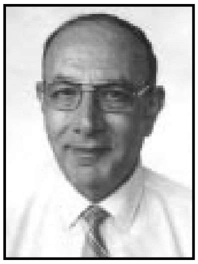

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Characterization of Deposits, Coatings & Electroforms—Methods for In-situ Studies

It is sometimes useful to observe the structure of electrodeposits while they are in the plating solution (*i.e., in situ*). There have been observations of the electrodeposition process in plating solutions, using optical microscopy. Resolution of the optical microscope has limited the usefulness of these observations, however. Scanning or transmission electron microscopes offer better resolution, but deposits can be examined only after they have been taken out of the plating solution. The reason is that these microscopes, as has been previously discussed, require that the specimen be kept in a vacuum. Recently, microscopes have been developed that allow observation in a liquid and that also have resolutions comparable to the transmission electron microscope. The three relevant types of instruments are the atomic force microscope (AFM), the scanning tunneling microscope (STM) and the scanning electrochemical microscope (SECM).

The AFM and the STM have a common feature. A very fine probe tip that is essentially only a few atoms across at the end, scans the surface. A precisely controlled feedback system keeps the distance between the tip and the specimen surface constant. In this way, the tip follows the surface topography. The tip is embedded in a cantilever beam. A laser then measures the deflection of the beam and thereby precisely the movement of the tip. The factors controlling the specimen-to-tip distance are the distinguishing features of the different types of microscopes. In these microscopes, resolution is not determined by the wavelength of the illuminating source, as is the case in the optical microscope. Rather, the size of the probe, which remains slightly separated from a particular surface feature, determines the resolution. The means of manufacturing probe tips of the required dimensions were the limiting aspects. Actually, the idea of having a fine-tipped probe move over a surface was suggested in the 1920s.

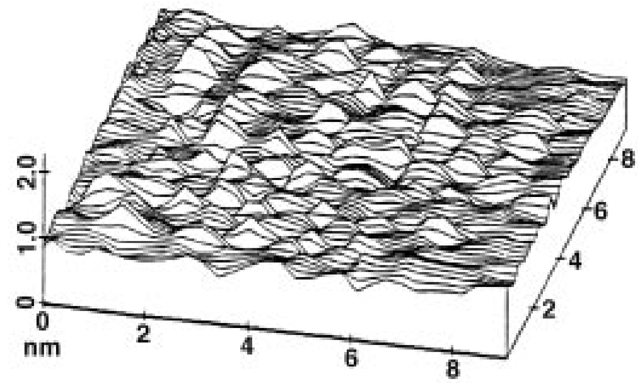

Fig. 1—Scanning tunneling electron micrograph of chromium deposited on electroless nickel.

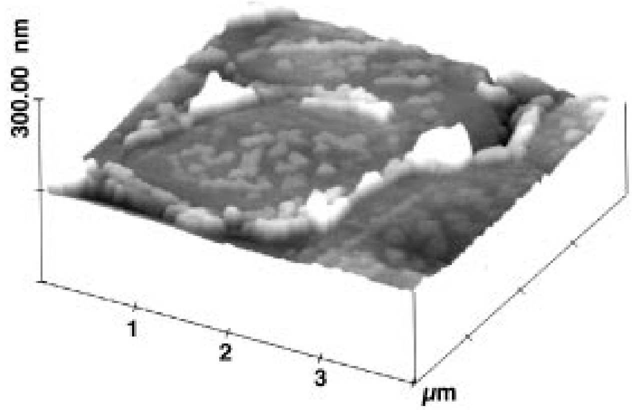

Fig. 2—Atomic force micrograph of copper deposited on gold. (Figure supplied by Dr. E. Eliadis, University of Illinois.)

The main disadvantage of the microscopes is that it is not possible to make continuous observations. The reason for this disadvantage is that the scanning by the probe is mechanical and therefore relatively slow. It usually takes several minutes to generate an image. In the scanning electron microscope, in which the surface of the specimen is scanned electronically, the image is generated much more rapidly.

The AFM and the STM are also useful for observations of surface structures outside of solutions. The resolution is comparable to that of the transmission electron microscope, but does not require thin foils. The AFM can be used to observe the topography of non-conducting surfaces that cannot be examined by the scanning electron microscope.

Scanning Tunneling Microscope

When two surfaces are in very close proximity, on the order of a few interatomic distances, a current can flow between them, even though the gap is not a conductor. This phenomenon is called tunneling. The tunneling current is a measure of the overlap of the wave functions of the two surfaces and, accordingly, a measure of the size of the gap. By maintaining the tunneling current constant, the probe tip follows the contours of the surface features. Figure 1 shows the surface structure of 10-nm-thick chromium, plated over electroless nickel, as taken with the scanning tunneling microscope (STM). It can be seen that the height of the crystallites is less than 1 nm, indicating the high resolution. Actually, the scanning tunneling micrograph shown in Fig. 1 was not taken in the plating solution. There is a possible problem that makes the STM not the best for the *in-situ* study of electrodeposition. This problem is that the tunneling current can change the local current density and thereby the structure. Also, because a tunneling current is required for operation of the STM, only conducting or semiconducting surfaces can be examined. The electrodeposition of copper in a plating solution containing benzotriazole was studied *in situ* with the STM by Armstrong and Muller.[1]

Atomic Force Microscope

The atomic force microscope, which is also called the scanning force microscope, relies on the repulsive force between the tip and the surface to be studied. Whenever surfaces are brought into very close proximity they repel each other. Because a current does not flow between the tip and the specimen, the current density is not changed; consequently, there is not the disadvantage of the STM, nor do the surfaces need be conductive. The only requirement is that the specimen be relatively rigid. The repulsive force is on the order of 10^{-6} to 10^{-8} newtons. Accordingly, there is no damage to the surface unless it is very soft. When the AFM is operated in air, the ambient humidity can bring about a viscous attractive force. This force is absent if the operation takes place in a liquid or a vacuum.

The AFM has been used to study *in situ* the structure of copper electrodeposited on gold.[2] Figure 2 shows an AFM image of the initial stage of copper electrodeposition on a {111} surface of gold. The acid-sulfate plating solution contained an additive that results in a smoother deposit. In the absence of the additive, there would be preferential deposition at grain boundaries. The AFM is also useful in the study of the deposition of reactive metals, such as lithium, which, if taken out of the plating solution, would immediately oxidize.[3] Another useful application of the AFM is in the study of organic coatings. *In situ* studies, using the AFM, are not limited to electrodeposition, but are also useful to investigate corrosion phenomena.

Scanning Electrochemical Microscope

The scanning electrochemical microscope (SECM) is, in principle, the same as the AFM and STM. It differs in that it uses a probe that is a microelectrode. The electrochemical current passing through the probe is monitored. The probe generally hovers over the surface at a constant distance and therefore does not follow the surface topography. The SECM is most useful in mapping the electrochemical activity of the surface and in the detection of species formed by oxidation or reduction. A paper by A.J. Bard *et al*.[4] describes the use of the SECM.

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