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ELECTRODEPOSITION OF ZnTe THIN FILMS

CIENKIE WARSTWY ZnTe WYTWARZANE METODĄ ELEKTROCHEMICZNĄ

Zinc telluride thin films were prepared in a system with rotating disc electrode (RDE) by potentiostatic or galvanostatic electrodeposition from an aqueous sulfate and sulfate-citrate solutions. The influence of the electrolyte variables and operating parameters on the composition and morphology of the deposited film was investigated. For optimized electrode-position parameters a compact ZnTe layers of the composition close to stoichiometry with a regular nodular morphology were obtained.

Keywords: zinc telluride, electrodeposition, citrate electrolytes.

Warstwy tellurku cynku wydzielano z wodnych roztworów siarczanowych i siarczanowo-cytrynianowych metodą potencjostatyczną lub galwanostatyczną w układzie z wirującą elektrodą dyskową. Badano wpływ zmiennych elektrolitu i parametrów operacyjnych na skład i morfologię osadzanych warstw. Przy optymalnych parametrach elektroosadzania uzyskano zwarte, drobnokrystaliczne warstwy ZnTe o składzie zbliżonym do stechiometrycznego.

1. Introduction

Zinc telluride is one of the important AII-BVI – type compound semiconductor materials for photovoltaic (PV) heterojunction structures [1-3]. ZnTe thin films are ultimately meant to serve as a window material in PV cells, especially the p-type doped window materials [4]. The electrodeposited polycrystalline ZnTe can also be used as a passivation layer in CdTe based bulk crystals for room temperature X-ray detectors [5]. In addition, p-type ZnTe has been used in high efficiency CdS/CdTe/ZnTe cells due to their high absorbance coefficient [1,6]. Figure 1 shows the achievable efficiency for a single junction solar cell as a function of the bandgap. As can be observed zinc telluride is characterized by the wide direct optical bandgap of 2.25 eV.
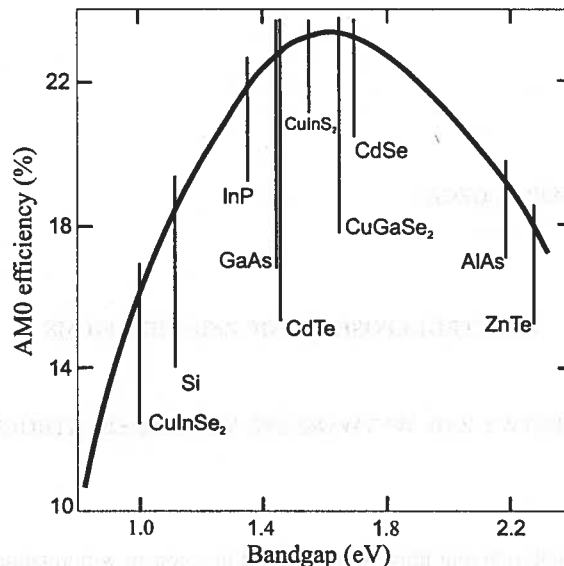
Fig. 1. Achievable efficiency for a single junction solar cell as a function of the bandgap
(Landis et al. 1989)

ZnTe layers have been usually prepared by expensive techniques including molecular beam epitaxy (MBE) and chemical vapor deposition (CVD) [7, 8]. Electrodeposition (ED) is an alternative method for the preparation of such semiconducting films. It is an inexpensive low-temperatured method to cover large area and the physical properties of the films can easily be controlled by the deposition conditions. In recent years various electrochemical methods (including deposition from complex baths) to prepare the ZnTe films have been reported [9-11].

The present work is aimed at determination of electrocrystallization conditions for deposition of ZnTe films from simple sulfate and complex sulfate-citrate electrolytes. The co-discharge kinetics and the influence of electrolyte variables ([Zn(II)]/[Te(IV)] concentration ratio, pH, complexing agent content) as well as mass transfer to the cathode on the microstructure and the chemical composition gradient of ZnTe thin films were determined.

2. Experimental procedure

The zinc telluride films (0.1 – 1μm) were electrodeposited on conducting copper substrates from sulfate solutions containing Zn(II) and Te(OH)$_3^+$ ions with and without the addition of citrate (Na$_3$C$_6$H$_5$O$_7$) complexing agent. The bath pH was varied between 0.5 – 6.0. The chemical composition of the electrolytes is given in Table 1. To ensure constant and controlled hydrodynamic condition, the electrolysis was carried out in an experimental system with rotating disc electrode (RDE), supplied

by a PARA 273A potentiostat. The cathode potentials were referred to a saturated calomel electrode (SCE) and were corrected for ohmic drop (CI method). The cathode was the polycrystalline copper disk (0.071 cm^2) rotating at 11 – 68 rad/s. A Pt sheet (5 cm^2) was used as the anode. Zinc telluride thin films were prepared potentiostatically and galvanostatically. The chemical compositions of the deposits were determined by electron dispersive spectroscopy (EDS) analysis using a LINK-ISIS apparatus. The morphology of ZnTe films was evaluated by scanning microscopy on a SEM Philips XL-30. The thickness of the deposited film was evaluated from deposition charge and current efficiency.

TABLE 1

The electrolyte chemical composition (Cit = $C_6H_4O_7$)

pH	Te(IV) [M]	Na$_2$SO$_4$ [M]	ZnSO$_4 \cdot$ 7H$_2$O [M]	Na$_3$HCit [M]	No
1.0	$5 \cdot 10^{-4}$	0.2	—	—	1
1.0	—	0.2	0.2	—	2
1.0	$5 \cdot 10^{-4}$	0.2	0.2	—	3
2.0	$5 \cdot 10^{-4}$	0.2	0.1	0.2	4
3.0	$5 \cdot 10^{-4}$	0.2	0.1	0.2	5
4.0	$5 \cdot 10^{-4}$	0.2	0.1	0.2	6
5.0	$5 \cdot 10^{-4}$	0.2	0.1	0.2	7
6.0	$5 \cdot 10^{-4}$	0.2	0.1	0.2	8
4.0	$5 \cdot 10^{-4}$	0.2	0.01	0.2	9
4.0	$5 \cdot 10^{-4}$	0.2	0.001	0.2	10
5.0	$5 \cdot 10^{-4}$	0.2	0.2	0.2	11
5.0	$5 \cdot 10^{-4}$	0.2	0.1	0.4	12

3. Results and discussion

A stock solution of Te(IV) (1 $\cdot$ 10^{-2} M) was obtained by dissolving 1.6 g TeO$_2$ in 2M H$_2$SO$_4$. This highly acidic solution of pH equals – 0.7 is stable against precipitation. During two years there was no visible precipitation of tellurium species. The electrolytes were prepared by blending suitable amount of the Te(IV) and Zn(II) stock solutions and diluting with water to a final nominal concentrations. The investigated [Zn]/[Te] concentration ratio was in the range of 2 – 400 for a constant content of Te(IV) equals 5 $\cdot$ 10^{-4} M.

The standard reduction potentials of zinc and tellurium are nearly 1.4 V apart. Despite the large difference in these potentials, the deposition is thermodynamically possible because of the free energy of ZnTe formation according to the following equation: Zn + Te $\rightarrow$ ZnTe; ΔG^0 = –114.6 kJ/mol (25°C). The negative free energy of formation of ZnTe leads to a positive shift in the deposition potential of zinc allowing the final electrochemical deposition of ZnTe given by reaction: Zn^{2+} + Te(OH)$_3^+$ +

$3H^+ + 6e \rightarrow ZnTe + 3H_2O$. Hence, the electrodeposition of ZnTe is conducted at a more positive potential than the redox potential of the less noble Zn(II) species and more negative to that for Te(IV), as can be seen from the runs of potentiodynamic polarization curves recorded for separate reduction of Te(IV) and Zn(II) as well as for their co-discharge (Fig. 2).
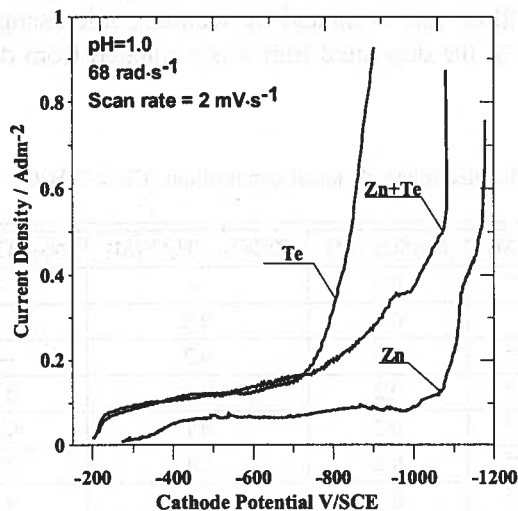
Fig. 2. Potentiodynamic polarisation curves for Te(IV) and Zn(II) separate reduction as well as their co-discharge from simple sulfate baths (Nos 1, 2, 3 in Table 1)

At more negative potentials the zinc discharge is predominant whereas at less negative tellurium is preferentially deposited. Fig. 3 shows the cathode potential range calculated for the preparation of ZnTe films (for investigated conditions). As can be seen, in dependence of the pH values, ZnTe films could be electrodeposited in the various potential ranges: e.g. -0.2 to -1.2 V/NHE at pH $= 0.5$ and -0.2 to -1.7 V/NHE at pH $= 6.0$.

Zinc telluride was electrodeposited from simple sulfate baths at relatively negative potentials with a parallel reaction of hydrogen evolution, which reduces the current efficiency of the electrochemical process. Hence, the higher pH values of the solutions should be profitable. However, increasing pH limits the solubility of TeO_2 (Fig. 5). For example, the pH $= 1.5$ is the highest possible value for solution containing $5 \cdot 10^{-4}$ M Te(IV). Moreover, for a simple sulfate baths, under potentiostatic condition, an abrupt change of the chemical composition from tellurium-rich to zinc-based deposits within the narrow potential range (0.02 V) causes the difficulties in determination of the operating parameters leading to the stoichiometric ZnTe films (Fig. 4).

The presence of citrate complexing agent in sulfate solution containing Te(IV) and Zn(II) improves the solubility of tellurium species, indicating the complex formation (Fig. 5) as well as allowing to increase the bath pH up to 6. At pH $5 - 6$ domina-
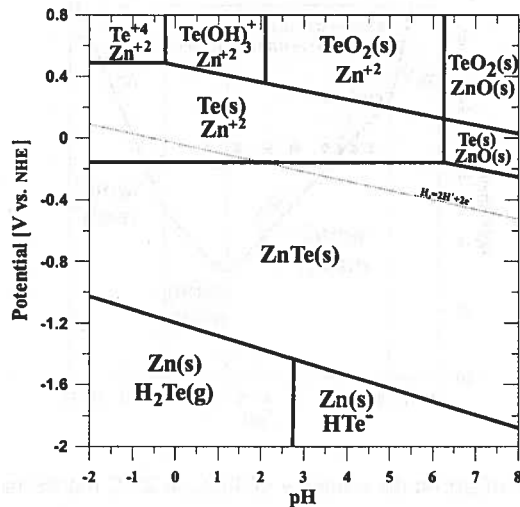
Fig. 3. Potential — pH diagram of Zn–Te–H$_2$O in aqueous electrolyte (at 25°C) calculated for $5 \cdot 10^{-10}$ M Te(IV) and 0.1 M Zn(II)
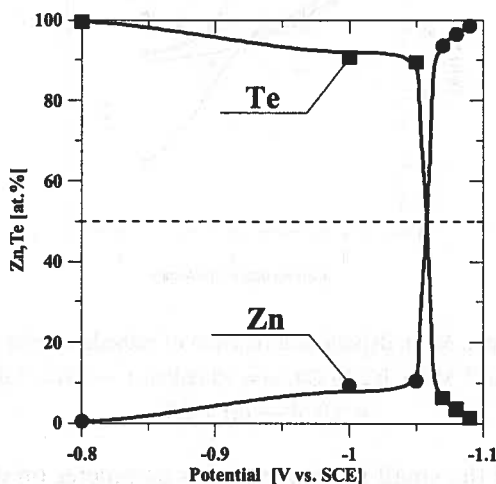

Fig. 4. Average composition of Zn Te layers as a function of the cathode potentials (thickness $\approx$ 1 μm)

tion ZnHCit$^-$ citrate complexes occur, whereas there is no available data for that of Te(IV)-Citrate [11]. Apart from the high solubility of TeO$_2$, citrate electrolytes ensure a stable pH value and more compact deposits.

An increase in pH causes a significant decrease of the slop of the curves presenting the chemical composition of deposits in function of current densities (Fig. 6).

As the citrate concentration in the bath containing 0.1 M Zn(II) increased from 0.2 M to 0.4 M, the Te content decreased at lower current densities (eg.79.1 to 61.8 at.
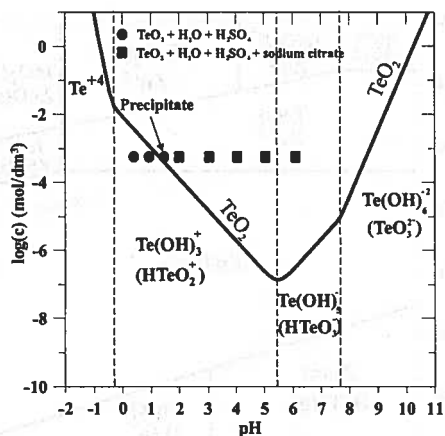
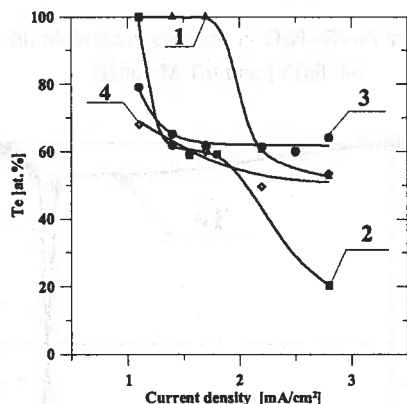Fig. 5. Influence of pH on the solubility of TeO$_2$, at 25°C (on the basis of [12])

Fig. 6. Tellurium content (atom. %) in deposit as a function of cathode current density for electrolytes of different pH (0.1 M Zn, 5 · 10^{-4} M Te, 0.2 M Cit, ω = 10 rad/s); 1 — pH = 3.0, 2 — pH = 4.0, 3 — pH = 5.0, 4 — pH = 6.0

% for 1.1 mA/cm^2) and the small influence of this parameter on chemical composition of the deposits have been observed under investigated conditions, allowing the deposit formation of composition Zn : Te close to 50 : 50 % at. (Table 2).

A trend to a composition gradient as a function of the ZnTe film thickness occurs, owing to the mechanism of co-deposition. The film composition stabilizes at the thickness depending on operating variables. Moreover, as the citrate concentration in the bath and pH increased as well as Zn(II) content decreased, the composition gradient in the deposit gradually reduced.

The morphology of ZnTe films was found to be strongly dependent on the plating baths. The SEM pictures of ZnTe films electrodeposited from simple and complex electrolytes are shown in Fig. 7.

Operating variables and composition of electrodeposits

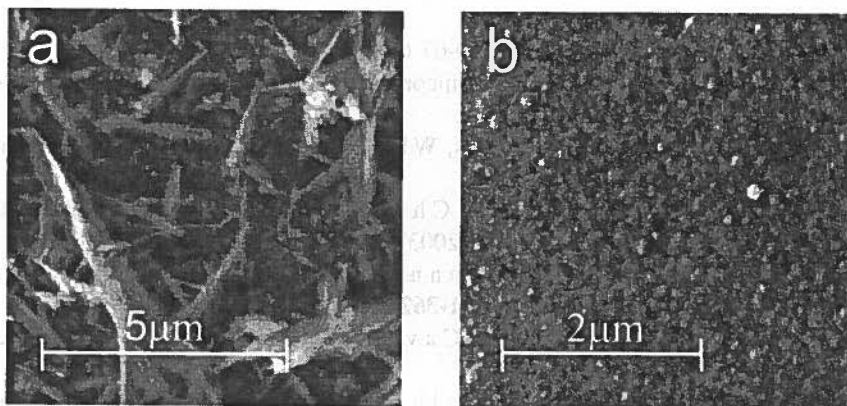| [Zn(II)]/[Te(IV)] concentration ratio	Na₃HCit [M]	pH	Current density or Cathode potential	Zn at %	Te at %	Zn:Te content ratio
400	—	1.0	-1.07 V/SCE	95.9	4.1	23.4
400	—	1.5	-1.50 V/SCE	1.5	98.5	0.01
400	0.2	5.0	0.20 A/dm²	52.8	47.2	1.1
400	0.2	5.0	0.22 A/dm²	46.0	54.0	0.9
200	0.2	6.0	0.20 A/dm²	50.4	49.6	1.0
200	0.2	5.0	0.22 A/dm²	45.0	55.0	0.8
200	0.2	6.0	0.25 A/dm²	46.5	53.5	0.9
200	0.4	5.0	0.22 A/dm²	49.1	50.9	1.0
20	0.2	4.0	0.31 A/dm²	49.2	50.8	1.0

Fig. 7. SEM images of ZnTe films electrodeposited from simple (a) and complex solution (b): a — Cathode potential — 1.05 V/SCE, [Zn(II)]/[Te(IV)] = 400, pH = 0.5, 10.6% at. Zn, 89.4% at. Te, b — Current density 0.22 A/dm², [Zn(II)]/[Te(IV)] = 200, pH = 5.0, 0.4 M Cit, 49.1% at. Zn, 50.9% at. Te

It was found that film deposited from simple solution exhibited a rough surface and there is no define grain structure as can easily be observed (Fig. 7a). Contrary for deposits obtained from complex bath, the SEM picture shows a smooth surface with small crystallites (Fig. 7b).

4. Conclusion

- The ZnTe electrodeposition is mainly controlled by mass transfer of the tellurium species to the cathode.
- Under potentiostatic condition, for a simple sulfate baths, an abrupt change of the chemical composition from tellurium-rich to zinc-based deposits occurs

within the very narrow potential range causing the difficulties in determination of operating parameters leading to stoichiometric ZnTe films.

- ZnTe films deposited from complex citrate baths of the wide range of the [Zn(II)]/[Te(IV)] concentration ratio (400 – 20) at pH 4 – 6 exhibited a stoichiometric composition of Zn/Te in the ratio approximate 50:50 at. %.

- A trend to a composition gradient as a function of the film thickness occurs, owing to the mechanism of ZnTe electrodeposition. The film composition stabilizes at the thickness depending on operating variables.

- The films deposited from complex baths showed a shiny reddish-brown or blackish- gray appearance with granular and compact morphology. The surface coverage is almost completed and the grains represent aggregates of very small crystallites.

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