

# Oxygen chemisorption on a stepped Ru ( $\sim 001$ ) crystal<sup>a)</sup>

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The 300 K chemisorption of oxygen on a stepped Ru ( $\sim 001$ ) single crystal  $[17(001)\times(100)]$  gives  $2\times 2$  complete half-order,  $1\times 2$  complete or incomplete half-order, and  $1\times 1$  integral-order LEED patterns depending on oxygen exposure and sample annealing. The corresponding relative AES oxygen signals are 0.25, 0.50, and 1.0, respectively. Under certain surface conditions, the presence of the steps is seen to break the threefold degenerate growth habit of  $1\times 2$  domains. The  $1\times 1$  pattern forms at 300 K only after lengthy exposure at relatively high pressure ( $10^{-5}$  Torr) and is stable to 600 K. Prolonged exposure gives rise to relative AES oxygen signals greater than unity suggesting penetration into the subsurface region.

## INTRODUCTION

A number of UHV surface studies have been reported on the interaction of oxygen with single-crystal Ru.<sup>1-8</sup> Among these, low-energy electron diffraction (LEED) experiments on Ru(001)+O<sub>2</sub> have shown the existence of a complete half-order diffraction pattern. Madey, Engelhardt, and Menzel<sup>2</sup> (hereafter MEM) further report that the intensity of the half-order beams reaches a maximum at a coverage corresponding to one-half the saturation value, declines with further oxygen exposure, and finally increases to a new maximum at saturation. In addition, the change in work function ( $\Delta\phi$ ) with exposure rises markedly at the point where the first maximum in LEED spot intensity occurs. No abrupt differences in sticking coefficient accompany these adsorption effects.<sup>2</sup> Finally, although MEM do not know with certainty the absolute coverage at saturation, they believe that it corresponds to a one monolayer  $1\times 2$  structure (where one monolayer has an equal number of adsorbate and surface adsorbent atoms).

This paper presents some interesting LEED and Auger electron spectroscopy (AES) results for oxygen adsorption on a stepped Ru ( $\sim 001$ ) single crystal  $[17(001)\times(100)]$  which are in complete agreement with the observations of MEM but clarify the relationship between surface structure and coverage. In particular, our results indicate the presence of a fully developed  $2\times 2$  oxygen overlayer at the first half-order LEED intensity maximum. Consequently, further increase in oxygen coverage results in the growth of a combination of three  $1\times 2$  degenerate domains up to the saturation value of MEM.

The experiments were done in a UHV system equipped with a four-grid LEED optics and a cylindrical mirror analyzer (CMA). A base pressure of  $1.5\times 10^{-10}$  Torr was maintained in the vacuum chamber using a 450 l/sec turbomolecular pump. Temperatures were measured using a W-26%Re-W thermocouple.

The Ru crystal face was prepared and polished using standard techniques.<sup>2</sup> Analysis by Laue backscattering showed that the surface was tilted  $2\frac{3}{4}^\circ$  from the (001) plane in a direction giving the surface designation  $[17(001)\times(100)]$ . A perfectly ordered Ru surface of this orientation would consist of terraces seventeen lattice spacings wide which are separated by straight (100) ledges. The extent of random kinking along these ledges cannot be measured and, although the real surface ledges undoubtedly are not perfectly straight, our results are consistent with a model in which kinks do not play a dominant role.

Following introduction into the vacuum chamber, the sample was cleaned by sputtering and heating cycles according to previously reported methods.<sup>2,9</sup> AES showed no difference between this surface and a thermally cleaned surface which was treated using repeated heating and cooling cycles (300–1550 K) in  $5\times 10^{-7}$  Torr of oxygen followed by heating *in vacuo* to 1600 K.<sup>10</sup> After the first cleaning treatment, the sample could usually be restored to a clean state by a flash *in vacuo* to 1600 K, but occasional retreatment in oxygen was required. Following an extended period of experimentation, heating the crystal in oxygen caused a "tenacious oxygen" to form that could be removed only by many heating cycles in vacuum.

## RESULTS

As described below for the stepped Ru ( $\sim 001$ ) surface, oxygen was found to form  $2\times 2$ ,  $1\times 2$ , and  $1\times 1$  LEED patterns with relative coverages of 0.25, 0.5, and 1.0 as determined by Auger peak-to-peak heights.

When the crystal was exposed to  $2\times 10^{-7}$  Torr oxygen at 300 K a complete half-order spot pattern was visually observed to increase in intensity up to 1.5 L. With additional exposure up to  $\sim 10$  L, the pattern became more diffuse and less intense until finally reintensifying as saturation was approached (We define saturation as the coverage reached after a 50 L exposure at 320 K but it should be noted that oxygen continues to accumulate slowly at higher exposure). These results reproduce the earlier work of MEM. We denote the complete half-order pattern at  $\leq 1.5$  L as a  $2\times 2$  pattern.

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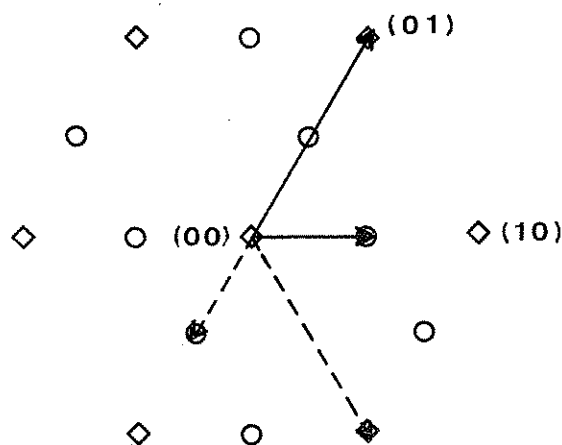


FIG. 1.  $1 \times 2$  oxygen LEED pattern from a stepped Ru( $\sim 001$ ) surface. ( $\diamond$ ) are integral order substrate spots. ( $\circ$ ) are half-order spots produced by oxygen chemisorption. The solid and dashed vectors indicate two reciprocal meshes used to generate the observed LEED pattern.

After the crystal was exposed to 1.5 L of oxygen at 300 K and heated to 700 K *in vacuo*, the  $2 \times 2$  pattern still persisted, but appeared to be sharper. Further exposure to  $\sim 20$  L oxygen at  $2 \times 10^{-7}$  Torr and 300 K converted the  $2 \times 2$  pattern into the incomplete half-order or  $1 \times 2$  pattern shown in Fig. 1. Auger measurements showed that the saturation oxygen coverage for this  $1 \times 2$  pattern was the same as that for the complete half-order pattern formed by saturating the surface at 300 K and twice the coverage for the  $2 \times 2$  pattern formed by a 1.5 L exposure at 300 K. The  $1 \times 2$  pattern converted into a complete half-order pattern upon heating to 500 K; this occurring without change in the oxygen AES signal.

After a 1.5 L  $O_2$  exposure, an anneal to 700 K and a 10 min exposure at  $10^{-5}$  Torr at 300 K (6000 L), only the integral order or  $1 \times 1$  diffraction features were observable. Within an experimental uncertainty of about 15%, the Auger peak-to-peak height for oxygen was twice that of the saturated  $1 \times 2$  pattern at  $2 \times 10^{-7}$  Torr and four times that of the  $2 \times 2$  pattern formed from 1.5 L exposure. A relative coverage of unity was assigned to this surface condition. It was stable to temperatures as high as 600 K. Heating to higher temperatures and then cooling gave a complete half-order pattern and reduced Auger signal indicating some dissolution.<sup>11</sup>

The Auger signal corresponding to the  $1 \times 1$  LEED pattern described above was measured in the following way. Once a complete half-order pattern had been established,  $O_2$  was leaked into the chamber at  $10^{-5}$  Torr and the LEED display periodically examined until the half-order spots vanished. Then after cleaning the sample, the same  $O_2$  exposure was repeated in the absence of any electron beam. The  $1 \times 1$  pattern was present immediately upon placing the crystal under the LEED beam. Subsequent Auger analysis gave a signal twice as large as the  $1 \times 2$  pattern at  $2 \times 10^{-7}$  Torr saturation. More detailed characterization of this  $1 \times 1$  pattern will be done in the future using photographic analysis.

After extended exposures at  $10^{-5}$  Torr and 300 K ( $> 10^5$  L) the oxygen Auger signal grew slowly while the

$1 \times 1$  LEED pattern persisted. Oxygen Auger signal intensities as high as eight times that attributed to the  $2 \times 2$  pattern at 1.5 L were observed. A small deterioration ( $< 5\%$ ) of the oxygen signal was noted when using the AES electron beam. This occurred during the first three minutes of beam time and extended time ( $\sim 40$  min) did not produce further changes. No detectable surface degradation was produced by the LEED electron beam ( $0.4 \mu A$  beam current and incident energy  $\sim 100$  eV). Furthermore, it is important to note that an electron beam was not required to form any of the above LEED patterns.

Since the CO background pressure tends to rise somewhat during such lengthy and high pressure  $O_2$  exposures, it is necessary to consider whether the  $1 \times 1$  pattern involves coadsorbed CO and  $O$ .<sup>3,10</sup> Flash desorption measurements have shown that CO is adsorbed by an oxygen-covered Ru(001) surface.<sup>11</sup> However, in the present study deliberate exposure of the  $2 \times 2$  or  $1 \times 2$  oxygen overlayers to CO at pressures as high as  $10^{-5}$  Torr resulted in a higher background and fuzzier spots but not a  $1 \times 1$  pattern. Electron beam exposure time was kept to less than 10 s. The partial pressure of water also rises during high pressure  $O_2$  exposures and, thus, its role in forming the  $1 \times 1$  pattern at 300 K must also be considered. Yates and Madey<sup>12</sup> have studied thermal desorption, ESDIAD and LEED of water adsorbed on Ru at 90 K. They found what appeared to be a small amount of dissociation of water during thermal desorption (indicated by  $H_2$  and  $O_2$  desorption). Our own evidence<sup>11</sup> from heating Ru in  $1 \times 10^{-8}$  Torr of  $H_2O$  shows that appearance of oxygen due to activated dissociation of water occurs readily only at temperatures in excess of 400 K. At 300 K, exposure of the  $1 \times 2$  oxygen overlayer to  $5 \times 10^{-8}$  Torr  $H_2O$  for 25 min (equivalent to that produced during high pressure  $O_2$  exposure) did not influence the LEED pattern. Even at higher temperature and more exposure of  $H_2O$  ( $1 \times 10^{-6}$  Torr for 10 min at 420 K) no  $1 \times 1$  pattern was observed. Although not conclusive, since  $O_2(g)$  was absent, this result suggests that  $H_2O$  is not responsible for the  $1 \times 1$  LEED pattern. The same experiment even with the electron beam of the AES gun constantly on the sample gave a  $2 \times 2$  pattern. In other experiments, to be reported elsewhere,<sup>11</sup> we have investigated the activated decomposition of water on Ru(001) in more detail.

## DISCUSSION

The following model is consistent with both the present and previously reported data. We assume that the absolute coverages corresponding to the  $2 \times 2$  (formed at 1.5 L exposure),  $1 \times 2$ , and  $1 \times 1$  LEED patterns are 0.25, 0.50, and 1.0 monolayer atomic oxygen, respectively. The  $1 \times 2$  pattern would be observed if the oxygen atoms on the surface were located in nearest neighbor sites on alternate substrate rows running in the same direction. On the Ru(001) surface where there are three geometrically equivalent directions for  $1 \times 2$  domains to grow, the superposition of diffraction features from the three domains gives a complete half-order LEED pattern.<sup>1-3</sup> For the stepped surface of this study, comparison of the crystal orientation obtained from the x-ray

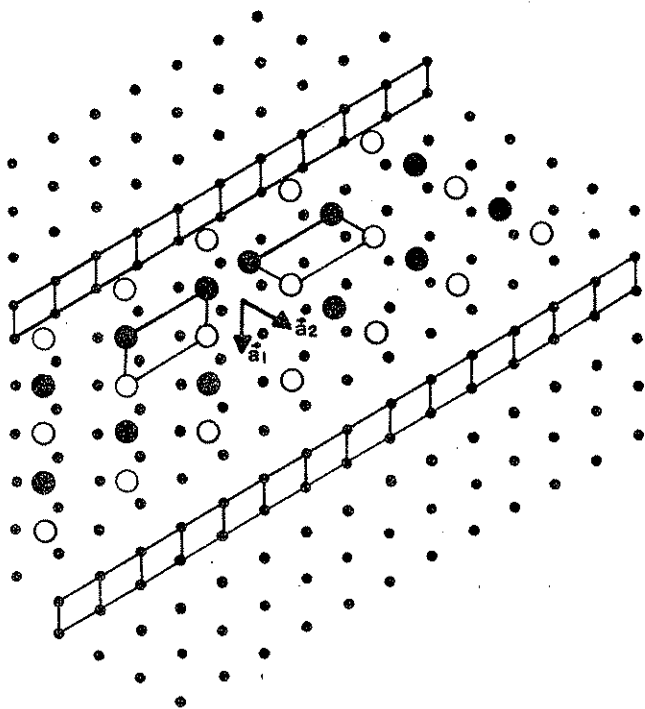


FIG. 2. One-site model for oxygen chemisorption on the stepped Ru( $\sim 001$ ) surface. (001) terraces—smaller than for actual surface—are separated by perfectly ordered (100) ledges. Small dots are substrate atoms. Circles are oxygen atoms forming  $2 \times 2$  overlayer. Large dots are oxygen atoms added to well-ordered  $2 \times 2$  to form  $1 \times 2$  domains.  $a_1$  and  $a_2$  indicate the two degenerate directions along which the  $1 \times 2$  domains grow in the absence of appreciable  $2 \times 2$  domain boundaries to give a LEED pattern similar to that of Fig. 1.

data with that of the  $1 \times 2$  domains obtained from the incomplete half-order LEED pattern (Fig. 1) indicates that oxygen atoms under the proper conditions prefer to form nearest-neighbor chains in the two equivalent directions shown in Fig. 2.

We believe that 300 K adsorption (up to 0.25 monolayer) gives rise to a  $2 \times 2$  structure in which the atoms have relatively low mobility, thereby limiting the long-range order to that readily detectable by broadening of the LEED beams, i.e., 100 Å.<sup>13</sup> Further adsorption at 300 K forms nearest-neighbor oxygen chains on alternate substrate rows, where the size of the  $1 \times 2$  domains is apparently limited by the long range order of the  $2 \times 2$  structure. Thus, the adsorption of 0.5 monolayer oxygen at room temperature results in the formation of  $1 \times 2$  structures oriented along three different directions—each  $1 \times 2$  domain being terminated by a boundary in the original  $2 \times 2$  structure. The combination of these three orientations of  $1 \times 2$  structure gives a complete half-order pattern.

However, heating the crystal after forming the  $2 \times 2$  pattern at 1.5 L increases the mobility of the surface oxygen atoms and the sharper  $2 \times 2$  pattern observed upon cooling to 300 K indicates that larger  $2 \times 2$  domains have

been formed (apparently over the width of the terraces on our crystal). Subsequent oxygen exposure at room temperature then results in the formation of ( $1 \times 2$ ) domains growing in the two degenerate directions of Fig. 2—the growth being directed in some way by the step ledges.

It is evident that the oxygen environment changes significantly with the onset of  $1 \times 2$  domain growth. That the oxygen atoms in the  $2 \times 2$  and  $1 \times 2$  domains have markedly different geometric and electronic properties is indicated by the sharp break in the  $\Delta\phi$  vs exposure curves,<sup>2</sup> the local maximum in the half-order beam intensity,<sup>2</sup> and the large change in the adsorption-desorption properties of carbon monoxide<sup>11</sup> when the  $O_2$  exposure at 300 K exceeds 1.5 L. As in MEM and in agreement with the present LEED data, the individual oxygen atoms within each domain type are thought to be essentially the same so that the growth of a  $1 \times 2$  domain involves changes in the dipole length and charge transfer associated with oxygen already present in the  $2 \times 2$  domains. Indeed, unlike the model of Fig. 2, the  $2 \times 2 \rightarrow 1 \times 2$  transformation may involve a change of bonding site.

The slow growth of the relative oxygen Auger signals during high exposures is very interesting and suggests slow penetration into the subsurface region at relatively low temperatures. Other evidence of penetration, based on higher temperature exposure, will be given in a separate publication.<sup>11</sup>

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