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Comparison of the oxidation of polycrystalline bulk bismuth and thin bismuth films on the Au(111) surface

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Auger-electron spectroscopy, electron-energy-loss spectroscopy, and work-function measurements have been used to make a comparison between the oxidation of bulk polycrystalline bismuth and thin bismuth films (of the order of one-monolayer thickness) on the Au(111) surface. Because the gold acts as an inert support, the thin films may be used to model bulk oxidation kinetics in a layer-by-layer fashion. The results indicate that a two-monolayer-thick oxide, BiO, grows laterally across the surface of bulk bismuth and reaches completion at an oxygen exposure of about 12 000 langmuirs [1 langmuir (L) $\equiv 10^{-6}$ Torr s]; no precursor stage of chemisorbed oxygen has been observed. This is followed by the continued growth of the oxide at a much slower rate. The same oxide occurs for Bi on Au(111), even for submonolayer quantities of Bi for which the oxide is only one layer thick. Chemical reactivity measurements of thicker films of Bi on Au(111) suggest that a cooperative two-layer reconstruction of the surface occurs upon oxidation, which probably takes place during the oxidation of bulk Bi, as well. The common bulk oxide of bismuth, Bi_2O_3, was never observed on either surface. There is evidence to suggest that the surface oxide lattice parameter relaxes to that of the bulk oxide when the oxide achieves a thickness of about seven monolayers. Most of the conclusions reported here are similar to those of an earlier study involving the oxidation of lead.

I. INTRODUCTION

The comparison of the oxidation of bulk Bi and thin Bi films on the inert Au(111) surface at room temperature is part of a continuing study by our laboratory of the oxidation of metals. Other investigations have been made for Pb (Ref. 1) and are being made for Sn.[2] Such comparisons are useful in the understanding of the oxidation kinetics of thin metal films, as well as for providing better insight into oxide growth on a bulk sample, and can illuminate any possible transitions from a surface to a bulk oxide phase. This information is important, especially in the field of corrosion science.

To our knowledge this is the first ultrahigh-vacuum (UHV) study of the oxidation of monolayer (ML) deposits of Bi on a noble metal and, in particular, on the Au(111) surface. The oxidation of bulk Bi or Bi films has been investigated by several authors.[3-7] From ultraviolet photoelectron studies, Benbow and Hurych[4,5] characterized the oxidation of Bi(0001) in three stages: (1) nucleation of chemisorbed surface oxygen preceding (2) rapid growth of an oxide layer, followed by (3) a much slower oxide growth. The transition from rapid to slow growth has been attributed to the oxide behaving as a thin protective layer on the metal substrate, resulting in diffusion-limited oxidation.[3,6] Taylor *et al.*[3] have stated that the rapid growth produces an oxide layer 3 ML thick on the Bi(0001) surface. They have identified the oxide as BiO by low-energy electron diffraction (LEED). Others have also made this identification through electron-diffraction measurements[8,9] and x-ray photoelectron spectroscopy.[10]

The one previous Auger-electron spectroscopy (AES) study of the oxidation of bulk Bi (Ref. 3) showed the evolution of Auger signal strengths for oxygen only; no information was presented concerning the Bi signal behavior, other than one oxygen-to-Bi Auger signal ratio at about 10^6 langmuirs (1 L $\equiv 10^{-6}$ Torr s). However, the Bi signal was a composite of oxide and pure metal components. To understand fully the oxidation behavior, these two components must be separated from each other. Henceforth, the components will be referred to as the Bi component (for the metal) and BiO component (for the oxide). The separation has been accomplished in this work for the Bi Auger spectra ($N_{6,7}O_{4,5}O_{4,5}$ doublet transition) by using a decomposition procedure described by Peeters and Slavin.[1] Decomposition of the Bi spectra enables one to compare the Bi and BiO components, and the oxygen signal, rather than just monitor the oxygen signal as is commonly done. This information, plus results obtained from work-function measurements and electron-energy-loss spectroscopy (EELS) on oxidized bulk Bi and Bi on Au(111), enables us to determine accurately the growth kinetics of the bulk oxide. As well, the type of oxide present for oxidized Bi layers on Au(111) and the reactivity of the Bi deposits toward oxygen can be studied.

II. EXPERIMENTAL

All experiments were performed at room temperature in UHV with a base pressure of 2×10^{-10} Torr. The apparatus has been described in Refs. 1 and 11–13. The polycrystalline Bi sample (99.999 95% pure, Alfa Products) was spark cut from a 1-cm-diameter rod, mechanically polished and etched in concentrated HNO_3.[14] The gold single crystal (99.999% pure) was cut to within 1° of the (111) plane and is the same one used for the Pb study by Peeters and Slavin.[1] The Au and Bi samples were cleaned in vacuum by argon-ion bombardment, while heated at 850 and 475 K, respectively, and then annealed at the same temperatures for 10 min. No contamination of the samples was detected by AES within the sensitivity of the four-grid LEED-type analyzer. The procedure for Bi vapor depositions on the Au(111) surface has been given previously.[13] Ultrahigh-purity oxygen gas (Linde Division, Union Carbide Corporation) was used and cold trapped to remove water vapor before being admitted to the UHV chamber through a leak valve. For oxygen exposures up to 2×10^4 L, a pressure of 10^{-6} Torr was used, and for 2×10^4 to 10^6 L, a pressure of 10^{-4} Torr was used. Above 10^6 L, pressures of the order of several millitorr were required to oxidize further the sample in a reasonable amount of time.

All Auger spectra were obtained in the $dN(E)/dE$ mode using peak-to-peak modulation voltages of 2.0 V for Au ($N_{6,7}VV$ doublet transition at 69 eV) and Bi ($N_{6,7}O_{4,5}O_{4,5}$ doublet transition at 102 eV) and 11.3 V for oxygen (at 517 eV). All Auger peak energies quoted refer to the minimum in the Auger spectrum. Electron-beam currents of 15 μA at 1500 eV were used and the analyzer had a resolution of 0.3% (Ref. 15). Thus, all Auger peak heights presented in this paper, and for which numerical values are given, can be compared directly, except for Fig. 7 as discussed in Sec. IV B. The peak heights given are in arbitrary units. Work-function measurements, accurate to within 0.04 eV, were made by observing the onset of the secondary electron peak (Ref. 16). EELS measurements were recorded in the $dN(E)/dE$ mode using a 2.8-V peak-to-peak modulation and an electron-beam current of 3.0 μA at an energy of 125 eV.

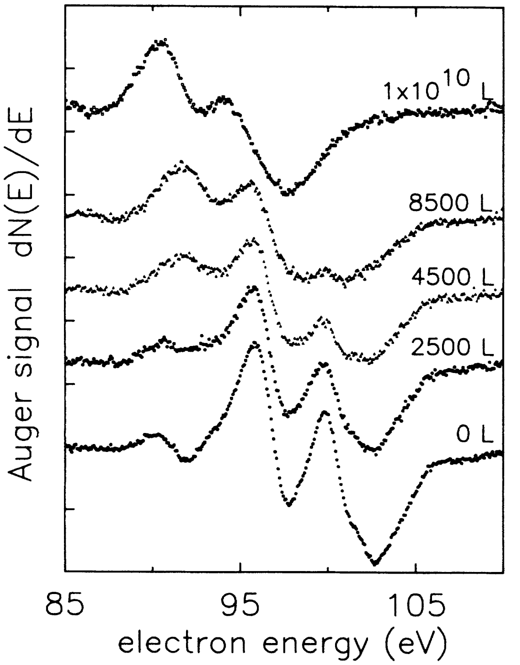

FIG. 1. Auger line shapes of bulk Bi for five different oxygen exposures.

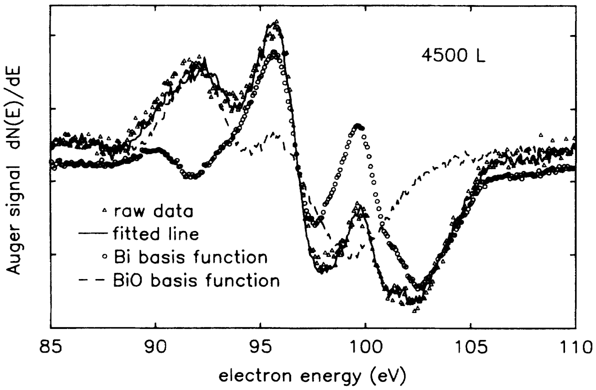

FIG. 2. Decomposition of bulk Bi line shape, after exposure to 4500 L of oxygen, into metallic and oxide components.

The procedure for decomposing the Bi signal into its metallic and oxide components requires one to know the Auger line shapes for the clean Bi metal and for completely oxidized Bi. It is assumed that the line shape of the BiO signal is independent of oxygen exposure. These basis functions were obtained experimentally and are shown as the bottom and top line shapes in Fig. 1, which also shows the composite line shapes for three intermediate oxygen exposures. The composite line shapes were decomposed into a linear sum of Bi and BiO components by allowing the basis functions to shift in energy position and peak height until the best fit was achieved. One such decomposition for an oxygen exposure of 4500 L is shown in Fig. 2. The fitted (solid) line agrees very well with the raw data, and this is typical of all of the decompositions throughout the entire exposure range (0–10^{10} L). Another indication of the validity of this procedure is obtained by adding the Bi and BiO Auger signals from the oxida-

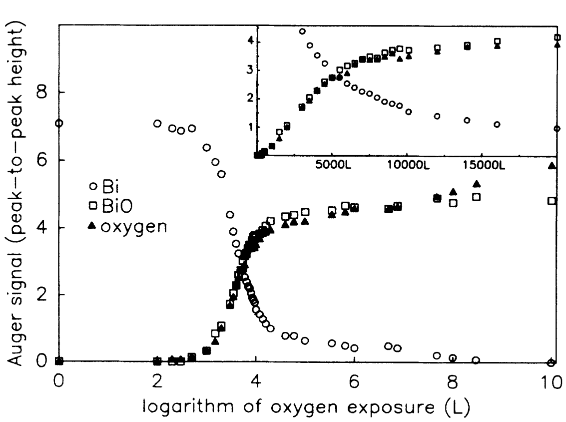

FIG. 3. Metallic Bi, BiO, and oxygen Auger signals as a function of oxygen exposure on bulk Bi. Inset shows the signals plotted linearly in exposure up to 2×10^4 L.

tion of bulk Bi (shown in Fig. 3), after normalizing them to their values before oxidation and for saturation oxidation, respectively.[1] The sum should be unity and experimentally it is 1.03±3 % for all oxidations carried out.

III. RESULTS

A. Oxidation of bulk bismuth

1. *Auger-electron spectroscopy*

As clean bulk Bi was exposed to increasing amounts of oxygen, the Bi Auger peak energy decreased, shifting by 4.7 eV at the point of oxygen saturation. This behavior is illustrated in Fig. 1. Shifts of such magnitude and direction are typical when an electronegative gas like oxygen interacts with a metal.[17] It was known that the sample was saturated when the Bi Auger signal no longer changed in line shape or energy position for larger additional oxygen exposures.

The spectra decompositions resulted in the Bi and BiO signal strengths shown in Fig. 3, along with the oxygen strength. The inset shows the Bi, BiO, and oxygen Auger signals as a function of oxygen exposure on a linear scale for the purpose of identifying the exposure at which a change from a rapid to slow oxide growth occurs. The inset clearly shows that the initially rapid increase in the BiO and oxygen Auger signals slows to a gradual increase above about 12 000 L. At this point the relative values of the Auger signals for Bi, BiO, and oxygen are 1.4, 3.9, and 3.6, respectively. It should be noted that the oxygen signal increases significantly in the exposure range of 10^6-10^{10} L (Fig. 3), whereas the Bi and BiO signals have remained almost constant. This is explained by the fact that the 517-eV electrons from oxygen have an attenuation length of about twice that of Bi 102-eV electrons (to be shown later); hence, oxygen electrons are able to escape from deeper within the sample as oxidation progresses. One measurement, taken at 10^{12} L, showed that the oxygen signal strength remained essentially unchanged above 10^{10} L.

The above experiments were repeated and found to agree well with the results shown in Fig. 3.

2. *Work-function changes*

The change in the work function of bulk Bi exposed to increasing amounts of oxygen is shown in Fig. 4. The work function drops rapidly by about 1.6 eV in the exposure range from a few hundred langmuirs of oxygen to about 12 000 L, giving further support that a transition from rapid to slow oxide growth occurs at about 12 000 L. Taylor *et al.*[3] observed a decrease in the work function of greater than 1 eV for the oxidation of the Bi(0001) surface; however, no sharp break coinciding with the completion of an oxide layer was evident in their curve.

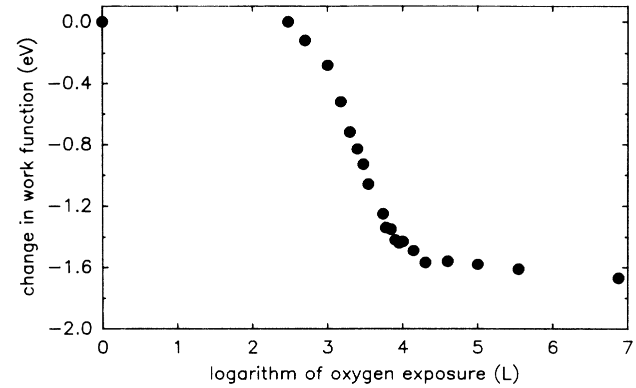

FIG. 4. Change in the work function of bulk Bi as a function of oxygen exposure.

3. *Electron-energy-loss spectroscopy*

Several EELS studies have been done for the oxidation of Bi. Taylor *et al.*[3,6] obtained EELS results for the oxidation of Bi(0001) and Wehenkel and Gauthé[7] and Singh[18] have each presented results for Bi oxide films. In order to make an effective comparison with the EELS results of oxidized Bi on Au(111), it was necessary to obtain our own EELS results for the oxidation of bulk Bi, as shown in Fig. 5. For convenience, the EELS peak maxima have been used to identify all loss transitions. EELS spectra for clean and oxidized bulk Bi are shown in curves *a* and *b*, respectively. Each of these curves shows the $5d_{3/2}$ and $5d_{5/2}$ Bi core-energy losses that correspond to the first two core levels beneath the valence band.[4,19] Based on the positions of the transition maxima the core levels have both shifted 1.8±0.2 eV to higher binding energies upon oxidation. This agrees well with the results of Taylor *et al.*[3] and the UPS study of Benbow and Hurych,[4,5] demonstrating that the oxide present on bulk Bi in this study is also BiO. The energy loss in the clean Bi spectrum (curve *a*) at about 17 eV has been attributed to a bulk plasmon and the 9-eV loss has been associated with a surface plasmon.[7,18,20] Another possible contribution to the 17-eV loss is an interband transition from the $O_{4,5}$ core levels to the valence band.[13] The shoulder present at about 22 eV is thought to be a combination of losses from the bulk plasmon and a 6-eV transition from the valence band to the Fermi level.[18] The loss at, ap-

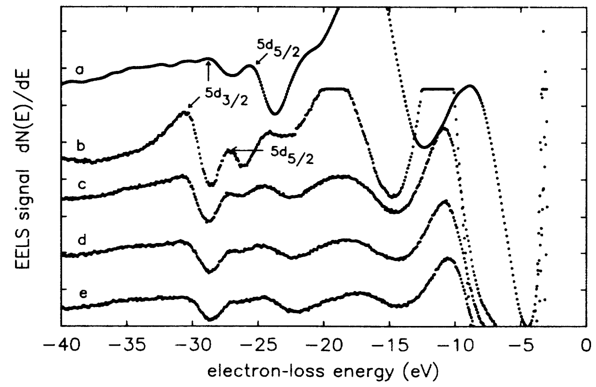

FIG. 5. EELS spectra for: *a*, clean bulk Bi; *b*, fully oxidized bulk Bi (BiO); and fully oxidized Bi deposits on Au(111) of *c*, 2.5 ML; *d*, 1.1 ML; *e*, 0.6 ML.

proximately, 19 eV in the BiO spectrum (curve *b*) corresponds to the bulk plasmon of the oxide[7,18] and the loss at 12 eV is most likely a result of the BiO surface plasmon.[7] Both of these peaks have been clipped by the detection electronics. Curves *a* and *b* have identical form to those reported by Taylor *et al.*[3]

B. Oxidation of Bi deposits on Au(111)

1. Introduction

A previous study[13] has been carried out on the evaporation of thin Bi layers on the Au(111) surface held at room temperature. The results of the prior study that pertain to the present work will be summarized. It was shown that Bi first forms a monolayer on top of the Au, with a $(2\sqrt{3}\times2\sqrt{3})R30°$ unit cell containing about 8 Bi atoms for every 12 Au atoms below it. Subsequent deposits produce a Bi-Au alloy, most likely BiAu, underneath the Bi surface layer. The work function decreased 1.56 ± 0.04 eV during the deposition of the first monolayer and then remained constant. This indicated that the Bi atoms, of lower electronegativity than the Au, formed the surface layer.

In order to investigate, quantitatively, the oxidation of Bi on Au(111) it was first necessary to deposit accurately known amounts of Bi onto the Au(111) surface. This has been accomplished by means of the calibration curve shown in Fig. 6. The Bi and Au Auger peak-to-peak signals have been plotted as a function of Bi evaporation time as described in the earlier study.[13] The break in the curves at 600 s corresponds to 1 ML of Bi on Au(111). The procedure was repeated three times and in all cases the 1 ML points agreed to within 3%. All subsequent Bi deposits were calibrated in monolayers deposited using Fig. 6 and the ratio of the Bi-to-Au signal strengths.

On exposure of these Bi-Au surfaces to oxygen, no change was evident in either the line shape or position of the Au Auger peak, indicating that the Au remained completely unoxidized.

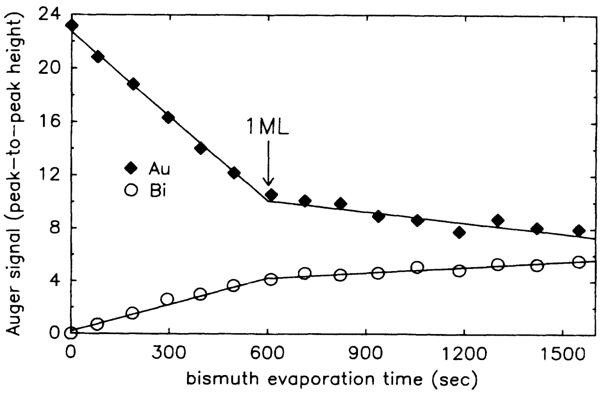

FIG. 6. Calibration curve for the deposition of Bi onto the Au(111) surface. Linear regression lines have been drawn through the data points.

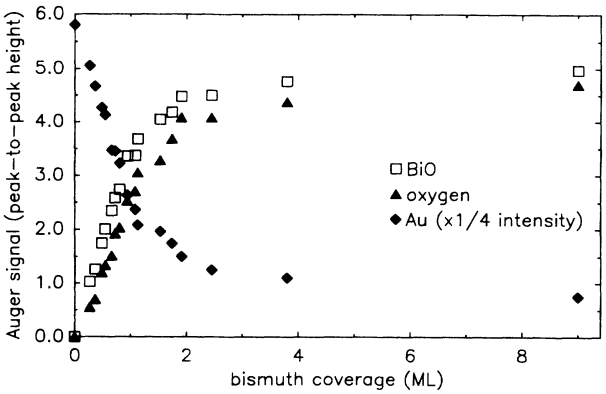

FIG. 7. BiO, oxygen and Au Auger signals for the oxidation of calibrated Bi deposits on Au(111).

2. Auger-electron spectroscopy

Figure 7 shows the results of the complete oxidation of Bi deposits on Au(111). After each calibrated Bi deposition the sample was saturated with oxygen (typically 5×10^{8} L) so that only the oxide was present and not the unoxidized Bi metal. The resulting Bi oxide line shape was essentially identical to that of the BiO observed on bulk Bi (Fig. 1), and will, henceforth, be referred to as BiO. Further evidence for this stoichiometry will be given later. The Au, BiO, and oxygen curves all show straight segments separated by breaks at depositions of 1 and 2 ML of Bi.

Oxygen exposures of 1400 L and 3200 L were also performed on Bi on Au(111) to study the reactivity of Bi with oxygen. The resulting oxygen Auger signal strengths are shown in Fig. 8.

3. Work-function changes

Changes in the work function directly following the deposition of Bi (circles) and following subsequent saturation oxidation (squares) are shown in Fig. 9. The lines have been added to guide the eye. Work-function measurements pertaining to a 1400 and 3200 L exposure (tri-

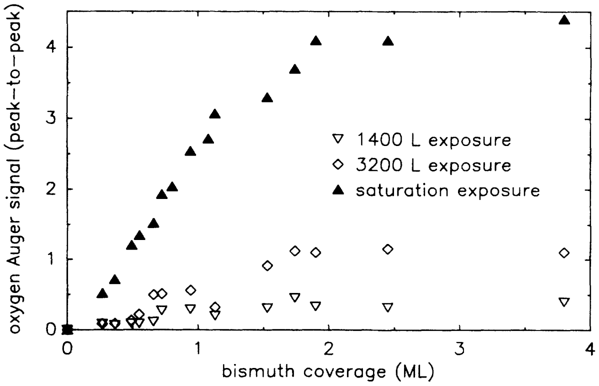

FIG. 8. Oxygen uptake as a function of gas exposure and Bi coverage.

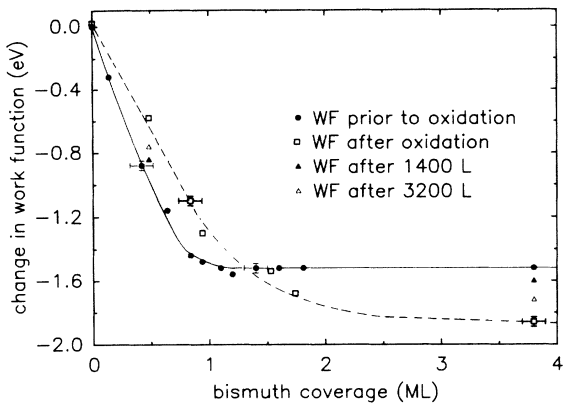

FIG. 9. Work-function changes of Bi on Au(111) prior to oxidation, at 1400 and 3200 L, and after saturation exposure to oxygen.

angles) have also been included for intermediate Bi depositions of 0.5 and 3.8 ML. The work function decreased by about 1.7 eV from the clean Au surface to a completely oxidized 2-ML deposit of Bi. Above 2 ML the work function remained almost constant. Note that the decrease in magnitude of the work function from clean Au to oxidized Bi on Au(111) is similar to that from the oxidation of bulk Bi (Fig. 4).

4. Electron-energy-loss spectroscopy

Curves *c*–*e* in Fig. 5 show EELS spectra for 2.5, 1.1, and 0.6 ML of Bi on Au(111) that have been oxidized to saturation. It is evident that the form of the curves for oxidized Bi deposits approaches that for oxidized bulk Bi, as the Bi deposit increases. The loss feature occurring at about 17 eV in curve *e* is probably due to the $O_{4,5}$-to-valence-band transition.[13] The peak maximum shifts slightly to higher loss energy with an increasing amount of Bi and lies near 18 eV for the 2.5-ML deposit. This shift may be due to the emergence of the bulk BiO plasmon loss which occurs near 19 eV. However, some shift is evident even for the 1.1-ML deposit. Since a bulk plasmon would not be expected for such a thin film, this shift may also result from small changes in the valence band upon oxidation which affect the $O_{4,5}$-to-valence-band transition. The $5d_{5/2}$ core level cannot be seen clearly in curves *d* and *e* because of the obscuring presence of the Au bulk plasmon peak occurring at about 26 eV.[13,18] The loss at 11 eV in curves *c*–*e*, similar to that of the bulk oxide shown in curve *b*, is a result of a surface plasmon associated with the oxide.[18] It is interesting that this peak is well developed even for the 0.6-ML deposit, although it appears to shift to larger loss energy by about 0.4 eV between the 0.6- and 2.5-ML coverages.

Note that the energy positions of the surface plasmon, bulk plasmon, and the $5d_{3/2}$ core levels of the oxide in curves *b*–*e* (with the obvious omission of the bulk plasmon for 0.6 ML of BiO) are all in agreement with each other within the experimental uncertainty of 0.3 eV. As well, EELS spectra of unoxidized Bi deposits of 0.6 and 1.1 ML thickness on Au(111) (Ref. 13) show that the position of the electron core levels agree with those for clean bulk Bi (curve *a*). Hence, the core-level shifts for the oxidized films are the same as those for oxidized bulk Bi.

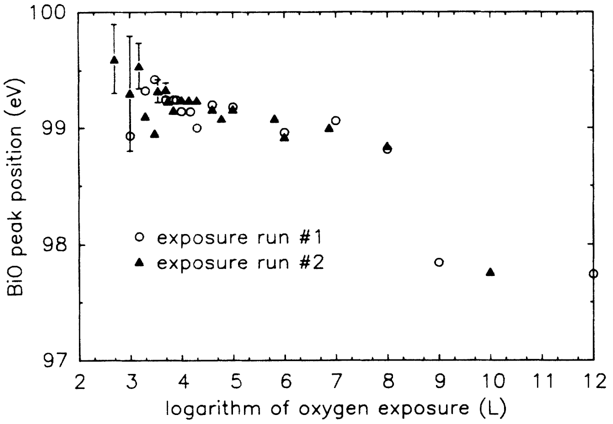

FIG. 10. BiO Auger peak position as a function of oxygen exposure on bulk Bi. Uncertainties in peak positions for exposures greater than 10^4 L are typically 0.03 eV.

C. Auger-energy shifts in BiO

Figures 10 and 11 show the change in BiO Auger energy position during the oxidation of bulk Bi and Bi on Au(111), respectively. For the latter case, each Bi deposit was oxidized to saturation and, therefore, only the oxide component was present, whereas for the oxidation of bulk Bi, the BiO component was separated from the metallic Bi signal by the decomposition procedure. Two different runs on bulk Bi are shown in Fig. 10 and the agreement between them is excellent. Both Figs. 10 and 11 show that at the onset of oxidation the BiO peak position has shifted to a lower energy from the clean Bi position (102.3 eV) by about 2.5 eV. The BiO peak then gradually decreases in energy as more Bi is oxidized. The outstanding feature that occurs in the bulk Bi oxidation is the large decrease (≅1 eV) in BiO peak position at about 10^9 L.

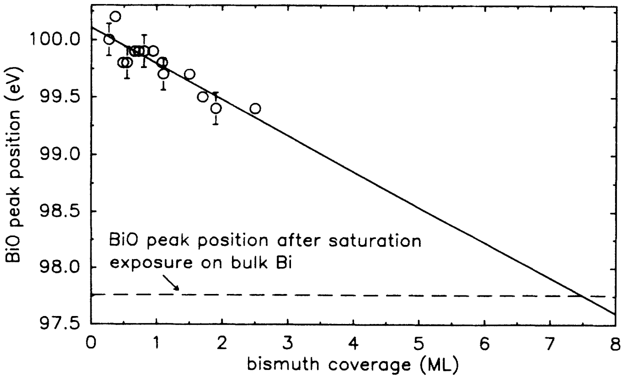

FIG. 11. BiO Auger peak position as a function of Bi deposited. All deposits have been saturated with oxygen. The solid line is a linear extrapolation through the data.

IV. DISCUSSION

A. Oxidation of bulk bismuth

In order to determine the thickness of the protective BiO layer occurring at 12 000 L in Fig. 3, a knowledge of the attenuation length of electrons through BiO is needed. This information may be obtained from the Bi Auger signal due to a 1-ML Bi coverage in the calibration curve of Fig. 6 and the clean bulk Bi Auger signal shown in Fig. 3. Assuming that the density in the first Bi monolayer on Au(111) is the same as that in each layer of bulk Bi, then the attenuation length, $\lambda_{102\,\mathrm{eV}}$, of Bi 102-eV electrons is given by,

$$\lambda_{102\,\mathrm{eV}} = -d[0.74\ln(1-\mathrm{Bi}_d/\mathrm{Bi}_{\mathrm{bulk}})]^{-1} , \tag{1}$$

where Bi_d is the Auger signal due to a layer of Bi of thickness d, $\mathrm{Bi}_{\mathrm{bulk}}$ is the Auger signal from clean bulk Bi, and 0.74 is a geometrical factor required for our analyzer.[21] The attenuation length for the incident electron beam is large enough (about 8 ML) that the transmission factor is close to unity (about 0.9 per atomic layer). Thus, the small differences in the attenuation length of the incident electrons expected[22] for the bulk Bi and Bi overlayer, will not affect the result of Eq. (1) appreciably. The backscatter coefficients of bulk Bi and Bi on Au have been assumed to be the same. This is reasonable because Bi and Au have similar atomic numbers. Substituting the appropriate values from Figs. 3 and 6 into Eq. (1) yields an attenuation length of 1.5±0.1 ML for the 102-eV electrons through Bi. A comparison of the Au Auger signal at 1 ML in Figs. 6 and 7 shows that the electron attenuation through Bi and BiO is identical within the experimental error. This is consistent with a calculation by Penn,[23] who shows that the attenuation lengths of electrons through Bi and BiO are expected to differ by only about 2%. This information can be used to determine the BiO thickness at 12 000 L from

$$d = -0.74\lambda_{102\,\mathrm{eV}}\ln(\mathrm{Bi}_{\mathrm{below}}/\mathrm{Bi}_{\mathrm{bulk}}) , \tag{2}$$

where $\mathrm{Bi}_{\mathrm{below}}$ is the measured metallic Bi signal from below the oxide of thickness d. Solving Eq. (2) with the values from Fig. 3 shows the BiO layer on bulk Bi to be 1.9±0.2 ML, or 2 ML thick. It will be shown later that the oxidation of Bi on Au(111) provides further evidence for a thickness of this amount. The only other published attempt to determine the oxide thickness concluded that an oxide layer 3 ML thick existed on the Bi(0001) surface at an exposure of 10^6 L.[3] We believe our results to be more reliable, because the 3-ML figure was obtained using tabulated attenuation lengths rather than experimental ones, and the metallic Bi and BiO signals were not separated from each other.

Knowledge of how the oxide grows on bulk Bi can be obtained by a plot of the BiO (or Bi) signal against oxygen signal. This plot (open circles, Fig. 12) results in a line of constant slope up to a BiO Auger signal strength corresponding to 2 ML. The absence of any break before 2 ML indicates that BiO does not grow a layer at a time; rather, a 2-ML-thick oxide grows laterally across the surface. A similar result and interpretation to that of Fig. 12 was obtained for the oxidation of bulk Pb.[1]

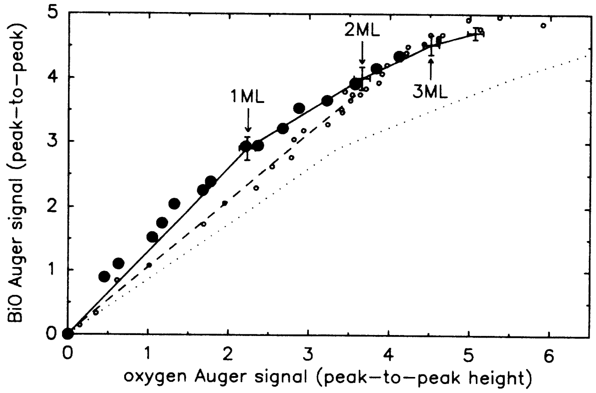

FIG. 12. Bi oxide vs oxygen Auger signal strengths for the oxidation of bulk Bi and Bi on Au(111). Oxidation of Bi on Au: ●, experimental; ——, theoretically based on oxidation of bulk Bi to BiO; oxidation of bulk Bi: ○, experimental; — — —, linear fit to 2 ML; · · · ·, theoretically expected for Bi_2O_3.

Information on the bonding of oxygen to the Bi may be obtained from the work-function behavior shown in Fig. 4. The decrease in the work function from 500 to about 12 000 L indicates the formation of positive-outward dipole moments at the surface. Since the electronegativity of oxygen (3.5) is greater than that of Bi (1.9) (Ref. 24) this implies that the oxygen is bonded below the Bi surface layer, in agreement with Taylor *et al.*[3] Since the work function never increases relative to clean bulk Bi, this demonstrates that oxygen is not chemisorbed on the Bi surface in any significant quantity, contradicting the conclusions of Benbow and Hurych,[4] but agreeing with the work by Taylor *et al.*[3]

B. Oxidation of Bi deposits on Au(111)

One of the most interesting aspects of this study is the search for differences in the type of oxide present on bulk Bi and on very thin Bi films on Au(111). We will begin by showing that the oxide which forms on the Bi films on Au(111) is BiO, as for bulk oxidation. Figure 12 (solid circles) shows the Bi oxide and oxygen Auger signal strengths of Fig. 7 plotted against each other. The raw data was decreased by 13% to correct for the fact that both the oxide and oxygen signal strengths for Bi on Au at 2 ML were 13% greater than on bulk Bi after an exposure of 12 000 L. The solid line that passes through these points has been calculated using the attenuation lengths, in BiO, of electrons from Bi (1.5 ML) and oxygen (2.9 ML), and using equations similar to that of Eq. (1). No adjustable parameters have been used in calculating the solid line. Therefore, the solid line is what one would have expected for the oxide on bulk Bi if it grew a single layer at a time. The error bars indicate the uncertainty in the calculation as a result of the uncertainties in the attenuation lengths of electrons from Bi and oxygen. The good agreement of the oxidized Bi on Au data with the calculated solid line clearly shows that the oxide growing on Bi on Au(111) is the same as that on bulk Bi; that is, BiO. For comparison, the result of the calculation corresponding to Bi_2O_3, which is the most common bulk oxide of Bi, is also shown (dotted line, Fig. 12). Bi_2O_5 is known to exist also,[9] and would produce a growth curve even farther from the measured data in Fig. 12. Therefore, it can be concluded that Bi on Au(111) only forms BiO for less than 3 ML of Bi. Moreover, the presence of a Bi oxide on Au with a composition other than 1:1 would be expected to have resulted in the oxide line shape being different from that observed in the oxidation of bulk Bi, whereas this did not occur.

Further evidence that the oxides in the two cases are both BiO is obtained from a comparison of the change in work function of oxidized bulk Bi (Fig. 4) and oxidized Bi on Au (squares, Fig. 9), measured relative to the initial work functions for clean Au (4.3 eV) and clean Bi (4.4 eV).[25] Both surfaces show the same work function of 2.7 ± 0.1 eV upon completion of a 2-ML-thick oxide. It would be expected that oxides of different stoichiometry would have different work functions.

The EELS spectra in Fig. 5 show that the $5d_{3/2}$ Bi core-level position for 0.6 to 2.5 ML of oxidized Bi on Au(111) agrees well with that of oxidized bulk Bi. Added to the fact that the energy positions of the electron core levels for the deposits prior to oxidation were essentially identical to that of clean bulk Bi (curve *a*),[13] gives strong evidence that BiO is the oxide formed in the oxidation of bulk Bi and of Bi deposits on Au(111), even for submonolayer Bi deposits. One previous study[10] of the oxidation of Bi films has shown that the change in position of the Bi electron core levels is proportional to the oxidation number; hence, one would expect a 50% larger shift in the core levels if the oxide for Bi on Au had been Bi_2O_3, for example.

We now consider the growth of the BiO film on Au(111) which forms after saturation exposures to oxygen. The breaks at 1 and 2 ML in the oxidation curve of Bi on Au (Fig. 7) show that the oxide will grow as a single monolayer. This is different from the bulk BiO situation discussed earlier in which the oxide grows laterally with a constant thickness of 2 ML. As well, the fact that the oxidation of Bi deposits of less than 2 ML on Au never resulted in an increase in the Auger signal from the Au substrate shows that Bi does not coalesce to form an oxide with a thickness of 2 ML. For reasons discussed in Sec. IV C, it seems likely that for single Bi depositions of 2 ML or greater, the oxide on Au also grows initially as a double layer.

The oxidation of Bi on Au also supports that the oxide thickness on bulk Bi at 12 000 L is 2 ML as calculated. A comparison of the oxygen and BiO signal strengths at 2 ML in Fig. 7 with those for a 12 000 L oxygen exposure on bulk Bi (Fig. 3) shows that they agree within 13%. In addition, the work function is essentially constant for the Bi film on Au after oxidation of a 2-ML deposit (squares, Fig. 9), and for the bulk Bi after an exposure to oxygen of 12 000 L (Fig. 4).

A comparison of the behavior of the work function before oxidation to after oxidation of Bi on Au(111) (Fig. 9) gives some information of how the oxygen bonds to this surface. To about 1.3 ML of Bi, the work function after oxidation is increased relative to that before oxidation. This can be accounted for by dipole-moment considerations if the oxygen bonds above the plane of the Bi surface layer and if it is assumed that no changes occur in surface roughness upon oxidation. This is in contrast to the oxidation of bulk Bi, where it has been shown that oxygen bonds beneath the first Bi layer (this work and Ref. 3). For greater than about 1.3 ML of Bi, the work function decreases upon oxidation relative to that of the Bi-Au compound. This can be explained by the fact that Bi within the Bi-Au compound undergoes oxygen-induced surface segregation.[13] As more than one monolayer of Bi accumulates above the Au, oxygen which was initially on the surface will move below the surface, as for the oxide on bulk Bi, thereby decreasing the work function.

C. Surface reactivity to oxygen of Bi deposits on Au(111)

The surface reactivity of Bi on Au(111) towards oxygen is shown by the three oxygen-uptake curves in Fig. 8 taken for 1400 and 3200 L of oxygen at 4×10^{-6} Torr, and a more-than-saturation exposure of oxygen of 5×10^{8} L at 75 millitorr. These correspond to exposure times of 350, 800, and 6700 s, respectively. Decomposition of the Bi Auger signals into oxidized and unoxidized components for the unsaturated exposures showed that the oxide followed a similar trend to that of the oxygen signal strengths in Fig. 8.

We will begin by discussing the results for deposits of Bi of less than 1 ML. In this coverage range it is noticed that, for low-oxygen exposures, oxidation is negligible below a deposit of about 0.5 ML but increases rapidly above this, whereas for saturation exposures oxygen uptake increases almost linearly with Bi coverage. One possible explanation involves the process of accommodation of an incoming oxygen molecule, if we assume it desorbs immediately if it strikes a region of the surface not covered with Bi. This is reasonable since molecular oxygen does not adsorb on Au(111) near room temperature.[26,27] Tully[28] has shown that an incoming molecule can "bounce" several times on a surface before being accommodated or desorbed. For some of these bounces on the partially completed Bi overlayer, the oxygen molecule will encounter a Au region and desorb directly. It appears that the probability of this occurring is high below a Bi coverage of about 0.5 ML and decreases fairly rapidly at higher coverages. That a Bi coverage of 0.5 ML is necessary before oxygen adsorption becomes appreciable may seem high; however, oxygen has a very low-sticking probability even on pure Bi [about 10^{-4} on Bi(0001) (Ref. 3)]. This suggests that many bounces are necessary for accommodation on Bi, which increases the probability of encountering an uncovered Au region.

That the saturation curve is not correspondingly depressed below 0.5 ML is explained by the fact that if the exposure is high enough, eventually enough oxygen molecules will become accommodated to oxidize all of the Bi atoms. In fact, however, an extrapolation of the saturation curve in Fig. 8 back to a zero-oxygen signal does show a slight offset from the origin corresponding to a coverage of about 0.1 ML of Bi, suggesting that even this curve may not represent complete saturation oxidation at very low Bi coverages due to the low probability of oxygen accommodation.

At low exposures, increasing the exposure should proportionately increase the number of oxygen atoms that accommodate to the surface, which explains why the 3200 L curve is about twice as high as the 1400 L curve in the region of 0.5 to 1 ML of Bi.

Above 1 ML of Bi, the curve for the 3200 L exposure rises by a factor of about 2 between 1 and 2 ML of Bi and remains essentially constant thereafter. (There was no obvious explanation for the low data point at 1.1 ML.) This behavior demonstrates that Bi deposits of greater than 1 ML thickness oxidize more easily than smaller Bi deposits. If this increase was due merely to the incorporation of oxygen into the second Bi layer, then a comparison with the saturation curve shows that a 50% increase in the oxygen signal strength would be expected on going from 1 to 2 ML of Bi, rather than the 100% increase observed. This large increase in oxygen uptake may be explained by a surface reconstruction involving two layers, which would allow for strain relaxation to occur over a larger distance, thereby reducing the activation energy of oxidation. The absence of a further increase in the oxygen signal strength for the 3200 L exposure between 2 and 3 ML of Bi suggests that the reconstruction involves only two layers. However, by this argument one would expect also to find a 100% increase between 1 and 2 ML of Bi for the 1400 L exposure. The increase appears to be less than this, although the small signal-to-noise ratio at 1 ML makes this uncertain.

Two other pieces of evidence support a cooperative two-layer reconstruction upon oxidation of Bi deposits of over 2 ML on Au. (1) Exposure of bulk Bi to oxygen resulted in the lateral growth of a 2-ML-thick oxide, as discussed earlier. (2) Exposure of bulk Bi to 1400 and 3200 L at 4×10^{-6} Torr shows the oxygen strength to be 40% higher than for the same exposures at 1×10^{-6} Torr (as in Fig. 3), indicating that oxygen uptake was favored by a larger quantity of oxygen interacting with the surface in a given time.

A comparison of the oxygen signal strengths after 1400 and 3200 L exposures at 4×10^{-6} Torr, on both bulk Bi and on Bi deposits greater than 1 ML on Au(111), showed that the oxygen signal was about 110% higher for bulk Bi for a given exposure. This difference may be a result of the diffusion time of Bi through the Bi-Au compound which is not a factor in the oxidation of bulk Bi. This would also explain why the oxygen signal strength in Fig. 8 increased by a factor of 3 between 1400 and 3200 L for about 2 ML of Bi on Au, whereas the exposure to oxygen increased by a factor of only 2.3: the longer exposure time (800 versus 350 s) would allow more Bi to diffuse to the surface where it is oxidized. Since the Bi deposit is only 2 ML, this suggests a Bi atom jump time, τ, of the order of a few hundred seconds. Using the expression

$$1/\tau=\nu\exp(-E/kT)\ , \qquad (3)$$

where ν is of order the Debye frequency ($\cong10^{12}$ Hz), k is the Boltzmann constant, and T is the sample temperature, shows the corresponding diffusion energy, E, to be about 1 eV. Energies of this order are typical for diffusion processes in compounds.[29] However, it should be cautioned that the energy calculated does not rapidly vary with changes in the jump time assumed.

D. Comparison with the oxidation of bulk Pb and the Pb/Au system

The AES results of this study are very similar to those of the study of the oxidation of bulk Pb and Pb on Au(111).[1] It has been shown that a thin protective monoxide layer, PbO, also forms upon oxidation of bulk polycrystalline Pb, inhibiting further oxygen uptake. In both cases the thickness of this layer has been determined to be 2 ML, and it has been shown that both oxides initially grow laterally as 2-ML-thick layers across the surface of the bulk samples. A further similarity can be seen in the ratio of oxygen and oxide Auger signals up to the completion of the 2-ML-thick oxide. Since Bi and Pb have very similar Auger cross sections, this provides further support that the oxide present on bulk Bi is the monoxide BiO. The only major difference in the oxidation of bulk Bi and Pb is that Bi is significantly more resistant to oxidation than Pb, requiring nine times the 1300 L exposure used for Pb (Refs. 1 and 30–33) to complete the 2-ML-thick surface oxide.

Similarities that exist between the oxidation of these metals on Au(111) are (1) both systems will form a monolayer-thick oxide even though on the bulk the oxide grows laterally with a thickness of 2 ML, and (2) in neither system is there a transition observed between a surface oxide and a bulk oxide of different stoichiometry, at least within the depth probed by the Auger electrons.

E. Auger-energy shifts in BiO

In Fig. 10 a large decrease is seen in the BiO peak position at about 10^9 L. Incorporating the Auger signal strengths from the oxygen curve in Fig. 3 in a calculation similar to that of Eq. (2), shows that the oxide thickness at this exposure is 7±1 ML. For comparison, the thickness at 10^7 L is about 4 ML. A straight line extrapolation through the data points in Fig. 11 for oxidized Bi on Au also suggests that 7 or 8 ML of BiO needs to form in order to achieve an energy shift equal to that resulting from the 10^9 L exposure on bulk Bi. Unfortunately, no data points were taken in Fig. 11 beyond Bi deposits of 2.5 ML.

The shift of the BiO peak with increasing oxide thickness must be a result of extra-atomic relaxation[34,35] since the BiO core levels remain constant within 0.3 eV for all oxygen exposures on bulk Bi (Ref. 3) and all oxygen-saturated Bi deposits on Au(111) (this work). The behavior of the curves in Figs. 10 and 11 may indicate that the surface oxide does not relax fully to the bulk oxide lattice parameter until a thickness of about 7 ML is achieved.

V. CONCLUSIONS

The comparison of the oxidation of bulk Bi and thin Bi films on the Au(111) surface using AES, EELS, and work-function measurements has provided information relevant to both surfaces. It has been determined that on bulk Bi a BiO surface layer grows laterally with a thickness of 2 ML and is completed at an exposure of about 12 000 L, although the rate of oxidation increases with increasing pressure. The same oxide, BiO, also occurs for Bi on Au(111), even for submonolayer quantities of Bi; the oxide does not coalesce to form a single layer 2 ML thick. Surface reactivity measurements of oxygen with Bi on Au(111) indicate that about 0.5 ML of Bi on Au is required before significant oxidation will occur, for low-oxygen exposures. This has been attributed to oxygen desorbing immediately from Au patches in the Bi overlayer, aided by the low-sticking probability of oxygen on Bi. These measurements also suggest that the surfaces of bulk Bi and Bi on Au(111) undergo a cooperative two-layer reconstruction during oxidation. There is evidence that seven or eight layers of BiO are necessary on either the Au or the bulk Bi before the oxide lattice parameter relaxes to its bulk value. No sign was seen of the formation of the common bulk oxides, Bi_2O_3 or Bi_2O_5.

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