Dynamic microscopy of nanoscale cluster growth at the solid-liquid interface

MOVIES 1 AND 2: LIQUID PHASE DEPOSITION

Nucleation, growth and dissolution of Cu clusters on polycrystalline Au during electrochemical deposition and stripping. Ross-1 shows galvanostatic deposition and stripping at 5 $mAcm^{-2}$ and Ross-2 shows the same process at a higher current density of 50 $mAcm^{-2}$, in each case in an electrolyte containing 0.3M $CuSO_4$. The videos were recorded in a Hitachi H9000 TEM at 300kV using bright field imaging conditions. The field of view (horizontal distance) of 6.3 μm was chosen to give reasonable cluster statistics; smaller fields of view are possible.

In each sequence, the electron beam passes through the electrolyte, the SiN windows and the Au/Ti electrode. These contribute a uniform background. The grain size of the electrode is small (15nm) and individual grains are not visible. When the current is first applied a change of contrast occurs, caused by charging or liquid motion, but this rapidly fades and nucleation events become visible. Individual Cu clusters show as dark areas due to greater scattering allowing positions and diameters to be measured from single frames.

At 5 $mAcm^{-2}$, progressive nucleation is clearly visible and nucleation is complete after 2-3 seconds. No further growth occurs after 3 seconds due to depletion of ions in the solution. After 8 seconds the current source is turned off then a reverse (stripping) current is applied and the nuclei dissolve back into the solution.

At 50 $mAcm^{-2}$, the same processes occur but with a much shorter time scale: in this case nucleation requires less than 0.4 seconds. The nucleation density is higher and nuclei are smaller. Analysis of growth kinetics shows that depletion becomes important at an earlier time at this growth rate.

(Note - videos are shown speeded up x2 to reduce the file size.)