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3d metallic layers electrochemically deposited from nearly nonaqueous electrolyte[*]

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A method of electroplating shiny layers of Fe, Co, Ni, Cu and Zn from universal type of electrolyte has been reported. At the beginning of the process, the electrolyte consists only of dimethylketone and inorganic acid. Since the electrolyte contains small amount of reactive species, layers with thickness of 400 nm can be formed and removed out of an electrolytic cell. Magnetic properties of the Fe layer have been reported.

Key words: *electrodeposition; nonaqueous electrolyte*

1. Introduction

Electrodeposition of metallic layers has a wide range of technical applications. Processes of 3d metallic layer deposition are particularly important for electronics [1]. For example, we quote copper electrodeposition, known as the damascene process [2] used in chip production, or 3d magnetic layers used in magnetoresistive sensors [3]. Aqueous electrolytes are commonly used for metallic layers deposition. Usually electrolyte includes many substances for achieving a good quality of the deposited layer – a strong adhesion to the substrate and a flat surface. Thus multicomponent electrolytes are designed for rather limited compositions of the deposited layers. Nonaqueous electrolytes are used in electrodeposition of chemically reactive metallic layers like rare earths, aluminum or alkaline metals. The aim of this contribution was to demonstrate a new type of electrolyte which is almost nonaqueous and under similar condi-

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tions metallic layers of a few different 3d elements could be deposited. Some features of the deposited layers and the method of deposition have been presented.

2. The process of deposition

The electrolyte was composed of 95% dimethylketone and 5% ($HCl + H_2O$). Electrodeposits were obtained at room temperature on one side of the cathode discs (substrate) with the approximate surface area of 4 cm^2. Before electrodeposition, the substrates were mechanically polished.

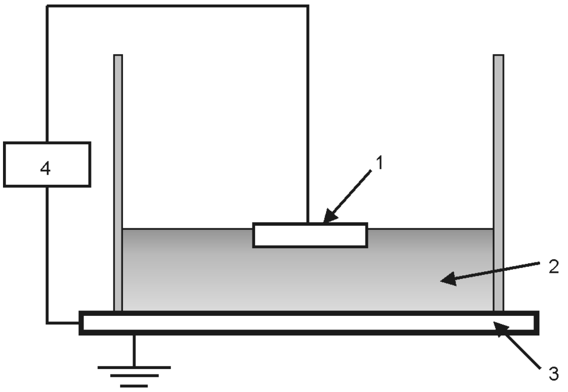

Fig. 1. The scheme of the electrochemical cell: 1 – anode, 2 – electrolyte, 3 – substrate, 4 – DC current source

The scheme of the electrochemical cell is shown in Fig. 1. The substrate was placed at the bottom of the cell. The anode was made of the element to be deposited. Approximately 5 cm^3 of electrolyte was used. Part of the anode was dissolved using DC current. After some time, concentration of ions in the electrolyte was self-adjusted and the process of deposition was performed. The density of cathodic current was stabilized to 5 mA/cm^2. The total time of the deposition was about 20 min. Under the same current conditions and nearly the same initial composition of the electrolyte, we were able to deposit shiny layers of five different elements: Fe, Co, Ni, Cu and Zn. Examples of Co layer deposited on Cu substrate and Cu layer deposited on Fe substrate are shown in Fig. 2.

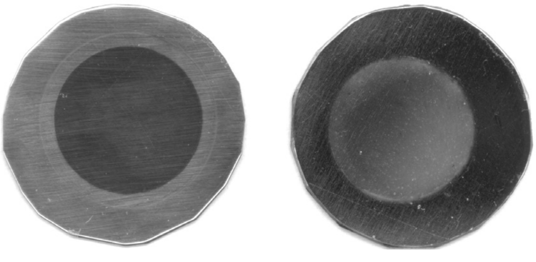

Fig. 2. Co layer on Cu substrate and Cu layer on Fe substrate obtained from nearly nonaqueous electrolyte

Small concentration of reactive HCl species does not result in fast corrosion of the deposited layers. Thus it is easy to safely remove smooth and shiny layer from the electrolytic cell.

3. Scanning electron microscopy results

To perform SEM measurements, samples were cut to pieces with the surface area of 1 cm^2. The pieces were covered by thermohardened resin and polished with emery paper and diamond powder suspension with decreasing gradation.

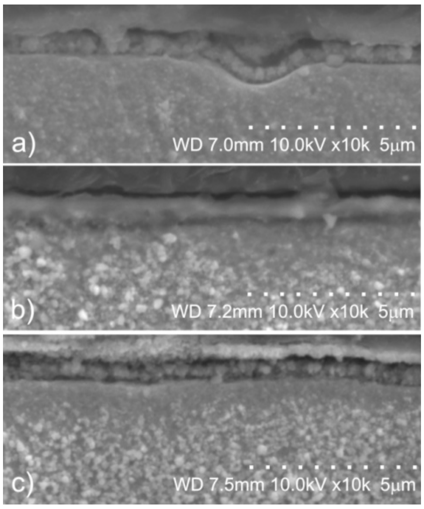

Fig. 3. The microstructure of the electrodeposited layers:
a) Co, b) Ni, c) Fe on the Cu substrate

The deposited layers of Fe, Co, and Ni obtained on Cu substrate were examined using the scanning electron microscopy with a beam size of approximately 1 µm. The microstructure of cross-sections of the layers are presented in Fig. 3. SEM measurements indicate that obtained layers are about 400 nm thick. Specific feature of the electrodeposition process is shown in Fig. 3a, where grove in the Cu substrate is covered by the Co layer of a uniform thickness.

4. Features of the process

Typical cation concentrations in electrolytes used are about 0.2–1.5 mol/dm^3 [4–6]. In the case of electrolyte used in our experiment, the cation concentration during the deposition process was about 0.03 mol/dm^3, over ten times smaller than typical concentrations used in electrodeposition processes. Low concentration of ions in the electrolyte is the apparent advantage of the method. It reduces costs of the process, especially in case of noble or expensive metals. The process can by used for deposition of layers of isotopically enriched samples. Another advantage of small ion concentrations is its potential applications in technologies of radioactive sources preparation. As an example, we quote ^{57}Co deposition which is used in Mössbauer spectroscopy [7]. We have found that small amount of water present in the electrolyte is essential for the deposition of metallic layers. The role of water molecules is, however, unclear.

5. Mössbauer measurements

The deposited Fe layer on Cu substrate was examined using the conversion electron Mössbauer spectroscopy (CEMS) with two geometries: the wave vector of photon **k** was perpendicular or almost parallel (approximately 2°) to the layer plane. Obtained CEMS spectra are shown in Fig. 4.

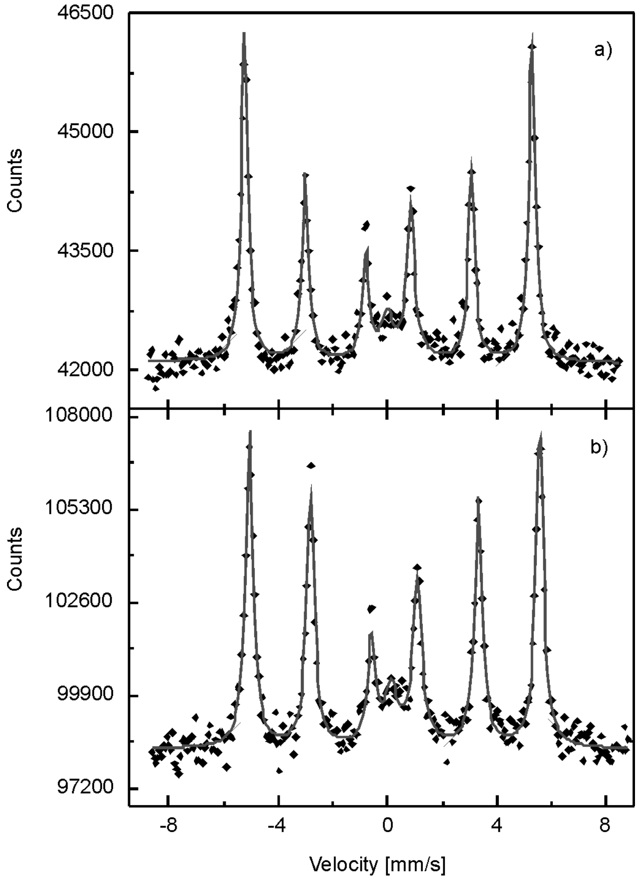

Fig. 4. The CEMS spectrum of an iron layer deposited on Cu and measured with **k** vector: a) perpendicular, b) almost parallel to the sample surface

Ratio of the intensities of the spectral lines observed in CEMS experiment depends on angle ϑ between directions of the **k** vector and the hyperfine magnetic field:

$$I_1:I_2:I_3:I_4:I_5:I_6 = 3(1+\cos^2\vartheta):4\sin^2\vartheta:(1+\cos^2\vartheta):(1+\cos^2\vartheta):4\sin^2\vartheta:3(1+\cos^2\vartheta) \quad (1)$$

It follows from Eq. (1) that in the case of magnetic moments arranged perpendicularly to the sample plane, $I_2/I_3 = 0$ for the **k** vector perpendicular to the surface, while $I_2/I_3 = 4$ for **k** parallel to the sample plane. In case of magnetic moments arranged in the sample plane, $I_2/I_3 = 4$ for **k** perpendicular while $I_2/I_3 = 4/3$ for **k** parallel to the surface. The Zeeman sextet and the doublet were fitted to the spectra. The obtained I_2/I_3 ratio is (1.73±0.04) for measurement with **k** vector perpendicular to the layer plane. This ratio increases to the value of (2.34±0.06) for measurement with low incidence angle. This indicates that magnetic moments have small preferential orientation, perpendicular to the sample plane.

6. Magnetization measurements

The magnetization measurements were carried out with the use of Vibrating Sample Magnetometer (VSM) model 7300 Lake Shore. Obtained magnetization curves

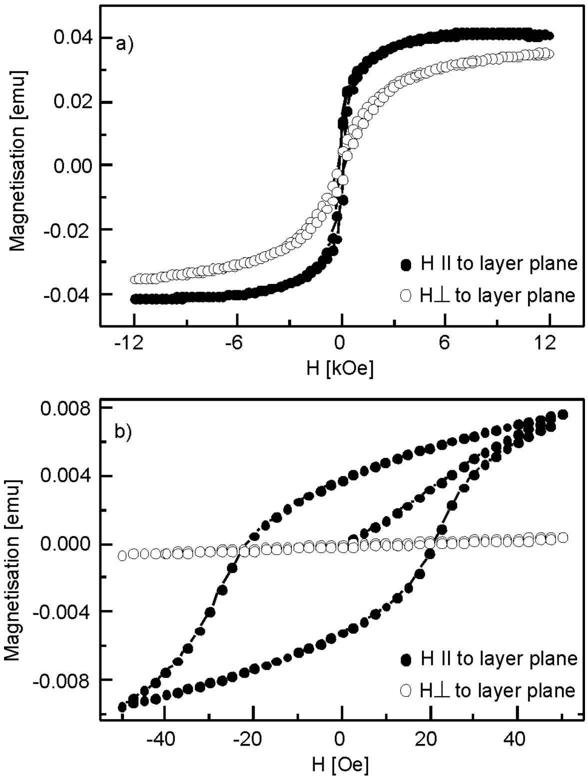

Fig. 5. Magnetization curves for Fe layer deposited on Cu substrate

measured at room temperature in strong (up to 12 kOe) and weak (up to 50 Oe) external magnetic field are shown in Figs. 5a and 5b, respectively. The shape of magnetization curves indicates that the Fe layer deposited on Cu substrate has an easy-plane type of magnetic anisotropy.

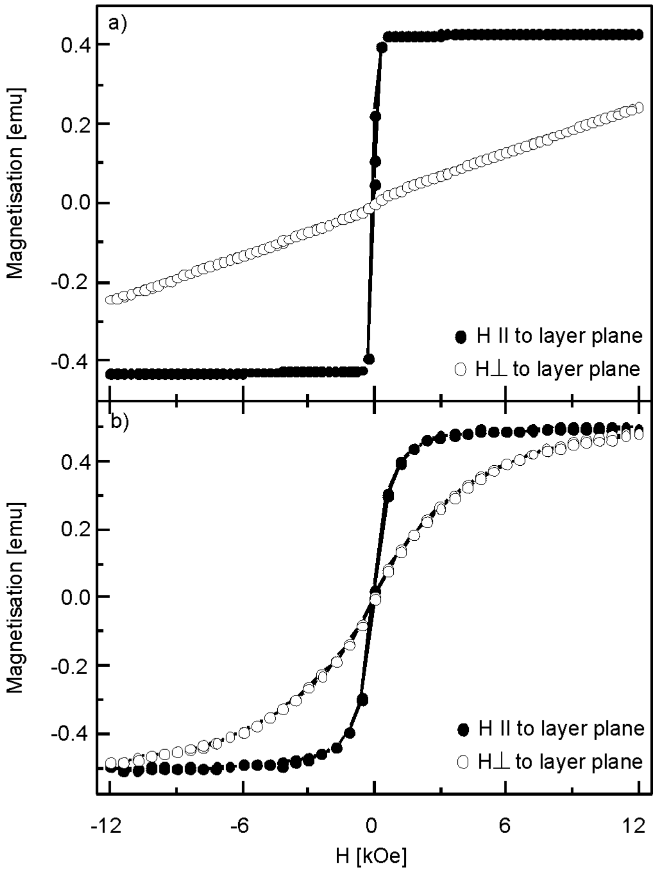

Fig. 6. Magnetization curves for: a) Fe foil, b) iron powder sample oriented in external magnetic field perpendicular to the sample plane

Two additional test samples with different types of magnetic anisotropies have been prepared. The first one was a pellet with the diameter of 1 cm, 1 mm thick, containing nonmagnetic filler (Li_2CO_3) and iron powder with the particle size about few micrometers. The iron particles and the filler were mixed with a two-component resin and exposed to magnetic field of about 1 T until solidification of the liquid components occurred. The magnetic field was perpendicular to the pellet plane. The procedure resulted in a preferred orientation of elongated iron particles [8]. The second test sample was pure iron foil of the thickness about 10 μm, rolled and annealed (900 °C for 1 h). Results of magnetization measurements are shown in Figs. 6a and 6b, respectively.

7. Discussion

CEMS measurements indicate that the magnetic moments are oriented in preferred direction, on average perpendicular to the sample plane. Magnetization measurements show that the deposited layer has rather an easy-plane type of anisotropy. However, the magnetization curves are substantially different from those measured for layer of magnetically soft material with clear shape anisotropy. Indeed, Fe foil is fully saturated in the magnetic field as small as 100 Oe (Fig. 6a) while the deposited layer saturates at the field as large as 6 kOe (Fig. 5a). Thus the in-plane magnetization processes in the deposited layer are strongly hindered. The possible reason for such behaviour is the presence of structural defects formed during the layer growth. Some inhomogeneities of the image of the Fe layer can be recognized in Fig. 3c. The magnetization curves (Fig. 5a) are similar to the magnetization curves of a pellet containing field oriented Fe particles (Fig. 6b). These similarities strongly suggest that there is a small perpendicular anisotropy in the deposited layer. The conclusion is in a full agreement with results of our CEMS observation. Details of the growth induced anisotropy are under investigation.

8. Conclusions

Nearly nonaqueous bath for deposition of the shiny metal layers has been reported. At the initial stage, the electrolyte does not contain cations of the deposited element. During the electrodeposition cation concentrations are much smaller than in typical electrolytes. We show that the same initial composition and the same current density is used for deposition of various 3d metals. Estimated thicknesses of the layers are of about 400 nm. Mössbauer measurements indicate that magnetic moments are preferentially oriented perpendicular to the film plane. Magnetization data of the deposited layer and the test samples were compared. It was concluded that small perpendicular anisotropy is present in the Fe layer deposited on the Cu substrate.

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References

[1] Mikhaylova M., Kim D.K., Toprak M. and Muhammad M., Mat. Res. Soc. Symp. Proc., 750 (2003), 51.
[2] Datta M., Electrochem. Acta, 48 (2003), 2975.
[3] Gomez E., Pellicer E., Duch M., Esteve J., Valles E., Electrochem. Acta, 51 (2006), 3214.
[4] Panda B., Das S.C., Hydrometallurgy, 59 (2001), 55.
[5] Chi-Chang Hu, Yau-Ruen Wu, Mater. Chem. Phys., 82 (2003), 588.

[6] MYUNG N.V., PARK D.-Y., URGILES D.E., GEORGE T., Electrochem. Acta, 49 (2004), 4397.
[7] STEPHEN J., Nucl. Instr. Meth., 26 (1964), 269.
[8] OLSZEWSKI W., SZYMAŃSKI K., SATUŁA D., DOBRZYŃSKI L., Nukleonika, 52 (2007), S17.

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