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Optimization of growth parameters of electrodeposited tin oxide thin films for PV applications

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Abstract

Tin oxide (SnO_2) is a promising photoactive semiconducting material due to its optoelectronics properties. Even though, growth of SnO_2 using the method of electrodeposition is advantageous, it has paved low attention among semiconductor researchers. In this study, well-adhered photoactive SnO_2 thin film was successfully electrodeposited on Cu substrates. The growth parameters, such as film deposition potential, bath temperature, and duration of deposition were optimized. Electrodeposition of SnO_2 layers was performed on copper substrates in a three-electrode electrochemical cell using a solution containing 30 mM $SnCl_2$ and 150 mM HNO_3 at a deposition potential of -0.85 V vs. Ag/AgCl. The fabricated best thin film resulted J_{SC} value of 410 μA cm^{-2} and V_{OC} value of 113 mV in 0.1 M $NaNO_3$ electrolyte. The best thin film obtained at a bath temperature of 85°C for a deposition time of 120 seconds. The Mott-Schottky analysis revealed that the fabricated SnO_2 thin film exhibits n-type conductivity, and it has a flat band potential of -0.51 V vs. Ag/AgCl.

Keywords

Electrodeposition, Photovoltaics, SnO_2, Thin film, Tin oxide

Introduction

Tin oxide (SnO_2) is considered to be a defect type photoactive semiconducting material. It has wide direct band gap of approximately 3.8 eV (Li et al., 2009). SnO_2 exhibits properties such as high mobility, excellent conductivity, great thermal stability and transparency in the visible region (Riahi et al., 2021). These properties are highly favorable for semiconductor applications. SnO_2 is already being using in solar cells (Xiong et al., 2018) as window layer as well as anode material for Li-ion batteries (J. S. Chen & Lou, 2013) and gas sensors (Das & Jayaraman, 2014).

Like all other metal oxide semiconductors (Kafi et al., 2020), SnO_2 thin films can be grown using techniques including chemical bath deposition (Khallaf et al., 2012), spray pyrolysis (Gordillo et al., 1994), sol-gel process (Chatelon et al., 1994), metal-organic deposition (Park et al., 2006), liquid flow deposition (Supothina, 2003) and electrodeposition (X. Chen et al., 2010). Among the range of techniques available for depositing SnO_2, fabrication of SnO_2 using the method of electrodeposition is less reported in literature. Additionally, the fabrication of SnO_2 using the method of electrodeposition owes advantages like cost effectiveness, easiness, and uniformity in growth of thin film layer.

Electrodeposition of SnO_2 thin films requires the presence of hydroxyl ions (OH^-) or O^- radicals on or near the working electrode (Therese & Kamath, 2000). Various types of oxygen precursors can be utilized for this purpose, including hydrogen peroxide

(Pauporté & Lincot, 2001), nitrate ions (Izaki & Omi, 1997), and blown oxygen (Peulon & Lincot, 1998). Generally, application of a potential to the working electrode causes a reduction of the oxygen precursor resulting creation of OH^- groups. Then, these anions create tin hydroxide ($Sn(OH)_4$) using the Sn^{4+} ions in the solution of SnO_2 film deposition bath. However, this $Sn(OH)_4$ is unstable. Thus, it quickly dehydrates and precipitates to form SnO_2, as presented in the following reaction:

$$Sn^{4+} + 4OH^- \rightarrow Sn(OH)_4 \rightarrow SnO_2 + 2H_2O$$

Many researchers have developed various film deposition baths for the fabrication of SnO_2 thin film employing electrodeposition technique is listed in the Table 1.

Table 1. *Reported film deposition baths for fabrication of SnO_2 thin films*

Working Electrode	Film deposition bath	Mode	References
Cu	20 mM $SnCl_2.2H_2O$ 100 mM $NaNO_3$ 75 mM HNO_3	Galvanostatically	(Chang et al., 2002)
Cu	25 mM $SnCl_2.2H_2O$ 150 mM HNO_3	Galvanostatically	(Chang et al., 2004)
Au	25 mM $SnCl_2.2H_2O$ 100 mM $NaNO_3$ 75 mM HNO_3	Potentiostatically	(Lai et al., 2006)
Pt	100 mM $SnCl_2.2H_2O$ 400 mM $NaNO_3$ 500 mM HNO_3 0.2 wt.% SDS	Potentiostatically	(Spray & Choi, 2007)
ITO	20 mM $SnCl_2.2H_2O$ 100 mM $NaNO_3$ 75 mM HNO_3 5 mM SDS	Potentiostatically	(Ishizaki et al., 2009)
Cu	20 mM $SnCl_4.5H_2O$ 80 mM HNO_3	Potentiostatically	(X. Chen et al., 2010)
ITO	30 mM $SnSO_4$ 1.07M HNO_3	Potentiostatically	(Vequizo et al., 2010)
Cu	100 mM $SnCl_2.2H_2O$ 500 mM $NaNO_3$ 400 mM HNO_3	Potentiostatically	(Kim, S., Lee, H., Park, C. M., & Jung, 2012)

ITO	40 mM $SnCl_2$ 100 mM HNO_3 100 mM $NaNO_3$	Potentiostatically	(Daideche, K., Azizi, 2017)

In this study, nitrate ion-based bath was used for the potentiostatically electrodeposition of the SnO_2 thin film followed by a pre-treatment of oxygen bubbling to the film deposition bath. The growth parameters such as potential of film deposition, temperature of the bath and duration of the film deposition were altered in order to find the optimum growth parameters. In literature, details of optimization of growth parameter for the SnO_2 film deposition is rarely reported. Further, the performance of photoactive SnO_2 thin films in sodium nitrate electrolyte is not reported. Thus, this study is significant to understand the electrical properties of electrodeposited SnO_2 thin films.

Methodology

SnO_2 thin films were potentiostatically electrodeposited on well-cleaned copper substrates using a Hokuto Denko Potentiostat / Galvanostat HAB-151 in a setup of three-electrode electrochemical cell. The aqueous film deposition bath consisted of 30 mM stannous chloride ($SnCl_2$ regent grade, 98%) and 150 mM nitric acid (HNO_3 regent grade, 69%). The working electrode was the copper foil and the counter electrode was a platinum foil. The reference electrode was a Ag/AgCl electrode. Initially, a pre-treatment step was carried out in order to oxidize the stannous ions (Sn^{2+}) into stannic ions (Sn^{4+}). Here, the oxygen gas was bubbled into the electrochemical bath for 1 hour at the relevant temperature of the electrodeposition bath. A cyclic voltammetry was taken to determine the deposition potential. Then, the growth parameters such as temperature of the film deposition bath and the duration of the film depositions were altered, in order to identify the optimum growth parameters. The tested temperature values of the film deposition bath were 70, 75, 80, 85, 90, 95 ℃ and the tested duration of the film deposition were 30, 60, 120, 150, 180, 240 seconds. After the SnO_2 thin film deposition, all the samples were washed with deionized water, then immersed in 0.1 M sodium nitrate ($NaNO_3$) and dried under ambient conditions in a desiccator.

A solution containing 0.1 M $NaNO_3$ was used as the photoelectrochemical cell (PEC) for the SnO_2 thin film characterization. The current-voltage (I-V) and capacitance-voltage (C-V) characterizations were implemented through Gamry G series potentiostat/galvanostat/ ZRA instrument. The I-V characterization was conducted under illumination with a mercury lamp.

Result and discussion

The Figure 1 depicts the cyclic voltammetry curve obtained using the Gamry instrument. From the curve of cyclic voltammogram shown in Figure 1, it is clear that well-defined cathodic peaks that can be observed around the potential values of -0.20 V and -0.77 V vs. Ag/AgCl. At the certain deposition potential value of -0.20 V vs. Ag/AgCl, no visible thin film was deposited on the working electrode. At the deposition potential value of -0.77 V vs. Ag/AgCl a thin film of SnO_2 was grown on the working electrode. However, the thin film formed at deposition potential value of -0.77 V vs. Ag/AgCl was not well-adhere to the substrate. Therefore, a set of samples was deposited across a range of potentials, varying from 0.60V to 0.90 V vs. Ag/AgCl. Thus, it is found that the best

adhered SnO_2 thin films were form at the deposition potential value of 0.85 V vs. Ag/AgCl.

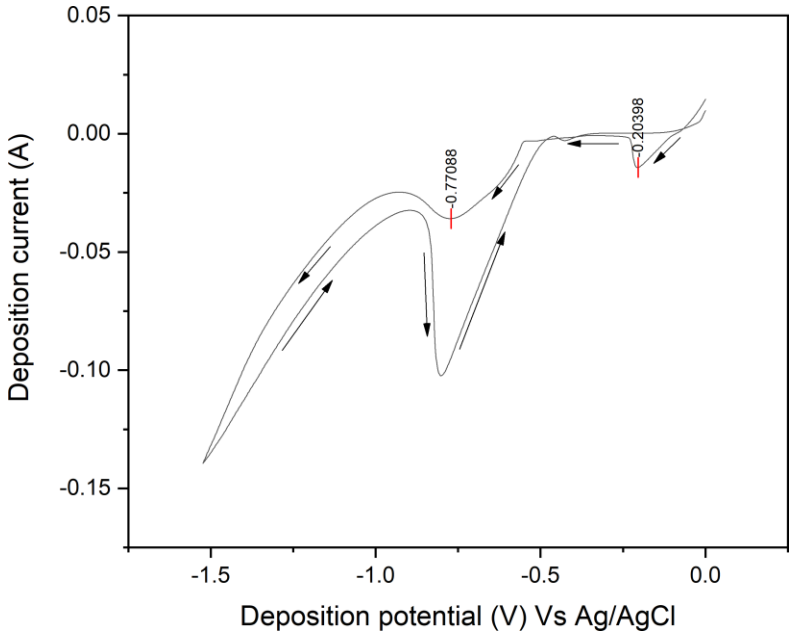

Figure 1. *Cyclic voltammetric curve of SnO_2 thin film deposition*

The Table 2 displays the values of short circuit current densities (J_{SC}) and open circuit voltages (V_{OC}) resulted for the SnO_2 thin films deposited at deposition potential value of -0.85 V vs. Ag/AgCl and at the bath temperature values of 80˚C, 85˚C, and 90˚C. The photoresponses resulted for the other temperature values are insignificant.

Table 2. *J_{SC} and V_{OC} values for the SnO_2 thin films deposited at different temperature values of film deposition for 120 seconds*

Temperature (˚C)	J_{sc} (μAcm^{-2})	V_{oc} (mV)
80	309	69
85	410	113
90	91	50

The Table 3 displays the J_{SC} and V_{OC} values for the SnO_2 thin films deposited at deposition potential value of -0.85 V vs. Ag/AgCl and at the deposition durations of 60, 90, 120 and 150 seconds. The photoresponses resulted for the other deposition durations were insignificant.

The optimal photoactive performance was achieved from the films grown in a bath consisting of 30 mM $SnCl_2$ and 150 mM HNO_3 at a deposition potential of - 0.85 V vs. Ag/AgCl and bath temperature of 85 ℃ for a deposition duration of 120 seconds. Light modulated I-V curve for the optimum sample is shown in Figure 02. Here the area exposed for the I-V characterization was 25 mm^2.

Table 3. *J_{SC} and V_{OC} values for the SnO_2 thin films deposited at different film deposition durations at the bath temperature value of 85* ℃.

Time (s)	J_{sc} (μAcm^{-2})	V_{oc} (mV)
60	59	9
90	254	51
120	410	113
150	227	42

Figure 3 represents the Mott-Schottky plot which was obtain for the optimum sample. According to the Figure 3 it is clear that SnO_2 film exhibits n-type conductivity and has a flat band potential of -0.51 V vs. Ag/AgCl.

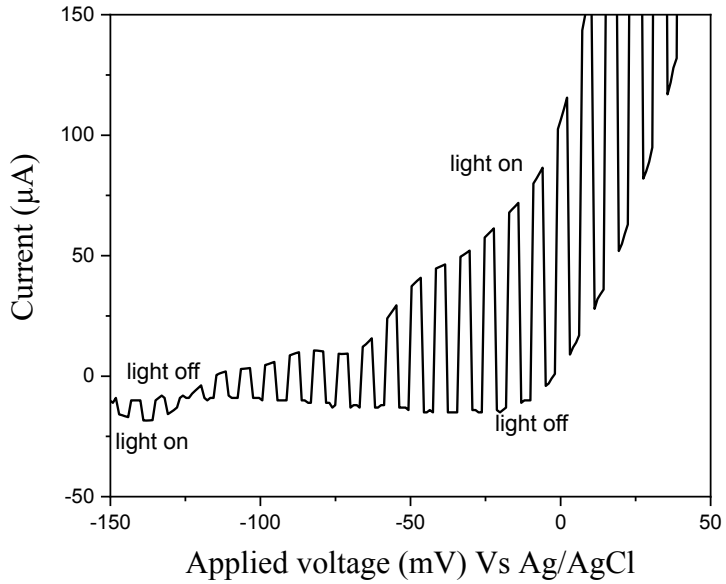

Figure 2. *Dark and light current-voltage characteristics for the film deposited at optimum growth condition*

Conclusion

In this study, it is found that successfully photoactive n-type SnO_2 thin films can be electrodeposited on Cu substrate. The best sample resulted the J_{sc} value of 410 μAcm^{-2} and V_{oc} value of 113 mV. The quality photoactive samples can be deposited in a three electrochemical cell consisting of 30 mM $SnCl_2$ and 150 mM HNO_3 at -0.85 V vs. Ag/AgCl for 120 seconds and bath temperature of 85°C. Moreover, the flat band potential resulted for the best SnO_2 thin films was -0.51 V vs. Ag/AgCl.

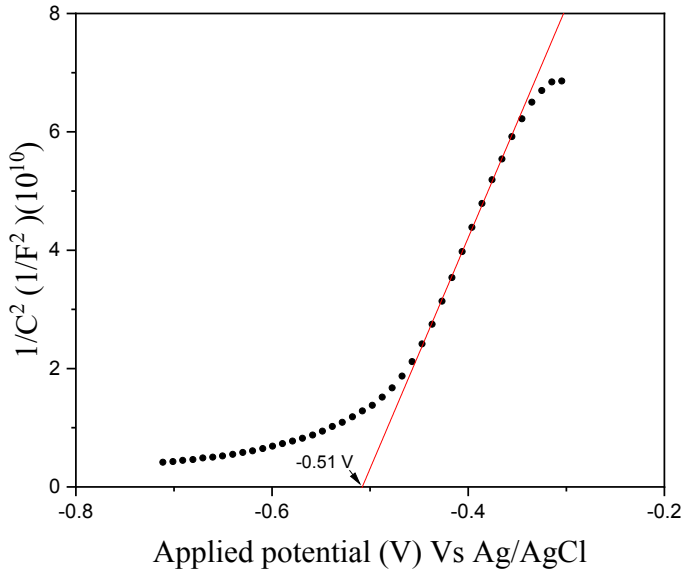

Figure 3. *Mott–Schottky plot obtained in a PEC containing 0.1 M sodium nitrate aqueous solution for SnO_2 thin film electrodeposited under optimum growth conditions.*

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