Spillover of Oxygen Adatoms from Ir to Au on an Ir/Au{111} Bimetallic Surface

Tianfu Zhang[a], Stephen M. Driver*, Stephanie J. Pratt, David A. King[b]

Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge, CB2 1EW, UK

a: present address: Petrochemical Research Institute, Petrochina Company Limitied, Haidian District, Beijing, People's Republic of China.

b: present address: Smith School of Energy and the Environment, University of Oxford, Hayes House, 75 George Street, Oxford, OX1 2BQ, UK.

* Corresponding author: smd37@cam.ac.uk

Abstract

We have used Auger electron spectroscopy (AES) and low-energy electron diffraction (LEED) to investigate oxygen adsorption on an Ir/Au{111} bimetallic surface. Chemisorbed oxygen stabilises Ir above the Au substrate, when it would otherwise dissolve sub-surface. At sufficient temperature, however, Au can nevertheless replace Ir in the outermost layer(s) in the presence of oxygen. Atomic oxygen is then found to be chemisorbed on both Ir and Au regions of the outermost layer, giving rise to co-existence of Ir{111}-(2×1)-O and Au{111}-($\sqrt{3}\times\sqrt{3}$)R30°-O LEED patterns. Since dissociative O_2 adsorption does not occur directly on Au{111} at low pressures, we conclude that a spillover process occurs, involving O_2 molecules dissociating on the Ir sites and migrating to adjoining Au sites.

Keywords: spillover, oxygen, iridium, gold, AES, LEED, bimetallic surface.

Introduction

It is well established that bimetallic surfaces can exhibit properties that are strikingly different to those of the surfaces of either constituent metal, motivating much effort aimed at exploring what the differences might be in individual cases. Our interest in Ir/Au bimetallic surfaces was triggered by a suggestion made to us by Toyota Motor Corporation that such surfaces might have advantageous properties for automotive exhaust catalysis, specifically for vehicles with lean-burn gasoline engines, where Ir-based (un-alloyed) catalysts have proved in service to be especially susceptible to S poisoning. Under lean-burn conditions, O_2 is present in excess of the stoichiometric ratio, prompting us to focus explicitly on the behaviour of the Ir/Au surfaces when exposed to oxygen. O_2 adsorbs dissociatively on Ir{111} at temperatures above 180 K under ultra-high vacuum (UHV) conditions [1], whereas O_2 dissociative adsorption on Au{111} requires high temperatures and pressures [2]. One might therefore anticipate that the activity of an Ir/Au surface towards O_2 dissociative adsorption would be somewhere in between the activities of Ir and Au surfaces.

In fact, our experiments revealed evidence of an unexpected spillover mechanism occurring on Au/Ir surfaces obtained by depositing Ir on Au{111}, which we report here. Spillover involves the transport of species adsorbed on one surface to another surface that does not adsorb the species under the same conditions [3,4]; most commonly, this is observed at the interface between a metal particle and an oxide support. In the present case, O_2 dissociates on Ir regions of the surface; the atomic O so generated then migrates onto regions of exposed Au, under conditions such that it would not be found in the absence of the Ir.

Experimental Details

Experiments were performed in a UHV chamber with a base pressure of 1×10^{-10} mbar. Ir was deposited on Au{111}, with the surface at 150 K, using an Omicron metal evaporator in which an Ir rod, 2 mm in diameter, was heated by electron bombardment from a W filament. The intensities of Au and Ir peaks in the Auger electron spectrum were used to monitor the deposition process. Due to significant overlap of the Au and Ir peaks, we chose to use the Au peak at 70 eV, and the Ir peak at 226 eV, as these showed (marginally) the least overlap with neighbouring peaks from the other element. After Ir deposition, the Ir/Au{111} surface was exposed to O_2 at 150 K, slowly heated (1 Ks^{-1}) to 500 K or 600 K and annealed at that temperature for about 10 minutes, before finally slowly cooling to temperatures below 350 K; the O_2 pressure was 7×10^{-6} mbar throughout the heating and cooling process. We used low-energy electron diffraction (LEED) to monitor the structure of the surface, and Auger spectroscopy (AES) to monitor changes of the chemical composition at the surface, occurring as a consequence of the oxygen and thermal treatments.

Results and discussion

Fig. 1 shows the effect on Au{111} Auger spectra of depositing Ir at 150 K and subsequent annealing. Deposition of Ir almost completely attenuates the Au peak at 70 eV in the spectra, and introduces Ir peaks at 38 and 54 eV; comparable changes are seen in the clusters of Au and Ir peaks centred on 150 and 230 eV. In the absence of knowledge of the growth mode or the coverage of Ir (no breaks in slope of the coverage dependence of the Auger peaks, which might give a reference point for complete layer formation, were observed: Fig. 2, for example, shows the attenuation of the Au peak at 70 eV), we conclude simply that the Ir layer thickness is sufficient to block all Auger electron emission from the Au substrate, implying multilayer coverage across the whole surface. Annealing, in this case to 1000 K, restores the spectrum to that of pure Au as the Ir dissolves into the bulk. The surface free energy of Au is lower than that of Ir [5], so thermodynamically one expects Au to cap Ir. However, there is a kinetic barrier to Au out-diffusion and Ir in-diffusion: the rates of diffusion are therefore dependent upon temperature. This can be seen from the Auger data in Fig. 3, which shows trends in Au and Ir Auger peak intensities when heating the crystal, after deposition of Ir, to successively higher temperatures for a fixed period of time at each temperature. The Ir peak drops steadily (after a slight initial rise) from 400 to 800 K, whilst the Au peak grows sharply from 400 K, and then more slowly from 600 K. We speculate, although we have no direct evidence for this, that the initial rise in the Ir peak arises from morphology changes, from 3-D islands as deposited to a more uniform morphology after gentle heating.

We next exposed the clean Au{111} surface to multilayer Ir (Fig. 4a) and then to O_2 at 150 K; a very blurred (1×1) LEED pattern was observed before and after O_2 exposure. Oxygen Auger peaks at 490 and 510 eV were observed after O_2 exposure. The surface was then slowly heated to 500 K, annealed at 500 K for 10 minutes, and cooled below 350 K at an oxygen ambient pressure of 7×10^{-6} mbar. In the Auger spectrum recorded afterwards (Fig. 4b), the Au peak at 70 eV was unchanged from its attenuated state in Fig. 4a, indicating that the Ir cap remained intact. By contrast, in a control experiment in which a similar Ir/Au{111} surface was heated for just 20 s to 500 K without exposure to oxygen, a significant increase in this peak was seen, indicating a partial replacement of Ir by Au at the surface. This is not surprising, given that Au has a lower surface free energy than Ir [5]. Taken together, these results indicate that the process of Au replacing Ir at the surface on heating is inhibited when oxygen is present at the surface. This can in part be rationalised thermodynamically: strong Ir-O bonding stabilises Ir at the surface, offsetting the high surface free energy of the clean Ir surface. However, as we argue later, we believe that this effect is in fact primarily kinetic in origin. The O Auger peak intensity slightly increased upon annealing at 500 K; there was no energy shift in the Ir peak position at 54 eV to indicate any IrO_x formation. The LEED measurement showed a clearer (1×1) pattern, indicating that the surface became more ordered after annealing.

We then repeated the experiment, but in this case going to 600 K instead of 500 K while exposing to O_2. In contrast to the lower temperature experiment, clear changes could now be seen in both the Auger spectrum and the LEED pattern. In the Auger spectrum (Fig. 4c) we see a substantial increase of the Au peak intensity at 70 eV, whilst the O peak intensities around 500 eV are comparable with those in the spectrum obtained after annealing at 500 K (Fig. 4b). These observations indicate that a significant fraction of the surface now consists of Au atoms, and that this does not lead to a decrease in oxygen coverage that might be expected. No energy shift of the Ir peak was observed. The LEED measurements revealed a superposition of an apparent (2×2) pattern and a (√3×√3)R30° pattern, as shown in Fig. 5a.

This mixed LEED pattern can be explained in terms of the known behaviour of O_2 on Ir{111} and Au{111} surfaces. It was previously reported that at temperatures above 180 K oxygen is adsorbed dissociatively on Ir{111} [1], giving rise to an apparent (2×2) LEED pattern [6]. Quantitative LEED analysis shows that the oxygen adatoms sit on threefold hollow sites [7]. Zhdan et al. [8] and Marinova et al. [1] deduced from XPS data that 0.5 ML is the saturation coverage of oxygen on Ir{111}, thereby confirming that the apparent (2×2) oxygen LEED pattern in fact arises from three domains of a (2×1) oxygen superstructure, rotated by 120° with respect to each other. The dissociative adsorption of O_2 on Au surfaces, on the other hand, requires elevated temperatures and high oxygen pressures: a (√3×√3)R30°-O structure on Au{111} has been reported, on the basis of LEED [2] and scanning tunnelling microscopy (STM) [9-11] measurements, to occur after such treatment. Using this information, we deduce that the LEED pattern in Fig. 5a arises from a combination of Ir{111}-(2×1)-O and Au{111}-(√3×√3)R30°-O domains coexisting at the surface. The sharpness of the spots indicates that all domains are of significant size, i.e. greater than a typical LEED transfer width (~ 100 Å). The domain size further implies that Au and Ir remain separate in the outermost layer, rather than intermixing. This is unsurprising, given that the high cohesive energy of Ir will drive it to agglomerate.

Because the recombinative desorption temperature of oxygen chemisorbed on Au{111} ranges from 505 to 535 K [12], we expect to see the disappearance of the (√3×√3)R30° LEED pattern from the mixed Ir/O and Au/O phase if we now heat the surface to 600 K in vacuo, and this was indeed what we observed. After the LEED pattern in Fig. 5a was recorded, we flashed the surface to 600 K. Upon cooling back down to 150 K, only the (2×1) LEED pattern of the Ir/O phase remained; the spots were now slightly sharper, as shown in Fig. 5b, indicating an improvement in the periodic order. The intensity of the Au peak at 70 eV was unchanged by the flash anneal, but that of the oxygen Auger signal at 510 eV decreased substantially, from 1.86×10^{-3} (a.u.) in Fig. 4c to 0.73×10^{-3} (a.u.) in Fig. 4d, suggesting that oxygen either desorbed from the Au surface or diffused into the sub-surface region. From this decrease in oxygen Auger peak intensity, we can estimate the fractional area A of

4

exposed Au surface and the global oxygen coverage prior to desorption. Assuming that oxygen initially saturates the whole surface, the fractional oxygen coverage on the Au surface (0.33 ML $\times$ A) and the fractional oxygen coverage on the Ir surface (0.5 ML $\times$ (1-A)) accounts for the 1.86×10^{-3} a.u. peak height. After desorption of the ($\sqrt{3}\times\sqrt{3}$)R30°-O overlayer from the Au regions, and neglecting any leaching of O from Ir to Au, the remaining fractional coverage on the Ir surface (unchanged at 0.5 ML $\times$ (1-A)) now accounts for the 0.73×10^{-3} a.u. peak height. Taking ratios and re-arranging gives A = 0.70, i.e. 70% of the surface was Au. It then follows that the global oxygen coverage was initially 0.38 ML.

O_2 can be dissociatively adsorbed on Ir{111} at just 180 K [1]; the dissociation barrier has previously been calculated to be only 0.06 eV [13]. O_2 dissociation on Au{111}, however, is much more difficult. No oxygen adsorption on Au{111} was detected when the surface was exposed to O_2 up to 10^{-4} Torr and temperatures up to 600 K [14], or at 5×10^{-6} mbar and 800 K [2], for example. In order to get atomic oxygen chemisorption on clean Au surfaces under UHV conditions, one typically has to resort to special methods, e.g. dosing O_2 through a hot filament [12,14], using O_2 DC reactive sputtering [15], decomposing O_3 on Au{111} [16], making N_2O_4 react with ice on Au{111} [17], or sputtering a condensed NO_2 layer on Au{111} [18,19]. Only in the presence of contaminants such as Si or Ca has O_2 dissociation been reported in UHV experiments on Au surfaces [14, 20-22]. The difficulty of O_2 dissociation on Au surfaces is attributed to a very high activation barrier, estimated experimentally to be 1.8 eV [16], and calculated to be ~ 2.2 eV [23].

We therefore propose the following scenario of 'oxygen spillover' to explain the oxygen adsorption on the Ir-Au bimetallic surface. During annealing in ambient oxygen, O_2 dissociates on the Ir surface, and O adatoms produced in this way migrate onto patches of Au surface that transiently form by Au out-diffusion (at high enough surface temperatures that the oxygen-enhanced kinetic barrier to Au out-diffusion is overcome), stabilising these patches and causing them to agglomerate. Since O is bound to Ir much more strongly than it is to Au, one might not expect the migration of oxygen atoms from Ir sites to Au sites. However, because the surface was annealed and cooled in O_2 ambient pressure, there was evidently sufficient oxygen diffusion that O atoms could diffuse onto the Au surface and be quickly replenished on the Ir regions by further dissociation of gas phase oxygen. Therefore a net flow of oxygen could occur from the gas phase O_2, across the Ir surface, to the Au surface.

An alternative interpretation of the presence of oxygen adatoms on Au is that O_2 molecules dissociate on low-coordinated Au atoms, as O_2 dissociation at such sites has previously been found to be much easier [18,23]. However, there is no reason to expect the presence of low-coordinated Au atoms at the surface in our experiments. Moreover, the process of oxygen adsorption on Au sites must take place during the cooling because the oxygen desorption temperature on the Au surface is ~ 500 K; and

from our experience we know that any low-coordinated Au atoms (e.g. from previous sputtering) mostly disappear after the surface is annealed at 600 K. Therefore we think the spillover mechanism is a more likely explanation of our results than a mechanism involving low-coordinated Au atoms.

We now deal with the observed diffusion of Au atoms from the Au{111} substrate / Ir film interface to the gas / surface interface, which occurs in particular at 600 K in the presence of O_2 at 7×10^{-6} mbar (Fig. 4b); the arguments developed here are shown schematically in Fig. 6. We have already noted that the surface free energy of Au is lower than that of Ir [5]. One can anticipate, thermodynamically, that an Ir layer (in the absence of oxygen) will become capped by Au, given sufficient time and temperature, and this is indeed what we observe experimentally (e.g. Fig. 1). However, the temperature-dependence seen in Fig. 3 also emphasises that Au out-diffusion and Ir in-diffusion are activated processes. At 600 K in the presence of O_2, broadly similar amounts of O-covered Au and O-covered Ir are formed, from which we infer that the surface free energies of the two O-covered metals are comparable. When the O is desorbed from the Au regions by re-heating to 600 K without O_2, the clean Au remains co-existing with the O-covered Ir. We therefore infer that the surface free energies of clean Au and O-covered Ir are also comparable. Given the similar surface free energies of Au, Au-O and Ir-O, we might expect to find Au-O co-existing with Ir-O in the experiment performed at 500 K; the fact that we do not indicates that the absence of Au-O is kinetic in origin: the presence of oxygen raises the activation barrier to Au out-diffusion and Ir in-diffusion, and at 500 K, this is sufficient to block these processes completely. Only when the temperature is raised to 600 K does the surface become sufficiently dynamic in the presence of oxygen for the system to achieve its most stable configuration.

Oxygen spillover has long been observed on metal oxide support catalysts, eg. Pt/Al_2O_3 [24] and MoO_3/Sb_2O_4 [25]. It plays a significant role in catalysis, especially for catalysts where the metal has different oxidation states [24]. Spillover of oxygen from one metal to another has, however, rarely been observed. Schrader found that Ca impurities on Au{111} promote oxygen adsorption on Au and suggest that the effect of Ca involves dissociative chemisorption of O_2 at Ca sites followed by migration of oxygen atoms to Au sites [20]. Our observation provides more direct evidence of oxygen spillover between metals. Spillover of oxygen atoms from Ir sites to Au sites is potentially important in oxidation reactions. In catalytic reactions on Au catalysts, dissociation of O_2 to yield atomic oxygen is likely to be the rate-limiting step in the oxidation of CO and hydrocarbons [18]. The addition of an active metal to the Au catalyst may dramatically enhance its catalytic activity.

Another interesting finding is the Au{111}-($\sqrt{3}\times\sqrt{3}$)R30°-O LEED pattern revealed in this study. There are only a few reports of a ($\sqrt{3}\times\sqrt{3}$)R30° structure forming when oxygen is adsorbed on Au{111}. The first observation is that by Cao et al. [2], who

formed a chemisorbed state of oxygen on Au{111} by annealing the surface between 870 and 1100 K at an O_2 pressure of 5×10^{-6} mbar. LEED measurements revealed a 'twisted oxide' (AuO_x) overlayer and a ($\sqrt{3}\times\sqrt{3}$)R30° structure, the latter attributed to chemisorbed oxygen adatoms on Au{111}. Huang et al. observed the ($\sqrt{3}\times\sqrt{3}$)R30° structure by STM, after annealing Au{111} at temperatures between 770 and 1070 K in 1 bar of O_2 [9-11]. However, in other studies of oxygen adsorption on Au{111}, no ($\sqrt{3}\times\sqrt{3}$)R30° LEED pattern was observed. In these studies, surface preparation conditions varied from annealing Au{111} (presumably Ca- or Si-contaminated) at O_2 pressures higher than 1×10^{-6} mbar and temperatures higher than 600 K [21,22], through O_3 exposure [16], to O_2 dosing through a hot filament [12]. It is not yet clear why no ($\sqrt{3}\times\sqrt{3}$)R30° LEED pattern was observed in these studies. All these studies seem to indicate that the appearance of the Au{111}-($\sqrt{3}\times\sqrt{3}$)R30°-O structure strongly depends on the surface preparation conditions. Our findings provide evidence of another route to prepare the Au{111}-($\sqrt{3}\times\sqrt{3}$)R30°-O structure.

Summary

Chemisorbed oxygen inhibits Ir deposited on Au{111} from dissolving into the bulk on heating. However, at sufficiently high temperature, Au does migrate to the surface, forming patches co-existing with Ir regions. A spillover process is found to occur, whereby O_2 molecules dissociating on the Ir regions can migrate to the Au regions and remain chemisorbed. This gives rise to a mixed Ir{111}-(2×1)-O + Au{111}-($\sqrt{3}\times\sqrt{3}$)R30°-O LEED pattern. On this basis, addition of Ir to Au catalysts may help oxygen adsorption on the Au surface and hence enhance their catalytic properties.

Acknowledgement

References

[1] T.S. Marinova, K.L. Kostov, Surf. Sci. 185 (1987) 203.

[2] J.M. Cao, N.J. Wu, S.X. Qi, K. Feng, M.S. Zei, Chinese Phys. Lett. 6 (1989) 92.

[3] W.C. Conner, J.L. Falconer, Chem. Rev. 95 (1995) 759.

[4] U. Roland, T. Braunschweig, F. Roessner, J. Mol. Catal. A 127 (1997) 61.

[5] Cohesion in metals: transition metal alloys, F.R. De Boer, R. Boom, W.C.M. Mattens, A.R. Miedema, A. K. Niessen, Elsevier, 1988.

[6] D.I. Hagen, B.E. Nieuwenhuys, G. Rovida, G.A. Somorjai, Surf. Sci. 57 (1976) 632.

[7] C.-M. Chan, W.H. Weinberg, J. Chem. Phys. 71 (1979) 2788.

[8] P.A. Zhdan, G.K. Boronin, A.I. Boronin, W.F. Egelhoff, W.H. Weinberg, Surf. Sci. 61 (1976) 25.

[9] L. Huang, J. Chevrier, P. Zeppenfeld, G. Comsa, Appl. Phys. Lett. 66 (1995) 935.

[10] L. Huang, P. Zeppenfeld, J. Chevrier, G. Comsa, Surf. Sci. 352 (1996) 285.

[11] J. Chevrier, L. Huang, P. Zeppenfeld, G. Comsa, Surf. Sci. 355 (1996) 1.

[12] K.A. Davis, D.W. Goodman, J. Phys. Chem. B 104 (2000) 8557.

[13] Y. Xu, M. Mavrikakis, J. Chem. Phys. 116 (2002) 10846.

[14] N.D.S. Canning, D. Outka, R.J. Madix, Surf. Sci. 141 (1984) 240.

[15] J.J. Pireaux, M. Liehr, P.A. Thiry, J.P. Delrue, R. Caudano, Surf. Sci. 141 (1984) 221.

[16] N. Saliba, D. Parker, B.E. Koel, Surf. Sci. 410 (1998) 270.

[17] J. Wang, B.E. Koel, Surf. Sci. 436 (1999) 15.

[18] X. Deng, B.K. Min, A. Guloy, C. M. Friend, J. Am. Chem. Soc. 127 (2005) 9267.

[19] B.K. Min, X. Deng, D. Pinnaduwage, R. Schalek and C.M. Friend, Phys. Rev. B 72 (2005) 121410.

[20] M.E. Schrader, Surf. Sci. 78 (1978) L227.

[21] M.A. Chesters, G.A. Somorjai, Surf. Sci. 52 (1975) 21.

[22] P. Legaré, L. Hilaire, M. Sotto, G. Maire, Surf. Sci. 91 (1980) 175.

[23] Z.-P. Liu, P. Hu, A. Alavi, J. Am. Chem. Soc. 124 (2002) 14770.

[24] W.C. Conner, J.L. Falconer, Chem. Rev. 95 (1995) 759.

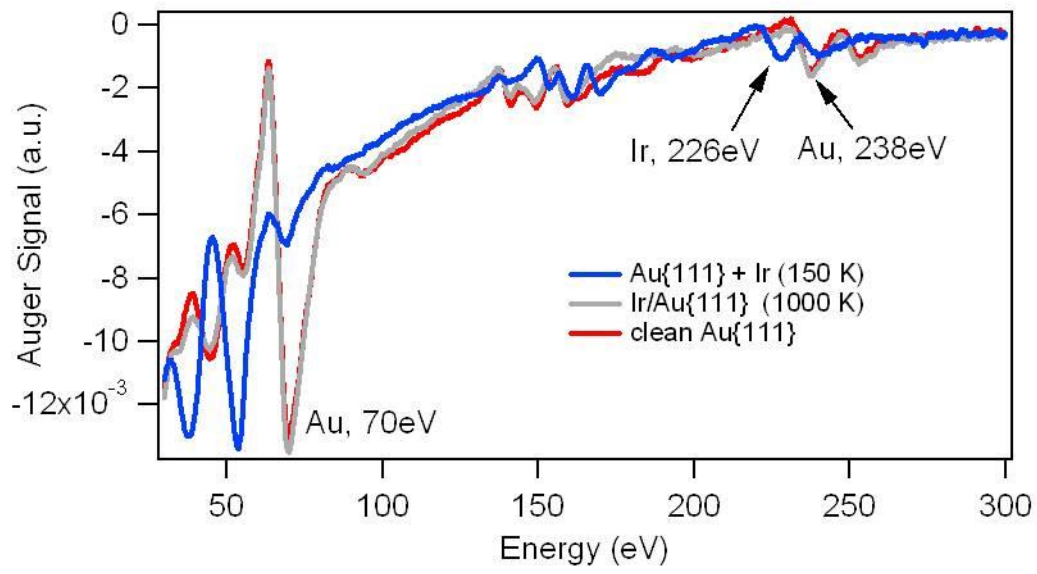[25] L.T. Weng, B. Delmon, Appl. Catal. 81 (1992) 141.

Figures

Fig. 1. Auger electron spectrum of Au{111}, before and after exposure to Ir at 150 K and subsequent annealing.
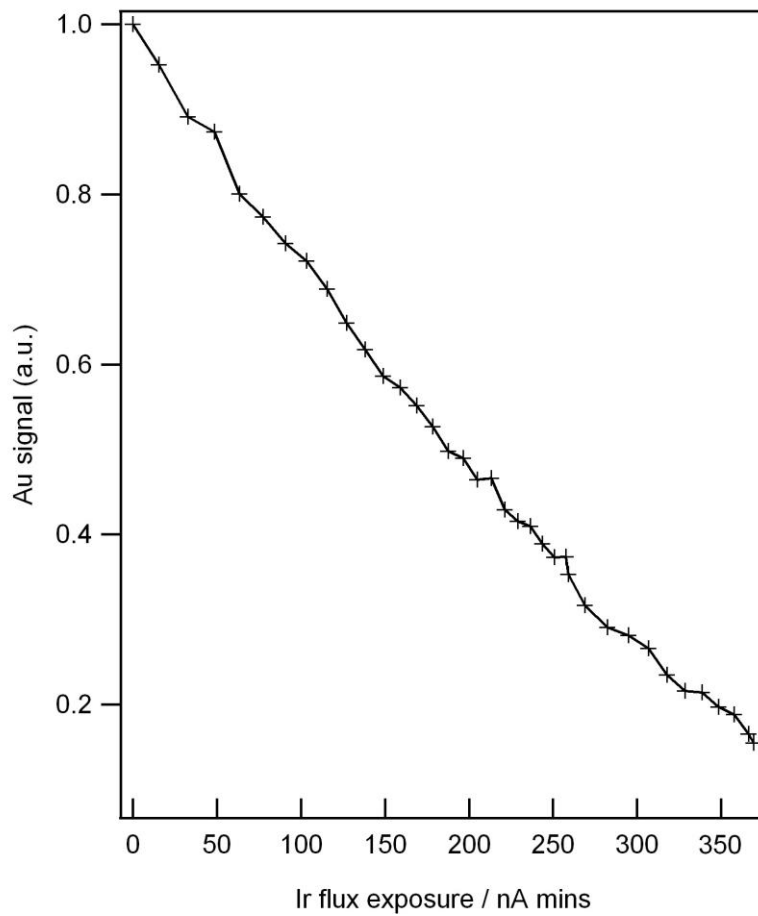
Fig. 2. Plot of the intensity of the Au Auger peak at 70 eV as a function of exposure to Ir. The exposure is calculated in units of nA.min to account for the tendency of the flux from the Ir evaporator (measured in nA) to drift with time.
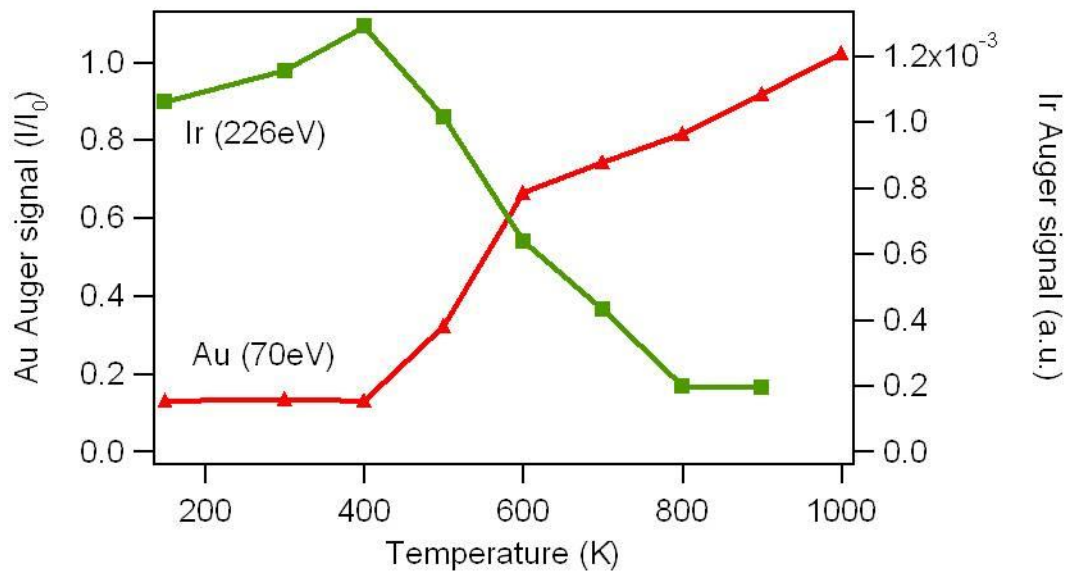
Fig. 3. Trends in Ir and Au Auger electron peak intensities when heating the Ir/Au{111} surface to successively higher temperatures for a fixed time interval (20 s). The Au peak intensity I is normalized to the clean-surface value I_0, and is given as I/I_0; no such reference point exists for Ir, so its peak intensity is simply given in arbitrary units.
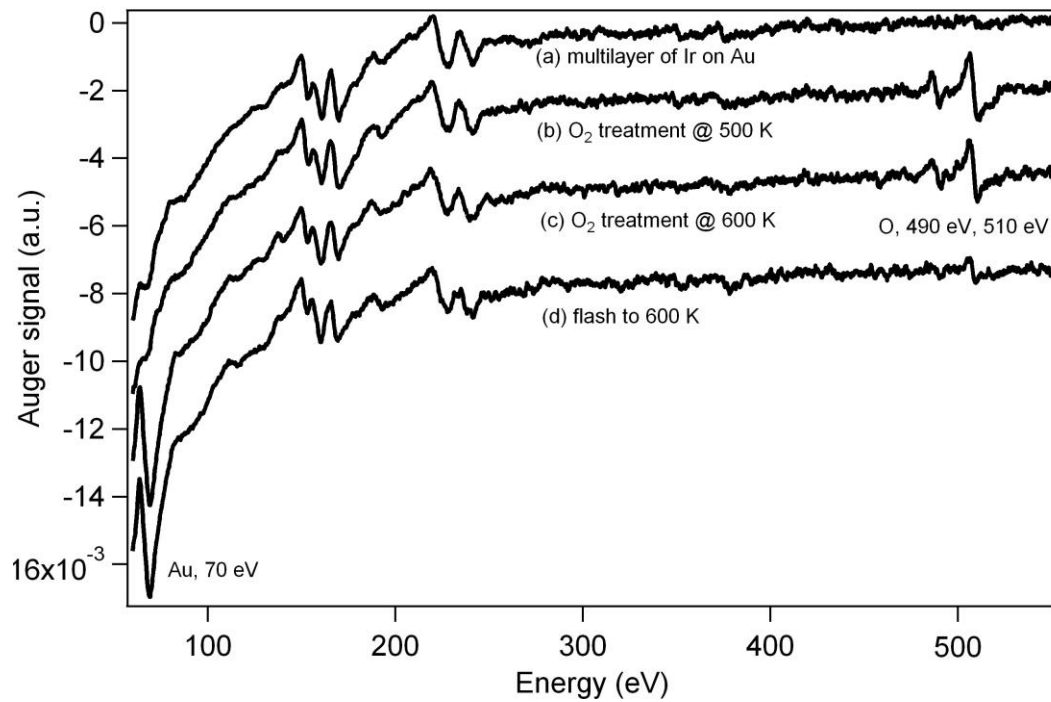
Fig. 4. Auger spectra of Ir/Au{111} surface before and after O treatment. (a) multilayer of Ir was deposited on Au{111} at ~150 K; (b) the surface was heated (1 Ks^{-1}) to 500 K, annealed at 500 K for 10 minutes, and cooled to 350 K at an oxygen pressure of 7×10^{-6} mbar; (c) as (b) but annealing to 600 K (d) the surface was flashed (4 Ks^{-1}) to 600 K.

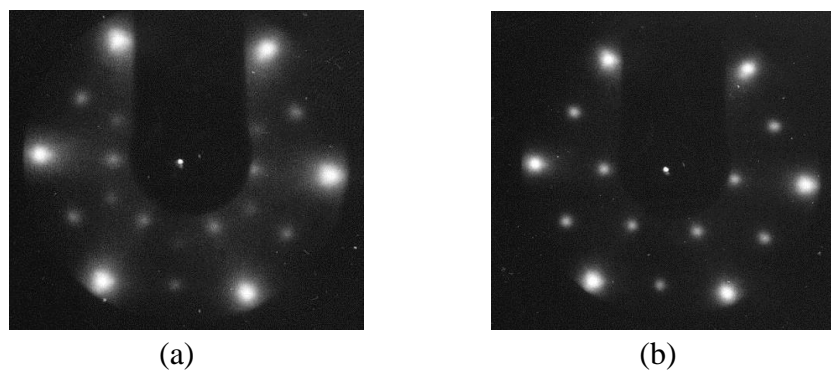(a)   (b)

Fig. 5. LEED patterns obtained after adsorption of oxygen on Ir/Au{111} surface. LEED measurements were made at ~ 150 K. (a) LEED pattern (65 eV) of Ir{111}-(2×1)-O plus Au{111}-(√3×√3)R30°-O, corresponding to Auger spectrum (c) in Fig. 3. (b) LEED pattern (63 eV) of Ir{111}-(2×1)-O, corresponding to Auger spectrum (d) in Fig. 3.
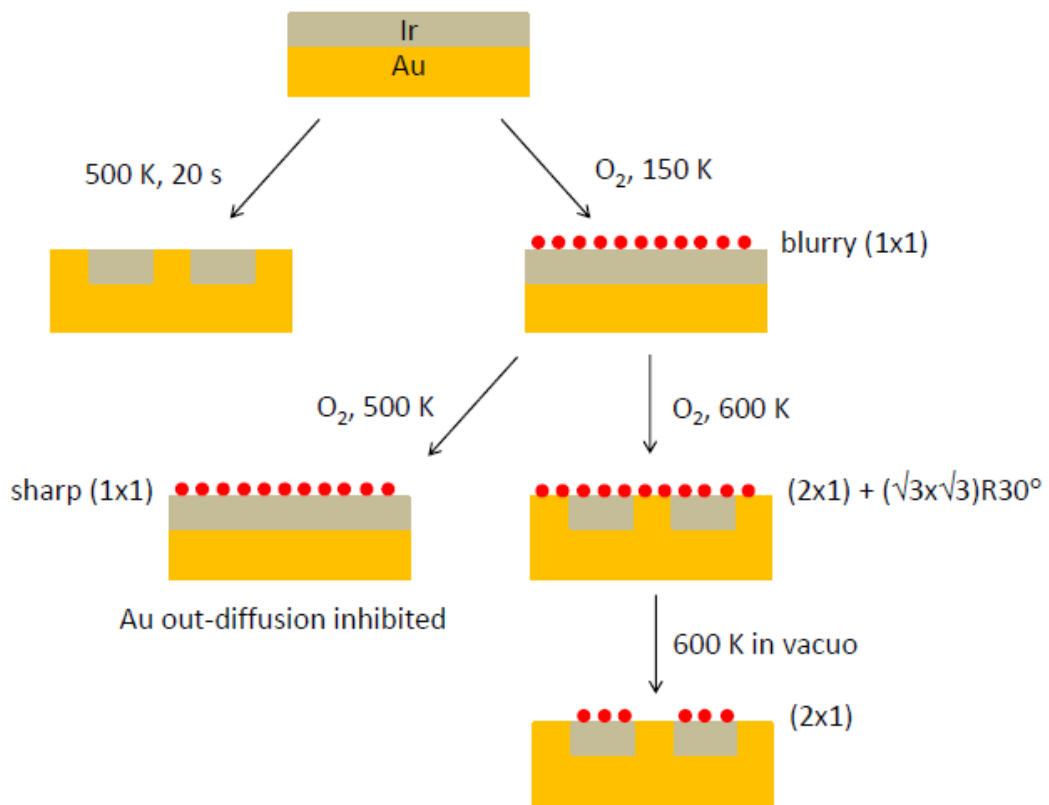
Fig. 6. Schematic summarising the behaviour of the Ir/Au{111} bimetallic surface under various conditions of temperature and oxygen exposure.