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

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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) crystallographic 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 x 10¹⁸ 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 devices¹–⁷, THz detectors¹ and window material for CdTe-based solar cells⁸. Various techniques have been reported for the fabrication of ZnTe thin films, such as thermal vacuum evaporation⁹, vapor-phase epitaxy⁵, and window material for CdTe-based photovoltaic devices. Various techniques have been investigated for the electrodeposition of ZnTe thin films, such as thermal vacuum evaporation⁹, vapor-phase epitaxy⁵, molecular beam epitaxy², and electrochemical deposition⁴–¹⁵. 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 ethylene glycol for ZnTe or DMSO for Ag,Te electrodeposition is an alternative approach for avoiding this problem⁸,¹⁴. The aim of current paper is to explore the possibilities of using a DMSO bath for the galvanostatic electrodeposition of ZnTe on monocristalline InP substrates. As elemental tellurium has a low solubility in this solvent, TeCl₄ 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 ± 1º C. The electrodeposition process was performed galvanostatically, using Ag/AgCl and platinum wire as a reference and counter electrode, respectively. All the potentials are expressed versus Ag/AgCl 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 ethylene glycol. Following their interpretation, for tellurium electrodeposition in DMSO current contribution indexed as C₁ (see Fig. 1) can be related to the charge transfer reaction:

\[ \text{Te}^{4+} + 4e^- \rightarrow \text{Te} \] (1)

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

\[ 2\text{Te} + 2e^- \rightarrow \text{Te}_2^{2-} \] (2)

Te₂⁻ ions can react with Zn²⁺ through the precipitation reaction:

\[ \text{Zn}^{2+} + \text{Te}_2^{2-} \rightarrow \text{ZnTe}_2 \] (3)

However, ZnTe₂ may undergo the disproportion reaction,

\[ \text{ZnTe}_2 \rightarrow \text{ZnTe} + \text{Te} \] (4)

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:

\[ \text{Te} + \text{Zn}^{2+} + 2e^- \rightarrow \text{ZnTe} \] (5)

\[ \text{Te}^{4+} + \text{Zn}^{2+} + 6e^- \rightarrow \text{ZnTe} \] (6)

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

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 ± 1º 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 reference.

Cyclic voltammetry, impedance, and galvanostatic measurements were carried out using an IM6e Potentiostat/Galvonostat (Bas – Zahner) in unstirred water, and then dried with a stream of argon gas. The spectra were recorded with a Philips PW3710 diffractometer. The spectra were recorded with a Philips PW3710 diffractometer. The spectra were recorded with a Philips PW3710 diffractometer. The spectra were recorded with a Philips PW3710 diffractometer. The spectra were recorded with a Philips PW3710 diffractometer. The spectra were recorded with a Philips PW3710 diffractometer. The spectra were recorded with a Philips PW3710 diffractometer. The spectra were recorded with a Philips PW3710 diffractometer. The spectra were recorded with a Philips PW3710 diffractometer.
**Cathodic hemicycle recorded onto n – InP (100) of the system 0.1 M LiCl + 0.1 M ZnCl₂ + 0.5 mM TeCl₄, in DMSO.** ν = 0.05 Vs⁻¹. T = 115 ºC, 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 Te⁴⁺. 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.

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 nucleation on the electrode surface can take place when the concentrations of the ions (Zn²⁺, Te₂⁻ and Te⁴⁺) 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

<table>
<thead>
<tr>
<th>Sample</th>
<th>j / µA cm⁻²</th>
<th>Calculated thickness d / µm</th>
</tr>
</thead>
<tbody>
<tr>
<td>M1</td>
<td>500</td>
<td>0.5</td>
</tr>
<tr>
<td>M2</td>
<td>400</td>
<td>0.5</td>
</tr>
<tr>
<td>M3</td>
<td>500</td>
<td>1.0</td>
</tr>
<tr>
<td>M4</td>
<td>444</td>
<td>0.5</td>
</tr>
<tr>
<td>M5</td>
<td>540</td>
<td>0.5</td>
</tr>
</tbody>
</table>

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 stablished. 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).

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

<table>
<thead>
<tr>
<th>Sample</th>
<th>Zn atomic %</th>
<th>Te atomic %</th>
<th>Zn:Te</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.18</td>
<td>2.27</td>
<td>1:1.9</td>
</tr>
<tr>
<td>2</td>
<td>4.34</td>
<td>20.10</td>
<td>1:4.4</td>
</tr>
<tr>
<td>4</td>
<td>2.52</td>
<td>17.96</td>
<td>1:7.1</td>
</tr>
<tr>
<td>5</td>
<td>8.98</td>
<td>19.14</td>
<td>1:2.1</td>
</tr>
</tbody>
</table>

The structural XRD analysis of samples grown at different current densities and shown in figure 4 reveal 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 2θ = 31.81° corresponding to the (200) reflection of the closed packed cubic structure, which is a little more intense for the film grown at 500 µA 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.

**Structural and optical Characterization.**

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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 values agrees with that reported in the literature

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.

CONCLUSIONS

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REFERENCES