Characterization of electrodeposited nanocrystalline Ni-Mn thin films for MEMS applications

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Nanocrystalline (crystallite size 18.319 nm to 22.512 nm) Ni-Mn alloy coatings were produced from chloride – citrate bath at different temperature on copper substrate. The effects of temperature on the structure, surface morphology, elemental composition, magnetic properties and mechanical properties of electrodeposited Ni-Mn thin films were studied. The structural and surface properties of Ni-Mn thin films were studied by using X-ray Diffractometer (XRD) and Scanning Electron Microscopy (SEM). Elemental compositions of the films were measured by means of Energy Dispersive X-ray Spectroscopy (EDAX). Magnetic properties of the thin films were studied with the aid of Vibrating Sample Magnetometer (VSM). The deposited Ni-Mn films were found to be crystalline in nature due to the increment of temperature. The deposits of Ni-Mn thin films were found to be shiny, smooth and good adherence to the substrate. The deposits were found to have face centered cubic (FCC) structure. Due to the increment of grain size, coercivity of the films were found to increase.

(Received June 6, 2013; accepted May 15, 2014)

Keywords: Ni-Mn, Thin films, Electrodepsition, Magnetic properties

1. Introduction

Electrodeposition is an easy, speedy and economical technique for preparing nano structured thin films. The electrodeposition of metals, alloys and semiconductors has found widespread use in the manufacture of micro electro mechanical system (MEMS). Nickel based alloys employ more practical materials for MEMS application due to their immeasurable usage in the form of mechanical and magnetical elements such as motors, flexure spring arms, precision gears, latches, magnetic shield, high performance transformer cores, high density recording media and magnetic actuators [1]. Ni-Mn thin films possess superior ductility, high strength and little stress used in Microsystems and in probe spring applications [2, 3]. The ferromagnetic and paramagnetic materials (Ni and Mn) come together to fabricate Ni-Mn alloys with astonishing magnetic properties. $Ni_{75}Mn_{25}$ shows paramagnetic behavior and $Ni_{80}Mn_{20}$ shows ferromagnetic behavior at room temperature [4]. Current density, pH, bath temperature and complexing agent, etc., are the parameters used to organize the process of deposition. In the leading part of the investigations, Ni-Mn alloys were deposited from sulfate and sulfamate baths and only a few from chloride bath. The efficiency of cathode has improved by chloride ions and films were deposited even at low voltages due to the high conductivity of chloride bath [5, 6].

To our knowledge, no literature discussed the effect of temperature in the NiMn thin films. The present work reports the synthesis and characterization of nanostructured Ni-Mn thin films at various temperatures. The effects of temperature on the elemental composition, structure and magnetic properties were examined.

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 bath with citrate as an additive by galvanostatic method. A copper substrate of size 2.0X6.0 cm 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 hide the entire area of the substrate except the area on which the deposition was required. Former to the deposition, Cu substrates were buffed to remove 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 temperature. All the chemicals used in the experiment were of analytical grade. 25 gl^{-1} of $NiCl_2$. $6H_2O$, 25 gl^{-1} of $MnCl_2$. $4H_2O$, 10 gl^{-1} of NH_4Cl were used to prepare the bath and 20 gl^{-1} Tri sodium citrate was used as a complexing agent. Solution pH was adjusted to 4 by means of adding few drops of diluted ammonia solution. The films were galvanostatically deposited on a copper substrate by applying constant 5 mA cm^{-2} current density at three different temperatures 30°C, 50°C and 70°C.

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

The chemical composition of the films was measured by using the EDAX analyzer (JEOL 6390). 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 Bruker AXS D8 Advance X-ray Diffractometer employing CuK$_\alpha$ radiation. The crystalline size of the Ni-Mn thin films were calculated from XRD data by using the Scherrer's formula $D = 0.94\ \lambda / \beta \cos\theta$, where λ, β and θ indicates viz., the wavelength of the radiation (1.5406 Å), the full width at half maximum and the Bragg's angle respectively. The magnetic studies were carried out for the thin films deposited at various temperatures by Lakeshore 7404 Vibrating Sample Magnetometer. Hardness of the films was measured by using the Mitutoyo HM 113 Vickers Microhardness Tester.

3. Results and discussion

3. 1. Elemental composition of the deposits

The elemental composition (Ni and Mn) of each electrodeposited Ni-Mn thin film was confirmed by the EDAX analysis and it is shown in Fig. 1. The atomic percent of manganese content present in the films were 4.9, 2.29 and 0.47 and the nickel content present in the films were 95.1, 97.7 and 99.56 for 30°C, 50°C and 70°C respectively were observed. The atomic percent of Mn content present in the film decreases with an increment of temperature and it was almost equal to zero at 70°C. The coercivity of the thin film increases as a result of the paramagnetic manganese content present in the film decreases.

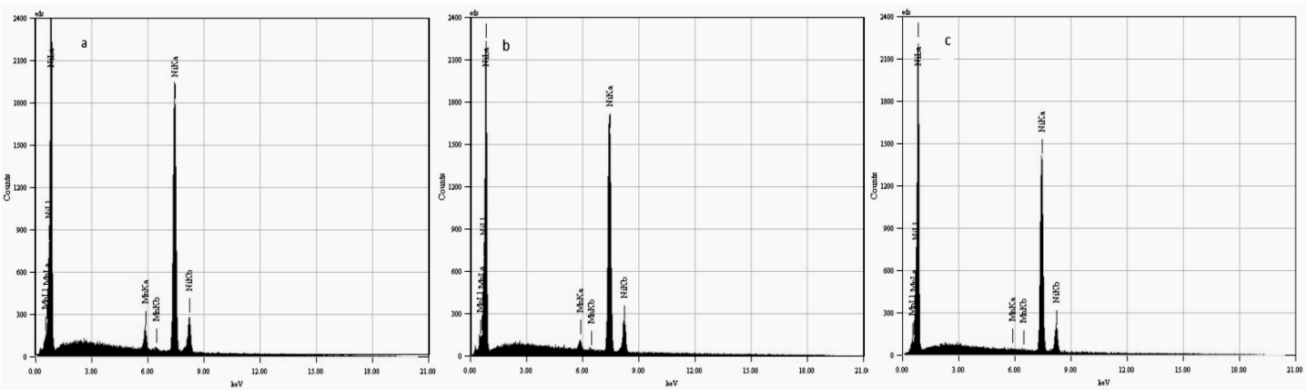

Fig. 1. EDAX spectrum of Ni-Mn thin film at various temperature (a) 30°C, (b) 50°C and c) 70°C.

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 chloride-citrate bath at three different temperatures of 30°C, 50°C and 70°C as shown in Fig. 2, enclose sharp peaks that point out films were crystalline in nature. The XRD pattern of the Ni-Mn thin films were matched well with the standard pattern [7, 8], the predominant peak centered at 45.291° with (111) reflection is related to Ni (JCPDS card no. 88-2326) and the intensity of the peak at this point increases with the increment of temperature as 356, 1445 and 4899 counts which is confirmed by EDAX result where Ni content increases with respect to temperature. Also, it seems that deposits have face centered cubic structure (FCC). The effect of temperature on the structural properties of NiMn thin film deposited at different temperatures is given in Table 1. This temperature was contributed to the formation of highly crystalline thin films and it affects structural parameter like grain size, stress, strain and dislocation density. The grain size was found to be increased while the other parameters like stress, strain and dislocation density decreases with the increment of temperature and it is shown in Fig. 3.

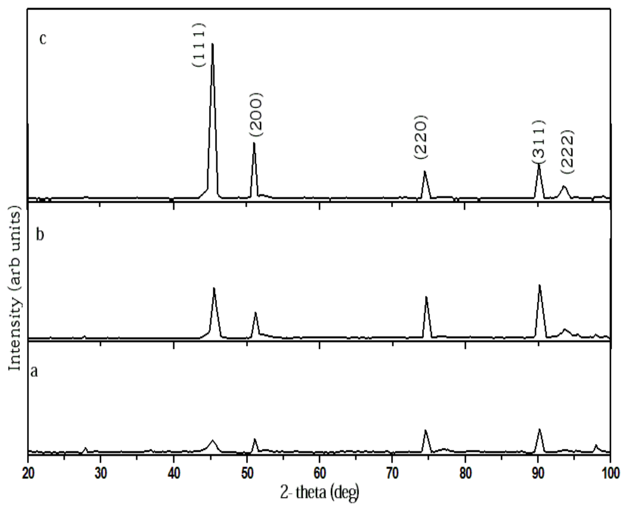

Fig. 2. XRD patterns of Ni-Mn thin film at various temperatures (a) 30°C, (b) 50°C and c) 70°C.

Table 1. Effects of Temperature on the structural properties of the Ni-Mn thin film at (a) 30°C, (b) 50°C and c) 70°C.

S. No.	Current Density mA/cm^2	Time hour	Temperature °C	Grain size nm	Stress MPa	Strain $x10^{-3}$	Dislocation density $x10^{15}m^2$
1	5	1	30	18.319	432.64	2.277	4.610
2	5	1	50	20.399	352.30	1.854	2.751
3	5	1	70	22.512	306.01	1.610	1.982

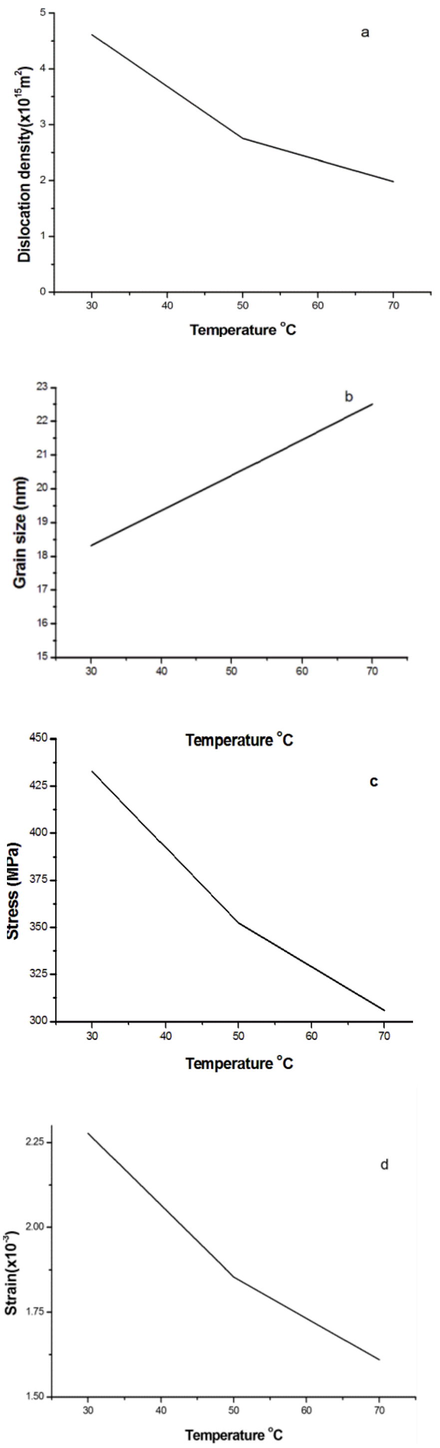

Fig. 3. Effect of Temperature on Structural properties of Ni-Mn thin film at various temperature.

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 without micro cracks. At a low temperature, the surface is uniform, bright and smooth as shown in Fig. 4(a). At a temperature of 50° C, the surface is granular and bright as in Fig. 4(b) and at the corner of Fig. 4 (b) shows the magnified image (x5000) indicates ball like structure. At a higher temperature of 70°C the surface shows large and bright granular structure as in Fig. 4 (c).

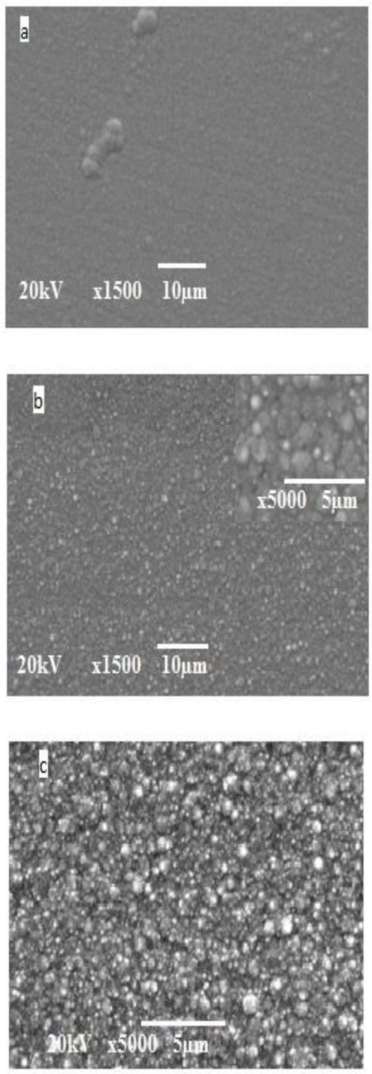

Fig. 4. SEM images of electrodeposited Ni-Mn thin films at different temperatures (a) 30°C, (b) 50°C and (c) 70°C.

3. 3. Hardness of the deposits

Fig. 5 shows the effects of temperature on the hardness of the samples. Hardness of the thin films at various levels were found to be about 240 VHN, 254 VHN and 173 VHN for the temperature of 30°C, 50°C and 70°C respectively. The hardness of the sample was high at the temperature of 50°C.

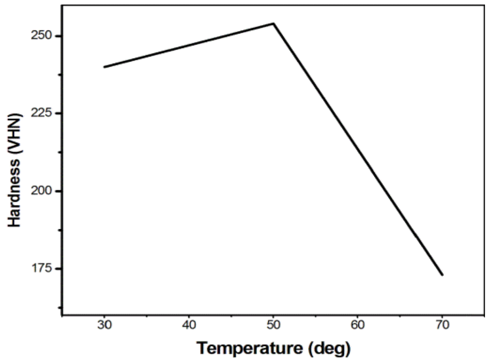

Fig. 5. Effect of temperature on hardness of Ni-Mn thin film at various temperature.

3. 4. Magnetic properties of the deposits

Fig. 6 shows a hysteresis loop of Ni-Mn alloy thin film deposited at (a) 30°C, (b) 50°C and (c) 70°C. The magnetic properties of Ni-Mn films were observed from vibrating sample magnetometer and are tabulated as shown in Table 2. The temperature has great impact on magnetic properties of electrodeposited Ni-Mn alloy thin films. Manganese content present in the film would disorder the alignment of the magnetic moments. Since the increment of temperature decreases the manganese content present in the film, it increases the grain size as well as the coercivity. Effects of grain size on magnetic properties such as coercivity, retentivity, magnetic saturation and squarness are shown in Fig. 7. Grain size has major role in magnetic properties. Quite a few single magnetic domains (having smaller grain size) are easier to rotate when subjected to magnetic field instead of a larger domain. Therefore, larger grain size implies in larger magnetic domains which are not easy to rotate and in addition it increases coercivity [9]. From the magnetic studies retentivity and squareness were found to decrease at 50°C and then increase at 70°C. Maximum value of magnetization 1.3452emu/g was obtained at the temperature of 50°C.

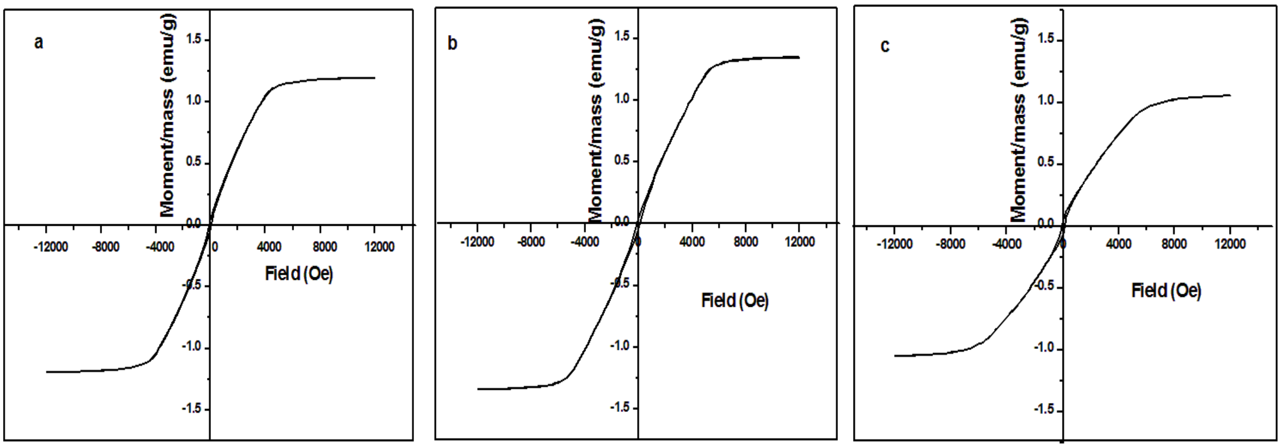

Fig. 6. Magnetic Hysteresis loop of the electrodeposited Ni-Mn film at various temperature (a) 30°C, (b) 50°C and c) 70°C.

Table 2. Effects of Temperature on the magnetic properties of the Ni-Mn thin film at (a) 30°C, (b) 50°C and c)70°C.

S. No.	Temperature °C	Grain size nm	Coercivity Hc Oe	Magnetization Ms emu g^{-1}	Retentivity Mr 10^{-3} emu g^{-1}	Squareness S
1	30	18.319	76.948	1.1978	41.966	0.03504
2	50	20.399	97.349	1.3452	38.898	0.02892
3	70	22.512	113.84	1.0525	58.116	0.05522

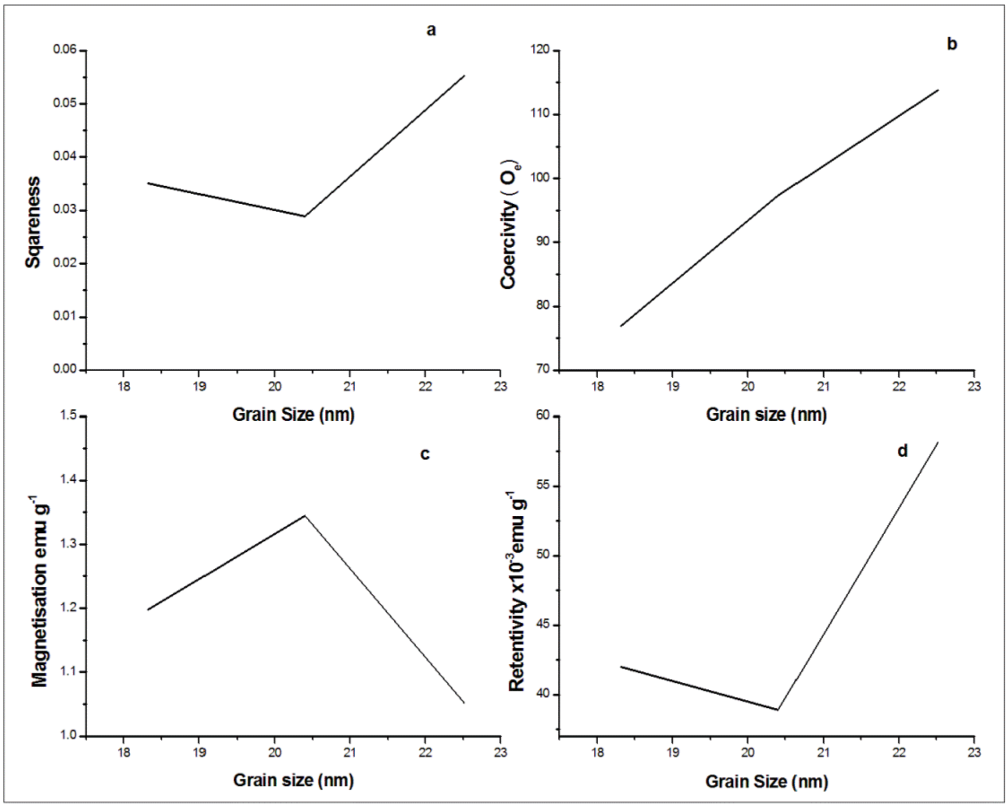

Fig. 7. Magnetic properties of the electrodeposited Ni-Mn film at various temperatures.

4. Conclusions

In the present revision, Ni-Mn films were electrodeposited from the chloride-citrate bath. The effects of temperature 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 increased with the increase of temperature. The Mn content present in the film decreases with an increment of temperature and as a consequence the stress involved in the film was reduced. The deposits were uniform and granular at 50°C. Meanwhile coercivity was increased with the increment of temperature and high value of magnetization obtained at 50°C. Due to the increment of temperature, the films became mechanically hard and maximum value of hardness of 254 VHN was obtained at 50°C. Thus the present study concludes that, at 50°C the magnetic and mechanical property of the Ni-Mn thin film could well be improved which is used well in the MEMS (Micro Electro Mechanical Systems) application.

Acknowledgements

Author wishes to thank the Govt. College of Technology for the financial support through TEQIP Phase-II to complete this work and Dr.L.Baskar for helpful discussion and support on this study.

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