

THE EFFECT OF MAGNETIC FIELDS ON THE ELECTRODEPOSITION OF Co AND Cu

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Introduction. The influence of magnetic fields up to $\mu_0 H = 1$ T differently aligned to the electrode surface on the electrodeposition process and the resulting structure has been investigated. The MHD effect in electrodeposition was firstly mentioned by Fahidy *et al.* [1]. A magnetic field applied perpendicular to the ion current induces a Lorentz force $\mathbf{F}_L = \mathbf{I} \times \mathbf{B}$, which causes an additional convection in the hydrodynamic layer of the thickness δ_H (Fig. 1) close to the electrode. For diffusion-limited systems a decreasing thickness of the diffusion layer δ_D (Fig. 1) and an increasing deposition rate is the consequence. Two additional magnetic forces derived from the magnetic energy ε_{mag} act inside the diffusion layer and lead to the so-called magneto-convection. The paramagnetic force F_P results from the gradient of paramagnetic ions in the vicinity of the electrode surface, which leads to a gradient in the magnetic susceptibility [2]:

$$\mathbf{F}_P = \chi_m \cdot \frac{B^2}{2\mu_0} \cdot \nabla c, \quad (1)$$

where χ_m is the molar magnetic susceptibility, \mathbf{B} the magnetic flux density, μ_0 the permeability of the free space and ∇c the concentration gradient. As derived from (1), the force drives paramagnetic ions (positive algebraic sign) away from the electrode and thus reduces the deposition rate. If the magnetic field is inhomogeneous because of its source [3] or the magnetic behavior of the electrode [4], the field-gradient force $\mathbf{F}_{\nabla B}$ acts on the ions. For magnetically saturated electrodes resp. layers and homogeneous magnetic fields, as in the case considered here, this force can be neglected.

Aogaki *et al.* [4] has demonstrated, that so-called micro-vortexes appear in the vicinity of the electrode. This phenomenon is attributed to micro-MHD-cells and leads to magneto-convective effects in the diffusion layer usually being considered as free of convection. The micro-vortexes can originate from different physical sources. Here we present a model considering the paramagnetic force as driving force for this kind of convection.

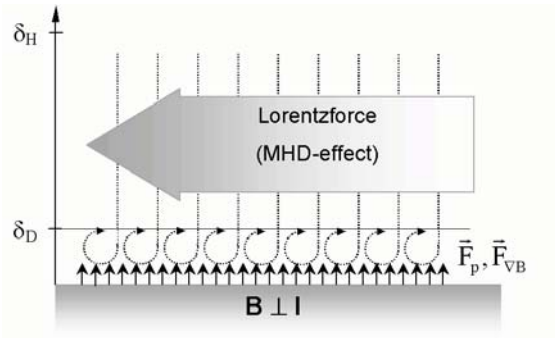


Fig. 1. MHD-effect and magneto convective effects.

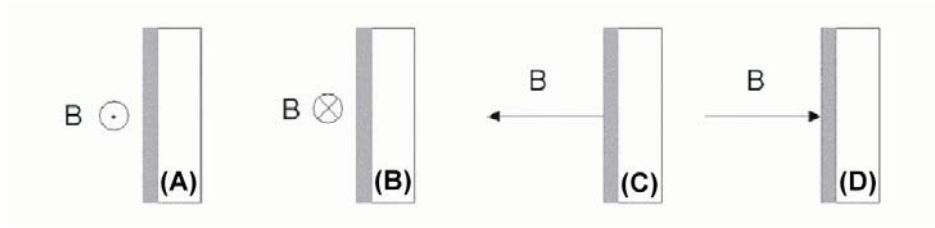


Fig. 2. Magnetic field to electrode orientations.

1. Experimental. 0.01 M CoSO_4 (or CuSO_4) + 0.1 M Na_2SO_4 , (pH 3) was used as electrolyte. The working electrode was a gold-coated quartz slice or a copper-coated Si(100)-wafer for the investigation of the layer structure.

The electrochemical cell is detailed described in [6]. In order to reduce edge effects the working electrode was placed under a viton-seal. The counter-electrode was a round-shaped platinum sheet with the inner diameter of the cell. It was positioned parallel to the working electrode surface to ensure parallel electrical field lines and a constant distance between the electrode. All potentials were measured versus a saturated Ag/AgCl-electrode. The used quartz-micro-balance system (QMB) is in detail described in [6].

The cell was placed horizontally in the gap of an electromagnet. Four different magnetic-field-to-electrode orientations has been investigated (Fig. 2), two parallel (A),(B) and two perpendicular (C),(D).

2. Results and discussion, Co deposition. Fig. 3a shows the change of the deposited mass calculated from the frequency change (QMB) and the limiting current density after one minute deposition time at a potential of $E = -1000$ mV_{SSE} depending on the orientation of the magnetic field ($\mu_0 H = 1$ T). In magnetic fields oriented parallel to the electrode surface ((A) and (B)) an increase of the limiting current density i_L and deposited mass was observed, caused by the classical MHD effect. In fields perpendicular to surface ((C) and (D)) i_L increases to the same order. Surprisingly, the deposited mass obtained from the frequency change decreases significantly with increasing field strength, indicating a suppression of the deposition rate due to F_P [6], caused by the relatively high magnetic susceptibility of Co^{2+} ($\chi_m = 10^{-8}$ m³/mol). Considering a linear concentration gradient and a diffusion layer thickness of $\delta = 100$ μm a value of $F_P = 400$ N/m³ at $\mu_0 H = 1$ T is calculated, which is about 40 times higher than the value of F_L for this system. Since ∇c increases exponentially with reducing the distance to the electrode it can be predicted that the real value in the very vicinity of the electrode surface is some orders of magnitude higher. Since F_P acts against the ion flow the interaction between both causes micro-vortexes as sketched in Fig. 1. When the deposited mass is reduced and the limiting current increased due to the magnetic field, the current efficiency decreases. It was shown in [6] that the current efficiencies for the orientation (A), (B) increase, but decrease for the orientations (C) and (D) in the order of 10%. This leads to the conclusion, that the hydrogen reaction is influenced by the magnetic field as well. It was shown recently by the authors, that the surface pH-value is also influenced by a magnetic field [7]. The transport-controlled discharge leads to a decrease of the proton concentration in the vicinity of the electrode and thus to an increase of the pH-value. If a magnetic field is applied parallel to the electrode ((A) and (B)), the depletion of proton concentration is lower due to the induced convection. In consequence, the pH-value increases to a less extend but more protons are discharged. The enhanced hydrogen evolution in perpendicularly oriented magnetic fields can not be explained by the MHD effect since no F_L acts when \mathbf{B} is parallel to \mathbf{I} .

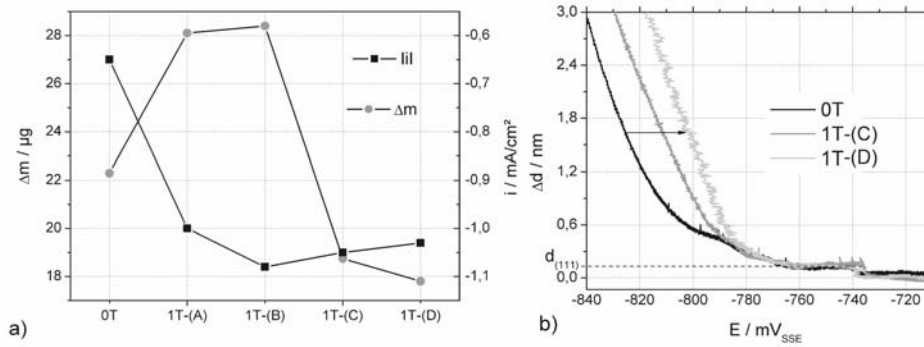


Fig. 3. (a) Influence of magnetic fields ($\mu_0 H = 1\text{T}$) on the i_L and Δm for the potentiostatic deposition of Co ($E = -1000\text{ mV}_{\text{SSE}}$; $t = 60\text{ s}$); (b) Quasi-potentiostatic $\Delta d(E)$ -curves in fields aligned perpendicular to the electrode ($dE/dt = 1\text{ mV/s}$).

Fig. 3b shows the quasi-potentiostatic QMB measurement for the orientations (C) and (D). At potentials more negative than $E = -740\text{ mV}_{\text{SSE}}$ the formation of one monolayer Co can be observed independent on the magnetic field. A second monolayer is formed at about $E = -780\text{ mV}_{\text{SSE}}$. In the presence of magnetic field the further growth of the layer starts significantly earlier, which is caused by an enhanced desorption of hydrogen atoms from the electrode surface. The mechanism of the enhanced desorption is still not clear. A diamagnetic effect is improbable because of the very small χ_m of $\mathbf{H}_{2(\text{g})}$. Otherwise, χ_m for $\mathbf{H}_{(\text{l})}$ is three orders of magnitudes higher. If the magnetic properties of the adsorbed atomic hydrogen are closer to liquid hydrogen than to gas the diamagnetic effect cannot be excluded. Another explanation is the micro-vortex theory proposed by Aogaki *et al.* [5]. If the magneto-convection acts close enough to the electrode surface desorption of adsorbed species could be the consequence.

It was shown by the authors in [8] that the surface roughness of the deposited films decreases for the orientations (A) and (B) but increases for the orientations (C) and (D). The TEM images (Fig. 4a,b) of the cross sections of the Co layers exhibit a homogenous structure and a very smooth surface for the orientation (B). In the case of orientation (C) a very disturbed microstructure and a high roughness was observed. The high roughness results from a wave-like surface (Fig. 4b), which is probably caused by the magneto-convection. Since the roughness is in the range of $R_m = 10\text{ nm}$ it is clearly proven that magneto-convection acts not only in the diffusion layer but also in the diffuse Helmholtz layer.

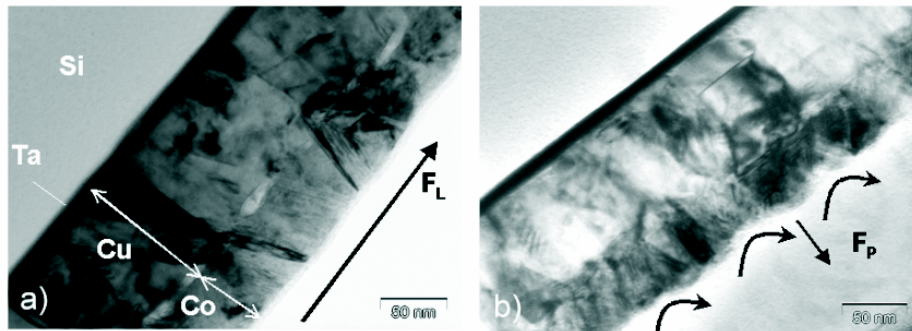


Fig. 4. TEM images of the cross section of Co layers ($d = 50\text{ nm}$, $E = -1000\text{ mV}_{\text{SSE}}$, $\mu_0 H = 1\text{T}$) (a) orientation (B), (b) orientation (C).

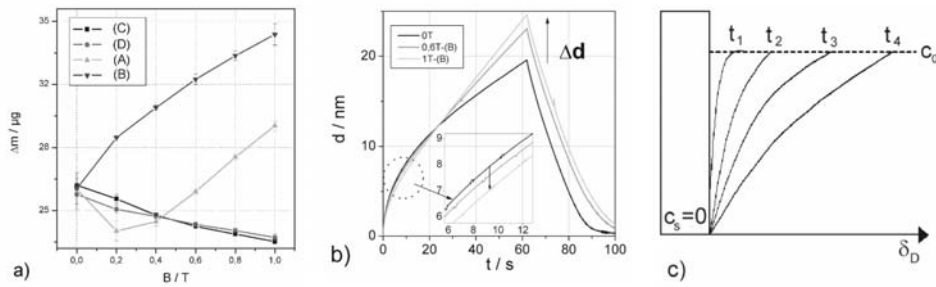


Fig. 5. (a) $\Delta m(B)$ -curves ($E = -500 \text{ mV}_{\text{SSE}}$) for Cu deposition in dependence on field direction and strength, (b) $d(t)$ -curves depending on magn. field strength, orientation (B), (c) time dependency of the concentration gradient ∇c .

3. Cu deposition. For the deposition of Cu at a potential of $E = -500 \text{ mV}_{\text{SSE}}$ in principle the same effects were found as for the Co-deposition (Fig. 5a). This was expected for the field-to-electrode orientations (A) and (B) but not for (C) and (D) since the χ_m of Cu is about one order of magnitude smaller than that of Co.

Fig. 5b exhibit for the orientation (B) that the layer thickness after 60s deposition time increases with the magnetic field strength, but decreases in the time range $0 \leq t_{\text{dep}} \leq 20 \text{ s}$. That means, that a strong F_P must act at the beginning of the deposition. The scheme in Fig. 5c explains this phenomenon. It shows clearly that ∇c is significantly higher in the first seconds of the deposition for low concentrations of metal ions. The increase of F_P and the reduction of deposition rate follow from equation (1). Therefore, the effect can only be measured for short deposition times.

4. Conclusion. Beside of the classical MHD effect we observed a magnetoconvection in the diffusion layer and the diffuse Helmholtz layer. Micro vortexes appear in these zones, caused by F_P , and increase the roughness in a nanometer scale. In the case of Co deposition F_P is mainly caused by the high χ_m , in the case of Cu deposition by a high ∇c in the first seconds of the deposition.

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