The Electrodeposition Division: Full of Surprises

by John Dukovic

It is fascinating that an atom, at the mere offer of an electron or two, will surrender its freedom of motion in a liquid phase and "settle down" with like-minded atoms into a densely populated and utterly rigid community. Such atoms are clearly crazy. The people who study them may be crazy too, but, fortunately, there is a long-standing, well-established support group for such people: the ECS Electrodeposition Division.

If electrodeposition were not useful, it would still be fascinating. But it is useful of course, and its uses range from the mundane to the exotic, from the industrial age to the information age (not to mention the space age). Wherever you are reading this article, you are probably surrounded by more things that are made or modified by electrochemical deposition than you realize. You may be wearing a watch or buttons or a belt buckle that's been plated. Your car might have rusted out by now without the Zn alloy coating on the sheet metal. Doorknobs, lamps, faucets, and handlebars are some of the many things obviously plated. Others are not so obvious. The computer on your desk is loaded with components that are made by electrochemical deposition: connectors, circuit boards, packaging modules, recording heads; the microprocessor chip may not have any plated metal on it, but your next one very well might (see page 32).

The theme of this article is that despite electrodeposition's long standing as a research field, rich and varied surprises keep arising. These surprises can be fundamental discoveries, practical inventions, new techniques of observation, unexpected properties, novel processes, new uses for old processes, etc. The landscape (the electrodescape?) continues to change.

It can be enlightening to pause once in a while to consider the kinds of developments that are afoot in the field. Only three and a half years ago, *Interface* featured the Electrodeposition Division with a cluster of articles on contemporary research areas.[1,2] Even more recently, a trio of short *Interface* articles gave an additional snapshot of the field.[3] There is some unavoidable carry-over of topics

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Our Featured Division

Electrodeposition Division

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into the present issue, but it's remarkable how much new work there is to tell about today.

It's folly, of course, to think that one can portray the state of a field by showing a few examples, no matter how well chosen they are. The resulting view will be imperfect at best. To enlist eminent research pioneers as spokesmen for specific topics is a good start, but something is lost in defining major topics in the first place. The very newest work will escape the search for not having achieved "critical mass." This said, it is hoped that the reader will find the suite of three feature articles in this issue to be, aside from interesting reading, representative of the "surprises" that are animating electrodeposition research at present.

Walther Schwarzacher leads us on a tour of ongoing research on metal nanostructures, a term that encompasses various materials and structures having lengths on the order of nanometers or tens of nanometers in at least one dimension. The most celebrated members of this class of materials are magnetic multilayers that exhibit giant magnetoresistance (GMR), a property of great value in magnetic recording technology. From an early point, electrodeposition has been an important contender among methods use to prepare such compositionally modulated materials.

Also under the banner of metal nanostructures are nanowires formed by electrodeposition into nano-porous membranes or templates. Such ultra-slender bodies, especially when additional structure is imparted along the axial dimension by potential or current modulation, exhibit extraordinary properties such as giant magnetoresistance, spin-dependent electron scattering, and elevated critical temperature for superconductivity. Finally, structures containing ultra-thin oxide layers acting as tunnel barriers, which can be formed anodically, are introduced. These have shown peculiar electronic characteristics such as Coulomb blockade and have engendered single-electron transistors and other devices that are replete with technological possibilities.

The burgeoning research on metal multilayers, magnetic nanostructures, nanowires, tunnel junctions, and the like is particularly engaging because it is so wide open. Many new properties and behaviors are being discovered, and the prospect of revolutionizing the electronics industry is always present. The emphasis on devices and the race to deliver the highest GMR are redolent of some recurring themes in electrodeposition. The field has in many ways been animated by the spirit of *making something.* Beyond this, there is an obsession with imbuing the deposit with certain *properties.* What can be done to make copper more ductile for circuit boards, chromium a better barrier to the diffusion of gold, to give nickel-iron a higher magnetic moment, or to make CdS a more efficient solar collector? The key to this game, of course, is understanding how the infinitely variable process conditions affect deposit structure and how structure, in turn, determines properties. A recent symposium entitled "Processing-Structure-Property Relationships in Electrochemically Prepared Materials" embraced this central theme.

Dieter Kolb and Marie Anne Schneeweiss describe the powerful impact of scanning-tunneling microscopy (STM) on our understanding of electrodeposition. It is a treat to have a high-level overview of this topic from the Kolb group, which has continually been at the forefront of research on in-situ STM at electrodes. The article begins with the fascinating and long-studied subject of underpotential deposition, in which atoms of one metal deposit from the electrolyte onto a single crystal of a different metal, forming mono- or submonatomic layers of highly distinctive structure. As the authors explain, this system is *made* to be studied by STM, which goes far beyond determining the overall pattern of the adsorbed metal atoms on the surface and reveals highly detailed structural information about immobilized anions, topography, and defects, which can be very important to the transition to bulk growth. The tendency for bulk growth to begin at defects, such as steps, is vividly illustrated. Bold strides from classic UPD into the swampy (but commercially significant) world of organic plating additives are recounted, showing the large, mostly untapped potential of scanning-probe methods to explore the molecular basis for the action of leveling and brightening agents. Back to purely inorganic systems, the authors go on to discuss astonishing findings about the *exact* point during layer-by-layer epitaxial growth of Cu on Ag(100) or on Au(100) at which a sudden transition occurs to a less-strained structure. Finally, the STM's capacity to *manipulate* electrode surfaces rather than merely to *image* them is invoked by illustrating a technique for creating small metal clusters at assigned locations on the electrode surface.

It was only a short time ago that we had to be satisfied mainly with characterizations of electrodeposition processes by ex-situ analysis of the deposits, by electrochemical techniques, and by a handful of in-situ methods. Most of these now seem quite limited and indirect by comparison to real-time, real-space imaging of individual atoms during deposition.

Many of us cheered the inception of the scanning tunneling microscope (STM) and the atomic-force microscope (AFM). In a decade and a half, scanning-probe methods have fulfilled high

Electrodeposition Division
Future Symposia Plans

Seattle — May 1999

Electrochemical Processing in ULSI Fabrication and Semiconductor/Metal Deposition II (co-sponsored by the Dielectric Science and Technology and the Electronics Divisions); *Spectroscopic Tools for Analysis of Electrochemical Systems* (co-sponsored by the Physical Electrochemistry Division).

Hawaii — October 1999

Interconnects and Contact Metallization for ULSI (co-sponsored by the Dielectric Science and Technology and the Electronics Divisions); *Fundamental Aspects of Electrochemical Deposition and Dissolution including Modeling; Third International Symposium on Electrochemical Technology Applications in Electronics; Electrochemistry of Ordered Interfaces* (co-sponsored by the Physical Electrochemistry and the Energy Technology Divisions); *Twelfth International Symposium on Molten Salts* (co-sponsored by the Physical Electrochemistry and the High Temperature Materials Divisions).

expectations for revealing the structure and nature of surfaces. It is not altogether inappropriate that the STM and the venerable electron microscope were recognized together with the 1986 Nobel prize for physics. For electrodeposition, scanning probes have clearly brought much new understanding, particularly of the incipient stages of growth but also for the advanced stages. It has been very gratifying to see how these in-situ techniques have evolved and how much insight has been gained.

Panos Andricacos gives a first-hand description of an exciting new *application* of copper plating, fabrication of the vast network of fine wires that interconnect the transistors on integrated-circuit chips. This article recounts some of the twists and turns in industrial research and development that led to the selection of electrodeposition as the preferred means, indeed perhaps the enabling means, of creating copper wiring structures on silicon wafers. The advantages of copper over aluminum as an interconnect metal are spelled out. The method of integrating plating with other unit processes into the overall fabrication sequence, which calls for “Damascene” plating, as opposed to “through-mask” plating, is explained. The author describes the associated need for superconformal coverage of highly topographic profiles and the remarkable way that electrodeposition meets this challenge. Finally, some of the properties of the electrodeposited copper are discussed, including a peculiar grain-growth/resistivity-change behavior that occurs after deposition and appears to be related to vital reliability properties.

The story of plated copper interconnects is compelling in a number of ways. It seems, looking back casually, that it was *bound* to happen—copper being so conductive and so readily plated, plating being so fast and so inexpensive. In fact there were many reasons it almost never happened: fear of contamination, competing deposition techniques, industry reluctance to adopt a new material, and lack of infrastructure. Those who rooted for plated copper interconnects all along, but expected it to be achieved by through-mask plating, were in for a surprise when Damascene plating prevailed. The shape-evolution properties of copper plating necessary to make Damascene copper filling succeed are extraordinary indeed. Finally, the emergence of plated copper interconnects, it goes without saying, is very gratifying for those who champion electrochemical processing in the electronics industry.

The Electrodeposition Division’s scope and focus naturally continue to change. Its main business is to stage symposia at ECS meetings. A glance through the titles of recent and upcoming symposia provides a very good picture of the topics and themes that are being developed in the field: ULSI fabrication; semiconductor/metal deposition; spectroscopic tools; fundamental aspects of electrochemical deposition and dissolution; modeling; molten salts; electrochemistry of ordered interfaces; tribology of electrodeposited and composite layers; processing-structure-property relationships; scanning-probe microscopy for electrode characterization and nanometer-scale modification; magnetic materials, processes and devices; morphological evolution; nanoscale and nanophase materials; and molecular structure of the solid liquid interface and its relation to electrodeposition.

The ECS Electrodeposition Division is a unique vehicle for bringing together those doing research on electrochemical deposition. We share the stage of course, with the Gordon Research Conference on Electrodeposition, the International Society of Electrochemistry, the American Electroplaters and Surface Finishers Society, and other organizations, but we occupy a central and special place: rooted in history, large in membership, international in scope, richly documented, pure and applied, and full of surprises! ■

References

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2. B. Loechel, *Interface*, Vol. 4, No. 3, p. 43 (1995).
3. A. A. Gewirth, P. C. Andricacos, Jay A. Switzer, with J. O. Dukovic, *Interface*, Vol. 7, No. 1, p. 22 (1998).

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