Effect of pH on the Electrodeposition of ZnTe Film from a Citric Acid Solution*1

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Potentiostatic cathodic electrodeposition of ZnTe was investigated from the viewpoint of the effect of pH on the deposits’ composition and crystallinity using citric acid electrolyte baths, in which Zn(II) and Te(IV) species were dissolved to form ZnH2Cit⁺, ZnHCit, ZnCit−, Zn(Cit)4− and HTeO2−, H2TeO3−, respectively (Cit: citrate) at various pH. The complex equilibrium calculation was carried out to examine the most predominant complex ion for Zn-Cit system at different pH. Deposition of three kinds of deposits, i.e., polycrystalline ZnTe with closely stoichiometric composition, crystalline Te, and the mixed crystal due to Te and ZnTe, can be controlled by changing the pH and [Zn(II)]/[Te(IV)] concentration ratio of the baths. All the deposits obtained at pH 4.0 were well crystallized with a ZnTe cubic preferential orientation along the (111) plane without any post-treatment. The difference of the electrodeposition behavior at various pH was also discussed.

1. Introduction

Thin film ZnTe compound semiconductor has found application as window material in multijunction solar cells based on chalcogenide and chalcopryte type semiconductors due to its optimum energy gap 2.2 eV, low electronic affinity and its p-type conductivity characteristics have improved the ohmic contact on CdTe or GaAs p-type semiconductors, which are absorber material in high-efficiency photovoltaic devices. ZnTe thin films have been prepared by several techniques including molecular beam epitaxy (MBE), vacuum evaporation, r.f. sputtering and electrodeposition. Among these techniques, electrodeposition offers several advantages: it is relatively economical; it can be used on a large scale; and it is conducted at low-temperature. Although there has recently been a growing interest in the electrodeposition of ZnTe film due to these advantages, two issues have concerned us. The first is that heat-treatment is necessary after deposition in order to adjust the Zn/Te stoichiometry, thus forfeiting the advantages of a low-temperature process. The second is that electrodeposition is often performed at a relatively negative potential, indicating that a sub-reaction of hydrogen evolution reduction could arise, leading to a reduction in current efficiency. For these reasons, we have been strongly interested in achieving a single electrodeposition of ZnTe film at a low overpotential (i.e., a more positive potential) and without heat-treatment.

Recently, we have overcome these two issues and have successfully deposited ZnTe films at pH 4.0 from a solution containing ZnSO4, TeO2, H3Cit and Na2Cit (Cit = C6H5O2−). It is well known that Zn and citrate ions form the complex as ZnH2Cit⁺, ZnHCit, ZnCit− and Zn(Cit)4− as shown in the literature. In these complex ion species, the relatively predominant ion species in the electrolytic solution depends on pH of the solution. It is considered that the variations of pH could affect the electrodeposition behavior of ZnTe. Thus, it is necessary to investigate the effect of pH on the electrodeposition of ZnTe.

In this study, the electrodeposition from a citric acid solution was carried out to examine the effect of pH on the electrodeposition behavior and the properties of the resulting ZnTe films.

2. Experimental

Citric acid aqueous electrolytes containing 99.99% pure ZnSO4 (Kanto Kagaku), 99.0% TeO2 (Kanto Kagaku), C6H5O2−, H2O (H2Cit·H2O; Kanto Kagaku) and Na2Cit·2H2O (Kanto Kagaku), and Na3C6H5O7·2H2O (Na3Cit·2H2O; Kanto Kagaku) were employed for electrodeposition of ZnTe. All the chemicals were of reagent grade and were used without pretreatment. Deionized water (7.5 × 105 Ωcm) was obtained from an Autostill water system (YAMATO Co., Ltd. WG25). Table 1 summarizes the concentrations of Zn and Te, and the pH of the citrate electrolytes employed in this study. Each Zn-Cit solution was obtained by dissolving the required amounts of Zn and Te for their respective experimental conditions.

The pH of the solutions was adjusted by changing the mixed ratio of citrate and sodium citrate, i.e., [Na2Cit]/[H2Cit]. The temperature was maintained constant by a rubber heater at 363 K. Cathodic electrodeposition was performed under potentiostatic conditions using a conven-

Table 1  List of aqueous electrolytes containing citrate (Cit) employed for potentiostatic electrodeposition of ZnTe. (M = kmol m⁻³)

<table>
<thead>
<tr>
<th>pH</th>
<th>[H2Cit] (M)</th>
<th>[Na2Cit] (M)</th>
<th>[Cit]total (M)</th>
<th>[Zn(II)] (mM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5</td>
<td>0.50</td>
<td>0</td>
<td>0.50</td>
<td>a1, b1, c1</td>
</tr>
<tr>
<td>2.6</td>
<td>0.45</td>
<td>0.05</td>
<td>0.50</td>
<td>a2, b2, c2</td>
</tr>
<tr>
<td>2.75</td>
<td>0.075</td>
<td>0.425</td>
<td>0.50</td>
<td>a3, b3, c3</td>
</tr>
<tr>
<td>4.0</td>
<td>0.25</td>
<td>0.25</td>
<td>0.50</td>
<td>a4, b4, c4</td>
</tr>
<tr>
<td>5.6</td>
<td>0.05</td>
<td>0.45</td>
<td>0.50</td>
<td>a5, b5, c5</td>
</tr>
</tbody>
</table>

Cathode potential was −0.65 V vs. Ag/AgCl. Te(IV) concentrations were 0.16 mM (M = kmol m⁻³) under all conditions.

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tional three-electrode setup comprised of a potentiostat (Hokuto Denko HA-501) connected to a function generator (Hokuto Denko HB-104) and a coulometer (Fuso Seisakujyo HEC5-343B). An Ag/AgCl electrode immersed in saturated KCl was used as a reference. A gold-plated copper sheet (20 mm × 40 mm) and a platinum sheet (50 mm × 50 mm) were employed for the working and counter electrodes, respectively. The gold-plating (thickness ca. 2 μm) was carried out using a gold-plating aqueous solution (EEJA microfab Au310) under galvanostatic conditions of 4 mA cm⁻² at 323 K. Before gold-plating, the copper sheet was polished with 6, 1 and 0.3 μm diamond paste, cleaned with distilled water and degreased. The electrolytic solution was agitated at 400 rpm with a magnetic stirring unit for all runs. In order to avoid any influence from dissolved oxygen, the electrolyte was deaerated by bubbling pure argon gas through it for about 20 min, following which the flux was kept over the solution. Film deposition was carried out potentiostatically with the total quantity of electricity being 1.0 C cm⁻². The composition of the films was determined quantitatively using energy dispersive X-ray analysis (EDX) (HORIBA EX200). X-ray diffraction (XRD) (RIGAKU RAD-IIIC) was conducted to examine the crystal structure of the Zn-Te compound film. XRD data were obtained using a powder diffractometer with CuKα radiation. The XRD peaks were assigned based on JCPDS data.

3. Solution Chemistry

In order to examine the relatively predominant complex ion for Zn-Cit system at different pH, the complex equilibrium calculations were carried out. In aqueous solution, Zn(II) soluble species form various complexes with citrate ligands (expressed as Cit³⁻ = C₆H₅O₃³⁻). The total amounts of Zn(II) species, C₉Zn, and citrate, C₉Cit, in the electrolytic solution are expressed by the following equations

\[
C_{Zn} = [Zn^{2+}] + [ZnH₂Cit³⁺] + [ZnHCit] + [Zn(Cit)²⁻] + [Zn(Cit)³⁻] \tag{1}
\]

and

\[
C_{Cit} = [H₂Cit] + [H₂Cit⁻] + [HCit²⁻] + [Cit³⁻] + [ZnH₂Cit³⁺] + [ZnHCit] + [ZnCit⁻] + 2[Zn(Cit)²⁻] \tag{2}
\]

The concentrations of each species can be calculated using eqs. (1) and (2), formation constant, β, of the Zn²⁺–citrate complexes, the dissociation constant, K, of citric acid, the total amounts of Zn(II), C₉Zn, and citrate, C₉Cit, and the pH value. The values for β and K are listed in Table 2.

Figure 1 indicates the results obtained with the Zn(II)-citrate bath. The relative predominant ion species are Zn²⁺, ZnH₂Cit³⁺, ZnHCit, Zn(Cit)²⁻ at pH from 0 to 2, pH from 2 to 2.7, pH from 2.7 to 2.8, and at pH > 2.8, respectively. As the contribution of other ion specie, i.e., ZnCit⁻, is less than 10% at pH between 0 and 7, it is assumed that this ZnCit⁻ specie does not contribute the main electrodeposition behavior for the reduction of Zn due to the formation of ZnTe.

The relative predominant ion species for tellurium in the acidic electrolytic solution are HTeO₂⁺, HTeO⁻ at pH between 0 and 5.45, 5.45 and 7, respectively. Although it is considered that Te soluble species could form a complex with citrate ligands, there is no available complex formation data for them. Thus, the reduction reactions for Te were treated as the reaction used in Pourbaix-type diagram.

Consequently, the pH used in this study were 1.5, 2.6, 2.75, 4 and 5.6.

4. Results and discussion

Our recent study concluded that citric acid bath of pH 4.0 with composition: [Zn(II)] = 5–50 mM (M = kmol m⁻³), [Te(IV)] = 0.16 mM, and [Cit] = 0.5 M, gave ZnTe deposits of close stoichiometry under potentiostatic electrodeposition potential at −0.65 V. The deposition behavior is inferred to be (i) cathodic electrodeposition of Te atoms, followed by (ii) underpotential deposition of the Zn(II) ions to form ZnTe. It is necessary for the formation of stoichiometric ZnTe that the depositions of Te atoms are quantitatively followed by that of Zn atoms. Thus, the deposition of Zn should occur immediately after the deposition of Te to prevent codeposition of bulk Te. As stated above, however, the relative predominant ion species in the citric acidic solution depend on the pH. If the predominant species in the bath change, it is predicted that the reduction rate of the deposition could be different.

According to the complex equilibrium calculations, it was indicated that the concentration of relatively predominant ion specie was considerably higher than that of other ion species. Thus, assuming that the reactions of relatively predominant ion species proceed mainly, the reduction reactions for...
tellurium can be as follows:

$$\text{HTeO}_2^+ + 3\text{H}^+ + 4e^- = \text{Te} + 2\text{H}_2\text{O} \quad (0 \leq pH \leq 5.45)$$

(3)

$$\text{HTeO}_3^- + 5\text{H}^+ + 4e^- = \text{Te} + 3\text{H}_2\text{O} \quad (5.45 \leq pH \leq 7)$$

(4)

The reduction reactions for the formation of ZnTe can be given by

$$\text{Te} + \text{Zn}^{2+} + 2e^- = \text{ZnTe} \quad (0 \leq pH \leq 2)$$

(5)

$$\text{Te} + \text{ZnH}_2\text{Cit}^+ + \text{H}^+ + 2e^- = \text{ZnTe} + \text{H}_2\text{Cit}^- \quad (2 \leq pH \leq 2.7)$$

(6)

$$\text{Te} + \text{ZnHCl}^- + \text{H}^+ + 2e^- = \text{ZnTe} + \text{H}_2\text{Cl}^- \quad (2.7 \leq pH \leq 2.8)$$

(7)

$$\text{Te} + \text{Zn(Cit)}_2^{2+} + 4\text{H}^+ + 2e^- = \text{ZnTe} + 2\text{H}_2\text{Cit}^- \quad (2.8 \leq pH)$$

(8)

It can be considered that the differences of complex ion species have an effect on the deposition amount of Zn, since the amounts of Zn$^{2+}$ ions concentration in the bath, which are necessary to deposit Zn atom, are different. The effects of the difference in these reaction paths on the electrodeposited film’s composition and crystallization were then investigated. Figure 2 shows the XRD diffraction patterns of the deposits obtained at pH 5.6 gave a diffraction peak corresponding to ZnTe, except the deposit obtained at pH 5.6. The deposit from samples b1-b4 were well crystallized with a ZnTe cubic preferential orientation along the (111) plane. Although the deposition potential, leading to that Te deposition proceeds preferentially at this pH. In contrast, the deposits obtained from samples b1-b4 were well crystallized with a ZnTe cubic preferential orientation along the (111) plane. 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Although the deposition potential, leading to that Te deposition proceeds preferentially at this pH.
\[ E(V) = -0.729 - 0.0295 \text{pH} - 0.0295 \log[H_3\text{Cit}] + 0.0295 \log[\text{ZnH}_2\text{Cit}^+] \]  

(9)

This suggests that not only increasing \([\text{ZnH}_2\text{Cit}^+]\) but also decreasing citrate concentration leads to a positive shift of the potential and to a promotion of the zinc deposition.

On the other hand, at pH 4.0, the deviation from the stoichiometric composition of the deposits was hardly observed despite the increase of the \([\text{Zn(II)}]\) concentration. The deposits had a diffraction peak only from \(\text{ZnTe}(111)\). According to these results, it is revealed that the difference of the electrodeposition behavior at various pH has an effect on the composition and crystallinity of the electrodeposited films. This can be ascribed to that \(\text{Zn(II)}\) soluble species form various complexes ion with citrate ligands and their dissociation degrees from solvated to unsolvated ions are different. It is concluded that the electrodeposits at pH 4.0 are the most suitable for the crystalline \(\text{ZnTe}\) film with the closely stoichiometric composition within the pH range investigated.

5. Conclusions

The effect of pH on cathodic electrodeposition of \(\text{ZnTe}\) from citric acidic solution was investigated and the complex equilibrium calculation was carried out to examine the most predominant complex ion at different pH. Based on the condition established for \(\text{ZnTe}\) deposition, the pH and \(\text{Zn(II)}/\text{Te(II)}\) concentration ratio were optimized so as to electrodeposit \(\text{ZnTe}\) with close stoichiometric composition. There was a tendency for the Zn content of the deposit from citric acidic baths to be higher with the increase of the \([\text{Zn(II)}]\) concentration. The results of composition and crystallinity suggest that the deposition behavior changes within the pH range investigated, since the relative predominant species in the baths changes. Consequently, polycrystalline \(\text{ZnTe}\) can be deposited potentiostatically by control of the pH and \(\text{Zn(II)}/\text{Te(II)}\) concentration ratio.

REFERENCES

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