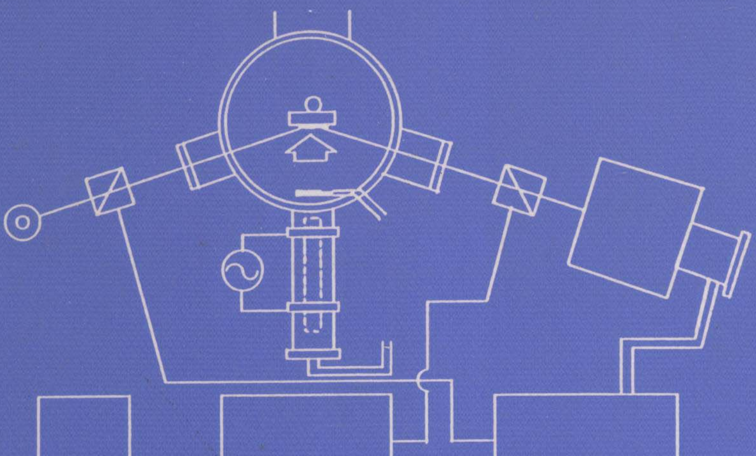
New Trends and Approaches in Electrochemical Technology

Edited by
N. Masuko, T. Osaka and
Y. Fukunaka



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and Yasuhiro Fukunaka

KODANSHA
Tokyo

VCH
Weinheim · New York
Basel · Cambridge

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Library of Congress Cataloging-in-Publication Data

New trends and approaches in electrochemical technology/edited by
Noboru Masuko, Tetsuya Osaka, and Yasuhiro Fukunaka.
p. cm.
Includes index.
ISBN 1-56081-781-X : $120.00 (est.)
1, Electrochemistry, Industrial. I. Masuko, Noboru, 1935— ,
II. Osaka, Tetsuya, 1945— . III. Fukunaka, Yasuhiro, 1944— .
TP257. N49 1993
660'.297--dc20 92-46440
CIP

Die Deutsche Bibliothek-CIP-Einheitsaufnahme

New trends and approaches in electrochemical technology/ed.
by Noboru Masuko...-Tokyo: Kodansha; Weinheim; New
York; Cambridge; Basel: VCH, 1993
ISBN 3-527-28574-1 (VCH, Weinheim...)
ISBN 1-56081-781-X (VCH, New York...)
ISBN 4-06-206137-6 (Kodansha)
NE: Masuko, Noboru [Hrsg.]

A CIP catalogue record for this book is available from the British Library.

Published jointly by
Kodansha Ltd., Tokyo (Japan),
VCH Verlagsgesellschaft mbH, Weinheim (FRG) and
VCH Publishers Inc., New York, NY (USA)

Printed in Japan

New Trends and Approaches in Electrochemical Technology

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Exclusive sales rights for
Japan, Taiwan, Hong Kong, Republic of Korea and People's Republic of China:
Kodansha Ltd., 12-21, Otowa 2-chome, Bunkyo-ku, Tokyo 112-01 (Japan)
Distribution for
Switzerland: VCH Verlags AG, P. O. Box, CH-4020 Basel (Switzerland)
Great Britain and Ireland: VCH Publishers(UK), Ltd., 8 Wellington Court, Wellington Street, Cambridge, CB1 1HZ (Great Britain)
USA and Canada: VCH Publishers, Suite 909, 220 East 23rd Street, New York, NY 10010-4606 (USA)
for all other countries: VCH Verlagsgesellschaft, P. O. Box 101161, D-6940 Weinheim (Federal Republic of Germany)

ISBN3-527-28574-1 VCH Verlagsgesellschaft
ISBN1-56081-781-X VCH Publishers
ISBN4-06-206137-6 Kodansha Ltd.

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Preface

Over the past few decades, the electronics industry has gone through a very rapid evolution towards microscale surface finishing, where high-tailored surface finishing including film formation, etching and ion implantation plays an important role.

Electrochemists and electrochemical engineers have developed many new processes and techniques, including plating and etching with photo-mask technology which permits micron and sub-micron dimensions, plating with extremely tight thickness and composition control, and plating with tightly controlled agitation and current distribution. Nowadays some of the most advanced techniques include electroless plating of a cobalt alloy with a very thin and homogeneous thickness for high-density magnetic disks, electroplating of a permalloy alloy with high compositional control in narrow places for the thin-film magnetic recording head and electroless plating of copper with very reliable connectors for more than 60 multi-layer boards. The demands of the electronics industry thus present a tremendous challenge to electrochemists and electrochemical engineers worldwide.

The International Symposium on Electrochemical Technology in Electronics held in October 1987 in Honolulu, Hawaii, as a part of the 172nd meeting of the Electrochemical Society Inc. was cosponsored by the Electrochemical Society of Japan and the Japan Society of Applied Physics. In September 1989, symposia on Electronic Materials in Electrochemical Technology and Electrochemical Processing for Tailored Materials were held in Kyoto, Japan, as part of the 40th International Society of Electrochemistry (ISE) Meeting. Some of the coorganizers of these symposia decided to publish review books on this field to stimulate further high-tailored research in electrochemical technology.

Hence, the editors selected various topics from these three symposia as the basis for this volume. We hope the topics discussed will contribute to the development of a higher level of electrochemical processing and create new areas of research and development.

January 12, 1993

Noboru Masuko
Tetsuya Osaka
Yasuhiro Fukunaka

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I

New Trends in Electrochemical Technology

1

Future Perspectives in Electrochemical Processing and Technology

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1.1 Introduction

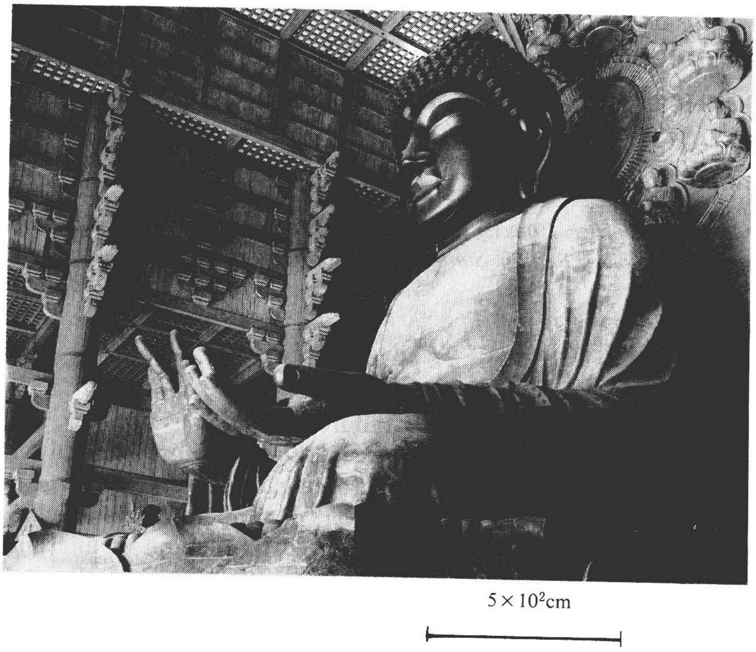
While the subject of thin film growth on tailored materials is not new, its fundamental basis has not been fully established. It is possible to trace work back to AD 752–757 in Japan, when ancient craftsmen applied a gold-amalgam process to a large bronze statue 15 meters high, to plate a uniform gold layer of 5 micrometers thickness. Today, sophisticated wet processes are applied to advanced fabrication of micron size devices. For instance, magnetic thin film heads are fabricated utilizing micro-pattern electroplating technology through polymeric mask (see photo). Nevertheless, the development on electrodeposition processes still seems to remain as a state-of-art technology, and the theory of electrodeposition tends to limp behind the art to some extent. Further progress in basic understanding of electrodeposition processes will be essential for process optimization and, more importantly, for creative designs of innovative electrochemical systems, despite the wide variety of electrodeposition processes and the complicated chemistry involved.

In this short overview, the two key factors affecting the microscopic morphology, on a scale (microns) comparable to the thickness of solid phases on a substrate, of electrodeposited layers are discussed. Morphology of electrodeposit is influenced by various process variables, e.g. substrate materials, current density or cathode potential, electrolyte temperature, concentration of metal ion (*i.e.* major discharged species), other cations, anions, complexing ligands, inhibitors and pH, agitation of electrolyte which occasionally is not well-defined quantitatively, etc. From a phenomenological point of view, the electrodeposit becomes noncoherent, spongy, dendritic and/or powdery in general in the specific current density range, namely, at or below the exchange current density i_0 and at or above the mass-transfer limiting current density i_L. Compact deposits are obtained in a certain current density range in between i_0 and i_L, to the contrary. It should be noted that the aim of this overview is to provide a framework of ideas, in view of both kinetic and mass transfer parameters, which can be used to visualize various industrial electrodeposition processes in perspective.

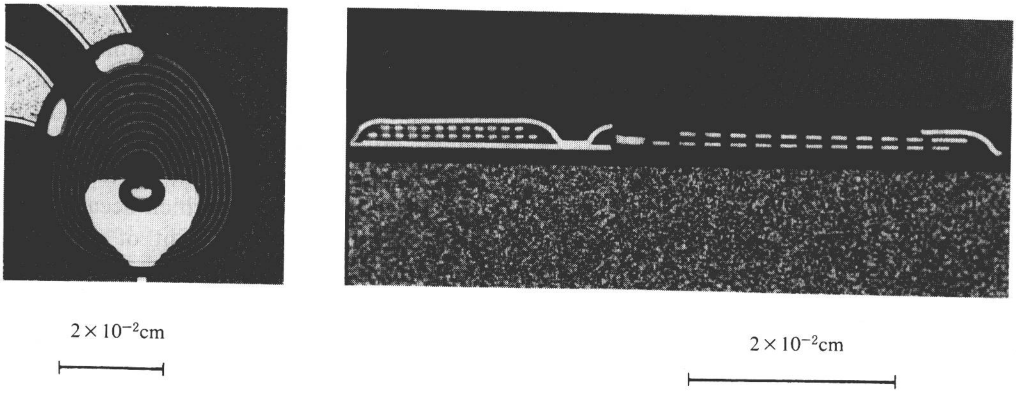
1.2 Electrodeposition Process

1.2.1 Kinetic and Transport Aspects of Electrodeposition

A relation between flux of electrodeposited species $N_{(j)}$ and partial current density $i_{(j)}$ is represented in Faraday's law equation for each species j:



(a) The gold plated statue of Buddha in Nara



Top view

Cross-sectional view

(b) Electroplated Cu inductive coils and Ni-Fe (permalloy)
Plated pole pieces of magnetic thin film heads

Photo 1. Tailored materials manufactured by wet-processes in ancient and modern Japan.

$$N_{(j)} = i_{(j)}/Z_jF \tag{1.1}$$

where Z_j is the number of electrons transferred in the cathodic reaction, and F is the Faraday constant. The average growth rate normal to the substrate of electrodeposited layer in the presence of simultaneous side reactions, such as hydrogen co-evolution, is then given by,

$$R_g = i\varepsilon_F M/ZF\rho \tag{1.2}$$

where R_g denotes the growth rate, i the total plating current density, ε_F plating current efficiency, M molecular weight, ρ the density of electrodeposited metal, and Z the number of electrons consumed or released in an electrochemical reaction.

Thin boundary layer approximation leads to the separation of the electrodeposition process into two parts. Firstly, the description of the kinetics very close to the cathode in the reaction layer (of the order of 1–10 nm), and secondly the description of the mass transfer of ionic species through the diffusion boundary layer from the bulk of solution to just outside the reaction layer.

Electrodeposition rate may be expressed by the Tafel equation in case $|\beta ZF\eta/RT| \gg 1$

$$i = i_0 \exp[-\beta ZF\eta/RT] \tag{1.3}$$

or in the rate constant form, assuming first-order rate process,

$$k_R = k_R^0 \exp[-\beta ZF\eta/RT] \tag{1.4}$$

$$N_{(j)} = k_R C_S \tag{1.5}$$

where i_0 stands for exchange current density, β transfer coefficients, η surface overpotential, R gas constant, T absolute temperature, k_R heterogeneous rate constant, k_R^0 value of k_R at $\eta = 0$, C_S denotes the concentration of metallic ions just outside the double layer.

General equation for the mass transfer of species j in a dilute electrolyte[1)] may be written as a summation of the electric migration term, diffusion term and convection term.

$$\tilde{N}_{(j)} = -Z_jU_jFC_j\nabla\Phi - D_j\nabla C_j + C_j\tilde{V} \tag{1.6}$$

Here, the subscript j designates species j, $\tilde{N}_{(j)}$ vector flux of species j, U the mobility, Z the ionic charge, C the concentration, d the diffusion coefficient, and $\tilde{V}$ the fluid velocity vector. Influence of the ionic migration can be neglected in the presence of excess supporting electrolyte, thus Eq. (1.6) reduces to the convective-diffusion case.[2)] By introducing mass transfer coefficient k_M, the flux being transported through the diffusion layer δ_D towards the outside of the double layer is then

$$N_{(j)} = k_M(C_\infty - C_S) \tag{1.7}$$

and

$$k_M = D_j/\delta_D \tag{1.8}$$

where, C_∞ is the bulk concentration of metallic ions to be electrodeposited. Substitution of Eqs. (1.7) and (1.8) to Eq. (1.5) gives,

$$C_S = \frac{C_\infty}{1 + (k_R/k_M)} \tag{1.9}$$

$$N_{(j)} = C_\infty\left(\frac{1}{k_R} + \frac{1}{k_M}\right)^{-1} \tag{1.10}$$

Limiting current density can be obtained when $C_S = 0$, for Eq. (1.7), and combining Eq. (1.1),

$$N_L = k_M C_\infty \tag{1.11}$$

or

$$i_L = ZFDC_\infty/\delta_D \tag{1.12}$$

The degree of electrodeposition uniformity is characterized by the Wagner number, which represents the ratio of the electrochemical reaction to the Ohmic resistances.

$$W = \frac{\kappa}{L} \cdot \frac{d\eta}{di} \tag{1.13}$$

or

$$W = \frac{\kappa RT}{Li\beta ZF} \quad \text{for Tafel polarization} \tag{1.14}$$

Here, κ is the conductivity of electrolyte, and L is the characteristic length dimension. The larger the Wagner number, the more negligible the primary current distribution. For microscopic topography of electrodeposits in the length order of microns, where $L \ll 1$, microscopic current distribution would be nearly independent of ohmic potential differences in the electrolyte, corresponding to very large W.

1.2.2 Electrocrystallization of Metal

The driving force of electrocrystallization[3)] may be written as,

$$\Delta\mu = kT \ln(1+\sigma) \tag{1.15}$$

where k is the Boltzmann constant and σ is the supersaturation expressed by

$$\sigma = \exp\left[-\frac{ZF\eta}{RT}\right] - 1 \tag{1.16}$$

On a parallel with the vapor deposition of metals, growth rate R_g and nucleation rate would be increased as supersaturation is increased. Unfortunately, there is so far no comprehensive model of electrocrystallization, relating atomistic scale processes to microscopic morphological development, due to the complexity arising from the presence of metal-solution double layer, adsorbed molecules or ions, desolvation of charged species, etc. As a first approximation, surface overpotential η in Eq. (1.3) may be associated with supersaturation σ in Eq. (1.16), although η is not divided into charge-transfer and crystallization overpotentials as individually defined by Vetter.[4)] Thus, we may expect enhanced nucleation and growth, increasing surface overpotential η, which is also an increasing function of the fraction i/i_0, and vice versa.

According to Fischer's classification of polycrystalline deposits,[5)] it is known that morphology of electrodeposit varies with surface overpotential η, in the following order:

$$\text{FI} \rightarrow \text{BR} \rightarrow \text{FT} \rightarrow \text{UD} \rightarrow \text{D or P}$$

where FI is "field oriented isolated crystal type," BR is "basis oriented reproduction type," FT is "field oriented texture type," UD is" unoriented dispersion type," and D or P is "dendritic and/or powdery crystal type."

Ibl[6)] pointed out that instability of surface roughness could occur for a diffusion-controlled process due to difference in the diffusion boundary layer thickness between peak and recess. Namely, i_{peak} will be greater than i_{recess}, because δ_{peak} is smaller than δ_{recess}, resulting in evolution of dendritic growth at peaks. Popov *et al.*[7-9)] studied the spongy deposit formation, which is caused by mass-transfer limitations under conditions of low nucleation rate (e.g. low overpotential η and small i_L). Pavlovic *et al.*[29)] interpreted copper dendrite formation in terms of the ratio i_L/i_0. Typically, metals with high exchange current

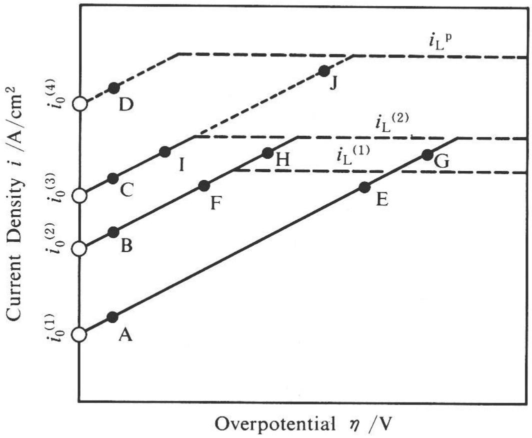


Fig. 1.1 Schematic diagram of operational windows for various electroplating systems.

	Exchange current density		Limiting current density	Process variables window
case I	[$i_0^{(1)}$	,	$i_L^{(1)}$]	Line A–E
case II	[$i_0^{(1)}$	,	$i_L^{(2)}$]	Line A–G
case III	[$i_0^{(2)}$	,	$i_L^{(1)}$]	Line B–F
case IV	[$i_0^{(2)}$	,	$i_L^{(2)}$]	Line B–H
case V	[$i_0^{(3)}$	,	$i_L^{(2)}$]	Line C–I
case VI	[$i_0^{(3)}$	,	i_L^p]	Line C–I for i C–J for η

densities, such as silver or aluminum in chloroaluminate melt, form nodular, dendritic and/or powdery deposits during electrodeposition more readily than the metals with low exchange current densities, such as nickel or iron.

Along the lines of Winand's diagram,[10] Fig. 1.1 illustrates the conceptual basis for the optimal range of process variables (i, η) to obtain compact deposits, for a given electrodeposition process characterized in terms of the kinetic parameter i_0 and the mass transfer-related parameter i_L. Coherent deposit is obtained when $i_0 < i < i_L$. Ideally, i should be much higher than i_0, and it is also recommended that i not exceed about half of i_L. Wider operational windows are achieved by lowering i_0 and/or increasing i_L values, which can be easily seen by comparing cases I, II, III and IV. Organic additives, such as thiourea, poly acrylamides, polyethylene glycol, etc., are often introduced in the electrolyte in very minute amounts to inhibit the kinetics of electrodeposition by adsorption mechanism in practice. For metal deposition with high exchange current densities close to limiting current densities, such as seen in case V, application of pulse plating may offer the possibility of higher overpotential deposition, as in case VI, for tailoring the quality of deposits.

1.3 Hydrodynamic Effects

As described in the previous section, electrodeposition process is a multi-successive process, involving mass transfer and kinetic reaction at the cathode surface. Mass transfer depends greatly on convection, which is governed by the fluid velocity field in the system.