Surface Science 88 (1979) L29–L34

SURFACE SCIENCE LETTERS

STRUCTURE DETERMINATION OF THE RECONSTRUCTED Au(110) SURFACE

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Received 12 June 1979; accepted for publication 10 August 1979

The LEED pattern of the Au(110) surface shows a (1 × 2) and also a (1 × 3) superstructure. The (1 × 2) superstructure has been determined by comparison of LEED intensities with model calculations. The missing row model is the most probable model. A minimum of the averaged $\bar{r}$-factor, $\bar{r} = 0.36$, has been found for 15% contraction of the first layer spacing without atomic displacements in the second layer.

The clean (110) faces of gold are known to exhibit a reconstruction of the atomic arrangement in the surface layers with respect to the bulk structure. Until now a (1 × 2) superstructure with a doubling of the lattice spacing in [001] direction has been reported [1,2]; now also a (1 × 3) superstructure has been found. Characteristic for both structures are diffuse LEED beams, significantly broadened in [001] direction. The angular half width of the beams depends on energy and angle of incidence. This behaviour has been interpreted previously for the (1 × 2) superstructure, applying a disordered missing row model with a slightly roughened surface [2,3]. This model can be used as well to explain the existence of the (1 × 3) superstructure. Similar superstructures have been observed at the (110) faces of platinum and iridium [4] and a first structure analysis by LEED for Ir (110)-(1 × 2) [5] shows, that the missing row model is the most probable one. Here we present a LEED structure determination, assuming a well-ordered superstructure, neglecting the effect of the disorder of the (110) surface.

The Au crystal of 5N purity has been oriented within 0.5° of the [110] direction by X-ray diffraction and was cut and planed by spark erosion. Electrochemical etching in 5N H_2SO_4 followed by electrolytical polishing in a cyanide solution produced a smooth reflecting surface. After argon ion bombardment the LEED pattern exhibits a very diffuse (1 × 2) superstructure – fig. 1a – which coalesces after tempering up to 800 K into the pattern of a (1 × 2) or (1 × 3) structure.

The conditions at which the (1 × 3) superstructure appears are not quite clear; it seems to be dependent on the special ion bombardment conditions and probably on the cooling rate after tempering. In both cases the spots are broadened in [001] *

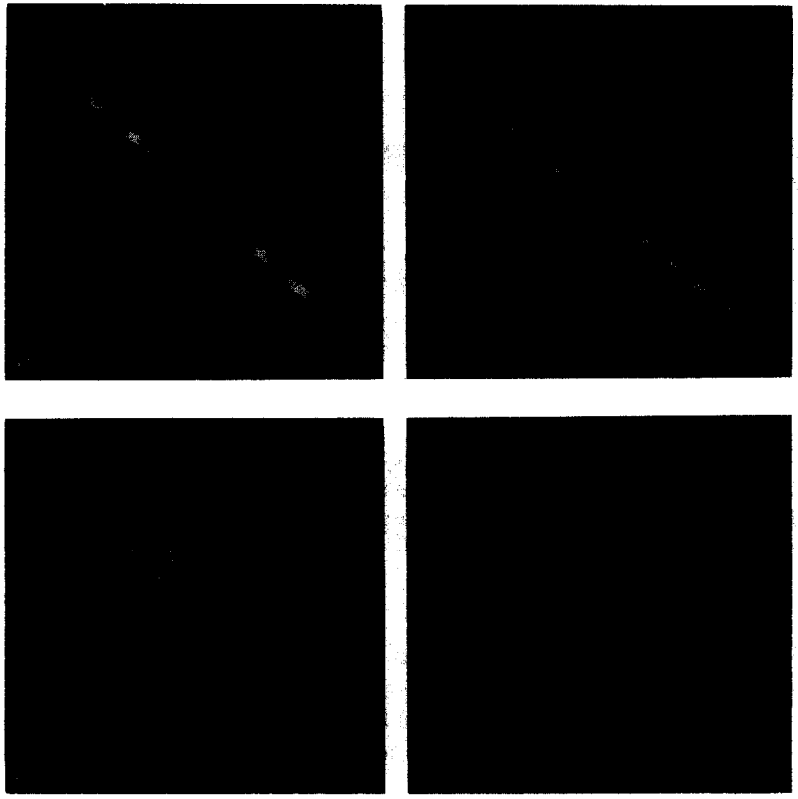

Fig. 1. Diffraction pattern of the Au(110) surface, E_p = 48 eV: (a) diffuse spots after ion bombardment, T = 300 K; (b) (1 × 3) superstructure, T = 300 K; (c) (1 × 2) superstructure, T = 300 K; (d) (1 × 1) structure, T = 750 K.

direction – figs. 1b and 1c. The superstructures cannot be caused by adatoms since no impurities could be detected by Auger electron spectroscopy. The (1 × 3) structure is stable up to 350 K. Above this temperature an irreversible transition to the (1 × 2) structure is found, which is stable up to 670 K. Above 670 K a rapid decrease of the integral intensity of the half order beams, correlated with broadening of the angular intensity profile is observed. At 720 K only integer order beams can be seen visually on the screen – fig. 1d. A detailed study of the thermal stability of the superstructures and the transitions (1 × 3) → (1 × 2) → (1 × 1) will be published. The following structure analysis only deals with the (1 × 2) superstructure.

Nineteen LEED intensity–voltage spectra at normal incidence – 11 integer order and 8 half order beams – have been measured, using a special LEED diffractometer, consisting of a movable electron gun [3] and a computer-controlled Fara-

day cup. For integral intensity measurements the diffracted beams have been collected with a detector of 4° aperture. All beams have been remeasured several times after ion bombardments and annealing, achieving in this way highly reproducible beam measurements.

Intensity calculations have been done for the missing row model – fig. 2a – a modification of the missing row model including small displacements in the second layer – fig. 2b – and a row-pairing model – fig. 2c. Two further models could be possible: a distorted hexagonal top-most layer as has been proposed recently [6] and an up-down row model.

Model calculations for the first of the latter two models have not yet been done; the first results for the second model show this model to be most unlikely. A detailed *r*-factor analysis for the up-down row model has been omitted since only poor correspondence could be found between experimental and theoretical curves by visual comparison.

The calculations were performed using the RFS-scheme and the layer-doubling method [7]. Up to eight phase shifts have been included and up to sixty symmetrically nonequivalent beams have been used. The phase shifts resulted from a relativistic band structure potential and were spin-averaged [8], the inner potential

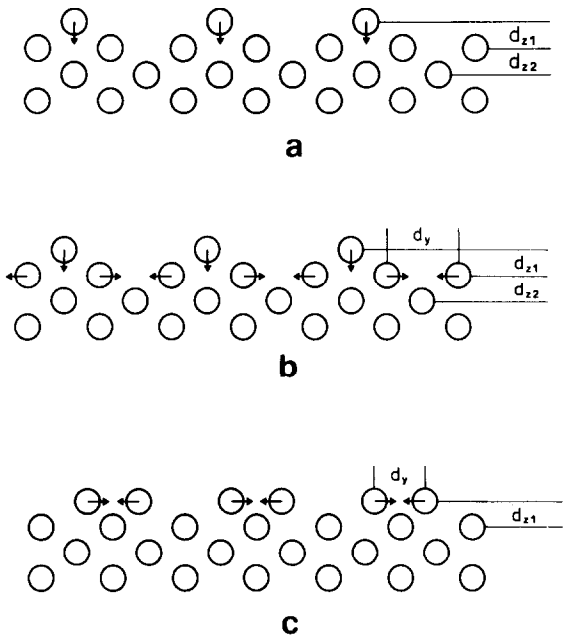

Fig. 2. Side views of surface models: (a) missing row model; (b) missing row model with additional displacement in the second layer; (c) row-pairing model. The z-direction is perpendicular to the crystal surface, x- and y-directions are in the surface plane.

related to this set of phase shifts has been found to be $V_0 = 9$ eV. All calculations have been done with a bulk Debye temperature $T_D = 170$ K [9], and a damping constant varying between 4 and 6 eV. The best agreement of theoretical and experimental curves is reached for 5 eV. Some examples of measured and calculated intensity–voltage spectra are shown in Fig. 3.

The agreement between theory and experiment has been determined quantitatively by the *r*-factor analysis, using the computer program developed by Zanazzi and Jona [10]. Some *r*-factor curves for the missing row model are displayed in fig. 4. A significant minimum is existent for 15% contraction of the first layer spacing, that is a distance $d_{z1} = 1.225$ Å compared to the bulk value of $d_{zb} = 1.442$ Å, the variation having been done in steps of $\Delta d_{z1} = 0.036$ Å, which is 2.5% of the bulk distance. The results indicate that there are none or only small displacements within the second layer. As can be estimated from fig. 4, a d_z-shift of the atoms within the second layer must be smaller than $\Delta d_{z2} = \pm 0.05$ Å. Also all displacements in the y-direction in the second layer, ranging from $d_{y2} = 3.88$ Å to $d_{y2} = 2.86$ Å, which is

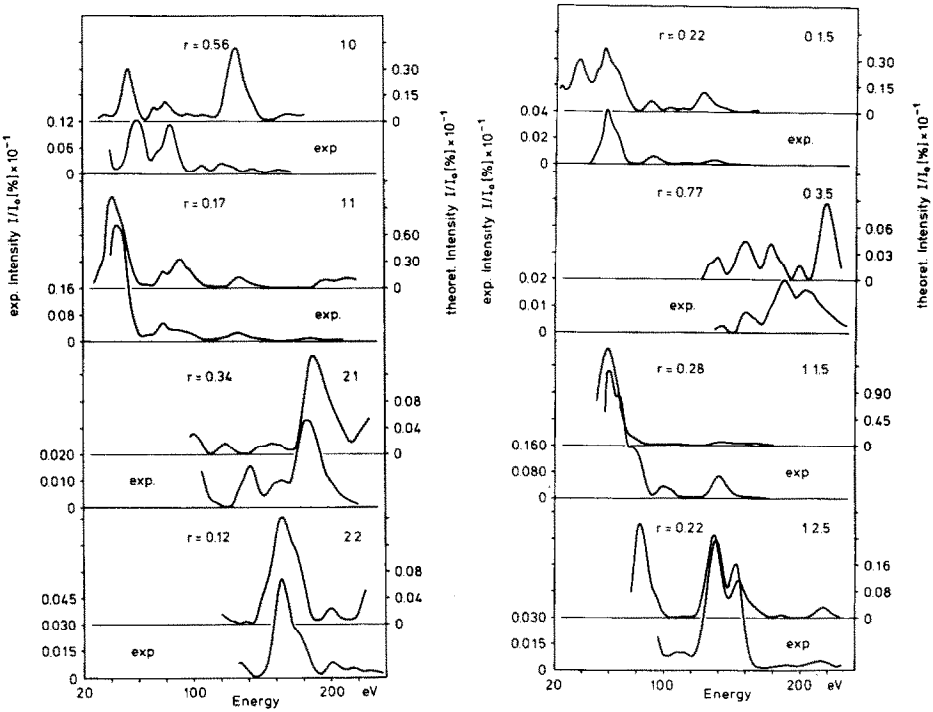

Fig. 3. Experimental and theoretical LEED spectra for normal incidence. The calculated spectra corresponds to the missing row model with 15% contraction of the first layer spacing. The *r*-factors are given.

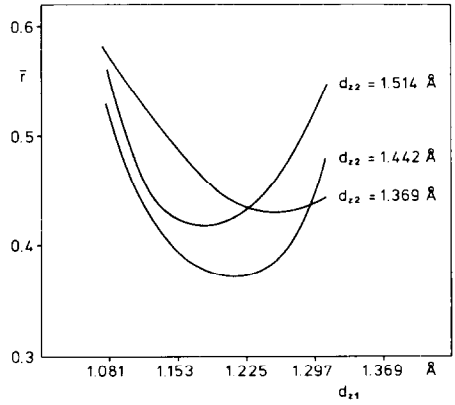

Fig. 4. Mean reliability factor $\bar{r}$ for the missing row model as a function of the first and second layer spacing d_{z1} and d_{z2}; $\bar{r}_{min} = 0.36$.

a variation of the bulk value $d_{yb} = 4.08$ Å between −5% and −30%, produced increasing r-factors; possible displacements must be smaller than $\Delta d_y = 0.1$ Å.

The averaged r-factor for the row-pairing model, calculated for all lateral chain distances between $d_y = 4.08$ Å and $d_y = 2.8$ Å in steps of $\Delta d_y = 0.2$ Å, is always greater than $\bar{r} = 0.5$; this result cannot be improved by variation of a second parameter, the first layer spacing d_{z1}, between $d_{z1} = 1.5$ Å and $d_{z1} = 1.2$ Å.

For the missing row model the minimum of the averaged r-factor calculated for 19 beams is $\bar{r} = 0.36$ with a structure R-factor [10] of $R = 0.28$. For some beams the experimental intensity spectra are found to agree well with the calculated profiles, equivalent to $r \leqslant 0.15$, while some other beams show only a poor correspondence with the experiment ($r \geqslant 0.5$). This is especially the case with the (10) and the (03.5) beam. Nevertheless, no other model calculation produced a lower r-factor for these two beams. The misfit which is still present may have two reasons: first, the inner potential and the damping constant have been assumed to be independent from energy, and the temperature factor has been set equal for all layers; second, the disorder of the surface has been neglected. Though the averaged r-factor $\bar{r} = 0.36$ is relatively high, we conclude that the missing row model with a contraction of the first layer spacing of 15% is the most probable model.

Grateful acknowledgement is made to the Deutsche Forschungsgemeinschaft – Sonderforschungsbereich 128 – for financial support. We thank Dr. M. Van Hove for helpful discussions and supplying the layer-doubling program. We are grateful to Mr. H. Plöckl and Mr. J. Csiszar for technical assistance.

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