Spontaneous near-substrate composition modulation in electrodeposited Fe–Co–Ni alloys

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Abstract
Conventional and reverse depth profile analysis of electrodeposited Fe–Co–Ni alloys was performed by secondary neutral mass spectrometry (SNMS). It was found that the reverse sputtering method gave a much better depth resolution at the vicinity of the substrate. The reverse SNMS spectra showed that the deposition of Fe–Co–Ni alloys starts with the formation of an Fe-rich zone followed by an increase in Co concentration, then the nickel content increases and a steady-state alloy composition is achieved. At high current density, the initial depth pattern reproduces itself twice before the composition becomes stable. It was concluded that the varying depth profile is a consequence of the anomalous nature of the codeposition of the alloy components, the depletion of the electrolyte with respect to the metal salts, and the dependence of the intensity of the hydrogen evolution on the deposit surface composition.

1. Introduction
Research of electrodeposited magnetic materials is powered by the needs of the microelectronic industry. Fe–Co–Ni alloys are in the forefront of research nowadays because higher saturation magnetization and lower coercivity can be achieved with the ternary alloys than with the binary ones. Electrodeposition of high moment magnetic materials is a viable alternative of the physical production methods due to the flexibility of electrodeposition in the sense that patterned surfaces can be covered with an alloy of pre-defined composition at low cost.

Several recent papers are available on crystallinity, magnetization, coercivity, high-frequency behaviour and annealing of electrodeposited Fe–Co–Ni alloys [1–6]. Composition of the alloys was mostly characterized with the average molar fraction of the components. In some studies, a systematic composition change was found for deposits obtained from agitated electrolytes and with total deposit thicknesses within the 50–1000 nm range [1,7], accompanied by a corresponding variation in the sample properties. In contrast, the depth profile analysis showed an even component distribution for 450 nm thick [2] and for 70 nm thick [4] Fe–Co–Ni samples.

It was shown recently that the deposition of Co–Ni alloys leads to deposits with gradually changing Co:Ni ratio [8,9]. The interplay of the anomalous nature of codeposition and the electrolyte depletion were identified as the origin of the composition gradient along the growth direction.

In this work, Fe–Co–Ni deposits were obtained and the depth distribution of the components was measured. An uneven component distribution with characteristic zones was found in each sample close to the substrate, and then a steady-state composition was achieved. The thickness of the subsequent zones with varying composition indicates that the deposit thickness has to achieve a lower limit for obtaining the desired magnetic properties of the alloy with bulk composition.

2. Experimental
Fe–Co–Ni samples were obtained by galvanostatic electrodeposition with an EF453 type potentiostat/galvanostat from the following electrolyte: NiSO₄ 0.2 mol dm⁻³, CoSO₄ 0.075 mol dm⁻³, FeSO₄ 0.025 mol dm⁻³, H₃BO₃ 0.4 mol dm⁻³. The electrolyte pH was adjusted to 2.8. The electrolyte composition was very similar to those applied in earlier works [1,3–6]. Electrodeposition was performed at ambient conditions in a tubular cell with an upward facing horizontal cathode as described in Ref. [10]. The substrate was a metal-coated Si wafer with a Cr adhesive layer (5 nm) and a conductive Cu seed layer (20 nm). The mean surface roughness of the substrate was around 1 nm.

The depth profile of one Fe–Co–Ni deposit was investigated with the conventional sputtering direction, i.e., starting the analysis...
from the final deposit surface. In case of other Fe–Co–Ni layers, however, the electrolyte was changed after the deposition of the Fe–Co–Ni layer and the samples were covered with a Zn layer in order to mark the end of the Fe–Co–Ni layer. The final step of the sample preparation was the deposition of a supporting Ni layer. Thus, samples with the following structure were obtained: Si/Cr/Cu//Fe–Co–Ni//Zn//Ni where "/" denotes the interface of the sputtered metal layers and "//" indicates the boundary of layers obtained with different electrolytes.

After the electrochemical sample preparation, the Si wafer was broken behind the sample in a manner that the deposit itself remained intact. Then, the deposit could be easily pulled off from the Si wafer and the separation took place at the Si/Cr (i.e., semiconductor/metal) interface. The surface of the resulting Cr-capped sample was equally smooth as the Si wafer, and hence it was particularly appropriate for a sensitive depth profile study. This analysis method will be shortly called hereinafter as the reverse depth profile analysis [11,12]. The reverse sputtering method could be routinely done for the Zn/Ni coated samples and occasionally only for the uncoated ones due to their low tensile strength.

The depth profile analysis of the samples was performed by Secondary Neutral Mass Spectrometry (SNMS, type INA-X, SPECS GmbH) in the direct bombardment mode by using Ar+ ions with a fairly low energy for sputtering ($E_{\text{Ar}^+} = 350$ eV). The erosion area was confined to a circle of 2 mm in diameter by means of a Ta mask. The lateral homogeneity of the ion bombardment was checked by a profilometric analysis of the depth of the craters sputtered. The method of the determination of the sputtering rates was described earlier ([8] and references cited therein). The uncertainty in the sputtering rate due to the varying composition is lower than 5% of the average value.

3. Results

Fig. 1 shows the conventional depth profile of a Fe–Co–Ni sample. Although the signals obtained were somewhat scattered, the composition of the sample seems to be fairly constant along the entire sample thickness including the near-substrate zone. The average composition of the sample is Fe$_{35}$Co$_{12}$Ni$_{53}$ (indices refer to the molar percentage). This corresponds to the composition obtained with 2.5 times larger current density with the same electrolyte when the bath was agitated [1]. The full width at half maximum of the Cr signal is 55 nm, indicating that the smooth 5 nm thick Cr layer under the 1.25 μm thick Fe–Co–Ni layer cannot be resolved with a good enough accuracy. The reason of the enhanced apparent layer thickness is the roughness of the final surface of the Fe–Co–Ni deposit.

Fig. 2 presents the reverse depth profile for the same sample as shown in Fig. 1. It can be seen that the Cr/Cu and Cu/Fe–Co–Ni interfaces are very sharp, as expected for smooth layers and low sputtering depths. The component distribution in the first 140 nm thick layer of the Fe–Co–Ni deposit is built up by zones that are rich in various components. The initial 20 nm is very rich in Fe, but the Fe molar fraction steadily decreases while the Ni molar fraction increases. The molar fraction of Co increases till its maximum at $d_{\text{Fe-Co-Ni}} \approx 15$ nm. There is a maximum in the Ni molar fraction at $d_{\text{Fe-Co-Ni}} \approx 90$ nm, then the composition becomes stable at $d_{\text{Fe-Co-Ni}} > 140$ nm. This spontaneous near-substrate composition modulation in the neighbourhood of the substrate was always seen in the reverse depth profiles even if the electrolyte composition or the deposition current density were changed.

The composition oscillation at current densities higher than $-16$ mA/cm$^2$ does not stop after the first triplet of waves. The first Ni-rich zone is followed by an increment in the Fe and Co molar fraction again, then the oscillation is slowly damped (at least, the depth profile analysis cannot resolve more than two triplet of waves). The oscillatory behaviour as a function of deposition current density is demonstrated by Fig. 3. At $-24$ mA/cm$^2$ current density, the stabilization of the deposit composition is achieved after about 400 nm deposit thickness only. The stabilized deposit composition at this current density is Fe$_{27}$Co$_{10}$Ni$_{64}$. The decrease in Fe and Co concentrations in the deposit with increasing current density indicates that these metals are deposited nearly at their mass transport limiting rate.

**Fig. 1.** Conventional depth profile of a Fe–Co–Ni sample. Deposition current density: $-16$ mA/cm$^2$, deposition time: 225 s, average current efficiency: 97%. The total sample structure is: Si/Cr(5 nm)/Cu(20 nm)//FeCoNi(1250 nm).

**Fig. 2.** Total and near-substrate (inset) reverse depth profile of the same Fe–Co–Ni sample as presented in Fig. 1.
4. Discussion

The occurrence of the near-substrate composition oscillation can be understood by taking into account the nature of the codeposition process of the constituent metals and the depletion of the electrolyte in the vicinity of the cathode. First, the metal with the highest deposition preference (Fe) is accumulated at the cathode surface. Since the electrolyte concentration of Fe$^{2+}$ is the lowest among the electroactive species in the bath used, the vicinity of the cathode soon becomes depleted and the metal next in the row of preference (Co) starts to discharge at a high rate. Since the increase in the partial current density of the Co deposition cannot fully balance the consumption of the Fe$^{2+}$ ions in the vicinity of the cathode, the decrease in the Fe deposition rate is immediately followed by the increase of the deposition rate of the least preferred metal (Ni) to maintain the constant current. This composition change in the deposit is analogous to that found earlier for Co–Ni deposits [8,9].

The occurrence of more than one set of concentration waves in the solid phase cannot be explained by merely the deposition preference. We assume that the Ni-rich deposit surface is more favourable for the hydrogen evolution than that of the previous zones, and the Ni enrichment in the deposit leads to a loss of current efficiency due to the increase of the partial current for the hydrogen evolution. The hydrogen evolved leaves the electrode surface, hence stirring the solution and giving rise to the flush of the cathode with fresh electrolyte. Hence, the cycle can start again, though with a lower intensity than at the very beginning of the deposition process. After the first drop in Ni molar fraction in the deposit, the variations in the Fe and Co concentrations are parallel, which is an indirect evidence of the effect of convection.

The trend in composition change as a function of deposit thickness is different from that observed earlier for Fe–Co–Ni deposits. It was found for various electrolyte compositions [1,7] that the Ni content of the deposit decreases and Co content increases as the layer thickness is varied in the 50–1000 nm range. This can be due to the Co counter-electrode used in these studies [1,7]. However, the arbitrary change in the coercive field as a function of the sample thickness below 200 nm [6] might be explained by composition fluctuations similar to those found in the present study.

5. Conclusions

It was demonstrated that the reverse depth profile analysis is particularly suitable for analyzing the subtle changes in sample composition close to the substrate. It was found that the electrodeposition of Fe–Co–Ni alloys starts with a damping oscillation of the deposit concentrations. The oscillation period includes successive zones in which the molar fractions of Fe, Co and Ni reach their maximum in this order. The zone sequence was explained by the anomalous nature of codeposition and electrolyte depletion, whereas the repeat of the zone triplet was attributed to the impact of the electrolyte agitation by the hydrogen evolution occurring on the Ni-rich deposit surface.

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References