Effects of current density on structural and magnetic properties of electrodeposited Ni-Mn alloy thin films from chloride bath

M. RAJESWARI[*], S. GANESAN[a], T. M. SELVAKUMARI[b]
[*,a] *Department of Physics, Government College of Technology, Coimbatore-641 013, Tamilnadu, India*
[b]*Department of Physics, Angel college of Engineering, Tripur-641665, Tamilnadu, India*

Nano structured Ni-Mn alloy thin films were electrodeposited on a copper substrate. The structural and surface properties of Ni-Mn thin film were studied by using X-ray Diffractometer (XRD) and Scanning Electron Microscopy (SEM). Elemental compositions of the film were measured by means of Energy Dispersive X-ray Spectroscopy (EDAX). Magnetic properties of the thin film were studied with the aid of Vibrating Sample Magnetometer (VSM). Hardness and roughness of the films were measured by using Vickers Hardness Number (VHN) and surface roughness tester respectively. Micro hardness testing was carried out to determine the relation between this mechanical property with crystallite size. The deposits of Ni-Mn thin films were found to be shiny, smooth, nanocrystalline and good adherence to the substrate. The deposits were found to have face centered cubic (FCC) structure.

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1. Introduction

The electrodeposition of semiconductors, metals and alloys has established an extensive utilize in the fabrication of micro electro mechanical system (MEMS) for the past decades. Ni and its high strength alloys employ more useful materials for MEMS application due to their vast usage in the form of mechanical and magnetical elements such as motors, precision gears, latches, flexure spring arms, high density recording media, a magnetic shield, high performance transformer cores and magnetic actuators [1]. Electrodeposition is simple, rapid and inexpensive method for preparing nano structured metal and alloy as thin films [2]. Electrodeposited Ni-Mn thin film posses high strength, good ductility and low stress used in microsystems and in probe spring applications [3, 4]. The parameters used to control the process of deposition are pH, current density, bath temperature and complexing agent, etc [5-8]. In most of the investigations, Ni-Mn alloys were electrodeposited from sulfate and sulfamate baths and very few from chloride bath. Fathi *et al* reported that the percentage of Mn content presents in the film increases with increasing current density. Moreover the effectiveness of cathode has enhanced by chloride ions and films were deposited even at low voltages due to the high conductivity of chloride bath [9, 10]. The Ni-Mn alloy is an intellectual combination to investigate further in their abundant inimitable properties viz, the contradictory type of magnetic alignment in their fundamental state is one among them. The ferromagnetic nickel and paramagnetic manganese come together to produce Ni-Mn alloys with attractive magnetic properties [11]. Babanov *et al* reported that $Ni_{75}Mn_{25}$ shows paramagnetic behavior at room temperature and $Ni_{80}Mn_{20}$ shows ferromagnetic behavior [12]. By keeping this context in mind, in the current investigation Ni-Mn alloy thin films were electrodeposited from chloride bath by means of glycine used as an additive. Additional properties like the effects of current density on the elemental composition, structure and magnetic properties were examined. The present effort was carried out to study the effects of bath parameter such as current density of deposition on the structural, mechanical and magnetic properties of the Ni-Mn thin film.

2. Experimental part

2. 1. Electrodeposition of Ni-Mn thin films

The Ni-Mn alloy thin films were electrodeposited on a copper substrate from acidic chloride-glycine bath. A copper substrate of size 2.0×6.0 cm (breadth and length) as the cathode and pure nickel of the same size as an anode were used for the electrodeposition of Ni-Mn thin film. A regulated direct current unit was used to pass the current for deposition. An adhesive tape was used to cover up the entire area of the substrate but free from the area on which the deposition was required. Prior to the deposition, Cu substrates were buffed to eradicate scratches in a mechanical polishing wheel which contains buffing cloth covered with aluminium oxide abrasive. Subsequently they were degreased with acetone, followed by ultrasonic cleaning with deionised water. Electrodepositon was carried out on the cleaned substrates at different current density. All the chemicals used in the experiment were of analytical grade. The chemical composition and operating conditions of the electroplating bath are as shown in Table 1. Solution pH was adjusted to 4.5 by adding few drops of ammonia solution. The films were galvanostatically deposited on a copper substrate by applying current density in the range of 3 to 7 mAcm^{-2}.

Table 1. Chemical composition and operating conditions for electroplating Ni-Mn.

S.No	Chemical Composition	Weight gl^{-1}	Time (hr)	pH
1	$NiCl_2 . 6H_2O$	25		
2	$MnCl_2 . 4H_2O$	25	1	4.5
3	NH_2CH_2COOH	20		
4	NH_4Cl	10		

2. 2. Characterization of Ni-Mn alloy thin films

The chemical composition of the films was measured by using the EDAX analyzer (JEOL model 6390LV). The surface morphology of the thin films was measured by using Scanning Electron Microscope (JEOL 6390). Various phases present in the film were studied by using a computer controlled X-ray Diffractometer (Bruker AXS D8) employing Cu K$_\alpha$ radiation. The crystalline size of the Ni-Mn thin films were calculated from XRD data by using the Scherrer's formula as follows,

$$D = \frac{0.94\lambda}{\beta \cos\theta}$$

Where λ, β and θ denotes viz., the wavelength of the radiation (1.5406 Å), the full width at half maximum and the Bragg's angle respectively.

Internal stress present in the film was calculated by using the relation as follows,

Young's modulus = Stress / Strain

Dislocation density (δ) was calculated from the following relation,

$$\delta = \frac{1}{D^2}$$

The magnetic studies were carried out for the thin films deposited at various current densities by Vibrating Sample Magnetometer (Lake Shore 7404).

Hardness and roughness of the films were measured by using Micro Vickers Hardness (Mitutoyo HM-113) and surface roughness tester (Mitutoyo SJ-400) respectively.

3. Results and discussion

3. 1. Elemental Composition of the deposits

The presence of elemental composition (Ni and Mn) of an each electro deposited Ni-Mn thin film was confirmed by the EDAX analysis and the EDAX pattern of the sample prepared at 7 mA cm^{-2} is shown in Fig. 1. Initially the nickel content of the thin film increases progressively with the current density from 3 mA cm^{-2} to 5 mA cm^{-2} and then decreases when it reaches 7 mA cm^{-2} on the other hand manganese content decreases initially from 1.56 to 1.38 Wt% and increases to 4.67 Wt% subsequently as shown in Table 2. It may be due to the incorporation of additive.

Table 2. Effect of current density on chemical composition.

S.No.	Current density mA cm^{-2}	Ni Wt%	Mn Wt%
1	3	98.44	1.56
2	5	98.62	1.38
3	7	95.33	4.67

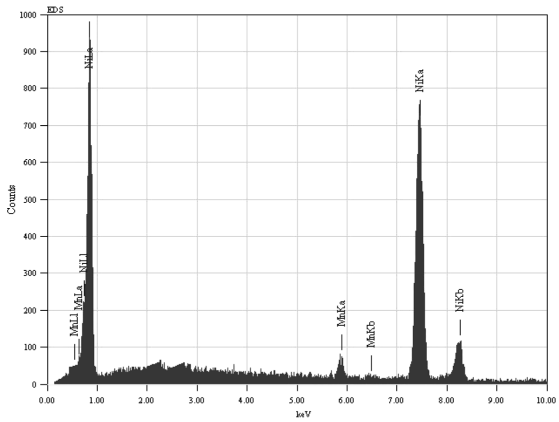

Fig. 1. EDAX spectrum of electrodeposited Ni-Mn thin film at 7 mA cm^{-2}.

3. 2. Structure and morphology of the deposits

3. 2. 1. X - Ray diffraction study of the deposits

The X-Ray Diffraction pattern of electrodeposited Ni-Mn films from the chloride - glycine bath as shown in Fig. 2, enclose spiky peaks that point out films were crystalline in nature. The XRD pattern of the Ni-Mn thin films were compared with standard pattern which matches with the reference pattern [2, 14], but the slight shift in peaks was obtained and it may be due to the stress in the film [16]. The peak centered at 45.069° is related to MnO_2 (JCPDS card no. 44-0992) and peaks at 2θ = 52.508° and 74.394° are due to electrodeposited $NiMn_2O_4$ (JCPDS card no. 71-0852). Also, it seems that deposits have face centered cubic structure (FCC). The peak corresponding to (111) reflection is considered as the predominant peak. The predominant peak intensity steadily decreases with the gradual increase of current density. This factor (current density) contributed to the formation of amorphous thin films. Similarly the other parameters like stress, strain and dislocation density increases with the increment of current density whereas the grain size of the film decreases with the increase in current density and are shown in Table 3. The variation of current density (3, 5 and 7 mA cm^{-2}) on the structural parameters of an individual film is shown in Fig. 3.

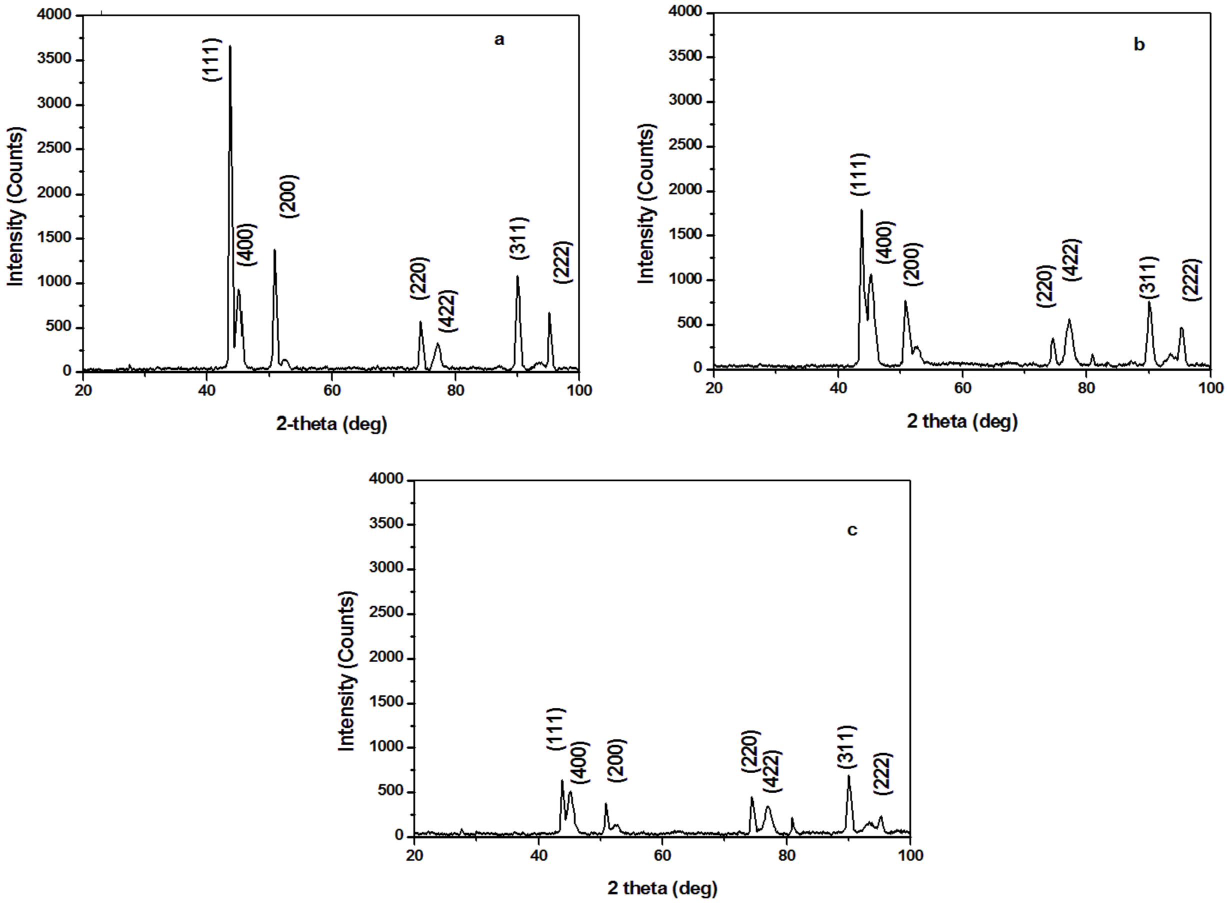

Fig. 2. XRD patterns of Ni-Mn thin film at various current densities 3 mA cm^{-2} (a), 5 mA cm^{-2} (b) and 7 mA cm^{-2} (c).

Table 3. Effects of current density on Grain size, Stress and Dislocation density.

S.No.	Current density mA cm^{-2}	FWHM deg	Peak intensity L Counts	Grain size D nm	Strain 10^{-3}	Stress MPa	Dislocation density δ Pm^{-2}
1	3	0.3020	3662	29.62	1.222	232.223	1.139
2	5	0.3677	1788	24.33	1.488	282.743	1.689
3	7	0.3780	639	23.62	1.533	291.259	1.793

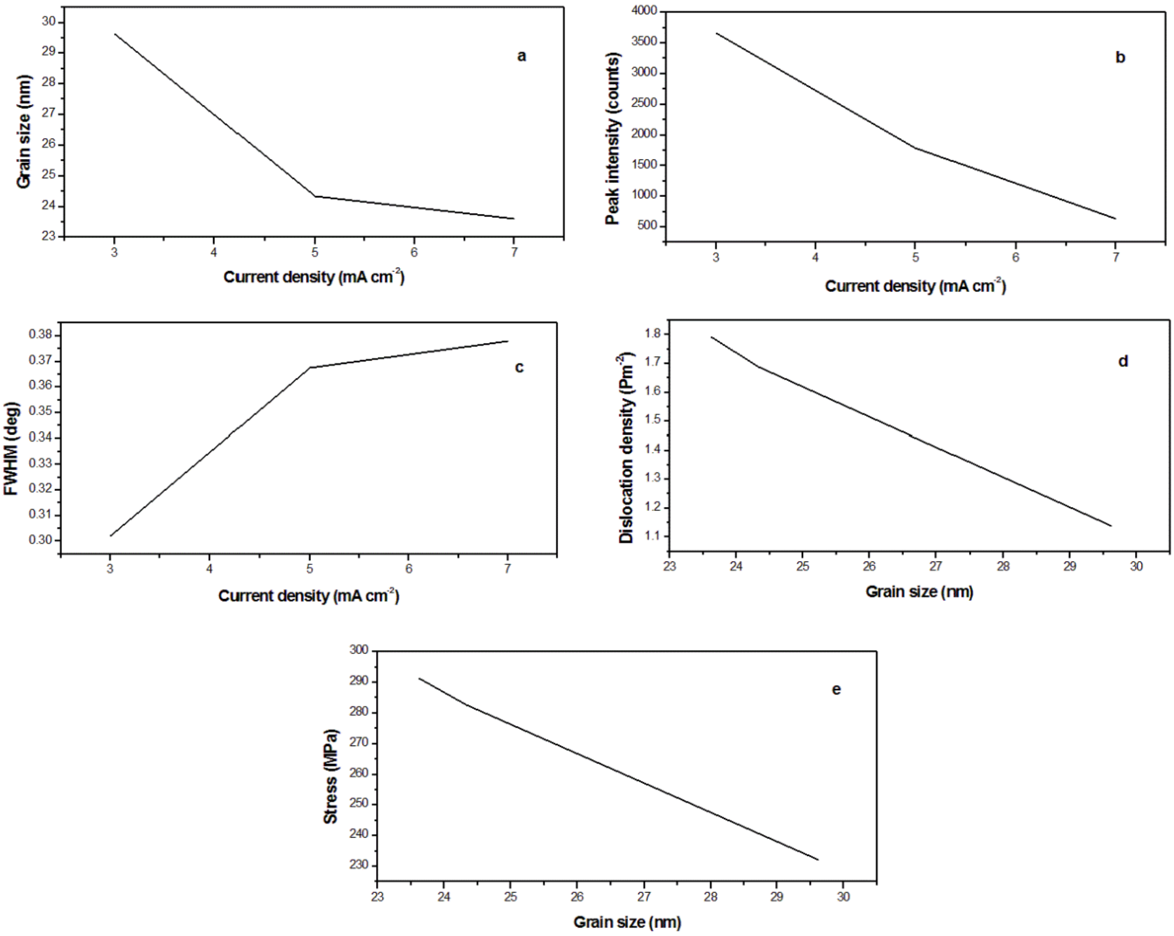

Fig. 3. Effects of current density on grain size (a), peak intensity (b) and FWHM (c);Effects of grain size on dislocation density (d) and stress (e).

3. 2. 2. Surface morphology of the deposits

Scanning electron micrographs of electrodeposited Ni-Mn thin films are shown in Fig. 4. The Ni-Mn films are obtained with micro cracks due to the internal stress. At a low current density, the surface is bright and smooth. At the current density of 5 mAcm^2, the surface is granular and bright. At a higher current density of 7 mAcm^{-2} the surface is bright and rough.

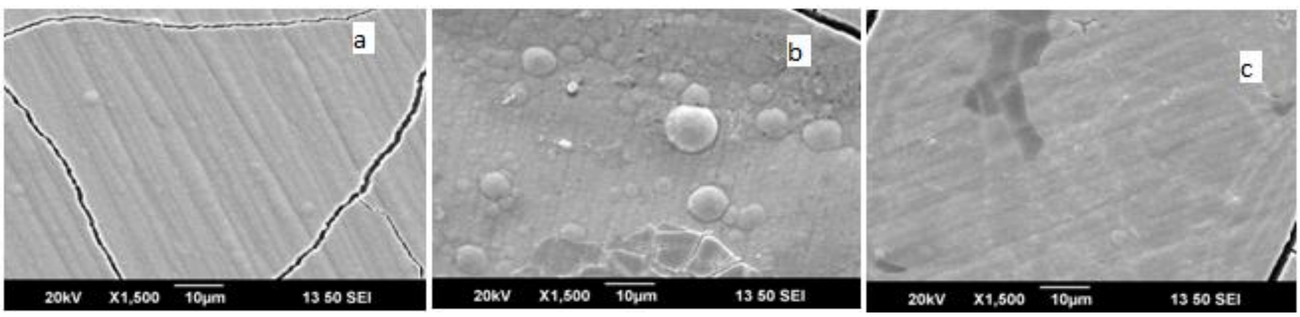

Fig. 4. SEM images of electrodeposited Ni-Mn thin films at different current densities 3 mAcm^{-2} (a), 5 mAcm^{-2} (b) and 7 mAcm^{-2} (c).

3. 3. Roughness and Hardness of the deposits

Table 4 shows the effects of current density on the hardness and roughness of the samples. Hardness of the sample was measured by using Vickers Hardness Number. Roughness of samples prepared by electrodeposition technique at various current densities were measured by using a surface roughness tester. The roughness of the samples were low at the current density of 3 mA cm^{-2}, and it increases with the current density. Hardness and roughness of the thin films were found to be increased due to the reduction of grain size [3].

Table 4. Effects of current density on hardness and surface roughness.

S.No.	Current density $mAcm^{-2}$	Grain size nm	Hardness VHN	Surface roughness R_a μm
1	3	29.62	267	0.04
2	5	24.33	310	0.05
3	7	23.62	366	0.07

3. 4. Magnetic properties of the deposits

Fig. 5 shows a hysteresis loop of Ni-Mn alloy thin film deposited at 7 $mAcm^{-2}$. The magnetic properties of Ni-Mn films were observed from vibrating sample magnetometer and are tabulated as shown in Table 5. Current density has great impact on magnetic properties of electrodeposited Ni-Mn alloy thin films. Magnetization, retentivity and squareness were found to decrease due to the increment of current density. Coercivity reduction depends on the magnetic domains of the material. Quite a few single magnetic domains are easier to rotate when subjected to magnetic field instead a larger domain.

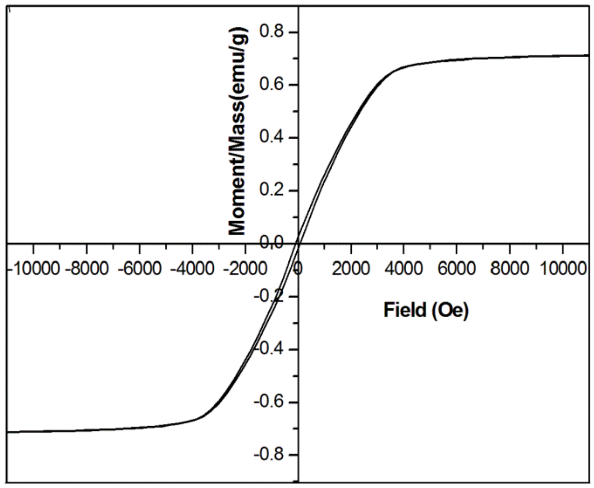

Fig. 5. Magnetic Hysteresis loop of the electrodeposited Ni-Mn film at 7 $mAcm^{-2}$.

Therefore, smaller grain size implies in more magnetic domains which are easy to rotate and in addition it reduces coercivity and makes the material magnetically soft. The random organization of an amorphous system favors the increase of magnetic domains and reduces as well [15]. The addition of glycine into the bath increases the retentivity value of 25.685 emu g^{-1} and it can be obtained even at a low current density of 3 mA cm^{-2}.

Table 5. Effects of current density on the magnetic properties of the Ni-Mn thin film.

S.No.	Current density mA cm^{-2}	Grain size nm	Coercivity Hc Oe	Magnetization Ms emu g^{-1}	Retentivity Mr 10^{-3} emu g^{-1}	Squareness S
1	3	29.62	115.321	0.78261	25.685	0.032819
2	5	24.33	99.291	0.74925	23.198	0.030962
3	7	23.62	82.073	0.71359	22.701	0.031812

4. Conclusion

In the present revision, Ni-Mn films were electroedeposited from the chloride-glycine bath. The effects of current density on the structural, compositional, morphological and magnetic properties of Ni-Mn thin films were revised. The results of the present study include viz., the electrodeposited Ni-Mn thin film has face centered cubic structure. The grain size of the films was found to be in nano size and it decreased with the increase of current density. The deposits were uniform and granular at 5 $mAcm^{-2}$ which encompass cracks due to the stress. Meanwhile Coercivity decreased with the increment of current density which makes the film magnetically soft. Due to the increment of current density, the films became mechanically hard and rough. Thus the present study concludes that the soft magnetic property of the material could well be improved by increasing current density which used well in the MEMS (Micro Electro Mechanical Systems) application.

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*Corresponding author: id- rajisdh@gmail.com