Structural properties electrodeposited of Ni-Mn thin films from chloride-citrate bath

Rajeswari M
Department of Physics,Government College of Engineering, Erode-638 316, Tamilnadu, India

In the present study electrodeposited NiMn thin films were prepared in tri sodium citrate bath at three different current densities and at three different concentrations of tri sodium citrate. Structural properties of the film were studied using X-ray diffraction technique (XRD), surface morphology of the deposits were analyzed using Scanning Electron Microscopy (SEM), Elemental composition of the deposits were found with Energy Dispersive X-ray spectroscopy (EDAX) and mechanical properties of the film were obtained with Vickers Hardness Test (VHN). X-ray diffraction (XRD) results indicated that the deposited film had crystalline size of 18 nm and hardness of the film was 240 VHN.

Keywords- NiMn, Electrodepostion, Structural Properties, Thin film

I. INTRODUCTION

Electroplating is a simple, rapid and cost-effective technique for preparing nano crystalline thin films. The electrodeposition of metals and semiconductors has found extensive use in producing micro electro mechanical systems (MEMS). Nickel based alloys have more practical materials for the application of MEMS due to their vast usage in the form of magnetical and mechanical elements for example motors, precision gears, magnetic shield, transformer cores and recording media [1]. NiMn thin films have better ductility, good strength and modest stress used in MEMS and in probe spring applications [2, 3]. Current density, bath temperature, time duration and complexing agent, etc., are the parameters used to organize the process of deposition. Nowadays, in most of the investigations NiMn films were deposited from sulfate and sulfamate baths and very few from chloride bath. The effectiveness of cathode found improved by chloride ions and films can be deposited even at minimum voltages because of the high conductivity of chloride bath [4, 5].

To our knowledge, there is no literature explaining the effect of citrate in the NiMn thin films. In the present study, NiMn thin films were prepared from the chloride-citrate bath by electrodeposition method [6]. The characterization of Ni-Mn thin films at different concentrations of tri sodium citrate is reported. The effects of tri sodium citrate concentrations on the elemental composition, structure and mechanical properties were examined.

II. EXPERIMENTAL PART

2.1 Electrodeposition of NiMn thin films from tri sodium citrate bath

A copper substrate of size 9 x 2 cm as the cathode and nickel of the same size as anode were used in this present work. The copper substrates were buffed and degreased using a detergent solution further it was cleaned with distilled water. Cleaned and dried substrate has been covered off with a cellophane tape except the area on which the deposition was required. Bath pH was varied from low to high pH and pH 4.0 was opted for the present work. The structural, morphological and mechanical properties of the NiMn thin films from tri sodium citrate bath [6] were studied with the help of XRD, SEM, EDAX and Vickers hardness test. The thickness of the films was determined by digitalmicroscope.

III. RESULTS AND DISCUSSION

3.1. Elemental composition of the deposits

The NiMn alloy thin films were deposited on the copper substrate by electrodeposition method. The elemental composition of the NiMn film deposited from tri sodium citrate bath (20 gl^{-1}) has been obtained from the EDAX study and it is shown in Figure 1. The weight percentages of the films electrodeposited with different tri sodium citrate bath concentrations are tabulated as in Table 1. EDAX results showed that the weight percentage of manganese found to be increased due to the increment of the bath concentration. The film prepared at 20 gl^{-1} citrate bath concentration having 4.90 wt% of manganese content.

Table 1 Results of EDAX analysis of NiMn thin films deposited from tri sodium citrate bath

S.No	Tri sodium citrate concentration (gl-1)	Ni wt%	Mn wt%
1	10	98.14	1.86
2	20	95.10	4.90
3	30	94.62	5.38

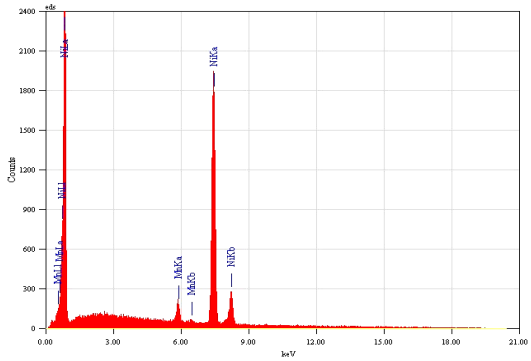
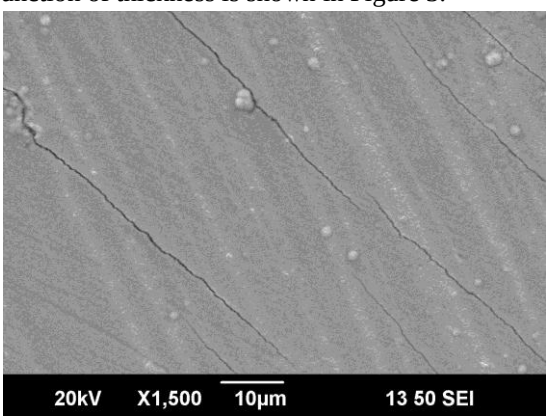


Figure 1 EDAX spectrum of NiMn thin film deposited from tri sodium citrate concentration of 20 gl^{-1}

3.2 Surface morphology of the deposits

The scanning electron micrographs of the NiMn thin films obtained from SEM studies and their images are shown in Figure 2. The films obtained from 20 gl^{-1} of tri sodium citrate bath concentration have no micro cracks as a consequence of stress relief. Thickness of the NiMn thin films were determined by using a digital micrometer and it is shown in Table 2.The effect of citrate bath concentration as a function of thickness is shown in Figure 3.



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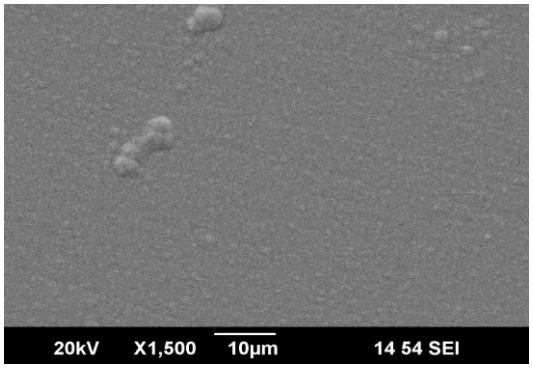

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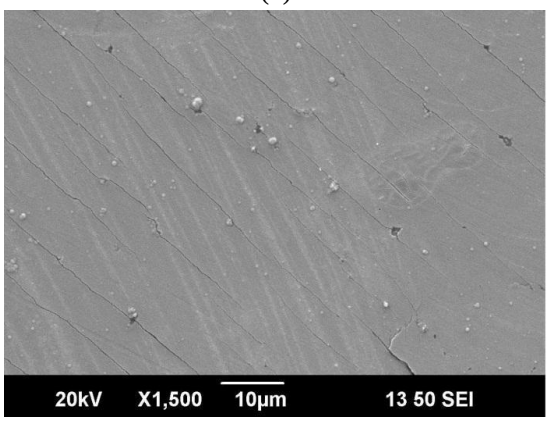


(c)

Figure 2 SEM images of NiMn thin films electrodeposited from different citrate concentrations (a) 10 gl^{-1}, (b) 20 gl^{-1} and (c) 30 gl^{-1}

Table 2 Thickness of NiMn thin films electrodeposited from chloride-citrate bath

S.No	Citrate bath concentration (gl^{-1})	Film thickness (µm)
1	10	7.0
2	20	7.5
3	30	7.5

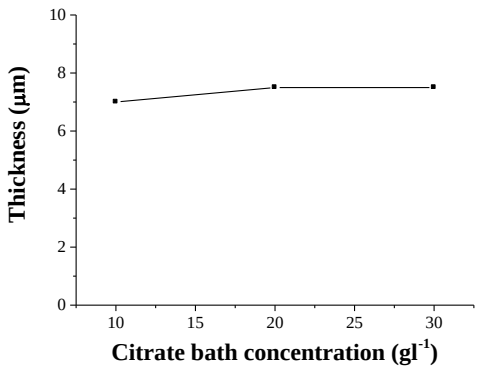


Figure 3 Effect of citrate bath concentration on the thickness of the NiMn thin films

3.3 Structural properties of the deposits

The crystalline nature of the NiMn thin films electrodeposited from chloride-citrate bath has been studied by X- ray Diffractometer and their XRD patterns are shown in Figure 4. The presence of sharp peaks in the XRD pattern of the NiMn films clearly reveals that the films are crystalline in nature. The crystalline size of the electrodeposits has been calculated from the XRD pattern using the Scherrer's formula

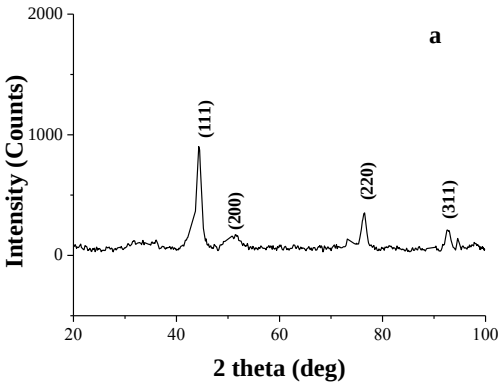
$$D = \frac{0.9\lambda}{\beta cos\theta}$$

The crystalline size of the NiMn thin films were found to be less than 25 nm. The structural parameters of NiMn alloy thin films obtained from various concentrations of tri sodium citrate bath are tabulated as shown in Table 3. The XRD patterns of NiMn films confirmed the existence of FCC phase with (111), (200), (220), (311) and (222) diffraction peaks. The variation of bath concentration affects the crystalline size of the electrodeposited NiMn thin films.

Due to the increment of the bath concentration, tensile stress of the film may also increase, which leads to the reduction in coercivity. This is because tensile reduces the coercivity of electroplated nickel based alloy thin films. Hence the NiMn films can be used to manufacture devices like magnetic recording heads.

Table 3 Structural properties of NiMn alloy thin films from tri sodium citrate bath

Citrate bath concentration (gl-1)	Crystalline size (nm)	Strain (x10-3)	Dislocation density (x1015/m2)	Lattice parameter (Å)
10	21.630	1.249	2.137	3.640
20	18.319	2.277	4.610	3.536
30	23.110	1.249	1.872	3.607



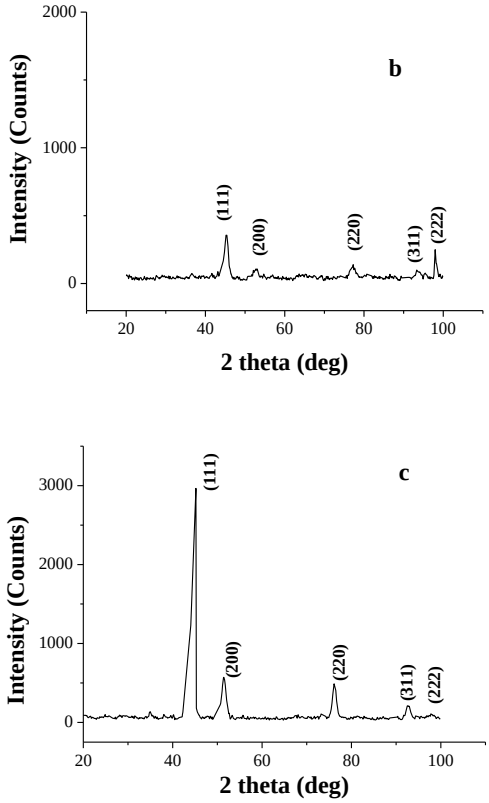


Figure 4 XRD patterns of NiMn thin films deposited from various tri sodium citrate bath concentration (a) 10 gl^{-1}, (b) 20 gl^{-1} and (c) 30 gl^{-1}

3.4. Mechanical properties of the deposits

Adhesion of the NiMn thin film to the copper substrate was tested by bent and scratch method. From this analysis, the films were found to have good adhesion to the substrate. Hardness of the film was examined using Vickers hardness test by the diamond intender method and the results are tabulated and shown in Table 4.

Table 4 Hardness of the electrodeposited NiMn thin film from tri sodium citrate bath

S.No	Citrate bath concentration (gl-1)	Crystalline size (nm)	Vickers hardness (VHN)
1	10	21.630	230
2	20	18.319	240
3	30	23.110	225

The results showed that the hardness varied by increasing the concentration of trisodium citrate bath. The decrease in grain size shows the increase in hardness of the electrodeposited NiMn thin films. The dependence of Vickers hardness on the bath concentration is shown in Figure 5.

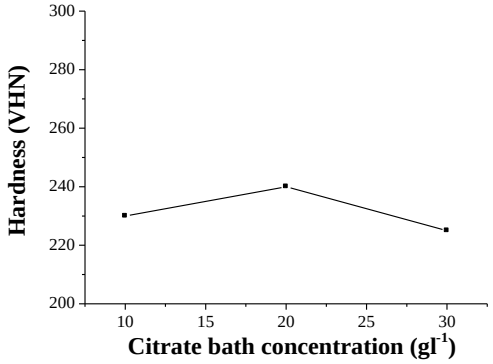


Figure 5 Vickers hardness as a function of citrate bath concentration

IV. CONCLUSION

In this investigation, NiMn alloy thin films were prepared from various citrate concentrations. The increase in the citrate bath concentration affected the properties of NiMn thin films. The electroplated NiMn films from chloride-citrate bath concentration of 20 gl^{-1} have good hardness. This is due to the reduction in grain size of the thin film. Film prepared at this concentration is having a uniform surface morphology and smooth surface.

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