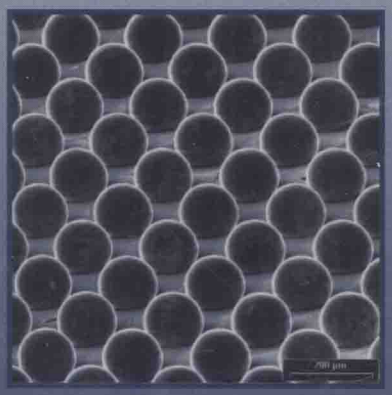
MODERN ELECTROPLATING

FIFTH EDITION



Edited by
MORDECHAY SCHLESINGER
MILAN PAUNOVIC

WILEY

The Electrochemical Society Series

MODERN ELECTROPLATING

Fifth Edition

Edited by

MORDECHAY SCHLESINGER
University of Windsor, Windsor Ontario, Canada

MILAN PAUNOVIC
IBM T.J. Watson Research Center, Yorktown Heights, NY (Retired)

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MODERN ELECTROPLATING

PREFACE

Ours is the information age. Consequently, the demand for high-performance, low-cost, and nonvolatile information storage systems is on a constant rise. There are a great variety of information storage systems, with varying degrees of development and commercialization. Those include, but are not limited to, magnetic tape drives, hard disc drives, magnetic floppy disc drives, magneto-optic (MO) disc drives, phase change optic disc drives, semiconductor flush memory, magnetic random-access memory (RAM), and holographic optical storage. Electrochemical deposition techniques are essential in the production of most of the above. This, among many others, is the raison d'être for the present (fifth) and the earlier (fourth) editions.

The fourth edition of *Modern Electroplating* appeared some 10 years ago. A great deal of progress has taken place in those years in the area of electrochemical plating and related fields. It is these developments that make this new edition both desirable and necessary. Those profound changes are reflected in the present edition in a number of different ways. Essentially, all chapters were rewritten, some by different authors, and/or updated. Unfortunately, two authors who contributed to the fourth edition (Drs. Rolf Wyle and Ned Mandich) have since passed on. Two chapters have been removed altogether and new ones are replacing them. The two new chapters are titled "Electrochemical Deposition Process for ULSI Interconnection Devices" by Osaka and Yoshino and "Electrochemical Synthesis of Metal Alloys for Magnetic Recording Systems" by Sugiyama, Yoshino, Hachisu, and Osaka. Four new chapters have been added: "Applications to Magnetic Recording and Microelectronic Technologies" by Brankovic, Vasiljevic, and Dimitrov; "Microelectromechanical Systems" by Zangari; "Analysis of Electroplated Films Using Dual-Beam FIB/SEM and TEM Techniques" by Meng-Burany; and "Ionic Liquid Treatments for Enhanced Corrosion Resistance of Magnesium-Based Substrates" by Petro, Schlesinger, and Song. These and most other changes, including the publication of the new second edition in 2006 of *Fundamentals of Electrochemical Deposition*, reflect the present tendency of the applications of electroplating more and more in the arena of nanoelectronics in particular and nanotechnology in general as alluded to above. Typically, it may be observed that whereas the fourth edition is comprised of 26 chapters on about 800 pages, the present edition contains 30 chapters and is about the same number of substantially enlarged pages. In this edition as in the previous the chapters are self-contained in that those may be read in any order that the reader finds useful. Thanks are due to the over 30 contributors/authors who made this edition possible.

MORDECHAY SCHLESINGER

Windsor Ontario, Canada

MILAN PAUNOVIC

Port Washington, New York

PREFACE TO THE FOURTH EDITION

In planning this new edition of *Modern Electroplating*, we have realized from the start that it would be impossible to include in one volume both the fundamental aspects and the technology itself. For this reason we have decided to publish the recent developments in the science of deposition in a separate volume titled *Fundamentals of Electrochemical Deposition*. That volume was published in November 1998. Therefore, the present volume includes only a brief summary of fundamental technological advancements, and this is presented in the first, introductory chapter.

Since the last edition of *Modern Electroplating* in 1975, electrochemical deposition has evolved from an ill-defined area, as the Preface to the previous edition calls it, into an exact science. This development is, in the first place, seen as responsible for the ever-increasing number and widening types of applications of this branch of practical science and engineering.

The most significant developments in any field of science or technology in general, and in electrochemistry in particular, are made by those who possess a good understanding of the fundamental aspects of the discipline, which in this case is electrochemical deposition. We, the editors, found it necessary and highly desirable to seek and present to the reader a companion volume that, for all intents and purposes, makes essentially a completely new contribution and not just a revised version of the earlier editions. Thus, for the sake of illustration, the present edition includes a chapter devoted to the electrodeposition of semiconductors. Another deals with environmental issues. Last, but not least, in this connection, neither of the editors nor the vast majority of the contributors were associated with any of the earlier editions.

Technological areas in which the possession of technical knowledge of electroplating is found to be essential include all aspects of electronics; macro-, micro-, and nano-optics; opto-etectronics; and sensors of most types. In addition, a number of key industries, such as the automotive industry, employ methods of electroplating. This is so even when other methods such as evaporation and sputtering CVD (chemical vapor deposition) are an option. Electroplating is therefore often used for reasons of economy and/or convenience.

This volume is divided into 26 chapters. After a three-part introductory chapter by Paunovic, Schlesinger, and Weil come 13 chapters dealing with the electrodeposition of copper (Dini), nickel (DiBari), gold (Kohl), silver (Schlesinger), tin (Abys et al.). chromium (Snyder et al.), lead and alloys (Jordan), tin-lead alloys (Jordan), zinc and alloys (Winand), iron and alloys (Izaki), palladium and alloys (Abys et al.), nickel and cobalt alloys (DiBari), and semiconductors (T. E. Schlesinger). Closing this series of chapters is one on deposition on nonconductors (Schlesinger), and conductive polymers (Osaka et al.). Next come 6 chapters dealing with electroless deposition of copper (Paunovic), nickel (Schlesinger), cobalt (Osaka), palladium and platinum (Ohno), gold (Okinaka), and electroless alloys (Ohno). Finally, 4 chapters close the book, and these are on preparation for deposition (Dexter Snyder), manufacturing technologies (Turner), manufacturing control (Turner), and environmental considerations (Tomkiewicz).

In the preface to *Fundamentals of Electrochemical Deposition* we stated that it may be considered a lucky coincidence that this volume is published close to the time that copper interconnection technology is introduced in the microelectronic industry. This is still the case. There has been a truly revolutionary change from physical to electrochemical techniques in the production of microconductors on silicon, and developments in electrochemical deposition are bound to generate and maintain in the twenty-first century an increased interest and urgent need for up-to-date information regarding

the technology. The present volume together with the *Fundamentals* volume should be of great help in understanding these advancements.

The chapters were written by different authors and so differences in style and approach will be evident. We the editors have tried to smooth those differences without changing the basic message present in each chapter. We also intend this volume to be a useful reference for practitioners of deposition as well as for individuals who are about to enter this modern ever-evolving field of practical knowledge. For this reason each chapter is complete and may be read and consulted separately, and certainly the book can be read in any order.

Our thanks and heartfelt gratitude go to many members of the Electrochemical Society and in particular to those of the Electrodeposition Division. Our thanks also go to our respective families for their patience and understanding during the hectic long hours we spent in preparing this volume.

MOROECHAY SCHLESINOER

Windsor Ontario. Canada

MILAN PAUNOVIC

Yorktown Heights. New York

CONTRIBUTORS

Joseph A. Abys Cookson Electronics–Enthone Inc., Orange, CT

Stanko R. Brankovic Cullen College of Engineering, University of Houston, Houston, TX

Jack W. Dini Lawrence Livermore National Laboratory, Livermore, CA (Retired)

George A. Di Bari INCO, Saddle Brook, NJ (Retired)

Norma R. de Tacconi University of Texas at Arlington, Arlington, TX

Nikolay Dimitrov Department of Chemistry, Binghamton University–SUNY, Binghamton, NY

Takuma Hachisu Waseda University, Tokyo, Japan

Masanobu Izaki Toyohashi University of Technology, Toyohashi, Japan

Manfred Jordan Dr. Ing. Max Schlotter, Geislingen/Steige, Germany

Paul A. Kohl School of Chemical Engineering, Georgia Institute of Technology, Atlanta, GA

Sinichi Komaba Department of Applied Chemistry, Tokyo University of Science, Shinjuku-ku, Tokyo, Japan

Masaru Kato Kanto Chemical Co., Soka Saitama-ken, Japan

Nenend V. Mandich (Deceased)

Toshiyuki Momma Waseda University, Tokyo, Japan

Xianying Meng-Burany University of Windsor, Windsor, ON, Canada

Tetsuya Osaka Waseda University, Tokyo, Japan

Izumi Ohno Tokyo Institute of Technology, Tokyo, Japan (Retired)

Yutaka Okinaka Waseda University, Tokyo, Japan

Milan Paunovic IBM T J Watson Research Center, Yorktown Heights, NY

Robert Petro University of Windsor, Windsor, ON, Canada

Krishnan Rajeshwar University of Texas at Arlington, Arlington, TX

Tom Ritzdorf Semitool, Inc., Kalispell, MT

Mordechay Schlesinger University of Windsor, Windsor, ON, Canada

Dexter D. Snyder GM Research and Development Center, Warren, MI (Retired)

Donald L. Snyder ATO Tech, Cleveland, OH

T. E. Schlesinger Carnegie Mellon University, Pittsburgh, PA

Atsushi Sugiyama Waseda University, Tokyo, Japan

Guang-Ling Song GM Research and Development Center, Warren, MI

Micha Tomkiewicz Department of Physics, Brooklyn College–CUNY, Brooklyn, NY

Natasa Vasiljevic Physics Department, University of Bristol, Bristol, UK

René Winand University of Bruxelles, Bruxelle, Belgium (Retired)

Masahiro Yoshino Waseda University, Tokyo, Japan

Yun Zhang Cookson Electronics–Enthone Inc., Orange, CT

Giovanni Zangari University of Virginia, Charlottesville, VA

CONVERSION FACTORS

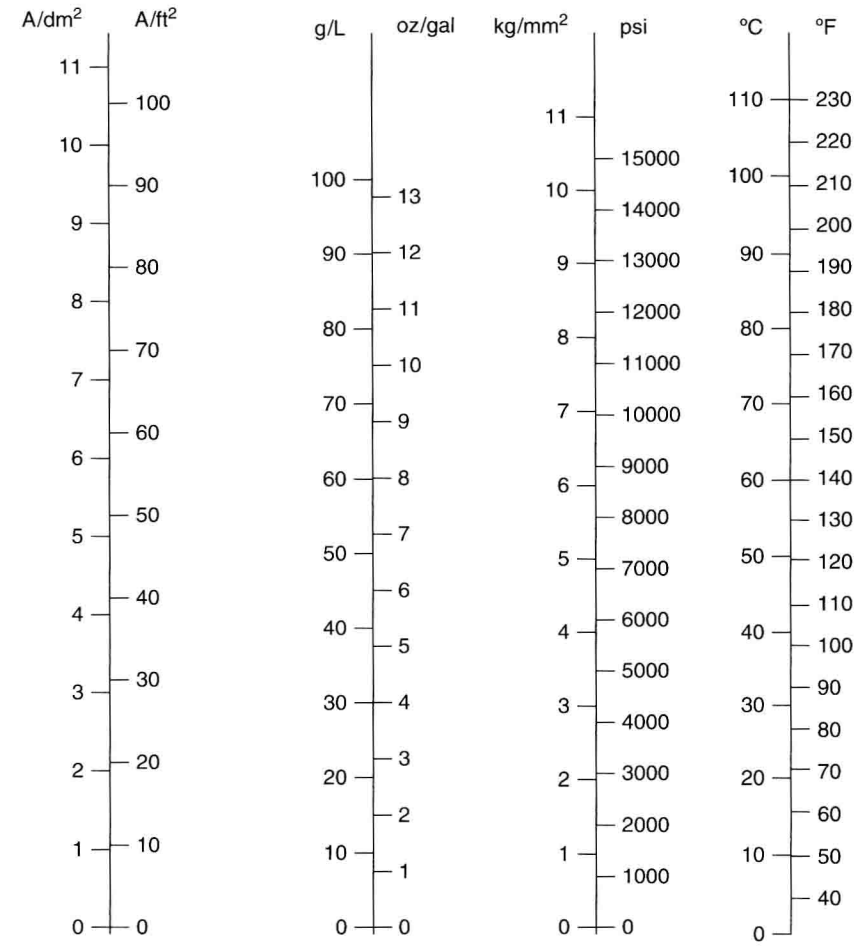
1 centimeter (cm) = 0.934 inch (in.)
1 millimeter (mm) = 0.0394 inch (in.)
1 micrometer (μm, micron) = 0.0394 mil = 39.37 microinch (μin.)
1 square decimeter (dm^2) = 15.5 square inch ($in.^2$) = 0.1076 square foot (ft^2)
1 square centimeter (cm^2) = 0.155 square inch ($in.^2$)
1 square millimeter (mm^2) = 0.00155 square inch ($in.^2$)
1 kilogram (kg) = 2.205 pound (lb)
1 gram (g) = 0.0353 ounce (oz) avoirdupois = 0.0321 ounce Troy
1 liter (L) = 0.264 gallon U.S. (gal) = 0.220 gallon British
1 ampere per square decimeter (A/dm^2) = 9.29 ampere per square foot (A/ft^2)—sec chart
1 gram per liter (g/L) = 0.133 ounce per gallon. U.S. (oz/gal)—see chart
1 kilogram per square millimeter (kg/mm^2) = 1.422 pounds per square inch $lb/in.^2$, psi)—see chart;
strictly, unit should be kilogram-force, or kgf/mm^2; in SI units, 1 $kgf/mm^2 = 9.806 \times 10^6$ newton/square meter (N/m^2) = 9.806 MN/m^2; 1 N/m^2 = 1 Pa (pascal)

Approximate Conversion Factors for Mental Calculation (accurate to 10% or better)

To convert from	To	Do this
A/dm^2	A/ft^2	Multiply by 10
A/dm^2	$A/in.^2$	Divide by 15 (multiply by 2, divide by 30)
Celsius (Centigrade)*	Fahrenheit, F	Multiply by 9/5 (1.8) and add 32
g/L	oz/gal	Divide by 7.5 (multiply by 4, divide by 30)
kg/mm^2	$lb/in.^2$(psi)	Multiply by 1500
mm	in.	Divide by 25 (multiply by 4, divide by 100)
micrometers (m)	mil	Divide by 25 (multiply by 4, divide by 100)

*Exact.

GRAPHICAL CONVERSIONS



(1 A/dm²=9.29 A/ft²) (1g/L=0.133 oz/gal) (1kg/mm²=1422 psi)

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CONTENTS

1

FUNDAMENTAL CONSIDERATIONS

MILAN PAUNOVIC,[1] MORDECHAY SCHLESINGER,[2] AND DEXTER D. SNYDER[3]

1.1 INTRODUCTION

Already in the preparation of the fourth edition of *Modern Electroplating*, we realized that the first chapter in the third edition (1974) needed to be enlarged considerably in order to cover all the significant progress made since 1974. As the prospect of adding material to the chapter on fundamentals began to suggest an inbalance in the new edition, we chose to publish a separate volume titled *Fundamentals of Electrochemical Deposition (Fundamentals* in further text) that would treat the basic aspects of electrochemical deposition [1]. For this reason we provided in the fourth and now in the present fifth edition only a brief review of these fundamentals. The number of references in this chapter is also limited, and the reader is urged to consult the more extensive list of references given in both editions of *Fundamentals.*

This chapter is divided into three parts. Part A treats electrochemical aspects, part B treats physical aspects, and part C treats material science. For this presentation of the fundamentals our objective is to provide the basis for understanding only the electrochemical deposition processes treated in this volume. Information on a higher level is presented in the *Funamentals* volume.

PART A ELECTROCHEMICAL ASPECTS

In Part A we discuss (1) electrode potential, (2) kinetics and mechanism of electrodeposition, (3) growth mechanism, and (4) electroless and displacement depositions. All four topics are presented in a concise manner that emphasizes the most important points. Most concepts are clarified by solutions of numerical examples. These examples are useful for this chapter and for the chapters that follow.

1.2 ELECTRODE POTENTIAL

When a metal M is immersed in an aqueous solution containing ions of that metal, M^{z+} (e.g., salt MA), there will be an exchange of metal ions M^{z+} between two phases, the metal and the solution. Some M^{z+} ions from the crystal lattice enter the solution, and some ions from the solution enter the crystal lattice. Initially one of these reactions may occur

[1] Milan Paunovic, Part A.
[2] Mordechay Schlesinger, Part B.
[3] Dexter D. Synder, Part C.

Modern Electroplating, Fifth Edition Edited by Mordechay Schlesinger and Milan Paunovic

faster than the other. Let us assume that conditions are such that more M^{z+} ions leave than enter the crystal lattice. In this case there is an excess of electrons on the metal and the metal acquires negative charge, q_M^- (charge on the metal per unit area). In response to the charging of the metal side of the interphase, there is also a rearrangement of charges on the solution side of the interphase. The negative charge on the metal attracts positively charged M^{z+} ions from the solution and repels negatively charged A^{z-} ions. The result of this is an excess of positive M^{z+} ions in the solution in the vicinity of the metal interphase. Thus, in this case, the solution side of the interphase acquires opposite and equal charge, q_s^+ (the charge per unit area on the solution side of the interphase). This positive charge at the solution side of the interphase slows down the rate of M^{z+} ions leaving the crystal lattice (due to repulsion) and accelerates the rate of ions entering the crystal lattice. After a certain period of time a dynamic equilibrium between the metal M and its ions in the solution will result:

$$M^{z+} + ze \leftrightarrows M \tag{1.1a}$$

where z is the number of electrons involved in the reaction. Reaction from left to right consumes electrons and is called reduction. Reaction from right to left liberates electrons and is called oxidation. At the dynamic equilibrium the same number of M^{z+} ions enter, $\vec{n}$, and the same number of M^{z+} ions leave the crystal lattice, $\vec{n}$, (see Fig. 1.1):

$$\vec{n} = \overleftarrow{n} \tag{1.1b}$$

The interphase region is neutral at equilibrium:

$$q_M = -q_S \tag{1.1c}$$

The result of the charging of the interphase is the potential difference, $\Delta\phi$ (M, S), between the potentials of the metal, ϕ_M, and the solution, ϕ_S:

$$\Delta\phi(M, S) = \phi_M - \phi_S \tag{1.2}$$

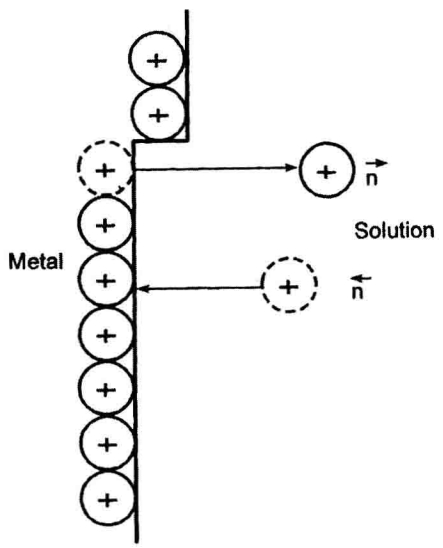

FIGURE 1.1 Formation of metal–solution interphase; equlibrium state: $\vec{n} = \overleftarrow{n}$.

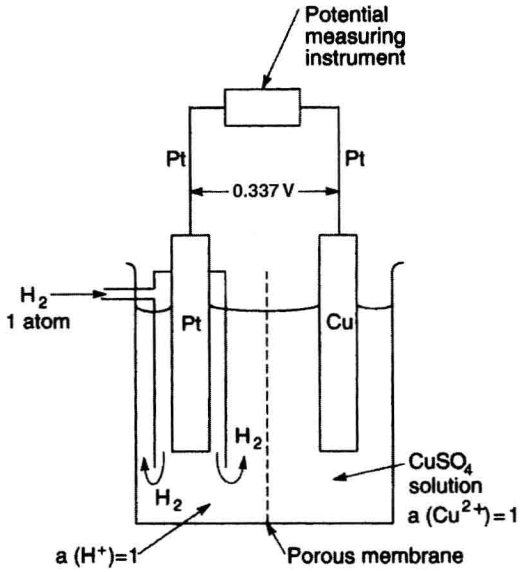

FIGURE 1.2 Relative standard electrode potential E^0 of a Cu/Cu^{2+} electrode.

In order to measure the potential difference of an interphase, one must connect it to another one and thus form an electrochemical cell. The potential difference across this electrochemical cell can be measured.

For example, consider the cell shown in Figure 2.2. This cell may be schematically represented in the following way:

$$Pt, H_2(p = 1)|H^+(a = 1)||Cu^{2+}(a = 1)|Cu|Pt$$

where the left-hand electrode is the normal hydrogen reference electrode; a stands for activity and p for the pressure of H_2. When $p = 1$ atm and the activity of H^+ ions is 1, the hydrogen electrode is called the standard hydrogen electrode (SHE) and its potential is zero by convention. The measured value of the potential difference of this cell is $+0.337$ V at 250°C. This measured cell potential difference, $+0.337$ V, is called the relative standard electrode potential of Cu and is denoted E^0. The standard electrode potential of other electrodes is obtained in a similar way, by forming a cell consisting of the SHE and the electrode under investigation. Standard electrode potentials at 25°C are listed in Table 1.1.

The potential E of the M^{z+}/M electrode is a function of the activity [see Eq. (1.5)] of metal ions in the solution according to the Nernst equation,

$$E = E^0 + \frac{RT}{zF} \ln a(M^{z+}) \tag{1.3}$$