

Electrodeposition of ZnTe Compound Semiconductors from Aqueous Solution

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Abstract. ZnTe compound semiconductors were synthesized in acidic aqueous solution using a pulsed current electrodeposition technique. The optimum condition to obtain ZnTe deposits was determined by the cathodic polarization curves measured at a wide potential range. During the co-deposition of Zn and Te, under potential deposition (UPD) of Zn was observed. Increasing the solution temperature up to 353 K, UPD of Zn was promoted by the formation of Zn(OH)₂. Crystal phase, structure and chemical composition of electrodeposited ZnTe was controlled by the solution composition and electrolysis condition. The band gap energy of ZnTe films annealed at 573 K was close to 2.26 eV.

Introduction

Zinc based II-VI compound semiconductors (ZnO, ZnS, ZnSe, ZnTe, *etc.*) with wide band gap energy can be applied to the opto-electronic devices such as light emission devices and photovoltaic solar cells [1-2]. Among of the zinc based II-VI compound semiconductors, ZnTe can be applied to green light emission devices and photovoltaic solar cells because the band gap energy of ZnTe is 2.26 eV. The ZnTe thin films grown at room temperature and high temperature are found to be polycrystalline in nature. Polycrystalline thin films of ZnTe have been prepared using different techniques such as, thermal evaporation [3], sputtering [4], chemical vapor deposition [5] and electrodeposition [6-10]. The equipment for liquid-based techniques is simple and much less costly than vacuum systems. Te can be electrodeposited from acidic aqueous solution and is not as harmful as the elements As, Cd, Pb and Se. Electrodeposition technique offers a low cost growth method to deposit good quality ZnTe thin films. This technique also allows the coating over large areas with good lateral control of the material quality. In this paper, to determine the optimum condition, electrodeposition process of Zn-Te compound semiconductors from acidic aqueous solution was investigated.

Experimental

Electrolytic solution was synthesized from ZnSO₄ and TeO₂ as shown in Table 1. The solution pH was adjusted by adding H₂SO₄ and NaOH. The solution temperature was maintained to 353K during the electrodeposition. Indium tin oxide (ITO) glass and gold wire were used as a cathode and an anode, while the Ag/AgCl electrode immersed in saturated KCl solution was used as the reference electrode. ZnTe film was potentiostatically electrodeposited on the ITO glass. Crystal structure of the deposited films was analyzed by using X-ray diffraction (XRD). The chemical composition was determined by means of energy dispersive X-ray spectrometer (EDX). Band gap energy of the deposited films was estimated by using ultraviolet and visible spectrophotometer (UV).

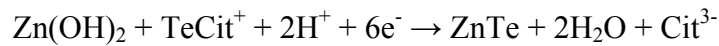
Table 1 Electrolytic solution composition for electrodeposition of ZnTe from aqueous solution.

sample	ZnSO ₄ ·7H ₂ O (mM)	TeO ₂ (mM)	Na ₂ SO ₄ (mM)	H ₃ Cit (mM)	Na ₃ Cit·2H ₂ O (mM)	
No.1	100	0.1	500	10	10	
No.2	100	0.1	500	10	10	H ₃ BO ₃ : 500mM
No.3	100	0.1	500	10	10	N ₂ gas Bubbling
No.4	100	0.1	500	—	—	Maric acid : 30 mM
pH : 5.0						
Concentration (M = mol dm ⁻³)						

Results and Discussions

1. Electrodeposition Process

Figure 1 shows cathodic polarization curves for Zn-Te electrodeposition. The polarization curves obtained from the solution containing H₃BO₃ (No.2) and the solution bubbled by blowing N₂ gas (No.3) are also shown in the figure. H₃BO₃ in the solution acts as pH buffer substance and N₂ gas in the solution prevents TeCit⁺ ions from oxidation. At the potential of ca. -0.2 V, H⁺ ions began to be reduced. With increasing the current up to 10⁻⁶ A, the potential polarized to around -0.5 V and Te began to deposit. With increase in the current over 10⁻⁵ A, the potential polarized from -0.5 V to -1.0 V. In this potential range, the pH in the vicinity of the cathode can increase up to around 6 due to the diffusion limit of H⁺ ions and TeCit⁺ ions, then Zn(OH)₂ forms in the vicinity of cathode. Electrodeposition of ZnTe will proceed by Zn UPD due to the formation of Zn(OH)₂ by the following reaction.



Zn-Te films deposited in the potential range from -0.8 V to -0.9 V mainly contained ZnTe phase with stoichiometric composition. Furthermore, with increase in the current more than 10⁻⁴ A, the potential polarized to less-noble than -1.0 V. In the potential range, massive metallic Zn began to deposit from Zn²⁺ ions.

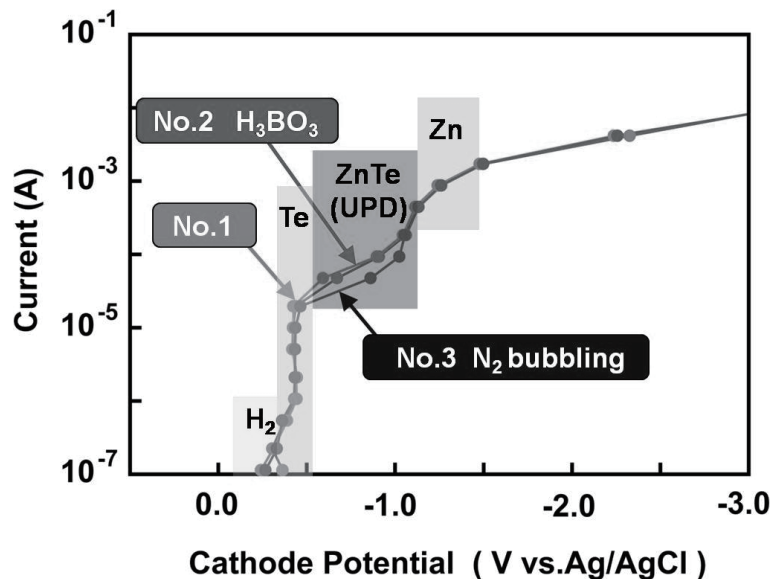


Figure 1 Cathodic polarization curves for Zn-Te electrodeposition. (No.1: standard solution, No.2: solution containing H₃BO₃, No.3: solution bubbled by blowing N₂ gas.)

2. Crystal Structure and Band Gap Energy

XRD patterns of electrodeposited films are shown in Fig.2. These XRD patterns correspond to (111) reflection planes of zincblende type ZnTe. During the electrodeposition of ZnTe, hydrogen ions are also reduced and pH in the vicinity of cathode increases up to around 6. At this pH, Zn(OH)_2 forms in the vicinity of cathode. UPD of zinc during ZnTe electrodeposition is caused by the formation of Zn(OH)_2 . H_3BO_4 in the solution acts as pH buffer substance and prevent Zn(OH)_2 from forming in the vicinity of cathode. Therefore, the sample obtained from the solution containing H_3BO_3 , consists of ZnTe and Te phase as shown in Fig.2-(b). ZnTe films with almost stoichiometric composition (Zn:Te=1:1) were obtained at under potential range more noble than -1.0 V vs. Ag/AgCl.

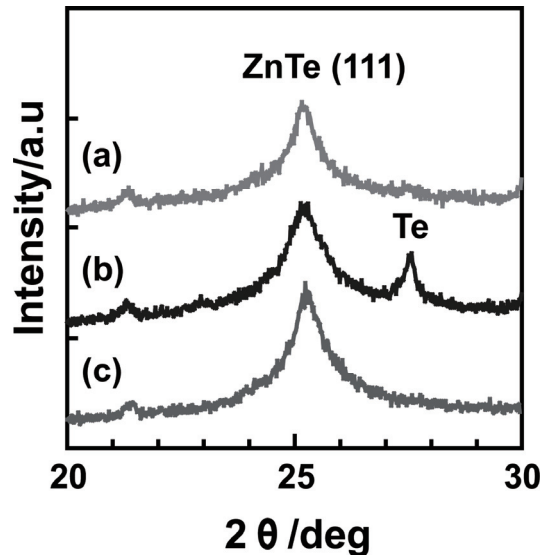


Figure 2 X-ray diffraction profiles of electrodeposited films obtained from three different conditions. Standard condition (a), solution containing H_3BO_3 (b) and bubbling with N_2 gas (c).

Table 2 and 3 show the band gap energy of electrodeposited Zn-Te films without heat treatment (Table 2) and with annealing at 573 K (Table 3). As shown in Table 2, band gap energy of as-deposited ZnTe films was less than 1.5 eV, which is smaller than the ideal band gap 2.26 eV of ZnTe. On the other hand, the band gap energy of ZnTe films after annealing at 573 K was close to 2.26 eV. This results from the disappearance of crystal defects and the recrystallization of the electro-deposited ZnTe fine crystals.

Table 2 Band gap energy of electrodeposited Zn-Te films without heat treatment.

Potential (V)	-0.6	-0.7	-0.8	-0.9	-1.0
No.1 (eV)	-	1.29	1.37	1.50	1.53
No.2 (eV)	1.10	1.22	1.44	1.44	1.38
No.3 (eV)	1.04	1.24	1.20	1.13	-
No.4 (eV)	1.28	1.15	1.03	0.88	-

Table 3 Band gap energy of electrodeposited Zn-Te films with annealing at 573 K.

Potential (V)	-0.6	-0.7	-0.8	-0.9	-1.0
No. 1 (eV)	-	1.68	1.84	1.84	2.18
No. 2 (eV)	1.67	1.22	1.30	1.48	1.50
No. 3 (eV)	1.14	<u>2.08</u>	<u>1.90</u>	<u>1.96</u>	-
No. 4 (eV)	1.43	<u>2.10</u>	<u>2.02</u>	1.08	-

Conclusions

Co-deposition of zinc and tellurium proceeded at potential region more noble than the equilibrium potential of zinc. Optimum deposition potential to obtain ZnTe single phase was determined to the range from -0.8 V to -0.9 V. By raising the solution temperature up to 353K, the formation of Zn(OH)₂ and the electrodeposition of ZnTe were promoted. Zn UPD due to the formation of Zn(OH)₂ promoted the electrodeposition of ZnTe with stoichiometric composition. Cubic zincblende type ZnTe compound semiconductor was potentiostatically electrodeposited on ITO glass from aqueous solution. The band gap energy of ZnTe films annealed at 573 K was close to the ideal value of 2.26 eV.

Acknowledgements

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