Surface Oxidation of Liquid Sn

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Introduction

Motivation:

Chemical reactions at surfaces and interfaces attract significant scientific interest since these reactions, often resulting in new materials not existing in the bulk, can be important for nanotechnology

Free liquid metal surfaces have recently attracted considerable attention because of the structural order at the liquid surface interface. At the same time there are almost no studies of reactive properties of free liquid metal surfaces

Idea:

Study the oxidation process of the free liquid Sn surface using specular and off-specular X-ray scattering as well as the grazing incidence diffraction (GID)

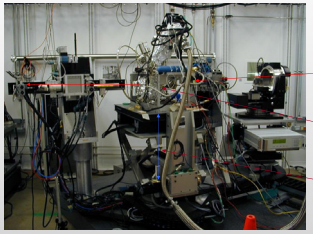
Tools:

Sn sample prepared and exposed to oxygen *in situ* in UHV chamber as mounted on the liquid reflectometer in sector 15-ID ChemMatCARS at APS

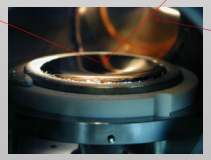
Experimental Details

Atomically clean surface of liquid Sn was prepared in UHV at $p < 1 \times 10^{-9}$ Torr by sputter etching of the liquid sample held at 240C.

UHV chamber at 15-ID ChemMatCARS beamline



Liquid sample in the chamber



X-ray beam comes through that window, the approximate beam path is shown
(in real experiment viewports are replaced by beryllium windows)

X-ray scattering:

Specular

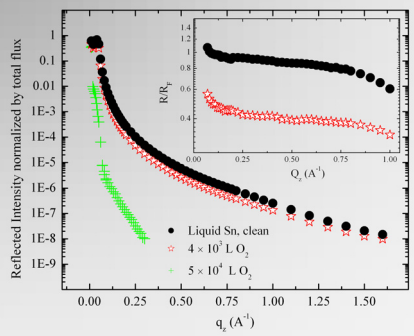


FIG. 1: Specular X-ray reflectivity from clean liquid Sn surface (black); after oxygen dose of 4×10^3 L at 2×10^{-5} Torr pressure (red); and from a strongly oxidized sample (green). The inset shows reflectivities normalized by Fresnel reflectivity

Off-Specular

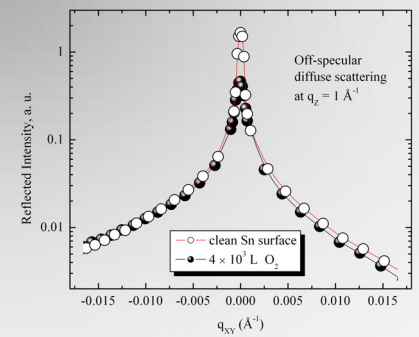


FIG. 2: Off-specular scattering scans measured at an incident angle equivalent to the $q_z = 1$ Å^{-1} from clean Sn surface (open symbols) and oxidized sample (closed symbols) - 4×10^3 L at 2×10^5 Torr

• **Specular reflectivity.** The x-ray reflectivity from the rough heavily oxidized Sn surface becomes unmeasurably small at small q_z. The reflected intensity from a weakly oxidized surface is ~ 50% less than that of the unoxidized surface however, it has essentially the same shape. This behavior could occur if ~50% of the surface was covered by a rough oxide.

• **Off-specular diffuse scattering.** If the above hypothesis were correct the central peak and wings of the off-specular scan should loose intensity in the same proportion. This is not the case and suggests that the fraction of the surface that is covered with rough, non-reflecting oxides, is much less than ~50%. Rather this data suggests that a smaller fraction of rough oxide patches distorts the surface to deflect the reflected signal away from the specular condition. This reduces the specular peak more than the wings.

Oxidation Kinetics

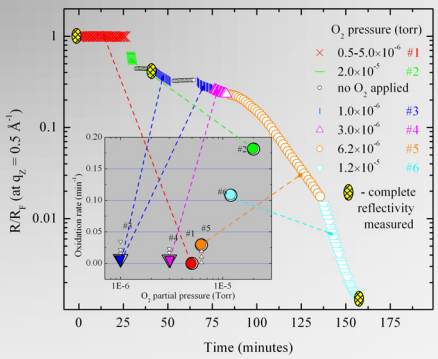


FIG. 3: Reflected x-ray signal at $q_z = 0.5$ Å^{-1} during surface oxidation as a function of time. Inset shows the rate of the reflected intensity change which is a function of the oxidation rate.

• No observable effect of oxidation until oxygen pressure exceeds 5×10^{-6} Torr. > Oxidation activation pressure is needed to start oxidation process at liquid Sn surface

• Subsequent changes were observed at oxygen pressure below threshold (#3 and #4 at the plot). > Oxidation proceeds around nucleation sites generated above the activation pressure

Crystal Structure of Sn Oxide

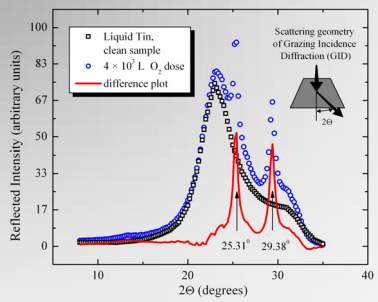


FIG. 4: GID from clean liquid Sn surface and after exposure to oxygen dose of 4×10^3 L at 2×10^{-5} Torr (after #2 in Fig.3). Broad peak at 2Θ=23 degrees corresponds to the bulk liquid structure factor of Sn.

Two sharp diffraction peaks observed after oxidation correspond to a polycrystalline sample (proved in an additional experiment) with a crystal structure that is best described by a cubic structure (NaCl type)
Fm(-3)m space group. This structure has never been observed before for Sn oxides and can be proposed to be a Sn oxide that forms at the liquid Sn surface due to the surface ordering (*O. Shpyrko et al., in preparation for PRB*).

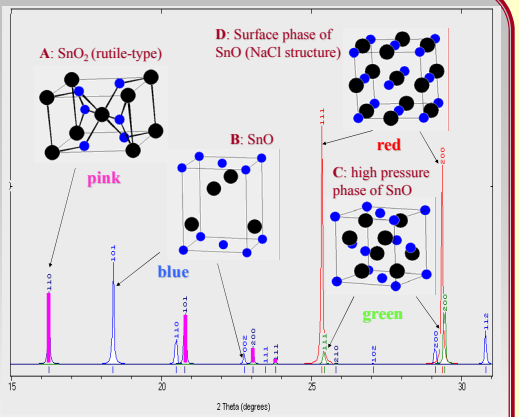


FIG. 5: Theoretical models of different possible crystal structures of a Sn oxide. Native oxide structures (dioxide **A** and monoxide **B**) can be ruled out as candidates to fit the experimental results since their diffraction patterns include strong peaks not observed on the experiment. The high pressure phase of SnO (*J. Haines et al., Science* ***271****, 629 (1996)*) *Pa(-3)* space group (**C**) can fit the experiment but the Sn-O closest neighbor distance is considerably smaller than molecular Sn-O ionic bond length. The halite structure (**D**) fits the experimental data if the lattice constant $a = b = c = 3.77$ Å that is used is the same lattice constant as $a = b$ of the tetragonal monoxide structure. In this case the Sn-O closest neighbor distance matches the molecular Sn-O ionic bond length within 5%. Moreover, the halite structure along (111) crystallographic direction consists of hexagonally packed layers which should be native atomic packing for the free liquid metal surface. Thus one can imagine that the oxygen atoms embed in between of surface layers of liquid metal to form an epitaxial oxide.

Summary

- A threshold oxygen pressure of the order of 5×10^{-6} Torr is required to initiate oxidation of a clean liquid Sn surface.
- Oxide patches form homogeneously when the oxygen pressure exceeds the threshold. Once oxide patches have formed further oxidation will occur for pressures below threshold.
- Sharp diffraction pattern observed in GID measurements of an oxidized liquid Sn surface show solid polycrystalline Sn oxide growth.
- The measured diffraction pattern does not correspond to native Sn monoxide or dioxide crystal structure. The best fit of the observed pattern is with the halite crystal structure using the same lattice constant of *3.77 Å* that applies to the tetragonal native Sn monoxide.
- It is proposed that the atomic ordering at the liquid Sn surface is responsible for epitaxial growth of the cubic halite-type structure at the surface.

Acknowledgements

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