Direct Imaging of Carbon-Covered and Clean Gold (110) Surfaces

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Results are presented on the atomic structure of gold (110) surfaces obtained by high-resolution electron microscopy. When covered by carbon, the 1×1 surface without surface relaxations is stable. Without carbon, a rough 2×1 reconstruction occurs with the missing-row structure, a $20\%\pm5\%$ outer-atom expansion and a 10% occupancy of atoms displaced outwards by $40\%\pm20\%$ down the channels. Local regions of 1×1 surface also exhibit a $10\%\pm5\%$ expansion of the outermost atoms.

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The detailed structure of the 2×1 reconstruction of the fcc (110) surface has been a subject of debate for several years. The most common structure proposed has been the missing-row model,[1] but solutions for the low-energy electron-diffraction (LEED) intensities[2] required very large surface relaxations which appeared physically unrealistic. It has recently been shown[3] that modern high-resolution electron microscopes are capable of directly imaging the atomic structure of surfaces. With use of small metal particles as specimens (comparable in size to those employed in heterogeneous catalysts), morphological details of catalytic significance such as the distribution of surface steps, particle faceting, and surface reconstructions were obtained. The general results demonstrated that the 2×1 reconstruction was macroscopically rough and confirmed the missing-row model, in agreement with independent results recently obtained in a scanning tunneling microscope[4] and with x-ray diffraction.[5] In this Letter a more detailed analysis is presented including a direct analysis of the surface relaxations.

The type of specimen required for high-resolution electron microscopy is substantially different from those employed in macroscopic techniques. We used small gold particles (20–40 nm in diameter) epitaxially prepared by evaporation in UHV onto cleaved alkali-halide substrates, then transferred after coating with an amorphous carbon film onto microscope grids. These were tilted by 45° from the epitaxial (100) orientation and imaged down the (110) zone in the University of Cambridge high-resolution high-voltage electron microscope at 500 kV.[6] Interpretation of the images was performed by comparison of digitized microdensitometry of the experimental images with numerical image simulations employing the multislice algorithm.[7,8] (Refinement of the structure entailed, in general, showing that hypothesized structures did not fit the experimental results.)

As prepared, the gold particles contained small $(1\bar{1}0)$ facets with the 1×1 structure as in Fig. 1. Here the atomic columns (at the defocus of this image, the white spots) showed no relaxations at the surface relative to the bulk (with an error of about $\pm3\%$), presumably a consequence of the carbon covering. Under certain conditions the carbon film etched clear of the particle surface (probably involving the attack of either oxygen or water on the carbon film catalyzed by secondary electrons). This leads to a rough surface based upon the (2×1) reconstruction intermixed with areas of (1×1) surface as shown in Fig. 2 (for this defocus the atomic columns are black).

Despite the comparatively poor vacuum of the microscope ($\sim10^{-5}$ Pa), the images correspond to clean surfaces; amorphous or ordered overlays would, if present, be clearly visible. Gold is a sufficiently inert material that once the amor-

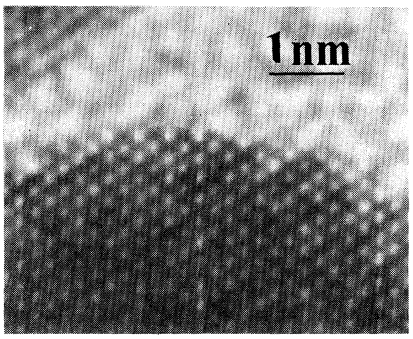

FIG. 1. Area of a gold particle as prepared showing a $(1\bar{1}0)$ 1×1 surface with white contrast at the atomic sites. The background contrast is due to the amorphous carbon substrate.

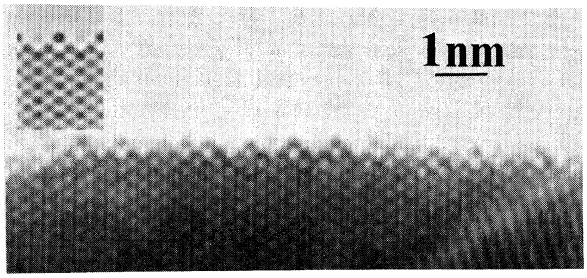

FIG. 2. Experimental image showing rough 2×1 reconstruction after etching of the carbon substrate. This may be compared to the image simulation shown as the inset.

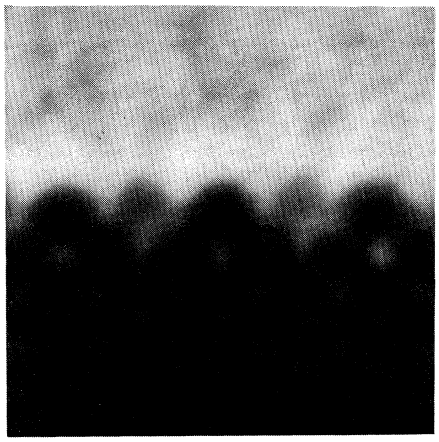

FIG. 3. Translational three-point average from the area of 2×1 surface marked in Fig. 2.

phous carbon has etched clear, residual-gas contamination is probably prevented by the high flux of electrons (primary and secondary) in the microscope.

In addition to the qualitative results detailed above, it is possible to refine the structure by detailed comparisons with the calculated images, employing translational averaging of the experimental images to reduce the contribution of statistical noise. (We employ a total dose of about 2.5×10^3 electrons/Å^2.) The result of a three-point translational average is shown in Fig. 3, and contains several features of importance. Firstly, the atomic columns at the top of the zig-zag surface are noticeably displaced outwards. This corresponds to a structural relaxation of $20\% \pm 5\%$ as shown by the comparison of the computed and experimental results in Fig. 4. (The error estimate includes uncertainties due to statistical noise and Fresnel effects at the surface which depend upon the microscope imaging conditions. At the particular defocus of this image, the sensitivity of the Fresnel effects to variations in the conditions of the microscope, e.g., the electron beam coherence, determined by comparing simulated images was small.) This relaxation is in excellent agreement with the LEED computations.[2]

The weak contrast in the channels of Figs. 2 and 3 can be fitted by either carbon atoms or a 10% occupancy of gold, both relaxed from the perfect (110) surface site by $40\% \pm 20\%$. Differentiation between the two possibilities requires careful comparisons between theory and experiment at more than one image defocus, and the image fit in Fig. 5 implies the presence of gold. [The results here are ambiguous. The match in Fig. 5 is for a channel relaxation of 30%, where carbon would show noticeable contrast at the defoci

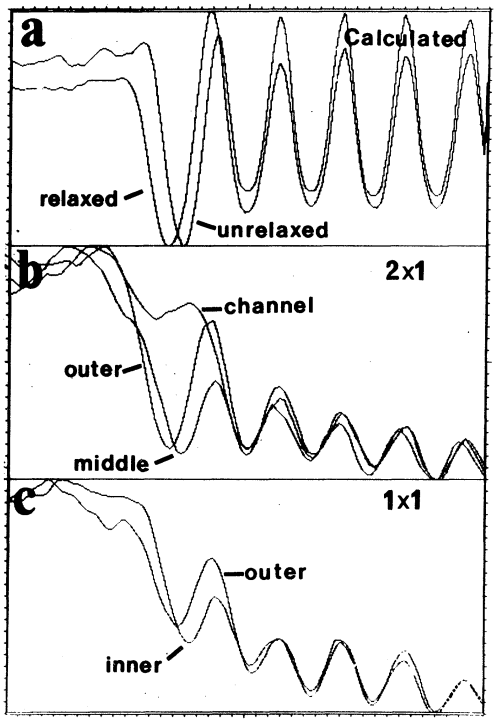

FIG. 4. Line traces normal to the surface from experimental and calculated images. (a) Calculated images with 23.5% and zero expansion of the outer atoms; (b) the 2×1 translational average through the outer atoms, the middle, and in the channels; (c) the 1×1 translational average through the outer atoms and the inner atoms. In the experimental graphs the intensities drop away from the surface because of increasing total thickness of the particle, an effect which has not been included in the simulations. For convenience, the graphs have been shifted in absolute location relative to each other.

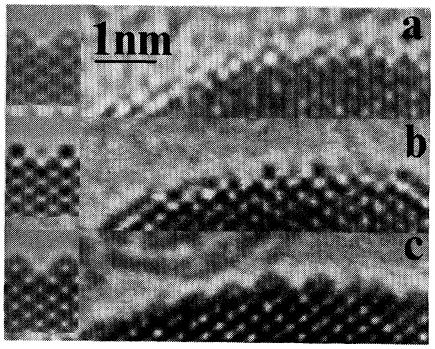

FIG. 5. Area of (110) surface showing images and calculations for defoci of (a) −20, (c) −60, and (c) −100 nm. Left-hand insets: calculated images with a 23.5% relaxation and a 10% gold occupancy in the channels with a 30% relaxation. The thickness for the calculations is 3.65 nm, with a chromatic abberation of 16 nm half-height and a convergence aperture of 2 mrad semi-angle. [For reference, in (a) and (c) the atom columns are white; in (b) they are black.]

of Figs. 5(a) and 5(c). Figures 3 and 4, however, imply a relaxation of 40%–50%. Hence the large error bounds associated with the channel relaxations.] We note that the precise occupancy of the gold cannot be determined to a high accuracy; our specimen is only about 5 nm thick, and so we are considering only two atoms in the channels with associated statistical uncertainties. The atoms could well be termination effects at the ends of the channels. We note that a low occupancy of highly relaxed atoms is consistent with fast atom diffusion down the channels.

Surface relaxations on the $(1\bar{1}0)$ surface were not confined solely to the perfect 2×1 areas. In Fig. 2 there is an area of two columns on the surface which also exhibit a 20% outer-atom relaxation. Areas of 1×1 surface also display large surface relaxations of $10\% \pm 5\%$ as measured by comparing translational averaged results with those of the simulations, as shown in Fig. 4.

To summarize, gold (110) surfaces covered with carbon have a 1×1 structure and no surface relaxations. Without carbon, an inhomogeneous 2×1 surface develops based upon the missing-row model with the outer atoms relaxed by 20%, and a 10% occupancy of highly relaxed gold atoms down the channels. Large relaxations of 10% also occur in local areas of 1×1 surface. Work is currently in progress to determine, *in situ*, the transition process between the two surface structures.

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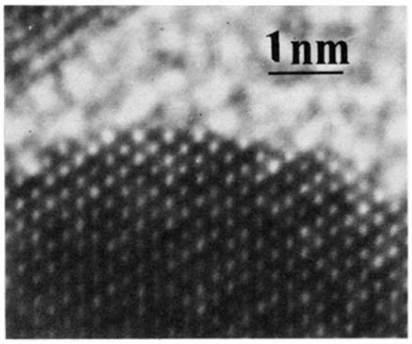

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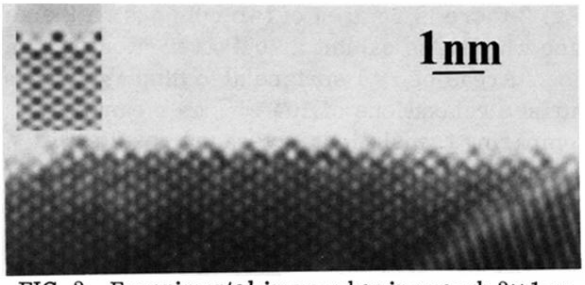

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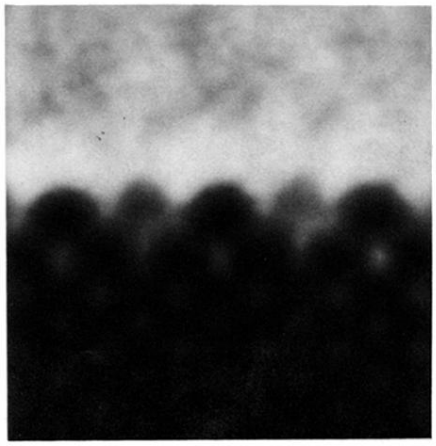

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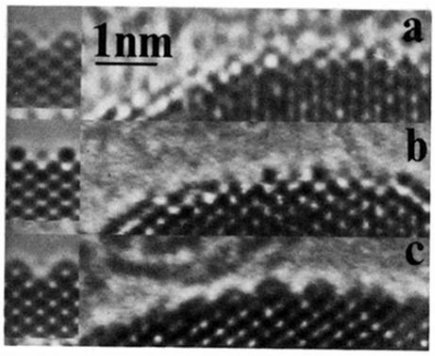

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