Two-Step Oxidation of Pb(111) Surfaces *

JIANG Peng(姜鹏)[1], WANG Li-Li(王立莉)[1], NING Yan-Xiao(宁艳晓)[1], QI Yun(齐云)[1],
MA Xu-Cun(马旭村)[1]**, JIA Jin-Feng(贾金锋)[2], XUE Qi-Kun(薛其坤)[1,2]

[1]*Institute of Physics, Chinese Academy of Sciences, Beijing 100190*
[2]*Department of Physics, Tsinghua University, Beijing 100084*

We report on a two-step method for oxidation of Pb(111) surfaces, which consists of low temperature (90 K) adsorption of O_2 and subsequent annealing to room temperature. In situ scanning tunnelling microscopy observation reveals that oxidation of Pb(111) can occur effectively by this method, while direct room temperature adsorption results in no oxidation. Temperature-dependent adsorption behaviour suggests the existence of a precursor state for O_2 adsorption on Pb(111) surfaces and can explain the oxidation-resistance of clean Pb(111) surface at room temperature.

Oxidation of metal surfaces has been studied intensively as a very common phenomenon in nature and for its applications in catalysis and electronics.[1−4] In spite of considerable experimental[5−10] and theoretical[11−14] efforts, a clear picture of the fundamental oxidation process is not achieved yet, partially because it varies for different metals. The commonly accepted oxidation process is characterized by formation of a series of states, a physisorbed state of O_2 at the initial stage, an intermediate molecularly chemisorbed state (for example at elevated temperature), and a dissociated chemisorbed state before formation of surface oxides.[9] A modified model is that O_2 molecules adsorb first, subsequently incorporate into the metal. The resulted sub-surface oxygen islands aggregate together, finally transit to oxide films.[12] In both the models, surface adsorption is an essential step in oxidation process.

In the case of Pb, recently, Thürmer *et al.*[8] investigated the oxidation behaviour of the (111) surface by using scanning tunnelling microscopy (STM) and found that pure Pb crystallites are very resistant to oxidation. Even at the O_2 dose up to 720 L, no surface oxidation was observed at 370 K. However, the oxidation could be significantly promoted by surface impurities, and Pb oxides grow at the vicinity of impurities via an autocatalytic process even after 9 L of O_2 exposure. In this Letter, we report a two-step method by which the Pb(111) surfaces could readily be oxidized without inclusion of surface impurities at room temperature. In situ STM observation reveals a new mechanism that has not been reported before.

Our experiments were carried out in a Unisoku ultrahigh vacuum (UHV) system, which consists of a preparation chamber and a low temperature (4 K) STM chamber. The base pressure of the system is better than 2×10^{-10} Torr. Crystalline Pb(111) islands were obtained by depositing Pb (99.999% purity) on the clean Si(111)-7×7 substrates as previously reported.[15] Molecular oxygen gas (99.999% purity) was introduced into the preparation chamber through a leak valve. During oxygen dosing, the substrate was either held at room temperature or at low temperature by liquid nitrogen, while the pressure of the preparation chamber was fixed at 2×10^{-7} Torr, similar to that in Ref. [8]. After oxygen exposure, the sample was immediately transferred into the STM chamber for imaging. All STM images were recorded in the constant current mode at about 80 K with electrochemically etched tungsten tips.

Figure 1(a) shows a typical STM image (100 × 100 nm^2) of the (111) surface of a Pb island of about 15 monolayers (ML) after 240 L of O_2 exposure at 90 K. Similar to O_2 adsorption on other metal surfaces, adsorbed oxygen molecules appear as protrusions in STM images.[16] Probably due to the attractive interaction between oxygen molecules,[5,6] they always tend to aggregate to form oxygen clusters. The smallest clusters of the adsorbed molecules seen in the image are about 1.2 nm, while the largest can be larger than 6.0 nm. At very low coverage (< 6 L), single oxygen molecules with a size of about 0.7 nm can be observed, similar to O_2 on Al(111), Cu(110), Pt(111) and Pd(111).[6,16]

When the above sample is warmed up to room temperature, oxide crystallites form (see Fig. 1(b)). The oxides are imaged as square patches featured with regularly separated stripes, which are more clearly seen

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**To whom correspondence should be addressed. Email: xcma@aphy.iphy.ac.cn

by the high resolution image in Fig. 1(d). Most of the oxide crystallites are identified as PbO with the characteristic linear chain structure. Due to the lattice overlapping of the PbO and underlying Pb substrate, individual lead oxide island displays the Moiré pattern with a unit cell size of 6.58 nm×1.35 nm, which agrees well with Ref. [8]. The unit cell of PbO can be determined to be $a = 0.548$ nm and $b = 0.482$ nm accordingly. Besides the PbO patches, smaller oxide clusters with well-defined shape, preferential orientation and size, also appear on the surface. The assignment of the clusters to oxides is based on their particular shape, which is defined by the certain Pb-to-O ratio of the corresponding form of oxides. The structure model and electronic properties of these oxide clusters will be discussed in detail elsewhere.[17]
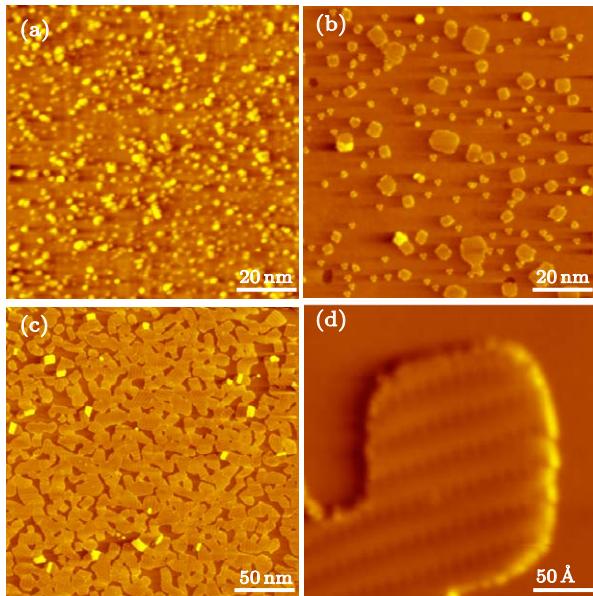

Fig. 1. (a) Topographic STM image (Imaging conditions: 0.1 nA, 2 V) of the Pb(111) surface after 240 L of O_2 exposure at about 90 K. (b) Topographic STM image (0.1 nA, 0.3 V) obtained after warming the sample in (a) up to room temperature. (c) STM image (0.1 nA, 1 V) obtained after further exposure of 360 L of O_2 to the surface in (b) at room temperature. (d) High-resolution image of the oxide patch (0.1 nA, 1 V). Image size: (a) 100 nm×100 nm, (b) 100 nm×100 nm, (c) 280 nm×280 nm, and (d) 30 nm×30 nm.

We argue that the oxidation observed in the present experiment is not related to impurities. High resolution STM images of the clean Pb islands (not shown) reveal that the surface is essentially impurity-free.[15] Some impurities might not be detectable by STM, but their contribution must be insignificant in terms of the high nucleation density of the oxides in Fig. 1(b). Once the oxides crystallites and clusters are formed, further oxidation of the surfaces proceeds in an autocatalytic manner.[8] This case is demonstrated in Fig. 1(c): additional dose of 360 L is sufficient to
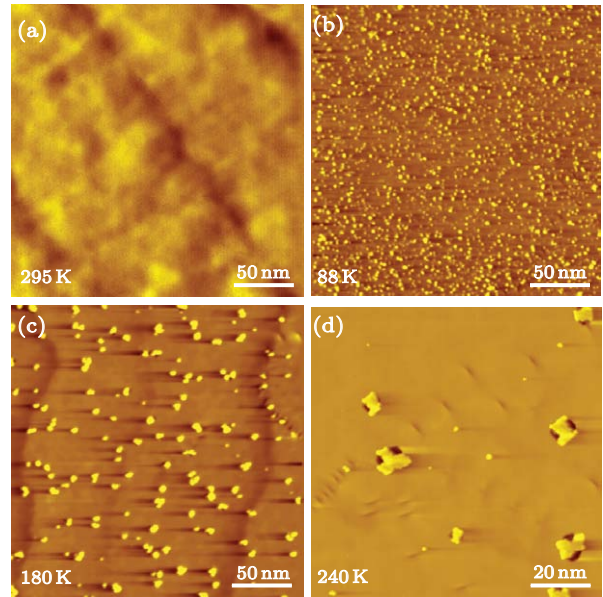
oxidize 90% of the Pb surface at room temperature.

Fig. 2. STM images showing the temperature dependence of oxygen adsorption on Pb(111). For the four different temperatures, the dose of O_2 was fixed at 120 L. The size of all images is 200 nm×200 nm. Imaging conditions in (a) and (b) are 0.1 nA and 2 V, in (c) and (d) are 0.1 nA and 1 V.

Remarkably, if the same amount of oxygen molecules is exposed to the Pb surfaces at room temperature, no oxidation occurs, as shown in Fig. 2(a), which is consistent with the previous report.[8] Here we just focus on low oxidation pressure (about 10^{-7} Torr) and small O_2 exposure (several hundreds of Langmuirs), because high pressure and exposure can make oxidation happen as in Ref. [8]. Considering that adsorption is a necessary step for oxidation,[9,12] we speculate that the inertness of Pb(111) at room temperature or above is due to the low sticking probability of oxygen molecules at these temperatures. In order to prove the speculation, a variable-temperature adsorption experiment was performed. Figures 2(b)–2(d) show the topographic STM images of oxygen-adsorbed surfaces at adsorption temperature of 88 K, 180 K and 240 K, respectively. All the surfaces were exposed to 120 L of O_2 at a pressure of 2×10^{-7} Torr. It is evident that, with increasing adsorption temperature, the average areal density (equivalent to the sticking probability) of adsorbed oxygen decreases. As already mentioned above, at room temperature oxygen adsorbate is not observed. Quantitatively the sticking probability has an exponential dependence on temperature (see Fig. 3). These observations strongly suggest that chemical adsorption, or even oxygen molecule dissociation, already takes place at low temperature such as 90 K (the lowest temperature we could reach in our system), and the bright features seen in Figs. 1(a) and 2(b) should correspond to chemically adsorbed oxy-

gen or some types of oxides. It is worthy to mention that Pb atoms are still active and can diffuse at a temperature range of 52–150 K, according to the previous reports.[18,19] This also suggests that oxygen molecules on the Pb surface have a few probabilities to impinge on the diffusing Pb atoms, and chemical bonding can form favourably with relatively low barrier. Otherwise, they will be desorbed from the surface as long as the sample is warmed up to room temperature if they were physically adsorbed O_2, as revealed by Fig. 2(a).
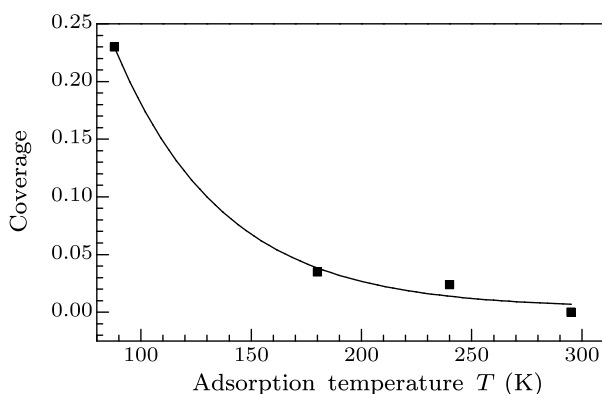

Fig. 3. Relationship between adsorbed oxygen coverage and adsorption temperature. The black squares indicate the measured values, and the solid line is the fitting curve according to the precursor model described in the text.

Under this context, the temperature-dependent adsorption behaviour can be explained by the precursor model.[20] Sticking probability is the competitive result of adsorption and desorption.[6,21] Depending on adsorption temperature, O_2 molecules can either enter molecular chemisorbed state or are desorbed from the surface. The almost zero sticking probability at room temperature means that the desorption process overwhelms the adsorption process. Based on the precursor model and using the formula $\ln(\nu_d/\nu_a) + (E_a - E_d)/RT = \ln[(1-S)/S]$,[6,21] we could fit to the experimental data well with $E_a - E_d = -34.8$ meV, as shown in Fig. 3. Here ν_d and ν_a are the desorption and adsorption pre-exponential factors, respectively. E_a and E_d are the relative barrier heights of adsorption and desorption from precursor state, and S stands for relative sticking probability. This further supports that the sticking coefficient decreases with increasing adsorption temperature. Adsorbed oxygen clusters at low temperature can act as nucleate centres for further oxidation at room temperature.

In summary, a novel two-step method is developed for effective room-temperature oxidation of the Pb(111) surface. We have demonstrated that the low-temperature adsorption of O_2 plays a very important role in the whole oxidation process. Temperature-dependent adsorption behaviour of O_2 on Pb(111) can be explained by the precursor model. This method might be extended to other oxidation-resistant metals.

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