

Structural determination of the unreconstructed and the reconstructed (110) surfaces of iridium

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An Ir(110)-(1×1) surface has been prepared by adsorbing 1/4 monolayer of oxygen at 850 K on a clean, reconstructed (1×2) surface. Good agreement was achieved between theoretical and experimental intensity-voltage (*I-V*) spectra for a surface model in which the oxygen is randomly and uniformly distributed over the crystal surface, and the (1×1) structure is the same as for a clean unreconstructed (1×1) surface with a topmost interlayer spacing of 1.26 ± 0.05 Å. Three different models have been tested for the reconstructed Ir(110)-(1×2) surface, namely, the missing-row model, the paired rows model, and the buckled surface model. Based on the comparison between experimental data (consisting of ten half-order beams and eight integral-order beams) and the theoretical calculations, the missing-row model with a topmost interlayer spacing of 1.22 ± 0.07 Å is the most satisfactory model tested.

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I. INTRODUCTION

Surface reconstruction presents a very important and interesting problem in the study of solid surfaces. Many surfaces have an atomic structure different from that obtained simply by terminating the bulk structure. Various studies have failed heretofore to determine the structure of any reconstructed surface.

The purpose of the present work is to study, by LEED, the atomic arrangements of both the Ir(110)-(1×1) surface resulting from oxygen deposition on the reconstructed (1×2) clean surface as well as the reconstructed (1×2) clean surface.

II. EXPERIMENTAL PROCEDURE

The experiments were performed in a UHV chamber which has a base pressure less than 1×10^{-10} Torr. The chamber is equipped with several probes for surface analysis, including LEED optics, a quadrupole mass spectrometer, and a single-pass cylindrical mirror energy analyzer for Auger spectroscopy. Two sets of Helmholtz coils were used to reduce the effect of the earth's magnetic field on the electron beam during LEED measurements. Crystal temperatures up to 1600 K could be achieved by resistive heating. The crystal temperature was measured with a 5% Re/95% W and 26% Re/74% W thermocouple which was spotwelded to the back of the crystal.

The Ir sample was cut from a single crystal and aligned within $1/2^\circ$ of the (110) orientation by the back-reflection Laue x-ray method. Both sides of the crystal were polished mechanically using standard techniques. After Ar⁺ bombardment and a series of treatments in 5×10^{-8} Torr oxygen at 800 K, followed by brief annealing in vacuum at 1600 K, the surface was shown to contain less than 2% carbon and no other impurities detectable by Auger electron spectroscopy. The clean (110) surface, after further annealing at 1600 K in

vacuum, exhibited a (1×2) superstructure with no detectable impurities present.

Intensity-voltage (*I-V*) beam profiles were measured at normal incidence at approximately 2 eV intervals using a rotatable Faraday cup collector. All *I-V* beam profiles have

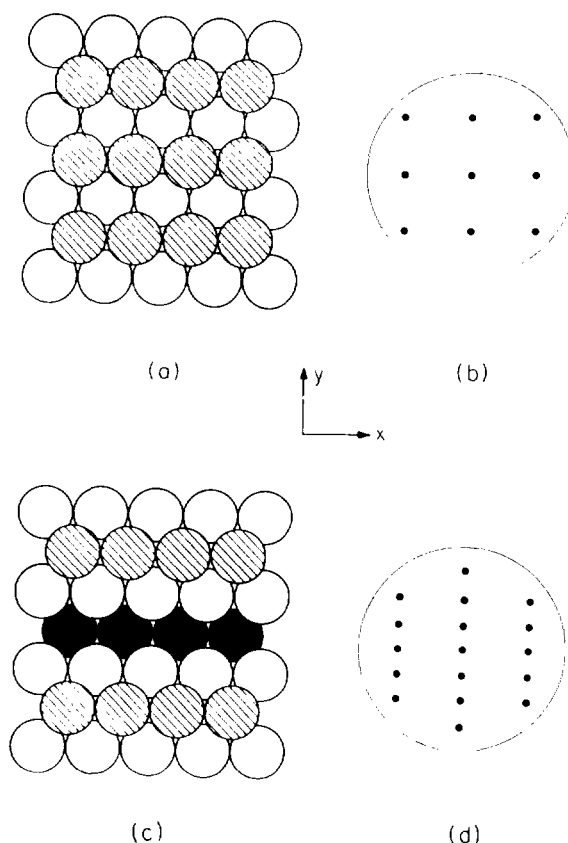


FIG. 1. (a) Schematic hard sphere model of the unreconstructed Ir(110)-(1×1) surface; (b) the reciprocal space representation of (a); (c) schematic hard sphere model of the reconstructed Ir(110)-(1×2) surface for the missing row model; (d) the reciprocal space representation of (c).

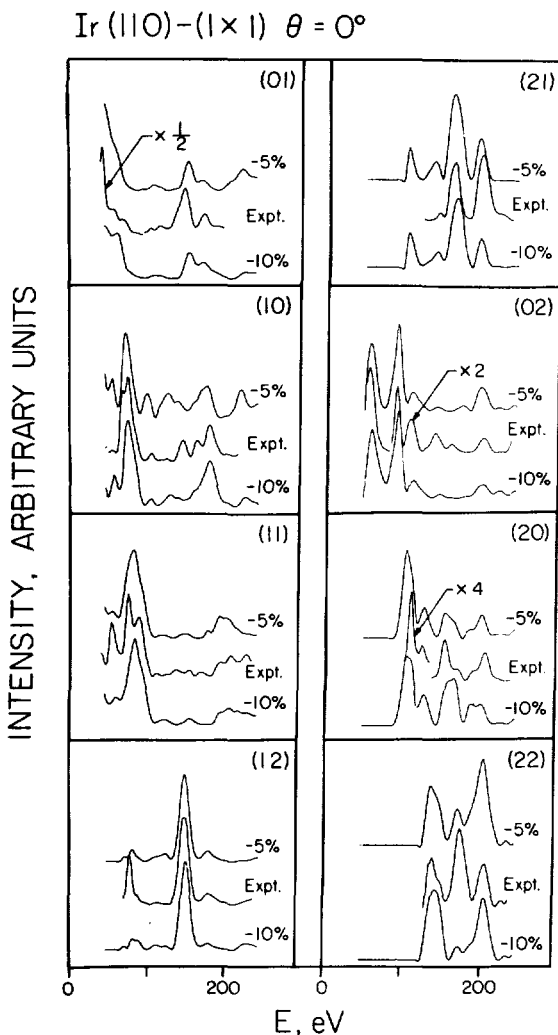


FIG. 2. Comparison between experimental I - V spectra modified with an inner potential of 8 eV for a topmost layer spacing ranging from -10% to -5% and the experimental I - V spectra from the Ir(110)-(1 × 1) surface. $\theta = 0^\circ$ corresponds to normal incidence.

been normalized to unit incident beam current. The achievement of normal incidence was verified by the satisfactory agreement between equivalent nonspecular beams. The beams are indexed so that the longer side of the real space unit cell is the y direction. The real space unit cell and the LEED pattern of both the (1 × 1) and (1 × 2) structures are shown in Fig. 1.

III. Ir(110)-(1 × 1) SURFACE

When the clean reconstructed (1 × 2) surface of Ir(110) is heated in 5×10^{-8} Torr oxygen at 850 K for approximately two minutes, a (1 × 1) surface structure is formed.¹ The amount of surface oxygen required to form the (1 × 1) structure from a clean (1 × 2) structure was estimated using Auger electron spectroscopy to be 1/4 monolayer. This conclusion is in agreement with independent contact potential difference measurements performed in this laboratory.² Intensity-voltage profiles for eight different nonspecular beams of the (1 × 1) surface structure were measured at normal incidence at approximately 2-eV intervals.

A convergent perturbative scheme³ known as the layer-

doubling method was used to calculate LEED intensity-voltage spectra for the Ir(110)-(1 × 1) structure at normal incidence for the eight nonspecular beams. The oxygen atoms were assumed to be distributed randomly and uniformly over the surface, so that the presence of oxygen on the surface would not contribute to the structure of the I - V spectra but could possibly modulate the spectral intensities. Hence, the presence of oxygen on the surface was neglected in the calculations of the I - V spectra, and the calculations were performed as for a clean, unreconstructed Ir(110)-(1 × 1) surface structure. The atomic potential used for Ir is a band structure potential⁴ and includes full Slater exchange. The real part of the inner potential was assumed to be 15 eV, and this quantity was allowed to change by a rigid shift of the energy scale for the comparisons between theoretical and experimental I - V spectra. A constant inelastic damping of 5 eV was used. Symmetry properties of the beams at normal incidence were exploited in the calculations. LEED I - V spectra were calculated for topmost layer spacings of the Ir(110)-(1 × 1) surface which were varied from -15% (percentage contraction of the bulk interlayer spacing of 1.36 Å) to +15% (expansion) in steps of 5%.

Comparisons between theory and experiment show that the best agreement occurs with a 5%-10% contraction and a modified inner potential of 8 eV. The experimental and calculated spectra are shown in Fig. 2. The good agreement between the experiment and theory further justifies the assumption that the oxygen atoms are distributed randomly and

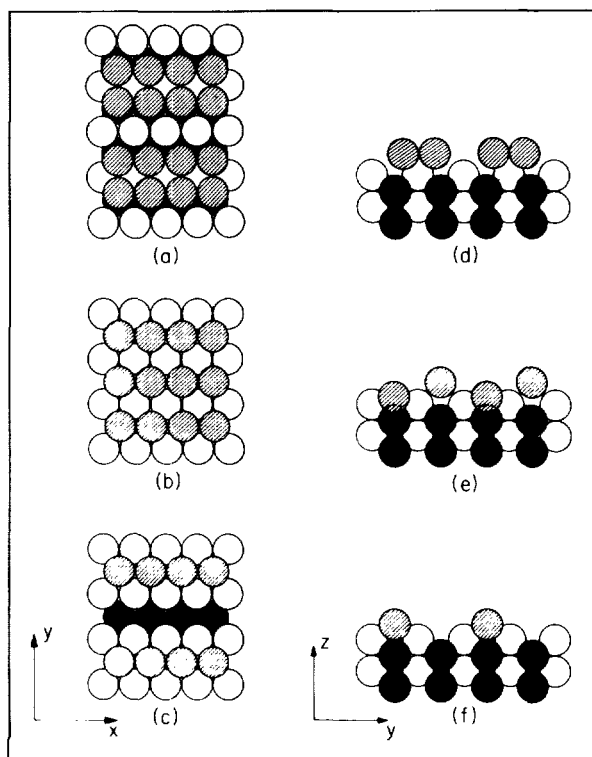


FIG. 3. Top views of a hard-spheres representation of (a) the paired rows model; (b) the buckled surface model; and (c) the missing row model. The corresponding side views are shown in (d)-(f), respectively. The x and y directions are in the plane of the crystal surface. The z direction is perpendicular to the crystal surface.

uniformly over the surface, stabilizing the (1×1) structure.

IV. Ir(110)- (1×2) SURFACE

It has been shown that a clean Ir(110) surface displays a (1×2) structure.^{5,6} Different models for this reconstructed surface have been proposed. The three simplest and most common ones are the missing row model, the paired rows model, and the buckled surface model. Figure 3 shows schematic hard-sphere drawings of these three models proposed for the reconstructed Ir(110)- (1×2) surface. In the missing row model, alternate rows of atoms are absent on the surface. The paired rows model suggests that every two adjacent rows of first layer atoms are paired to form one row. In the buckled surface model, adjacent rows of first layer atoms are relaxed in opposite directions perpendicular to the crystal surface. Previous investigations of the unreconstructed Ir(110)- (1×1) surface¹ indicate that the transformation of the (1×2) structure to the (1×1) structure occurs at a temperature of 850 K in 5×10^{-8} Torr oxygen and takes approximately two minutes, which is a long time for atomic rearrangements.

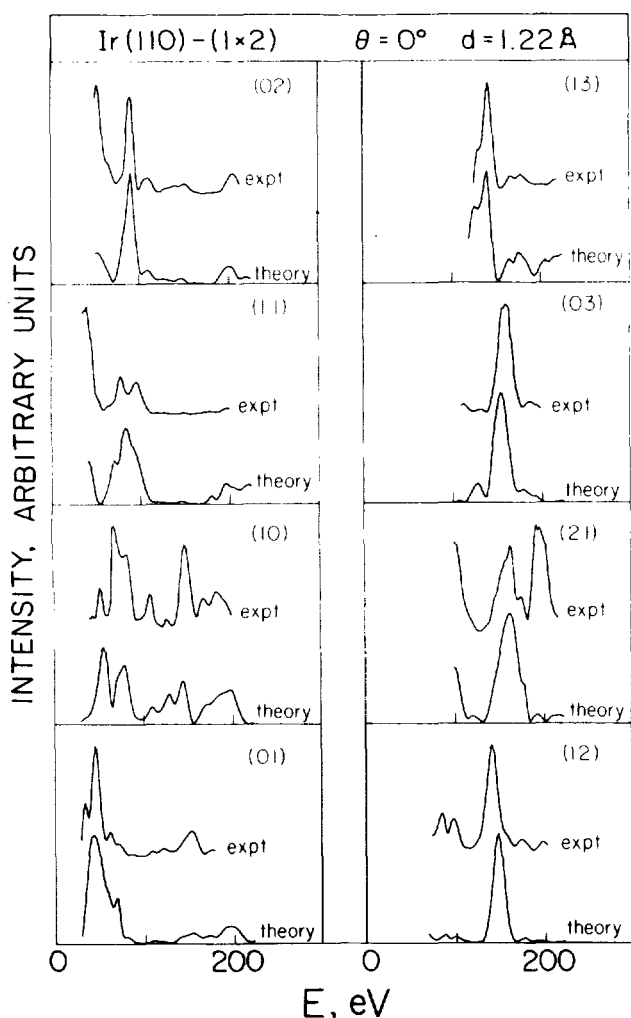


FIG. 4. Comparison between the theoretical I - V spectra for the missing row model (with a modified inner potential of 10 eV and a topmost interlayer spacing of 1.22 Å) and the experimental I - V spectra of integral-order beams from the Ir(110)- (1×2) surface.

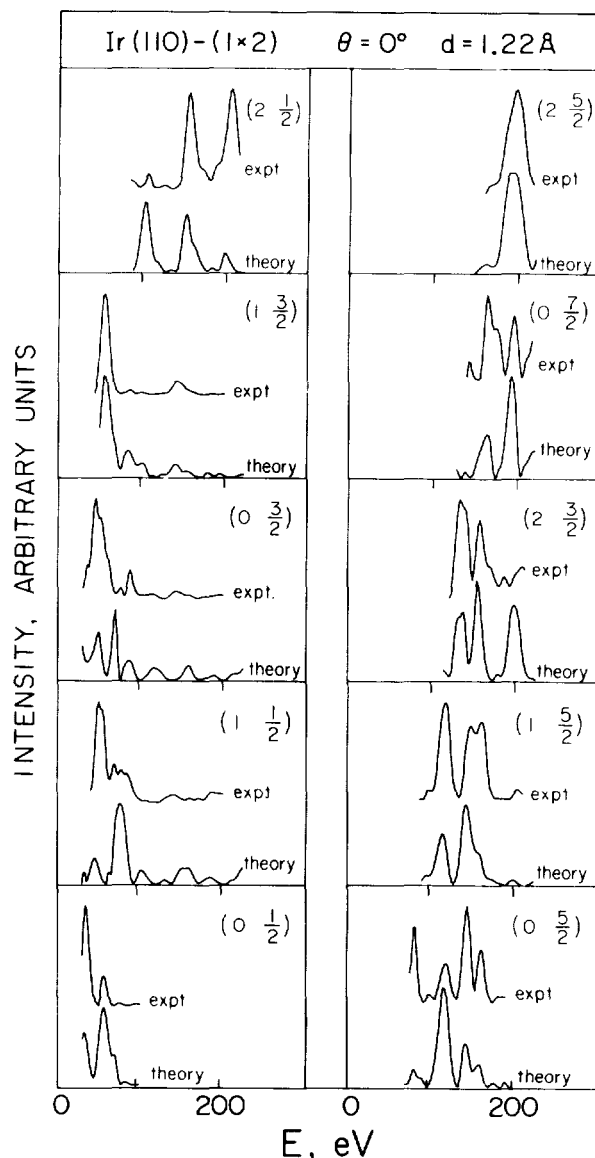


FIG. 5. As in Fig. 4, except for half-order beams.

This fact indicates that a substantial atomic rearrangement has occurred in the transformation of the (1×2) structure to the (1×1) structure. *A priori*, this evidence makes the missing row model a highly possible candidate for the reconstructed surface since its formation would involve movement of entire rows of atoms.

Eighteen LEED I - V spectra consisting of ten half-order beams and eight integral order beams were collected for the (1×2) surface structure. To confirm that the data are reproducible, ten spectra were retaken after repolishing the Ir crystal. The agreement between the two independent sets of data is excellent.

The calculations for the theoretical I - V spectra were performed as described in the previous section. Comparisons between the experimental data and the results of the calculations using the missing row model, the paired rows model, and the buckled surface model show that the missing row model is the most likely one considered. In the calculations of the LEED I - V spectra for the missing row model, the topmost interlayer spacing of the Ir(110) surface was allowed

to relax from -15% to $+5\%$ in steps of 5% . The best agreement between the theoretical and experimental $I-V$ spectra was obtained for the missing row model with a topmost interlayer spacing of 1.22 \AA (-10%) modified with an inner potential of 10 eV . Figures 4 and 5 show the comparisons between experiment and theory for the integral order beams and the half-order beams, respectively.

Among the 18 experimental $I-V$ spectra displayed in Figs. 4 and 5, fourteen show good correspondence between theory and experiment; whereas two integral order beams, the (11) and the (21), as well as two half-order beams, the ($0 \frac{3}{2}$) and the ($1 \frac{1}{2}$), exhibit only mediocre agreement. The minor disagreement between experiment and theory is probably due to roughness of the (110) surface.^{7,8} However, the missing row model, with a topmost interlayer spacing of $1.22 \pm 0.07 \text{ \AA}$, is certainly the most probable structure for the (1×2) reconstructed surface based on the good agreement between experiment and theory for the majority of beams.

A detailed R -factor analysis developed by Zanazzi and Jona⁹ will be used to determine quantitatively the level of agreement between theory and experiment for the different models considered.¹⁰ Work is in progress also to include a slight movement (row pairing) of the second layer within the framework of the missing row model.¹⁰

V. CONCLUSIONS

(1) *The Ir(110)-(1 × 1) surface*: Results of the LEED analysis indicate that the Ir(110)-(1 × 1) structure formed by the deposition of $1/4$ monolayer of oxygen on a clean, reconstructed Ir(110)-(1 × 2) structure is the same as the bulk structure, with a topmost interlayer spacing of $1.26 \pm 0.05 \text{ \AA}$. These results corroborate our assumption that the oxygen atoms are randomly and uniformly distributed over the crystal surface, stabilizing the (1×1) structure. The transformation

of the (1×2) structure to the (1×1) may involve an extensive atomic rearrangement on the surface.

(2) *The Ir(110)-(1 × 2) surface*: Based on the good agreement between experiment and theory for the majority of the LEED beams examined, the missing row model, with a topmost interlayer spacing of $1.22 \pm 0.07 \text{ \AA}$ is the most probable structure for the (1×2) reconstructed surface.

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