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Surface oxidation of liquid Sn

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Abstract

We report the results of an X-ray scattering study that reveals oxidation kinetics and formation of a previously unreported crystalline phase of SnO at the liquid–vapour interface of Sn. Our experiments reveal that the pure liquid Sn surface does not react with molecular oxygen below an activation pressure of $\sim 5.0 \times 10^{-6}$ Torr. Above that pressure a rough solid Sn oxide grows over the liquid metal surface. Once the activation pressure has been exceeded the oxidation proceeds at pressures below the oxidation pressure threshold. The observed diffraction pattern associated with the surface oxidation does not match any of the known Sn oxide phases. The data have an explicit signature of the face-centred cubic structure, however it requires lattice parameters that are about 9% smaller than those reported for cubic structures of high-pressure phases of Sn oxides.

Keywords: X-ray scattering, diffraction, and reflection; Oxidation; Surface chemical reaction; Surface structure, morphology, roughness, and topography; Tin; Tin oxides; Liquid surfaces; Polycrystalline thin films

1. Introduction

Chemical reactions at interfaces are of the fundamental and practical scientific interest. They sometimes exhibit both unusual kinetics and new phases that are unstable in the bulk [1–3]. There are considerable differences between the ways oxidation develops in various materials. One

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commonly cited example is the surface of solid aluminum. Although the oxidation of Al is rather rapid in the presence of even trace amounts of molecular oxygen, the formation of a relatively thin surface oxide layer effectively passivates the bulk from further oxidation [4]. By contrast, oxidation of metals like Fe proceeds well into the bulk. In spite of the fact that the free surfaces of liquid metals have recently attracted considerable attention because of the atomic ordering at the liquid–vapor interface [5–7] there have been very few studies of their reactive properties [8–11]. Oxidation of such surfaces are of particular interest because they lack the types of defects at which homogeneous nucleation occurs on solid surfaces namely steps, pits and dislocations [1]. In addition, surface oxidation of liquid metals can drastically change the surface tension which will have a profound effect on the way the liquid metal wets different surfaces [10]. This is important for practical processes such as soldering, brazing, casting, etc.

The only two liquid metals for which the structure of the surface oxide has been studied by X-ray scattering technique are In and Ga, which were found to behave differently [8,9]. Oxidation of the liquid Ga surface is similar to that of solid Al in that it saturates at a 5 Å (1 Å = 10^{-10} m) depth to form a uniform layer protecting the metal from further oxidation [12]. By contrast, oxidation of liquid In produces a rough oxide film from which there is negligible X-ray reflectivity signal [8]. Grazing incidence diffraction (GID) of the Ga surface oxide did not reveal any Bragg peaks, indicating that this oxide is amorphous. A direct comparison with In is not possible since GID measurements were not done for the surface oxide. In the present paper we report both X-ray reflectivity and GID studies of the oxide growth on the liquid Sn surface. In addition to the static features of the structure, these measurements also provide important information on the oxidation kinetics of the liquid Sn surface.

2. Background

2.1. Surface scattering of X-rays

X-ray reflectivity and GID are widely used for the determination of the structure of surfaces and interfaces, while off-specular diffuse scattering is used to probe surface homogeneity and roughness [13,14]. The present study makes use of all three techniques to characterize the oxidation of the liquid Sn surface. The geometry for these techniques is shown in the Fig. 1. X-rays of wavelength λ and wave-vector $k = 2\pi/\lambda$ are incident at an angle α to the surface. For specular reflectivity the detected wave-vector is in the plane of incidence, $\Delta\Theta = 0$, at an angle $\beta = \alpha$ to the surface. The scattering is measured as a function of wave-vector transfer along the normal to the surface $q_z = 2k\sin\alpha$. For GID, the incident angle is generally less than the critical angle, α_c, for total external reflection [14], and scattering is measured as a function of both the surface-parallel, $q_{xy} = k \times \sqrt{\cos^2\alpha + \cos^2\beta - 2\cos\alpha\cos\beta\cos(\Delta\Theta)}$ and surface normal, $q_z = k[\sin\alpha + \sin\beta]$, components of the wave vector. Small angle off-specular diffuse scattering is measured in the plane of incidence, $\Delta\Theta = 0$, as a function of β for fixed α with $q_y = k[\cos\alpha - \cos\beta]$ and $q_z = k[\sin\alpha + \sin\beta]$.

The reflectivity $R(q_z)$ is commonly expressed as

$$\frac{R(q_z)}{R_\mathrm{f}(q_z)} = |\Phi(q_z)|^2 \exp[-\sigma(q_z)^2 q_z^2],\qquad \sigma(q_z)^2 = \sigma_\mathrm{int.}^2 + \sigma_\mathrm{cw}(q_z)^2, \tag{1}$$

where $R_\mathrm{f}(q_z)$ is the Fresnel reflectivity that can be calculated from classical optics for a flat and structureless surface, $\Phi(q_z)$ is the surface structure factor, and $\sigma(q_z)$ is the effective surface roughness consisting of the intrinsic roughness σ_int and the

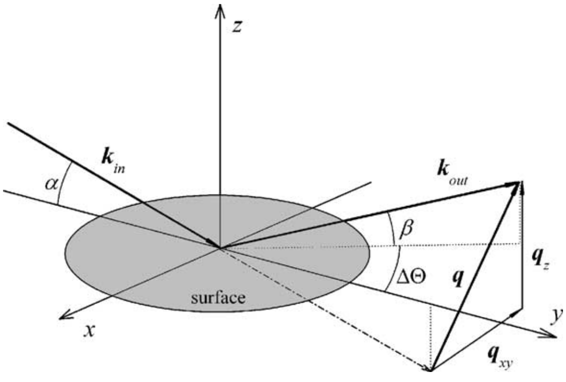

Fig. 1. Kinematics of the X-ray scattering used in the present study.