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Preparation of Nickel Sulphide Nano Films

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ABSTRACT

In present work Ni-S films were prepared by electro deposition method. Sprayed SnO_2:F Films on glass to be used as electrodes. Characterization was done by 'XRD' analysis and TGA analysis. The observed 'd' values were compared with standard ASTM data. Good matching was observed in data and observed values. The bulk X-Ray diffractogram was used to calculate grain size. The thermo gravimetric studies of sample gave us the information regarding the thermal properties of a material. TGA & DTG data also supports to the formation of Nickel sulphide with Nickel having plus two (II) Oxidation state (Ni_7S_6).

Keywords: Electroplating, Electrodes, XRD, TGA, Ni-S, etc.

INTRODUCTION

The preparation method for obtaining the amorphous alloys by the plating techniques has some merits which are different from those of other techniques. For example rapid quenching, sputtering and evaporation. It is possible to prepare wide or bulky amorphous materials as well as covering a material with complicated shape by an amorphous material. There is no need of vacuum equipments or furnaces for electroplating. The composition and microstructure of the alloy can be varied by changing the composition of electrolyte. It has been reported that electrodeposited Ni-P, Ni-S glasses are most stable.

The mass production of electroplating by continuous operation is possible. It has been thought that the amorphous materials prepared by the electroplating technique have high probability as new technologically viable materials.

METHODOLOGY

Preparation of Sprayed SnO_2: F Films on Glass to be used as electrodes:

SnO_2:F Films were deposited on Corning 7059 glass substrates using spray pyrolysis technique. Details of the experimental setup are given in paper (25). The F/Sn atomic ratio in the solution was kept constant and methanol to water volume ratio was maintained to 9:1. All the films were grown at 450^0C (+ 5^0C) using a solution flow rate of 4 ml per minute. The films of about 15 - 20 $ohm^{-1}cm^{-1}$ conductivities were prepared by spraying 10 ml of solution which was prepared by taking 7 g of $SnCl_4$ $5H_2O$ (Stannic chloride) + 1.5g of Nh_4F (Ammonium fluoride) + 90 ml (Methanol) CH_3OH A.R. Grade +10ml H_2O. These Sno_2:F film deposited substrates were used as cathode in the present experiment.

Electrochemical Deposition of Ni-S films:

Ni-S films were prepared by electrode position method. Experimental setup is arranged properly for the deposition of Ni-S films. The electrolyte solution was prepared by mixing 20 g of Nickel Ammonium Sulfate, 2.00 g of Sodium Thiosulfate and 3.0 g of Sodium Citrate ($Na_3C_6H_5O_7$. $5H_2O$) as a buffer in a fixed volume of double distilled water (200ml). The above prepared solution was transferred to a five necked flask (electrolytic bath). The pH of the solution was maintained constant by using sodium citrate and was maintained between 6.2 to 6.5 by adding Ammonical water or dilute H_2SO_4 solution. From the central neck, the SnO_2:F film as a cathode was inserted. It was previously checked for proper contact with the help of a multimeter by checking the resistance of the SnO_2: F film. From the second neck of electrolytic bath the platinum electrode was inserted which was previously washed with distilled water. The distance between platinum anode and (SnO_2: F coated on glass) cathode was kept constant throughout the deposition. The cathode area was also

maintained constant for successive deposition. The third neck of electrolytic bath was utilized for bubbling nitrogen gas with the help of bubbler during deposition process to prevent oxidation of electrolyte by dissolved oxygen in electrolyte. The fourth neck was used for temperature measurements during deposition and was maintained constant throughout the deposition with help of heater and magnetic stirrer. A regulated D.C. Power Supply was used for deposition purpose, supplied by 'CONEL', whereas the micro ammeter was supplied by 'Simpson'. The Ni-S films were deposited for different time intervals between one hour to three hours. The cathodically electrodeposited films of Ni-S shows brownish (thin) or Black (thick) colour. The films are then analysed by using XRD analysis and TGA analysis.

RESULT AND DISCUSSION

The nickel sulphide is an attractive material from physical as well as application point of view. In the hexagonal form it exhibits a transition at 295^0K. The band gap of the order of 0.4 eV opens up at low temperature while the hexagonal lattice remains undistorted. The semiconductor to metal transition has been described by Mott-Hubbard Model. Nickel sulphide is however not a Mott insulator. The semiconductor to metal transition has been studied by various researchers and the query still remains unresolved. Small stoichiometric changes in nickel sulphide are expected to influence the semiconductor-metal transition. Electroplating can be conveniently used to obtain nonstoichiometric Ni-S films by simply varying the current density, molarity, composition and pH of electrolyte. We have prepared Ni-S films by cathodic reduction of metal ion containing suphide in electrolyte solution or they can also be deposited from aqueous solutions containing soluble metal and chalcogen compounds.

$$M^{++} + S^- \longrightarrow MS$$

The nickel sulphide coating in aqueous medium has been obtained first by "Sawada" et. al. However, they report crystalline film formation only after annealing at 100^0C. We were successful in obtaining crystalline Ni-S films on chemically inert SnO_2: F films with

slightly higher nickel content by electroplating method for various time intervals. Ni-S can be used as an anti-corrosive layer in catalysis and in photochemical solar energy conversion. The band gap of Ni-S is 0.4 eV; it absorbs all the photons in visible and U.V. range. Hence it can be used in photo thermal energy conversion.

The typical diffractogram for the thickest Ni-S sample was shown in above Figure 1. The diffractogram exhibits highly oriented crystallites, (0 2 2) peak which is dominant. While for all other planes epitaxial intensity is less than 30%. The grain size cannot be obtained correctly from glancing incidence X-ray diffractogram. We have used the glancing incidence X-ray diffractogram for determining crystal structure or phase of Ni-S. The bulk X-ray diffraction pattern was used to calculate the grain size Figure.

Interplanar spacing is obtained by using well known Bragg's relation. The observed 'd' values are compared with standard ASTM data (Card 22-1193). Good matching was observed in data and observed values. The standard deviation is given in Table 1, Card 22-1193 Ni_7S_6 Orthorhombic a_o = 9.180, b_o=11.283, c_o =9.457.

Nickel rich Ni_7S_6 phase was obtained. The bulk X-ray diffractogram for the sample deposited for highest time interval is shown in Figure 2. This was used to calculate the grain size. Although the complications due to diffraction pattern from the substrate SnO_2: F is unavailable. This method is useful in estimating grain size. Note that the X-ray diffraction is inferior to microscopic examination in the accurate measurement of grain size. Diffractogram can yield semi quantitative information about the grain size together with the information about crystal perfection and orientation.
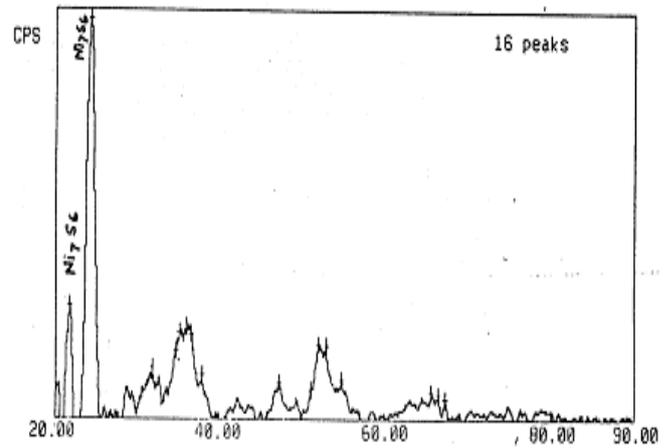

Fig 1: Typical diffractogram of the thickest Ni-S film

Table 1: X-ray diffractogram data

Obs. No.	d(Calculated)	D (Standard)	SD	(h k l)
01.	4.077	4.14	0.063	2 0 1
02.	3.672	3.93	0.258	1 1 2
03.	2.815	3.02	0.205	0 2 2
04.	2.379	2.33	0.049	2 4 1
05.	1.787	1.795	0.008	0 2 5
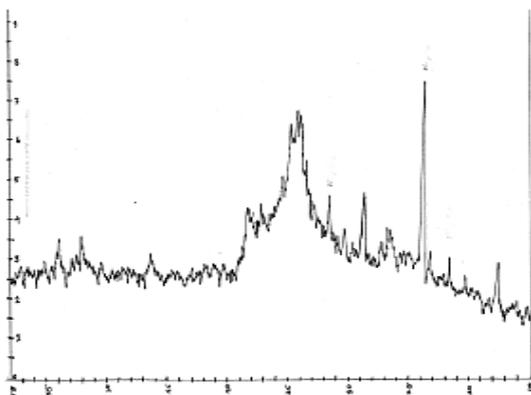
Fig 2: X-ray Diffractogram of Ni-S film
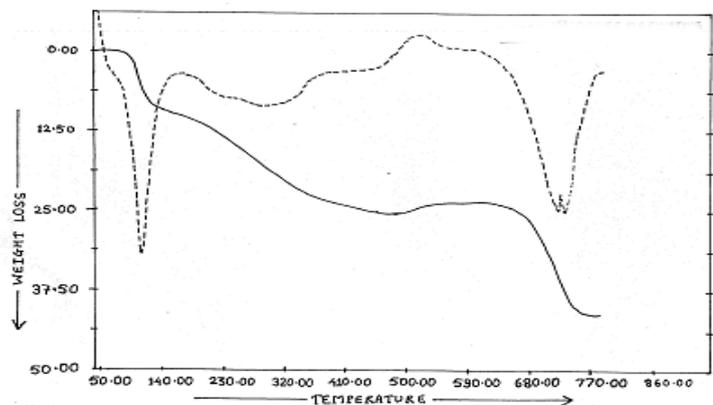
Fig 3: TGA for Typical Ni-S Film

The governing effect is due to the number of grains which take part in diffraction. This number in turn related to cross-Sectional area of the incident beam and its depth of penetration and also the sample thickness. When the grain size is coarse only few crystals diffract and diffraction consists of superimposed lines, one from each crystal due to white radiation present. For finer grains the pattern exhibits broad lines.

Additional broadening due to finite temperature is present. We estimated the grain size from the diffractogram as shown in Figure. A typical grain size was about 500^0A.

The TGA of Ni-S film is shown in Figure 3. The initial small loss of weight must be due to trapped solvent molecules in the film not maintained in vacuum. The loss of weight about 30 % corresponds to the loss of sulphide from the matrix. However, it extends over a large temperature range from $140^{o}C$ to $770^{o}C$ indicating that the sulphide matrix has strong bonding. This data also indicates that the film must be corresponding to the formation of nickel suphide with Ni having plus two oxidation state. However, the emphasis was laid on aqueous electrolyte; cathodic deposition of Ni-S films, X-ray diffraction, and this technique is used in solid state physics and Chemistry and is employed for phase and particle size determination.

Conflicts of interest: The authors stated that no conflicts of interest.

REFERENCES

1. Hasegawa R and Issue CC, *Phys. Rev*.B2 1632
2. Pampillo A, *J.Mater.Sci*.10,1194 (1975)
3. Berry BS, Gilman JJ & Leamy HJ, *Amm. Society for metals*, Leveland (1977)
4. Harris R, Plischte M, Zuckermann MJ, *Phys.Rev.Lett.* 31,160 (1973)
5. Chandhary P, Cuomo JJ, Gambino RJ. *IBM J. Res. Dev.* 17,66 (1973).
6. Rhyne JJ, Picort SJ, Alperine HA, *Phys.Rev.Lett.*,1972; 29,1568.
7. Paul DI. In proceedings of the 2nd international conference on amorphous magnetism, R.A. Lavy & R. Hasegawa, Edj. (Plenum, New York 1977) P.403.
8. Weaire D, Ashby MF, Logan J, Weans MJ. *Acta.Metall*, 1971; 19, 779(1971)
9. Dingle RB and Slater JE, *Corrosion*, 1976; 32, 155.
10. Hashimoto K and Masumoto J. *Mater, Sci. Epg*. 1976; 23,285.
11. Polk DE and Glessen BC. In Metallic Glasses Edg, J.J.Gilman and H.J. Leamy
12. Pond RB, Maringer RE, Mobley CE, In New trends in material Processing, American Society for Metals, New York (1979) P.128.
13. Goldstein AW, Rostoker W and Schossfergere F, *J. Electrochemical Soc*.1957; 104.
14. Sead Satal and Herbert Herman in Trestise on Material Science and Technology, Vol. 20 ed. Herbert Herman Academic Press, New York (1981)
15. Chaudhary P, GuomoJJ, Gambino RJ, Appl.Phys.Lett., 1973. 27, 337.
16. Surago K., Matsushita S, SakuraiY, IEEE Trans., Magn. MAG 12,776 (1976)
17. Minumura Y, Manura NI, Kobyasni T, Ibid P. 779
18. Hans-Werner Schroeder in Rapidly quenched metals, Vol.II, ed.S. Steeb.
19. Warlimont H, Elsevier Science, Publishers, B.V. (1985), P.1027
20. Narita A, Watnable J and Tanade Y. In rapidly Quenched Metals Vol. I ed. S. Steels, H.Warlimont, Elsevier Science Publishers, B.V. (1985) P. 133
21. Bestegen H. In Rapidly Quenched Metals, Vol. I ed. S. Steels, H. Warlimant Elsevier Science Publishers, B.V.(1985) P. 445.
22. Asami K, Kawashima A, SatoT, Hashimoto K, Lizawa KL and Plaito K . In Rapidly Quenched Metals, Vol. II ed.S. Steels, H. Warlimont, Elsevier Science Publishers, B.V.(1985) P. 1027.
23. Hashimoto K and Masumoto T. In Proc. Second International Conference on Repidly Quenched Metals Section II .