

In- Situ STM Study of Surface Ordering During Pb UPD on Cu (111)

N. Vasiljevic¹, N. Dimitrov² and K. Sieardzki¹

¹ *Ira A. Fulton School of Engineering
Arizona State University
Tempe, AZ 85287-6106*

² *Department of Chemistry
State University of New York at Binghamton
Binghamton, NY 13902-6016*

Ultrahigh vacuum (UHV) experiments demonstrated that the initial stage of Pb deposition on Cu (111) is dominated by a large atomic size mismatch of 37 % [1]. Surface alloy formation at submonolayer coverage of Pb has been observed even at room temperature [1]. This system is an archetype of large atoms on a small substrate, illustrating the effect of atomic size mismatch that favors surface-confined intermixing [2]. A recently reported [3] feature of the Pb/Cu(111) system at elevated temperatures is a domain self-assembly of two coexisting phases: (i) a random surface alloy phase and (ii) a close-packed (4×4) overlayer phase. Currently, this is the only reported system in which the elastic interaction resulting from surface stress difference drives self-assembled domain stabilization. The unusual behavior of this system observed in UHV, motivated the in-situ electrochemical STM study that we discuss here.

It is known that Pb forms one epitaxial wetting layer on Cu (111) in the potential region positive to the reversible potential of bulk Pb deposition (underpotential deposition – UPD) [4-7]. This highly irreversible UPD process shows unusual behavior that is strongly dependent on the system pre-polarization history, solution pH and anion content of the solution. So far, this process has been analyzed by conventional electrochemical techniques such as cyclic voltammetry, chronoamperometry and rotating ring disc electrode [4-7]. The structural analysis of a complete lead UPD layer has been done by ex-situ LEED and in-situ X-ray diffraction techniques [7, 8]

In this work we will present the first in-situ STM study of Pb UPD on Cu (111) in 0.2 mM $\text{Pb}(\text{ClO}_4)_2$ at different pH values. High resolution STM results show (4×4) Moiré pattern of a complete closepacked Pb UPD layer formed on Cu (111) as shown in Figure 1. The structure of the as-deposited layer is identical to the one observed in UHV experiments [1]. Dynamic STM experiments showed a modulated topmost copper layer after stripping of Pb. Depending on the solution pH value, STM results revealed different types and dimensions of nano-scale organization: (a) an anion-induced reconstruction on Cu (111) at pH 2 and (b) a star pattern dislocation network at pH 1 (Figure 2). The observed changes could be explained by Pb assisted anion adsorption and/or Pb playing a catalytic role on the kinetics of electrode processes sensitive to presence of oxygen species in the solution. The conclusions are supported by in-situ STM experiments on Cu (111) in lead-free perchlorate solutions at different pH values.

References

1. C. Nagl, O. Haller, E. Platzgummer, M. Schmid and P. Varga, *Surf. Sci.*, **321**, 237 (1994).
2. J. Tersoff, *Phys. Rev. Lett.*, **74**(3), 434 (1995).

3. R. Plass, N.C. Bartlet and G.L.Kellogg, *J. Phys: Condens. Matt.*, **14**, 4227 (2002).
4. H. Siegenthaler and K. Juttner, *J. Electroanal. Chem.*, **163**, 327 (1984).
5. J.R. Vilche and K. Juttner, *Electrochim. Acta*, **32**(11), 1567 (1987).
6. A. Bewick J. Jovicevic and B. Thomas, *Farad. Simp. Chem. Soc.*, **12**, 25 (1977).
7. G.M. Brisard, E. Zenati, H.A. Gasteiger, N.M. Markovic and P.N. Ross Jr., *Langmuir*, **11**, 2221 (1995).
8. Y.S. Chu, I.K. Robison and A.A. Gewirth, *Phys. Rev. B*, **55**(12), 7945 (1997).

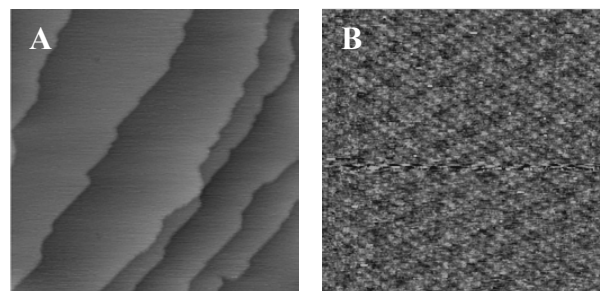


Figure 1 (A) Pb UPD monolayer on Cu (111) surface in perchlorate solution pH 2. Scan size 100×100 nm. (B) (4×4) Moiré superstructure of Pb UPD monolayer. Scan size 10.5×10.5 nm.

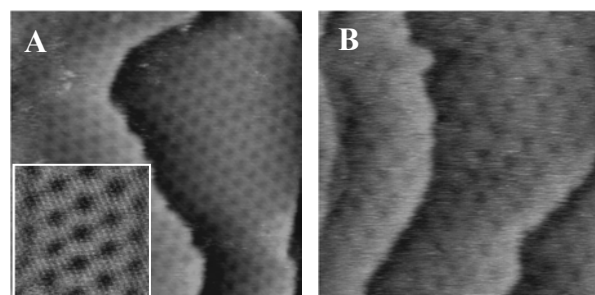


Figure 2 Nano-structured Cu (111) surface after stripping of Pb UPD layer in perchlorate solutions. Scan size of both images is 60×60 nm. (A) Solution pH 2; Inset size is 16.5×16.5 nm. (B) Solution pH 1.