

Effect of Gravitational Level on the Initial Stage of Cu Electrodeposition

Hirofumi INARI, Takao WAKATSUKI, Youko KONISHI, Yasuhiro FUKUNAKA¹ and Richard C. ALKIRE²

¹ Graduate School of Energy Science, Kyoto University, Yoshida Hon-machi, Sakyo-ku, Kyoto, Japan
fukunaka@energy.kyoto-u.ac.jp

² Department of Chemical and Biomolecular Engineering and National Center for Supercomputing Applications, University of Illinois at Urbana-Champaign, Urbana, Illinois, USA
r-alkire@uiuc.edu

Abstract

Copper was electrodeposited potentiostatically in 0.05 M CuSO₄ - 0.05 M H₂SO₄ aqueous solutions onto a TaN film sputtered on a silicon substrate. Two different electrolytic cell configurations were designed in order to discuss quantitatively the effect of gravitational level on the nucleation and growth of metal electrodeposition in detail: (a) a horizontal cathode surface facing downward over an anode (C/A) and (b) an anode over cathode (A/C). FE-SEM image demonstrates the progressive nucleation model on TaN substrate. A/C configuration introduces more number of nuclei than the case of C/A at a constant applied potential. Moreover, the comparison of nearest-neighbor distance distribution among precipitated particles with Poisson random distribution confirms the existence of "exclusion zone". The growth rate of the exclusion zone is surely influenced by the gravitational level. Then, the potentiostatic electrodeposition was engaged in A/C configuration inside a centrifugal field. The nucleus number density becomes slightly increased with increasing the gravitational level. It is saturated above 100 G.

1. Introduction

The copper wiring technology has been intensively studied because it has more reliability, lower resistance and cheaper than the aluminum. It is mainly due to the higher resistivity against electromigration for Cu than Al metal. IBM adopted the dual-damascene process as the copper wiring technology in 1997. This process involves the deposition of a diffusion barrier layer and a copper seed layer prior to electrochemical deposition of the copper. The diffusion barrier, typically Ta, TaN, TiN, or TiSiN, isolates the metallization from the silicon dioxide layer and prevents the diffusion of Cu metal into the dielectric layer. As the feature size of trenches and vias continues to shrink, the deposition of a continuous defect-free copper seed layer becomes increasingly difficult. Furthermore, the seed layer will produce a significant fraction of the metallization with feature sizes decreasing below 100 nm. As a result, the clean strategies for direct deposition on the barrier layer are being explored.

Nucleation kinetics and the growth of the first metallic nuclei formed on the initial substrate are critical steps determining the physicochemical properties of the electrodeposited metals. Therefore, a detailed understanding of nucleation and growth during electrodeposition is critical to design the deposition processes for void-free features and appropriate interface structure between copper and barrier layer for complex structures with small length scales, such as trenches and vias in integrated circuits. For this purpose, the essential effects of additive have been examined by trial and error in electrochemical processing. However, there are few quantitative examinations about the coupling phenomena between the ionic mass transfer rate and

the nucleation and crystal growth phenomena, although it provides the more fundamental information. [1-4].

We have introduced various parameters like gravitational levels and magnetic field fluxes as another degree of freedom to control the non-equilibrium electrochemical processing in order to tailor the unique nanostructured influence to create the advanced physical properties. These researches have demonstrated that the initial stage of electrodeposition including nucleation phenomena might be influenced by the change of gravitational level or the magnetic field flux, because the electrochemical phase transformation inherently involve the non-equilibrium heterogeneous surface reaction. These new reaction environments certainly change the ionic mass transfer rate to couple with the morphological variation of electrodeposited metals. In fact, it has been confirmed that effects of gravitational levels and magnetic field fluxes produce the drastic shape evolution variation of metals or the interesting behavior of bubble evolution [5-12]. Morisue et al. also showed that the difference of G level introduced a morphological difference of copper electrodeposition or even the nucleus number on polycrystalline copper substrate or TiN substrate [13,14].

We are now planning to engage in further experiments on electrodeposition in the drop shaft. The longer duration experiment in ISS is our goal. Here is a preliminary report to analyze the effect of gravitational level on the initial stages of copper electrodeposition on TaN substrate installed in a centrifuge.

2. Experimental

Copper was electrodeposited potentiostatically in 0.05 M CuSO_4 - 0.05 M H_2SO_4 aqueous solutions on a TaN substrate using a cavity-type electrolytic cell. 25 nm thick TaN diffusion barrier layer was sputtered on a silicon wafer (International SEMATECH). The electrolytic cell is illustrated schematically in Fig. 1. The effective cathode surface was limited to a circle with a 2 mm diameter by insulating a polycrystalline copper substrate with a silicon rubber sheet. The perforated anode with a 20 mm diameter was made of copper foil (Nilaco Inc.). A Teflon coated copper wire 0.5 mm in diameter (Nilaco Inc.) was utilized as a conventional reference electrode. Its edge was placed perpendicularly 2.5 mm away from the cathode surface. In order to apply the current to TaN substrate, copper foil was used. Cathode is fixed at the center of the copper foil by silicon sheet and acrylic sheet because the distance from the electrical contact has an influence on the electrodeposition behavior of copper [15].

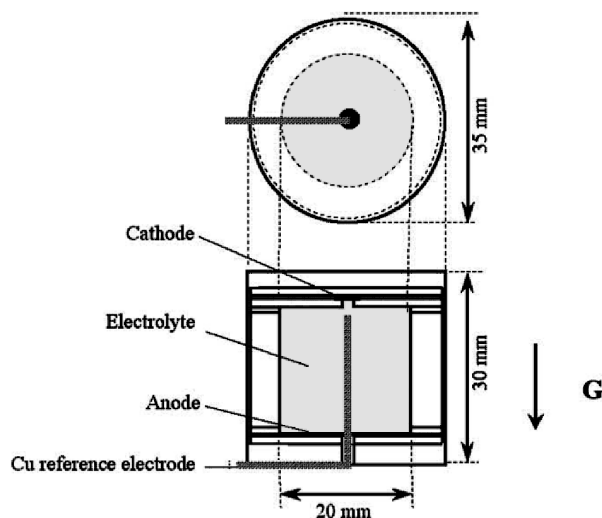


Fig.1 Cavity-type electrolytic cell in C/A configuration.

All solutions were adjusted with high-grade copper sulfate and sulfuric acid (Nacalai Tesque Inc.). Influence of oxide thickness on electrodeposition of copper on TaN substrate is known to be serious [16]. TaN substrates were immersed in 70% HNO_3 (Nacalai Tesque Inc.) for 30 s and then rinsed with distilled water prior to each experiment. The electrolyte was then deaerated for 1.5 hours by bubbling nitrogen gas. All experiments were performed at 25 °C and all potentials were measured vs. Cu^{2+}/Cu .

The effect of gravitational level to the initial stage of electrodeposition or the nucleation related phenomenon was examined by using two kinds of electrolytic cell configuration under 1-G

environment; one is a horizontally installed cathode surface facing downward over a horizontal anode (C/A), and another is an anode over a cathode (A/C). In the C/A configuration, the less concentrated and lighter electrolyte solution remained adjacent to the downward facing cathode surface. The gradient of the electrolyte density profile thus becomes parallel to the gravitational field vector. For produce high G environment, the centrifuge machine (Labnet International Inc.) was used.

Fig. 2 shows the centrifuge facilities equipped with an electrolytic cell. The centrifuge has a swing out rotor. Therefore the resultant force of the earth gravity force (1-G) and the centrifugal force always acts perpendicular to an anode and a cathode.

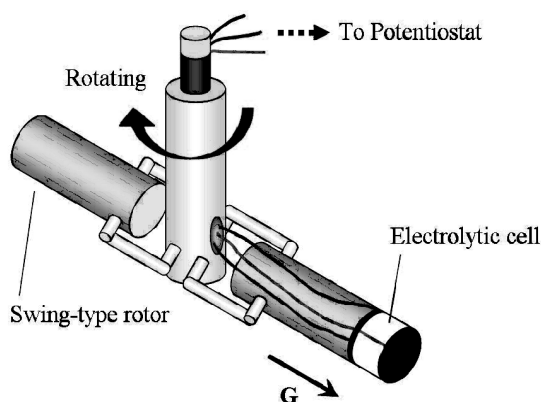


Fig.2 Centrifuge facilities equipped with an electrolytic cell.

3. Results

3.1 Electrodeposition under Normal G level (1-G)

Potentiostatic electrodeposition was carried out at various applied potentials. The amount of electricity was maintained constant at 31.8 mC/cm^2 as the experiment of copper on TiN substrate in our laboratory [14]. Firstly, the growth process of electrodeposited copper grains was examined in order to characterize the morphological variation of electrodeposited TaN substrate surface.

The current transients curve shows a significant differences between two configurations of C/A and A/C. The current transient curve apparently fluctuates after the current reaches to a peak in A/C configuration, while those in C/A decrease steadily. Bernard type natural convection should be inevitably induced with electrolysis in A/C configuration under normal gravity. Thus, the surface concentration of Cu^{2+} ion is maintained at a higher level than that in C/A after at least 20 seconds. Such a convection rotates inside a cell A/C configuration. Current fluctuation must be deeply related to this convection.

Next, the time dependence of copper grains electrodeposited at -1100 mV vs. Cu conventional reference electrode in A/C configuration was

examined. Copper grains were randomly precipitated on the TaN substrate, though the detailed image analysis indicates precipitated grains varying from 10 to 150 nm in size. The nucleus number densities N determined from FE-SEM images increased with time i.e. the amount of electricity. These results suggest that the copper electrodeposition on TaN substrate in our experimental system is “progressive nucleation” mode [17,18]. It is clearly contrast to the case on TiN substrate; “instantaneous nucleation” [14].

Copper was electrodeposited on TaN at various applied potentials vs. Cu^{2+}/Cu reference electrode in C/A and A/C configurations. In all experiments, the amount of electricity was set at 31.8 mC/cm^2 as mentioned before. At this amount of electricity, it was conformed that N was substantially saturated. Then N_0 is defined as this saturated nucleus number density. Fig. 3 shows FE-SEM images of copper precipitates electrodeposited on TaN substrate at -1100 mV . The image (a) corresponds to the sample electrodeposited in C/A configuration and (b) to that in A/C. A higher N_0 was obtained in A/C configuration than in C/A. The same tendency was found for the images obtained at other applied potentials.

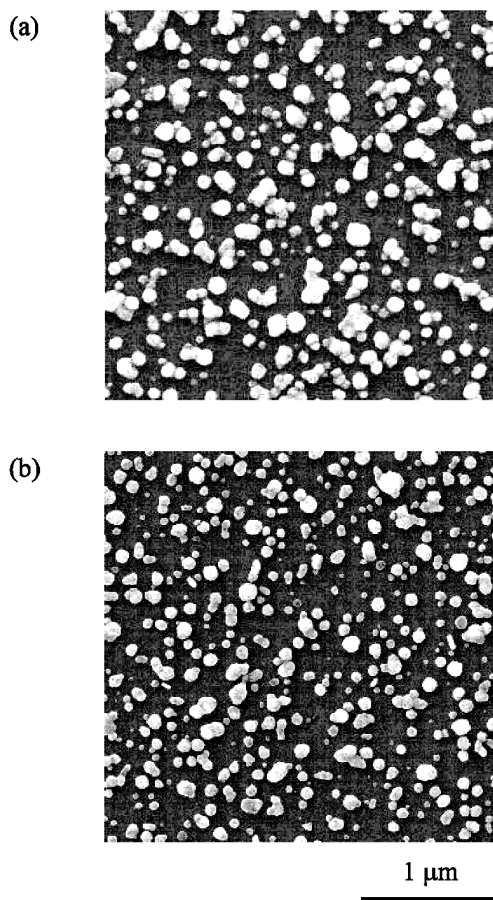


Fig.3 FE-SEM images of copper electrodeposited on TaN at 31.8 mC/cm^2 and -1100 mV under 1-G; (a) C/A and (b) A/C configuration.

Then image analysis were engaged in order to examine the applied potential dependence of N_0 obtained from $3 \times 3 \text{ μm}$ FE-SEM images. An exponential dependence of N_0 on the applied potential was recognized as expected. N_0 in A/C configuration are higher than in C/A over a wide range of applied potential. It well agrees with the previous experiment of copper onto TiN or silver onto HOPG in our laboratory. Moreover, the grain size distribution determined from the FE-SEM images indicates that the larger grain size is obtained with C/A configuration than that with A/C. It is simply because the lower N_0 was obtained with C/A configuration than with A/C at the same amount of electricity.

It is known that the diffusion fields growing around nuclei plays an important role in determining the kinetics of the early stages of electrodeposition. This concept of “exclusion zone” around the nucleus has been discussed in [19-29]. Similarly to the electrodeposition of copper on TiN substrate, the spatial distribution of precipitated nuclei will be examined from the aspect of correlation analysis. That is, the mean distance between the j th-neighbor nuclei r_j^* , the standard deviation σ_j and the ratio σ_j/r_j^* are examined with image processing technique. The correspondence between an experimental and a Poisson random distribution is quantitatively discussed. In both cell configurations, the quantities σ_j/r_j^* are smaller than the theoretical ones in all cases. Such a deviation from Poisson distribution surely confirms the presence of the exclusion zone.

The difference of mean distance r_j^* between in C/A and A/C configurations represents the degree of the influence of the exclusion zone on the nucleation phenomena. Consequently, the growth rate of diffusion layer around the growing nucleus is smaller in A/C than in C/A, because the surface diffusion rate of nuclei must be significantly influenced by the induced convection of electrolyte in A/C configuration.

3.2 Electrodeposition under High G Level in A/C Configuration

Under 1-G, N_0 in A/C configuration is higher and d_{mean} is smaller than those in C/A due to a kind of natural convection. Then, in A/C configuration, we introduce high G level force as another degree of freedom using centrifugal facility. The effect of high G level on the initial stage of copper electrodeposition is examined. The current transient accompanied with potentiostatic electrodeposition of copper on TaN at -1100 mV in A/C configuration is at first examined. The current transient is followed by the appearance of peak current. It usually starts dumping out with current fluctuation after the appearance of peak current, as clearly demonstrated in A/C configuration on TiN substrate [14]. The current transient is influenced by increasing in gravitational level. That is, the current peak

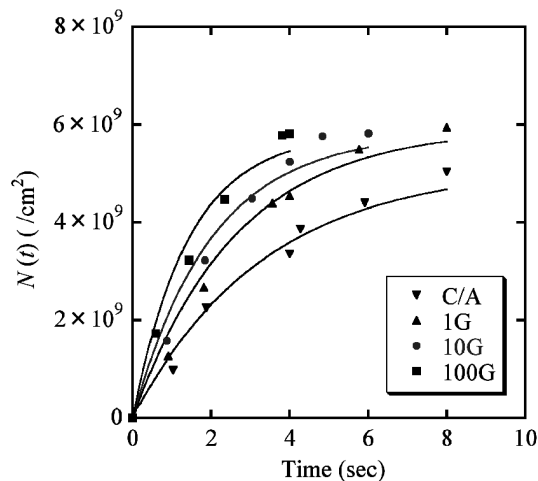


Fig.4 Time variation of the N under several G levels in A/C and C/A configuration (only 1-G).

significantly increases and the current fluctuation after the peak is dumped out with increasing in gravitational level. It is simply because the ionic mass transfer rate accompanying Bernard type convection due to the concentration difference between the electrode surface and the bulk electrolyte is enhanced under high G level in A/C configuration. It is expected that the period of current fluctuation becomes shaper with increasing in gravitational level. However, the current peak increasing with gravitational level is almost saturated under G level greater than 100 G. Then, the current fluctuation also disappears. 3D numerical calculation is necessary to understand the gravitational level effect of current transient.

Next, the nucleation phenomena are examined under several G levels. Copper is electrodeposited on TaN at 31.8 mC/cm^2 at -1100 mV and various G levels in A/C configuration. N_0 slightly increased with G level and saturated under the G level over 100 G as the current transients. But remarkable change such as the current transients was not seen. In this case, it is guessed that high G level have much more effects on the crystal growth than on the nucleation.

The time variation of nucleus number is examined under various G levels. Fig. 4 summarizes the time variation of nucleus number density N under several G levels at -1100 mV in A/C and C/A. In C/A configuration, only data under 1-G is shown. It is tried to correlation the measured time variation of nucleus number with a simple first order kinetic equation.

$$N(t) = N_0 [1 - \exp(-k_n t)] \quad (1)$$

where $N(t)$ is the time-dependent nucleus number density, N_0 is the saturated nucleus number density, and k_n is the nucleation rate constant. Eq. (1) provides a good fit to the experimental data under

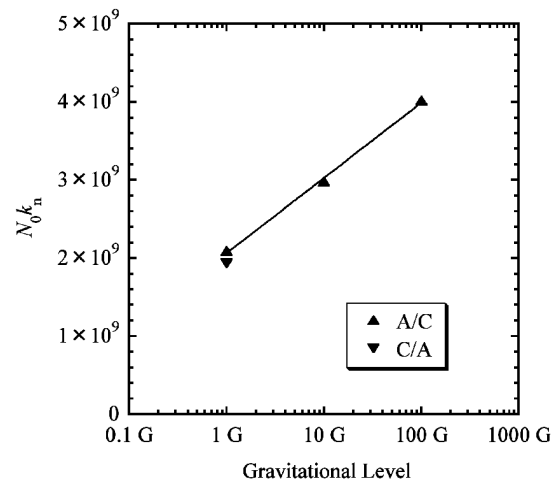


Fig.5 Effect of G level on the nucleation rate ($k_n N_0$) in A/C and C/A configuration (only 1-G).

various gravitational levels. It suggests that the present experiment of copper electrodeposited by the progressive nucleation and the characteristics of progressive nucleation phenomena is described well by first order kinetics and a nucleation rate constant k_n . Fig. 5 shows the nucleation rate ($N_0 k_n$) linearly increased with the gravitational level at -1100 mV in A/C configuration. However, the experimental results suggest an upper limitation to increase the nucleation rate ($N_0 k_n$) by applying the high gravitational level over 100 G, as mentioned above.

4. Discussion

Our previous experiments showed many effects of gravitational level on copper deposition on polycrystalline copper substrate [13]. Galvanostatic electrodeposition was conducted in a quasi 2 D electrolysis cell with $200 \mu\text{m}$ thickness horizontally installed. When the electrodeposition of copper in 0.9 M CuSO_4 aqueous solution on polycrystalline copper substrate was engaged in during a free-fall experiment in a drop shaft, a common path microscopic interferometry was newly designed. The growth of the diffusion boundary layer of Cu^{2+} ions associated with galvanostatic electrodeposition of copper was successfully measured in situ under $\mu\text{-G}$. It was confirmed that natural convection was certainly induced even in such a shallow and horizontal electrolyte layer of $200 \mu\text{m}$ thick. Measured voltage drop between both electrodes showed an abrupt increase during galvanostatic electrodeposition, which suggested that the surface concentrations of Cu^{2+} ion reached zero under microgravity conditions. After only 8 s, a significant different morphology of copper appeared on Cu substrate in galvanostatic electrodeposition. Larger grains with preferential growth of lower indexes were obtained under $\mu\text{-G}$. It corresponds to a smaller nucleation rate under $\mu\text{-G}$.

For the potentiostatic electrodeposition of copper

on TiN substrate in 1-G environment, even in “instantaneous nucleation” mode was confirmed. Moreover, the nucleus number density was smaller in C/A than in A/C configuration. This means that the effect of G level appears in the initial stage of electrodeposition. From these results, in experiment under μ -G, it is expected that the nucleus number density decreases and the grain size become larger than that under ground level and high G level.

The progressive nucleation mode was confirmed in the potentiostatic electrodeposition onto TaN substrate. The effect of G level on nucleation and crystal growth of copper electrodeposition was confirmed similarly to the case of TiN substrate in spite of the difference of nucleation mode; a significant difference was found in two different C/A and A/C configurations under 1-G environment. The reason why such a difference of the nucleation rate (N_0k_n) is introduced by increasing in gravitational level may be understood as follows. The different propagation rate of diffusion layer is introduced in the electrolysis cell by the enhanced ionic mass transfer rate accompanying a kind of Bernard type natural convection. Higher surface concentration is maintained. It surely accelerates the enhancement of nucleation rate for the case of progressive nucleation mode. This deduction why the nucleation rate increases at higher gravitational level can be acceptable provided that the nucleation phenomena is governed by the progressive nucleation mode.

Although the potentiostatic electrodeposition can be regarded to be instantaneous nucleation mode, the existence of exclusion zone around the nuclei has been surely confirmed. The surface diffusion of cluster toward the precipitated nuclei might be governed by a microscopic fluctuation of electrolyte or such a microscopic convection may not be dumped out as long as the experiment was conducted under 1-G environment. This may explain the effect of gravitational level on the nucleation associated with potentiostatic electrodeposition.

Hence, the coupling phenomena of the diffusion and migration mechanism to electrocrystallization under several G levels particularly under μ -G must be further examined.

5. Conclusion

Copper was electrodeposited potentiostatically for 31.8 mC/cm^2 on TaN substrate. Under normal G level (1-G), two kinds of electrolysis cell configuration of cathode over anode (C/A) and anode over cathode (A/C) were employed. The current transient curves are significantly influenced by electrolytic cell configuration. Moreover, it was found that the nucleation mode was progressive on TaN substrate. The nucleus number density was higher in A/C than in C/A configuration. The gravitational effect on the nucleation related phenomena seems to appear much earlier than the induction of macroscopic natural convection. With

the statistical spatial analysis, the deviation from the random Poisson distribution should be ascribed to the presence of exclusion zones. The exclusion zone length in C/A is larger in A/C configuration.

Under higher G level, the effect of gravitational level on the current transient is quite significant. The nucleus number density $N(t)$ is saturated under high G level earlier than under low G level. The saturated nucleus number density N_0 becomes slightly increased with increasing in gravitational level and is substantially saturated over 100 G. This is because the ionic mass transfer rate due to the concentration difference is significantly enhanced to increase the nucleation rate $k_n N_0$.

It was found that the nucleation and crystal growth process was significantly influenced by introducing various high G levels as new parameters into the non-equilibrium electrochemical processing on TaN substrate. Hence, it is desired that more experiments should be done under a wider range of gravitational level from μ -G to high G and at longer electrodeposition time. Such kind of information may be useful whenever the centrifugal field is applied to the non-equilibrium processing to create or tailor the unique interface structure in nano space.

References

- 1) P.C. Andricacos et al., *IBM J.Res.Develop.*, **42**, 567, 1998
- 2) P. C. Andricacos, *Electrochem. Soc. Interface*, 1999
- 3) T. Sugii, T. Nakamura, *FUJITSU*, **52**, 4, 2001
- 4) T. Yoda et al., *TOSHIBA*, **59**, 8, 2004
- 5) M. Ishikawa and T. Okubo, *J. Crystal. Growth*, **233**, 408, 2001
- 6) P. RV and R. LL, *Acta Astronaut*, **48**, 163, 2001
- 7) M. H. Johnston and C. Griner, *Metall. Trans.* **8A**, 77, 1977
- 8) X. Y. Liu, *J. Chem. Phys.*, **11**, 1628, 1999
- 9) H. Matsushima, T. Nishida, Y. Konishi, Y. Fukunaka, Y. Ito and K. Kuribayashi, *Electrochim. Acta*, **48**, 4119, 2003
- 10) H. Matsushima, Y. Fukunaka and K. Kuribayashi, *Electrochim. Acta*, **51**, 4190, 2006
- 11) M. Motoyama, Y. Fukunaka and S. Kikuchi, *Electrochim. Acta*, **51**, 897, 2005
- 12) H. Matsushima, Y. Fukunaka, Y. Ito, A. Bund and W. Plieth, *J. Electroanal. Chem.*, **587**, 93, 2006
- 13) Y. Fukunaka, K. Okano, Y. Tomii, Z. Asaki and K. Kuribayashi, *J. Electrochem. Soc.*, **145**, 1876, 1998
- 14) M. Morisue, Y. Fukunaka, E. Kusaka, R. Ishii and K. Kuribayashi, *J. Electroanal. Chem.*, **559**, 155, 2003
- 15) A. Radisic, Y. Cao, P. Taephaisitphongse, A. West, and P. Searson, *J. Electrochem. Soc.*, **150**, C362, 2003
- 16) A. Radisic, G. Oskam, and P. Searson, *J. Electrochem. Soc.*, **151**, C369, 2004
- 17) B. Scharifker and G. Hills, *Electrochem. Acta*,

- 28, 879, 1983
- 18) A. Milchev, "ELECTROCRYSTALLIZATION: Fundamentals of Nucleation and Growth", Kluwer Academic Publishers., 2002
- 19) A. Milchev, *J. Electroanal. Chem.*, **312**, 267, 1991
- 20) A. Milchev, *Electrochem. Acta*, **37**, 2229, 1992
- 21) E. Michilova and A. Milchev, *Electrochem. Acta*, **37**, 2233, 1992
- 22) A. Milchev, W. Kruijt, M. Sluyters-Rehbach, and J. Sluyters, *J. Electroanal. Chem.*, **362**, 21, 1993
- 23) W. Kruijt, M. Sluyters-Rehbach, J. Sluyters, and A. Milchev, *J. Electroanal. Chem.*, **371**, 13, 1994
- 24) A. Milchev, E. Michailova, and I. Lesigiarska, *Electrochem. Com.*, **2**, 407, 2000
- 25) E. Garcia-Pastoriza, J. Mostany, and B. Scharifker, *J. Electroanal. Chem.*, **441**, 13, 1998
- 26) A. Serruya, J. Mostany, and B. Scharifker, *J. Electroanal. Chem.*, **464**, 39, 1999
- 27) E. Budevski, G. Staikov, and W. Lorenz, *Electrochemical Phase Formation and Growth – An Introduction to the Initial Stage of Metal Deposition*, VHC, Weinheim, 1996
- 28) A. Radisc, J. G. Lomg, P. Hoffmann, and P. Searson, *J Electrochem.Soc.*, **148**, C41, 2001
- 29) A. Milchev, W. Kruijt, M. Sluyters-Rehbach and J. Sluyters, *J. Electroanal. Chem.*, **350**, 89, 1993

Received October 23, 2006

Accepted for publication, May 30, 2007