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Autocatalytic Oxidation of Lead Crystallite Surfaces

Konrad Thürmer,¹ Ellen Williams,¹ Janice Reutt-Robey^{2*}

Growth of an ultrathin lead oxide layer causes massive changes in the shape of lead crystallites. The dynamics of this process was investigated with time-lapsed scanning tunneling microscopy. Pure lead crystallites proved extremely resistant to oxidation. Once nucleated by surface impurities, monolayer films of lead oxide grew readily on lead (111) microfacets in an autocatalytic process. The anisotropic growth of orthorhombic lead oxide films (massicot structure) was most rapid along the direction of weakest lead-oxygen bonding, which suggests that the growth edge autocatalyzes oxygen dissociation by providing proximal sites for oxygen dissociation and attachment.

Thin oxide films, formed by direct reaction between metal surfaces and gaseous O₂, are widely used as catalysts, sensors, dielectrics, and corrosion inhibitors. Studies of the kinetics of oxide growth have shown that once a stable oxide layer forms, the rate of oxidation is limited by field-enhanced transport of ionic species across the oxide film [the Mott-Cabrera model (1)]. Oxide growth thus occurs most rapidly for thinner films but then slows dramatically by transport through thicker films, resulting in a parabolic growth law.

Unfortunately, the Mott-Cabrera model omits the initial stage of oxidation, which is crucial for growing uniform ultrathin oxides of current technological interest, and there have been surprisingly few experimental studies of this critical regime. The initial stage is generally assumed to proceed via the formation of a chemisorbed O monolayer, followed by the nucleation, growth, and coalescence of two-dimensional oxide islands. The saturating O monolayer offers a simple, yet often invalid, assumption: Transition metal systems, such as O/Ru(0001) (2) and O/Ag(110) (3), support chemisorption beyond the monolayer via the dissolution of atomic O and the formation of a variety of O species. For example, emergent RuO₂ patches strongly mediate O uptake by increasing the dissociative sticking coefficient of O₂ by up to six orders of magnitude (4, 5) by the adsorption and subsequent dissociation of O₂ on RuO₂ (6). Simple metal surfaces, in contrast, cannot easily dissociate molecular O₂ (7), hindering the accumulation of even

monolayer quantities. We now report the direct imaging and temporal evolution of PbO films in the nanometer-thickness regime at elevated temperatures. Trace surface impurities are needed to form oxide nuclei on a Pb crystallite surface. Once nucleated, PbO grows autocatalytically in two dimensions. The growth anisotropy of individual PbO grains implicates the dissociation of O₂ as the rate-limiting step. The applicability of this mechanism to other materials systems and technologies is discussed.

Pb crystallites were selected as the model system for these investigations because of the extensive knowledge of the pure crystallite shape derived from scanning electron microscopy (8, 9), scanning tunneling microscopy (STM) (10, 11), and first-principles theoretical calculations (12). Defect-free Pb crystallites can be prepared on a Ru(0001) [or graphite or Cu(001)] support with exposed (111) top facets and (111) and (100) side facets. The rounded crystallite edges display a 3/2 power law (13), indicating that the crystal shape is locally equilibrated. Energetic values for both step and kink formation energies have also been evaluated for this system (10). Pb crystallites are inert with respect to all chamber residual gases (H₂, CO, and CO₂), and the effects of O₂ are thus easily isolated.

We prepared ~1- μ m Pb crystallites under ultrahigh vacuum (UHV) conditions by the room-temperature deposition of a 20- to 30-nm Pb film onto a clean Ru(0001) substrate and subsequent dewetting at temperature (T) ~620 K, or 20 K above the Pb melting temperature, T_m (10). The molten Pb droplets were then cooled at a rate of 0.3 K s⁻¹ to solidify the droplets into crystallites with few (and in some cases no) imperfections. The crystallites were then typically held at elevated temperatures (T ~380 K) for a period of 2 days in order to

achieve stable near-equilibrium crystal shapes. We then used variable-temperature (VT) STM to follow the oxidation of these supported Pb crystallites during in situ exposure to oxidizing gases (14). In lower resolution measurements, we resolved the movements of individual crystallographic steps and the correlated development of PbO grains. For atomistic details on the structures of these PbO grains, we subsequently imaged the grains with atomic resolution at room temperature (15).

We briefly review the structural features of these truncated Pb crystallites. The uppermost part of a Pb crystallite (Fig. 1A) is capped with a (111) facet that is atomically smooth and has a characteristic diameter of about one-half that of the crystallite. The "noisiness" of the monatomic steps that descend to join the (111) and (100) side facets is caused by fluctuations in the step positions (16). The relatively small kink formation energy of 40 meV (10) leads to substantial edge-atom motion at the 380 K temperature of measurement.

After prolonged O₂ exposures under UHV conditions [5000 Langmuirs (L) of O₂, or 1 \times 10⁻⁶ torr for 5000 s] at 370 K, Pb crystallites undergo massive structural transformation (Fig. 1B). Although the Pb mass is conserved overall, the crystallites develop sharp edges. The curved facet boundary of the Pb crystallite, in particular, yields to oxide-stabilized orientations (see the comparison in Fig. 1C). On the oxidized surface, steps assume the extremely straight (stiff) structures characteristic of an oxide crystal. Remarkably, this gross transformation is accomplished by an oxide layer that is only ~0.5 nm thick. The crystallite can be remelted to remove the oxide layer and restore the Pb crystallite to its neat rounded shape.

These ultrathin oxide-coated crystallites are the results of the billions of surface chemical events. In order to identify these molecular-level processes, we decreased the O₂ pressure to 1 \times 10⁻⁷ torr and limited the exposures to capture the initial stages of this transformation with time-lapsed STM imaging. We determined that impurities play a key role under practical oxidation conditions.

We first examined the oxidation of ultrapure Pb crystallites. Because of the impracticality of imaging the entire crystallite with high resolution, we identify impurity-free surfaces as (i) those which exhibit no impurities when random patches of the surface are imaged with atomic resolution and (ii) those with freely fluctuating step configurations that are completely undistorted

¹Department of Physics, ²Department of Chemistry and Biochemistry, University of Maryland, College Park, MD 20742, USA.

*To whom correspondence should be addressed. E-mail: rrobe@wam.umd.edu

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by impurity pinning. A surface purity level of ~ 10 parts per billion is estimated for such crystallites. A portion of one such crystallite at 370 K (Fig. 2A) contains two distinct structural elements: monatomic steps [which cascade to the (001) facet] and a screw dislocation (shown in the center). Conceivably, both of these edge structures could facilitate oxide growth by acting as nucleation sites or by serving as reservoirs of Pb adatoms, yet this crystallite region proved to be remarkably resistant to oxidation. After exposure to 70 L (Fig. 2B) and 150 L (Fig. 2C) of O_2 , the crystallite remained oxide-free. The screw dislocation and the perimeter steps continued to fluctuate freely with no apparent oxide formation. Even prolonged O_2 exposure (720 L) produced no evidence of oxide formation (Fig. 2D). Pure Pb crystallites showed similar chemical resistance to H_2O and N_2O .

In order to study the role of impurities, we

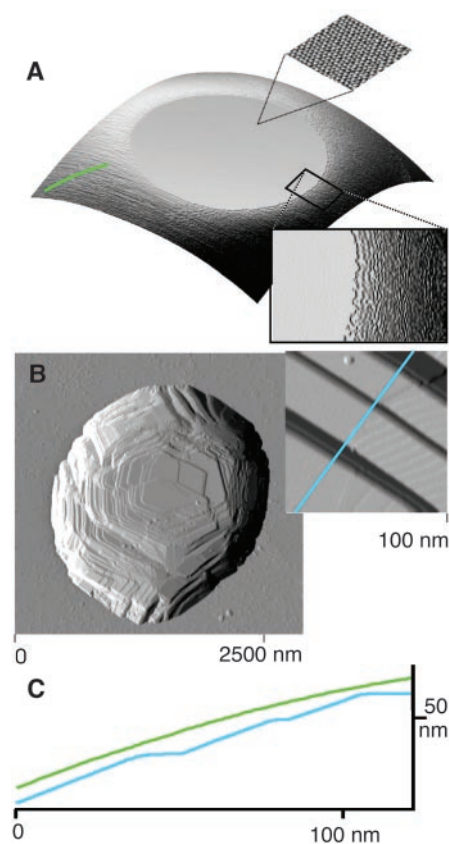


Fig. 1. (A) STM images of the uppermost portion of a Pb crystallite taken at 380 K. Enlarged insets show the (111) atomic structure and the immediate curved region of descending monatomic steps. Curvature (green line) is profiled in (C). (B) Large field-of-view STM image of a Pb crystallite after exposure to 5000 L of O_2 (1×10^{-6} torr) at 370 K and the formation of an ultrathin oxide film. Enlarged inset shows new facet orientations that are profiled (blue line) in (C). (C) Comparison of small-scale surface profiles of Pb (green) and PbO (blue) crystallites.

simply adapt our method of crystallite preparation. Before crystallization, molten Pb droplets can dissolve foreign atoms, which then become trapped upon solidification. Buried impurities had no measurable effect on surface oxide formation, but we could raise shallow impurities (located within ~ 20 nm of the surface) to the surface by utilizing the temperature dependence of the Pb crystallite shape: Upon temperature reduction, Pb crystallites evolved toward their less rounded equilibrium shapes through the monolayer-by-monolayer peeling of the upper (111) microfacet (11). Such peeling (Fig. 3, A and B) can lead to an eventual exposure of buried impurities, such as those located within the two circles in Fig. 3B and profiled in the line scans of Fig. 3C.

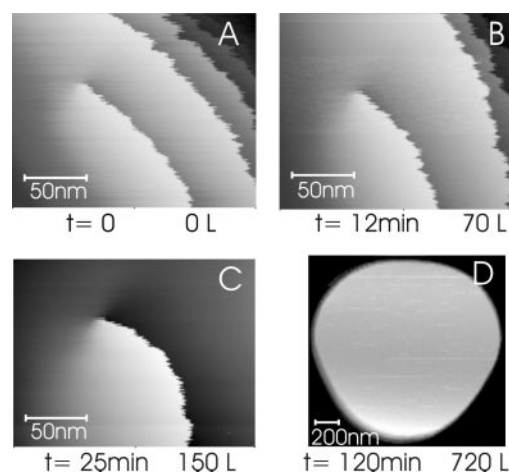


Fig. 2. (A to C) A series of STM images of a crystallite at 370 K upon exposure to 1×10^{-7} torr O_2 , in which the position of a screw dislocation is tracked as it undergoes thermal motion (fluctuations): (A) before oxygen exposure; (B) after exposure to 70 L of O_2 ; and (C) after exposure to 150 L of O_2 . Time (t) is relative to the onset of O_2 exposure. Persistent thermal motion of steps and dislocation, and the absence of oxide formation, show that these morphological elements have little direct impact on Pb oxidation. (D) Larger-scale STM image after 720-L exposure shows an oxide-free top facet.

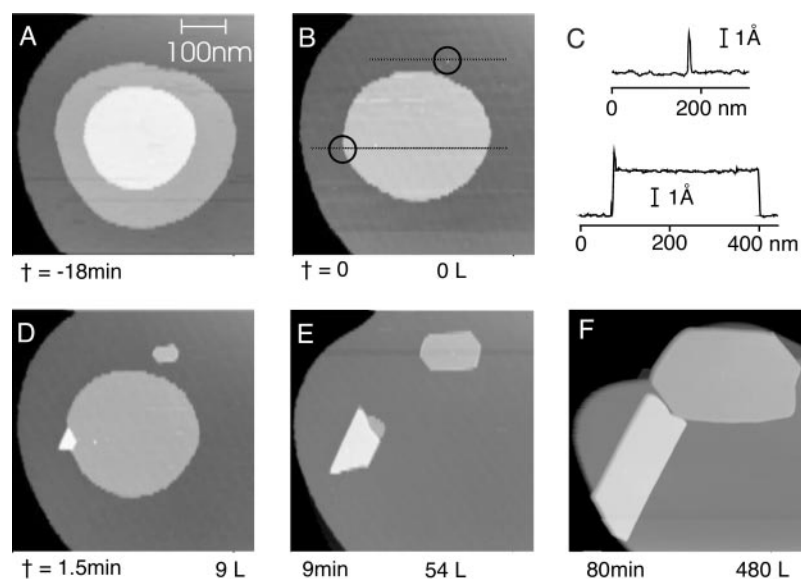


Fig. 3. Time-lapsed STM images of the upper (111) Pb microfacet, after a thermal quench to 370 K, where time (t) is relative to the onset of O_2 exposure. (A and B) The system evolves to its equilibrium shape by the peeling of the topmost layers, which exposes buried surface impurities indicated within the circles. (C) Line scans pinpoint the exposed impurities. (to F) After impurities were raised to the surface, it was exposed to 1×10^{-7} torr of O_2 : (D) Within 1.5 min (9 L), oxide nuclei readily appeared at the impurity sites. (E) After 9 min (54 L), the oxide grains continued to grow rapidly but anisotropically. (F) After 80 min (480 L), they span the top (111) facet along the rapid growth axes and have collided. A more complete sequence is available in fig. S1.

Under identical oxidizing conditions (1×10^{-7} torr O_2 , 370 K), the clean crystallite surface underwent no oxidation after an exposure of 25 min (Fig. 2C), but the impurity-decorated crystallite surface, after 21 min of O_2 exposure, produced 200-nm-long PbO grains. The $>400,000$ atoms incorporated into such a grain require substantial surface atom mobility. Indeed, a Pb adatom surface hopping rate of 10^{11} s^{-1} is estimated from the 62-meV theoretical value for the Pb adatom hopping barrier (17) and a typical 10^{12} s^{-1} prefactor. We thus conclude that PbO forms by heterogeneous nucleation under the conditions of our experiment (18).

The distinct shapes of the two PbO grains of Fig. 3, E and F, identify them as the two distinct polymorphs of lead monoxide—massicot (lower left) and litharge (upper right) (19). Time-lapsed images show that once a polymorph is nucleated, its structure is preserved during subsequent grain growth. Because the orthorhombic form, massicot (Fig. 4, A to C), is most prevalent in Pb oxidation (20, 21), we discuss its growth characteristics (22). The emergent massicot grains exhibit growth shapes that are particularly anisotropic, with two very straight edges characteristic of an oxide grain and two more irregular rapid-growth edges. An analysis of characteristic moiré patterns (fig. S2) in high-resolution STM images and a comparison of atomically resolved images with the known structure allowed us to determine that the a edge of the massicot grains is the active growth edge, whereas the b edge is the more stable edge.

By correlating the atomic-scale structure of the PbO grains to their growth shapes, we now infer the autooxidation mechanism. In the massicot structure, Pb and O atoms arrange themselves in zigzag

chains that parallel the surface. Each massicot unit cell contains two such chains (Fig. 4B), in which each Pb atom coordinates to four O atoms: Two short Pb-O bonds (0.221 and 0.222 nm) make up the Pb-O chain structure (shown as thick solid lines in Fig. 4, B and C), whereas two longer Pb-O bonds (0.249 nm) connect the Pb-O chains (thin solid lines in Fig. 4, B and C) (19, 23). Stronger intrachain Pb-O bonds thus run parallel to the massicot a edge ($a = 0.549$ nm), and weaker interchain bonds run along the massicot b edge ($b = 0.475$ nm). The growth edge of the Pb-O grains is the a edge that parallels the Pb-O chains. PbO grains thus grow most rapidly at the sides of the oxide chains. Rapid growth occurs in the direction of weaker Pb-O bonding, instead of at the more strongly bonding chain ends.

The rate of oxidation is not limited by the attachment of atomic species. In that case, the grains would grow most rapidly at the sites with the strongest covalent bonding, at the Pb-O chain ends or b edge. Instead, O (Pb) atoms attach along the side of the Pb-O chains, in the direction of weaker interchain bonding. This preferred atomic attachment along massicot's a edge reveals the dissociation of O_2 as the rate-limiting step. Along this growth edge, a distance of just 0.34 nm separates Pb atoms and allows both atoms to interact with O_2 (Fig. 4D). After stretching O_2 and lowering the transitional energy for O_2 dissociation, proximal Pb atoms provide accessible attachment sites for both O atoms. Once PbO grains are nucleated at impurity sites, the grains can catalyze their continued growth.

On Pb crystallites, we have observed the nucleation of oxide grains by as yet unidentified surface impurities with imaged heights of 0.1 to 0.2 nm and diameters ranging from <1 to 10 nm. Nucleation

centers thus appear to range in size from several atoms to hundreds of atoms. The thermal stabilities of the impurities suggest that they are not pure metal (elemental Ru) but are more likely compounds of O or C, the main impurities detected by Auger electron spectroscopy. RuO is a plausible candidate for the nucleation center because of its ability to dissociate molecular oxygen (8). Autooxidation holds technological promise and suggests the possibility of planting surface impurities for controlled nanooxide deposition.

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Supporting Online Material

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Figs. S1 and S2

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Fig. 4. (A) Atomically resolved STM image of a PbO grain (massicot structure). (B) Ball-and-stick model of a massicot grain shown in the top-down view, for direct comparison to the atomically resolved STM image. The red rectangle denotes the massicot a - b unit cell. Thick black lines denote stronger Pb-O intrachain bonds in massicot; thin black lines denote weaker Pb-O bonds that couple Pb-O chains in the orthorhombic structure. (C) Side view of massicot structure shown along the a edge (parallel to the Pb-O chains), where growth occurs. (D) Ball-and-stick model for the proposed mechanism of Pb-O-catalyzed dissociation of oxygen along the massicot a edge. Schematically, Pb atoms along the Pb-O chain stretch the O molecule and provide attachment sites, facilitating O_2 dissociation.

