



Electrodeposition: A Technology for the Future

by *Walther Schwarzacher*

Electrochemical deposition, or electrodeposition for short, has been around for a very long time now; so why should serious scientists and technologists still get excited by it? There are several answers. To begin, electrodeposition is a fascinating phenomenon. That one can put a shiny coating of one metal on another simply by donating electrons to ions in a solution is remarkable, and studies of the process at an atomic level continue to yield surprises. Electrodeposition is exceptionally versatile, and valuable applications keep being invented. In this article we can give only a brief and incomplete overview, but we hope at least to whet your appetite to learn more.

A good story should always start at the beginning; however, nobody knows for sure when and where electrodeposition began. Electrodeposition by passing a current through an electrochemical cell from an external source (electrolytic deposition) had to await the invention of such a source, by Alessandro Volta in 1800, but electroless deposition, where no external current flows, predates it by centuries. Figure 1 shows an example of electroless deposition from nearly 2,000 years ago. The decorative gold coating was formed by replacement plating, which occurs when a copper surface is exposed to gold ions because the former is the more reactive metal. A direct descendant of this process, in which the electrons that participate in the electrochemical reaction are supplied by a chemical reducing agent, was invented by Grace Riddell and Abner Brenner in the 1940s, and is now an extremely important method of applying protective coatings to metal components used in industries ranging from mining to aerospace. Electroless deposition remains an area of active research and innovation.¹

Meanwhile, electrolytic deposition really took off with the development of effective electrolytes for silver and

gold deposition around 1840. These became the basis of an extraordinarily successful decorative plating industry, with the technology spreading from Great Britain and Russia to the rest of Europe. However, the electrolytes were extremely toxic, as they incorporated cyanide, and the search for better, safer substitutes continues. Finding environmentally friendly alternatives to established electrodeposition processes is still an important general challenge, and, recently, the Electrodeposition Division of ECS has initiated a symposium series entitled "Green Electrodeposition."

In parallel with the development of new processes, considerable effort has been devoted to gaining a fundamental understanding of electrodeposition. Breakthroughs included the establishment of the linear relationship between overpotential and the logarithm of the deposition current by Tafel in 1905, and its explanation on the basis of statistical thermodynamics. Some exceptionally elegant experiments on perfect silver crystals by Kaischew, Budevski and co-workers in Bulgaria in the 1960s led to a much deeper understanding of the role of defects, in particular screw dislocations, in

the growth of electrodeposited metals; but experimental studies at an atomic level were hindered for a long time because the experimental techniques using electron scattering that were developed so successfully for studying surfaces under vacuum could not be used in an electrolyte.

Some researchers have applied these tools successfully to electrode surfaces following withdrawal from the electrolyte, but the development of powerful techniques such as synchrotron X-ray diffraction and scanning tunneling microscopy (STM) that enable researchers to study electrode surfaces while still inside an electrochemical cell have led to a revolution in experimental studies. STM is particularly useful, because not only is it possible to obtain images of electrode surfaces showing the positions of individual atoms but also to manipulate them, for example, depositing tiny clusters of atoms at predetermined positions.²

While electrodeposition continues to be widely used for protective or decorative coatings, challenging new applications have been found in the electronics industry. More detail is given in the box by Deligianni, but particularly exciting developments include the development of thin film magnetic recording heads for hard disks, and the recent replacement of aluminum and its alloys by electrodeposited copper for interconnects in ultralarge scale integrated circuits.³

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Fig. 1. Miniature copper mask from the site of Loma Negra on the far north coast of Peru, ca. 200 C.E. Removal of the green copper corrosion products reveals a bright gold surface. The extremely thin layer of gold was applied to the sheet copper by electrochemical replacement plating. [Figure reprinted with permission from Heather Lechtman, *Sci. Amer.*, 250(6), 56 (1984).]

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Getting material into arbitrary three-dimensional geometries is a great strength of electrodeposition compared to other methods, and has led to its widespread adoption in nanotechnology. Nanocomponents fabricated using electrodeposition include wires consisting of alternating magnetic and non-magnetic layers each only a few nanometers thick and single-electron transistors using niobium.⁴ Electrodeposition is also a low energy process and therefore uniquely suited to dealing with modification of soft matter of various types. It may be combined with self-assembled templates to prepare nanomaterials with exciting properties.⁵ This is described in more detail in the box by Schwartz.

What does the future hold? High resolution surface probes will become faster and therefore even more useful for studying electrodeposition. Traditional applications of electrodeposition will continue, while new ones will emerge rapidly, especially in the fields of nanoelectronics, biotechnology, and energy engineering. The electrodeposition of nonmetallic materials will become more important and the combination of electrodeposition with other processes will lead to whole new classes of nanostructured material. These are exciting times for the subject!

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Electrodeposition and Microelectronics

by H. Deligianni

Magnetic data storage has typically followed advances in modern computers and has seen explosive growth, with an increase of several orders of magnitude in the areal density in the last 50 or so years.¹ The different technologies implemented in order to achieve this were the thin film inductive head, the magnetoresistive (MR) read head, the giant magnetoresistive (GMR) head and antiferromagnetically coupled (AFC) media. Progress in the electrodeposition of high-moment magnetic materials contributed greatly to the implementation of these technologies. During the last decade huge improvements were demonstrated with ever higher moments, from 1.0 Tesla for permalloy (NiFe) to 2.4-2.5 Tesla with CoFe. Electrodeposition of these alloys requires precise compositional control of the alloy in confined geometries since alloy composition greatly affects the magnetic properties of the material.

Semiconductor chips are the heart and brain of the Information Age and the Internet Revolution. Everything from supercomputers to personal computers, personal digital assistants, cellular phones, computer games, modern cars, airplanes, household appliances and medical devices need sophisticated chips to run. The ubiquitous semiconductor chips have altered the way people communicate, do business, and receive education and entertainment. Along the way the semiconductor industry has grown to become a gigantic \$225 billion worldwide business in less than five decades. Key technological breakthroughs and innovations include the flip-chip and copper interconnects. A common element of these technologies is that they use electrodeposition and other electrochemical micro and nanofabrication methods.

In 1969 a new chip joining method known as the flip-chip was developed. This connection utilizes an array of solder balls allowing a high density of input/output leads and therefore higher utilization of the logic circuits on the chip. Electrodeposited flip-chip solder connections were introduced in 1995 as the first application of electrodeposition on a semiconductor chip. Electrodeposition offers significant cost, reliability and environmental advantages over the previously used evaporation technology and can accommodate the whole range of vastly different length scales found on a large 200mm or 300mm diameter wafer.² Electrodeposition also offers unique spatial selectivity. A continuous conductive layer is deposited at the bottom of a photoresist mask that acts as the mold for the solder layer. The solder is then electrodeposited only in the openings of the photoresist. The deposit grows up from the bottom where the seed layer lies, replicating the exact shape of the resist opening. The seed and adhesion layers are then removed to isolate the flip-chip solder connections from each other electrically. Removal of the seed and adhesion layers is performed by a series of electrochemical and chemical steps utilizing the solder as a mask. The end result is to produce an area array of highly ordered solder chip connections that assume a spherical shape once the solder is melted.

In the late 90s as the number of transistors on a chip increased with a concurrent reduction in size, on-chip wiring issues posed a huge challenge. The semiconductor industry decided to pursue new materials, processes, and integration schemes. The implementation of copper wiring resulted in a 40% lower wire resistance, a 20-30% anticipated boost in chip performance, improvements in wire reliability and a 10-15% lower chip cost. Today copper metallization is being used in every major semiconductor fabrication facility

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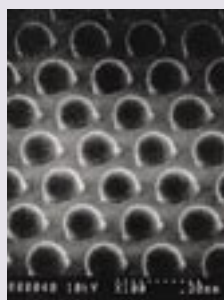
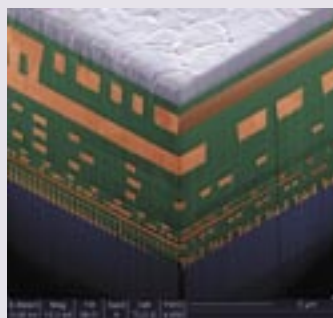


Fig. 1. Electrochemically fabricated flip-chip interconnects.²



Courtesy of International Business Machines Corporation. Unauthorized use not permitted.

Fig. 2. A ten level copper on-chip interconnect scheme of 90 nm CMOS node fabricated in low dielectric constant material.⁷

Electrodeposition and Nanobiosystems

by Daniel Schwartz

As seen elsewhere in this section on electrodeposition, electrodeposition is a key method for making the materials used in computer chips and magnetic data storage systems; every day it helps lower the cost and improve the performance of our information society. However, electrodeposition is also emerging as a uniquely capable method for making materials and structures needed for a nanotechnology- and nanobiotechnology-based future. It also provides some unique opportunities for directly writing materials onto a surface without going through the photoresist masking steps that are used in conventional electrochemical microfabrication.

Electrodeposition has three main attributes that make it so well suited for nano-, bio- and microtechnologies.

- It can be used to grow functional material through complex 3D masks.
- It can be performed near room temperature from water-based electrolytes.
- It can be scaled down to the deposition of a few atoms or up to large dimensions.

The first attribute of electrodeposition is being exploited now to make complex 3D electrical interconnects in computer chips, as shown in the sidebar on microelectronics. The key concept is that electrodeposited materials grow from the conductive substrate outward, and the geometry of the growth can be controlled using an insulating mask (so-called through-mask electrodeposition). Moreover, the insulating mask need not have a straight line-of-sight path between the substrate and the electrolyte; even tortuous masks can be filled with materials, so long as the whole path through the mask is wetted with the electrodeposition electrolyte. The resulting deposit is a high fidelity negative replica of the mask itself. Through-mask electrodeposition has been used extensively to pattern metals, semiconductors, and polymers on conductive substrates.¹ Emerging techniques for electrochemical nanofabrication often exploit masks that self-organize, such as anodic alumina and molecular crystals like amphiphilic surfactants and block copolymers.² Few other methods can so easily grow material through tortuous masks.

The second attribute of electrodeposition has several implications. As a water-based process, it is often more environmentally friendly than deposition methods that require hazardous solvents and reactive precursor chemicals (like organometallic compounds, for instance). But, perhaps

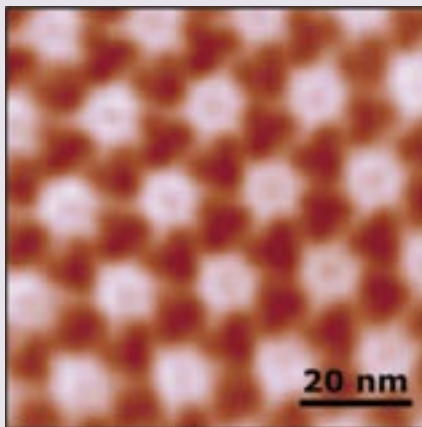


Fig. 1. Nanometer-scale cuprous oxide (colored red) can be electrodeposited through the openings in the hexagonally packed intermediate layer protein (white regions) from the bacterium *Deinococcus radiodurans*. Purified crystalline protein sheets are first adsorbed to a conductive substrate, and then electrodeposition is carried out to fill the nanometer-scale pores in the protein (see scale bar). Details of the method are given in Ref. 4.

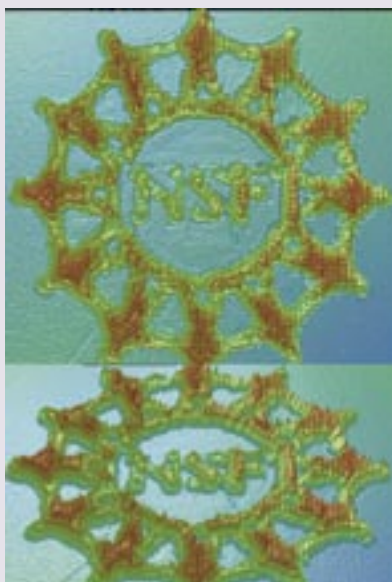


Fig. 2. Electrochemical printing (ECP) involves localized electrodeposition beneath a rastering print head; no masking step is needed. Two different viewing angles show the topography of a complex ECP pattern that is 1.8 mm across and 700 nm high. In this case, copper was ECP patterned with a 1000 dots per inch lateral resolution. This single image shows the multiscale nature of electrodeposition, where the thin film is easily controlled at the nanoscale while lateral dimensions can be macroscopic. Details of ECP can be found in Ref. 6.

the most exciting implication of room temperature, water-based processing is that electrodeposition is compatible with proteins, Mother Nature's orchestrators of biological fabrication. Proteins are responsible for the nucleation, growth, composition, and shape of functional biological structures like bones, teeth, and shells.³ Using proteins to control the growth of electrodeposited materials is truly a frontier area where biology meets nanotechnology. One way that proteins are being used in electrochemical nanotechnology is as masks for through-mask electrodeposition.⁴ Proteins can self-organize into complex structures representing all possible two-dimensional (2D) space groups built from chiral molecules. Moreover, they are readily engineered through molecular biology, providing an attractive foundation for nanotechnology. Figure 1 shows an example of electrodeposition through the 2D crystalline surface layer protein known as the hexagonally packed intermediate layer protein from *Deinococcus radiodurans*. This protein crystallizes into a hexagonal array of pores that are accessible to

electrolytes. When placed on a conductive surface, the pores can be used as an electrodeposition mask (the protein is an insulator). Figure 1 is a false-color transmission electron microscope image showing an ordered array of reddish cuprous oxide dots a few nanometers in diameter organized as a hexagonal periodic array with an 18 nm repeat distance. The dots of cuprous oxide were grown through the holes in the protein. As noted above, there are proteins that crystallize into virtually every 2D periodic structure.

The final attribute of electrodeposition is its ability to be scaled down and scaled up. A single wafer of computer chips can have kilometers of electrodeposited copper wires that are less than 100 nm wide! This versatility means that electrodeposition is being explored for a wide array of unconventional micro- and nanofabrication methods, ranging from nanopatterning with a scanning tunneling microscope,⁵ all the way to patterning large substrates using a process called

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in the world. The Damascene method involves etching trenches and vias in an insulating layer which is then filled with barrier layers and copper and planarized.³ Electrodeposition of copper has played a key role because it can fill high aspect ratio features without defects such as seams or voids. This unique property is due to a phenomenon called superfilling in which the organic additives present in the electrolyte act to accelerate the rate of copper deposition within the trench.^{4,5} State-of-art equipment for electrodeposition of 300 mm diameter wafers with 10 Dual-Damascene layers of copper is extremely advanced.⁶ These tools include single wafer plating cells that meet three key requirements: (i) the solution composition remains constant over time, (ii) the overpotential on the wafer surface is constant, and (iii) the mass transport conditions are uniform.

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electrochemical printing (ECP), where an image drawn in software can be directly electroplated as a thin metal film using no mask whatsoever.⁶ Figure 2 shows two views of a 1000 dot-per-inch ECP pattern of the National Science Foundation logo made from copper directly printed on the surface. The electrodeposited film is only 700 nm thick, but the whole pattern

is 1.8 mm wide. Thus Figure 2 serves to further reinforce the notion of scalability in electrodeposition, all within the same pattern.

Taken together, the unique attributes of electrodeposition as a material deposition method, augur well for a bright future, whatever directions technology moves. ■

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