Electrical Properties of Semiconducting Nickel Sulphide Thin Films

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Abstract

Thin films of Nickel Sulphide (NiS and NiS_2) were grown on glass substrates at room temperature and 50°C for NiS, and 55°C for NiS_2 using Chemical Bath Deposition (CBD) technique. In NiS, the chemical bath contained nickel sulphate ($NiSO_4$), sodium thiosulphate ($Na_2S_2O_3.5H_2O$) and triethanolamine ($C_6H_{15}NO_3$) solutions. In NiS_2, nickel chloride hexahydrate ($NiCl_2.6H_2O$), sodium thiosulphate ($Na_2S_2O_3.5H_2O$) and ammonia (NH_3) solutions were mixed at 55°C in the chemical bath. The aim of the present study was to observe electrical properties of NiS and NiS_2 thin films using Four-Point Probe method. The NiS films showed not too much different in the resistivity and conductivity at room temperature and 50°C with increasing deposition time. The resistivity of NiS_2 films increased with increasing annealed temperatures except for an un-anealed one. The films also exhibited decreasing conductivity with increasing annealed temperatures except for an un-annealed one.

Introduction

Nickel sulphide (NiS) thin films belong to VIII-VI compound semiconductor materials. They have a number of applications in various devices such as solar cells, sensors, photoconductors and infrared detectors. A variety of methods, including electrodeposition, SILAR, pulsed laser ablation, metal-organic chemical vapour deposition, thermal and photochemical chemical vapour deposition can be used for the preparation of nickel sulphide thin films. Chemical bath deposition method is an attractive choice due to its simplicity, low cost, low temperature and potential for large-scale production. Up-to-date, chemical bath deposition method has been successfully used to deposit many different semiconductors thin films including CdS, Sb_2S_3 and CdSe, Cu_4SnS_4 and $Zn_xCd_{1-x}S$. So far, there is no report on deposition of NiS thin films from aqueous solution using triethanolamine as complexion agent at room temperature and 50°C by chemical bath deposition method.

Nickel sulphide (NiS_2) thin films also belong to group VIII- VI compound semiconductor materials and have diverse applications in the areas of optoelectronics and electro-optic devices. The deposition of chalcogenide thin films has been carried out by many researchers, using CBD techniques, sol-gel method, vacuum evaporation, radio frequency sputtering, cathodic electron deposition, etc. Following the successful deposition of the NiS_2 thin films, four samples were annealed at various temperatures. The resistivity and conductivity of NiS and NiS_2 thin films were measured by Four-Point Probe method. The use of thin films as resistors, contacts and interconnections in modern technology has also led to extensive study of their electrical properties.

Experiment

All the chemicals used for the deposition were analytical grade and all the solutions were prepared in deionized water. The nickel sulphide thin films (NiS) were prepared from

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aqueous solutions of nickel sulphate ($NiSO_4$) and sodium thiosulphate ($Na_2S_2O_3.5H_2O$) acted as a source of Ni^{2+} and S^{2-} ions, respectively. Triethanolamine (TEA) was used as a complexing agent during deposition. The glass substrates were used as the substrates for the chemical bath deposition of nickel sulphide thin films. Before deposition, the glass substrates were degreased with acetic acid and soap, and rinsed with water. Then, they were cleaned with acetone. Finally, they were washed with distilled water and dried in oven for 10 min.

Deposition of thin films was carried out at room temperature and 50 °C in the following manner. 25 ml of $NiSO_4$ (1.0 M) was taken in a 100 ml beaker and 16.7 ml of the concentrated TEA was mixed in it. Subsequently, 25 ml of $Na_2S_2O_3.5H_2O$ (1.0 M) and 10 ml of distilled water were added in it with constant stirring. The cleaned glass substrates were immersed vertically into beaker. The deposition was carried out at different deposition times (1, 2 and 3 hours) at room temperature and 50°C in order to determine the best conditions for the deposition of thin films. After the completion of deposition, the films were removed from the beaker and dried in air for 10 hours before analysis. The experimental conditions for NiS were tabulated in Table 1.

Table 1 Experimental setup for the deposition of NiS thin films on glass substrates

Sr No	Composition in NiS ($NiSO_4$:$Na_2S_2O_3.5H_2O$:$C_6H_{15}NO_3$) (ml)	Deposition Time (hr)	Deposition Temperature (°C)
1.	(25:25:16.7)	1	Room temperature
2.	(25:25:16.7)	2	Room temperature
3.	(25:25:16.7)	3	Room temperature
4.	(25:25:16.7)	1	50
5.	(25:25:16.7)	2	50
6.	(25:25:16.7)	3	50

The Nickel Sulphide thin films (NiS_2) were prepared from aqueous solution of nickel chloride ($NiCl_2.6H_2O$) and sodium thiosulphate ($Na_2S_2O_3.5H_2O$) as sources of Ni^{2+} and S^{2-} ions respectively. Ammonia (NH_3) solution was used as a complexing agent during the deposition. Cleaning methods for glass substrates were the same as that in NiS compound. The cleaned glass substrates were then inserted vertically in the reaction bath.

The composition of the 100 ml bath consists of 5ml of $NiCl_2.6H_2O$ (1.0 M) solution, 15 ml of $Na_2S_2O_3.5H_2O$ (1.0 M), 10 ml of NH_3 and 30 ml of distilled water. The mixture was stirred thoroughly with magnetic stirrer (IKA® C-MAG HS 7) at each stage and made up to 90 ml with distilled water. For optimization of the thin films, four different mixtures of $NiCl_2.6H_2O$: $Na_2S_2O_3.5H_2O$: NH_3 [(5:15:10) ml, (5:15:15) ml, (5:20:15) ml, (10:10:20) ml] were prepared in an oven at 55 °C and left undisturbed for six hours. The deposited thin film samples were then annealed in an oven heating at temperatures of 50°C, 100°C, 150°C and

200°C leaving one un-annealed sample. All the samples were further washed in distilled water and air-dried for analysis. The optimum conditions to be analyzed were shown in Table 2.

Table 2 Experimental setup for the deposition of NiS_2 thin films on glass substrates

Sr No	Composition in NiS_2 ($NiCl_2.6H_2O:Na_2S_2O_3.5H_2O:NH_3$) (ml)	Deposition Time (hr)	Deposition Temperature (°C)	Annealing Temperature (°C)
1.	(5:15:10)	6	55	-
2.	(5:15:10)	6	55	50
3.	(5:15:10)	6	55	100
4.	(5:15:10)	6	55	150
5.	(5:15:10)	6	55	200

Results and Discussion

The resistivity of NiS and NiS_2 thin films were measured by the Four-Point Probe method. Silver paste was applied to the polishing surfaces of the films to provide electrical contact. The resistivity ρ is given by

$$\rho = R_s \times t$$

where R_s is the sheet resistance and t is the film thickness. 1/ρ gives the electrical conductivity, σ. Table 3 and Table 4 show the electrical properties of NiS and NiS_2 thin films with their conditions. Figure 1 and Figure 2 display resistivity versus temperatue for NiS and NiS_2 thin films. Their corresponding conducitvity values are shown in Table 5, Table 6, figure 3 and figure 4. In NiS, the values of resistivity and conductivity at room temperature and 50°C with increasing deposition time were not too much different. In NiS_2 films, resistivity increased with increasing annealed temperatures except for an un-annealed one. Consequently, the films revealed decreasing conductivity with increasing annealed temperatures except for an un-annealed one. The schematic diagram of sheet resistance measurement was shown in figure 5.

Table 3 Electrical properties of NiS thin films

Temperature(°C) (deposition time, hour)	Film Thickness (μm)	Resistance R (x 10^8 Ω)	Sheet Resistance R_s (x 10^8 Ω)	Resistivity ρ (Ωm)
Room temperature (1)	0.215	9.16	0.84	18.1
Room temperature (2)	0.216	6.11	1.52	32.8
Room temperature (3)	0.223	7.73	1.19	26.5

Temperature(°C) (deposition time, hour)	Film Thickness (μm)	Resistance R (x 10^8 Ω)	Sheet Resistance R_s (x 10^8 Ω)	Resistivity ρ (Ωm)
50 (1)	0.213	5.35	0.62	13.2
50 (2)	0.250	3.67	0.98	24.5
50 (3)	0.255	6.57	0.76	19.4

Table 4 Electrical properties of NiS_2 thin films

Annealing Temperature (°C)	Film Thickness (μm)	Resistance R (x 10^8 Ω)	Sheet Resistance R_s (x 10^8 Ω)	Resistivity ρ (Ωm)
As grown	0.558	9.47	0.16	8.928
50	0.540	8.97	0.02	1.08
100	0.554	9.24	0.08	4.432
150	0.570	14.75	0.12	6.84
200	0.560	11.19	0.27	15.12

Table 5 Conductivity of NiS thin films

Temperature(°C) (deposition time, hour)	Conductivity σ(x 10^{-2} $\Omega^{-1}m^{-1}$)
Room temperature (1)	5.52
Room temperature (2)	3.05
Room temperature (3)	3.77
50 (1)	7.58
50 (2)	4.08
50 (3)	5.15

Table 6 Conductivity of NiS_2 thin films

Annealing Temperature (°C)	Conductivity σ(x 10^{-2} $\Omega^{-1}m^{-1}$)
As grown	11.2
50	92.59
100	22.56
150	14.62
200	6.61

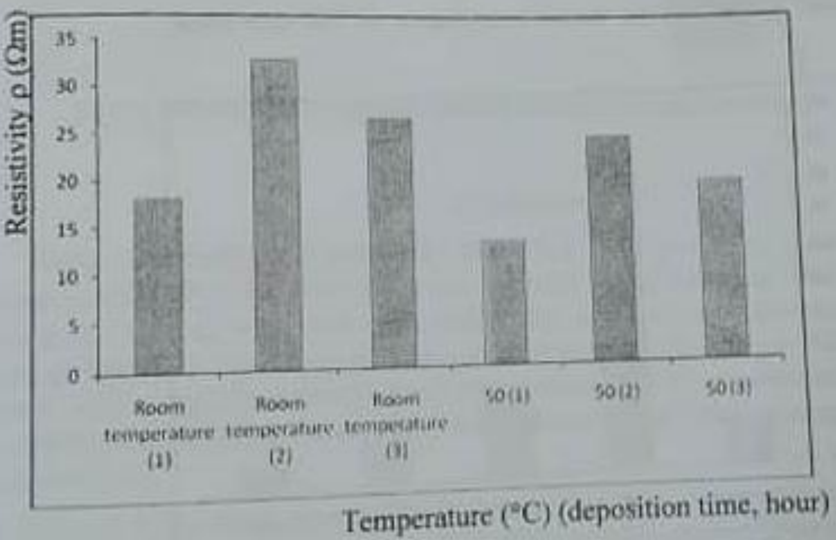

Figure 1 Resistivity versus temperature for NiS thin films

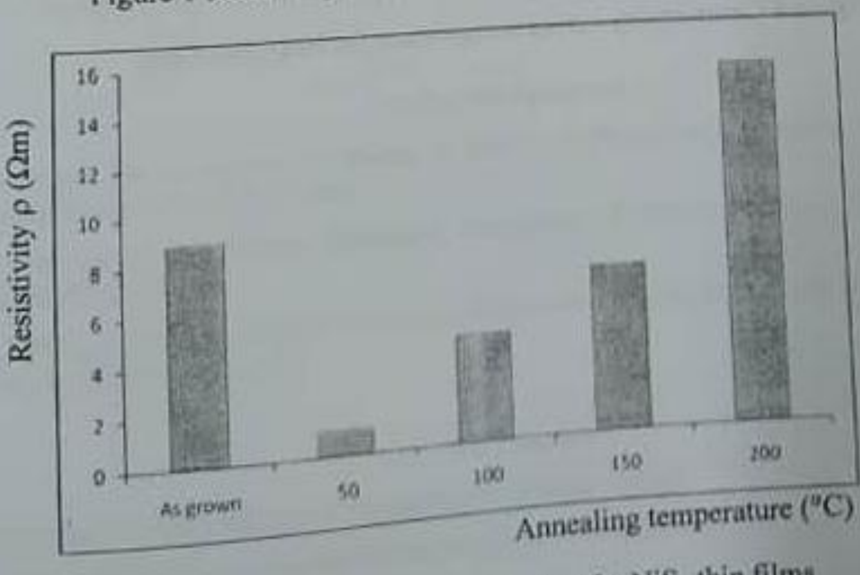

Figure 2 Resistivity versus temperature for NiS_2 thin films

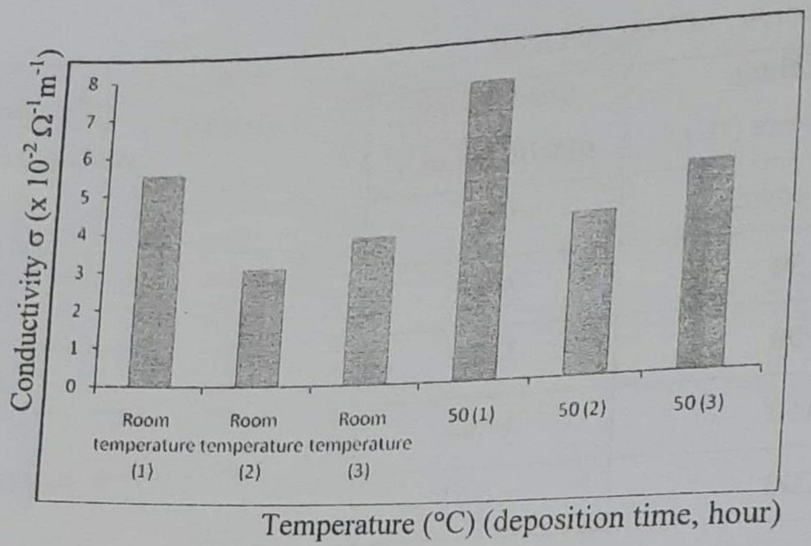

Figure 3 Conductivity versus temperature for NiS thin films

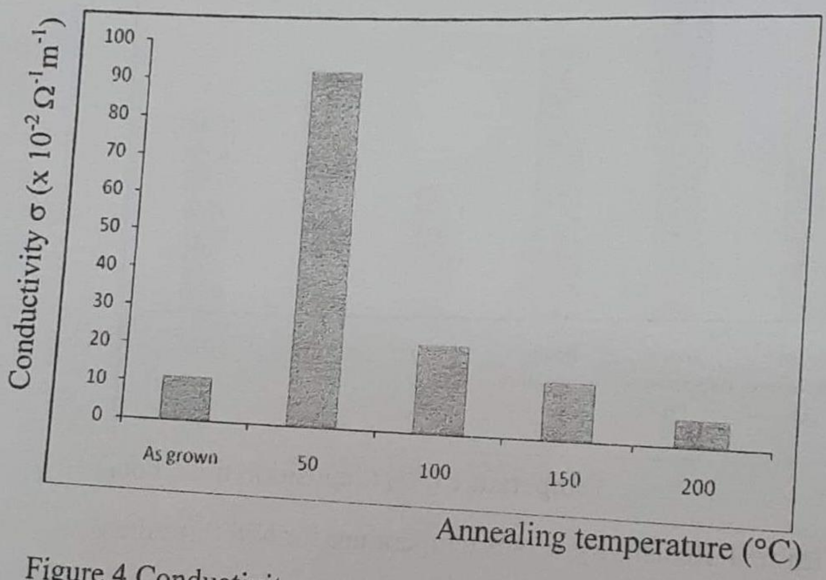

Figure 4 Conductivity versus temperature for NiS_2 thin films

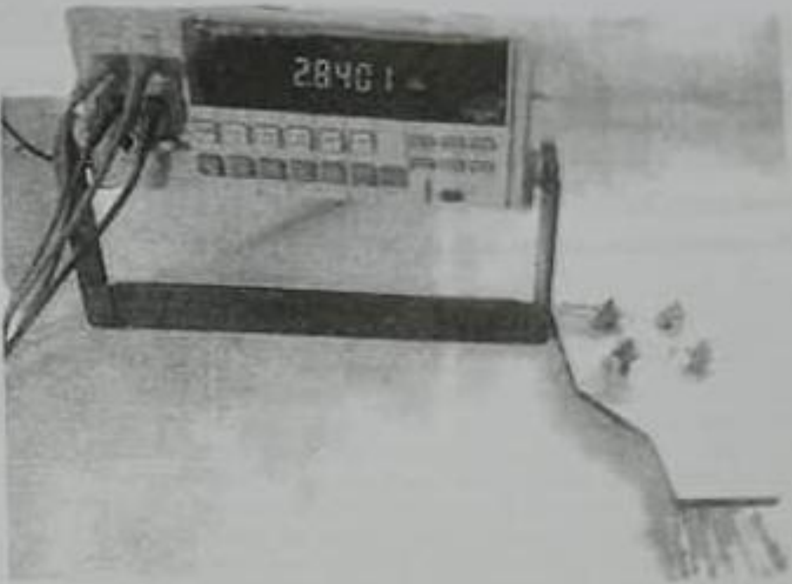

Figure 5 Schematic diagram of sheet resistance measurement

Conclusion

Nickel Sulphide (NiS and NiS_2) thin films were grown on glass substrates at room temperature and 50°C for NiS, and 55°C for NiS_2 using Chemical Bath Deposition (CBD) technique. In NiS, the resistivity and conductivity values at room temperature and 50°C with increasing deposition time were not too much different. In NiS_2 films, the values of resistivity increased with increasing annealed temperatures except for an un-annealed one. As a result, the films exhibited decreasing conductivity with increasing annealed temperatures except for an un-annealed one.

Both NiS and NiS_2 are p type semiconductors. If another n type semiconductor is obtained semiconductor solar cells can be made. Thin films are also applied in area of infrared detectors, window coatings, filters, photoconductors and others.

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