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RECONSTRUCTION OF A STEPPED Fe (111) SURFACE DUE TO OXYGEN ADSORPTION

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Single crystal surfaces with high Miller index are of much interest in their thermal stability under ultra-high vacuum (UHV) condition, besides in their peculiarities in gas adsorption and in catalytic activities. Oxygen adatoms are well-known to play an important role in reconstruction of iron surfaces as inferred from the fact that either the epitaxial growth of FeO-like oxide layers¹⁻⁸⁾ or the thermal faceting⁹⁾ occurs on the oxygen-covered surface, depending on amount of the adatoms. In the present note, some results of LEED study where oxygen adsorption on a stepped Fe (111), Fe(s)-4(111) × (110) surface, was examined with a special interest in the effect of oxygen adatoms on the thermal stability are represented.

The stepped (111) surface was prepared by cutting a single crystal at $\sim 4.0^\circ$ from the (111) face towards the (110) plane. The surface orientation was determined by a back-reflection Laue X-ray technique with an accuracy of $\pm \frac{1}{2}^\circ$. Repeated argon-ion bombardment with 500 eV at 10^{-5} Torr, while keeping the sample at 700 K, and annealing at 900 K in vacuum produced the clean stepped (111) surface in accordance with Fig. 1. LEED patterns were taken around 300 K throughout the present study.

Oxygen adsorption around 300 K at the low exposures (< 20 L)* enhanced the background intensity with decrease in intensity of LEED spots from the stepped (111) surface and around the exposures of 20 L all the spots became invisible. After further exposing the surface to oxygen (30 L), very broad, weak LEED spots with quasi-hexagonal

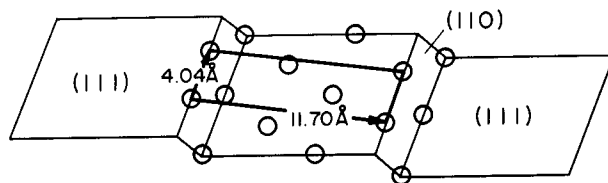


Fig. 1. Schematic representation of the Fe(s)-[4(111) × (110)] surface structure.

*) $1\text{L} = 10^{-6} \text{ torr} \cdot \text{sec.}$

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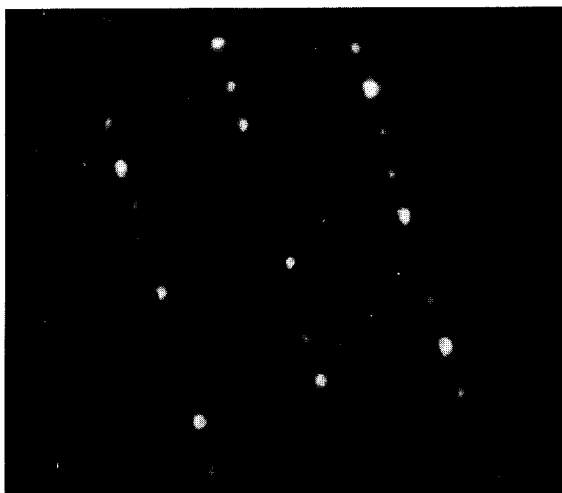
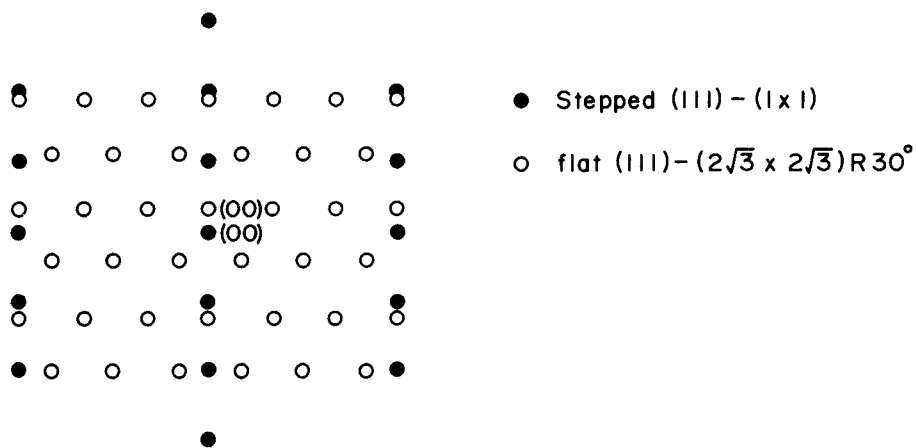


Fig. 2. The LEED pattern of the ordered stepped (1×1) surface structure obtained after flashing the oxygen-covered stepped (111) surface to ~ 700 K (~ 60 eV).



25 V

Fig. 3. Schematic diagram of the LEED pattern of the stepped (111)-(1×1) and flat (111)-(2√3 × 2√3) R 30° surface structures obtained after flashing the oxygen-covered stepped (111) surface to ~ 800 K (25 eV).

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symmetry began to appear, from which the surface atomic spacing was found to be somewhat larger than that on the clean (111) surface. The quasi-hexagonal pattern remained unchanged at the exposures up to 40 L. After flashing the surface up to 700 K a weaker stepped (111)-(1×1) pattern recovered. Upon flashing the surface up to 800 K, this pattern further changed into a flat (111)-(2√3 × 2√3) R 30° pattern accompanied by additional spots. All the additional spots were found to be arised from neither the flat nor the stepped (111) surface. The faint stepped (111)-(1×1) pattern observed at 20 L, on the other hand, became a very bright one after flashing to 700 K, see Fig. 2. After subsequent flashing to 800 K the bright pattern was accompanied by LEED spots indicating a flat (111)-(2√3 × 2√3) R 30° surface structure as shown in Fig. 3.

With the flat (111) surface covered with oxygen, flat (111)-(4×4) (~0.5 monolayers) and -(2√3 × 2√3) R 30° (above one monolayer) patterns have been observed after flashing the surface to 700 K.^{10,11} From such a "super" or a "coincidence" pattern from the flat (111) surface, it is usually difficult to draw informations on whether the surfaces are subjected to surface-reconstruction due to oxygen adsorption and the subsequent flashing or not. However, the flat (111)-(2√3 × 2√3) R 30° pattern observed here with the stepped (111) surface covered with much oxygen clearly shows a drastic reconstruction of the stepped (111) surface such as a (111) faceting. On the other hand, the flat (111)-(4×4) pattern was never observed with stepped (111) surface at the lower coverages even after flashing to 800 K. It follows from this that the drastic surface reconstruction, the (111) faceting, has not to occur on the stepped surface under these conditions. The additional spots accompanied with the flat (111)-(2√3 × 2√3) R 30° pattern are arised probably from {112} or {110} facets with lower surface free energy, because such facetings have usually been observed after heating the heavily contaminated flat (111) surface with oxygen around 800 K, as will be reported in detail elsewhere.

UPS,^{12,13} XPS,^{12,14,15} and AES⁹ studies have shown that γ -Fe₂O₃ or Fe₃O₄ is formed on iron surfaces at 300 K in case of high oxygen coverages and that the oxide is readily reduced to FeO by heating at 800 K under UHV conditions. And, the apparent surface coverage of oxygen has been estimated at about two monolayers after the heating. Taking these observations into consideration, the observed surface-reconstruction, therefore, can be regarded as being a consequence of incorporation of oxygen adatoms into the flat (111)-(2√3 × 2√3) R 30° surface structure. The formation of oxide, γ -Fe₂O₃ or Fe₃O₄, at 300 K surely suggests that a reconstruction such as interchanges of the sites between the substrate atoms and the oxygen adatoms can occur even around 300 K. The recovery of the stepped (111)-(1×1) surface structure in greater or lesser degree after flashing the oxygen-covered surface around 700 K informs us, however, that the drastic surface-reconstruction does not occur under the present adsorption conditions, laying aside the small displacement of substrate atoms or the partial interchange be-

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tween adatoms and substrate atoms which was predicted from a change caused by oxygen adsorption around 300 K in work function⁹⁾ or in sticking probability^{6,7,13)}. Furthermore, XPS and UPS studies^{12,13)} suggest that the interchange between the adatoms and the substrate atoms proceeds as the exposure increases. The quasi-hexagonal pattern observed above 30 L can be referred to an interchange of this kind, also.

In summary, the stepped (111) surface covered with much oxygen reconstructs drastically on flashing at 800 K, forming the FeO-like oxide layer with $(111)-(2\sqrt{3} \times 2\sqrt{3}) R 30^\circ$ surface structure. On the other hand, in the case of lower oxygen coverages, there appears to be no drastic surface-reconstruction even at 800K on the stepped (111) surface as supposed from their thermal stability under UHV condition.

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