NOVEL FEATURES OF INITIAL STAGE ELECTRODEPOSITION OF SN AND SB ON AU AND CU BY IN-SITU STM

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By employing in-situ scanning tunneling microscope, underpotential as well as overpotential deposition of practically important Sn and Sb on Au(hkl) and Cu(hkl) electrode surfaces are investigated systematically. It is emphasized that the characteristic adlayer structures as well as dynamic behavior of the underpotential deposition (UPD) are determined by interactions between the substrate surface atoms, adatoms and ions from the electrolyte as well as among themselves.

In the absence of anion adsorption, metal UPD and their corresponding adlayer structures are entirely determined by the crystallography of substrate and adatom-substrate interaction. For example, size-confined clustering and anisotropic growth behavior are the characteristics of Sn UPD on Au(111)(1×1) and Au(111) (√3×22), respectively. With an increasing adatom-substrate interaction via directional bonding and electron back donation, Sb UPD on Au(111) is observed to induce relaxation of the (√3×22) reconstruction to corrugation lines of trigonal network as well as surface alloying. In the case of Sb on Au(100), formation of a stable chemisorbed-type surface complex suppresses surface alloying on the more open (100) surfaces.

In the presence of anion adsorption, however, UPD processes are determined by the relative strength of all interactions between adatom-substrate, adatom-anion, anion-substrate and anion-anion. In the case of Sn UPD on Cu(111) in sulfuric acid solution, both the anion-substrate and anion-anion interaction are sufficiently large. This severely restricts the Sn UPD process so that the UPD starts with breakthrough sites at the periphery of the anion adlayer, and proceeds by displacing the anions and releasing the bare surface sites for further deposition.

Sb is a semi-metallic element with covalent bond nature. And there is a large crystallographic mismatch between the rhombohedral Sb and fcc metals of Au and Cu. The overpotential deposition of Sb also displays a novel growth behavior with the formation of well-orientated three-dimensional nanostripe architecture. This is attributed to the occurrence of lattice coincidence between Sb and Cu(100), which is normally observed in the semiconductor growth. Under this circumstance, a layer-by-layer epitaxy of nanostripes can be achieved to as thick as several tens of monolayers even in the overpotential range.

The results demonstrate that subtle electronic and crystallographic differences of the substrate as well as the nature of the depositing metal may lead to significantly different UPD and OPD behaviors. The observed features provide new insights into the dynamics of initial stage electrodeposition and related fundamental processes such as surface reconstruction, competitive adsorption and surface alloying.

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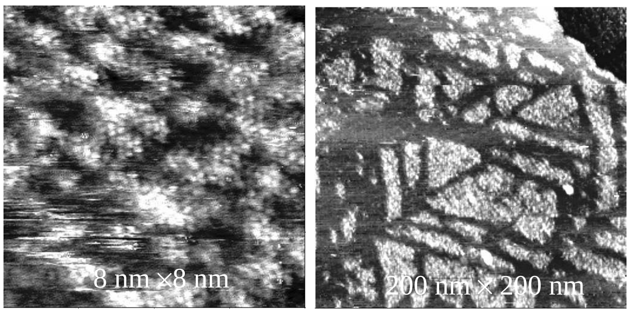

Fig.1 Size-confined clustering and anisotropic growth of Sb on Au(111) (1×1) (left) and Au(111)(√3×22) (right).

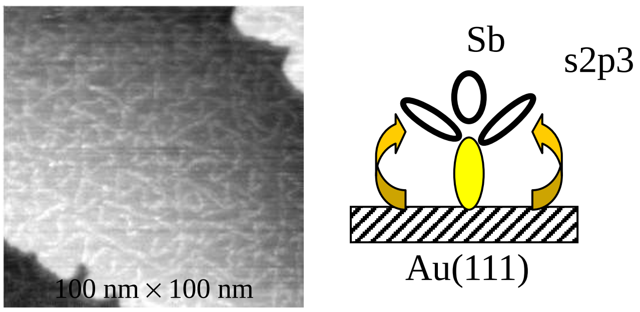

Fig. 2. Sb adlayer induced relaxation of Au(111)(√3×22) reconstruction

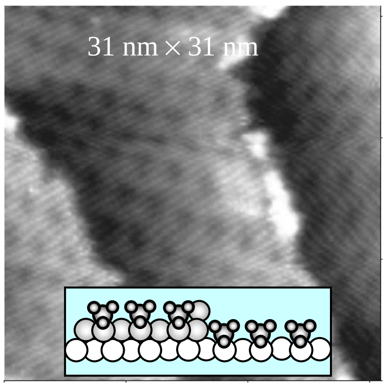

Fig. 3. Competitive adsorption of Sn and SO_4^{2-} on Cu(111).

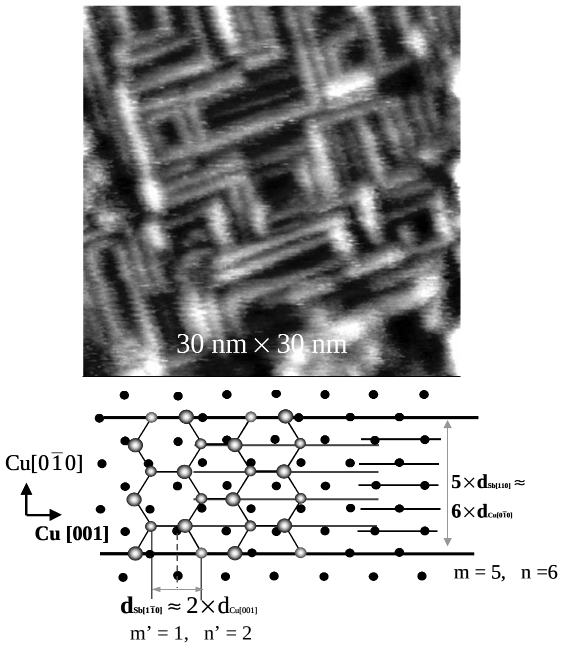

Fig. 4. Formation of Sb Nanostripes on Cu(100) via Coincidence Lattice.