Structural Transformations in Chemical Bath Deposited Nickel Sulphide Thin Films.

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ABSTRACT

In this paper, we presented the results of X-ray diffraction and scanning electron microscopy of the nickel sulphide thin films prepared by using simple and cost effective chemical bath deposition method. The effects of deposition time and solution concentration toward the structural and morphological properties of the thin films were investigated. Based on the X-ray diffraction data, the films deposited for 30 min using 0.15 M of nickel sulphate and sodium thiosulfate indicated the formation of single phase of cubic structure of Ni_4S_3. However, both cubic and hexagonal phases were presented for the films prepared at longer period and higher concentration. These observations were supported by scanning electron microscopy results.

(Keywords: nickel sulphide, thin films, X-ray diffraction)

INTRODUCTION

Nickel sulphide thin films are very attractive materials for a wide variety of technological applications such as solar cells, light-emitting diodes, laser devices, and electroluminescent devices. Various methods are used for the preparation of nickel sulphide thin films such as successive ionic layer adsorption and reaction [Sartale and Lokhande, 2001], chemical bath deposition [Anuar et al., 2010a], metal-organic chemical vapor deposition [Nomura and Hayata, 2001], pulsed laser ablation [Lee et al., 1993], electro-deposition [Anuar et al., 2004], laser, and thermal vapor deposition [Cheon et al., 1997]. Among various other methods, the chemical bath deposition method is found to be a cheap and simple way to deposit metal chalcogenide thin films such as ZnS (Goudarzi et al., 2008), CuS (Anuar et al., 2010b), CdS (Moualkia et al., 2009), $CuBiS_2$ (Sonawane et al., 2004), and Cu_4SnS_4 (Anuar et al., 2010c).

In this work, for the first time, we report the deposition of nickel sulphide thin films using Na_2EDTA as a complexing agent by chemical bath deposition method. In order to get good quality of thin films, the deposition parameters such as solution concentration (0.15, 0.2 and 0.3 M) and deposition time (0.5, 1 and 2 h) are optimized. The thin films have been characterized by X-ray diffraction (XRD) for structure determination and scanning electron microscopy (SEM) for surface morphology study.

MATERIALS AND METHODS

All chemicals used for the deposition were analytical grade reagents and all the solutions were prepared in deionized water (Alpha-Q Millipore). The nickel sulphide thin films were prepared from an acidic bath using aqueous solutions of nickel sulphate and sodium thiosulfate which provided Ni^{2+} and S^{2-} ions, respectively. The ethylenediaminetetraacetic acid disodium salt (Na_2EDTA) was served as complexing agent to chelate with Ni^{2+} to obtain Ni-EDTA complex solution. The microscope glass slide was used as the substrate for the chemical bath deposition of nickel sulphide thin film. Before deposition, the microscope glass slide was degreased with ethanol for 15 min. Then, ultrasonically cleaned with distilled water for another 15 min and dried in desiccators. Deposition of nickel sulphide thin films was carried out using following procedure. 20 ml of

nickel sulphate was complexed with 20 ml of 0.15 M Na_2EDTA. Then, 20 mL of sodium thiosulfate was added slowly to the mixture. The cleaned glass slide was immersed vertically into beaker. In order to determine the optimum conditions for the deposition process, the films were deposited at different deposition periods (0.5, 1, and 2 h) and solution concentration (0.15, 0.2, and 0.3 M). The pH was adjusted to 1.5 by adding hydrochloric acid using pH meter. During deposition process, the beaker was kept undisturbed. After the completion of deposition, the glass slide was removed, washed several times with distilled water and dried naturally in desiccators for further characterization.

In order to investigate the crystallographic properties of the nickel sulphide thin films, we carried out the X-ray diffraction analysis using Philips PM 11730 diffractometer with CuK_α (λ=1.5418 Å) radiation. The surface morphology was observed by a scanning electron microscopy (JEOL, JSM-6400).

RESULTS AND DISCUSSION

Table 1 shows the X-ray diffraction (XRD) data for the films prepared at various deposition periods using 0.15 M of nickel sulphate and sodium thiosulfate. At shorter deposition time (30 min), three prominent peaks which correspond to (211), (220), and (311) planes, respectively are detected. All of the peaks are coincident well with the corresponding diffraction peaks of cubic phase (a=b=c=5.14 Å) of Ni_4S_3 compound [Kitakaze and Sugaki, 2001] (Joint Committee on Powder Diffraction Standard (JCPDS) reference code: 00-052-1027). Based on the XRD data, the number of Ni_4S_3 reduced to 1 while NiS peaks increased to 2, respectively, as the deposition time is increased to 1 h. However, at longer deposition period (2 h), all peaks are belonging to NiS structure, which is a clear indication of a structural phase transition. The significant peaks attributed to NiS appear at 2θ=33.4°, 34.9°, 45.7°, and 53.2° can be observed. The experimental *d*-spacing values are in good agreement with the standard JCPDS *d*-spacing values confirming that the material is hexagonal structure (a=b=3.4361 Å, c=5.29 Å) of NiS [Campbell and Heinz, 1993] [JCPDS reference code: 00-065-0830] as shown in Table 1.

Table 1: Comparison of the JCPDS *d*-spacing Data for Nickel Sulphide Thin Films to Experimentally Observed Values for the Samples Deposited at Various Deposition Periods Using 0.15 M of Solution Concentration

Deposition time (h)	2θ	*hkl*	d-spacing (Å) observed	JCPDS	Compound
0.5	43.1	211	2.09	2.10	Ni_4S_3
	50.2	220	1.82	1.82	Ni_4S_3
	59.5	311	1.55	1.55	Ni_4S_3
1	34.9	101	2.57	2.59	NiS
	45.6	102	1.98	1.98	NiS
	50.1	220	1.82	1.82	Ni_4S_3
2	33.4	002	2.67	2.65	NiS
	34.9	101	2.57	2.59	NiS
	45.7	102	1.96	1.98	NiS
	53.2	110	1.72	1.72	NiS

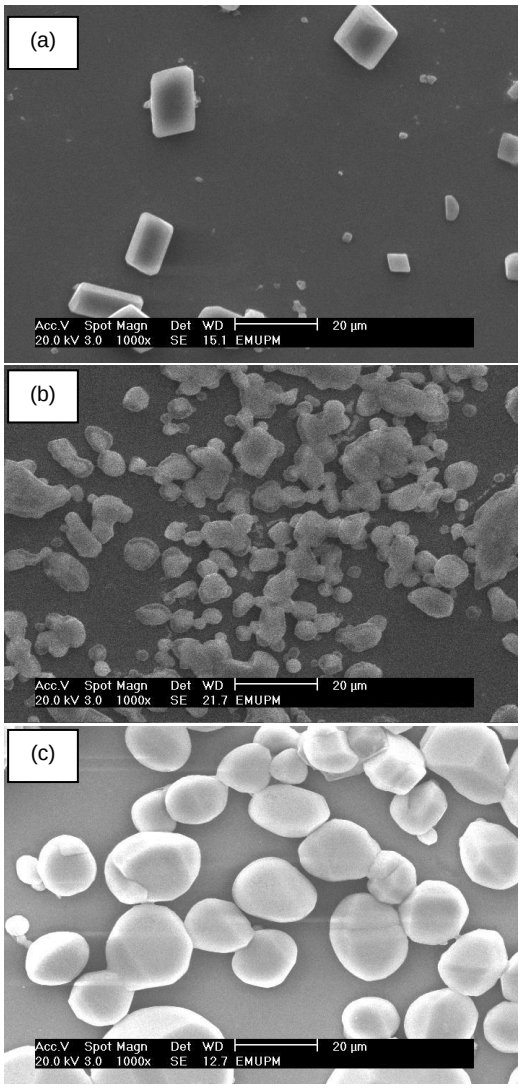

Figure 1: The Scanning Electron Microscopy Micrographs of Nickel Sulphide Thin Films Deposited at Various Deposition Periods Using 0.15 M of Solution Concentration. (a) 30 min (b) 1 h (c) 2 h.

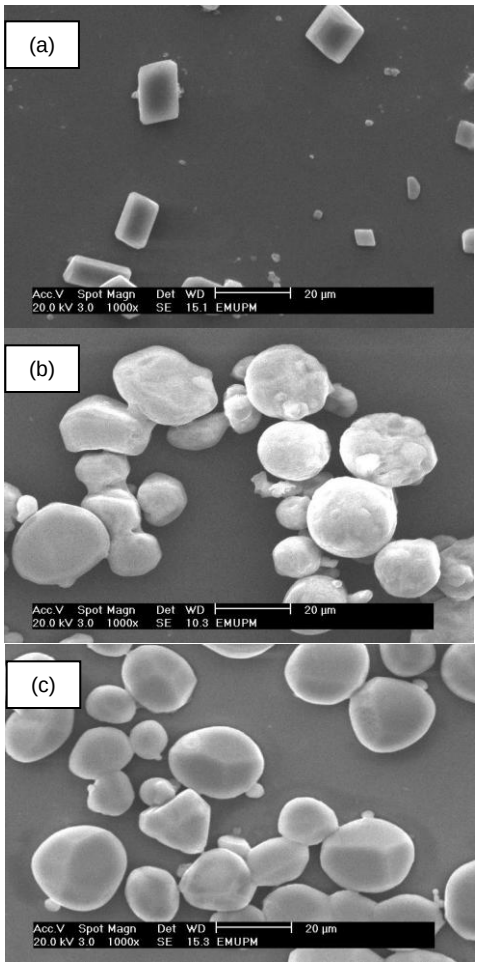

Figure 2: The Scanning Electron Microscopy Micrographs of Nickel Sulphide Thin Films Deposited for 30 min at Various Concentrations (a) 0.15 M (b) 0.2 M (c) 0.3 M

Table 2: Comparison of the JCPDS *d*-spacing Data for Nickel Sulphide Thin Films to Experimentally Observed Values for the Samples Deposited for 30 min at Various Concentrations

Concentration (M)	2θ	hkl	d-spacing (Å)		Compound
			observed	JCPDS	
0.15	43.1	211	2.09	2.10	Ni_4S_3
	50.2	220	1.82	1.82	Ni_4S_3
	59.5	311	1.55	1.55	Ni_4S_3
0.2	42.9	211	2.11	2.10	Ni_4S_3
	45.4	102	1.98	1.98	NiS
	53.1	110	1.72	1.72	NiS
0.3	34.9	101	2.57	2.59	NiS
	43.3	211	2.09	2.10	Ni_4S_3
	45.4	102	1.98	1.98	NiS
	53.2	110	1.72	1.72	NiS

The surface morphology of nickel sulphide thin films was determined by scanning electron microscopy (SEM). All the samples taken at 20 kV with a 1000 X magnification. The Figure 1a indicates that the grain shape is in cubic structure and has irregular in size. For the Figure 1b, the morphology is not in obvious cubic shape and some of it clustered together which show the incomplete growth while for Figure 1c, it shows that the grains are in irregular size and having the orthorhombic structure.

The XRD data of the films deposited under different concentrations of nickel sulphate and sodium thiosulfate for 30 min is shown in Table 2. The XRD data show the dominance of the cubic phase for the films deposited using 0.15 M of nickel sulphate and sodium thiosulfate. However, at higher concentration (0.2 M and 0.3 M), both cubic (Ni_4S_3) and hexagonal phases (NiS) are present. Comparison between thin films deposited at lower and higher concentration reveals that the number of Ni_4S_3 peaks increased in the films prepared using lower concentration.

Figure 2 shows the scanning electron microscopy (SEM) micrographs of nickel sulphide thin films deposited at different concentrations of nickel sulphate and sodium thiosulfate for 30 min. From Figure 2a, the SEM micrograph indicates that only cubic structure can be seen and this observation is supported by the data obtained from XRD. On the other hand, several different morphologies are obtained for the films deposited using higher concentration (0.2 M and 0.3 M). Except the presence of hexagonal shape deposits, there are also some cubic crystals and aggregates. These aggregates made up of many tiny crystals assembled into a sphere may be formed during the nucleation and crystal growth stage. The grains are distributed randomly over the surface of substrate. The sizes of the grains exhibit random orientation as these grains vary from one to another. From the SEM micrographs obtained, we can conclude that the surface morphology of the films is very much dependant on the solution concentration.

CONCLUSION

The nickel sulphide thin films could be chemically deposited by using nickel sulphate, sodium thiosulfate and Na_2EDTA solutions. Based on the X-ray diffraction data, the films deposited for 30 min using 0.15 M of nickel sulphate and sodium thiosulfate indicated the formation of single phase of cubic structure of Ni_4S_3. However, both cubic and hexagonal phases were presented for the films prepared at longer period and higher concentration. These observations were supported by scanning electron microscopy results. From the above results obtained, we concluded that the structure and surface morphology of the films were very much dependant on the deposition time and solution concentration.

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