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Authors
Mattera, A.M.
Goodman, R.M.
Scraorjai, G.A.

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LOW ENERGY ELECTRON DIFFRACTION STUDY OF THE (100) FACE OF SILVER, GOLD, AND PALLADIUM

A. M. Mattera, R. M. Goodman, and G. A. Somorjai

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Low Energy Electron Diffraction Study of the (100) Face of Silver, Gold, and Palladium.

A. M. Mattera, R. M. Goodman, and G. A. Somorjai

Department of Chemistry and Inorganic Materials Division of the Lawrence Radiation Laboratory, University of California, Berkeley, California 94720

Abstract

The clean (100) surfaces of silver, gold, and palladium were studied as a function of temperature from 25-830°C. Several surface structures, ordered and disordered, were found which are stable only within well-defined temperature ranges. The ordered surface structures form during annealing after ion bombardment. They are parallel to the substrate surface and are characterized by lattice parameters which are integral orders of the substrate lattice parameter. The properties of these ordered surface structures can be explained by assuming they are comprised of ordered arrays of vacancies situated in the first atomic plane. The structures are produced as stable intermediates during annealing of the greatly disordered surface. The disordered surface structures are characterized by either ring-like diffraction patterns or the appearance of new diffraction spots. They appear at high temperatures above the stability range of the ordered surface structure. They are stable and can only be removed by ion bombardment. Apparent interatomic distances assigned to the disordered surface
structures are always larger or smaller than the nearest neighbor distance in the substrates. Good correlations have been found between the properties of the surface structures of gold and platinum and of silver and palladium, respectively.
INTRODUCTION

Recent low energy electron diffraction studies on different low index faces of high purity platinum single crystals [including the (100) orientation]\(^1,2\) have revealed the existence of ordered and disordered surface structures with well-defined temperature ranges of stability. All of the experiments indicated that these surface structures are the property of the clean platinum substrates. Many physical properties of platinum (crystal structure, binding energy, work function, melting point, etc.) can be correlated with its neighbors in the periodic table. Therefore, it was thought that similar surface structures might also exist on other clean face centered cubic metal substrates.

The purpose of this paper is to report on the properties of the surface structures found on the (100) substrates of gold, silver and palladium. Several surface structures appeared during heat treatment in the temperature range 25-830°C. These surface structures have properties similar to those found on the (100) face of platinum. They are ordered or disordered, exist only in well-defined temperature ranges, and are reproducible on the different samples. All of the studies were carried out in ultrahigh vacuum using several samples of high purity single crystal of each metal.
EXPERIMENTAL

The single crystals* were oriented by X-ray, cut within 1° to the (100) face, polished and etched. The etching solutions which gave the most uniform surfaces were nitric acid (50% solution) for silver, aqua regia for gold and dilute nitric acid and hydrochloric acid solution for palladium (H₂O:HNO₃:HCl = 20:5:1). No impurities in concentration greater than 10 ppm were found in any of the samples except 10³ ppm silver in gold, and 5x10³ ppm platinum, and 3x10³ ppm copper in palladium. The samples (5x5x1 mm) were mounted on a tantalum holder after experiments showed that this holder material did not effect the results. The diffraction chamber** was evacuated and after bake-out an ambient pressure of 10⁻¹⁰–10⁻⁹ torr was achieved and maintained during all of the experiments. The samples were then ion bombarded with ultrahigh purity argon or xenon in order to remove the surface damage which was due to the crystal preparation. Typical experimental conditions for ion bombardment were 340 eV accelerating potential and 4.0x10⁻⁵ torr total pressure for 2-10 hours. No diffraction pattern of the freshly prepared sample was obtained at room temperature without ion bombardment. When the sample was heated near to its melting point (gold) or to a temperature at which marked

*The crystals were obtained from Materials Research Corporation, Orangeburg, New York.

**Varian low energy electron diffraction apparatus was used in all of these studies.
evaporation of the surface occurred (silver, palladium), high
temperature surface structures formed irreversibly even without
ion bombardment. These structures prevent the investigation
of surface structures which exist at lower temperatures, thus
ion bombardment was used at the start of most of our studies.
Once a clean diffraction pattern was obtained, any further
"ion bombardment cleaning" of the surface required no more
than 0.5-4 hours at 140-340 eV at 4.0x10⁻⁵ torr argon or
xenon.

In order to study the structure of the (100) substrates
as a function of temperature the samples were heated (D.C.
resistance heating) in 50° steps. The heating time at each
temperature was 0.5-4 hours. When any change of the diffraction
pattern could be detected the heating time was extended to
explore the properties of the new diffraction features. This
way we can be reasonably certain that no surface structure
remained undetected. Once the temperature range of stability
of the different structures was established the structures
were reproduced several times by heating the sample after ion
bombardment directly to the desired temperature. The temper-
ature was monitored by thermocouples spot-welded onto the
sample and/or the crystal holder. The temperature ranges of
study were 25-800°C for silver, 25-850°C for gold, and 25-830°C
for palladium. Several single crystal samples of each metal
have been used in the experiments. The surface structures
reported here were reproducible from sample to sample. The
heat treatment of the substrates was always carried out in ultrahigh vacuum.

RESULTS

The (100) face of silver, gold, and palladium does not appear to be faceted in the temperature range of this investigation. Some of the samples showed a small degree of faceting after heat treatment at the highest temperatures (>700°C).

The surface structures detected on the different face centered cubic metal substrates have several common characteristics. Their diffraction patterns are concentric about the (00)-reflection of the substrate and behave similar to the diffraction spots attributed to the substrate unit mesh. Thus, all of the surface structures reported here are parallel to the substrate plane. The diffraction features which are due to the surface structures are discernible only at low electron energies (approximately 10-150 eV). At higher energies electrons penetrate deeper below the surface and the relative contribution of atoms in the surface plane to the total scattered intensity diminishes.

We have listed in Table I the different surface structures which were found to exist on the (100) face of silver, gold, and palladium with their approximate temperature ranges of stability. In order to facilitate the correlation of the observed surface structures on the different face-centered cubic crystals we have included the surface structures found on the (100) face of high purity platinum. The notation used to
designate the different surface structures is that suggested by Wood. The disordered surface structures which give rise to a ring-like diffraction pattern are designated by a circle. The surface structures may be divided into two groups, ordered and disordered. We shall describe and then discuss them separately.

Ordered Surface Structures

Au(100)-(5x1) and Au(100)-(5x5)

The surface structures form in the temperature range 150-550°C and their temperature ranges of stability overlap. The (5x1) diffraction pattern appears at first which after prolonged heating converts to the (5x5) pattern (Figs. 1a and 1b). Unlike the platinum (5x1) surface structure,\(^1,2\) the intensities of the fractional order spots in both x and y directions are similar. The (5x5) structure persists at higher temperatures than the (5x1) structure. The intensities of both regular and fractional order diffraction features diminish above 500°C. Disorder structures begin to appear above this temperature.

Ag(100)-c(2x2)

Annealing after ion bombardment in the temperature range 50-600°C produces the diffraction pattern which is characteristic of the clean substrate. When the substrate is heated above 600°C the c(2x2) surface structure appears (Fig. 2). This type of structure has been observed to exist on several metal surfaces.\(^4,5\) Its stability range extends up to 750°C. Above that temperature the disordered surface structure forms.
When the palladium substrate is heated after ion bombardment in the temperature range 200-550°C, the (2x1) surface structure appears first (Fig. 3). After prolonged heating streaks develop in the diffraction pattern which slowly resolve into the (2x2) surface structure. This is shown in Fig. 4. When the substrate is heated above 550°C this structure gradually transforms into the centered c(2x2) surface structure. This structure is the only one which persists at the highest temperature employed in these experiments (830°C).

Disordered Surface Structures

Au(100)-Ω and Ag(100)-Ω

When the gold (100) substrate is heated in high vacuum above 550°C the intensity of the diffraction features due to the substrate and the 5x5 surface structure diminish. At the same time eight new diffraction spots appear (Fig. 5a). These are detectable only at low electron energies (15-40 eV), are concentric about the (00)-reflection of the substrate, and show diffraction features which are characteristic of other surface structures. The apparent lattice parameter which can be assigned to this pattern indicates a marked expansion with respect to the bulk lattice spacing (Table II). Further heating above 750°C results in the appearance of a set of new ring-like diffraction features (Fig. 5b). These diffraction rings are
narrow and well-defined, are concentric about the (00)-reflection of the substrate, and show up at electron energies 10-150 eV. The apparent lattice parameters which may be assigned to the new sets of rings are markedly smaller than the nearest-neighbor distance in the gold substrate (Table II). The formation of these new diffraction patterns is irreversible. Once formed they can only be removed by ion bombardment. The properties of the narrow ring-like diffraction patterns are similar to those diffraction patterns which were observed on the different crystal faces of platinum at high temperatures.¹²

When the (100) face of silver is heated to above 750°C new diffraction spots appear (Fig. 6). These show twelve-fold symmetry, are concentric about the (00)-reflection of the substrate, and, like any other surface structure, are detectable only at low electron energies. It is somewhat troublesome to develop this disordered surface structure since the evaporation rate of silver is appreciable at these temperatures.

No ring-like diffraction features could be detected on the clean (100) substrate of palladium up to 830°C. It is possible, however, that they may appear above this temperature. Excessive evaporation of the samples has prevented further studies at higher temperatures.

In Table II we list the diffraction patterns which may be attributed to the disordered surface structures. We designate as "first" the pattern which gives rise to diffraction features (spots or rings) which are nearest to the (00)-reflection. The ratio \( \frac{d_\circ}{d_{\text{substrate}}} \) is given where \( d_\circ \) is the
apparent lattice parameter which could be assigned to the disordered structure and $d_{\text{substrate}}$ is the nearest neighbor distance in the substrate plane. It is difficult to determine absolute values of these lattice dimensions with any certainty from the experimental results. There are other parameters such as the inner potential, field distortions in the diffraction chamber, possible expansion or contraction of the lattice which introduce uncertainties. In order to avoid these difficulties we give only the ratio of the lattice parameters which were measured in the experiments. We also list the same lattice parameter ratios which were obtained for the ring-like diffraction patterns on the (100) face of platinum for comparison. It is apparent that none of the ring patterns overlap the diffraction spots which are due to the substrate unit mesh.

DISCUSSION

The results of these low energy electron diffraction studies on the (100) face of gold and platinum, and of silver and palladium, respectively, show that great similarity exists between the surface structures which form. Gold and platinum exhibit surface structures with larger unit cells (5x1 and 5x5) than those on the silver or palladium surfaces [2x1, 2x2, or c(2x2)]. It is believed that most, or maybe all, of the surface structures are attributable to the clean surface. The hypothesis that impurities might be the cause of the observed surface structures appears to be unsupported by the experimental facts. The possibility cannot be ruled out,
however, that the formation of some of the surface structures may have been catalyzed by trace amounts of impurities. The experimental results which primarily indicate that the surface structures are the property of the clean substrate are:

(1) There is a similarity in the types of surface structures which form on the different metal substrates.

(2) They are present only in well-defined temperature ranges. The type of surface structures varies on the same substrate as a function of temperature.

(3) The surface structures show a broad spectrum of physical properties. They are ordered or disordered and are reproducible on all of the samples which were studied.

(4) Impurity concentrations in platinum\(^2\) and silver are below the detection limit which is postulated to exist for low energy electron diffraction experiments.\(^2\)

(5) The surface structures are parallel to, and in registry with, the substrate unit mesh for all of the ordered structures. The ring-like diffraction features are characterized by different apparent lattice parameters on the different metal surfaces.

(6) Metals which contain large concentrations of an impurity metal have surface structures which are in no way similar to the surface structures of that impurity metal. Thus, gold which contains \(10^3\) ppm silver exhibits surface structures which are in no way comparable with the surface structures of silver. Palladium which is contaminated with
platinum (10^3 ppm) has surface structures which are different from that of platinum.

If any of the observed surface structures are caused by impurities in the samples one would expect that irreproducibilities under certain experimental conditions would be revealed. For example, impurities which segregate at the surface would be removed by successive ion bombardments or heat treatments and the impurity surface structure would not be reproducible after prolonged studies. Other types of impurities may have low diffusion rates and remain uniformly distributed throughout the crystal. In this case one would expect irreproducibilities between two single crystal samples grown under different conditions with different impurity concentrations.

Surface structures on the (100) substrates of gold, identical to those reported in this paper, have been reported by Fedak et al. \(^6\) It was suggested that these structures are due to "unidentified impurities." We believe, however, that the evidence that identical surface structures were detected to be present on the surface of different gold single crystals which were grown and prepared under entirely different experimental conditions is an indication that these surface structures are the property of the clean gold (100) substrate.

**Correlations Between Ordered Surface Structures**

The following statements give a summary of some of the properties of the ordered surface structures on the (100) crystal face of silver, gold, and palladium. Those properties are
depicted which could be correlated for these face-centered cubic metals.

(a) Similar surface structures have formed on the silver and palladium and on the gold and platinum surfaces, respectively. These surface structures are reproducible on all of the samples which were studied.

(b) These structures exist only in well-defined temperature ranges and are unstable outside these ranges. The stability range of some of the surface structures can overlap.

(c) The intensity of the fractional order diffraction features for most of the observed surface structures are of the same order of magnitude as those due to the substrate.

(d) All of the ordered surface structures were obtained after ion bombardment. The formation of these structures was independent of the type of ions (xenon or argon) which were used and from other conditions of the ion bombardment.

The surface structures could be due to the presence of either ordered arrays of vacancies or atoms at the (100) crystal face. There are experimental observations which suggest that the surface structures consist of ordered arrays of vacancies in the topmost atomic plane. These are:

(1) The intensities of the diffraction features which are due to the surface structure are of the same order of magnitude as the intensities of the diffraction spots due to the substrate.

Structure analysis has been carried out on the (5×1) and (5×5) surface structures. The model which was used was one of singly reflected electrons from a substrate consisting of a
surface of 50x50 atoms. Ten planes were taken into account beneath the substrate. The structure factor was calculated by summing over all of the scattering centers. The absorption of electrons as they penetrate below the surface plane and possible lattice expansion or contraction have been taken into account. The atomic scattering factor was calculated using partial wave analysis and the Thomas-Fermi-Dirac potential. The only model which gave intensities similar to those observed in the experiments was one in which vacancies were introduced in the substrate. Extra atoms which are placed above the surface plane in regular arrays gave rise to intensities for the fractional order diffraction spots which were two orders of magnitude lower than intensities due to the substrate unit mesh.

(2) When two surface structures can exist in the same temperature range the transition, in general, occurs during annealing from the higher density surface structure to the more open low density structure. For example, Au(100)-(5x1) $\xrightarrow{200-550^\circ C}$ Au(100)-(5x5). Thus the high vacancy concentration anneals out as a function of heating time. If atoms were responsible for the surface structures their concentration would be expected to increase as a function of heating time.

A vacancy model provides a possible explanation for the properties of the ordered surface structures. The substrate becomes disordered after ion bombardment. A large fraction of the surface atoms occupy nonequilibrium surface sites. This is clearly seen from the high background intensity of the
diffraction patterns and the diffuse diffraction features of the substrate after ion bombardment. This damage cannot be annealed out at room temperature for the face-centered cubic metals which were studied because the diffusion of the substrate atoms is apparently very slow. When the substrate temperature is increased the substrate atoms diffuse to positions which are energetically more favorable. These appear to be domains of vacancy surface structures in which long range order can be established. The more stable surface structures form gradually through several intermediate structures.

It is likely that one of the most stable arrangements of surface atoms is that in the clean substrate, i.e., the absence of any surface structure. One of the more important results of this study is to show that there are other arrangements of surface atoms which exhibit long range order and are remarkably stable in a given range of temperatures.

Since all of the ordered surface structures were obtained after ion bombardment, it is possible that atoms may have to be placed into nonequilibrium positions before they are able to participate in forming any of the vacancy structures. Thus, nonequilibrium concentration of vacancies must be created at the surface. In order to determine whether these structures may be formed in a substrate which has equilibrium vacancy concentration cleaved or vapor-etched surfaces should be used.

It is interesting to note that on both gold and platinum substrates the surface structures with five times the lattice dimensions of that of the substrate are favored, while silver
and palladium seem to prefer surface structures with only two times the substrate unit cell.

**Correlation Between Disordered Surface Structures**

The disordered surface structures begin to form only at elevated temperatures. These structures develop gradually, new diffraction spots appear at first then slowly a ring-like diffraction pattern forms. Thus, the substrate atoms enter gradually into the disordered phase. The ring-like diffraction patterns which are also concentric about the (00)-reflection of the substrate indicate that the disordered domains can freely be rotated about the (100)-axis with respect to the substrate orientation.

The diffraction features which characterize the disordered surface structures do not overlap the diffraction spots of the substrate unit mesh. There is always an apparent expansion or contraction when the disordered phase forms. This is clearly indicated by the lattice parameter ratios which are given in Table II. Also, only in the case of silver does the "second" diffraction ring correspond to truly second order diffraction features.

The formation of the disordered phase is irreversible for all of the face-centered cubic crystals studied with the exception of palladium where no such disordered surface structure was found to exist in the temperature range of this study (25-830°C). The intensity of the disordered diffraction features seem to increase as the melting temperature is approached.
while the intensity of the substrate diffraction features decreases with increasing temperature. Thus, the surface shows signs of disorder at a temperature which is appreciably below the melting point while no apparent disorder is known to occur in the bulk of the crystals at the same temperature. Since the surface Debye temperatures and surface diffusion rates\(^{10}\) were found to be markedly smaller than in the bulk this result is not too surprising. Studies on thin films at elevated temperatures have indicated that surfaces may even melt below the melting temperature for the bulk.\(^{11}\)

Unlike the ordered surface structures the disordered structures could be obtained without ion bombardment. Prolonged heating to the proper temperature always developed the ring-like diffraction patterns. Thus, these appear to be stable equilibrium surface structures at elevated temperatures.

It is likely that the formation of most of the surface structures is surface diffusion limited. Therefore the rate of formation is not only a function of temperature but also the surface topology such as the step, ledge, and kink concentration in a given surface. These, of course, depend on the history of surface preparation prior to the heat treatment of the substrate. In addition, since heating of the substrate is carried out mostly by passing current through the sample, the temperature across the sample surface may not be uniform in steady state or while steady state temperature is approached. The nature of the temperature gradient depends mainly on the geometry of the sample, the sample holder, and the contact
between them. The presence of such a temperature gradient may accelerate the formation of a given surface structure at certain portions of the crystal while other parts of the substrate remain free of surface structure. This has been frequently observed on many of the metal substrates. Thus, it is difficult to assign an accurate temperature range in which a given surface structure is stable. We gave, in Table I, an approximate temperature range which is indicated by many experiments which were aimed at obtaining the surface structure. The relative temperatures at which the different surface structures appear however, should remain unchanged [for example, the Au(100)-(5x1) always appears at lower temperature with respect to the Au(100)-(5x5)]. Until the activation energies of formation for the different surface structures is determined or the sample sample-holder geometry is standardized, there is a degree of uncertainty in the temperature range of stability reported for most of the surface structures.

Acknowledgement—This work was performed under the auspices of the United States Atomic Energy Commission.
Table I. Surface structures on the (100) substrates of gold, platinum, silver, and palladium, and their approximate temperature ranges of stability.

<table>
<thead>
<tr>
<th>Surface Structures on the (100) Substrates</th>
<th>Approximate Temperature Range °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au</td>
<td></td>
</tr>
<tr>
<td>(5x1)</td>
<td>200-400</td>
</tr>
<tr>
<td>(5x5)</td>
<td>350-550</td>
</tr>
<tr>
<td>ring (⊙)</td>
<td>&gt;550</td>
</tr>
<tr>
<td>Pt</td>
<td></td>
</tr>
<tr>
<td>(2x1)</td>
<td>300-500</td>
</tr>
<tr>
<td>(5x1)</td>
<td>350-500</td>
</tr>
<tr>
<td>ring (⊙)</td>
<td>&gt;600</td>
</tr>
<tr>
<td>Ag</td>
<td></td>
</tr>
<tr>
<td>c(2x2)</td>
<td>600-750</td>
</tr>
<tr>
<td>ring (⊙)</td>
<td>&gt;750</td>
</tr>
<tr>
<td>Pd</td>
<td></td>
</tr>
<tr>
<td>(2x1)</td>
<td>200-300</td>
</tr>
<tr>
<td>(2x2)</td>
<td>250-550</td>
</tr>
<tr>
<td>c(2x2)</td>
<td>&gt;550</td>
</tr>
</tbody>
</table>
Table II. The lattice parameter ratios, \( \frac{d_0}{d_{\text{substrate}}} \) for the ring-like diffraction patterns on the (100) substrates of silver, gold, and platinum. We designate as "first" the ring which is nearest to the (00)-reflection.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Ring</th>
<th>( \frac{d_0}{d_{\text{substrate}}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>I</td>
<td>1.14 ± 0.01</td>
</tr>
<tr>
<td></td>
<td>II</td>
<td>0.58 ± 0.01</td>
</tr>
<tr>
<td>Au</td>
<td>I</td>
<td>1.99 ± 0.01</td>
</tr>
<tr>
<td></td>
<td>II</td>
<td>0.79 ± 0.01</td>
</tr>
<tr>
<td></td>
<td>III</td>
<td>0.55 ± 0.01</td>
</tr>
<tr>
<td>Pt</td>
<td>I</td>
<td>0.76 ± 0.03</td>
</tr>
<tr>
<td></td>
<td>II</td>
<td>0.43 ± 0.03</td>
</tr>
<tr>
<td></td>
<td>III</td>
<td>0.41 ± 0.03</td>
</tr>
</tbody>
</table>
References


7. A. Chutjian and G. A. Somorjai, to be published.


Figure Captions

Fig. 1a and 1b. Diffraction patterns of the (a) Au(100)-(5x1) and (b) Au(100)-(5x5) surface structures at $E = 58$ eV.

Fig. 2. Diffraction pattern of the Ag(100)-c(2x2) surface structure at $E = 70$ eV.

Fig. 3. Diffraction pattern of the Pd(100)-(2x1) surface structure at $E = 77$ eV.

Fig. 4. Diffraction pattern of the Pd(100)-(2x2) surface structure at $E = 75$ eV.

Fig. 5a and 5b. The new (a) diffraction spots (20 eV), and the (b) diffraction rings (100 eV) which appear on the (100) face of gold above 500°C.

Fig. 6. The segmented diffraction ring which appears on the (100) face of silver above 750°C at $E = 70$ eV.
Fig. 1b
Fig. 3
Fig. 5b
Fig. 6
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