative deposition potentials are applied and vice-versa.

1. Introduction

Cadmium chalcogenide semiconductors, formed between elements of 12th (zinc group) and 16th (chalcogens; oxygen group) groups of the periodic table, e.g. CdSe and CdTe, present some specific characteristics on which their particular applications are based: energy gap, electron donor or acceptor character and capability in conversion of solar energy to electricity or chemical energy [1–8]. They possess direct energy gaps (1.7 and 1.5 eV, respectively), which are more efficient to the absorption of electromagnetic radiation. Moreover, using these compounds, the exploitation of a large part of the photons present in the solar spectrum can be achieved.

In particular, binary and ternary chalcogenide semiconductors, such as CdSe, CdTe and Cd(Se,Te) alloys [CdSe_xTe_{1-x} (0 ≤ x ≤ 1)] have received widespread interest in the field of photocatalysis and conversion of solar energy [9]. As they can easily be obtained, by numerous techniques, onto various substrates, in the form of thin polycrystalline layers presenting considerable application potential, the research on cadmium chalcogenides photoelectrodes is currently conducted exclusively in the field of thin films. The latter can be conveniently and inexpensively synthesized by electrochemical methods employing cathodic, mainly, or anodic routes from aqueous or non-aqueous electrolytes of the appropriate soluble species. Electroless techniques, such as evaporation, co-evaporation, spray pyrolysis, slurry painting, pellets sintering, chemical bath deposition *etc.*, have also been applied in the field of photoconversion applications [10–13]. Cathodic electrodeposition of Cd chalcogenides is extensively investigated [14,15], where the concept of potential preparation of compact, polycrystalline, semiconductor compound films by underpotential deposition of Cd, in a potentiostatic manner, is described.

Photoelectrochemical research has a far-reaching interest in cadmium chalcogenide semiconductors since they can be effectively used as active electrodes in relatively stable photoelectrochemical cells (PEC) for solar energy conver-

sion. Moreover, polycrystalline anodes, particularly of CdSe, have signified the potential advantages of the liquid–solid junction compared to solid state ones. Photoelectrochemical

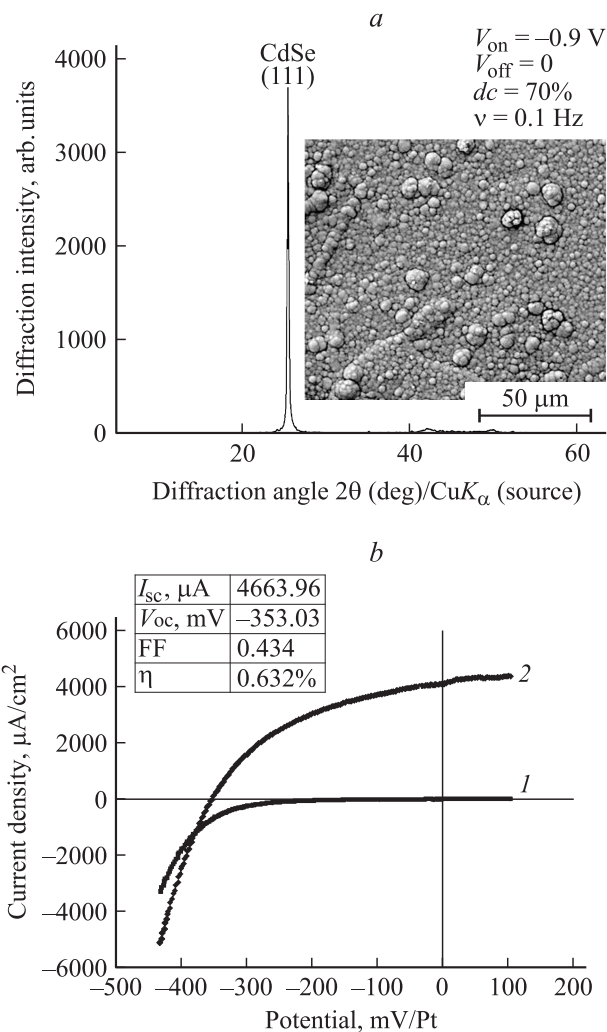


Figure 1. XRD diagram, SEM micrograph (a), and diagram of current density (b) vs electrochemical PEC potential (I — in the dark, 2 — under illumination of 1000 W/m²) given by a CdSe thin film prepared at -900 mV/SSE under PC: V_{off} = 0, dc = 70%, ν = 0.1 Hz.

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Photoelectrochemical parameters of CdSe electrodeposits prepared under direct current (DC) and pulse current (PC) regime

Current regime	Duty cycle (%)	V_{on} (mV)	ν (Hz)	I_{sc} (μ A)	V_{oc} (mV)	FF	η (%)	Crystal structure
DC	–	–900	–	1221.86	–309.82	0.259	0.0867	Cubic
DC	–	–1000	–	1875.06	–332.65	0.323	0.178	Cubic/hex
DC	–	–1100	–	2116.18	–283.32	0.284	0.151	Cubic/hex
PC	70	–900	10	2743.96	–312.58	0.394	0.298	Cubic
PC	70	–1000	10	972.76	–268.61	0.279	0.0645	Cubic/hex
PC	70	–1100	10	4635.26	–378.92	0.33	0.514	Cubic/hex
PC	70	–900	1	4531.97	–347.82	0.306	0.426	Cubic
PC	70	–1000	1	4592.45	–360.23	0.309	0.452	Cubic
PC	70	–1100	1	5125.66	–347.82	0.195	0.307	Cubic/hex
PC	70	–900	0.1	4663.96	–353.03	0.434	0.632	Cubic
PC	70	–1000	0.1	870.96	–261.87	0.287	0.0579	Cubic
PC	70	–1100	0.1	3228.46	–277.19	0.293	0.232	Cubic/hex
PC	50	–900	10	1176.26	–358.08	0.305	0.114	Cubic
PC	50	–1000	10	1168.76	–358.08	0.308	0.114	Cubic
PC	50	–1100	10	4922.16	–351.96	0.296	0.453	Cubic/hex
PC	50	–900	1	103.86	–203.66	0.0287	0.0054	–
PC	50	–1000	1	2813.76	–247.62	0.347	0.214	Cubic
PC	50	–1100	1	1919.6	–35.90	0.0369	0.0255	Cubic/hex
PC	50	–900	0.1	157.6	–161.53	0.0495	0.0111	Cubic
PC	50	–1000	0.1	2549.46	–242.72	0.345	0.189	Cubic/hex

efficiencies estimated as high as 5–7%, after the deposits underwent various post deposition annealing and (photo-) chemical treatments or/and donor diffusion have been reported [16,17]. The lattice structure of CdSe can be found in the forms of sphalerite (cubic) and wurtzite (hexagonal). The former is a metastable phase, nearly constituting the exclusive product of an electrochemical formation process, while the latter is the thermodynamically stable structure obtained either by annealing the cubic phase [4] or directly by various, electroless preparation techniques.

According to the literature, pulse plating is essentially an interrupted direct current plating technique. While using direct current (DC) the main electrolysis parameter is the current density J , the application of pulse current (PC) technique introduces two more parameters to the electrolysis ones: the pulse frequency ν , and the duty cycle, $dc = [T_{on}/(T_{on} + T_{off})] \times 100$, where T_{on} the deposition time and T_{off} the relaxation time [18]. It has been proved that the modification of the PC parameters can affect the crystal growth of the deposits and, consequently, their properties. Pulse electrolysis is thus a powerful mean of perturbing the adsorption/desorption phenomena occurring at the cathod–electrolyte interface during the relaxation time T_{off} and hence offers the opportunity of preparing deposits exhibiting modified structure and better controlled properties [18,19].

In the frame of this work, the influence of pulse electrolysis on the structure, the microscopic characteristics and the semiconductive properties of CdSe thin films, deposited on Ti substrates from acidic electrolytic baths, was studied.

2. Experimental

CdSe thin films were electrodeposited under direct (DC) and pulse current (PC) regime, using a potentio-scan system with a conventional three electrode setup and a pulse generator, as well. Pulse plating parameters were adjusted as follows: $\nu = 10, 1$ and 0.1 Hz, and $dc = 70$ and 50% . The cathode was a rotating Ti disc electrode ($\varnothing = 12$ mm; $\Omega = 500$ rpm) and the counter electrode was a large platinum plated grid. The potential of the working electrode was monitored against an Hg/HgSO₄ saturated sulfate reference electrode (SSE). The electrolytic bath was an additive-free aqueous solution containing typically 0.2 mol/l CdSO₄ and $2 \cdot 10^{-3}$ mol/l SeO₂ being kept constant at $85 \pm 1^\circ\text{C}$. The electrolyte pH was adjusted to 2.2. All semiconductive deposits of typically 1 to $4 \mu\text{m}$ thickness were examined by XRD and SEM techniques. Compositional data were obtained by EDAX analysis. Photoresponse studies were performed in a PEC. An alkaline sulfide-polysulfide solution (S_x^{2-} 1M NaOH, 1M Na₂S and 1M S solution) was used as the working red-ox electrolyte. The PEC measurements were conducted under a white light generated by a halogen lamp and focused in front of the quartz window of the cell. Illumination intensity was 1000 W/m^2 .

3. Results and discussion

CdSe thin films were plated under DC and PC regime at $V_{on} = -900, -1000$ and -1100 mV/SSE and, for all deposits, $V_{off} = 0$. At these potentials, as it is known by previous works [1–8], a co-deposition of Cd and Se to CdSe

exists. The X-Ray crystallographic analysis and the EDAX measurements confirmed, as it is expected, the formation of a CdSe layer, presenting a metastable cubic sphalerite (zinc blende) structure with a predominating crystalline orientation towards to the [111] axis. The photocurrents obtained, using the PEC method, are always anodic, a fact already observed for the CdSe semiconductors prepared by electrodeposition, characteristic of an *n*-type behavior due to the variations of stoichiometry. Table summarizes the parameters of the photoconversion curves (short circuit current j_{sc} , open circuit potential V_{oc} , fill factor FF , and photoelectrochemical efficiency η) as well as the crystal structure for all deposits prepared. Figs. 1–3 present the XRD diagrams, the SEM micrographs and the current-potential photoresponses for the electrodeposits presenting the best efficiencies (see below).

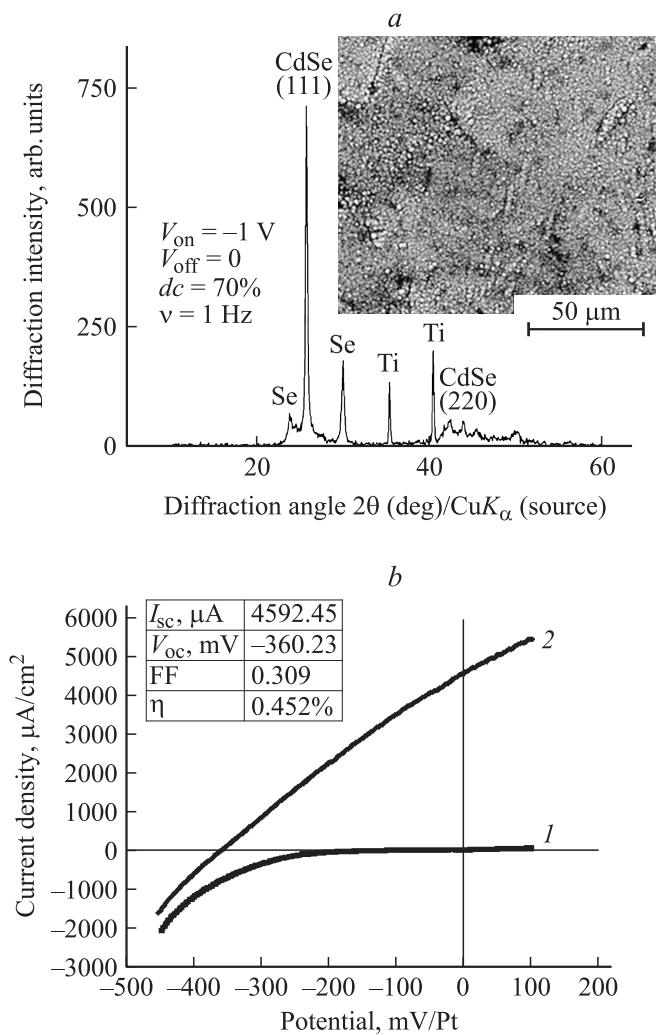


Figure 2. XRD diagram, SEM micrograph (a), and diagram of current density (b) vs electrochemical PEC potential (*I* — in the dark, 2 — under illumination of 1000 W/m²) given by a CdSe thin film prepared at -1000 mV/SSE under PC: $V_{off} = 0$, $dc = 70\%$, $\nu = 1$ Hz.

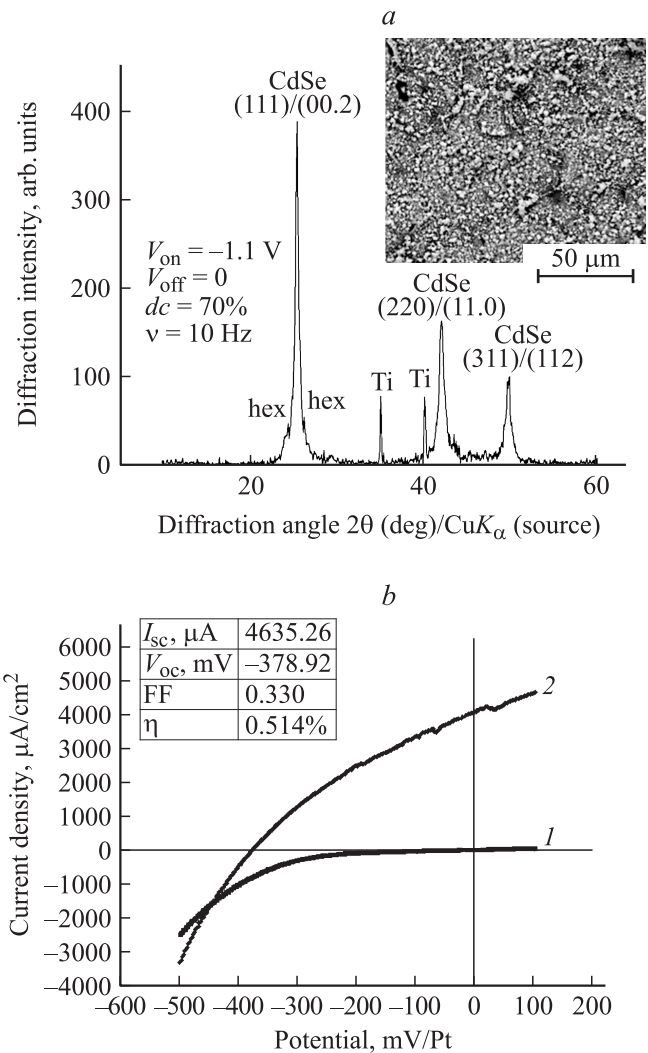


Figure 3. XRD diagram, SEM micrograph (a), and diagram of current density (b) vs electrochemical PEC potential (*I* — in the dark, 2 — under illumination of 1000 W/m²) given by CdSe thin films prepared at -1100 mV/SSE under PC: $V_{off} = 0$, $dc = 70\%$, $\nu = 10$ Hz.

Most CdSe layers plated under PC regime present better photoelectrochemical efficiencies in comparison to them prepared using DC at the same potentials. The composition of the deposits, their crystal structure and surface morphology sensibly depend on the PC parameters. It is observed that deposits prepared at more negative potentials (-1000 and chiefly -1100 mV/SSE) tend to obtain a mixed cubic-hexagonal crystal structure (see Table and Fig. 3, a). On the other hand, deposits plated at -900 mV/SSE present a purely cubic structure and better crystallinity (Fig. 1, a). The X-Ray crystallographic analysis and the EDAX measurements confirmed also the presence of free Se in some deposits. This elemental Se, that deteriorates the quality of the CdSe thin films, leading to much lower efficiencies, may be removed by appropriate thermal treatment [4].

It was found that electrodeposits prepared at higher $dc = 70\%$ generally exhibit better photoelectro-chemical efficiencies. Specifically, optimal efficiencies are observed at $V_{on} = -900$ mV and $\nu = 0.1$ Hz (Fig. 1, *b*), $V_{on} = -1000$ mV (Fig. 2, *b*) and $\nu = 1$ Hz and $V_{on} = -1100$ mV and $\nu = 10$ Hz (Fig. 3, *b*).

For deposits prepared at $dc = 50\%$, the best efficiency is observed at $V_{on} = -1100$ mV and $\nu = 10$ Hz. It is worth noting that, for both dc values, increased efficiencies are observed to so higher pulse frequencies as more negative deposition potentials are applied and vice-versa. This fact is more obvious for deposits plated at $dc = 70\%$.

These as prepared CdSe thin layers are convenient to be used as substrates for the development of new hybrid–inorganic/organic–semiconductors [20].

4. Conclusion

Thin films of CdSe semiconductors electrodeposited from acid aqueous electrolytes onto Ti substrates have been developed using periodically modified currents, such as pulse current. All deposits obtained by pulse electrolysis, comparing to those prepared under a direct current regime, may modulate their composition, crystal structure and surface morphology, according to the imposed pulse current parameters. A mixed cubic-hexagonal structure, probably associated with better photoresponses, can be observed to deposits prepared at negative enough potentials.

Moreover, most CdSe thin films plated under PC regime present better photoelectrochemical efficiencies in comparison to them prepared using DC at the same potentials. Better PEC efficiencies are obtained for the higher $dc = 70\%$. It was also found that, for both duty cycles, increased efficiencies are observed to so higher pulse frequencies as more negative deposition potentials are applied and vice-versa.

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