A Review of Recent Results on Cyclic Voltammetry Studies of Metal Chalcogenide Thin Films

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Abstract: Cyclic voltammetric studies were done in an electrochemical bath to monitor the electrochemical reactions as described by many researchers. The study reviews recent results on cyclic voltammetry technique applied to the semiconductor thin films. All the voltammometric curves were scanned in the cathodic and anodic direction in order to find the optimum potential region where the formation of metal chalcogenide thin films. Ag/AgCl and saturated calomel electrode were used as reference electrode during the experiment.

Key words: Cyclic voltammetry, reference electrode, counter electrode, working electrode, metal chalcogenide, thin films

INTRODUCTION

Cyclic voltammetry plays a major role in the field of electrochemistry by investigating the electro chemical behavior of a system (Bard and Faulkner, 2001; Compton and Banks, 2007; Randles, 1948). It is one of the most important analytical characterizations (Paul, 1990) which measures the current that produces in an electrochemical cell (Wang and Eric, 2011). The excess voltage is predicted by the equation given by Nerst. It is performed by the working electrode by cycling the potential and the resultant current is measured. The transfer of electron can be analyzed by using this characterization study. The needful information regarding the thermodynamic process of redox and the mechanism of electron-transfer reactions are carried out using the power of this cyclic voltammetry. The prominent transfer of charge from donor to acceptor, charge transport and the collection of charge at the electrodes are the most essential parameters for standardizing the photovoltaic devices. The operating mechanism is which the electric potential is scanned before approaching to reverse direction after coming to the final potential and again scans the initial potential. It is used to study the various processes of redox and the determination of stability of reaction products (Kumar et al., 2016). Also the reversibility of a reaction, its kinetics of electron transfer and the presence of intermediates in redox reactions are studied. The limitation of this cyclic voltammetry is which applies only when there is no current that flows through the electrode. When there is a flow of current, the activity of ions at the surface of the electrode changes. Also, it results in additional over potential and resistive loss terms which approach towards the measured potential.

In the present research, we report the synthesis of thin films using electrochemical deposition technique. Electrochemical behavior of thin films was studied using cyclic voltammetry. The cyclic voltammograms were recorded in order to establish the appropriate experimental conditions for the formation of sulphur, selenium and tellurium based metal chalcogenide thin films.

Literature review: Nowadays, metal chalcogenide thin films are under intense investigation because of they have unique properties. They are used in a huge number of applications such as optoelectronic devices, laser devices, photovoltaic cell, microelectronic and nano electronics. To date there are a plenty of reports related to the synthesis of sulfur-based (Kassim et al., 2010a, b, 2011a-d, Anuar et al., 2008; Ahmad, 2017; Ho and Pan, 2014; Gao and Shen, 2012; Kul, 2014; Lugo et al., 2014; Jaid et al., 2017; Anuar et al., 2009, 2011a, b; Jelas et al., 2009; Ho, 2014), selenium-based (Khatri et al., 2017; Edelman et al., 2017; Singh et al., 2017; Kumar et al., 2016, 2017; Forster et al., 2017; Kwon et al., 2017; Guillen and Herrero, 2017; Abraham et al., 2017) and tellurium-based (Ho and Pan, 2014; Okuyama et al., 2017; Zheng et al., 2014; Sudarshan et al., 2017; Rogacheva et al., 2016;
Yamauchi and Takashiri, 2017; Takashiri et al., 2007; Poudel et al., 2008; Kuznetsov et al., 2016, 2017) metal chalcogenide thin films using a variety of deposition methods.

Cyclic voltammetry is a powerful electro analytical tool (Bengi and Sibel, 2011) for confirming the electrode potential during the deposition process (Daubinger et al., 2014). It is a potential sweep method (Nasirpour, 2016) in which the potential of the working electrode is varied continuously with time and the current from a redox event is measured (Peter and William, 1983). Now a days, cyclic voltammetry is the most common electrochemical techniques in use by researchers due to it is an elegant and could be carried out with relatively simple equipment (Budnikov and Kazakov, 2000) for studying redox reactions at the electrode solution interfaces. Generally, cyclic voltammetry has become increasingly employed in all fields of Chemistry and Material Sciences (Bocarsly, 2002). A standard cyclic voltammetry experiment uses a cell fitted with three electrodes, namely reference electrode, working electrode (the reduction or oxidation reaction takes place) and counter electrode. This combination is called as a three-electrode setup. In the experiment, the species of interest is dissolved along with some electrolyte which promotes conductivity in the solution. Then, three electrodes are inserted into the solution. The working electrode has a small disc of electrode exposed, so, the reaction can take place in a carefully controlled area. The counter electrode is made from gold, platinum wire or graphite (Sangeeta and LaGraff, 2004) completes the circuit (Wipf and Wightman, 1989). The reference electrode with a known potential is a very important component in cyclic voltammetry which is used to measure the potential applied to the cell. There are various types of reference electrodes such as standard hydrogen electrode, saturated calomel electrode and the silver-silver chloride electrode (Aryan et al., 2014). According to researchers, cyclic voltammetry gives additional data that can be interpreted to make conclusions about the reduction or oxidation reaction and the stability of the species resulting from the electron transfer.

**METAL SELENIDE SEMICONDUCTOR THIN FILMS**

Electrodeposited zinc selenide thin films have been prepared onto transparent conducting oxide coated glass substrates (Chandramohan et al., 2004). Deposition potential range of -700 to 1100 mV was selected for the deposition of ZnSe films as described in their research. Reduction waves for H2SeO3 to Se centered about -550 mV and the hydrogen evolution happens at more negative potentials could be seen in cyclic voltammetry studies. Gromborti et al. (2012) have reported that the preparation of zinc selenide films onto Au substrate in acidic conditions by using electro deposition method. Cyclic voltammograms display that reduction of Au oxides could be supported by the cathodic peak at 0.9 V (Ag/AgCl). Additionally, the current of cathodic peak increases in the presence of Se (IV), indicating that selenium deposition is occurring.

Electro deposition of iron selenide thin films was described by Thanikaiarasan et al. (2009). FeSe films were deposited onto substrate (indium doped tin oxide coated conducting glass) in the aqueous bath containing FeSO4 and SeO32-. Cyclic voltammetric studies were carried out in the range from 0-1200 mV (SCE). The reduction peak at -900 and -540 mV is due to the reduction of Fe3+ to elemental Fe and reduction of H2SeO3 to Se, respectively. Chen et al. (2011) reported the synthesis of iron selenide using same deposition method. The obtained results show there are two cathodic peaks (-0.63 V versus Ag/AgCl (Fe3+ to Fe) and -0.86 V (Se to Se3+)) could be detected in cyclic voltammograms. A slight difference in deposition potential is because of external factors such as substrate type, stirring solution, pH, bath temperature and concentration of the electrolytic solution. Pawar et al. (2007) also agreed their explanation.

The electrochemical behavior of Cu-Se was studied using cyclic voltammetry (Fernandez et al., 2017). Reduction of Cu2+ to Cu+ could be supported by cathodic peak at -100 mV. The formation of Cu2Se occurs at more negative potential (-700 mV versus Ag/AgCl). On the other hand, reduction peak at -600 mV could be observed for the formation of Ga2Se5. In their research, CuGaSe2 films were successfully produced as Ga2Se5 films react with the CuSe films.

Rohom et al. (2016) have synthesized copper indium diselenide thin films using potentiostatic electrochemical method (at room temperature and in acidic medium). The cyclic voltammograms obtained without agitation indicate that reduction of copper and selenium ions happened at lower cathodic potentials such as +100 to -400 mV versus Ag/AgCl. Lastly, indium is proposed to be electrodeposited along with copper and selenium in order to produce ternary films (copper indium diselenide) at -400 to 700 mV by the charge transfer reaction.

**METAL TELLURIDE SEMICONDUCTOR THIN FILMS**

Gomez et al. (2005) have reported voltammetric investigations were done in order to understand the
cadmium telluride nucleation and growth mechanism on silicon. The voltammogram shows a small cathodic peak at -0.325 V versus SCE which can be associated to HTeO$_4^-$ reduction to tellurium (through a four electron process). Further, the reduction of Te to H$_2$Te (at a potential of -0.5 V) and deposition of metallic Cd in the bath (at a potential of -0.6 V) could be seen as the scan towards more negative potentials.

Electro deposition method was used to synthesis cadmium telluride thin films onto nickel foil substrate as described by Wang et al. (2015). In their research, reduction of cadmium ions to elemental cadmium and tellurium ions to elemental tellurium could be observed at a potential of -800 and 250 mV, respectively. Finally, good quality of CdTe films were produced in a potential of -500 mV. These results agree with those obtained earlier as reported by Echendu et al. (2016) electro deposition of CdTe.

Sonawane and Chaure prepared zinc telluride films and copper zinc telluride films using electrochemical deposition method. These films were deposited onto glass substrate (fluorine doped tin oxide) in aqueous solution (TeO$_2$, ZnSO$_4$ and CuSO$_4$), at room temperature and pH = 2.5. The potential was optimized in the range of -0.9 to 1.1 V versus Ag/AgCl based on the cyclic voltammetry studies.

John et al. (2005) have reported that the preparation of copper doped zinc telluride thin films using electro deposition technique in acidic bath (ZnSO$_4$, TeO$_2$ and CuSO$_4$). Cyclic voltammetry analysis was performed to identify the deposition potential of ZnTe and ZnTeCu. There are two cathodic peaks could be seen in their works, indicating reduction of HTeO$_4^-$ to tellurium (-0.4 V versus SCE) and formation of ZnTe on the substrate (-0.78 V). The current increased as the potential increased more than -0.8 V due to the high concentration of Zn$^{2+}$ in the bath.

Hatsuta et al. (2016) have synthesized p-type Sb$_2$Te$_3$ films onto stainless steel substrate using electro deposition technique. There are two cathodic peaks could be observed, representing an electrodeposition of Te (-1.00) and Sb (-2.20 mV versus Ag/AgCl), respectively.

Xiao et al. (2006) have reported the synthesis of lead telluride thin films using electro deposition method in acidic conditions. There are few peaks could be detected as shown in cyclic voltammetry studies. For example, the first peak at -0.2 V (Ag/AgCl) was attributed to HTeO$_4^-$ to Te. Second peak at -0.5 V is two steps reaction, involve the electrochemical generation of HTe$_2$Te as an intermediate species followed by chemical reduction to elemental Te. Meanwhile, in the lead electro deposition, the reduction wave at -0.43 V due to the reduction of lead (II) ion to lead.

Metal sulphide semiconductor thin films: Kim et al. (2013) have prepared Cds films onto ITO glass using electro deposition method in aqueous solution. The reduction of Cd$^{2+}$ to Cd (-1.14 V versus Ag/AgCl) and reduction of thiosulfate ion to Cds (-0.95 versus Ag/AgCl) could be observed. The current looping in the reversal sweep direction indicating nucleation and growth deposition process (Zhang et al., 2009; Inamdar et al., 2007).

Ebrahim et al. (2012) have prepared CuInS$_2$ thin films using electrochemical deposition method. These films were deposited onto fluoride doped tin oxide substrate in the presence of doceylbenzene sulfonic acid in order to prevent the precipitation of the sulfur element. They conclude that the increasing of pH shifts the electrodeposited voltage to more negative. The obtained films were thin and adherent to the substrates. Pulsed electro deposition method was used to prepare antimony sulfide thin films onto fluorine doped tin oxide coated glass substrate (Garcia et al., 2016). The obtained films were brown colour, spatial uniformity and good adherence to the substrates. Deposition of Sb from SbCl$_3$ was observed in between -380 and 840 mV. Also, the cathodic current sharp increases beyond -70 mV which attributed to the reduction of thiosulfate to sulfur. Lastly, they conclude that the best deposition potential was -720 mV versus SCE.

Potentiostatic cathodic electro deposition method was employed to synthesis silver tin sulfide films on indium tin oxide coated glass substrate, at pH 2 and temperature of 55$^\circ$C (Almessiere et al., 2015). There are several peaks could be seen in their experiment results. For example, reduction of thiosulfate ion to sulfur (-600 mV) and the formation of silver sulfide compound (-900 mV). Finally, they reported that black colour, homogeneous and uniform films with good adherence have been obtained at the best cathodic potential peak (-1000 mV vs. Ag/AgCl).

A Successive Ionic Layer Adsorption and Reaction (SILAR) method has been used to prepare PbS films. Cyclic voltammetry studies have been carried out in the potential value of -800 and 50 mV (Ag/AgCl). An anodic peak could be seen at a potential of 230 mV due to oxidation of lead sulfide films on gold electrode in basic solution (Ust et al., 2016). On the other hand there are two cathodic peaks could be detected (-490 and -560 mV), representing cathodic stripping of either elemental sulfur of lead sulfide films.

ZnS films were prepared using electrodeposition method in aqueous solution (Zinc (II) acetate and sodium
thiosulfate) as described by Arbi et al. (2015). They figure out that the reduction of thiosulfate ion to sulfur (-1000 mV versus Ag/AgCl) and the formation of ZnS onto ITO coated glass substrates (-1300 mV) in acidic solution can be seen in cyclic voltammetry studies.

Zhang et al. (2013) synthesized quaternary thin films (copper zinc tin sulfide) using co-electrodeposition method. Reduction of copper ion and tin ion could be seen in the cathodic peak at -750 mV (Ag/AgCl) and 1400 mV, respectively. However, no obvious cathodic peak was observed from the ZnSO4 solution. They observe that the deposition of multi-elemental compounds is more complex when compared to the electrodeposition of a single element. They explain that the different elements have different redox potentials and reduction kinetics.

Shao et al. (2015) have prepared Cu,ZnSnSe3 films onto the fluorine doped tin oxide coated glass substrate. They reveal that copper (II) ions are first reduced to copper (I) ions in acidic solution, then, reduced to elemental copper when the applied potentials are swept to more negative potentials. Further, they explain that the cathodic current increases as the applied voltage was more than -800 mV, indicating H+ ions were reduced to hydrogen.

Assaker et al. (2014) synthesized ZnInS3 thin films in acidic chemical bath (containing zinc chloride, indium chloride and sodium thiosulfate). Cyclic voltammetry technique has been used to investigate binaries (Zn-S, In-S) and ternary system. In Zn-S binary system, cathodic peak (-800 mV versus Ag/AgCl) is detected which is attributed to reduction of thiosulfate ion to sulfur. Further, they figure out that cathodic peak at -1050 mV because of the formation of zinc sulfide. In binary In-S mixture, the formation of indium sulfide could be supported by the reduction peak at -1050 mV. They conclude that the best potential was -1050 mV, successfully obtained brown films and uniform good adhesion to substrate.

Electro deposition method was used to produce ternary (silver indium sulfide) thin films onto fluorine doped tin oxide coated glass substrate (Wang et al., 2011). There are three reduction peaks at -0.2-0.38 V (Ag/AgCl), -0.8 V-1.4 V and -0.8-1.1 V could be detected for the reductions of silver, indium and sulfur ions, respectively. The reduction potentials of mixture were a little more negative than that of the single Ag+3, In+3 and S2O3-2 ions in the deposition bath. They further explain that an over potential caused by diffusion limitations of the ions in the solution used in the electrodeposition process.

CONCLUSION

Cyclic voltammetry technique has been used to investigate the electrochemical of the thin films as reported by many researchers. A series of cyclic voltammetry experiments were carried out. The cyclic voltammetry curve was first scanned in the cathodic direction and then in the anodic side. Reduction of metal ions, followed by thin film formation could be seen in cyclic voltammogram.

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REFERENCES


