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## Novel process for electrodeposition of Bi<sub>2</sub>S<sub>3</sub> thin films

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## **Novel Process for Electrodeposition of Bi<sub>2</sub>S<sub>3</sub> Thin Films**

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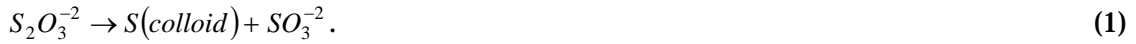
**A novel method for electrochemical deposition of Bi<sub>2</sub>S<sub>3</sub> from an aqueous acid bath comprising Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> and Bi(NO<sub>3</sub>)<sub>3</sub> complexed with Na<sub>2</sub>EDTA is proposed using SO<sub>3</sub><sup>-2</sup> ions as a sulfur source. For stoichiometric deposition, the initial concentrations of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> and Bi(NO<sub>3</sub>)<sub>3</sub> in the solution are determined from the experimental current-potential relations based on a current model under diffusion control. X-ray diffraction reveals that the deposits have no single substance and compound other than Bi<sub>2</sub>S<sub>3</sub> within experimental uncertainties. This indicates that the system in this study obeys the current model under diffusion control.**

**Keywords: Bi<sub>2</sub>S<sub>3</sub>, complexing agent, electrodeposition, diffusion control, X-ray diffraction**

## Introduction

$\text{Bi}_2\text{S}_3$  thin films [1-6] for solar cells deposited chemically and electrochemically have been extensively studied in past ten years since they have an appropriate bandgap for conversion of solar energy into electrical energy. Especially electrodeposition is an attractive method, which easily allows to control the growth rate via the current density and applied potential. However, unfortunately there have been very few studies on the stoichiometry of  $\text{Bi}_2\text{S}_3$  thin films in electrodeposition under diffusion control [7]. We have interests in a problem of whether the stoichiometric Bi : S ratio can be under diffusion control determined by the initial compositions of the electrolyte.

Cathodic deposition of  $\text{Bi}_2\text{S}_3$  films [5] has been usually carried out from aqueous acid solutions of sodium thiosulfate ( $\text{Na}_2\text{S}_2\text{O}_3$ ) as a sulfide ion source. Instable thiosulfuric acid in acid solutions can spontaneously decompose into sulfurous acid and sulfur. Sodium thiosulfate disassociates in acid solutions producing colloidal sulfur particles according to the following reaction:



Subsequent reduction of bismuth via adsorption of the colloidal sulfur particles on cathode electrodes produces the compound of  $\text{Bi}_2\text{S}_3$ ,



However incorporation of colloidal sulfur particles of arbitrary radii into the thin films brings compounds except for  $\text{Bi}_2\text{S}_3$  and difficulties in control of the film quality.

In this study after the reaction (1) is fully run for 24 hr, the sulfur particles precipitate on the bottom of a glass jar. The top clear solution is used, in which no sulfur particles caused the light scattering are found by the use of a laser microscope. Instead of colloidal sulfur particles, we propose a cathodic deposition method for  $\text{Bi}_2\text{S}_3$  thin films using  $\text{SO}_3^{-2}$  ions as a sulfur ion source [8],



A complexing agent that forms a complex ion with a metal ion is known to change the deposition potential. The disodium salt of ethylene diamine tetraacetic acid ( $\text{Na}_2\text{EDTA}$ )

is used in this study, which has solubility in acid water. The deposits require the stoichiometric Bi : S ratio of 2:3 for the high convergence efficiency of the solar cells. The initial concentrations of bismuth nitrate ( $\text{Bi}(\text{NO}_3)_3$ ) and  $\text{Na}_2\text{S}_2\text{O}_3$  in a nitric acid solution are determined from the experimental current-potential relations based on the current model under diffusion control [7]. According to the current model under diffusion control, ionic species are transported to the cathode only by diffusion. Hence negatively charged ions can be electrodeposited on the cathode. Oppositely charged ions such as  $\text{Bi}^{+2}$  and  $\text{SO}_3^{-2}$  can move to the cathode. We can find the presence of the diffusion control region by measuring the current-potential relations. The deposits are investigated by X-ray diffraction in order to make clear the compounds formed by electrodeposition.

The purpose of this study is to present a novel method for  $\text{Bi}_2\text{S}_3$  thin films and the deposit stoichiometry that obeys the diffusion control model.

## 2. Experiments

$\text{Bi}_2\text{S}_3$  thin films were cathodically deposited in a three-electrode system from a nitric acid bath containing sodium thiosulfate ( $\text{Na}_2\text{S}_2\text{O}_3$ ), bismuth nitrate ( $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ ) and the disodium salt of ethylene diamine tetraacetic acid ( $\text{Na}_2\text{EDTA}$ ). A carbon sheet and ITO glass substrate ( $6\Omega$  sheet resistivity) were prepared for counter and working electrodes, which were cleaned ultrasonically in acetone, ethanol and distilled water. Saturated  $\text{Ag}/\text{AgCl}$  was used as a reference electrode to obtain the current-potential relations, which were used to determine the initial bath composition for stoichiometric deposition.

The detailed procedure of electrodeposition for stoichiometric deposits of  $\text{Bi}_2\text{S}_3$  was as follows:  $4 \times 10^{-2}$  M  $\text{Na}_2\text{S}_2\text{O}_3$  was dissolved in a solution mixed with 90ml distilled water and 10ml nitric acid. Colloidal sulfur instantaneously formed in the solution at room temperature changing the color of the mixture. For 24hr, the solution was kept still at room temperature and sulfur particles precipitated on the bottom of the glass jar. The top clear solution was used, in which no sulfur particles were found by observations of the light scattering using the laser microscope. In addition  $6 \times 10^{-3}$  M  $\text{Bi}(\text{NO}_3)_3$  and  $6 \times 10^{-3}$  M  $\text{Na}_2\text{EDTA}$  were dissolved into the solution. The ITO glass plate and carbon substrate for cathode and anode electrodes were located parallel in the still bath filled with the solution. The thin films were electrodeposited on the ITO glasses at a cathode potential of -1.5V. The deposits were investigated by X-ray diffraction with  $\text{CuK}\alpha$  radiation. Annealing treatments of the deposit were carried out in a flow of argon gas for 0.5hr at 423K.

### 3. Results and discussion

We first need to find the presence of a diffusion control region in which oppositely charged ionic species can move in the same direction. Such cathodic currents are known to obey the current-potential equation under diffusion control [7],

$$j = j_L \left( 1 - \exp \frac{zF\eta}{RT} \right), \quad (4)$$

where  $j_L$  indicates the limiting current when the concentration of the ion at the interface is equal to zero,  $z$  the ionic charge,  $F$  the Faraday's constant,  $\eta$  the overpotential,  $R$  the gas constant and  $T$  the temperature. A solution of  $\text{Na}_2\text{S}_2\text{O}_3$  was prepared by the procedure stated above. Fig.1 shows a plot of the current vs the cathode potential for (a)  $1.33 \times 10^{-2} \text{ M Bi(NO}_3)_3$  and (b)  $2 \times 10^{-2} \text{ M Na}_2\text{S}_2\text{O}_3$  in a nitric acid solution of 50ml. The cathodic currents appear to obey Eq. (4), especially for the small cathode potential the currents follow the relation  $j \approx -(j_L zF / RT)\eta$ . Fig.1 indicates that a larger negative shift in the deposition potential of bismuth is required to codeposit the bismuth and sulfur ions. In this study,  $\text{Na}_2\text{EDTA}$  is used as a complexing agent to change the deposition potential of bismuth ions.

Fig.2 shows the current-potential relations in (a) a nitric acid solution containing  $1.33 \times 10^{-2} \text{ M Bi(NO}_3)_3$  and  $1.33 \times 10^{-2} \text{ M Na}_2\text{EDTA}$ , and (b) that containing  $1.33 \times 10^{-2} \text{ M Bi(NO}_3)_3$ . The cathode potential in Fig.2 (a) becomes more negative than that in Fig.1(a) owing to the addition of  $\text{Na}_2\text{EDTA}$ . Moreover there appears to be a diffusion control region at about the cathode potential of  $-1.5 \text{ V}$  in the two cases. The diffusion control region is designated in Fig.2 as a rectangle. The cathodic currents in the rectangular region little change with the cathode potential. Hence we consider the two ionic components of  $\text{Bi}^{3+}$  and  $\text{SO}_3^{2-}$  to be under diffusion control that allows to transport only by diffusion. For the current  $j_i$  ( $i = \text{Bi}^{3+}$  or  $\text{SO}_3^{2-}$ ), using the current by diffusion [7]  $j_i = D_i z_i F (c_i - c_i^o) / [(1 - t_i) \delta_i]$  and the relations such as  $\eta = (RT / zF) \ln(c_i^o / c_i)$  and  $c_i^o / c_i = 1 - j_i / j_L$ , Eq.(4) can be rewritten as

$$j_i = \frac{z_i F D_i}{(1 - t_i) \delta_i} (c_i - c_i^o), \quad (5)$$

where  $D_i$  indicates the diffusion coefficient,  $t_i$  the transport number of the ion,  $\delta_i$  a thickness of the diffusion layer,  $c_i$  the initial concentration and  $c_i^o$  the concentration at

the interface. Consequently Eq.(5) yields

$$\frac{j_{Bi}}{j_{SO_3^{2-}}} \cong \frac{k_{Bi}c_{Bi}}{k_{SO_3^{2-}}c_{SO_3^{2-}}}, \quad (6)$$

where  $k_i = D_i z_i F / t_i \delta_i$ . Here we can ignore the term  $c_i^0$  because of  $c_i^0 \ll c_i$  under diffusion control. Unless the factor  $k_i$  in Eq.(6) is known, we cannot determine the initial concentration ratio of  $Na_2S_2O_3$  and  $Bi(NO_3)_3$  for stoichiometric deposition. However Eq.(5) indicates that the current is proportional to the initial concentration. This implies that from the current ratio obtained from the experimental current-potential relations we can determine the initial concentrations for stoichiometric deposition. Taking into consideration the current-potential relations in Fig.2 for  $Na_2S_2O_3$  and  $Bi(NO_3)_3$ , we can choose the following initial concentrations:  $4 \times 10^{-2}$  M  $Na_2S_2O_3$ ,  $6 \times 10^{-3}$  M  $Bi(NO_3)_3$  and  $6 \times 10^{-3}$  M  $Na_2EDTA$ .

Fig.3 shows X-ray diffraction patterns of the  $Bi_2S_3$  thin films electrodeposited from the solution at the cathode potential of  $-1.5V$ . X-ray spectrum of as the deposited  $Bi_2S_3$  film in Fig.3 (a) suggests that the deposit consists of so far fine grain structures. Some broad diffraction peaks are observed. The annealing treatment of the as-deposited  $Bi_2S_3$  films in a flow of argon gas for 0.5 hr at 423K results in an increase in the grain size. Fig4.(b) shows a typical X-ray diffraction pattern of the annealed  $Bi_2S_3$  thin film. As shown in Table 1, the observed diffraction peaks are consistent with those calculated from the plane indices in orthorhombic cell with the lattice constants [9] of  $Bi_2S_3$  as  $a=1.115, b=1.130$  and  $c=0.3981nm$ . We have found no single substance and compound other than  $Bi_2S_3$ . Hence we obtain the stoichiometric deposits within experimental uncertainties as predicted by the diffusion-control transport model. However more detailed studies are needed in order to characterize the physical properties of the  $Bi_2S_3$  thin films.

#### 4.Conclusion

A novel method for  $Bi_2S_3$  thin films electrodeposited from an aqueous acid bath comprising  $Na_2S_2O_3$ ,  $Bi(NO_3)_3$  and  $Na_2EDTA$  as a complexing agent is proposed. A solution of  $SO_3^{2-}$  and  $Bi^{+3}$  ions that includes no colloidal sulfur particles are used in cathodic electrodeposition. The initial concentrations of  $Na_2S_2O_3$  and  $Bi(NO_3)_3$  in the solution are determined from the current model under diffusion control. The X-ray diffraction patterns indicate no simple substance and compound other than  $Bi_2S_3$  within experimental uncertainties. This implies that the reactions in this experiment

**obey the current model under diffusion control.**

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## Figures captions

**Fig.1 Current-potential relations of (a)  $1.33 \times 10^{-2}$  M  $\text{Bi}(\text{NO}_3)_3$  and (b)  $2 \times 10^{-2}$  M  $\text{Na}_2\text{S}_2\text{O}_3$  in a nitric acid solution of 50ml. A solution of  $\text{Na}_2\text{S}_2\text{O}_3$  was kept still for 24 hr and the top clear solution was used.**

**Fig.2 Current-potential relations of (a) a solution containing  $1.33 \times 10^{-2}$  M  $\text{Bi}(\text{NO}_3)_3$  and  $1.33 \times 10^{-2}$  M  $\text{Na}_2\text{EDTA}$  as a complexing agent, and (b) a solution containing  $2 \times 10^{-2}$  M  $\text{Na}_2\text{S}_2\text{O}_3$  in a nitric acid solution of 50ml.**

**Fig.3 X-ray diffraction patterns of (a) as-deposited  $\text{Bi}_2\text{S}_3$  and (b)  $\text{Bi}_2\text{S}_3$  annealed in a flow of argon gas for 0.5hr at 423K. The  $\text{Bi}_2\text{S}_3$  thin films were electrodeposited from a nitric acid solution of  $4 \times 10^{-2}$  M  $\text{Na}_2\text{S}_2\text{O}_3$ ,  $6 \times 10^{-3}$  M  $\text{Bi}(\text{NO}_3)_3$  and  $6 \times 10^{-3}$  M. The rectangle indicates the diffusion control region.**

**Table 1 Comparison of calculated and observed  $\theta$  values of the  $\text{Bi}_2\text{S}_3$  thin films where  $\theta$  is the Bragg's angle. The lattice constants  $a_0=1.115\text{nm}$ ,  $b_0=1.130\text{nm}$  and  $c_0=0.3981\text{nm}$  are used for calculation of  $\theta$ . The observed  $\theta$  values are measured from the X-ray pattern of the annealed  $\text{Bi}_2\text{S}_3$  thin films.**

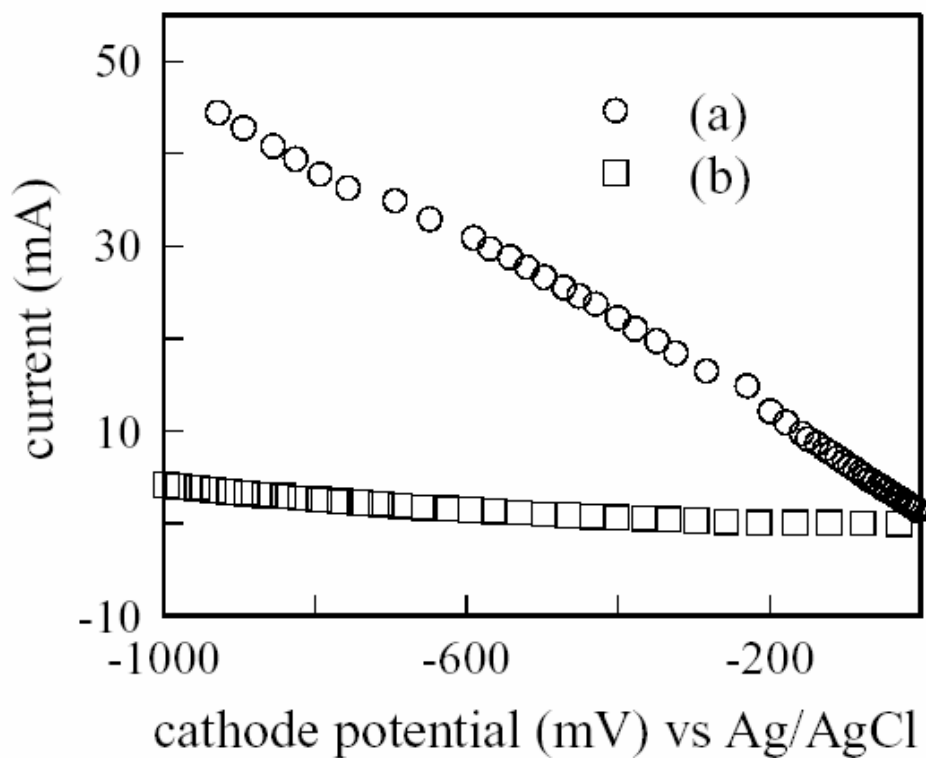


Fig.1 Current-potential relations of (a)  $1.33 \times 10^{-2}$  M  $\text{Bi}(\text{NO}_3)_3$  and (b)  $2 \times 10^{-2}$  M  $\text{Na}_2\text{S}_2\text{O}_3$  in a nitric acid solution of 50ml. A solution of  $\text{Na}_2\text{S}_2\text{O}_3$  was kept still for 24 hr and the top clear solution was used.

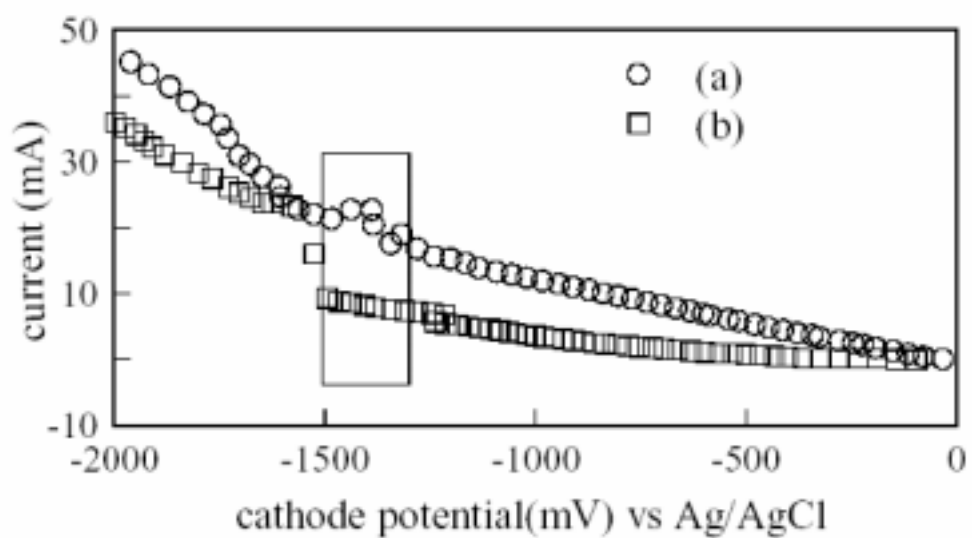


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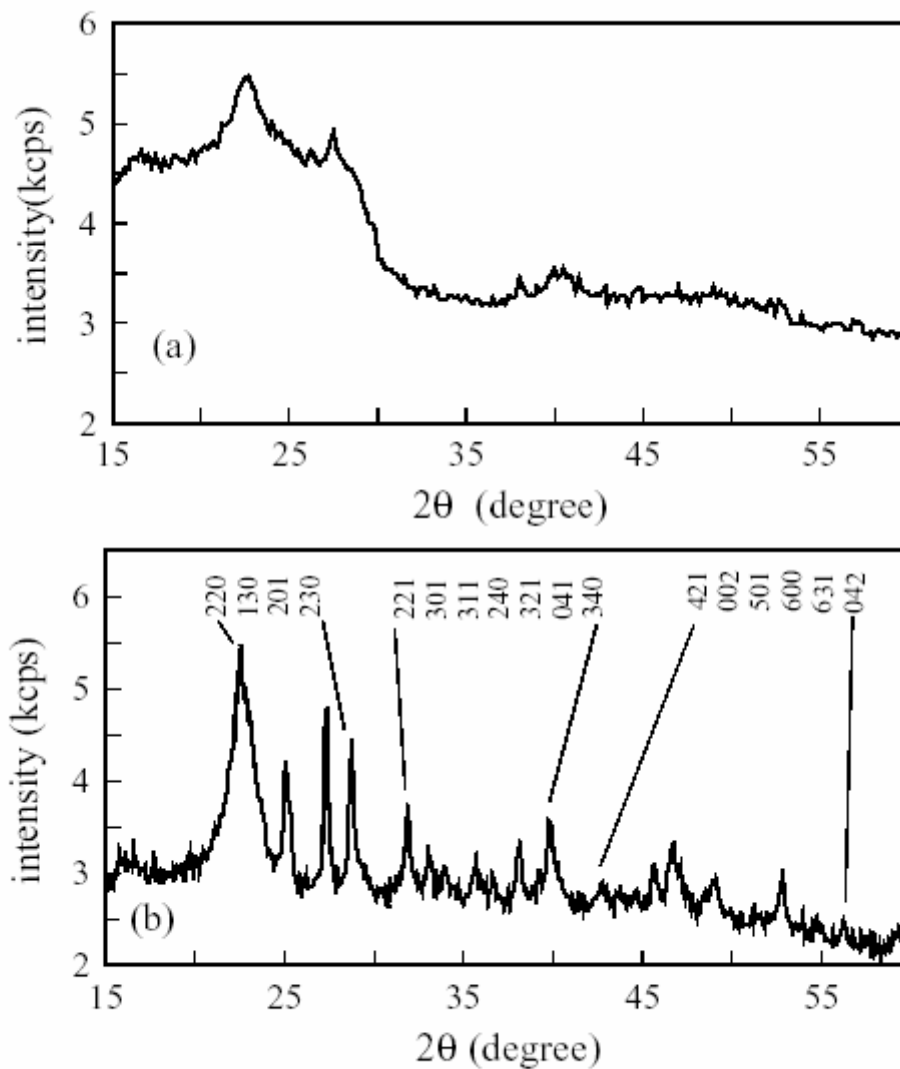


Fig.3 X-ray diffraction patterns of (a) as-deposited  $\text{Bi}_2\text{S}_3$  and (b)  $\text{Bi}_2\text{S}_3$  annealed in a flow of argon gas for 0.5hr at 423K. The  $\text{Bi}_2\text{S}_3$  thin films were electrodeposited from a nitric acid solution of  $4 \times 10^{-2}$  M  $\text{Na}_2\text{S}_2\text{O}_3$ ,  $6 \times 10^{-3}$  M  $\text{Bi}(\text{NO}_3)_3$  and  $6 \times 10^{-3}$  M. The rectangle indicates the diffusion control region.

Calculated $\theta$ (degree)	Observed $\theta$ (degree)	Reflection plane
11.20	11.29	220
12.48	12.54	130
13.77	13.68	201
14.30	14.37	230
15.92	15.95	221
16.49	16.52	301
16.97	16.96	311
17.82	17.86	240
18.35	18.30	321
19.55	19.11	041
20.05	19.92	340
21.36	21.38	421
22.79	22.80	002
23.35	23.37	501
24.51	24.47	600
26.49	26.41	531
28.28	28.11	042

Table 1 Comparison of calculated and observed  $\theta$  values of the  $\text{Bi}_2\text{S}_3$  thin films where  $\theta$  is the Bragg's angle. The lattice constants  $a_0=1.115\text{nm}$ ,  $b_0=1.130\text{nm}$  and  $c_0=0.3981\text{nm}$  are used for calculation of  $\theta$ . The observed  $\theta$  values are measured from the X-ray pattern of the annealed  $\text{Bi}_2\text{S}_3$  thin films.