Effect of pH on chemical bath deposited Nickel Selenide (NiSe) thin films.

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Abstract: *Thin film of Nickel Selenide (NiSe) was deposited on glass substrate at 303K using chemical bath deposition (CBD) technique. The films were deposited from aqueous solution containing* $Ni^{2}+$ *and refluxed sodiumselenosuphate* (Na_2SeSO_4)*. The pH of the solution baths were varied with constant time. The optical absorption data reveals that films of NiSe absorbs strongly at the ultraviolet range of 0.35µm and has above 90% transmittance in the VIS –NIR regions. The results show that the film has energy gap (εg) of 2.60eV – 2.70eV. Thickness ranges from 0.05µm – 0.51µm throughout the films. The film is found suitable as anti- reflection coatings.*

Key Words: Nickel Selenide, Chemical bath deposition, pH, thin films.

1.0 INTRODUCTION

In the past years, synthesis and physical characterization of thin film semiconductors have attracted significant interest. They have a wide variety of applications such as solar cells electroluminescent devices, photoconductors, sensor and infrared detector devices.(Prabahar 2009). Chemical bath deposition method has been used for the deposition of thin films of sulphides and selenides.

NiSe thin film using chemical bath deposition method so far. The basic principal involved in chemical bath deposition technique is the controlled precipitation of the desired compound from a solution of its constituents. This requires that the ionic product must exceed the solubility product. The use of complexing agent is very common in the preparation of thin films. Many researchers use various complexing agents such as sodium citrate, Ammonia, triethanolamine and disodium ethylenediamine tetra-acetate during deposition of thin films (Dhanam, 2005).

In the present investigation, thin films of NiSe were prepared from an alkaline bath using $NiCl_2 . 6H_2O$ and refluxed Na_2SeSO_4 acted as a source of nickel and selenide ion, respectively. DisodiumEthylene-diamine tetra-acetate EDTA $[Na_4(C_{10}H_{16}N_2O_8)]$ was used as a complexing agent during deposition process. The optical properties of NiSe thin films were determined. Two important factors that should be considered in producing these materials are the band gap energy matching the solar spectrum and the competitiveness of production cost. The rationale for this is that thin films modules are expected to be cheaper to manufacture owing to their reduced material costs, energy costs, handling costs and capital costs. Anua (2008). Nickel selenide is a semiconductor which is suitable for applications in solar cells, sensor and laser materials. Films of nickel selenide have previously been prepared by thermal evaporation and chemical bath deposition(CBD). (Okereke ,2010).

2.0 MATERIALS AND METHOD.

2.1 Chemicals Used

The reagents used are Nickel Chloride, SodiumSelenoSulphate Na_2SeSO_4, Ammonia Solution $NH_4(OH)$ which helps in adjusting the alkalinity of the solution used . Ethylene Diamine-Tetra Acetate (EDTA) serves as a complexing agent for the deposition of Nickel Selenide film. Mean while sodium sulphite in aqueous solution was used to reflux Selenium powder to obtain sodium selenosulphate (Na_2SeSO_4). Nickel Selenide (NiSe) was deposited by the reaction of solution containing [Nickel Chloride Dehydrate ($NiCl_2.6H_2O$)].

2.2 Film Deposition

The deposition baths were prepared as follows:

1.0ml of 0.1M of DisodiumEthylene-diamine tetra-acetate EDTA $[Na_4(C_{10}H_{16}N_2O_8)]$ was added to 3.0ml of 1.0M of $Nicl_2.6H_2O$ in a 100ml beaker, 2.0ml of 0.5M of freshly refluxed Na_2SeSO_4 was added and the volume was mae up to 50ml with water. The pH of the solution was adjusted by the use of 1.0ml, 3.0ml, 4.0ml, and 5.0ml of ammonia $NH_4(OH)$ in pH=8.9, pH=9.3, pH=9.7, & pH=10.0 baths, respectively. The degreased substrate were vertically suspended in the bath with a holder. After the 24hrs the substrate were taken out of the bath and rinsed with distilled water, which after it was dried in air

3.0 RESULTS AND ANALYSIS

The average of some of the optical and solid state properties of each film were calculated as shown in table 4.0 below. This enables us in analyzing the grown film in other to obtain its applications.

Table 1: Optical properties and thickness of NiSe films grown under varying pH

Reaction bath	Dip Time	Temp	pH	Average α	Average n	Average K	Average σ_{opt}	Thickness, t	Bandgap, E_g	Average ε_r	Average ε_i
	hr	^oC		(μm)			(S^{-1})	(μm)	(eV)		
8.9	24	303	8.9	211863.0	1.954787	0.008139	1.0505E+ 13	0.050401	2.6	3.848349	0.032838
9.3	24	303	9.3	72219.97	1.898311	0.007966	1.26946E+13	0.174229	2.6	3.705832	0.033693
9.7	24	303	9.7	239583.3	1.913801	0.009132	1.59867E+13	0.237931	2.65	3.80445	0.040622
10	24	303	10.0	495702.5	2.035661	0.015499	2.66477E+13	0.512032	2.70	4.300316	0.068787

3.1 Optical Properties of Nickel Selenide (NiSe) Thin Films

Fig 1: shows that film thickness increases proportionally with increase in pH value of the reaction bath. This is likely due to the variation in the volume of the ammonia $NH_4(OH)$ solution used.

Fig 2: Shows the variation of the optical absorbance spectra of the film with wavelength. Film prepared at pH=8.9 pH has low absorbance of (0.11- 0.115) at UV region of 350nm-400nm. At VIS-NIR-IR regions, it has (0.115-0.114). For films prepared at pH=9.3, pH=9.7,and pH=10 the absorbance decreases proportionally with wavelength increase from UV-VIS-NIR-IR regions respectively.

Fig 3: Shows the variations of the transmittance spectra of the film with wavelength. %transmittance for Films prepared at pH=9.3, pH=9.7 and pH=10.0, increases in all the regions between 70%-93% respectively. There was a slight curves in all the regions for the film prepared at pH=8.9 . This could be as a result of low thickness of the film.

Fig 4: Shows the variations of the reflectance spectra of the film with wavelength. Films prepared at pH=9.3,and pH=9.7 pH, has %reflectance decrease in all the regions of values between18%-6.7%, but film prepared at 10.0 pH has an increase in the UV region of (350nm – 400nm) which ranges from 13.4% - 21.0% . It then decreased from 21% to 4.1% at VIR-NIR-IR. Film prepared at 8.9 pH has slight curves constantly throughout the regions which ranges from 8%-5% .

Fig 5: Shows the plot of Refractive index against Photon energy of as grown films. The result shows that the films has high refractive index with its peak value at 1.5 -2.5. This makes it a suitable material for anti reflection coatings.

Fig 6: Shows the optical band gap (Eg) of the films estimated from $(\alpha hv)^2$ versus eV curve for prepared film at pH=8.9, pH=9.3, 9.7, and pH=10.0 pH, respectively. The straight nature of the plot indicates the existence of the photon energy axis at $(\alpha hv)^2 = 0$. It was found to be pH=8.9 = 2.7eV, pH=9.3 = 2.6eV, pH=9.7 = 2.7eV, and pH=10.0 = 2.65eV. This compares slightly with work of Anuar *et al.* (2011) who presented a bandgap of 2.11- 2.52eV. The wide bandgap possessed by NiSe film makes it likely candidate to replace GaN in light emitting laser diodes (Gutowski *et al*, 2002). It is also a good material for window layer coatings.

The surface morphology of sample was investigated using scanning electron microscopy (SEM). Figures7.0 and 8.0 shows the SEM micrograph of NiSe thin film deposited on the microscope glass slide at 100x magnification. The thin film is composed of largely irregular-shaped grains. This is due to several crystallites grouped together to form larger grains.

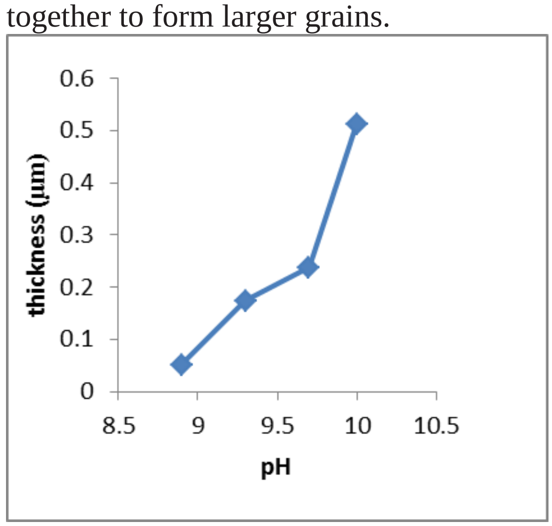

Fig 1.0 Variation of Thickness with pH of $NH_4(OH)$

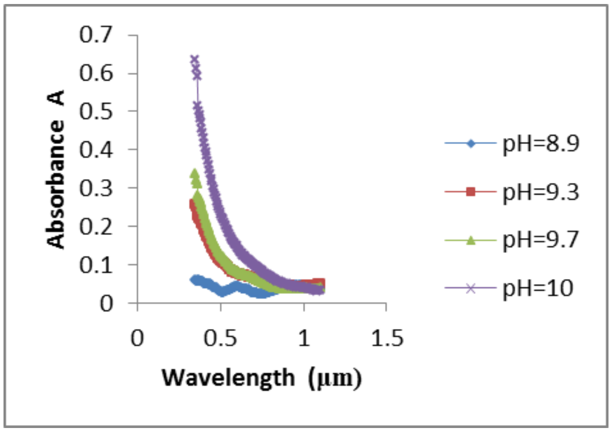

Fig. 2.0 Variations of Absorbance of NiSe with wavelength pH=8.9, pH=9.3, pH=9.7, pH=10.0 .

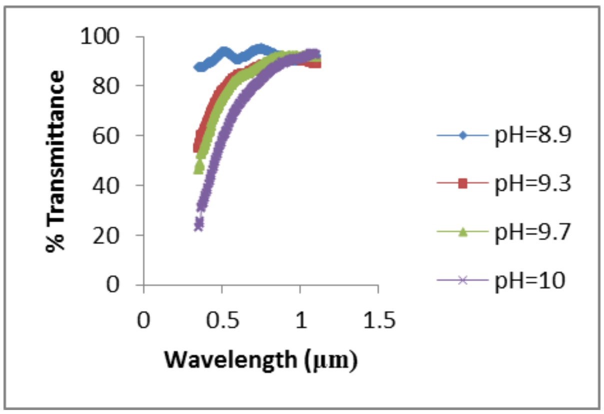

Fig 3.0 Variations of Transmittance of NiSe with wavelength for pH=8.9, pH=9.3, pH=9.7, pH=10.0 .

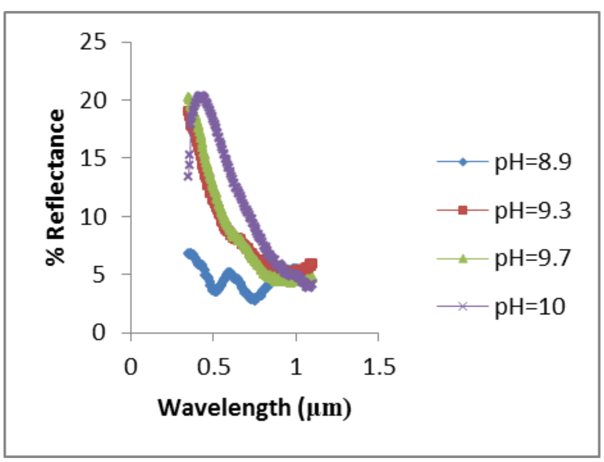

Fig 4.0 Variations of Reflectance of NiSe of as grown with wavelength for pH=8.9, pH=9.3, pH=9.7, pH=10.0.

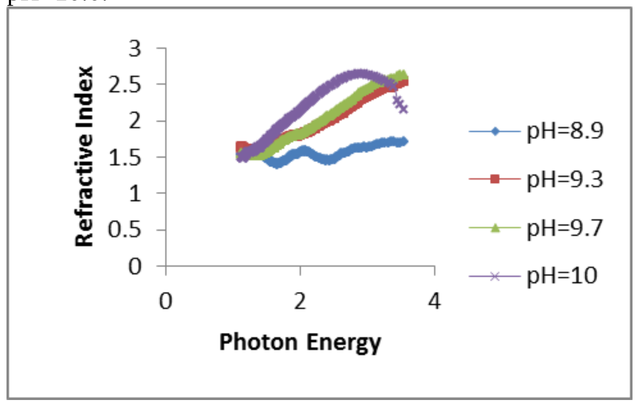

Fig 5.0 Variations of Refractive index of NiSe of as grown films against Photon Energy for pH=8.9, pH=9.3, pH=9.7, pH=10

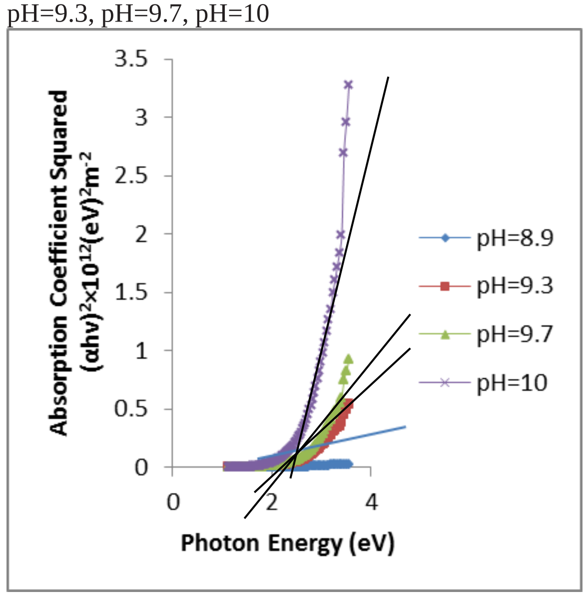

Fig 6.0 Plot of $(\alpha h\upsilon)^2$ versus photon energy of NiSe for pH=8.9, pH=9.3, pH=9.7, and pH=10

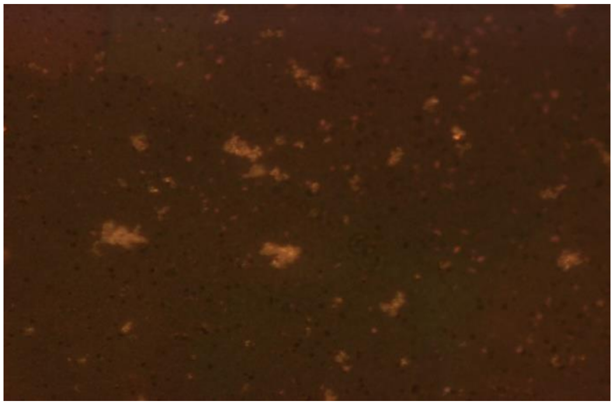

Fig 7.0 Micrograph of NiSe thin films for pH=9.3 slide at 100x

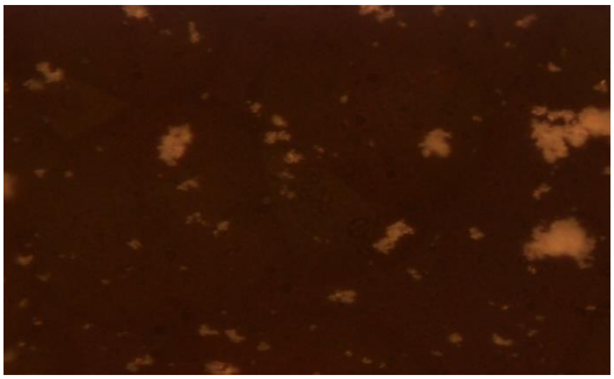

Fig 8.0 Micrograph of NiSe thin films for pH=9.7 slide at 100x

5.0 CONCLUSION

The completed deposition of Nickel Selenide (NiSe) thin film using cheap and simple solution growth technique, and characterization of the deposited films using the optical microscope and spectrophotometer to obtain the surface morphological and optical properties of the films.

The characterization of the films have revealed the following:

NiSe have band gaps (E_g) of 2.45eV – 2.7eV, thickness ranging from 0.05µm – 0.51µm.

Due to the high absorbance and low reflectance in the ultraviolet, visible and infrared regions, NiSe thin films are suitable for coatings on different types of solar collectors.

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