STRUCTURAL AND SEMICONDUCTING PROPERTIES OF ZnTe THIN FILMS GALVANOSTATICALLY GROWN ONTO MONOCRYSTALLINE InP SUBSTRATE FROM TeCl₄/DMSO SOLUTION.

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(Received 27th March 2007 – Accepted 12th June 2007)

ABSTRACT

ZnTe thin films were galvanostatically electrodeposited onto (100) InP substrates from an electrolytic solution containing TeCl₄ dissolved in DMSO. Cyclic voltammetry in the dark was used to identify the process involved in the complex electrochemical reduction of the Te(IV) precursor. Quantitative analysis of energy dispersive x-ray analysis results indicated that the composition ratio (Zn:Te) was not possible to determine due the presence of a tellurium excess in the deposits. X-ray diffraction results revealed that the thin films obtained showed a preferred (200) orientation with cubic structure indicating the existence of an epitaxial grow along the (100) crystalline planes of the InP substrate. The n-type character of the films was deduced from Mott-Schottky plots that also gave a donor density of $1.54 \times 10^{18} \text{ cm}^{-3}$. From the optical absorption measurements a bandgap of 2.21 eV was obtained.

Key words: ZnTe, electrodeposition, semiconductors.

INTRODUCTION

Zinc telluride is a wide-gap II-VI compound semiconductor which has shown great potential for optoelectronic device applications such as light-emitting devices^{1,2}, THz detectors³ and window material for CdTe-based solar cells⁴. Various techniques have been reported for the fabrication of ZnTe thin films, such as thermal vacuum evaporation⁵, vapor-phase epitaxy⁶, molecular beam epitaxy⁷, and electrochemical deposition⁸⁻¹³. ZnTe has usually been electrodeposited at a relatively negative potential, which indicates that hydrogen evolution reaction is also produced, reducing the current efficiency of the electrochemical process. In order to achieve higher efficiency, either a higher pH or more positive electrodeposition potential can be employed. The use of a nonaqueous solvent, such as ethyleneglycol for ZnTe or DMSO for Ag₂Te electrodeposition is an alternative approach for avoiding this problem^{8, 14}. The aim of current paper is to explore the possibilities of using a DMSO bath for the galvanostatic electrodeposition of ZnTe on monocrystalline InP substrates. As elemental tellurium has a low solubility in this solvent, TeCl₄ was employed as tellurium precursor which revealed a complex voltammetric behavior. A set of electrochemical and chemical reactions, including the electroprecipitation of the films, is proposed to reasonably interpret the overall processes involved.

EXPERIMENTAL

The zinc telluride films were electrodeposited on n-type (100) InP substrates using a plating solution containing 100 mM LiCl (Aldrich, 99.99 + %), 100 mM ZnCl₂ (Aldrich, 99.999 %) and 0.5 mM TeCl₄ (Merck) dissolved in Dimethyl sulfoxide (DMSO) was used without further purification. The InP working electrodes were cleaned for 10 min in boiling ketone, 3 min in boiling methanol, 3 min in cold methanol, then 20 s in a 0.2 % Br₂/methanol solution and finally rinsed with deionized water. Before each measurement the working electrode was rinsed with 3 M H₂SO₄ and then with deionized water. The electrochemical cell was immersed in a silicone bath at a temperature of $118 \pm 1^\circ \text{C}$. The electrodeposition process was performed galvanostatically, using Ag/AgCl and platinum wire as a reference electrode and counter electrode, respectively. All the potentials are expressed versus Ag/AgCl. After deposition the substrate was removed from the electrolyte and rinsed with deionized water, and then dried with a stream of argon gas.

Cyclic voltammetry, impedance, and galvanostatic measurements were carried out using an IM6e Potentiostat/Galvonostat (Bas – Zahner) in unstirred solutions in the darkness. The film structures were characterized by X-ray diffraction. The spectra were recorded with a Philips PW3710 diffractometer using CuK_α radiation. The accelerating voltage was set at 40 KV with a 25 mA flux. Scatter and diffraction slits of 1° and 0.1 mm collection slit were used. A JEOL 5900 LV SEM apparatus was used to image and characterize the ZnTe films by scanning electron microscopy (SEM). Chemical composition of the ZnTe samples was obtained by energy dispersive X-ray analysis (EDAX). This was done with the use of a THERMO NORAND VANTAGE (with a NORVARD window) device which is in the same equipment that was employed for obtaining the SEM images.

Optical transmission measurements on SnO₂:F (FTO) covered glass substrates were carried out using a SHIMAZDU UV-160 A double beam spectrophotometer. Spectra were recorded at room temperature against air as a reference.

RESULTS AND DISCUSSION.

• Voltammetry behaviour of the 0.1 M LiCl, 0.1 M ZnCl₂, 0.5 mM TeCl₄, DMSO solution.

In an earlier report Pandey *et al.*¹⁵ studied the thermodynamic and kinetic behaviour of tellurium deposition from TeCl₄ solution in ethylen glycol. Following their interpretation, for tellurium electroreduction in DMSO current contribution C₁ (see Fig. 1) can be related to the charge transfer reaction:

Following the negative scan, tellurium reduction takes place in the potential domain of peak C₂ according to:

Te₂²⁻ ions can react with Zn²⁺ through the precipitation reaction

However, ZnTe₂ may undergo the disproportion reaction,

It is highly probably that the excess of tellurium found in the EDAX analysis of the deposits be originated by this reaction (*vide infra*). Following the potential excursion, the wide current contribution indexed as C₃ involves two processes attributed to reactions:

Fig. 1 Cathodic hemicycle recorded onto n – InP (100) of the system 0.1 M LiCl + 0.1 M ZnCl₂ + 0.5 mM TeCl₄ in DMSO. $v = 0.05 \text{ Vs}^{-1}$. $T = 115^\circ\text{C}$, in the static hydrodynamic conditions.

Equation (5) accounts for ZnTe formation through an electroprecipitation reaction at the interface whereas reaction (6) corresponds to the direct six electron reduction of Te^{4+} . As a consequence of the overpotential associated to the presence of a ZnTe semiconducting layer that already coats the InP substrate, making more difficult the corresponding charge transfer reaction, the latter process appears shifted towards more negative potentials. Finally, the potential scan ends with a great current increase which is related to the massive electroreduction of zinc ions to metallic zinc.

•Galvanostatic ZnTe electrodeposition.

Figure 2 show; the E/t transients for the deposition of ZnTe on n – InP (100) substrates at different current densities. It is observed that independent on the applied current density, the final potential remains fixed around -1.3 V . This high value can be explained considering that at shorter times starts the sequence of reactions (1) to (6), producing the fast formation of a ZnTe/Te semiconducting layer which acts as a barrier that increases the resistance to the charge transfer at the interface.

Fig. 2 E/t Transients for the constant current ZnTe electrodeposition recorded in the dark in unstirred 0.1 M LiCl, 0.1 M ZnCl₂, 0.5 mM TeCl₄ in DMSO solution.

Table 1 presents the current densities that were applied in order to obtain deposits of different thickness together with the estimated thickness calculated from the charge involved in the E/t transients considering an overall 6 electron process. It is necessary to point out, that as the ZnTe formation is produced

through electroprecipitation, it is probably that the thickness is over estimated. In fact, the growth of the film on the electrode surface can be controlled by two nucleation processes: heterogeneous and homogeneous. According to the kinetics of each reaction (1) to (6), the process of heterogeneous nucleación on the electrode surface can take place when the concentrations of the ions (Zn^{2+} , Te_2^{2-} and Te^{2-}) approach to the over-saturation conditions. The charge involved in the processes (see Fig. 1) indicates that this condition was surpassed promoting the homogeneous nucleation outside of the interface electrode/solution. This affects directly to the final thickness of the film as well as the Faradic yielding of the overall process.

Table 1.- Current densities and calculated thickness for the galvanostatic electrodeposition of ZnTe on InP substrates

Sample	$j / \mu\text{A cm}^{-2}$	Calculated thickness $d / \mu\text{m}$
M1	500	0.5
M2	400	0.5
M3	500	1.0
M4	444	0.5
M5	540	0.5

Table 2.- Zn and Te atomic percentage and Zn:Te ratios

Sample	Zn atomic %	Te atomic %	Zn:Te
1	1.18	2.27	1:1.9
2	4.34	20.10	1:4.4
4	2.52	17.96	1:7.1
5	8.98	19.14	1:2.1

The composition of the samples, analyzed by EDAX, is depicted in Table 2. The analysis of the data reveals a great variation in the composition of both components, therefore no defined stoichiometry can be accurately established. A possible explanation for this behaviour is the presence of a variable amount of tellurium excess (clear coloration) in the SEM micrographs shown in figure 3. This implies that in the region of the surface selected for X-ray analysis is practically impossible to determine the exact atomic Zn:Te ratio. This, however, was not an obstacle for the further characterization of semiconducting properties of the films (*vide infra*).

M 1

M 5

Fig. 3.- SEM micrographs for samples grown at $500 \mu\text{A cm}^{-2}$ (M 1) and at $540 \mu\text{A cm}^{-2}$ (M 5).

• Structural and optical Characterization.

The structural XRD analysis of samples grown at different current densities and shown in figure 4 revealed a number of peaks corresponding to the InP substrate, as well as to ZnTe and Te. The location and intensity of Te peaks depends on the current densities values. The only reflection of the ZnTe was observed at $2\theta = 31.81^\circ$ corresponding to the (200) reflection of the closed packed cubic structure, which is a little more intense for the film grown at $500 \mu\text{A cm}^{-2}$. In spite that the peak is not strong, the presence of the (200) plane, parallel to the (100) reveals some epitaxial character of the film.

Fig. 4.- XRD spectra of ZnTe (o) films grown at: (A) 500 $\mu\text{A cm}^{-2}$ and (B) 540 $\mu\text{A cm}^{-2}$.

The optical absorption spectrum of the ZnTe film was used to determine the optical bandgap. From the calculated values of the absorption coefficients, a straight line plot of $(\alpha h\nu)^2$ versus $h\nu$ was obtained, as shown in figure 5, indicating a direct transition at the fundamental absorption edge. From the interpolation of this plot a value of 2.21 eV for the bandgap of the ZnTe film was determined. This value agrees with that reported in the literature¹⁶.

Fig. 5.- $(\alpha h\nu)^2$ vs. $h\nu$ plots calculated from characteristic transmission spectra of $\text{SnO}_2\text{:F} / \text{ZnTe}$ interface for the sample grown at 500 $\mu\text{A cm}^{-2}$ (M1).

In order to determine some characteristic semiconductor parameters of the ZnTe films, the variation of the interfacial capacitance with potential was extracted from impedance measurements at high frequency assuming a simple parallel RC equivalent circuit. The corresponding experimental data were recorded as a classical Mott-Schottky plots that is shown in figure 6 for sample M3, together with that for the InP substrate as comparison. The positive slope means that the substrate and the grown film present both a n-type electrical conductivity. The donor density, N_D , determined from the slopes of the plots give $N_{D\text{ZnTe}} = 1.54 \times 10^{18} \text{ cm}^{-3}$ and $N_{D\text{InP}} = 1.60 \times 10^{18} \text{ cm}^{-3}$, values that are typical of extrinsic doped semiconductors. Finally, the extrapolation of the straight line to $1/C^2 = 0$ gives for ZnTe a flat band potential, $V_{fb} = -0.474 \text{ V}$ vs Ag/AgCl. In general, V_{fb} is an important quantity for semiconductor electrodes that are employed in photoelectrochemical applications because it determines the band edge position at the semiconductor-electrolyte interface, which in turn, determine the energies of the conduction-band electrons and valence-band-holes reacting with the electrolytic solution.

Fig. 6.- Mott – Schottky plots for ZnTe and InP recorded in the darkness using an acetate buffer (pH = 4.50) at room temperature without stirring. $f = 100 \text{ KHz}$.

CONCLUSIONS

ZnTe has been successfully prepared by single step galvanostatic electrodeposition onto n-type (100) InP substrates from a solution containing TeCl_4 dissolved in DMSO as tellurium precursor. The presence of a X-ray diffraction peak corresponding to the (200) crystalline plane in the as grown films revealed the presence of epitaxy along the (100) plane of the monocrystalline substrate. The qualities of the films were evidenced by the donor number and the bandgap values, both coincident with those reported in the literature. The only constraint was the presence of a tellurium excess that could be easily eliminated by annealing in an air stream.

ACKNOWLEDGEMENTS

This work has been funded by FONDECYT, grant N° 1040650.

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