

Selective Deposition of Metallic Nanoclusters on Silicon by a Galvanic Displacement Process

L. Magagnin^a, P.L. Cavallotti^a,
R. Maboudian^b, C. Carraro^b

^a Dipartimento di Chimica, Materiali e Ingegneria
Chimica "Giulio Natta" - Politecnico di Milano
Via Mancinelli, 7 - Milano - Italy

^b Department of Chemical Engineering
University of California
Berkeley, California 94720-1462 - USA

Wet processes for the deposition of metallic films on silicon from fluoride containing solution are currently under investigation,¹⁻³ for applications in microelectronics and in micromechanical systems technology. This work presents a novel method for depositing nanostructured films of noble and platinum-group metals by galvanic displacement from water-in-oil microemulsions. One possible application of this process is coating of the interior walls of microchemical reactors⁴ for enhanced catalytic activity. The water-in-oil system investigated comprises an organic phase (n-heptane), a surfactant (AOT), and an aqueous solution of hydrofluoric acid and metallic ions. Metallic nanoclusters are deposited by galvanic displacement at the silicon substrate in contact with the fluoride containing water droplets. Nanoclusters with controlled size and distribution are obtained on silicon by regulating the micellar radius and deposition time. Scanning probe microscopy is employed to characterize the deposited films. Microscopic observations are correlated with X-ray diffraction and SEM/EDS analyses to investigate the nucleation and growth of the nanoclusters.

Figure 1 shows SEM images of gold nanoclusters on Si(100) obtained from microemulsions with R values of 50. A uniform coverage of the substrate is obtained. The cluster-size distribution also appears fairly uniform; however, some larger aggregates can be observed and are attributed to cluster coalescence. In the present case, it appears that cluster deposition by galvanic displacement from a single microemulsion is effective in reducing cluster aggregation.

The resulting cluster size values are shown in Fig. 2, together with the expected values of micelle size, which are known to follow the law:

$$R_{\text{micelle}} \text{ (nm)} = 0.175 \cdot R + 1.5$$

with $R = [\text{water}]/[\text{AOT}]$, and R_{micelle} the micelle radius in nanometers. Thus, the gold cluster size follows very closely the size of water droplet in oil.

Results about the deposition of palladium nanoparticles from microemulsions with R from 1 to 50 and with varying deposition time will be presented.

A novel method for depositing metallic clusters on silicon surfaces, conformally and selectively, is demonstrated. It is based on immersion plating in reversed micellar microemulsions of a plating solution containing metal and fluoride ions. A good correlation is found between metallic cluster size and micelle radius. The latter is easily controlled by selecting microemulsion composition.

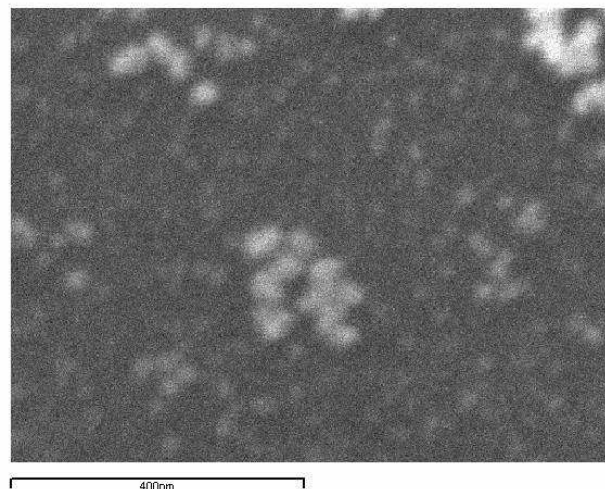


Fig. 1 - SEM micrographs of gold clusters on silicon after immersion for 15 s into a microemulsion with $R = 50$.

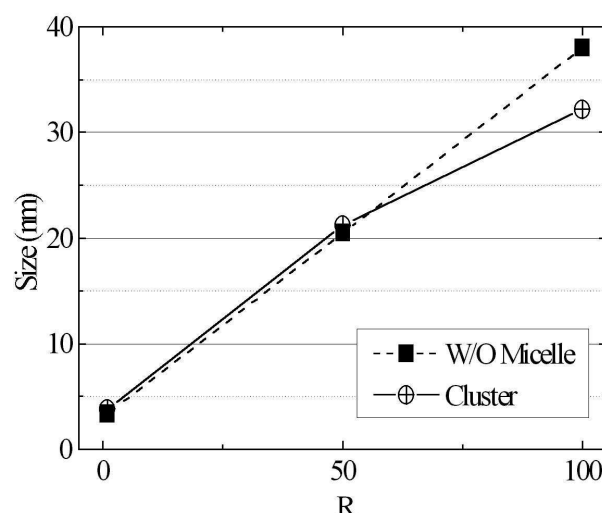


Fig. 2 - Cluster size vs. R for gold clusters on silicon after immersion for 15 s into a microemulsion with $R = 1, 50, 100$.

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