In Situ Scanning Tunneling Microscopy of Underpotential Deposition of Lead on Cu(100) in Sulfuric Acid Solutions

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In situ scanning tunneling microscopy (STM) has been used to examine underpotential deposition (UPD) of lead at Cu(100) electrode in 0.1 M hydrochloric acid containing 1 mM $Pb(ClO_4)_2$. **Figure 1** shows the cyclic voltammogram of Cu(100) electrode in 0.01 M HCl containing 1 mM $Pb(ClO_4)_2$. A negative-going potential sweep starting from 0.12 V results in UPD of sub-monolayer of Pb adatoms at –0.1 V and bulk deposition of Pb at –0.15 V. These corresponding oxidative stripping processes occur at –0.05 and –0.15 V, respectively. This result is consistent with those reported by others.[1,2]

The initial stage of Pb deposition results in well-defined strip patterns running parallel to the <001> direction, which are attributed to the formation of surface alloy with a chemical composition of Pb_3Cu_4. Continuous deposition of Pb atoms induces dealloying, where surface Cu atoms are forced Cu out of the alloyed domains, giving rise to a series of ordered structures of Pb adatoms as the coverage exceeds 0.5. The Pb adlayers are characterized by atomic resolution STM imaging as $c(2 \times 2)$, compressed $c(2 \times 2)$, and $(5\sqrt{2} \times \sqrt{2})R45°$. **Figure 2** presents the atomic resolution of the last structure, featuring alternating straight and zigzag Pb atomic chains. These results are consistent with those observed in an ultrahigh vacuum environment.[3,4]

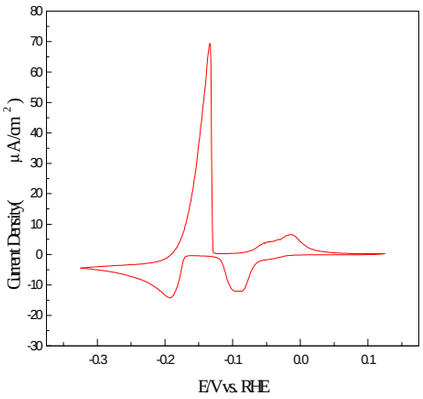

Figure 1. Cyclic voltammograms at 5 mV/s of Cu(100) in 0.01 M HCl containing 1 mM $Pb(ClO_4)_2$.

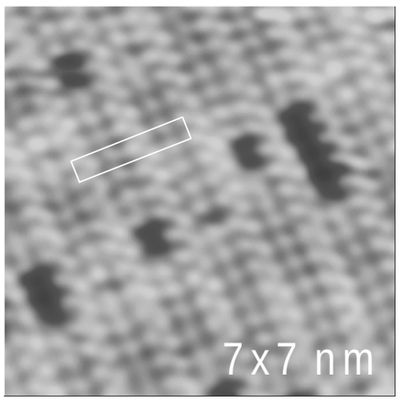

Figure 2. In situ STM atomic resolution of Cu(001) –$(5\sqrt{2} \times \sqrt{2})R45°$ - Pb. The imaging conditions are 50 mV bias voltage and 10 nA setpoint current.

References:

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3. Bocquet, F.; Robert, S.; Gauthier, S.; Duvault, J. L.; Klein, J. *Surf. Sci.* **1997**, *392*, 86.
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