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THE IRON-NICKEL-MOLYBDENUM (Fe-Ni-Mo) ELECTRODEPOSITED ALLOY ON n-TYPE SILICON

ABSTRACT

In the present work, the electrodeposition of iron-nickel-molybdenum (Fe-Ni-Mo) alloy on n-type silicon (Si) is investigated. A voltamperometric study has been carried out. According to the composition of the solution and of its pH, the properties of final deposit have been investigated and analyzed by X-rays diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS). Under our conditions an amorphous FeNiMo alloy was formed. The morphology of deposited layer was strongly influenced by the polarization and the molybdenum dominance in the final chemical composition of the deposited film. Moreover, high percentages of molybdenum can be obtained from high molybdate concentrations and grain size increase with increasing Mo concentration. We also noticed that an absence of nickel was accomplished by applying more negative potential.

Key words: *Electrodeposition, metallic alloy, pH solution*

INTRODUCTION

Electrodeposition is a very convenient technique for production of metallic films and alloys due to its low cost of implementation and ease of handling [1, 2]. Very recently this technique has been employed in the production of metallic nanostructures with very interesting magnetic, mechanical and thermal properties [3, 4].

A variety of metals can be electrodeposited, offering a wide selection of metallic properties. Thus electrodeposition of special alloys has added numerous materials to the list of the more commonly electrodeposited metals such as nickel, copper, and iron [5, 6].

Electrodeposition of alloys, binary and ternary ones, has received attention in recent years due to their magnetic properties [7–12]. Thus, different alloys can be electrodeposited to attain useful soft magnetic films and prepare materials for highly functional magnetic recording [13–18].

The presence of molybdenum in metal alloys increases their magnetic interests [19, 4, and 21] and constitutes a protection of these metals against corrosion [23]. Thus, the increase of Mo quantity in the metallic films composition increases their resistivity [4].

The electrodeposition of molybdenum with an iron-group element occurs through the so-called induced codeposition mechanism [23, 24]. Molybdenum cannot be fully reduced in aqueous solutions by itself. In contrast, it can be codeposited with an iron-group metal (inductor metal).

In this work, the ability of the electrodeposition method to improve the deposition of FeNiMo alloy on Si substrate is tested based on electrochemical characterization. A concentration of 0.008 M in molybdate is chosen to enhance Mo incorporation into the deposits [23, 25].

The influence of polarization, pH bath and Molybdenum concentration on the morphology and on the final composition of the deposits has been examined.

EXPERIMENTAL

The study of the electrodeposition process and the deposits were prepared in a conventional three-electrode cell using a microcomputer-controlled potentiostat. For the electrochemical study, n-type Silicon (111) with a resistivity of $0.015\Omega\text{cm}$ was used as working electrode. The reference electrode was a saturated calomel electrode (SCE); all potentials are referred to this electrode. The counter-electrode was made in platinum.

The used bath contains 0.05M $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, 0.24M $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, 0.008 M $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$, 0.69M $\text{CH}_3\text{COONH}_4$. The pH was adjusted with H_2SO_4 and maintained at 0.5.

In other hand and to examine the influence of the molybdenum concentration, we have used other electrolytes with different molybdate concentrations.

The morphology of the deposits was examined with a Philips 505 SEM and JEOL JSM-6360LV Scanning Electron Microscopy (SEM) and their elemental composition was determined by Energy Dispersive X-ray Spectroscopy (EDS).

RESULTS AND DISCUSSION

The electrochemical behaviour of the silicon electrode in the electrodeposition bath was assessed by cyclic voltametry (Fig.1). The obtained curve shows the presence of two plates corresponding to the metal reduction on silicon surface. The first one is around -1.2V and the second around -1.5V .

SEM micrograph of figure (2a) shows a uniform and *pitted film* obtained by a polarization of silicon sample at -2.9V for 5min. According to Popov et al. [26], these *pits* are due to the simultaneous hydrogen evolution during electrodeposition of Fe-Ni-Mo alloys which strongly influences the properties of these deposits.

For a polarization at $-0.37\text{mA}/\text{cm}^2$ and for the same deposition time (5 min) we observe an uniform structure with an appearance of *hillocks* growth which evolve with the electrodeposition time (Figure 2b). In literature, this form of deposit is also called *microcapsules* [27].

For a polarization time of 10min at the same current density as previously, the morphology of the deposit changes and becomes porous (figure 2c). This porosity is the most important property of good adherent and stressless metal coating [25]. It is probably due to hydrogen co-deposition.

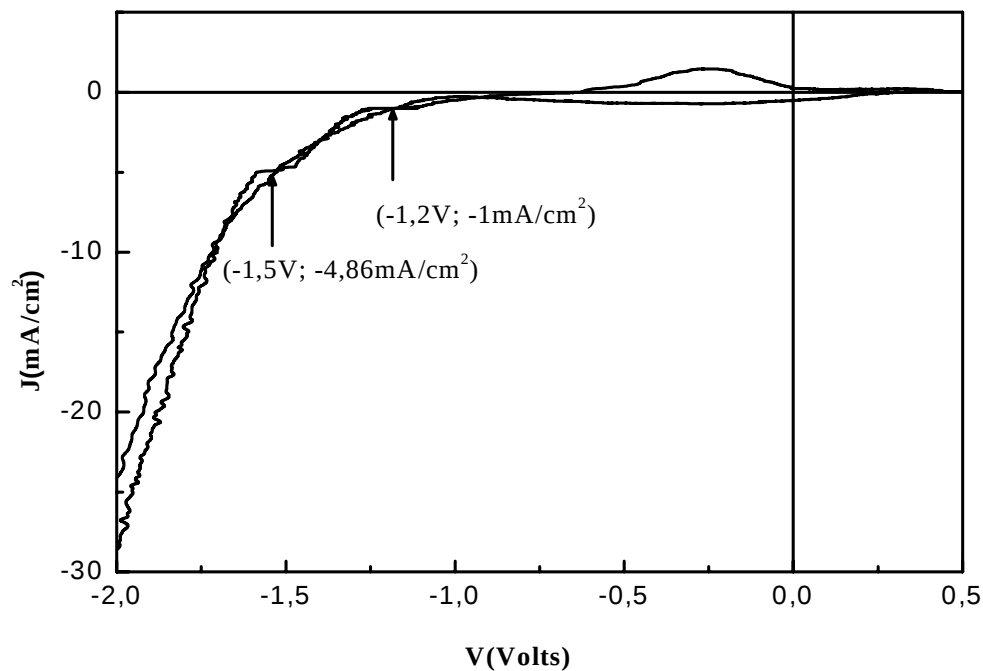


Fig. 1. Cyclic voltamograms obtained with an electrolyte containing: 0.009M $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ + 0.05M $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ + 0.008M $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ + 0.1M $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$

EDS analysis shows that nickel is not detected in the final composition of elements in all the previous films. While referring to the literature, we find that this absence of Ni is due to the strong acidity of the bath used ($\text{pH}=0.5$) [29]. In addition, the molybdenum dominates (Tab.1).

The majority of alloys containing Ni were carried out in non acid mediums which are not largely studied [30]. In this work we chose acid solutions with a pH of 0.5 and knowing that Ni is not electrodeposited in these mediums [22]. So, we tried to overcome this problem by applying a more negative potential (-4V). In this case, the deposit grows as leaves shape, Fig.2d, and the presence of FeNi dominate in final composition of elements (Tab.1). For the same polarization as previously but for higher electrodeposition time a cauliflower form (Fig.2e) of the deposit has been obtained. It has been found [31, 27] that the deposit presents a cauliflower shape when the film has a compact structure of coherent grains just after starting the deposition. The difference in the conductivity of the different grains will then lead to this cauliflower structure of the thicker films.

The phase structures of the coatings have been found all amorphous, which has been confirmed by XRD (not shown here); this is in agreement with published works [32, 33].

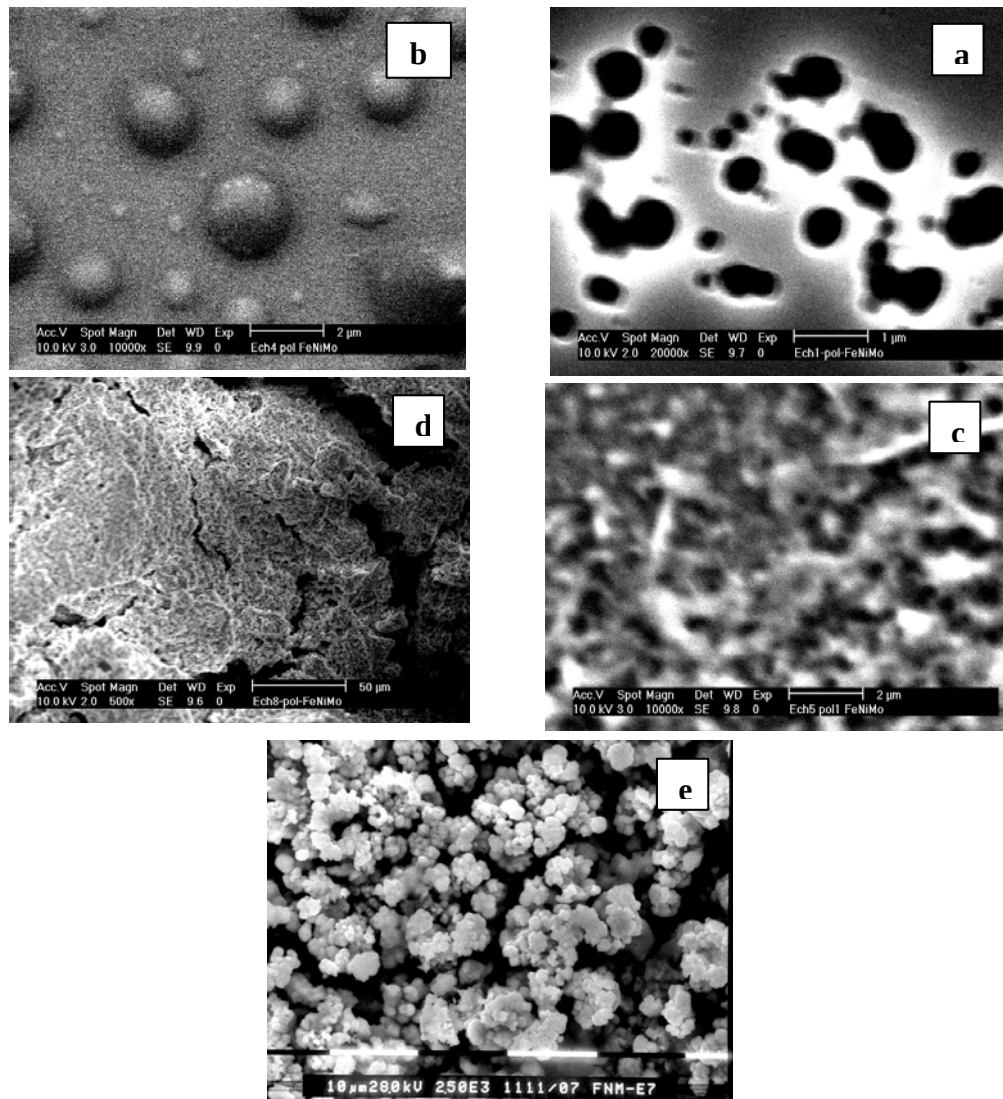


Fig. 2. SEM micrographs of different film morphologies obtained from: a) $V = -2.9V$, $t = 5\text{min}$; b) $I = -0.37\text{mA/cm}^2$, $t = 5\text{min}$; c) $I = -0.37\text{mA/cm}^2$, $t = 10\text{min}$; d) $V = -4V$, $t = 8\text{min}$; e) $V = -4V$, $t = 10\text{min}$

Table 1. Composition of deposited alloys obtained by EDS analysis

Samples	V(Volts)	J(mA/cm ²)	t(min)	Elements, weight% Fe/Ni/Mo
1	-2.9		5	57.84/ 0 /42.16
2		-0.37	5	36.92/ 0 /63.08
3		-0.37	10	3.55/ 0/ 96.45
4	-4		10	11.83/85.05/3.12
5	-4		8	13.45/81.73/4.82

Figure 3 presents EDS analysis spectrum for two deposited samples, 3 and 5 of table 1. These spectrums confirm the dominance of molybdenum in the first sample and the appearance of nickel in the second one.

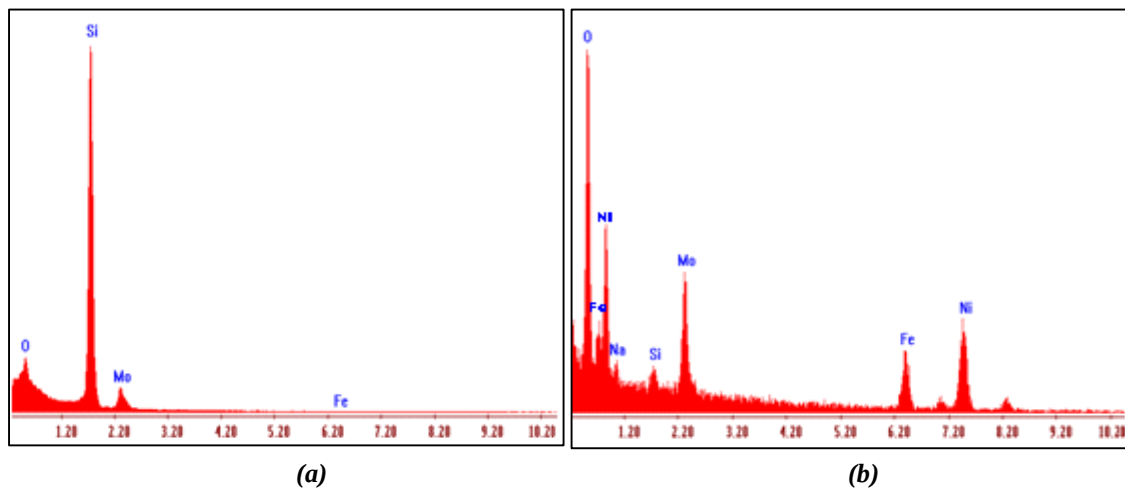


Fig. 3. EDS analysis spectrum for samples: a) 3 and b) 5

The intensity of the silicon peak observed in figure (3.a) compared to that of figure (3.b) indicates that the layer deposited at -4V is thicker than that deposited at current density of 0.37mA/cm^2 . Whereas, the figure (4. b) shows a high oxygen peak, indicating the deposited layer oxidation.

On the Figure 4 we present the morphologies obtained with variable Molybdate concentrations. The bath electrodeposition was $0.009\text{M FeSO}_4 \cdot 7\text{H}_2\text{O} + 0.05\text{M NiSO}_4 \cdot 6\text{H}_2\text{O} + x\text{M Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O} + 0.1\text{M Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$, $x=0\text{M}$ (fig. 5. a), $x=0.001\text{M}$ (fig. 5. b) and $x=0.008\text{M}$ (fig. 5. c). We observe an increase in clusters size as we increase the Molybdate concentration in the deposition bath. We also notice the increase in space (void) between the agglomerations of so formed grains on the substrate surface.

Knowing that the coercivity decreases with the reduction of grain size [28, 34], which is given by minimising molybdate concentration in the electrodeposition bath, it is essential to use weak molybdenum concentrations to obtain soft magnetic materials.

EDS analysis of the samples, allowed us to observe the influence of the molybdenum concentration on the chemical composition of the final deposit. Indeed, the percentage of Mo in the deposit increases linearly with the increasing of its bath concentration (fig. 6. a). While referring to the literature [4] it is very convenient to have metal layers rich in Mo because that increases the corrosion resistivity. Whereas for magnetic applications, we have to preserve a weak molybdenum percentage in the deposit.

In addition, the increase of molybdenum concentration in the solution supports the formation of molybdenum oxides. This was confirmed by EDS analysis of the samples carried out from solutions containing various Mo concentrations. Figure (6. b) shows the variation of oxygen composition with molybdate concentration in the deposition bath. An increase of the oxygen percentage in the finale deposit is remarqued. The presence of this oxygen is attached to molybdenum to form molybdenum oxides which were deposited before metal alloy [25].

So, although low molybdate concentrations favoured alloy deposition, higher concentrations led to the formation of molybdenum oxides, which hinders the deposit of metal alloy.

On figure (7) we represent the evolution of the FeNiMo deposition current density with the Molybdenum bath concentration. The curve has a Gaussian form with a maximum current density at 0.005 M. this indicates that a small quantity of molybdenum in solution clearly progresses the deposit compared with that of the solution containing only Nickel and Iron and for significant concentrations the current density decreases. Thus the presence of molybdenum in solution has caused and, more and more, favoured deposition process;

On figure (8) the deposition current density is traced as a function of the deposition time for 0.012M of molybdenum. When the FeNiMo were deposits were obtained at constant voltage an induction time was observed indicates a nucleation spike followed by an increase which attained a quasistationary value for deposition times higher than 3.5s.

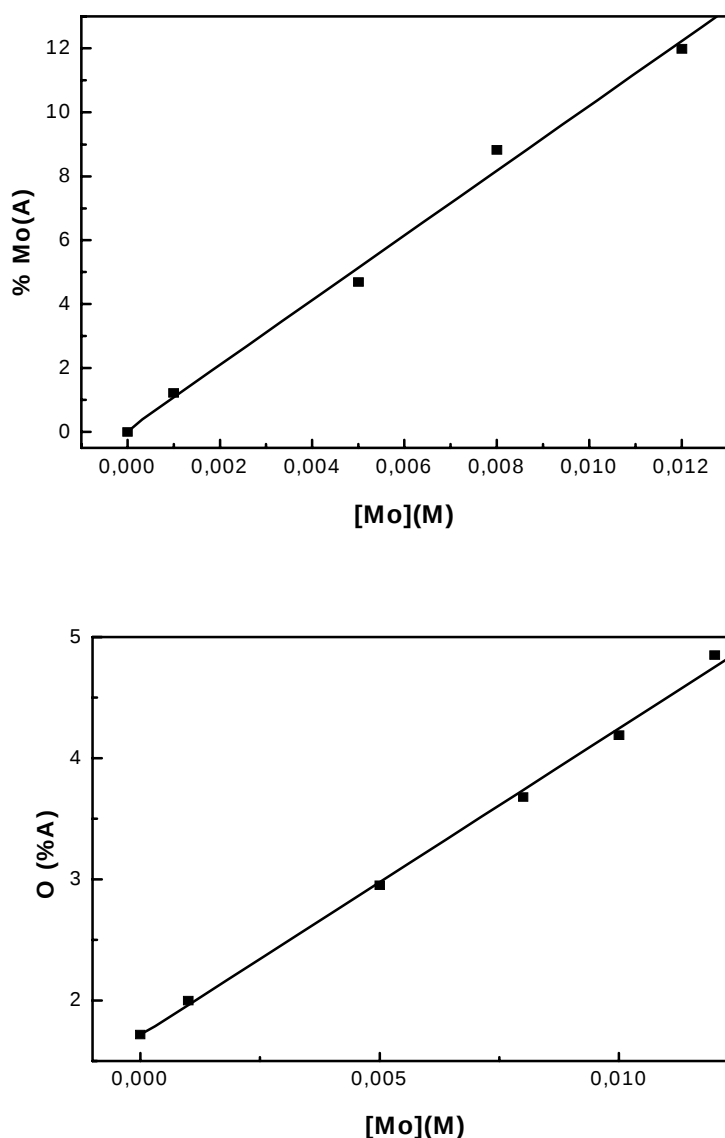


Fig. 6. Percentage (en %A), in the final deposit, of a) Molybdenum b) Oxygen as a function of Mo concentration in the electrodeposition bath

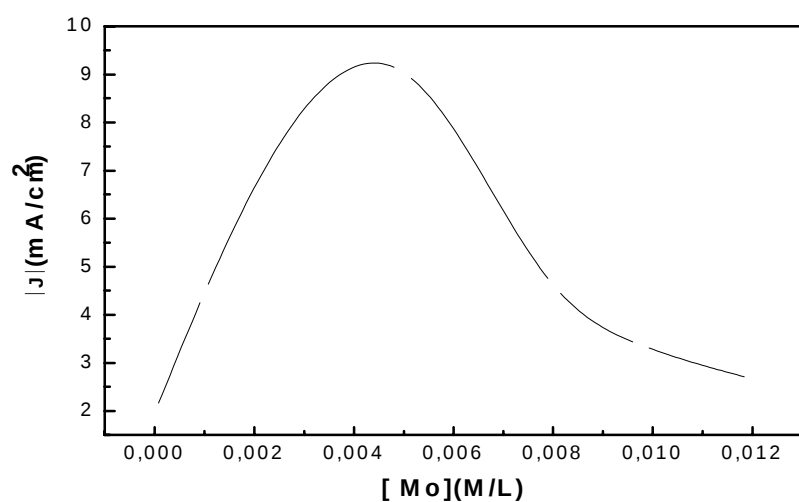


Fig. 7. Influence of Mo concentration on the deposition current density

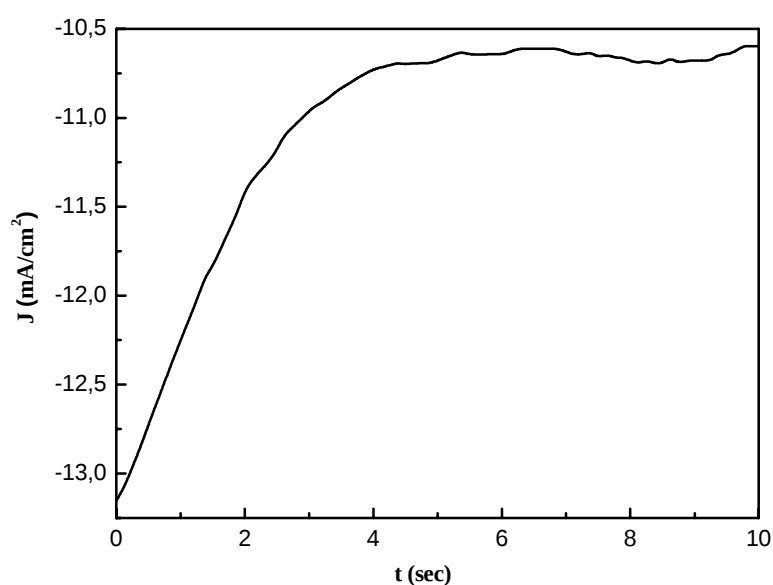


Fig. 8. Current density transients obtained for FeNiMo deposition

CONCLUSIONS

In this work we have studied the effect of deposition parameters (polarization, time, Molybdenum concentration) on the morphology and composition of the deposits. The results show that polarization at a constant potential leads to an uniform and pitted layer in contrast with that obtained with the corresponding current density polarization where it has

been shown an uniform structure with microcapsules growth on the deposited film. EDS analysis shows the dominance of Molybdenum in the case of current density polarization, the percentage of this element was increased in the deposited film by increasing the polarization time; in contrast there was no Ni in the film which is due to the very low value of pH [29]. The formation of Ni in the deposit could be accomplished by applying a more negative potential (-4V), where leaves like morphology and with dominance of Ni have been obtained. These forms of leaves have been evolved to dendrite shape which finishes with a cauliflower shape when increasing the deposition time of deposit. XRD has been shown that the FeNiMo is an amorphous deposit on silicon surface. Thus the results obtained have showed an increase of the Molybdenum incorporation in the final composition of deposited film and an increase of the grains size while increasing the Mo concentration in the deposition bath.

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