Comparison of Structural and Optical Properties of GaS_xO_y Thin Films Deposition by ECD and PCD Techniques

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Abstract: GaS_xO_y is a wide band gap semiconductor and suitable as a buffer layer in solar cells. GaS_xO_y thin films were deposited from an aqueous solution of $Ga_2(SO_4)_3$ and $Na_2S_2O_3$. The major area of interest is different deposition techniques; electrochemical deposition (ECD) and Photochemical deposition (PCD) on indium-tin-oxide coated glass substrates and fluorine-doped-tin-oxide-coated glass substrates respectively. Their structural and optical properties were investigated by Auger electron spectroscopy, scanning electron microscope and optical transmission spectroscopy. The film deposited under the optimum condition exhibited high transmission and a wide energy band gap of 2.9 eV for film by ECD and 3.5 eV for film by PCD.

Keywords : Semiconductors, PV, solar cell, thin films; ECD, PCD, optical transmission, buffer layer.

1. Introduction

Renewable energy will play a critical role in reducing emissions to mitigate climate change. Photovoltaic (PV) is one of the most promising and prominent techniques for electricity generation based on renewable solar energy. Thin film photovoltaic devices have high worldwide demand to generate an efficient, renewable and clean solar energy as fossil fuel sources will be exhausted in future. Now a day, more attentions are focusing on the nontoxic, environment friendly materials which can replace CdS used for a buffer layer in heterostructure solar cells. In_2S_3 has been considered as a substitute of CdS [1,2], but In is not abundant and its price is now increasing rapidly. Ga is nontoxic and the abundance of Ga in the earth's crust is 100 times that of In. Gallium sulfides (GaS and Ga_2S_3), gallium oxide (Ga_2O_3), and their alloy, gallium sulfide oxide (GaS_xO_y), are n-type wide-band-gap semiconductors and thus are promising as buffer layer materials in solar cells. So far, several studies have been

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performed on gallium sulfide fabrication techniques such as metal-organic chemical vapor deposition [3], a modified Bridgman method [4], a microwave glow discharge method [5], a chemical vapor- transport method [6], and chemical vapor deposition [7], and on gallium oxide fabrication techniques such as spray pyrolysis [8] and molecular-beam epitaxy [9]. In my previous reports, GaS_xO_y thin films were deposited using the ECD technique and PCD technique for the first time onto indium-doped tin oxide (ITO) and fluorine-doped tin oxide (FTO) coated glass substrates from an aqueous bath containing $Ga_2(SO_4)_3$ and $Na_2S_2O_3$ by DC biasing [10,11].

In this paper, the structural and optical properties of GaS_xO_y thin films using the ECD technique and PCD techniques were reported. The advantage of ECD method is the possibility to increase the control over film properties and thickness by means of the electrochemical variables, potential and current. Furthermore, by changing the deposition time, deposited film thickness can easily be controlled On the otherhand, the PCD technique is the advantageous because of its simplicity, cheapness, low cost of the starting materials and capability of large area deposition [12-15]. The deposition experiments were carried out under best condition to determine basic compositional, structural and optical characteristics of the as-deposited films [10,11].

2. Experimental details

2.1. ECD techniques

A three-electrode cell was used for ECD (Fig-1a) with a saturated calomel electrode (SCE) as the reference electrode. An indium-tin-oxide (ITO)-coated glass was used as the working electrode (substrate) and a platinum sheet was used as the counter electrode. In the following, all the potential values are referred to vs. SCE. Both the ITO substrate and the platinum sheet were washed ultrasonically in alkyl benzene and dried by nitrogen before the experiment. The deposition area was about 1x1 cm^2. An aqueous bath containing $Na_2S_2O_3$ and $Ga_2(SO_4)_3$ was used for the deposition at room temperature (22-25 ^oC). After the experiment, the deposited films were washed softly in pure water and naturally dried in air.

A gallium sulfide is expected to be formed by the following mechanism as reported for other sulfide [10] . Elemental sulfur is released from $S_2O_3^{2-}$ by the reaction

$$S_2O_3^{2-} + 2H^+ \longrightarrow S + H_2SO_3 \qquad (1)$$

Ga_2S_3, for example, will be formed at the cathode according to the apparent reaction:

$$2Ga^{3+}+3S+6e^- \longrightarrow Ga_2S_3 \qquad (2)$$

In parallel, gallium oxide is expected to be formed by the following reaction with dissolved oxygen.

$$3O_2 + 4Ga^{3+} + 12e^- \longrightarrow 2Ga_2O_3 \quad (3)$$

2.2.PCD techniques

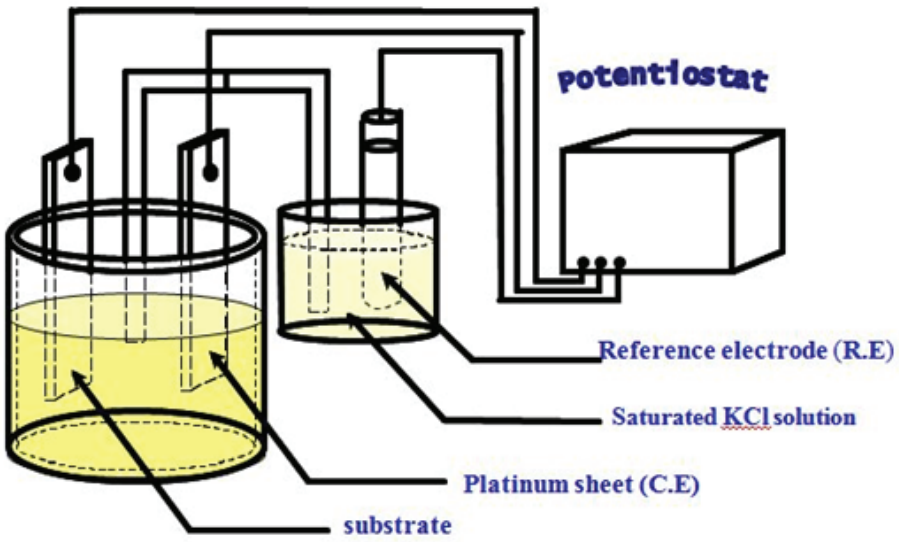
An aqueous solution of 50 ml containing 5 mM $Ga_2(SO_4)_3$ and 25 mM $Na_2S_2O_3$ was prepared. The apparatus for PCD is schematically shown in Fig.-1b. A degreased substrate was immersed in the solution and illuminated by a high-pressure mercury lamp through a spherical lens from above as shown in Fig-1B.The distance from the solution surface to the substrate was maintained about 2-3 mm. It was observed that the substrate position affects the deposited film thickness, and we could not precisely control this position. The diameter of the illumination region was approximately 10 mm.

GaS_xO_y is expected to be formed by the following mechanism. In the general process of sulfide PCD, the thiosulfate ions present in the solution absorb the UV light and are exited. These photo exited thiosulfate ions release solvated electrons and sulfur atoms [12].

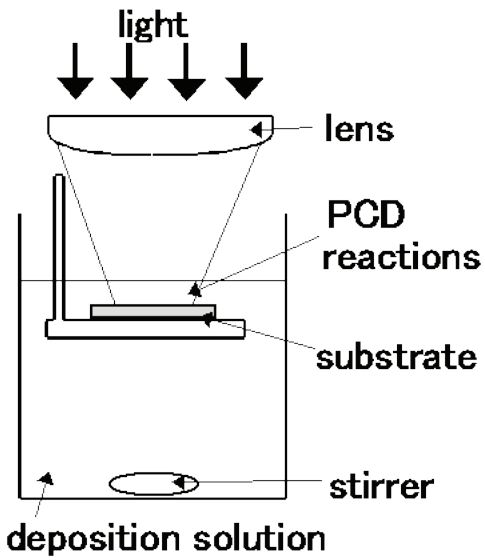
$$S_2O_3^{2-} + h\nu \rightarrow S + SO_3^{2-} \qquad (1)$$

$$2\ S_2O_3^{2-} + h\nu \rightarrow S_4O_6^{2-} + 2e^- \qquad (2)$$

We can expect that GaS_x is formed with S and e^- generated by the above reactions. However, GaS_x is hydrolytically unstable: we confirmed that pure Ga_2S_3 is vigorously dissolved in water. Thus GaSx once formed will react with water, and Ga_2O_3 and Ga $(OH)_3$ will be formed.



(a)



(b)

Fig.1. Schematic diagram of (a) ECD technique and (b) PCD technique.

The compositional analysis of as deposited films was carried out by Auger electron spectroscopy (AES) using a JEOL JAMP 7800 Auger microprobe at a probe voltage of 10 kV and a current of $2x10^{-8}$ A. Argon ion etching with an acceleration voltage of 3 kV and a current of 20 mA was used to sputter the film surface. The AES spectra were recorded after sputtering the surface for 6 to 10 s. The S/Ga and O/Ga atomic ratios were calculated using standard Ga_2S_3 and Ga_2O_3 compounds, respectively. The thickness of the films was measured by an Accretech Surfcom-1400D profile meter. The surface morphology of the film was analyzed using a Hitachi S-2000S scanning electron microscope (SEM) at a constant acceleration voltage of 10 kV and a magnification of 2000. The optical transmission measurement was performed using a JASCO U-570 UV/VIS/NIR spectrometer with the substrate as the reference.

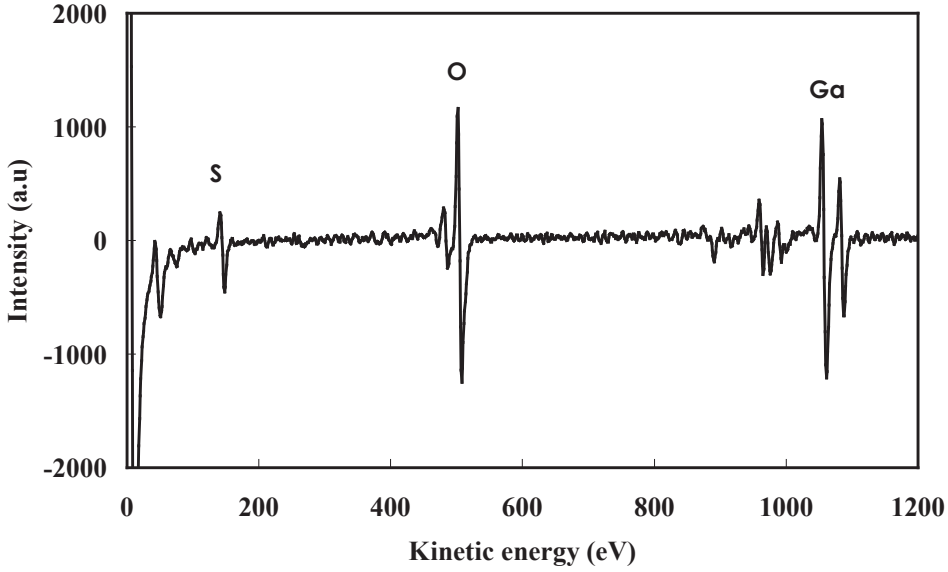
Results and discussion

The structural and optical properties of GaS_xO_y thin film deposited by ECD and PCD techniques from aqueous solution have reported in this paper. Fig. 2 shows the AES spectra were recorded after sputtering of the surfaces for 5 to 10 sec. As shown in table 1, O/Ga ratios of the deposited films are very close for different deposition techniques and these are Oxygen rich films. This can be explained as follow; We may expect that beside Ga_2O_3 formation, $Ga(OH)_3$ may be formed in the solution, and the high O/Ga ratio would be due to $Ga(OH)_3$ formation.

Table 1. Atomic composition and characteristics of the GaS_xO_y films deposited by different techniques.

Techniques	$Na_2S_2O_3$(mM)	$Ga_2(SO_4)_3$(mM)	Thickness(μm)	S/Ga	O/Ga
ECD	100	10	0.2	0.14	1.54
PCD	25	5	0.25	0.26	1.53

Fig.3 shows the surface morphology of the film deposited in case of optimum condition by (a) ECD and (b) PCD. In both the cases, the entire substrate surfaces were uniformly covered with a continuous layer of small grains.



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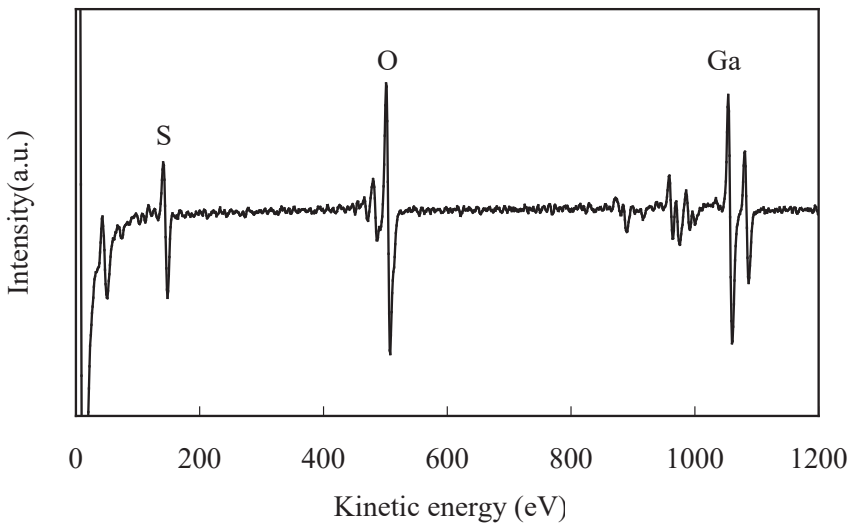
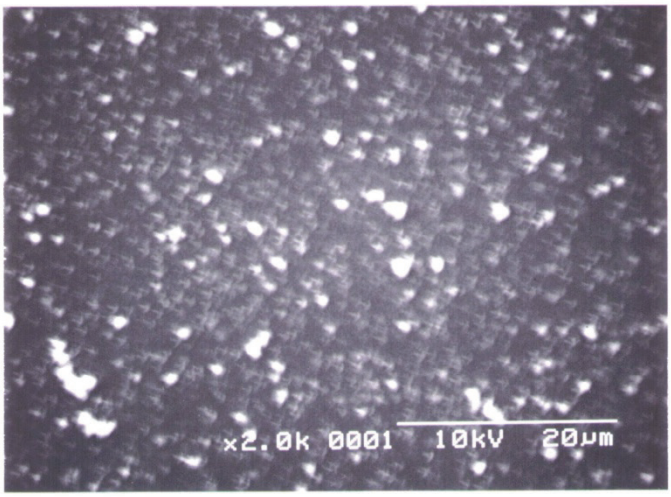


(b)

Fig.2. AES for GaS_xO_y thin film deposited at optimum condition for (a) ECD technique and (b) PCD technique.



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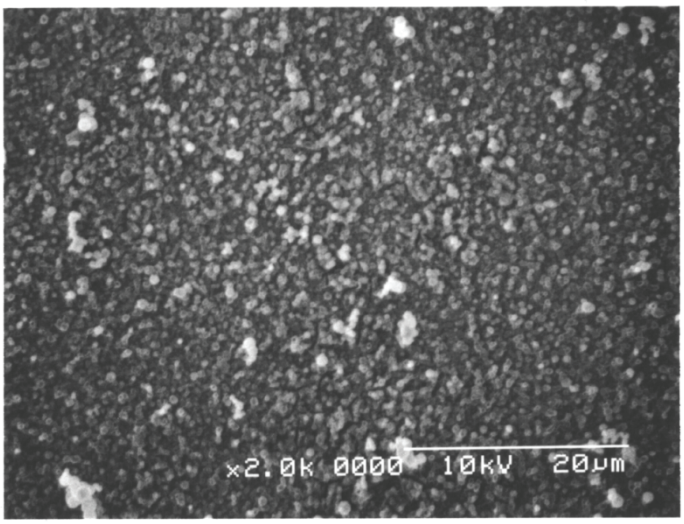
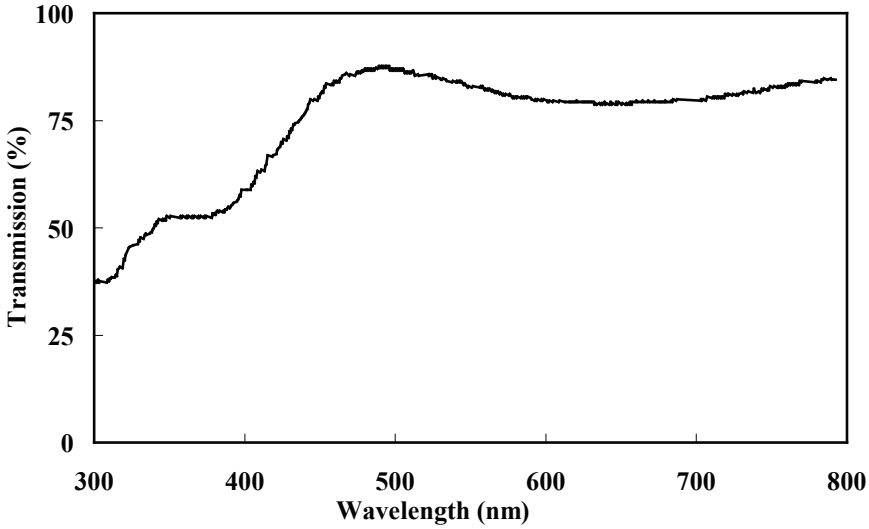


(b)

Fig.3. SEM of the film deposited for (a) ECD technique and (b) PCD technique.



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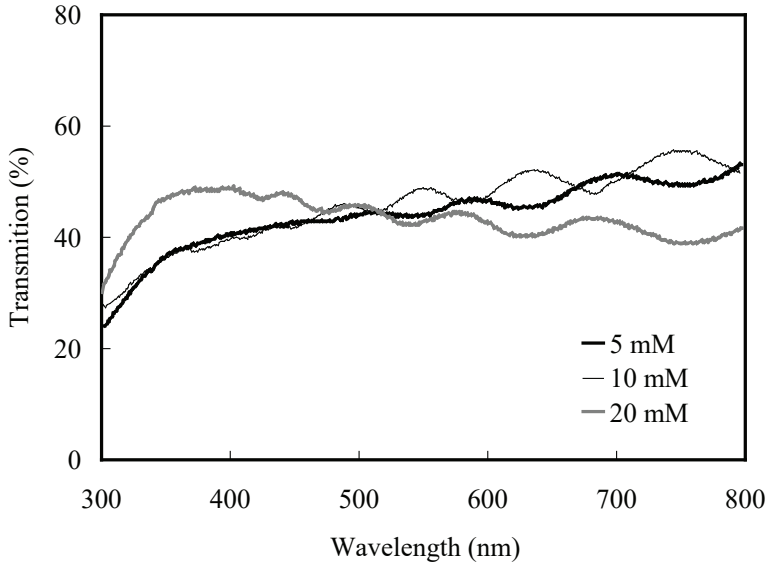
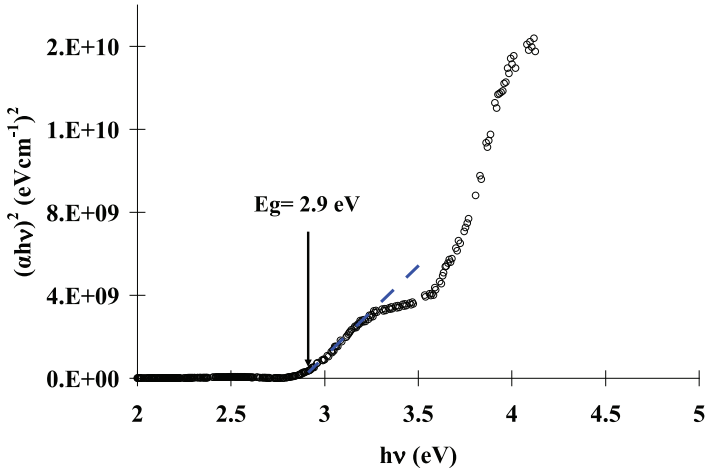


(b)

Fig.4. Optical transmission of the films deposited for (a) ECD technique and (b) PCD technique [$Ga_2(SO_4)_3$ = 5mm,10mm, 20mm].



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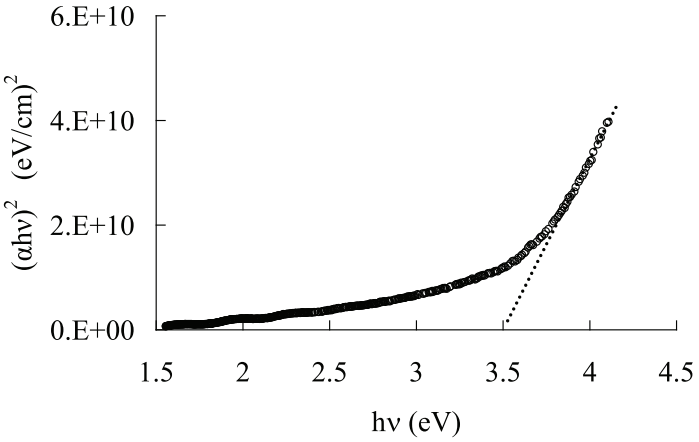

(b)

Fig.5. Band gap estimation of the film deposited for (a) ECD technique and (b) PCD technique.

Fig. 4 shows optical transmission of the films deposited by ECD and PCD techniques. In fig. 4(b) for PCD, it is observed that different amount of $Ga_2(SO_4)_3$ caused no significant difference in transmission. For both films deposited by ECD and PCD the transmission in the visible region is not so high, probably because of scattering by

the surface roughness. For this condition, the optical band gap energy was calculated from the classical relation for direct-band optical absorption, $\alpha = k(h\nu - Eg)^{1/2}/h\nu$, where k is a constant, Eg is the band gap and hν is the photon energy.

From fig.5 we can see that Eg indicated by the lower sharp onset is about 2.9 eV for film deposited by ECD and 3.5 eV for PCD. The reduction in Eg in fig 5(a) may be due to effects of random atom arrangement (amorphous nature) and band-gap bowing in the gallium sulfide oxide alloy.

4. Conclusions

GaS_xO_y thin films were deposited by two different deposition techniques; electrochemical deposition (ECD) and Photochemical deposition (PCD) from an aqueous solution of $Ga_2(SO_4)_3$ and $Na_2S_2O_3$. In the both method, the films are uniform and composition is oxygen-rich with growth rate of 0.2 to 0.25 μm/hour. The optical transmission observed in the visible region for both deposition techniques. The films deposited under optimized condition have a wide band gap of about 2.9 eV for ECD and 3.5 eV for PCD techniques. These properties make the film suitable for solar cell application as a buffer layer.

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