INFLUENCE OF DEPOSITION TIME ON ELECTRODEPOSITED NICKEL SELENIDE ($NiSe_2$) THIN FILMS FOR SOLAR/PHOTOELECTROCHEMICAL CELLS

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ABSTRACT: The present study investigates the role of deposition time on the structural, morphological, compositional, optical and semiconducting properties of electrodeposited $NiSe_2$ thin films. Nickel Selenide ($NiSe_2$) is a transition metal chalcogenide material suitable for its good chemical and optical properties. The films were deposited on Indium Tin Oxide (ITO) coated conducting glass substrates at deposition times between 10 – 30 minutes with the interval of 5 minutes. The structural analysis of the films reveals the polycrystalline nature with sharp and high intense peaks. Scanning electron micrographs (SEM) reveals that grains are in spherical shape, uniform and pin-hole free. Composition analyses through energy dispersive X-ray (EDX) studies confirm the presence of Se and Ni to its stoichiometry. The observed direct bandgap films reduced their energy gap values from 1.30 to 1.15 eV as the deposition time increases found by optical studies. Heat treatment of these films is annealed at 200°C for 1 hour yield the high crystallinity that also confirms by X-ray diffraction. Annealed films with longer deposition time of 30 minutes shown cracks in the surface observed by SEM. The energy gap reduced in 20% for the annealed films. This investigation confirms that the deposition time has greater influences for the grown films.

KEYWORDS: *$NiSe_2$; Electrodeposition; Deposition Time; Energy Gap; Pin-hole Free*

1.0 INTRODUCTION

Over the past years, great efforts have been made to develop novel material for electrochemical energy conversion by focusing on their appropriate electrochemical properties and affordable cost [1]. Hence, researchers have introduced thin film technology in photo-electrochemical application due to their affordable manufacturing cost, simple P-N junction formation, offers great efficiency fabrication technique, and suitable for large area production [2-3]. Surface coatings with thickness less than 1 μm known as thin films are controlled by its materials on their molecular and atomic scale. The surface modification, crystal structure and deposition prior are to improve its conductivity [4].

Lately, researchers have suggested Transition Metal Chalcogenide (TMC) materials for this purpose that possess suitable bandgap spectrum for the solar energy related applications. It also has good electrical conductivity with high optical absorption bandgap [5]. In line to this, the fabrication of group II–VI semiconductors that has transition metal chalcogenides such as MX_2 (where M refers the transition metal and X refers chalcogenides as Se, S and Te). Transition metal nickel (Ni) chalcogenides are in good physical, non-linear optical properties and chemical properties with promising luminescent properties [6]. Yu et al. [7] proposes to add complexing agent in electrolyte to create a feasible co-deposition condition. Previous works reports that various complexing agents namely EDTA (ethylene diamine tetra acetic acid) [8], thiourea, nitrilotriacetic acid, ammonia, triethanolamine (TEA), tartaric acid and disodium ethylene diamine tetra-acetate [9] have been used to deposit thin film chalcogenide. However, TEA has been widely applied in thin film studies [10-11] due to its stable condition for photo electrochemical application [12], improves thin film growth [13] and controls the diffusion of Ni^{+2} ions to react with chalcogenide [14].

$NiSe_2$ thin film has been identified as a satisfactory candidate for energy storage application since it possesses significant electronic and Pauli magnetic properties in conductivity and catalytic discipline [15-16]. The energy bandgap of Nickel Selenide is lying between Nickel Sulfide and Nickel Oxide. It is wider than its counterpart selenide and narrower than its oxide counterpart which successfully fitted as promising candidate for energy storage [17]. Moloto et al. [16] has claimed that Nickel Selenide identified as p-type semiconductor has

energy band gap of 2.0 eV (620 nm). Traditionally, various deposition methods used for TMC thin films synthesis. They can be prepared via electrodeposition [18], deposition by chemical bath [3], hydrothermal [19], One-pot [17] and low pressure – metal oxide chemical vapour deposition (LP-MOCVD) [20]. However, electrodeposition technique is always under the limelight due to its affordable cost for large scale production with simple equipment setup and reduce wastage [3, 18]. Thus, researchers have attempted in investigating numerous TMC material via electrodeposition method such as $NiSe_2$ [21], NiS_2 [3, 22], Bi_2Te_3 [23], ZnS [24], CuO [25], Sb_2Se_3 [26] and ZnSe [27] with various deposition parameters.

There is no previous research work on $NiSe_2$ prepared through electrodeposition with TEA combination that investigated the influence of deposition time or on its thickness characteristics. Considering that this study investigates the synthesis of $NiSe_2$ thin film via electrodeposition method in the presence of complexing agent Triethanolamine (TEA) with various deposition time parameters. The characterization of $NiSe_2$ thin film preparation specifically, influenced by the deposition time is thoroughly investigated.

2.0 EXPERIMENTAL PROCEDURES

2.1 Thin Film Substrate and Electrolytes Preparation

Thin film growth mainly affected by the adhesiveness of the substrate used. It is necessary to clean the ITO coated substrates ultrasonically cleaned in deionized water and ethanol. 50 ml of deionized water were used with respective metal and chalcogenides solutions. The electrodeposition of thin film semiconductors on ITO-coated glass substrates was carried out at 40±2ºC of temperature. The aqueous solution containing Nickel Sulphate Hexahydrate, $NiSO_4.6H_2O$ (1mM) + Sodium Selenide, Na_2SeO_3 (4 mM) as precursors for Nickel Selenide ($NiSe_2$) solution. The additive selected for this precursor is Triethanolamine (TEA) (0.1 M) that has been added into the solution bath. To maintain the nature of solution to be alkaline drop by drop of NaOH added to keep the value of pH to be ~ 10 (2.5 mM) [19].

2.2 Electrodeposited Thin Films and its Characterization

Thin film electrochemical behaviour of the $NiSe_2$ was studied by cyclic voltammetry (CV), galvanostatic charge - discharge and electrochemical impedance measurements in 6 M KOH aqueous

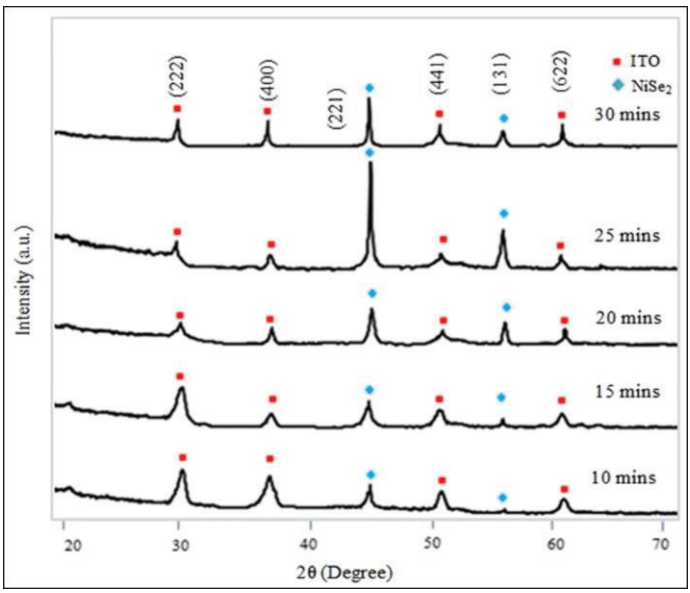
solution. Princeton Applied Research Model VersaSTAT 3 Potentiostat was used which is in three - electrode cell. In a cyclic voltammetry measurement, by applying desirable scan rate and potential window, the voltammograms of the electrode material can be recorded in a three electrode system. The three electrodes normally used as working electrode (WE), ITO-coated glass substrate, a counter electrode (CE) as graphite and as the reference electrode (RE) as Saturated Calomel Electrode (SCE) described in [28]. All the three electrodes kept as close to each other with the optimum distance of 1 cm for uniform deposition [29]. Film deposition was carried out at -1.0V after various deposition potential was studied. Characterization studies show that -1.0V is the suitable potential for preparing high crystalline film. Gravimetric weight difference method was used to find the film thickness. These $NiSe_2$ thin films used by sensitive microbalance by assuming film density close to its bulk counterpart [10]. PANalytical ZPERT PROMPD PW 3040/60 diffractometer used as X-ray diffraction (XRD) for 2θ range from 15 to 75° with Cu$K\alpha$ radiation and SEM ZEIZZEVO 50 scanning microscope used for both scanning election microscopy (SEM) analysis and its composition studies UV-Vis spectrophotometer utilized for determination of energy band gap of the films to study their optical properties and it consists of the thin film photo electrode and graphite as the counter electrode as illustrated in [22, 30].

3.0 RESULTS AND DISCUSSION

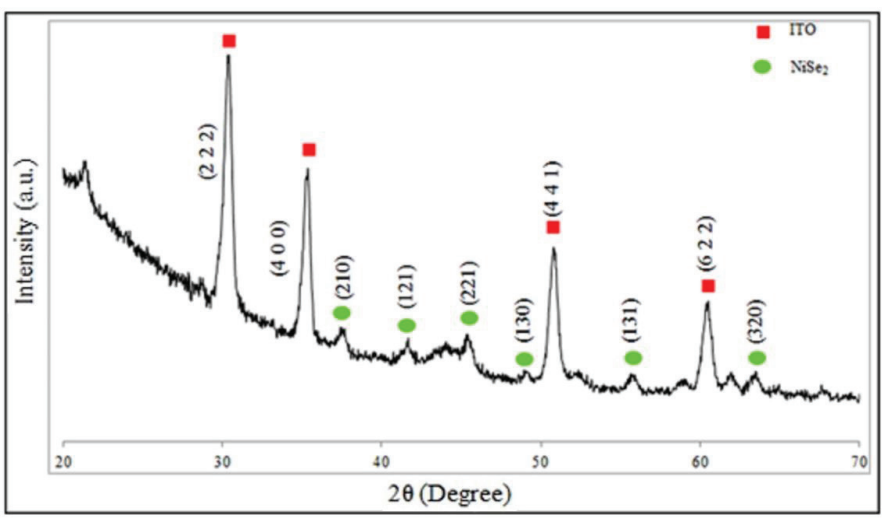
3.1 Crystallographic Analysis

XRD spectrum of $NiSe_2$ thin films deposited on ITO substrates at various deposition time with time interval of 5 minutes is shown in Figure 1(a). The XRD spectrum reveals two peaks of $NiSe_2$ at 47.176° and 55.733° corresponding to 221 and 131 orientation plan. The orthorhombic structure of these $NiSe_2$ films with the peaks fit into lattice parameters values. The lattice parameters are measured a = 4.892, b = 5.958 and c = 3.957nm. These values are well agreed with the standard values [31]. The experimental and standard JCPDS data of 'd' spacing of the $NiSe_2$ thin films are summarized in Table 1. The deposition starts only after about 10 minutes which is denoted as Induction time. The only $NiSe_2$ peak observed after 10 minutes' films with more distinct peaks appear for ITO glass slides. It could be due to insufficient film thickness attributed to low deposition time. Evidently, at deposition time of 15 minutes, low intense peak at $2\theta = 55.733^{o}$ start to become more distinct to its neighboring $NiSe_2$ film peak that

indicates (131) plane. On the other hand, the preferred orientation peak observed at (221) which is considered as the film peak grows with higher intensity compared to other peaks. It can be clearly seen that as the deposition time increases the $NiSe_2$ peak intensity also increases and it is observed as the maximum film crystallinity at 25 minutes thereafter the film crystallinity deteriorates.



(a)



(b)

Figure 1: (a) XRD pattern for $NiSe_2$ as-deposited thin films deposited at different deposition times and (b) $NiSe_2$ as-annealed film at 200°C for 1 hour

Therefore, it is evident that deposition time is directly proportional to its film thickness. As the film thickness reaches to certain level the internal grains are started to break. It can be observed in 30 minutes grown spectrum where by the intensity of the planes (221) and (131) that belongs to the film decreases while increasing tend observed for the intensity of ITO peaks (222), (441), (440) and (622) increases. This reveals that at stage the film peel off and internal structure crack. The calculated $NiSe_2$ crystallite size with Debye Sherrer formula [24] is in the range of 15-35 nm. On the other hand, film prepared at 25 minutes, considering as optimum crystalline film was annealed at 200°C for 1hour to analyse the heat influence on film characterization. Figure 2 (b) shows that annealed film has more film peaks with lower intensity and ITO peaks with higher intensity were obtained compared to as-deposited film. New film peaks in the spectrum shows that recrystallization has occurred, however, the film deteriorated at certain condition and made the influence of ITO substrate higher. Annealed film is also orthorhombic structure [23].

Table 1: Comparison of experimental 'd' values with JCPDS for as-deposited and annealed $NiSe_2$ film

Condition	Angle (2θ)	Planes (h k l)	STD (Å)	Experimental (Å)				
				10 min	15 min	20 min	25 min	30 min
As-deposited	47.176	2 2 1	1.9250	1.9311	1.9279	1.9110	1.8990	1.9186
	55.733	1 3 1	1.6480	1.6512	1.6441	1.6362	1.6207	1.6497
Annealed	38.856	2 1 0	2.2644	-	-	-	2.2433	-
	42.146	1 2 1	2.0951	2.0945	2.0932	2.0913	2.0902	-
	47.176	2 2 1	1.9250	1.9247	1.9237	1.9237	1.9231	-
	49.498	1 3 0	1.8400	1.8379	1.8374	1.8347	1.8328	-
	55.733	1 3 1	1.6481	1.6471	1.6462	1.6445	1.6442	-
	64.931	3 2 0	1.4350	1.4342	1.4327	1.4302	1.4302	-

The sharp and highly intensed diffraction peaks indicate that the film is polycrystalline with improved crystallinity as the deposition time increases [21]. This improvement is attributable to effective mass transfer resulting in increased film thickness during the film growth process [25]. It can be concluded, when the reduction process takes place the ITO peaks gradually decreases while the $NiSe_2$ peaks increases corresponding to 'ion-by-ion' growth mechanism. Hence, it can be mentioned that the influence of ITO in the spectrum decreases as the film thickness contributes for the film growth to reach optimum intensity. Thereafter the film is claimed to crack and peel due to severe stress. This is also supported in SEM result.

3.2 Surface Morphology of $NiSe_2$ Thin Films

Figures 2 (a)-(c) shows as deposited $NiSe_2$ film morphology. Morphology of the film is at granular shape at deposition time of 10 minutes. However, the film grows with time and forms in spherical shape at 25 minutes. It is observed that few crystallites are grouped together and forms bigger grains. It could be due to Se element become amorphous in alkaline bath and tend to aggregate to form bigger grains [33]. It is the effect of 'Ostwald ripening" process.

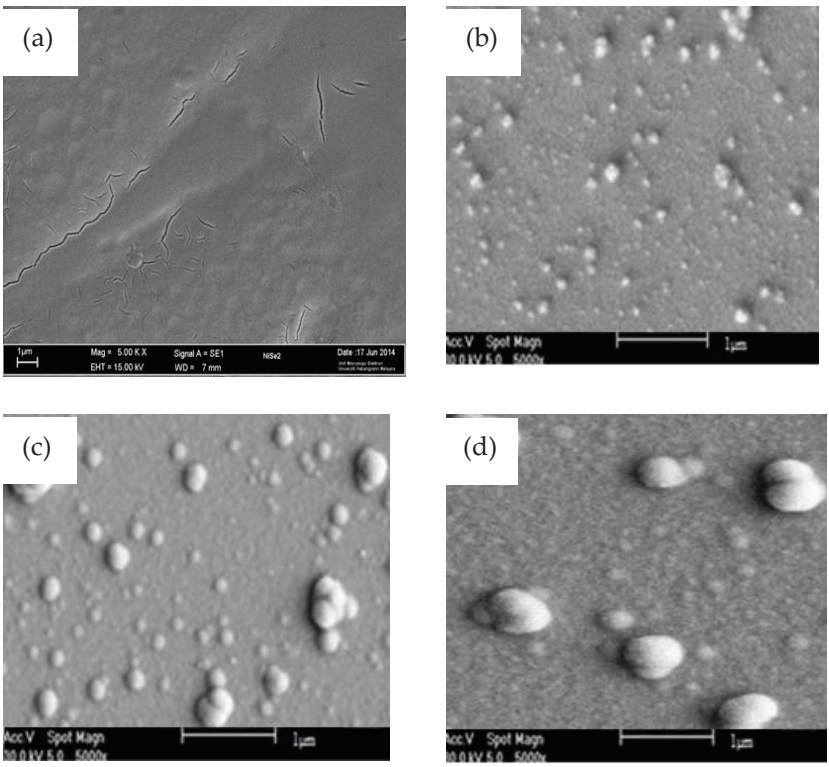


Figure 2: Surface morphology of $NiSe_2$ films with deposition time (a) 10 minutes (b) 20 minutes (c) 25 minutes and (d) 25 minutes-annealed at 200°C for 1 hour

The grain size were calculated from these studies are in the range of 0.13 – 0.38 μm. The synthesized films are continuous, homogenous and denser for thicker films. Since the temperature of the electrolyte bath is maintained at 40 ± 2°C throughout the growth process, the grain growth is contributed by longer deposition time [34]. However, it does not mean longer deposition time promises uniform film. This is proven in film prepared at 30 minutes. The grain size of the film

increases extensively resulting a thicker film with increase of strain energy. Hence the film cracks to release the accumulated stress and started to peel off [3]. Figure 2d shows the film prepared at 25 minutes annealed at 200°C for 1 hour. The film is smoother, smaller grains and with some cracks which could be possibly due to accumulated internal stress as the thickness increases during re-crystallization.

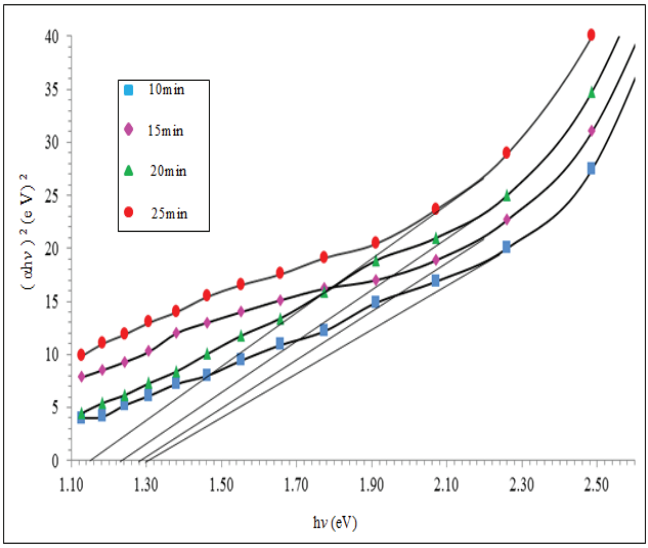
3.3 Energy Bandgap Studies of $NiSe_2$ Film

Optical studies revealed the absorption spectra of the as deposited $NiSe_2$ thin films. They focused their analysis in the wavelength range 200-1100 nm without considering losses due to reflection and transmission at room temperature atmosphere. Light intensity analysis of an optical spectrum of a material is imperative for solar cell application. This employed to determine key optical properties such as extinction coefficient (k), absorption coefficient (α), optical band gap (Eg) etc. The absorbance spectrum of these optical studies are considered as this value calculated for the synthesized samples to its light absorption nature. From this spectrum and its corresponding wavelength, the type of band transition and its energy gap were derived from the following equation [32] expressed as

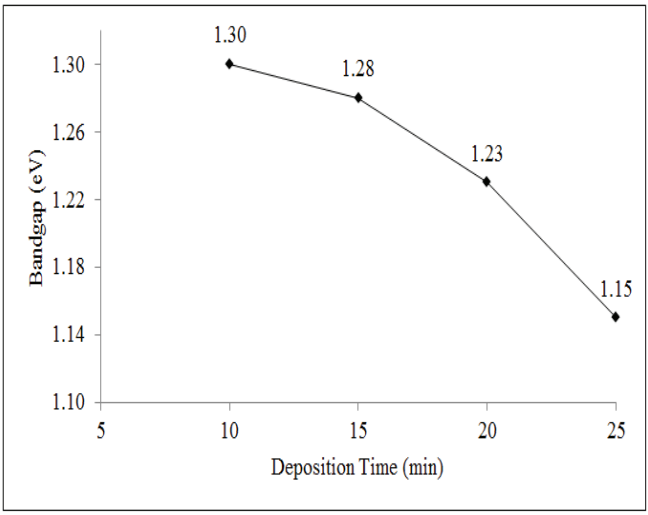
$$\alpha h\nu = A(h\nu - Eg)^n \quad (1)$$

where A is an energy dependent constant, Eg is the band gap energy (eV) and α is the photon energy and h is the plank constant (6.627 X 10^{-34}), v is light frequency, substituting the values of n as ½ (direct) and 2(indirect). The synthesized $NiSe_2$ thin films at different deposition times with their $(\alpha h v)^2$ vs. hv plots are shown in Figure 3 (a) whereas Figure 3 (b) shows the range of these band gap values for $NiSe_2$ films lying between 1.30 - 1.15eV. The obtained band gap range is very much similar to the reported [33]. It is observed that the energy bandgap is directly proportional to the deposition time. It is due to improved grain growth in thicker film has lower absorbance value in the absorption spectra compared to lower thickness film. Lower absorption spectra contribute for decrease of film bandgap [35]. It is also claimed that film reorganization by filling the voids in the film provides smaller energy bandgap. In this study, deposition time parameter influences the film reorganization. Thus, bandgap energy values strongly dependent on deposition time parameter. The change in the bandgap values corresponding to thickness increase with fixed deposition condition such as temperature, solution concentration etc [34]. It is reported that change of barrier height in

polycrystalline thin film can influence the film bandgap. Decrease in the barrier height corresponding to increase of grain size and thickness contributes for the smaller energy bandgap. Since the barrier height is lower as the thickness increase, the film's tendency to absorb more light is also decreases. Hence, bandgap decreases as films get thicker [36].



(a)



(b)

Figure 3: Optical absorbance variance of $NiSe_2$ film deposited at different deposition times (a) $(\alpha h\upsilon)^2$ vs. $h\upsilon$ and (b) bandgap vs. deposition time

4.0 CONCLUSION

It can be summarized that $NiSe_2$ films are successfully electrodeposited on Indium Tin Oxide conductive glass substrates. XRD results reveals that all films are in polycrystalline nature with sharp and more intense diffraction peak. Film crystallinity is deteriorated at deposition time beyond 30 minutes for as deposited film and in annealed film. This phenomenon is also confirmed in SEM studies. All films found to be continues, homogeneous and denser as the deposition time increases. However, the films are in peeled condition at the mentioned deposition time for $NiSe_2$. The film characterization followed by EDX analysis to determine the stoichiometric of $NiSe_2$ films and they are found to be in nearly stoichiometric. Presence of both Ni and Se primary elements with the stoichiometry close to the ratio of 1:2 that confirms the dichalcogenides (MX_2) nature by EDX. Then, optical and semiconductor studies are proceeded with the prepared films. Optical bandgaps are in the range of 1.30-1.15 eV for $NiSe_2$ films. Semiconductor studies reveals that all films are p-type semiconductor. Based on the results obtained, 25 minutes is the optimum deposition time to prepare $NiSe_2$ films.

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