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ANOMALOUS Au(111) SURFACES STUDIED BY LEED, AES AND OXYGEN CHEMISORPTION*

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Abstract: LEED patterns obtained from clean Au(111) surfaces, show that each integral order diffraction beam in the normal (1 x 1) pattern is surrounded by hexagonal arrays of reflections aligned along the <110>. The spacing between these additional diffraction features is ∿ 4% of that between the integral order beams and leads to the suggestion that the outermost layer of atoms is not completely coherent with respect to the bulk structure. Oxygen was found to adsorb on the clean surface at sample temperatures above 500°C but its presence did not effect the LEED pattern. An increased rate of adsorption was observed on surfaces which contained small quantities of Ca. This chemisorbed oxygen could be removed by ion bombardment but not by heating up to 800°C.

INTRODUTION

It has been determined from LEED investigations of clean Au(100) and (110) surfaces, that the atomic arrangements in the outermost layer are reordered relative to their ideal intraplaner arrangements in the bulk./1-4/ While the surface region of the (100) is now generally believed to consist of a single hexagonal Au layer on top of the normal bulk array, /4,5/ the exact atomic arrangement of the (110) surface is still in question. In contrast, results of studies with LEED on the Au(111) surface have suggested that this surface exhibits its normal bulk-like atomic arrangement./2,6,7/ However, published LEED photographs obtained during these studies,/2,7/ exhibit large areas or intensity at the integral order reflection positions instead of sharp narrow beams. We have obtained results, presented below, which now suggest that the Au(111) outermost surface layer is not completely coherent with respect to the bulk structure.

Although relatively inert, there has been interest in the adsorption properties of Au and a number of investigations specifically concerned with the chemisorption of oxygen at room and elevated temperatures have been performed since 1920. The contradictory results of some of these studies may possibly be attributed to surface preparation, treatment or cleanliness. Two recent studies performed on (111) oriented samples under UHV conditions have both reported chemisorption at elevated temperature but differ in their observations concerning adsorption below 500°C./7,8/ In view of the role of active sites and, thus, the specific dependence on both sample orientation and surface cleanliness in the chemisorption process, we have performed adsorption experiments on well characterized Au(111) surfaces.

EXPERIMENTAL

All LEED observations were made with a commercial three-grid LEED optics. While some initial Auger spectra were obtained by employing this optics as a retarding field analyzer, most data were acquired with a double pass CMA. Both analyzers along with an ion bombardment gun and quadrupole mass spectrometer were mounted in a stainless steel UHV chamber whose background pressure was typically in the low 10^{-8} Pa range.

The bulk Au sample used in this investigation was spark cut from a 5N pure ingot and then mechanically polished with abrasives to produce a surface oriented to within 0.5° of the [111]. An optically smooth, high-quality surface was subsequently obtained by electropolishing the sample in a cyanide base solution./9/ The thin film sample used was a self-supporting single crystal ≈ 6500 Å thick with a [111] orientation. This sample was grown epitaxially on a mica substrate and then transferred to a Au disk using procedures previously described./10/ A chromel-constantan thermocouple placed in contact with these samples was used for monitoring specimen temperatures.

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DISCLAIMER

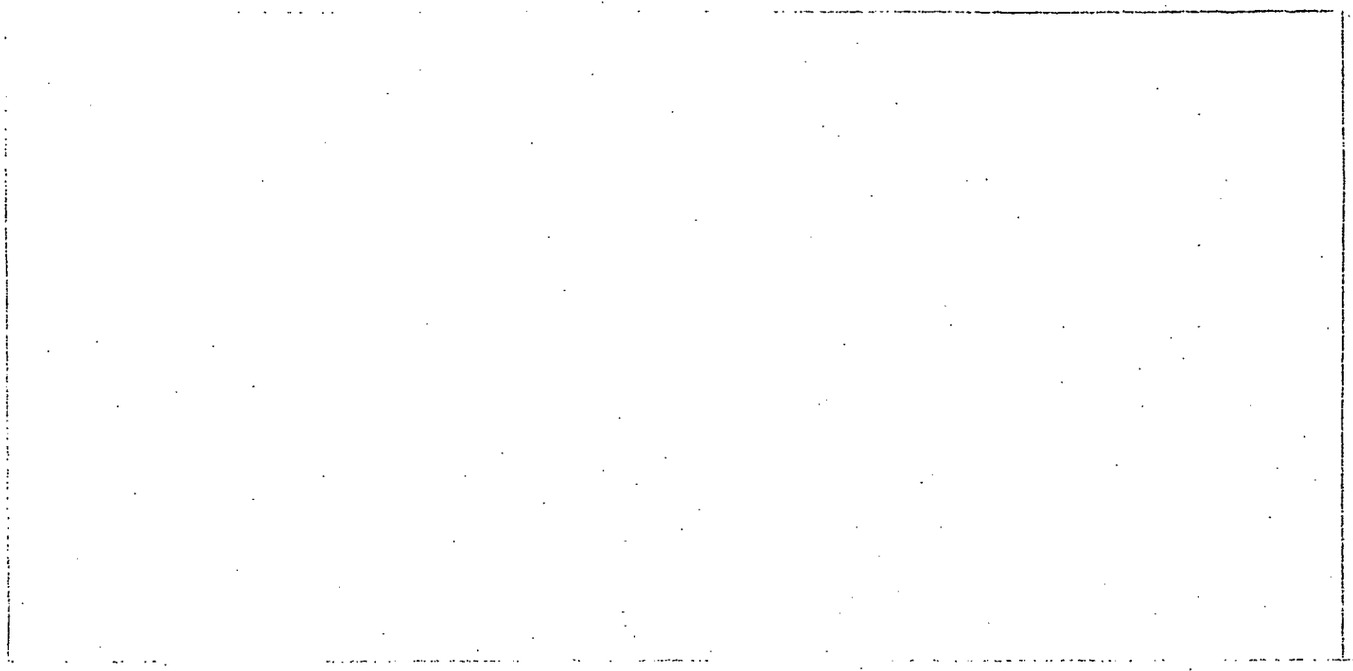

Fig. 1. a) LEED pattern at a primary beam energy of 54 eV from a clean Au(111) surface.
b) Orientation of sample with respect to LEED pattern. To be viewed from the prospective of looking through the crystal and projecting the first three layers, ABC, onto the screen, A = O, B = ◌, C = ●.

RESULTS

LEED observations from the bulk Au sample, as inserted in the UHV system, revealed only integral order reflections of weak intensity, detectable at energies above 200 eV, due to the intense diffuse background. Subsequent to Ar ion bombardment and annealing to ∿ 400°C the LEED pattern shown in Fig. 1a was observed. Each integral order beam is surrounded by hexagonal arrays of additional reflections whose intensities exhibit the three-fold rotational symmetry specific to this crystal orientation. An examination of the bulk atomic arrangement, oriented with respect to the LEED pattern and shown in Fig. 1b, reveals these additional reflections to be aligned with <110> directions. From additional observations, it was determined that heating to ∿ 200°C subsequent to ion bombardment was sufficient to anneal the surface such that this complex LEED pattern was then obtained. This atomic arrangement then persisted and similar LEED patterns were observed after annealing to temperatures as high as 850°C.

An Auger spectrum obtained from such a surface is shown in Fig. 2 and reveals that no impurity signals could be detected on this surface. Repeated sputter and annealing treatments had no effect on either the LEED patterns or Auger spectra. Therefore, it is believed that these measurements are indicative of a clean Au(111) surface.

Initial characterization of the thin film specimen was similar to that of the bulk sample. After Ar ion bombardment and annealing, the LEED pattern obtained from this surface was of the same quality as that exhibited in Fig. 1a. However, the intensities of the hexagonal arrays of reflections as well as the integral order beams exhibited six-fold rather than three-fold rotational symmetry. This results from a superposition of three-fold symmetric diffraction patterns from adjacent domains which have either ABC or ACB stacking arrangements formed during the epitaxial growth on the mica substrate. With the exception of this difference, all other observations on this surface were identical to those on the bulk sample surface.

No changes were observed in the clean surface LEED patterns or Auger spectrum from a sample subsequent to exposure to oxygen at room temperature at pressures up to 10^{-3} Pa and for periods up to 8 hrs. However, exposure of a freshly ion bombarded surface to 10^{-3} Pa for 2 hrs resulted in the adsorption of a very small amount of oxygen which rapidly desorbed upon standing in vacuum. This oxygen Auger signal was never more than ∿ 0.02 as intense as the 255 eV Au Auger signal.

Fig. 2. Auger electron spectra from a clean Au(111) surface and after exposure to O_2 at 700°C.

Oxygen was observed to begin adsorbing on a clean annealed surface at a crystal temperature of ∿ 500°C at a pressure of 10^{-3} Pa. The amount of adsorbed oxygen for a specific exposure increased with increasing temperature up to the maximum temperature employed, 800°C. The largest oxygen Auger signal was ∿ 0.2 as intense as the 255 eV Au Auger signal and its negative peak occurred at an energy of 507 eV. No other detectable Auger signals nor changes in LEED patterns were observed following these exposures. This chemisorbed oxygen could be removed by ion bombardment but not by heating to 800°C.

Ca could be segregated to the surface by heating the sample above 500°C for many hours, and the quantity increased with heating time or increased temperature. More oxygen was observed to adsorb for a specific exposure at an elevated temperature when Ca was initially present than on the clean surface. Depending on the initial conditions, this increase could be as much as a factor of 5. The oxygen Auger line shape and position with respect to energy were unchanged from that observed in the absence of Ca. An example of the most intense signal observed is shown in Fig. 2. With Ca present, the minimum temperature for adsorption of oxygen was lowered to ∿ 400°C. The amount of Ca segregating at the surface at a specific temperature increased when the sample was simultaneously exposed to oxygen.

DISCUSSION

The observation of identical LEED patterns obtained from samples prepared in totally different fashions from different source materials in conjunction with identical AES results strongly suggests that these patterns reflect the atomic arrangement on highly oriented clean Au(111) surfaces. The possibility that surface imperfections are responsible for these observations is reduced due to the complete stability of these surfaces with respect to extensive heating at temperatures up to 850°C and the additional fact that the thin film surface is known to have atomically smooth domains several thousand angstroms in extent. Moreover, our LEED observations on (100) and (110) oriented Au samples prepared from these same source materials are consistent with previous results and argue against some undetected impurity being responsible for stabilizing this atomic arrangement. The absence of similar observations of this complex LEED pattern during previous studies on (111) oriented Au samples may reasonably be attributed to either surface preparation or lack of angular resolution in the electron optics detection system./2,7/ While the reordered Au(100) and (110) surfaces can be converted to their normal atomic arrangements by adsorption of submonolayer quantities of impurities, the amounts of either O or Ca present as a result of the adsorption experiments have been insufficient to cause such a conversion of the (111).

A careful examination of the LEED patterns reveals that the spatial splitting between the additional reflections and the integral order beams is ∿ 4% of the distance between the integral order beams. This amount of splitting is comparable to that observed between the extra reflections in the Au(100) LEED patterns. In that case a hexagonal layer with an intralayer spacing ∿ 5% smaller than that in the bulk has been suggested as the top layer configuration./1-4/ The observations presented here suggest that a contracted hexagonal layer may also exist on the Au(111) surface. Because of the complexity of the pattern, accurate LEED intensity measurements are difficult, and while predictions of multiple scattering calculations may prove helpful, an approach which makes use of ion channeling may be the most suitable technique for determining whether or not the top layer is contracted./5/

The absence of any detectable oxygen adsorption at temperatures below 500°C on clean annealed surfaces is in complete accord with the only other LEED-AES investigation on a Au(111) surface reported by Chesters and Somorjai (C & S). /7/ However, these observations and the

lack of any significant adsorption on an ion bombarded surface are in disagreement with the recent results of Schrader./8/ He has postulated active sites, not present on highly ordered surfaces, to explain the difference between his results and those of C & S. While the absence of adsorption on our annealed surfaces may be due to a lack of such active sites, our results on the ion bombarded surface (which are known from LEED observations to be highly disordered) raise some doubts about the importance of such a site. Unfortunately, the lack of surface characterization with LEED raises the possibility that the (111) oriented samples of Schrader may differ significantly in their surface topography from ours and thus prevents a thorough evaluation of these differing results.

The observed adsorption of oxygen at temperatures above 500°C in a strongly chemisorbed form is consistent with previous observations./7,8/ Although it is difficult to estimate precisely the coverage due to many unknown factors affecting the Auger signal strength, the relative intensity of the oxygen signal and the absence of any new ordered structures or changes in LEED patterns, suggests that the coverage was much less than a monolayer. While these LEED observations are in conflict with the oxide structure reported by C & S, the difference may be due to the difference in surface order as indicated by the differing LEED observations from the surfaces on which the adsorption occurred. However, the relative strength of the oxygen Auger signal reported here is in agreement with that observed by others /7,8/ and suggests that the quantity of oxygen present is not sufficient to form an extensive oxide structure.

The effect of Ca on oxygen adsorption rates has not been reported previously; however, its effect on water vapor adsorption on Au has recently been reported by Schrader./11/ In accord with his observations, the amount of oxygen adsorbed for a specific Ca concentration increased, but not linearly, with increased Ca segregation. Moreover, since the Ca concentration could be increased by heating the sample in the presence of oxygen it appears that not only does the Ca increase the rate of oxygen adsorption but it segregates at the surface, bound in a complex that involves adsorbed oxygen. Because of this increased adsorption rate in the presence of Ca, it is possible that a small undetectable quantity was present on the clean surface; however, this quantity is extremely small.

CONCLUSIONS

While there is much agreement between the oxygen adsorption results presented here and those previously reported by others, the lack of extensive surface characterization in some of those investigations prevents a complete evaluation and understanding of the conflicting observations. Specifically, the new LEED patterns reported here suggest that highly oriented, clean, annealed Au(111) surfaces may not have been used in previous studies. Our LEED results imply an atomic configuration in the surface region of the (111) different from that in the bulk. Although details of the exact arrangement remain to be determined, a contracted intralayer spacing in the outermost layer may explain these observations and is consistent with previous findings on Au(100) reordered surfaces.

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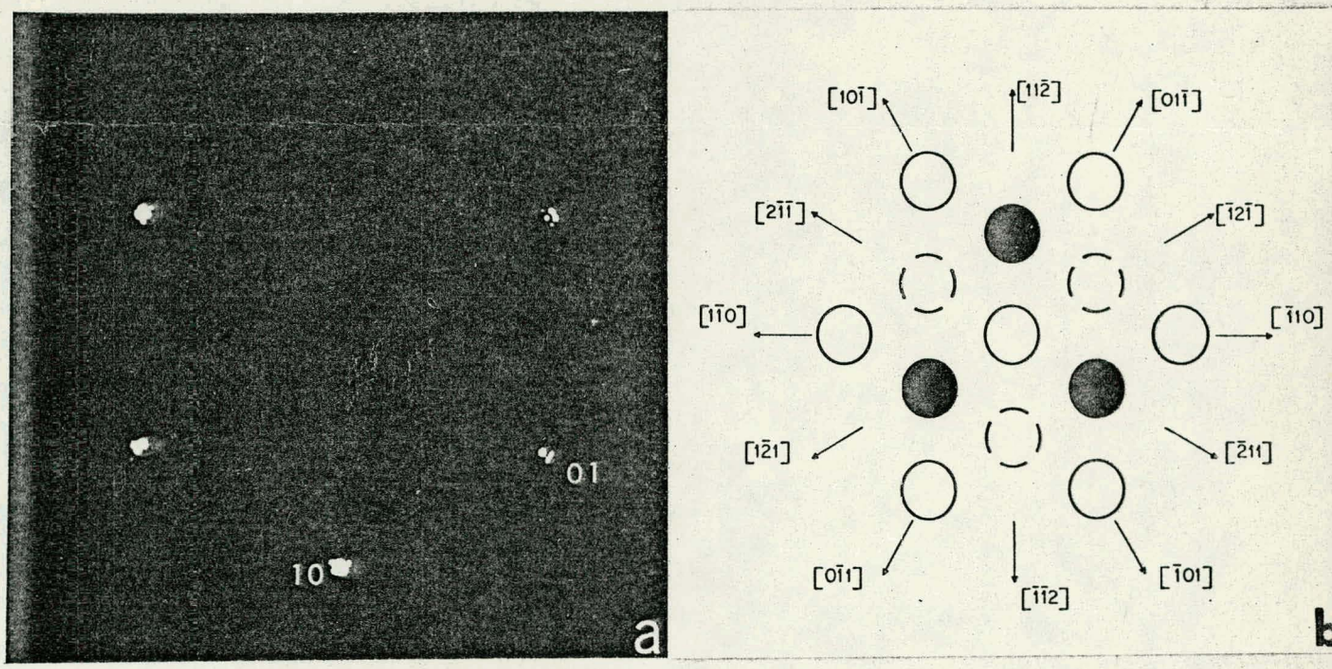
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b

Fig. 1

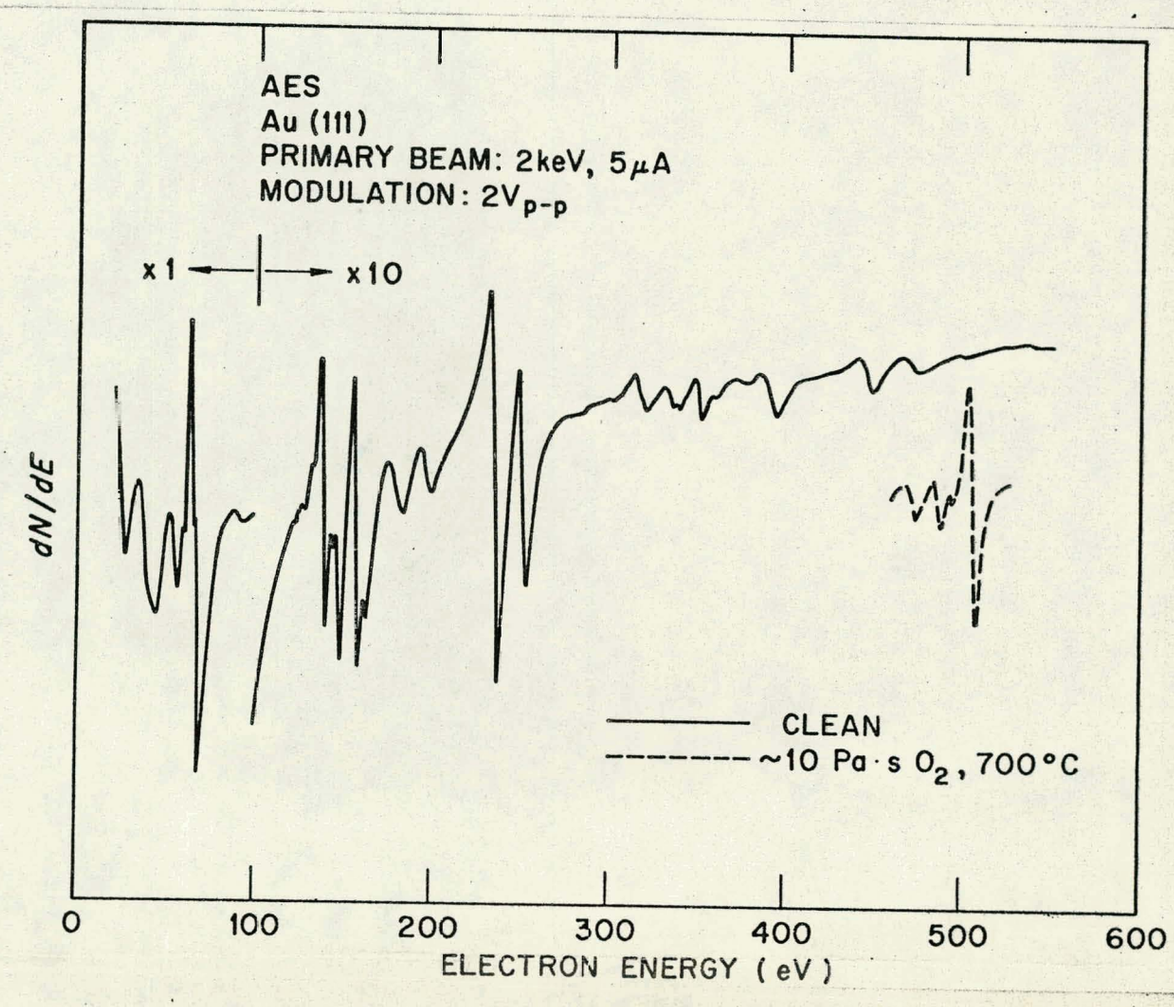
AES
Au (111)
PRIMARY BEAM: 2keV, 5μA
MODULATION: 2V$_{p-p}$
x1
x10
dN/dE
CLEAN
~10 Pa·s O$_2$, 700°C
0
100
200
300
400
500
600
ELECTRON ENERGY (eV)

Fig. 2