JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 8, No. 5, October 2006, p. 1889 - 1891

Effect of ultrasounds sonication on surface microstructure of the electrodeposited Ni-Zn thin films

N. SULIȚANU*, C. PÎRGHIE[a], F. BRÎNZĂ
Department of Solid State Physics and Theoretical Physics, Faculty of Physics,
"Al.I.Cuza" University, 11 Carol I Blvd., 700506 Iasi, Romania
[a]Faculty of Mechanical Engineering, "Stefan cel Mare"University, 720225 Suceava, Romania

This work is focussed on the preliminary results on surface microstructure of some Ni-Zn films electrodeposited in the presence or not of an ultrasound field. Different frequencies (20 kHz, 1 MHz) of ultrasounds were applied to electrolytic bath. Ultrasounds were applied perpendicular to the direction of deposition. The thickness of studied samples was in the range of 100-120 nm. The surface microstructure was investigated using an atomic force microscope (AFM) and a laser profilometer. The change in film surface microstructure was evidenced. Ultrasound keeps the electrode surface clean and improves mass transport such that uniform electrode reaction occurs across the area of a centimetre-scale electrode, with consequently greater reaction velocity at the electrodes. We found that 20 kHz irradiation using a cleaning bath allowed the formation of fine grained Ni-Zn films on the electrode. These films had fine structure features and a denser morphology than silent ones. Moreover, the use of a 1MHz higher-frequency bath interfered with formation of coarse grained films at the electrode, similar to those obtained from silent bath. The possibility of obtaining different surface microstructures of Ni-Zn electrodeposited thin films by applying ultrasounds of different frequencies to the electrolyte bath allows to control by structure the physico-chemical properties of the films.

(Received September 1, 2006; accepted September 13, 2006)

Keywords: Ni-Zn alloy, Electrodeposition, Ultrasounds, Thin film, Surface microstructure

1. Introduction

Alloying of zinc by iron group elements (Ni, Fe or Co) has been the subject of extensive research mainly directed towards two different fields: the corrosion resistance and the catalytic activity. From the first viewpoint, many authors reported on the important role of the alloy composition, indicated that the optimal corrosion resistance is reached for the zinc alloys containing between 12 and 13 % Ni, for example [1, 2]. From the second viewpoint, Ni-Zn films can have a porous structure or-and a high surface roughness depending on electrodeposition parameters: pH, current density, bath concentration and temperature, deposit growth rate, nature of additive reagents [3-7]. The electrodeposition by pulse-plating technique is an interesting case for microstructure of Ni-Zn films and their physico-chemical properties [8].

The aim of this work was to investigate the ultrasounds influence on surface microstructure of the Ni-Zn thin films and changes in surface roughness of these kinds of films.

2. Experimental

The Ni-Zn thin films were obtained by DC electrodeposition from an aqueous bath. The electrolyte was a mixed aqueous solution containing $NiSO_4 .7 H_2O$ = 250 g/l, $ZnSO_4$ = 50 g/l, H_2BO_3 = 20 g/l and natrium lauryl sulphate = 0.5 g/l. The pH value was fixed at 4.0 by a small addition of sulphuric acid. During deposition, the electrolytic cell was kept at a constant temperature of T=298K. The film substrate was copper. The electrolyte was irradiated with ultrasounds of 20 kHz and, respectively, 1MHz frequency applied perpendicular to the deposition direction. Ultrasound generator was applied to the cathode. For obtaining ultrasounds of 1 MHz frequency we used a piezoelectric transducer but for obtaining ultrasounds of 20 kHz frequency we used a magnetostriction transducer. The thickness of studied samples was in the range of 100-120 nm. The surface microstructure was investigated using an atomic force microscope (AFM) and a laser profilometer.

3. Results and discussion

Fig. 1 shows AFM images of Ni-Zn film surface obtained without ultrasounds and with ultrasounds applied perpendicular to the direction of the deposition.

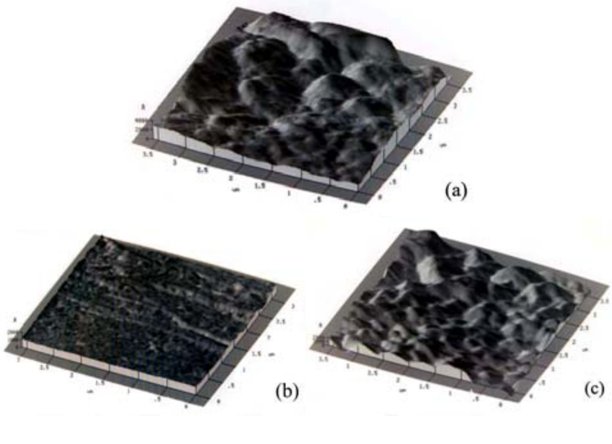

Fig.1. AFM 3D surface images of Ni-Zn thin films obtained (a) without ultrasounds, (b) with 20 kHz ultrasounds and (c) with 1 MHz ultrasounds. Aria of scanning is 3.6 x 3.6 µm.

Fig. 2 shows the top views of Ni-Zn film surfaces obtained by AFM.

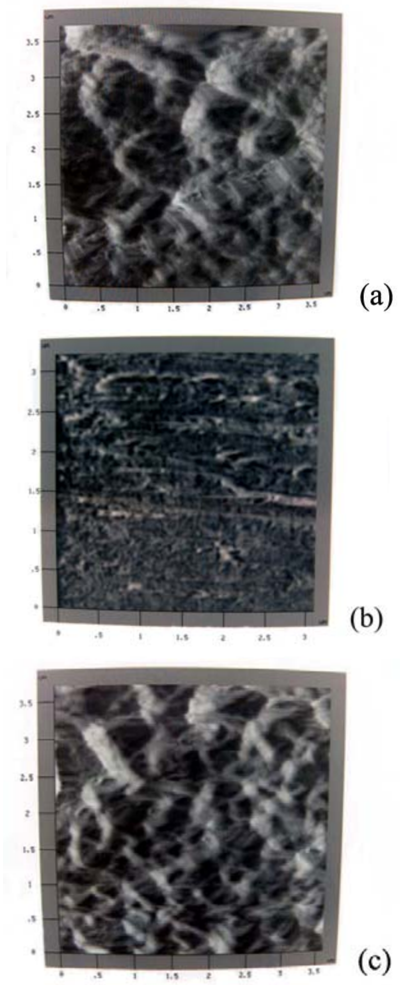

Fig. 2. AFM top view images of Ni-Zn film surface: (a) without ultrasounds, (b) with 20 kHz ultrasounds and (c) with 1 MHz ultrasounds.

The topographic characteristics of film surface measured with a laser profilometer are given in Table 1.

Table 1. Topographic characteristics of Ni-Zn film surface.

Topographic characteristics (nm)	Without ultrasounds	With ultrasounds 20kHz	With ultrasounds 1MHz
Median height	9.158	2.730	4.440
Average height	11.081	3.788	5.943
Peak to valley	5411.403	163.410	567.765
RMS roughness	90.049	17.870	91.921
AVE roughness	71.630	12.619	74.868

Fig. 3 shows Ni-Zn thin film profiles obtained through a laser profilometer. Surface samples from silent bath shows an average height topographic profile of approximately 9 nm and a RMS roughness of 90 nm (Fig. 3a). This is characteristic for quite large and well delimited grains what is in accordance with AFM observations and the alternation of zones with different grains sizes can be directly linked to the RMS roughness values (Figs 1a and 2a).

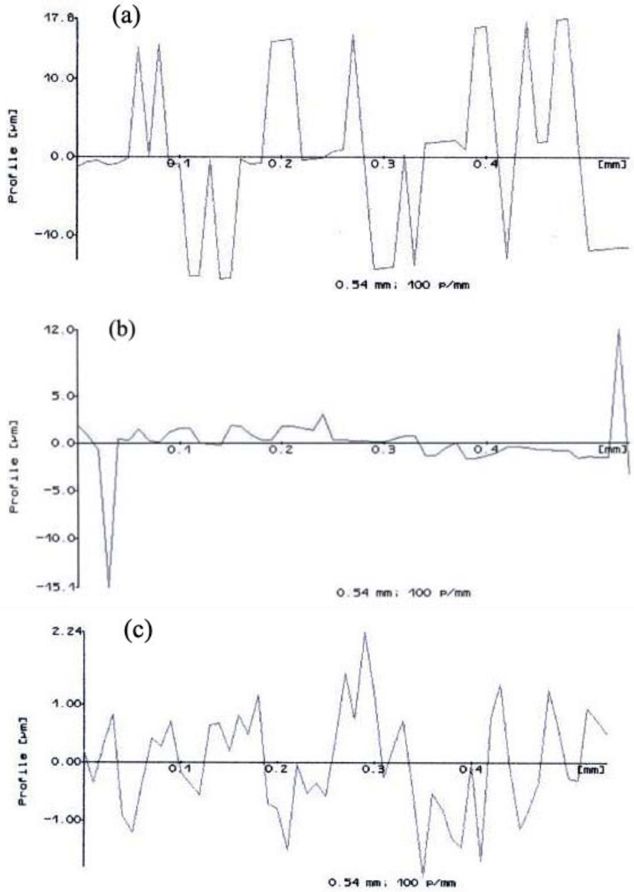

Fig. 3. Ni-Zn thin film profiles obtained by laser profilometer: (a) without ultrasounds, (b) with 20 kHz ultrasounds and (c) with 1 MHz ultrasounds.

For 20 kHz, the experimental results indicate a very smooth surface profile characterized by an average height profile of approximately 3.8 nm and surface roughness decreases up to 17.87. This is characteristics for fine grains structure evidenced by AFM observations (Figs. 2a and 3b). For very high frequency of about 1 MHz although the average height of surface profile is not so bigger (~ 5.9 nm) that those for silent bath the RMS roughness reaches similar values (around to 90 nm) (Fig. 3c). Otherwise a similar surface grain structure as for silent bath was evidenced by AFM investigation (Figs 2c and 3c). Therefore, an important change in surface structure may be obtained by irradiation of electrolytic bath with low frequency ultrasounds.

The ultrasounds influence on electrodeposited Ni-Zn films is due to the phenomena which take place at the electrode (substrate) during the deposition [9-11]. On the one hand, the ultrasonic irradiation accelerated the rates of charge transfer reactions on both the cathodic and the anodic processes and increased the capacitance of the double layer at the metal-electrolyte interface. Up to now, the mechanism of contributions of ultrasound to charge transfer processes has not been elucidated in detail. On the other hand, the imposition of ultrasound may decrease the thickness of the double layer, so that the potential at the outer Helmholtz plane may be energetic to accelerate both cathodic and anodic charge transfer processes. In the first instance, both processes may lead to the fine grains nucleation, but this depends on ultrasounds irradiation frequency.

5. Conclusion

In summary, a simple route to obtain nanocrystalline Ni-Zn film alloy under ultrasound irradiation at room temperature has been developed. The use of ultrasound has reduced the electrolyte pH and eliminated grained reagents using for these materials and the reaction conditions in our route are easy to maintain. High-intensity ultrasound sources are inexpensive, available from commercial sources and extremely reliable.

Ultrasound keeps the electrode surface clean and improves mass transport such that uniform electrode reaction occurs across the area of a centimetre-scale electrode, with consequently greater reaction velocity at the electrodes.

We found that 20 kHz irradiation using a cleaning bath allowed the formation of fine grained Ni-Zn films on the electrode. These films had fine structure features and a denser morphology than silent ones. Moreover, the use of a 1MHz higher-frequency bath interfered with formation of coarse grained films at the electrode, similar to those obtained from silent bath.

The possibility of obtaining different surface microstructures of Ni-Zn electrodeposited thin films by applying ultrasounds of different frequencies to the electrolyte bath allows to control by structure the physico-chemical properties of the films. Our preliminary magnetic property measurements come to sustain the started researches.

At present we try to determinate film morphology and magnetic properties as a function of film composition and ultrasound irradiation parameters: frequency and intensity of ultrasounds.

Acknowledgements

Part of this work was supported by the Romanian Ministry for Education and Research, programme CNCSIS under grant 33373-48-1321.

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* Corresponding author: sulitanu@uaic.ro