1-1-2002

Copper plating process control by SEM

Jorgen Akesson

Sudipta Seal
University of Central Florida

Satyajit Shukla

Zua Rahman

Recommended Citation

Akesson, Jorgen; Seal, Sudipta; Shukla, Satyajit; and Rahman, Zua, "Copper plating process control by SEM" (2002). *Faculty Bibliography 2000s*. 3037.
https://stars.library.ucf.edu/facultybib2000/3037

TECH SPOTLIGHT

Copper plating process control by SEM

*Jorgen Akesson, Sudipta Seal,**
Satyajit Shukla, Zia Rahman
University of Central Florida
Orlando, Florida

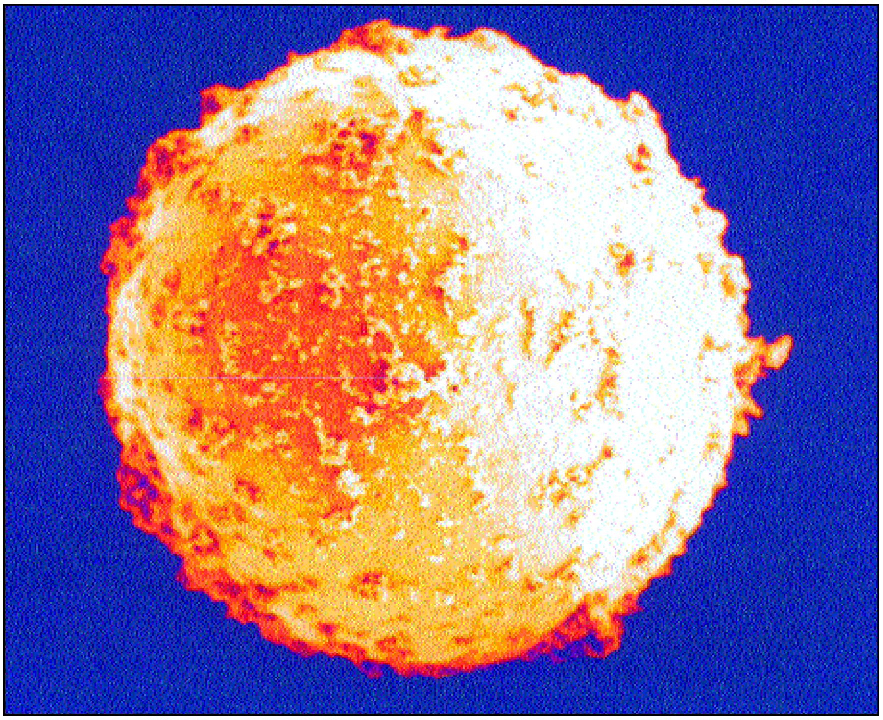

Fig. 1a — This colorized electron microscope photomicrograph shows a single fly ash

Electroless plating is a batch process consisting of a number of process sequences, any of which may affect the results of electroless copper plating. Electron microscopes are powerful instruments for analyzing and acquiring process information that can be subsequently applied to optimize the outcome.

This article describes an example of how electron microscopy could be successfully implemented in developing a novel electroless copper plating process applied on hollow ceramic cenospheres from coal combustion, to develop conductive fillers for EMI shielding.

Fly-ash spheres

In electroless plating, the part is immersed in different agitated solutions until it is plated and the surface is free of residue. The process as applied to fly-ash cenospheres consists of three steps:

- Sensitization in a stannous chloride solution
- Activation in a palladium chloride solution
- Plating in a complex copper sulfate solution

The copper sulfate solution also contains reducing agents, in which palladium acts as a catalyst. A few cleaning and drying steps are also required to complete the process.

Fly-ash particles are a by-product of coal-fired power plants. The particles are hollow spheres within a size range of 30 to 300 ? m. Although the chemistry of the particles varies depending on the coal-combustion process, they are mainly composed of silica and alumina.

The size distribution, chemistry, and amount of fly-ash, as well as the chemical composition and pH of the plating solutions, affect the coating process to a great extent. Furthermore, the plating process is highly complex and difficult to control, and it is also difficult to change. However, the process must usually be altered for new substrates and even for scale-up from laboratory processes.

When trying to establish a working electroless plating process for particles, the first rule to apply is the size rule: smaller-size particles have a higher surface area per volume. Therefore, a higher electroless bath concentration is needed throughout the process. Size distribution is easily determined by an electron microscope in combination with image analysis software (Fig. 1a and b).

An unsuitable plating composition results in either partially coated surfaces or some completely uncoated particles, which appear as charging areas in the SEM. Partially coated particles (Fig. 2) are caused by either an insufficient number of copper ions in solution, or insufficient amount of pH stabilizer in the plating solution. The pH stabilizer is needed to maintain an appropriate pH range for efficient copper reduction by formaldehyde. These two conditions may lead to thin and patchy

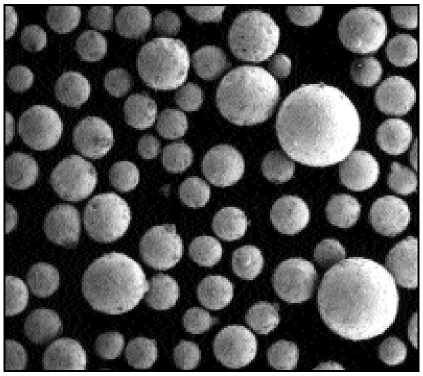

Fig. 1b — The size distribution among fly ash particles ranges from 30 to 300 mi-

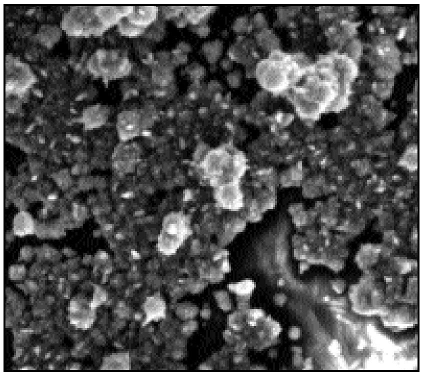

Fig. 2 — Partially coated particles may be caused by an insufficient number of copper ions in solution.

**Member ASM International*

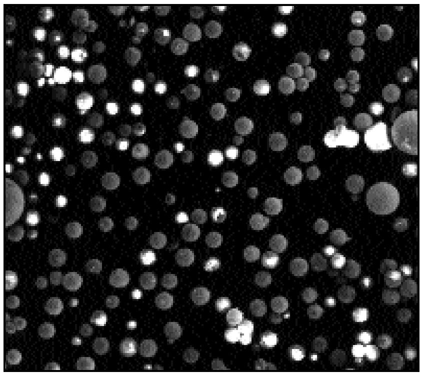

Fig. 3 — This photomicrograph shows 15% uncoated particles.

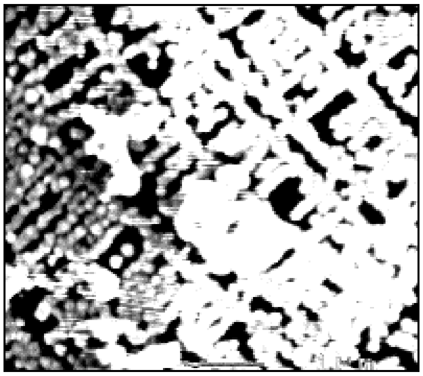

Fig. 4 — The coating process is initiated as an array of connected copper

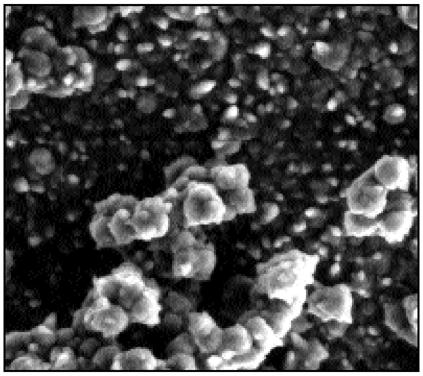

Fig. 5 — The nanoparticles grow and coalesce, forming layer after layer until the copper is depleted from the solution.

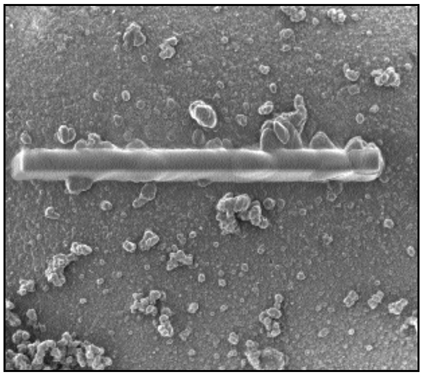

Fig. 6 — Focused ion beams deposit a protective layer of platinum as an upper reference.

coatings, and can be distinguished by the appearance of the plating solution, which in the first case turns clear and in the second case remains blue because of the extra copper ions.

Uncoated particles (Fig. 3) are caused by insufficient activation by palladium. This is resolved by making sure that enough palladium is present and by allowing longer stirring time. Some studies have suggested that copper loses its catalytic activity when thickness increases, which might be the reason for the remaining blue color of the solution.

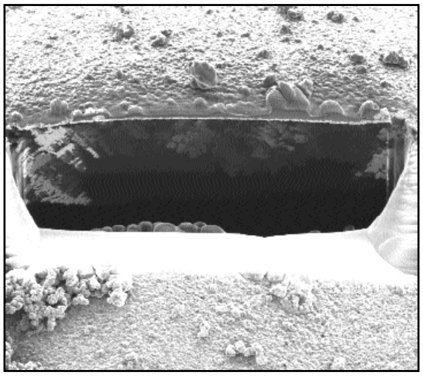

Fig. 7 — An ion-milled hole as seen at an angle of 45 degrees.

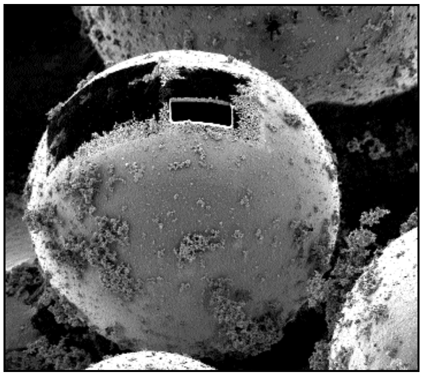

Fig. 8 — The same ion-milled hole, as seen at low magnification.

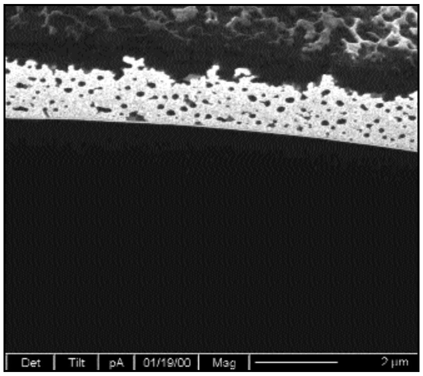

Fig. 9 — This thick porous coating was formed too fast, and trapped hydrogen gas inside the coating.

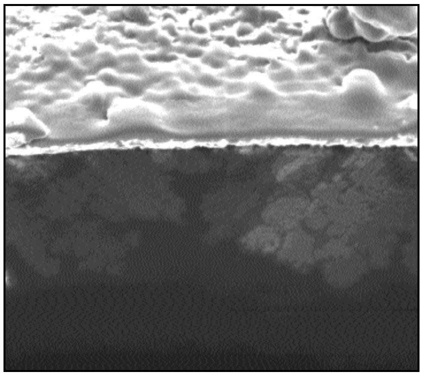

Fig. 10 — This thin uniform coating was the result of a controlled deposition rate and a sufficient concentration of

Growth morphology of the copper coating can be studied to understand the plating process further. If the sensitization and activation are done right, the copper coating builds up in a layered fashion.

The coating initiates uniformly over the surface as an array of connected copper nanoparticles in a single layer (Fig. 4). Slightly non-uniform deposition of the active palladium on the surface eventually creates complete coverage. This is because copper coatings build up from islands that are initially separated from each other, but which eventually coalesce and form a thicker and more non-uniform “first layer” (Fig. 5).

Cross-section thickness

SEM proves to be inadequate to measure the cross-section thickness of a coating on a small particle. The common sample preparation methods, such as pressing a pellet containing the particles, followed by polishing, consume too much time. To circumvent this problem, a focused ion beam instrument (FIB) was used to quickly and precisely measure and visualize the coating cross-section. The preparation consists of the following steps, all confined within and executed in-situ by the FIB:

- Depositing a protective layer of platinum as an upper reference
- Milling a hole through the coating
- Tilting the sample to view the cross-section.

All three steps are shown in Fig. 6, 7, and 8 (Figures 7 and 8 both represent a tilted sample). The coating thickness can then be easily measured, and the cross-section may be readily inspected at a very high magnification with enhanced resolution. The cross-section in Fig. 9 is thick and porous, which suggests that the copper deposited with excessive copper in solution and at a high rate, causing hydrogen gas (extracted during the copper reduction process) to be trapped inside the coating. By lowering the copper concentration and controlling the pH, the process yields very uniform and homogenous coatings with a sufficient coating thickness, as shown in Fig. 10.

Mechanistic aspects

As mentioned earlier, the coating process is achieved through sensitization, activation, washing, and coating in a copper sulfate bath in the presence of the reducing agent formaldehyde. Our detailed microscopy and X-ray photoelectron spectroscopy studies at each step reveals that the coating is initiated by palladium clusters (4 to 5 nm) and not by palladium-tin alloy formation during sensitization and activation. The coating bath first dissolves this sheath, exposing the palladium sites for actual copper deposition. The copper coating begins at this point, when copper atoms formed by the reduction of Cu^{2+} ions by HCHO, are deposited on the ceno-sphere particle surface, the reaction which is activated by Pd(0) sites. Deposited copper atoms then act as self-catalysts for subsequent deposition, and the result is development of a uniform coating via formation and growth of copper nanoparticles.

In conclusion, the coating thickness and coating quality are greatly improved by combining sound engineering skills with powerful analytical instruments, such as SEM and FIB. The thickness of the copper coating can vary from 200 nm to 1 ?m, depending on the coating conditions. The process was successfully scaled up for a pilot plant plating facility and was then transferred to an external company for possible commercialization. Recently, we have also developed cost effective-based activators in place of costly palladium chloride, which can reduce the coating cost considerably. ■

For more information: Sudipta Seal is a professor at the University of Central Florida, Advanced Materials, Processes and Analysis Center, Mechanical, Materials and Aerospace Engineering, Eng 381, 4000 University Blvd., Orlando, FL 32816; tel: 407/823-5277; fax: 407/823 0208; e-mail: sseal@pegasus.cc.ucf.edu. He is currently the Nanoinitiative Coordinator at UCF.

This article, in poster form, won an Honorable Mention in the 2001 IMS International metallographic contest.

The authors acknowledge Energy Strategy Associates Inc.(R. Order), USNR Coal Resources (R Carter), and I4 Corridor Initiative for financial support. Authors also thank AMPAC's Materials Characterization Facility.

How useful did you find the information presented in this article?
Very useful, **Circle 285**
Of general interest, **Circle 286**
Not useful, **Circle 287**