Characterization of zinc telluride thin films for photoelectrochemical applications

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Abstract

Zinc telluride (ZnTe) semiconducting thin films were prepared by cathodic electrodeposition on to tin-oxide-coated glass and titanium substrates. Studies revealed that stoichiometric ZnTe films were synthesized by maintaining the deposition potential, solution pH, zinc concentration, and bath temperature as -1.1 V versus a saturated calomel electrode, 3.5 ± 0.01, 0.15 M, and $90\,°C$ respectively. The effect of deposition potential on the structure of ZnTe films was investigated. The variations of the optical constants and dielectric constant of ZnTe thin films with wavelength were studied. The surface morphology and film composition were analysed by means of a scanning electron microscope and energy-dispersive x-ray analysis respectively. It is found that a minimum concentration of Zn^{2+} ions in the solution bath yielded stoichiometric films with smooth surfaces. Preliminary studies on photoelectrochemical solar cells based on ZnTe were carried out and the results are discussed.

1. Introduction

In recent years, research on zinc telluride (ZnTe) has gained momentum due to its potential applications in various opto-electronic devices and solar cell technology. ZnTe films are well suited for use in thin-film opto-electronic devices due to their high-absorption-coefficient, p-type conductivity with a direct optical band gap of 2.26 eV [1]. Polycrystalline ZnTe films and its alloys such as CdTe, CdSe, and CdS are successfully utilized in the fabrication of tandem solar cells and quantum well structures [2]. ZnTe films are usually prepared by techniques such as thermal evaporation [3], hot-wall evaporation [4], rf sputtering [5], liquid-phase epitaxy [6], molecular beam epitaxy [7], and electrodeposition [8]. Among these techniques,

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electrodeposition seems to be the most promising, especially for large-scale use. It has been shown that smooth, uniform, and good quality ZnTe films could be obtained from inexpensive raw materials by low-cost techniques such as electrodeposition [8].

In the present communication, we report our studies on the preparation and characterization of ZnTe thin films by cathodic electrodeposition with an emphasis on the effect of deposition conditions on structure, morphology, and elemental analysis. The optical properties, the effect of deposition potential on the surface morphology, and the use of polycrystalline ZnTe films in a photoelectrochemical (PEC) solar cell are also studied.
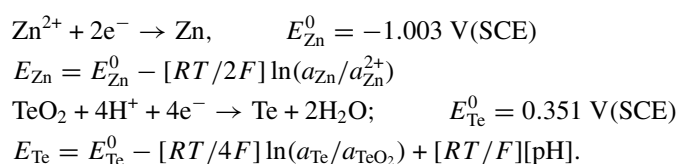
2. Experimental details

ZnTe thin films were electrodeposited from an aqueous solution containing 99.99% pure $ZnSO_4$ (0.15–0.21 M) and $HTeO_2^+$ (0.5 mM) using a scanning potentiostat (Model PAR 362, USA). The telluride ion was supplied in the form of TeO_2. The reference electrode was a commercial saturated calomel electrode (SCE) and the counter-electrode was a pure graphite rod. The substrates were tin-oxide-coated glass with a sheet resistance of 10 $\Omega/\square$. Prior to deposition, the substrate surfaces were degreased using a detergent for 10 s, rinsed in deionized water, and then dipped in a 2 M HCl solution for 10 s. Finally, the substrates were thoroughly rinsed in deionized water. The deposition potential of ZnTe was determined by plotting the cell current against the reference electrode potential; the potential corresponding to a sharp increase in the cell current was taken as the deposition potential of ZnTe. The films were found to be uniform and to adhere well to the substrates.

X-ray diffraction (XRD) analysis was carried out using a Philips PW 1710 x-ray diffractometer with Cu Kα radiation ($\lambda = 1.542$ Å). A UV–VIS–NIR spectrophotometer (JASCO Corporation; UV-530) was used to study the optical characteristics. The surface morphology of the deposited films was studied by a scanning electron microscope (SEM) (JEOL JSM 840) and the composition of the films was analysed by the EDAX microanalytical unit of the SEM. PEC measurements on as-deposited and annealed samples were carried out using a three-electrode compartment cell.

3. Electrochemistry of ZnTe films

The basic electrochemical reactions for the electrodeposition of ZnTe and their corresponding Nernst relations are

$$Zn^{2+} + 2e^- \rightarrow Zn, \qquad E_{Zn}^0 = -1.003 \text{ V(SCE)}$$
$$E_{Zn} = E_{Zn}^0 - [RT/2F]\ln(a_{Zn}/a_{Zn}^{2+})$$
$$TeO_2 + 4H^+ + 4e^- \rightarrow Te + 2H_2O; \qquad E_{Te}^0 = 0.351 \text{ V(SCE)}$$
$$E_{Te} = E_{Te}^0 - [RT/4F]\ln(a_{Te}/a_{TeO_2}) + [RT/F][pH].$$

Here $a_{Zn_{2+}}$ and a_{TeO_2} are the activities of Zn and TeO_2 in the electrolyte, while a_{Zn} and a_{Te} are the activities of Zn and Te in ZnTe. E_{Zn}^0 and E_{Te}^0 are the standard reduction potentials of Zn and Te; E_{Zn} and E_{Te} are the equilibrium potentials of Zn and Te. F is the Faraday constant, R is the universal gas constant, and T is the temperature of the bath.

It has been reported that [9] telluride anion formation from the six-electron reduction of Te (IV) ions is assumed negligible with the deposition potentials used. So the deposit is formed by solid-state reaction of plated Zn and Te atoms rather than precipitation of H_2Te and Zn^{2+}. Therefore Zn + Te $\rightarrow$ ZnTe with negative free-energy formation $\Delta G^0 = -141.6$ kJ mol^{-1}. From the equilibrium electrode potential of Te and Zn, it can be seen that the potential of Te

Table 1. Deposition conditions and ZnTe characterization. Solution pH: 3.5 ± 0.01; deposition potential: -1.1 V versus the SCE; bath temperature: $90\,^{\circ}$C.

Sample	Film thickness (nm)	Zn^{2+} concentration (M)	$HTeO_2^+$ concentration (mM)	Film appearance	Zn:Te (%)
A1	680	0.15	0.5	Reddish brown	49:51
A2	710	0.20	0.5	Orange	47:53
A3	700	0.25	0.5	Greyish brown	42:58
A4	715	0.30	0.5	Dark brown	46:54

is far more positive than that for zinc deposition. Further, to obtain simultaneous deposition of Zn and Te, the electrolyte concentration should be adjusted so as to bring the electrode potentials of the two deposits closer. It is desirable to use a high concentration of Zn and low concentration for the nobler component Te, so that the deposition potential of Zn shifts towards a positive value, approaching the Te deposition potential. The deposition of Te will be diffusion controlled due to the very low concentration of TeO_2 (and consequently of the $HTeO_2^+$). Based on these electrode reactions, a higher concentration of 0.15 M of Zn and very low concentration of 0.5 mM of Te have been taken in the bath for the deposition of ZnTe films. Since the electrodeposition of ZnTe is a six-electron transfer process, in each deposition, the number of transferred electrons was calculated from the total charge and the mass of the deposit. For all good films, the number of transferred electrons for the deposition of one molecule of ZnTe was found to be close to six.

4. Results and discussion

4.1. Sample preparation

ZnTe thin films of thickness of 0.1–1.2 μm were electrodeposited cathodically onto tin-oxide-coated glass and titanium substrates. The thicknesses of the films were measured using a multiple-beam interferometer in the thickness range 0.1–0.4 μm. A weight loss method was used to estimate the thickness of the ZnTe films in the range 0.4–1.2 μm. Since the film thickness was not uniform over the entire area, an average was taken. The surface profiling technique is not suitable for films deposited on conducting substrates owing to the roughness of the surface. The deposition parameter limits for yielding smooth, uniform, and well adhering films are found to be as follows: deposition potential: -0.8 to -1.1 V versus the SCE; solution pH: 3.5 ± 0.01; Zn concentration: 0.15–0.30 M; Te concentration: 0.5 mM; bath temperature: 30–90 $^{\circ}$C; plating duration: 10–60 min.

ZnTe films were electrodeposited at different concentrations of Zn and Te and their characteristic appearances are given in table 1. The $HTeO_2^+$ concentration was kept at a low value of 0.5 mM throughout all the depositions and the Zn^{2+} concentration was varied from 0.15 to 0.30 M. An approximate stoichiometric composition of 49:51 (Zn/Te) was obtained for a lower zinc concentration of 0.15 M. Also it was observed that the peak height of the XRD signal of the (111) cubic phase increases with decreasing Zn^{2+} concentration, indicating preferred orientation and improved crystallinity of ZnTe films deposited at lower Zn^{2+} concentration. The plating efficiency was estimated by calculating the total charge passed through the plating circuit during deposition, which gives the amount of material deposited. It was estimated that at a deposition potential -0.9 V versus the SCE, the plating efficiency was 0.25 C cm^{-2}, whereas at -1.1 V versus the SCE, the efficiency was 0.95 C cm^{-2}.
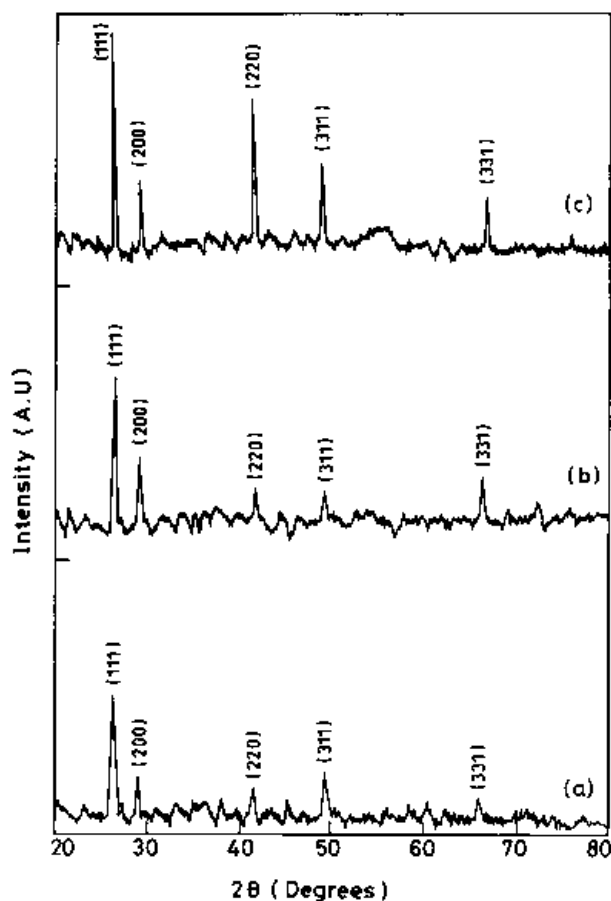
Figure 1. XRD spectra of typical ZnTe layers deposited at (a) 0.8 V versus the SCE; (b) −0.95 V versus the SCE; (c) −1.1 V versus the SCE (solution pH: 3.5 ± 0.01; bath temperature: 90 °C).

4.2. Structure of ZnTe layers

The structure of the electrodeposited ZnTe films was investigated by XRD analysis with Cu Kα radiation. The three samples fabricated under different plating potentials were analysed by means of XRD and their diffraction patterns are shown in figure 1. The patterns revealed that the films were polycrystalline in nature with cubic structure, and exhibited preferential orientation along the (111) direction. Examination of the peaks shows that electrodeposits are not formed from two separate elements, but correspond to a single alloy phase. It is seen from the figure 1 that the degree of crystallinity increased with decreasing deposition potential. The preferred orientation of the ZnTe films was weakened with decrease in the cathodic potential from −1.1 to −0.8 V versus the SCE, and was lost for the films prepared under −0.8 V versus the SCE or comparatively positive plating potentials. The relative intensities of the diffracted x-ray lines for the sample prepared at −1.1 V(SCE) exactly match those tabulated in JCPDS files. For the films deposited above −1.1 V versus the SCE, the XRD peak height decreases due to the interference of hydrogen evolution. This hydrogen evolution appearantly reduces the plating efficiency by ejecting already deposited material into the solution, and/or by further reduction of Te to Te^{2-}. A well crystallized phase was present in deposits from a solution
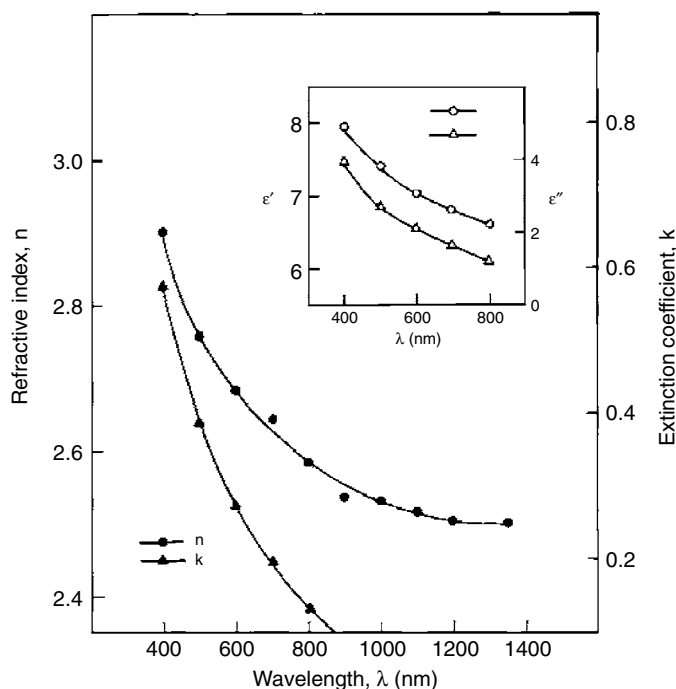
Figure 2. Dependences of n and k on wavelength for a typical ZnTe film. Inset: variations of ε' and ε'' with wavelength.

with lower $HTeO_2^+$ concentration. Deposits prepared in a solution with higher concentration of $HTeO_2^+$ were less crystalline. Samples deposited at 90 °C show narrower peaks than those deposited at 25 °C.

4.3. Optical characteristics

Figure 2 shows the variation of the refractive index (n), and the extinction coefficient (k), for a typical ZnTe thin film. The refractive index is found to decrease with increase in wavelength and tends to become constant at higher wavelengths. Absorption is a phenomenon of fundamental interest because of its relation to the dynamics of the electrons and ions of the medium under the influence of electromagnetic radiation. An absorbing medium is characterized by a complex dielectric constant $\varepsilon_c = \varepsilon' + i\varepsilon'' = (n + ik)^2$, where ε' and ε'' are the real and imaginary parts of the dielectric function respectively. From the optical constants, the real and imaginary parts of the dielectric function are estimated using the relations $\varepsilon' = n^2 - k^2$ and $\varepsilon'' = 2nk$. The variations of ε' and ε'' with wavelength for a typical ZnTe film are shown in the inset of figure 2. It is observed that both ε' and ε'' decrease with increase of wavelength and a similar observation was reported by Thutupalli and Tomlin [10] for ZnTe thin films.

4.4. Surface morphology

The surface morphology of the electrodeposited ZnTe films was analysed by SEM. The SEM photographs of the three deposited samples at different plating potentials are shown in figure 3. The morphology of the ZnTe films was found to be strongly dependent on the plating potential. This is partially due to the fact that Te plating from dilute electrolyte is a
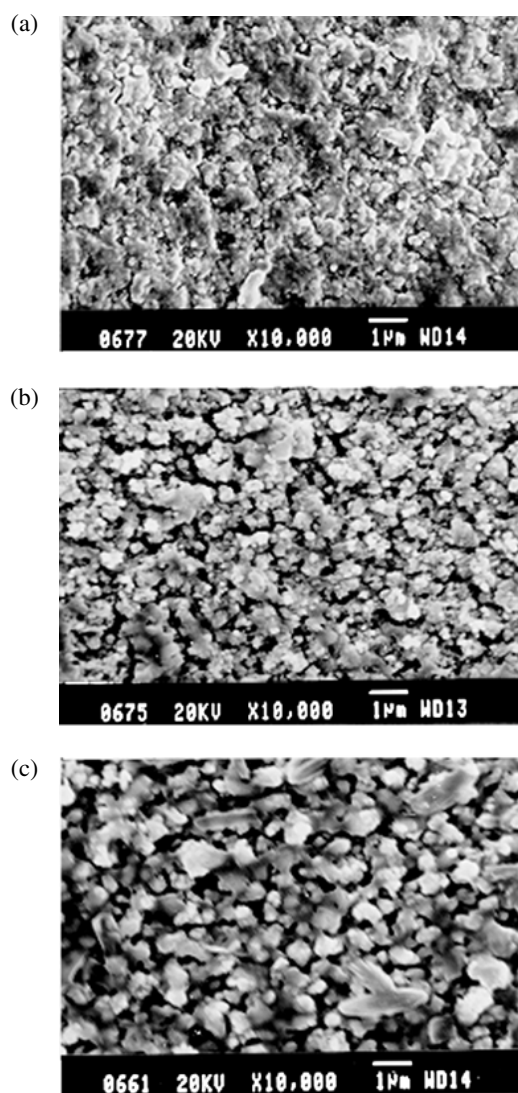
(a)

(b)

(c)

Figure 3. SEM pictures of typical ZnTe samples deposited at (a) −0.8 V versus the SCE; (b) −0.95 V versus the SCE; and (c) −1.1 V versus the SCE.

diffusion-limited process. Therefore, high plating potentials quickly deplete the Te species from the region near the cathode, and if $HTeO_2^+$ is not supplied fast enough through this diffusion region, discontinuous, non-adhering deposition occurs. It is observed from the SEM pictures that, at low cathodic potentials (−0.8 V) non-homogeneous and island-like crystallites were seen. Even though the surface coverage is good, there is no definite grain structure that can easily be observed in the surface. It has been found that a fine-grained globular structure is observed for the films deposited at −1.1 V versus the SCE. Moreover, the cathodic current density is an important factor, influencing the crystallite size. At low current densities, the deposits obtained have been found to be coarse and crystalline due to the slow discharge of ions. The rate of growth of nuclei would be more than the rate at which new ones are formed.
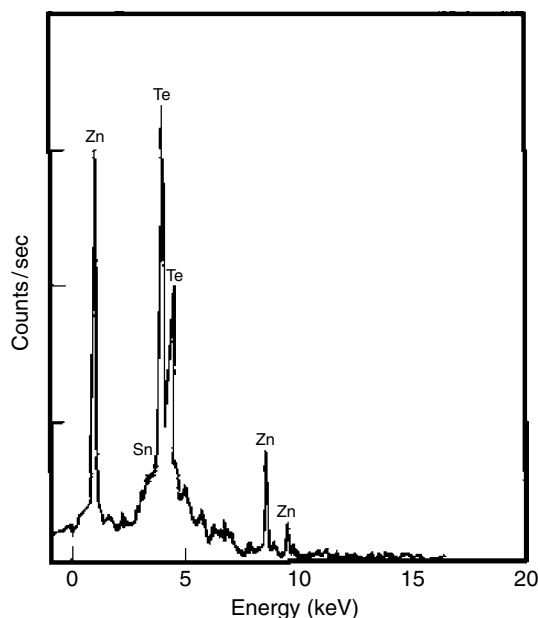
Figure 4. An EDAX spectrum of a typical ZnTe sample deposited at -1.1 V versus the SCE. (Zn^{2+} concentration: 0.15 M; $HTeO_2^+$ concentration: 0.5 mM).

As the current density is increased, the deposits become fine grained due to the higher rate of growth of nuclei. But at very high values of the current density, evolution of hydrogen occurs because of the depletion of metal ions in the vicinity of the cathode. Bubble formation leads to porous and spongy deposits. But some regions were seen to show a clearer contrast than the underlayer, indicating the presence of loosely adhering surface particles. The tendency of the film surface to accumulate loosely adhering surface particles has increased for thicker deposits.

4.5. Compositional analysis

The composition of the ZnTe thin films was analysed by the EDAX microanalytic unit attached to the SEM. The sharpness of the ZnTe peaks increases with cathodic potential, owing to an increase in grain size. A representative EDAX spectrum of a ZnTe film with a Zn^{2+} concentration of 0.15 M and a $HTeO_2^+$ concentration of 0.5 mM deposited at a potential of -1.1 V versus the SCE is shown in figure 4. It is observed that the emission lines of Zn and Te were present in the energy range investigated and also that the peak related to Sn represents the effect of SnO_2 coating of the substrate. The average Zn:Te atomic ratio was observed to be 49:51, indicating stoichiometric formation of ZnTe films. It is found that the gradual increase of the Zn^{2+} concentration in the electrolyte bath with a constant $HTeO_2^+$ concentration of 0.5 mM resulted in the deposition of ZnTe films with excess Te (table 1). The studies indicate that the optimum Zn^{2+} concentration in the bath for synthesizing stoichiometric ZnTe films is 0.15 M.
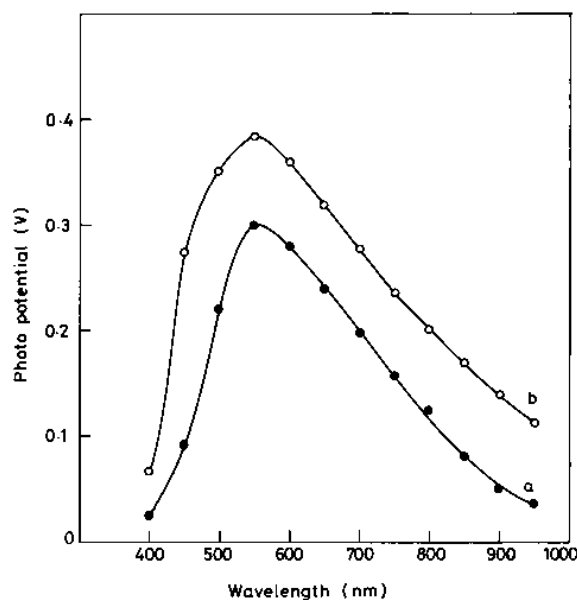
Figure 5. Variations of photopotential with wavelength for the ZnTe photoelectrode (a) as deposited and (b) annealed (350 °C in air).

4.6. PEC studies

From the point of view of PEC studies, p-type semiconducting materials endowed with acceptable stability and compatibility are required so that enhanced photoresponsiveness to illumination may become possible. The quality of an electrodeposited semiconducting film needed for photovoltaic applications depends to a large extent on the applied deposition potential, the composition, and the pH of the deposition bath. PEC studies of ZnTe thin films were carried out in a conventional three-electrode system with p-ZnTe as the photocathode, a platinum foil, and SCEs used as the counter-electrode and reference electrode. The electrolyte consisted of 1 M each of Na_2S, S, and KOH. A collimated light beam from a 150 W tungsten halogen lamp was used as the light source and photopotential measurements were carried out using a Keithley digital multimeter (Model 2000, USA). The variations of the photopotential with wavelength for as-deposited and annealed (350 °C in air) ZnTe films are shown in figure 5. It is observed that the photopotential is larger for the annealed photoelectrode, which may be attributed to an increase in grain size of annealed ZnTe samples.

5. Conclusions

Electrochemical synthesis was carried out successfully to prepare polycrystalline ZnTe films by a single-step electrodeposition process from an aqueous solution of $ZnSO_4$ and TeO_2. The effect of Zn^{2+} concentration on the film stoichiometry was studied and it was found that a minimum concentration of Zn^{2+} in the bath yielded nearly stoichiometric ZnTe film. The structure was found to be cubic and the degree of crystallinity increased with decreasing deposition potential. The surface morphology reveals uniform grain size for films deposited at more negative deposition potentials (-1.1 V versus the SCE). PEC studies were carried out and the effect of annealing on the photopotential was investigated.

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