

A COMPARISON BETWEEN THE OXIDATION OF BULK LEAD AND THAT OF LEAD DEPOSITS ON Au(111): AN AUGER STUDY

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A comparison of the oxidation of bulk lead with the oxidation of thin lead layers on an inert gold substrate provides important information on both processes, particularly on the transition from surface to bulk oxidation. The exposure to oxygen of bulk polycrystalline lead at room temperature rapidly produces an oxide layer which grows laterally as a film 2.0 ± 0.2 monolayers thick, followed by much slower oxygen uptake. The same oxide, PbO, forms for lead films of submonolayer to several monolayers thickness, deposited on a Au(111) surface. For lead deposits of less than one monolayer, the oxide grows with a thickness of one monolayer.

Computer decomposition of the lead signal into metal and oxide components has been carried out using the Auger lineshapes for unoxidized metal and thick oxide as basis functions. This method provides chemical information similar to that obtained from X-ray photoelectron spectroscopy.

1. Introduction

Thin metal films on metal substrates have been studied extensively [1]. Their chemical behaviour is of technological importance to the fields of corrosion science and bimetallic catalysis. In particular, numerous studies have been carried out on the oxidation of lead films deposited onto the noble metals [2–7]. Lead films on Cu and Ag were reported to oxidize to orthorhombic PbO for Pb coverages from submonolayer to several monolayer (ML) thickness [2–6].

Only one study has investigated the oxidation behaviour of lead films on a Au substrate [7]. Based on the low ratio of the oxygen to lead-oxide Auger signals, MacMillan-Jones et al. postulated that lead films, deposited onto a polycrystalline Au surface of predominantly (111) orientation, oxidize to lead clusters of about 4 to 5 Pb atoms per oxygen atom. This behaviour is surprisingly different from that using other noble metals as substrates. It was suggested that the presence of grain boundaries and residual oxygen in the experiments of MacMillan-Jones et al. may have affected the behaviour of the lead films. The present study has, therefore, eliminated grain boundary effects by using a single crystal Au(111) surface as substrate, and removed all residual

oxygen by ion bombardment and annealing prior to deposition of Pb. It confirms most of the experimental results of MacMillan-Jones et al., but modifies their interpretation.

Separation of the metallic lead and lead-oxide components of the Auger signal has been accomplished using reference lineshapes obtained in a study of the oxidation of polycrystalline bulk lead. The oxidation of polycrystalline and single crystal lead had been investigated earlier by several techniques [8-13]. Most authors agree that bulk lead oxidizes to orthorhombic PbO. In particular, low energy electron diffraction (LEED) studies by Joyner et al. [12] suggest that even for exposures as low as 100 L (1 L = 1 Langmuir unit = 10^{-6} Torr · s) orthorhombic PbO is formed.

In all investigations of the oxidation of bulk Pb the rate of oxidation appears to be greatly reduced once a certain oxide thickness has been reached. For polycrystalline Pb the oxygen exposure required for this is reported to be 800 L [8], 1300 L [9], 3400 L [10] and approximately 2000 L [11]. The oxide thickness at the "kneepoint" in the plot of oxygen or lead oxide versus exposure was calculated to be, variously, 1 ML [9] (ref. [12] for 100, 110 surfaces), 2 to 3 ML [8], and 6.3 Å or 2 ML [11].

To our knowledge only one previous Auger electron spectroscopy (AES) study on the oxidation of bulk Pb has been carried out [11]; it reports only spectra for the oxygen peak at 518 eV. Our decomposition of lead/lead-oxide Auger spectra into the Pb (94 eV) and PbO (91 eV) components enables a comparison of Pb, PbO and oxygen peaks for different lead oxide thicknesses (henceforth, the "PbO peak" refers to the oxide component of the lead Auger signal near 94 eV). The AES study of the oxidation of bulk lead not only provides reference Auger lineshapes for the Au(111) work, but also, by comparison with the Pb film work, provides information on the oxidation of bulk lead.

This study also shows that the decomposition of Auger spectra can provide chemical information similar to that obtained from XPS (X-ray photoelectron spectroscopy), given that the basis functions for the decomposition are available.

2. Experimental

The apparatus was the same as that used by MacMillan-Jones et al. [7] with the addition of an argon ion gun for sample cleaning. Auger spectra were recorded by a microcomputer interfaced with a 4-grid LEED-type analyzer operated in the derivative mode. The modulation voltage was 2 V peak-to-peak for the Pb and Au peaks and 11 V peak-to-peak for oxygen. All spectra were taken at a primary energy of 1500 eV and a beam current of 15 μ A. Reported peak positions always refer to the minima in the $dN(E)/dE$ spectra. The

polycrystalline Pb and a sparkcut and mechanically polished Au(111) sample were cleaned by argon ion bombardment at 500 K (Pb) and 900 K (Au). After annealing for 5 min the Auger signals of contaminants typical for Au and Pb (C, Ca, Cl, O) were below the detection limit of our apparatus, with the exception, for the lead sample, of a small oxygen signal typically 3% of that measured for the maximum O₂ exposure of 3 × 10⁹ L. Lead films on Au(111) were prepared by evaporation of lead previously deposited on a platinum ribbon [7]. All experiments were carried out at room temperature and background pressures of typically 2 × 10⁻⁹ Torr. During oxygen exposures O₂ was admitted into the chamber at pressures between 1 × 10⁻⁷ and 0.1 Torr as measured by a Bayard–Alpert gauge (BAG) and a Hastings gauge. All pressures and exposures are given as uncorrected BAG and Hastings gauge measurements as is common practice. The true O₂ pressure readings for exposures of less than 10⁴ L can be obtained by multiplying the uncorrected values by 2.76 ± 0.7%, determined by calibration against a Baratron capacitance manometer.

3. Results

3.1. Bulk lead

A typical sequence of lead/lead-oxide lineshapes found for different O₂ exposures of bulk lead is given in fig. 1. The spectra of clean bulk Pb, and of Pb exposed to 3 × 10⁹ L of O₂ (figs. 1a and 1e), were used as basis functions for the decomposition of the lead/lead-oxide lineshapes. Components obtained by allowing the two basis functions to vary in height and position independently produced reconstructed curves which showed excellent agreement with the original data (fig. 2). This decomposition procedure assumes that the PbO lineshape is independent of the exposure to O₂. Support for this assumption is obtained from the results on oxidation of lead films on a gold substrate discussed below.

Further evidence for the validity of the fitting procedure is obtained as follows. Assuming that the inelastic mean free paths (IMFP's) of the 94 eV electrons from Pb travelling through PbO (λ_{94}) and for the 91 eV electrons from PbO travelling through Pb (λ_{91}) are the same, the sum of the properly normalized coefficients for the Pb and PbO components is expected theoretically to be unity. This can be shown by the calculation of the signal from a PbO layer of thickness d (PbO_{*d*}) normalized to that of bulk PbO (PbO_{bulk}), and the signal from bulk Pb below a PbO layer of thickness d (Pb_{below}) normalized to that of clean bulk Pb (Pb_{bulk}). The constant 0.74 in these equations is a geometrical factor for our analyzer [14]:

$$\text{PbO}_d/\text{PbO}_{\text{bulk}} = 1 - \exp[-d/(0.74\lambda_{91})], \quad (1)$$

$$\text{Pb}_{\text{below}}/\text{Pb}_{\text{bulk}} = \exp[-d/(0.74\lambda_{94})], \quad (2)$$

$$\text{PbO}_d/\text{PbO}_{\text{bulk}} + \text{Pb}_{\text{below}}/\text{Pb}_{\text{bulk}} = 1, \quad \text{if } \lambda_{94} = \lambda_{91}.$$

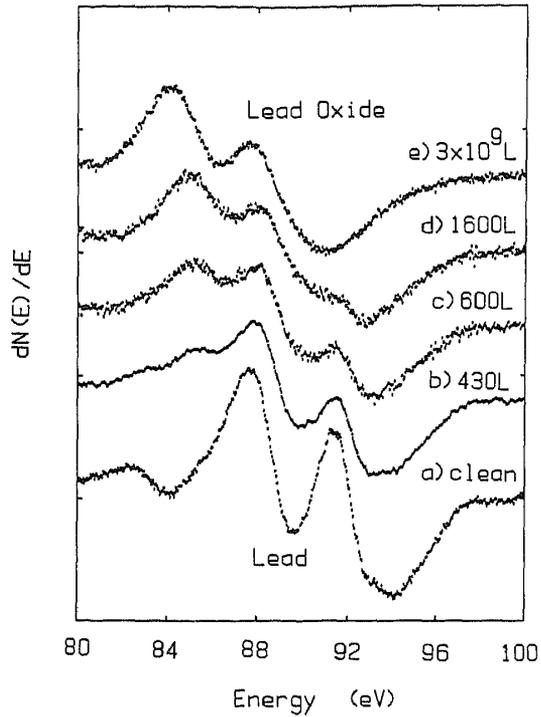


Fig. 1. Auger lineshapes of polycrystalline lead for different O_2 exposures: (a) clean lead; (b) 430 L; (c) 600 L; (d) 1600 L; (e) 3×10^9 L (lead oxide).

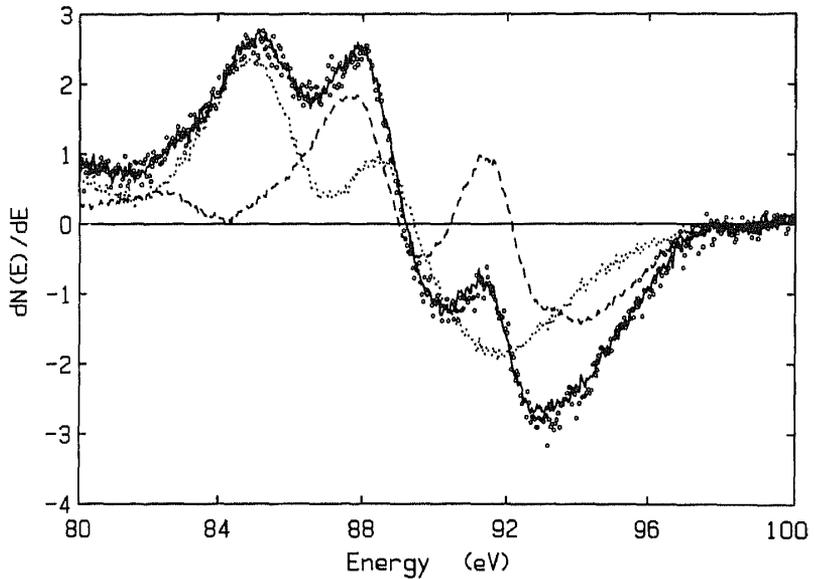


Fig. 2. Decomposition of the lead/lead-oxide lineshape for a 600 L exposure of polycrystalline lead: (●) original data; (—) fitted curve; (·····) PbO component; (---) Pb component.

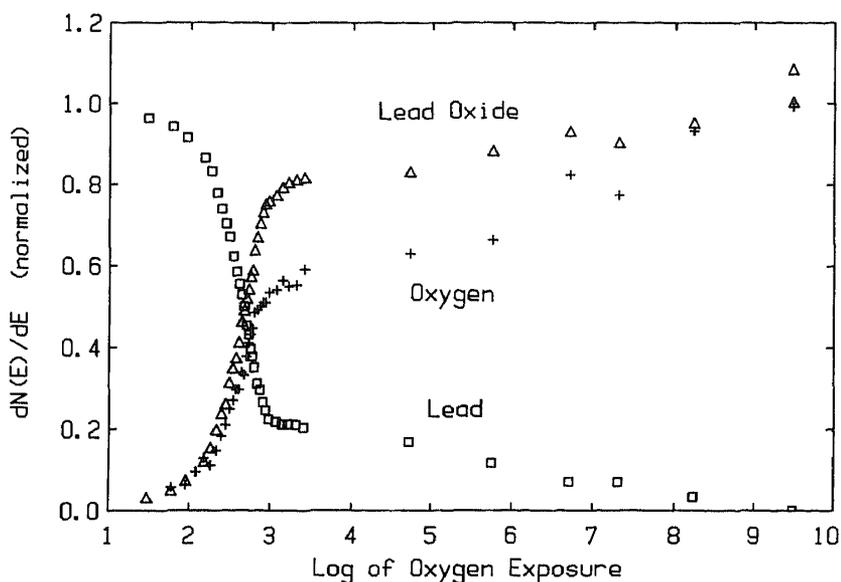


Fig. 3. Development with oxygen exposure of the peak-to-peak heights for the (Δ) PbO component; (+) oxygen peak; (\square) Pb component.

Experimentally this sum was measured to be $0.98 \pm 3\%$ for any curve decomposed. The low degree of variation and sums of very close to 1 indicate the validity of the fitting procedure.

For O_2 doses up to 1000 L (O_2 pressure 1×10^{-7} Torr) the PbO and the O Auger signals increased rapidly, while the Pb signal decreased (fig. 3), not reaching zero until an exposure near 3×10^9 L (at 0.1 Torr). The Pb signal is normalized to the clean Pb peak, while the PbO signal and the oxygen peak are normalized to the PbO and oxygen peaks after a 3×10^9 L O_2 exposure. At this exposure the absence of a metallic lead component shows that the lead was fully oxidized within the Auger sampling depth. The corresponding PbO and O signals will be termed "saturation values". In fact, because of the longer IMFP of the 518 eV electrons, the oxygen signal will be at only about 91% when the lead-oxide signal has already reached 99% of its saturation value. By 1300 L the PbO had already reached 79% and the oxygen 55% of their respective saturation values at 3×10^9 L O_2 , whereas the Pb peak had decreased to 21% of the clean bulk Pb value. It is difficult to choose a specific oxygen exposure at which the rate of oxygen uptake changes from rapid to slow. Since the plots in fig. 3 are essentially linear above 1300 L this exposure was chosen as the transition point. No attempt has been made to investigate the pressure dependence of the rate of oxidation above 1300 L. The pressures used were chosen for convenience and ranged from 1×10^{-7} to 0.1 Torr.

The oxide peak was shifted to a lower energy relative to the metallic lead peak by about 2.8 eV. The PbO peak continued to shift slightly with increasing

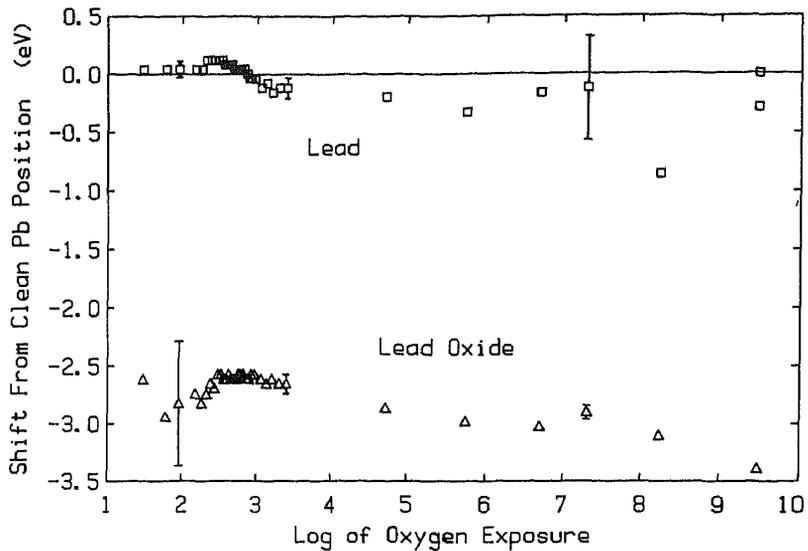


Fig. 4. Shifts of the Pb and PbO peaks relative to clean Pb for different O_2 exposures (in Langmuir units) of polycrystalline Pb: (Δ) PbO component; (\square) Pb component.

oxygen exposures (fig. 4). Because of the large uncertainty in the measurement of the metallic lead component at high oxygen exposures, it is unclear whether this peak position remains constant or also shifts slightly. It is not unreasonable that the PbO peak should continue to shift slowly as the oxide thickens.

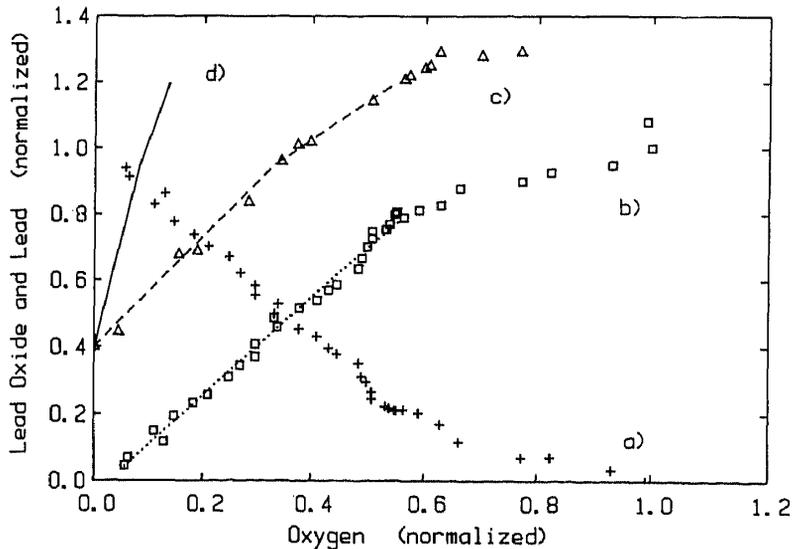


Fig. 5. Relationship between the lead oxide or lead and the oxygen Auger peak heights. (a) Pb peak for bulk lead: (+) experimental. (b) PbO peak for bulk lead: (\square) experimental; (\cdots) regression line for data up to 1300 L. (c) PbO peak for lead film on Au(111): (Δ) experimental; ($- - -$) expected for PbO with layer-by-layer growth. (d) Lead oxide for lead film on Au(111): ($-$) expected for Pb_4O with layer-by-layer growth. Curves (c) and (d) are shifted upwards by 0.4 eV for clarity.

The size of the uncertainty in the measurements also makes it unclear whether the maxima in shifts near an exposure of some 30 L are real or not. It was not possible to determine whether a similar shift occurred for the oxygen peak because the larger modulation voltage (11 V peak-to-peak) resulted in too low a resolution at this energy. The total shift from the clean lead peak (at 0 L) to fully oxidized PbO is 3.4 eV. This is close to the value of 3.7 ± 0.2 eV measured for the integrated spectra (these values are not expected to be exactly the same, because the first uses the minimum in the $dN(E)/dE$, and the second the maximum in the $N(E)$ spectrum, and the lineshapes are different).

The ratio between PbO, or Pb, and O Auger signals was found to be constant for normalized lead-oxide peak-to-peak heights of up to 0.80 ± 0.01 (fig. 5) obtained for exposures of about 1300 L. The slight offset from the origin for the PbO/O data is due to the presence of residual oxygen on the lead, and produces a negligible error. For exposures larger than about 1300 L the slopes of both plots changed to lower values.

3.2. Lead films on Au(111)

Exposure of the Au(111) surface to an increasing number of identical Pb evaporations resulted in Pb and Au Auger signals as shown in fig. 6. From the absolute values of the Pb signal at the first breakpoint in fig. 6, which is considered to represent a Pb coverage of 1 monolayer [7,15–17], and the clean bulk Pb signal of fig. 1a, an IMFP of 94 eV electrons from Pb through Pb can

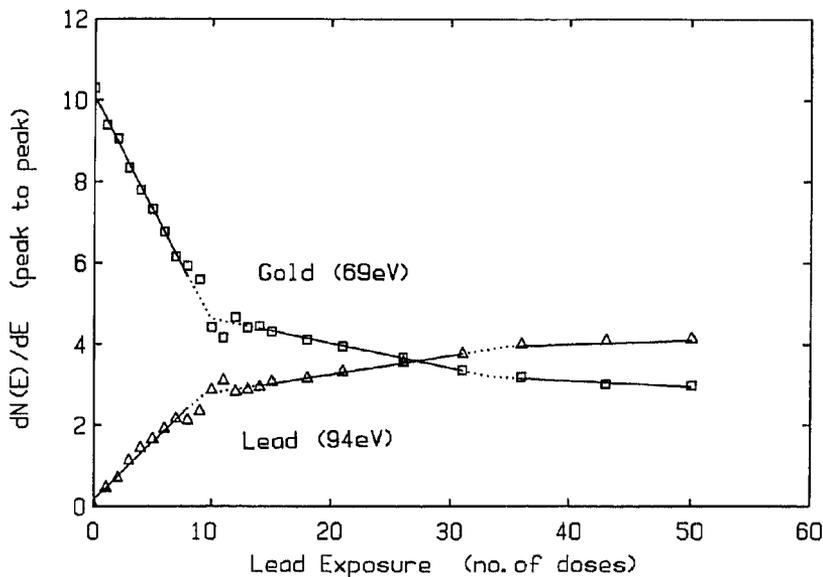


Fig. 6. Calibration of Pb deposits on Au(111). (Δ) Pb (94 eV); (\square) Au (69 eV); (—) regression lines; (·····) extrapolation.

be calculated as in eq. (1) to be 1.7 ± 0.1 ML. The unit of monolayers (ML) for a mean free path will be defined as that thickness of an overlayer causing an attenuation in the Auger signal equal to the attenuation produced by the Pb film on Au(111) at the first breakpoint. The calculation above assumes that the Pb density in the Pb layer at the breakpoint is the same as the Pb density in layers of bulk lead, and that backscattering factors are identical for both polycrystalline Pb and the 1 ML Pb film on Au(111). Once the data of fig. 6 was obtained, the amount of any lead deposited on the Au(111) surface could be determined by either the ratio of lead and gold Auger signals, or by the attenuation of the gold Auger signal, using the monolayer breakpoint as reference and assuming constant Pb sticking probability. The fact that the gold signal never approaches zero in fig. 6 indicates that dosages larger than 1 monolayer equivalent (ME) of Pb result in the formation of a lead-gold surface alloy, as discussed in earlier studies (ref. [7] and references therein). There is some evidence of a second breakpoint in the curves of fig. 6 for a deposition of 3 ME's of lead, but it is not clear enough to warrant further discussion.

Oxygen exposure of the clean Au(111) surface does not lead to oxygen uptake (ref. [7] and references therein). Pb films deposited on a Au(111) surface and then dosed with about 5000 L of oxygen (or 5×10^6 L in the case of Pb deposits larger than 6 ME) showed lead-oxide Auger lineshapes essentially identical to the PbO lineshape shown in fig. 1e. In fact, a decomposition of the lead/lead-oxide Auger peaks of oxidized lead deposits on Au(111) (fig.

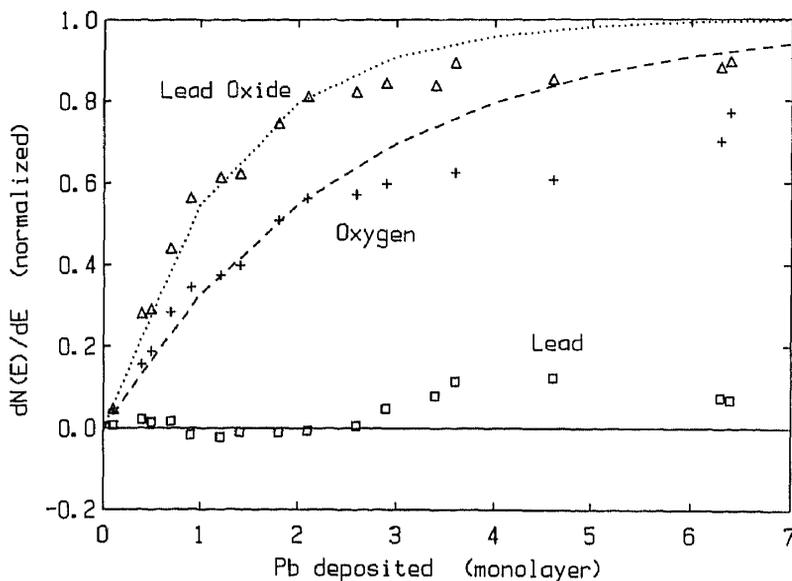


Fig. 7. Auger peak-to-peak heights for different Pb coverages. (Δ) lead-oxide component; (\square) Pb component; (+) oxygen peak (518 eV); (\cdots) calculated for layer-by-layer growth using the IMFP's for lead oxide and ($- - -$) for oxygen electrons through PbO.

7), using the same basis functions as for the decomposition of lineshapes on bulk lead, showed only an oxide component up to 2.5 ME of Pb. Above this value, the metallic-lead component is also present which indicates that the lead films were not fully oxidized at the oxygen exposures used. Both the oxygen and lead-oxide signals for oxygen-saturated lead films on Au(111) increased with the lead coverage (fig. 7). The dotted and dashed lines in fig. 7 were calculated with no adjustable parameters, assuming that: (1) the lead oxide grows layer-by-layer and (2) the electron IMFP's in PbO are the same as in Pb. The second assumption is supported by a comparison of the theoretical IMFP's in Pb and PbO, using a calculation developed by Penn [19], which shows that at 94 eV the IMFP's differ by less than 3%. The IMFP used for electrons from oxygen was $\lambda_{518} = 3.4$ ML, which will be calculated later.

The calculated values of the PbO and O signal strengths from fig. 7 have been used to plot the dashed line in fig. 5c. It involves no adjustable parameters. Agreement with the experimental data is excellent, including the break in slope at a lead deposit of 1 ME, and gives support for layer-by-layer growth of the lead oxide up to at least 2 monolayers. The ratio of the PbO and O signals was very similar to that found during oxidation of bulk Pb (fig. 5b).

For all Pb coverages the Au signal from the substrate after oxidation was smaller than the Au signal before oxidation as found previously [7].

LEED showed the expected 6-fold pattern for the clean Au(111) substrate. The more complex details observed by others [20] could not be resolved, which may be attributed to the limited quality of our analyzer. No clearly defined patterns for the lead films before or after oxidation could be identified although new but faint diffraction spots were observed after Pb deposition.

4. Discussion

4.1. Bulk lead

The Auger lineshape for lead oxide in fig. 1e and the separation of 3.7 ± 0.2 eV of the integrated metallic Pb and the PbO peaks at 3×10^9 L compare well with the lineshape and the shift of 3.8 eV reported for bulk PbO [18]. This indicates that the oxidation of polycrystalline Pb leads to the formation of PbO, which is in agreement with earlier studies [8,10–13].

Joyner et al. [12] concluded from LEED experiments on oxidized Pb(100) and Pb(110) crystals that orthorhombic PbO is formed on both substrates even for oxygen exposures as small as 100 L. If the stoichiometry of the lead oxide formed on polycrystalline Pb is independent of O₂ exposure, the PbO/O Auger signal ratio is expected to remain constant until a complete layer of lead oxide is formed. Further oxidation should result in a different ratio caused by the different IMFP's for lead and oxygen Auger electrons ($\lambda_{518} \approx 2.0\lambda_{94}$). Fig.

5 shows that the change in the ratio of the PbO/O signals occurs at a normalized PbO peak-to-peak height of 0.80 ± 0.01 , which corresponds to an O_2 exposure of approximately 1300 L. Just prior to this exposure the O_2 sticking probability decreased drastically (fig. 3). These observations indicate that at about 1300 L a complete PbO layer is formed, greatly inhibiting further oxidation of the lead underneath. This exposure of 1300 L agrees reasonably well with the “kneepoint” exposures reported in refs. [8,9,11]. The differences may be due to variations in the calibration of the gauges used, or the difficulty in defining the knee position.

Using the Auger peak heights for clean Pb and for the metallic lead component at 1300 L and assuming a homogeneous oxide layer, the thickness of the completed PbO layer can be calculated using the IMFP, λ_{94} , to be 2.0 ± 0.2 ML. This lead-oxide thickness is consistent with results obtained by ellipsometry [11], XPS and UPS [8], and is strongly supported by our results found for the oxidation of Pb films on Au(111). The PbO peak-to-peak height from fig. 7 for an O_2 -saturated lead film of 2.0 ± 0.2 ME on Au(111) agrees with the PbO peak-to-peak height found for the 1300 L exposure of bulk Pb.

The IMFP for oxygen electrons (518 eV) through PbO can be obtained from the oxygen peak-to-peak height at the 2 ML completion to be $\lambda_{518} = 3.4$ ML using eq. (1). Since both the PbO/O and Pb/O slopes remain constant up to the completion of the 2 ML thick PbO film on bulk lead (fig. 5), with no break in slope as seen for deposits on gold, oxygen exposures from 60 to 1300 L seem to result in the formation of a 2 ML thick lead oxide. This Pb appears to grow laterally with increasing O_2 exposure, until at about 1300 L a 2 ML thick PbO film is completed. This PbO film hinders further oxygen uptake so effectively that even for an exposure of 2×10^8 L the oxide formed can be estimated from the data of fig. 3 to be only 4.5 ML thick.

4.2. Lead films on Au(111)

In an earlier investigation [7] a comparison of lead-oxide and oxygen Auger peak heights with handbook data led to the suggestion that the oxidation of Pb films deposited on polycrystalline Au results in the formation of Pb_4O or Pb_5O . However, the Auger lineshape in fig. 1e for oxygen-saturated bulk lead is essentially identical to the lineshape for oxygen-saturated lead films on Au(111) (saturation was obtained for films up to 2.5 ME Pb). This suggests that oxygen adsorption either on polycrystalline lead, or on lead films deposited onto a gold substrate, leads to the formation of the same lead-oxide compound, namely PbO. Moreover, for Pb_4O or Pb_5O compounds the lead-oxide-to-oxygen ratio would be expected to be 4 to 5 times larger than the ratio found for PbO on bulk lead, whereas the lead-oxide/oxygen Auger ratios found for lead films deposited onto an Au(111) substrate and saturated with oxygen compare very well with the ratios found for PbO on bulk Pb (fig. 5).

Most of the data reported by MacMillan-Jones et al. [7] for a predominantly (111) polycrystalline Au substrate appear to be almost identical to the data reported here for the Au(111) surface. Therefore, the lead oxide formed in both studies appears to be orthorhombic PbO rather than clusters of Pb₄O or Pb₅O.

MacMillan-Jones et al. also suggested that for all thin lead films on Au some lead remained unoxidized even for large oxygen exposures, whereas the present results show complete oxidation to PbO under these conditions up to 2.5 ME. Above 2.5 Me the lead films have not been fully oxidized by exposures about 5000 L, or 10⁶ L in the case of 6 ML thick deposits. This is not surprising since an exposure of 10⁶ L was required for bulk lead to reduce the metallic Pb component to 9% of its original value, corresponding to an oxide layer 3 ML thick. The error in the earlier work resulted from the use of a single basis function, that of clean lead, in the decomposition of the lead Auger peak. A comparison of the present study with that of MacMillan-Jones et al. thus brings out two important points:

- (1) The scaling of amplitudes from Auger handbook data may result in estimates of surface concentrations which are in error by several hundred percent unless the chemical systems compared are very similar.
- (2) Reliable basis functions are needed in decomposing overlapping Auger spectra. Good agreement between original data and reconstructed curves does not in itself imply an acceptable decomposition.

The comparison between experiment and theory in fig. 7 for initial Pb coverages less than 2 ME indicates that it is possible to form a monolayer-thick oxide, although on bulk lead the initial oxide is 2 ML thick. This is further supported by the following argument. For coverages less than 2 ME of Pb, the formation on oxidation of a 2 ML thick PbO film as on bulk Pb would require coalescence of the lead on the surface, which should cause an increase in the Au Auger signal. However, in all experiments the Au signal was found to be decreased after oxidation. (For initial coverages greater than 2 ME Pb the ratio of the Au signal after oxidation to that before oxidation was very small, which can be explained by the migration of Pb atoms towards the surface of the lead-gold alloy as discussed in detail by MacMillan-Jones et al. [7].)

The discussion in ref. [7] of the reactivity of the Au/Pb surface vis-à-vis that on Cu/Pb or Ag/Pb also appears to remain essentially valid.

5. Conclusions

The technique of comparing oxidation of a bulk metal with the oxidation of thin layers of the same metal on an inert substrate can provide important information about both processes. The oxidation of bulk polycrystalline Pb leads initially to the formation of orthorhombic PbO which grows laterally as

a layer 2.0 ± 0.2 ML thick. At an exposure of about 1300 L this film is completed, reducing further oxygen uptake dramatically.

The oxidation of thin Pb films on Au(111) and polycrystalline Au also leads to the formation of orthorhombic PbO for all Pb coverages, rather than Pb₄O or Pb₅O as suggested earlier. Oxidation of Pb films of less than 2 ME does not result in coalescence of the lead to produce a 2 ML thick oxide layer.

Decomposition of Auger spectra can be used reliably to analyze overlapping Auger spectra provided that all required basis functions are available.

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