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Effects of well-defined magnetic field gradients on the electrodeposition of copper and bismuth

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ABSTRACT

Paramagnetic Cu^{2+}-ions have been electrodeposited under application of magnetic field gradients. Obtained deposits show a direct correlation of the distribution of magnetic flux density $\boldsymbol{B}$ at the electrode and the deposit thickness and morphology. In contrast to that no influence on the deposit structure has been observed for deposition of Bi from electrolytes containing diamagnetic Bi^{3+}-ions. This indicates that the structuring effect is mainly based on the action of the magnetic gradient force. A structuring-mechanism has been proposed that also discusses influences of the Lorentz force.

1. Introduction

Electrodeposition is a well-established method for production of thin metal layers and for surface finishing. In the past decades the influences of magnetic fields on electrochemical processes have been studied widely [1–15]. Although remarkable changes e.g. of the surface morphology of electrodeposits have been observed in non-homogenous magnetic fields, up to now no effort has been made to structure deposits with intent by application of magnetic field gradients (∇B-fields) [15–18]. For the first time we report on the structuring of Cu deposits by means of tailored moderate ∇B-fields generated by specifically designed magnetic field templates in comparison to Bi deposits that remain unaffected and we propose a structuring-mechanism.

2. Experimental

Electrochemical experiments have been performed at room temperature in an optimized three electrode Teflon® cell coupled to a potentiostat (Jaissle). A schematic of the cell geometry and electrode arrangement used is given in [19]. As working electrodes (WE) glass discs of 150 μm thickness evaporated with 200 nm of Au(1 1 1) (∅ = 13 mm) have been used. To establish well-defined ∇B-fields at the WE a magnetic field template prepared from 21 pure Fe wires (∅ = 1 mm, l = 3 mm) embedded in PVC (Fig. 1a) has been placed directly behind these discs. The wire axes have been aligned perpendicularly to the horizontal, downward facing WE and magnetized by a homogeneous magnetic field $\boldsymbol{B}_{ex}$ of 0.5 T (HV7, Walker Scientific). $\boldsymbol{B}_{ex}$ has been superimposed during electrodeposition in direction of the wire axes, i.e. perpendicularly to the WE. Thus not only a given gradient of $\boldsymbol{B}$ has been used, but a specific, well-defined ∇B-field has been generated at the WE. The B-distribution is easily adjustable by application of different magnetic field templates.

For comparison deposition experiments without the template in $\boldsymbol{B}_{ex}$ = 0.5 T as well as without $\boldsymbol{B}_{ex}$ have been performed. The electrolyte for Cu deposition contained 0.01 M $CuSO_4$ and 0.1 M Na_2SO_4 (as supporting electrolyte). Its pH value has been adjusted to 3.0 with H_2SO_4. To achieve comparable limiting current densities ($\boldsymbol{i}_{lim}$) for Bi deposition a solution of 0.01 M $Bi(NO_3)_3$ in 0.1 M HNO_3 has been used. Based on cyclic voltammograms potentials of $E = -160$ mV for Cu deposition and E = 140 mV vs. SHE for Bi deposition have been chosen for chronoamperometric depositions in the transport controlled regime. No side-reactions have been observed at these potentials. Simulations of B-distributions have been performed using the numerical 3D magnetostatic field solver *Amperes 6.0* (Enginia Research Inc.). Sample topographies and reflectivities have been analysed with an optical profilometer (MikroProf, FRT), morphologies have been characterized by SEM micrographs (LEO Gemini 1530, Zeiss).

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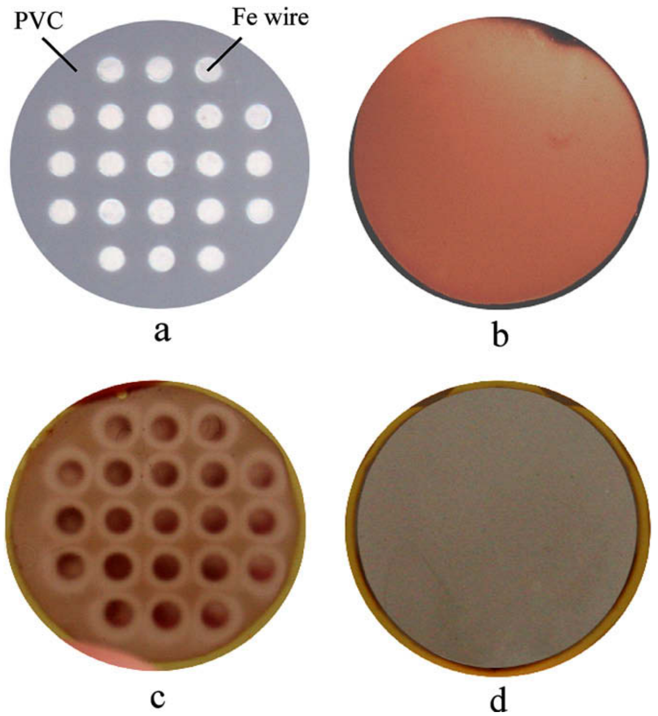

Fig. 1. Optical images of the used magnetic field template (a), a homogenous Cu layer deposited without the template (b), a structured Cu deposit (c) and a homogenous Bi layer (d) observed with the template behind the WE. Displayed deposits have been obtained by discharging 260 mC of Cu^{2+} or 400 mC of Bi^{3+} in $\boldsymbol{B}_{ex}$ = 0.5 T WE.

3. Results

As expected, electrochemical Cu depositions without $\boldsymbol{B}_{ex}$ and in a homogenous $\boldsymbol{B}_{ex}$ = 0.5 T yield homogenous layers (Fig. 1b). Chronoamperometric measurements do not show significant changes of $\boldsymbol{i}_{lim}$. Yet, structured Cu deposits and a strong increase of $\boldsymbol{i}_{lim}$ are obtained when the magnetized magnetic field template is placed behind the WE during the deposition process. The optical image of such a deposit is presented in Fig. 1c and displays, that the thickness distribution apparently correlates with the location of the Fe wires and hence the ∇B caused by these wires. The distribution of the magnetic flux density has been simulated and the product $B\nabla B$ at the WE is visualized in Fig. 2a. Obviously maxima of $B\nabla B$ are located near the Fe wire rims (indicated by black circles), whereas $B\nabla B$ is lower above the wire centre and decreases dramatically with increasing distance from the wire rim. In the centre of the WE the B-distribution above each wire is symmetric, whereas it is strongly non-symmetric above wires at the outer part of the template. This is a consequence of the interaction of the magnetic flux densities generated by neighboring wires.

The film thickness z exactly complies with this distribution. It is more than ten times thinner in regions of low $B\nabla B$ (z < 100 nm) than it is at the maxima of $B\nabla B$ ($z \approx 2$ μm) as profilometric studies of the Cu deposits reveal (Fig. 2b–d). Especially it has to be emphasized that in the central region of the WE where the B-distribution above one Fe wire is symmetric to its centre the same is valid for the deposit thickness (Fig. 2c). On the other hand non-symmetric deposit thicknesses result above Fe wires near the rim of the WE, where the B-distribution above one wire is strongly non-homogenous (Fig. 2d).

Additionally the roughness of the surface that can be visualized by reflectivity measurements (Fig. 2b) correlates to the B-distribution at the WE. In fact the deposit roughness is increased by at least one order of magnitude when regions of low and high $B\nabla B$ are compared. The remarkable influence of ∇B-fields on the surface morphology becomes obvious from SEM micrographs, as well. The rough surfaces that are obtained in regions of high $B\nabla B$ are characterized by columnar grain growth (Fig. 2e), whereas small grains and smooth surfaces are observed elsewhere (Fig. 2f).

In contrast to the structuring effect described above no influence of superimposed ∇B-fields could be observed for electrodeposition of equal amounts of bismuth. Homogenous Bi layers have been obtained in all cases. Neither optical images of the deposits (Fig. 1d) nor SEM micrographs of deposit morphologies (not presented here) indicate any difference as regions of high and low magnetic flux density are compared. Additionally no relevant influence of homogenous or non-homogenous $\boldsymbol{B}$ on $\boldsymbol{i}_{lim}$ has been found.

4. Discussion

The experimental data demonstrate that structuring of Cu electrodeposits is possible when ∇B-fields are superimposed during the deposition process. Maxima of deposit thickness correlate with maxima of $B\nabla B$, so evidently ∇B-fields can alter the current distribution at the WE. As the depositions have been performed in the mass-controlled regime this observation indicates enhanced mass-transport of Cu^{2+}-ions to these regions, leading to locally increased deposition rates. This assumption is reinforced by the columnar grain growth in regions of high $B\nabla B$, as it is typically observed at relatively high deposition rates [20]. Two different magnetic forces are known to be capable for such an effect: the Lorentz Force $\boldsymbol{F}_L$ and the magnetic field gradient force $\boldsymbol{F}_{\nabla B}$ [9,11]. Mostly, influences of B-fields on electrodeposition are attributed to a $\boldsymbol{F}_L$ induced convection, known as magnetohydrodynamic (MHD)-effect [1]. $\boldsymbol{F}_L$ results as cross-product of current density $\boldsymbol{i}$ and applied magnetic field $\boldsymbol{B}$:

$$\boldsymbol{F}_L = \boldsymbol{i} \times \boldsymbol{B} \quad (1)$$

Hence, it should be negligible in our optimized experimental setup [21], since $\boldsymbol{B}_{ex}$ is parallel to $\boldsymbol{i}$. The fact that without the Fe wire template no influence of $\boldsymbol{B}_{ex}$ on $\boldsymbol{i}_{lim}$ has been detected and that homogenous layers have been deposited (Fig. 1b) confirms this expectation. On the contrary $\boldsymbol{F}_{\nabla B}$ is only prominent in ∇B-fields and significant effects in moderate fields will result for processes involving paramagnetic species, especially. This becomes obvious as it is a function of the magnetic flux density $\boldsymbol{B}$ and its gradient ∇B applied at an electrochemical system containing species with molar magnetic susceptibility χ_m in a concentration c (μ_0 is the magnetic constant):

$$\boldsymbol{F}_{\nabla B} = \mu_0^{-1} \cdot c \cdot B \cdot \nabla B \quad (2)$$

$\boldsymbol{F}_{\nabla B}$ attracts paramagnetic ions to regions of high $B\nabla B$, whereas it only slightly repels diamagnetic ions, as their χ_m is essentially smaller [9,17]. Anyhow, if $\boldsymbol{F}_L$ were the main driving force for this structuring effect, it should only be affected by $\boldsymbol{i}$ and $\boldsymbol{B}$, but not by χ_m of the ions. This cannot be the case here, as although these parameters have been kept constant a structuring effect was observed for Cu but not for Bi depositions. Thus the structuring effect has to be attributed to $\boldsymbol{F}_{\nabla B}$ and χ_m of the deposited ions has to be taken into account. As mentioned above absolute values of χ_m are at least one order of magnitude smaller for diamagnetic ions like Bi^{3+} ($\chi_m \approx -0.5 \times 10^{-9}$ m^3/mol [22]) than for paramagnetic ions like Cu^{2+} ($\chi_m \approx 16 \times 10^{-9}$ m^3/mol [16]). Hence $\boldsymbol{F}_{\nabla B}$ attracts Cu^{2+}-ions to regions to of high $B\nabla B$ which results in an enhanced mass-transport to these regions, whereas $\boldsymbol{F}_{\nabla B}$ is not strong enough to alter the flux of Bi^{3+}-ions to the electrode, significantly. However, once $\boldsymbol{F}_{\nabla B}$ changed the flux of