STM and RHEED experiments on non-equilibrium surface structures of the Au(110) surface

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Abstract

The Au(110) surface is studied by scanning tunneling microscopy (STM) and reflection high energy electron diffraction (RHEED). The surface is rapidly cooled from above the order–disorder transition temperature of $T_c = 650$ K to room temperature. The STM reveals some details of the disordered state, i.e. a preference of $\langle 110 \rangle$ chains of varying lengths as the most obvious short range structural elements. The first long range order structural features are (1×3) rather than (1×2) islands. The (1×2) structure needs some energy input to be formed. The RHEED analysis is done while the target is heated in the range from room temperature to above T_c. The RHEED experiments give information about the disordered state, as well as the annealing and the order–disorder phase transition.

Keywords: Gold; Reflection high energy electron diffraction; Scanning tunneling microscopy; Surface structure

1. Introduction

Two-dimensional phase transitions on surfaces are of interest theoretically [1–3] and experimentally. The first experimental finding of such a case was the (1×2) reconstruction of Au(110) [4]. There was some controversy about the crystallographic nature of the (1×2) structure [5–19]. It is now agreed that it is a "missing row" structure with a small "pairing" in the 2nd layer and some buckling of the 3rd layer. The distance between the two outermost layers is contracted with respect to the equivalent bulk interplanar distances by about 20%. A more subtle problem is the order–disorder phase transition $(1 \times 2) \rightleftharpoons (1 \times 1)$-disordered at 650 K. The LEED analysis led to the

result that it is a phase transition of the 2D-Ising type [15]. The interpretation of that finding was questioned in view of the mass transport necessary to form the (1×2) structure from the disordered (1×1) phase while cooling down the surface [10,15]. The mass transport question can be overcome using the "saw tooth" model [10], which only needs short-range movement of atoms to change the (1×2) structure into the disordered (1×1) structure. For the "saw tooth" structure no experimental evidence was found and all recent theories show that long-range transport is not necessary to perform the phase transition [1–3].

More recently low energy ion scattering experiments [20], atom diffraction experiments [21,22] and STM studies [23] gave evidence for defects playing a role below the phase transition temperature. The ion scattering and atom diffraction experiments gave also evidence for a roughening

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transition to occur within 50 K of the 2D Ising phase transition in agreement with theoretical predictions [1]. Presently the experimental accuracy is not sufficient to decide whether T_c and T_R coincide or not. The sequence of the transitions, i.e. whether T_R is higher, lower or equal to T_c is interesting because it depends on the energy difference between the ordered flat and the reconstructed ground state [24]. For a recent review on the roughening problem see e.g. Ref. [25].

In the present paper we present experimental results using STM and RHEED on Au(110) surfaces which have been rapidly cooled down from above the phase transition temperature of 650 K. From previous experiments [20,23] it is known that surface ordering processes at room temperature on that surface are "slow". Step structures are rather stable, step "frizziness" is low and starts to built up at around 500 K [23]. Vice versa, in order to obtain well ordered (1 × 2) reconstructed surfaces long annealing times and slow cooling (100 K/h) down procedures seem to be necessary [20,26]. Therefore the rapid cooling experiment may give information on the local structures at higher temperatures if the cooling rate is fast compared to the experimentally proven annealing times.

2. Experiment

For the scanning tunneling microscopy (STM) we use a OMICRON[1] system. The vacuum in the STM and in the analysis chamber is below 10^{-10} mbar. The primary target preparation, Ar ion sputtering, is done in a separate chamber. The targets are transported from there to the analysis chamber. In the analysis chamber a standard two-axis manipulator is used. The structure of the targets on that manipulator can be probed at with LEED and RHEED. The LEED system is a OMICRON reverse LEED. For the RHEED experiments we use a STAIB-gun[2] and the LEED

screen. The diffraction patterns are monitored with a video camera and processed with a PC. The manipulator allows target heating. For the temperature measurement we use a thermocouple and a infrared sensitive pyrometer. From the analysis-manipulator the targets are transported to the STM using a wobble stick. If the target, mounted on a Mo-target holder, is grabbed while being at 700 K, it cooles down rapidly to about 400 K within 6 min, i.e. with a cooling rate of 50 K/min as measured with the pyrometer. This cooling rate is fast compared to the cooling rates of the order of 1 K/min necessary to obtain a surface with large terraces. We observe that the surfaces are not ordered after the rapid cooling. There is a mixture of local structures, and the ordering process at room temperature takes several days. First reproducible STM patterns can be monitored at about 325 K. Later on there is practically no thermal drift and atomic resolution along the [001] direction is preserved for up to four days without further target treatment.

3. Results

Previously [26,27] we reported results from Au(110) which had been prepared by sputtering cycles followed by lengthy annealing procedures. The data reproduced previous results with respect to the (1 × 2) reconstruction and step structures [23,28,29]. Additionally we found evidence for mass transport on the surface which proceeds rather slowly at room temperature in agreement with recent findings of Kuipers et al. [23]. These observations encouraged us to try to "freeze" the high temperature, rough phase of the surface by simply grabbing the hot sample (700 K) with the wobble stick and placing it into the STM.

The first image (Fig. 1a) is taken directly after cooling down at about 325 K, the second (Fig. 1b) one day afterwards. The data are untreated, i.e. no smoothing or other "beautification" have been applied. There are three planes of the metal visible. The obvious structural elements are rows of varying length in the $\langle 1\bar{1}0 \rangle$ surface direction. There is no obvious ordering along $\langle 001 \rangle$. The top layer (white) shows a hint of island formation. The

(a)

(b)
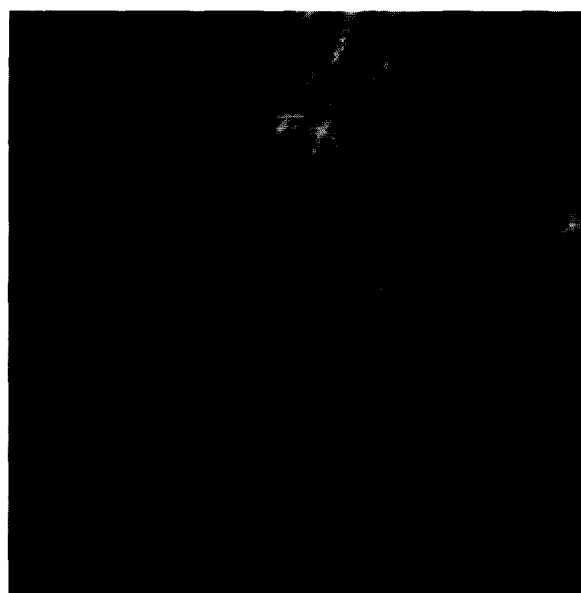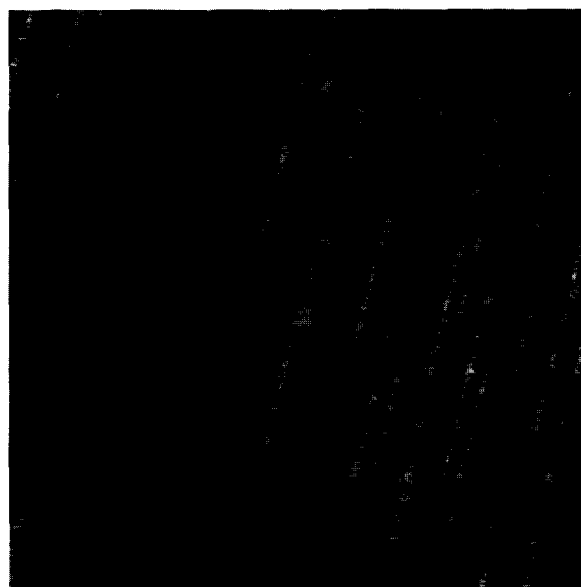
Fig. 1. (a) (500 Å)² scan of Au(110) at about T = 325 K directly after the rapid cooling. Full greyscale corresponds to 10 Å. (b) (500 Å)² scan of Au(110) at room temperature, one day after the rapid cooling. The visible rows belong to three different layers; total height is 5 Å. The orientation is ⟨1̄10⟩ along the prominent chains.
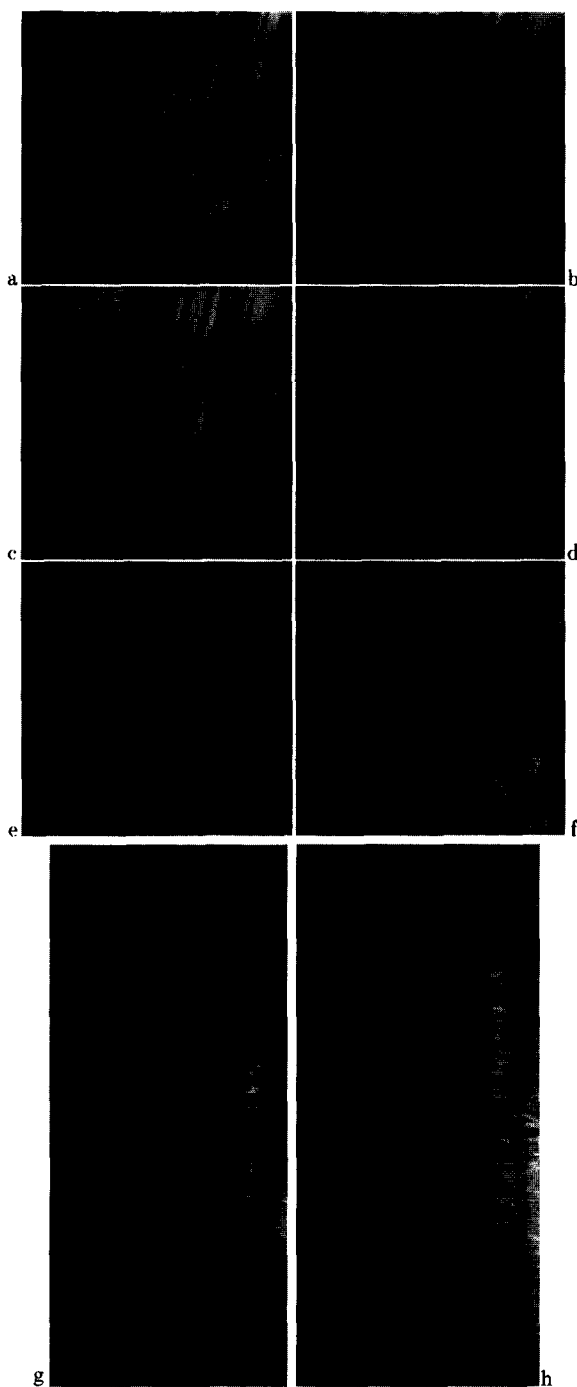

Fig. 2. (a)–(f) 500 × 500 Å² scans of Au(110) at room temperature in 6 min intervals one day after rapid cooling. The structure are (1 × 3) (light patches) and (1 × 2) (dark patches); unfiltered data. (g)–(h) 87 × 200 Å² scan of Au(110), also one day after the rapid cooling; Δt = 3 min.

second layer (grey) has "clearings" through which the third layer (dark) is visible.

Figs. 2a–2f show 6 frames (500×500) Å^2 of a series of 12 STM images obtained in time intervals of 3 min, i.e. the time interval in Fig. 2 is 6 min; each individual scan takes 3 min. The surface is rough indeed and shows as the most obvious feature long rows along the $\langle 1\bar{1}0 \rangle$ surface direction. There is obvious evidence for surface diffusion but in the top layer mainly. The first layers are arranged in "islands" (height differences between major grey levels correspond to one atomic plane) and "clearings" (dark). The dominating local reconstruction is (1×3) rather than (1×2). A statistical evaluation of the lattice distances was made by counting on 10 randomly chosen lines along the $\langle 001 \rangle$ directions of each frame. The results show a relative abundance of (1×3), (1×1) and (1×2) distances of 1.0, 1.5×10^{-2} and 2×10^{-3} respectively. The darker areas (clearings) in Fig. 2 are mostly (1×2) reconstructed but not well ordered. Closer inspection shows that these small areas contain steps along the $\langle 1\bar{1}0 \rangle$ direction. For that reason the counting procedure gives too low average contributions of (1×2) and (1×1), since the sampling does not include the length of the chains in the dark areas.

On 2000×2000 Å^2 scans long steps are seen, but 2 or 3 on each scan only at this point in time and temperature. The general orientation of the (1×2) patches is $\langle 1\bar{1}0 \rangle$ and $\langle 001 \rangle$, a result which may indicate that in some earlier experiments the samples have been cooled too fast [6], because a "mesalike" structure was proposed with steps along $\langle 1\bar{1}0 \rangle$ and $\langle 001 \rangle$. In recent STM studies $\langle 001 \rangle$ steps are not very common [26–29].

Out of the same series of measurements one day after the initial cooling we show two examples of scans (Figs. 2g and 2h). Here, details of the behaviour in time of the $\langle 1\bar{1}0 \rangle$ chains become visible. In the left image (2g) some interruptions in a chain are visible, which have been disappeared in the next image (right, 2h). These changes are not geometrical but due to kink movements faster than the y-scan velocity. The dominating local lattice distance in the $\langle 001 \rangle$ direction corresponds to (1×3). The changes are of this width too, which shows that kinks move in groups of three atoms at least, as seen at the right hand side of these

figures. In general, there is no clear tendency to develop the (1×2) structure, the (1×3) type distances between the surface chains remain dominant at this point in time.

A Fourier analysis (Fig. 3) of the patterns (Figs. 2a–2f) shows no contributions corresponding to (1×1), but to (1×2) and (1×3) corresponding spatial frequencies. There is also evidence for higher order periodicities which are integer multiples of the (1×3) type mainly. The (1×5.5) type frequency is a mixture of (1×2.5) and (1×3), for instance a step in a (1×3)-area. Here the apparent abundancy of (1×2) is more like the eyeball judgement of the "white to dark" area ratio in the real space. The counting in real space is limited by the fact that disordered and small (1×2) areas are neglected as discussed above. In the Fourier analysis they contribute to higher order periodicities and to the non-integer frequencies.

The next result is from 2 days after the first cooling (Fig. 4). We find evidence for step structures on the large area scans. However, the majority of the topography is still dominated by rather short $\langle 1\bar{1}0 \rangle$ chains which seem not to be able to arrange themselves into larger islands or to form large (1×2) areas. The difference between Figs. 2 and 4 is, that now the chains are more homogenously distributed which leads to an average distance of 6 lattice constants between the chains. The real space statistical evaluation leads to relative abundances of $(1 \times 3) : (1 \times 2)$ of $2 : 10^{-2}$ again too low compared to the Fourier analysis. It took another 2 days and a mild annealing $(50°C)$ before we found the "fish scale" structure typical for clean, well annealed Au(110)(1×2) (Fig. 5a). But even on that surface there are still some $\langle 1\bar{1}0 \rangle$ chains left and the step pattern is not as clear as in the case of the conventional prepared surface (Fig. 5b). It should be noted that the lateral resolution is practically not degraded compared to the situation after 1 day or 2 days (Figs. 2 and 4). This finding allows the conclusion that impurities play no major role in the structural changes observed here. On a contaminated surface the tip tends to pick up material followed by a loss in resolution. Impurities also tend to "pin" steps and thus inhibit the growth of the fish scale pattern.

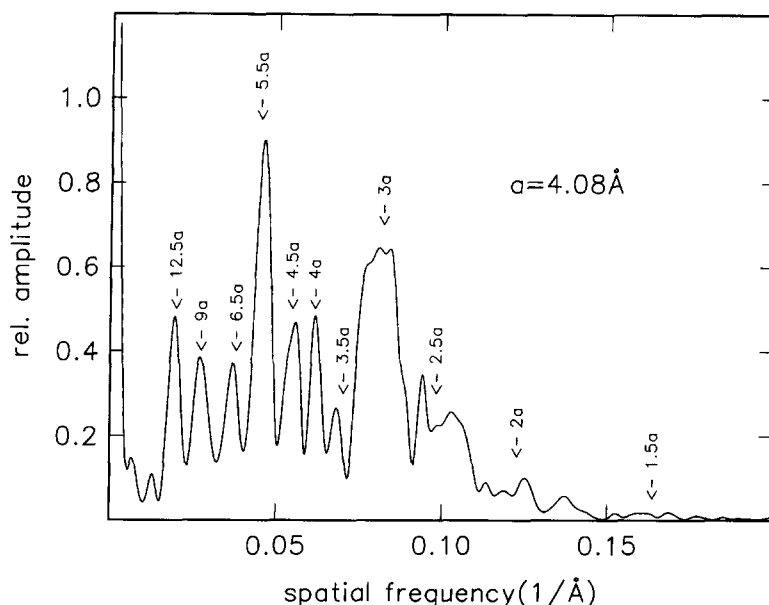The RHEED results agree qualitatively with the STM data. The ion beam bombarded surface

Fig. 3. Result of the Fourier analysis of the surface after one day. The dominating peaks correspond to (1 × 3) and (1 × 2) in real space and some multiples of the two; (1 × 1) is not present.

Fig. 4. 2000 × 2000 Å² scan of the Au(110) surface 2 days after the cooling. One greyscale corresponds to the interplanar distance; total height is 3 Å; top terrace at the lower left corner; unfiltered data.

shows a disordered state (Fig. 6a). Ordering is improved by annealing (Figs. 6b–6d). Firstly a (1 × 3) structure is developing but the diffraction spots are streaky. Between 500 K and 630 K the (1 × 2) structure is established, the diffraction spots become more circular (Fig. 6d). Around 660 K (Fig. 6e) the half order diffraction spots start to disappear and at 685 K (Fig. 6f) only spots due to the (1 × 1) disordered structure remain. If this surface state is rapidly cooled RHEED shows a disordered (1 × 2) but little evidence of (1 × 3). This is not in agreement with the STM finding (Fig. 2), where we find (1 × 3) predominantly. An explanation can be that the long range order of (1 × 3) is too poor to show up in RHEED. The structural changes become more evident from the intensity line scans through the diffraction spots as shown in (Figs. 6g–6l, right hand panels). We chose a linear cut as indicated, because this provides the information about the structure from the "satellites" of the (02) diffraction spots. The information about the disorder is seen from the varying extension or "streakiness" of the (00) into the region between the (02) spots. In Fig. 6g the intensity of the (00) spot extends "vertically" into the region between the (02) spots which is clear evidence for

(a)

(b)
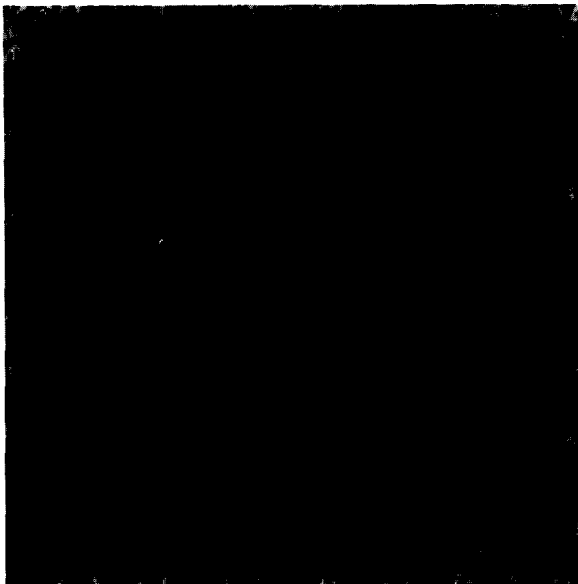
Fig. 5. 2000 × 2000 Å^2 scan of the Au(110) surface. (a) 4 days after the cooling. One greyscale corresponds to the interplanar distance as in Fig. 4; 16 visible terraces; top terrace at the upper left corner; no filtering. (b) Conventionally prepared "fish scale" pattern. Full greyscale corresponds to 8 Å.

strong disorder. Note: at the rocking angle chosen here the (01) spot are extinguished. Furthermore, closer inspection shows that the curvature of the

circular line connecting the diffraction spots in Fig. 6a is different from that in Figs. 6c and 6d. When the (1 × 2) structure is established the spots form the correct "Laue-circle" whereas in Fig. 6a contributions from bulk diffraction are evident. The annealing between 400 K and 630 K takes 20 more min to establish a "well" ordered (1 × 2) diffraction pattern. The change from (1 × 3) to (1 × 2) is obvious from the shift of the "satellites" (Figs. 6h–6j). The position of the 1/3 and 1/2 order spots agrees with the expected positions from kinematic diffraction. At the temperature (660 K) where the half order spots disappear we observe the reappearance of the "central intensity", i.e. the (00) intensity is streaky again (Fig. 6h). However in disagreement with STM results the first, even though very irregular structure, developing after the temperature is lowered rapidly is a (1 × 2) rather than a (1 × 3) structure. However the (1 × 3) diffraction spot may be hidden in the comparatively broad (1 × 2) spot. Furthermore the change in the curvature, as mentioned before, indicates a contribution of bulk diffraction in case of the premordial rough surface. It should be noted that in a LEED study [6] also (1 × 3) structures have been found during the cooling of Au(110). The appearance of these structures was reported to depend on the cooling rate.

4. Discussion

The Au(110) surface has been hitherto known to reconstruct in the (1 × 2) missing row structure. It is known to change into a (1 × 3) structure under the influence alkali metal adsorption [30,31]. The role of defects has been discussed [6,9,20,21,23] in the past, but it took the STM to clearly show the "mesoscopic" structure of the surface [23–29], i.e. the formation of long ⟨1̄10⟩ steps on "dirty" surfaces and the formation of the "fish scale" structure on "clean" surfaces with small misorientation. With respect to the phase transition the new STM results of Kuipers et al. [23] seem to indicate that the order–disorder transition at 650 K is preceded by step roughening. Partly, the increase of "point defects" with temperature observed by ion scattering [20] may in fact be due to step roughen-
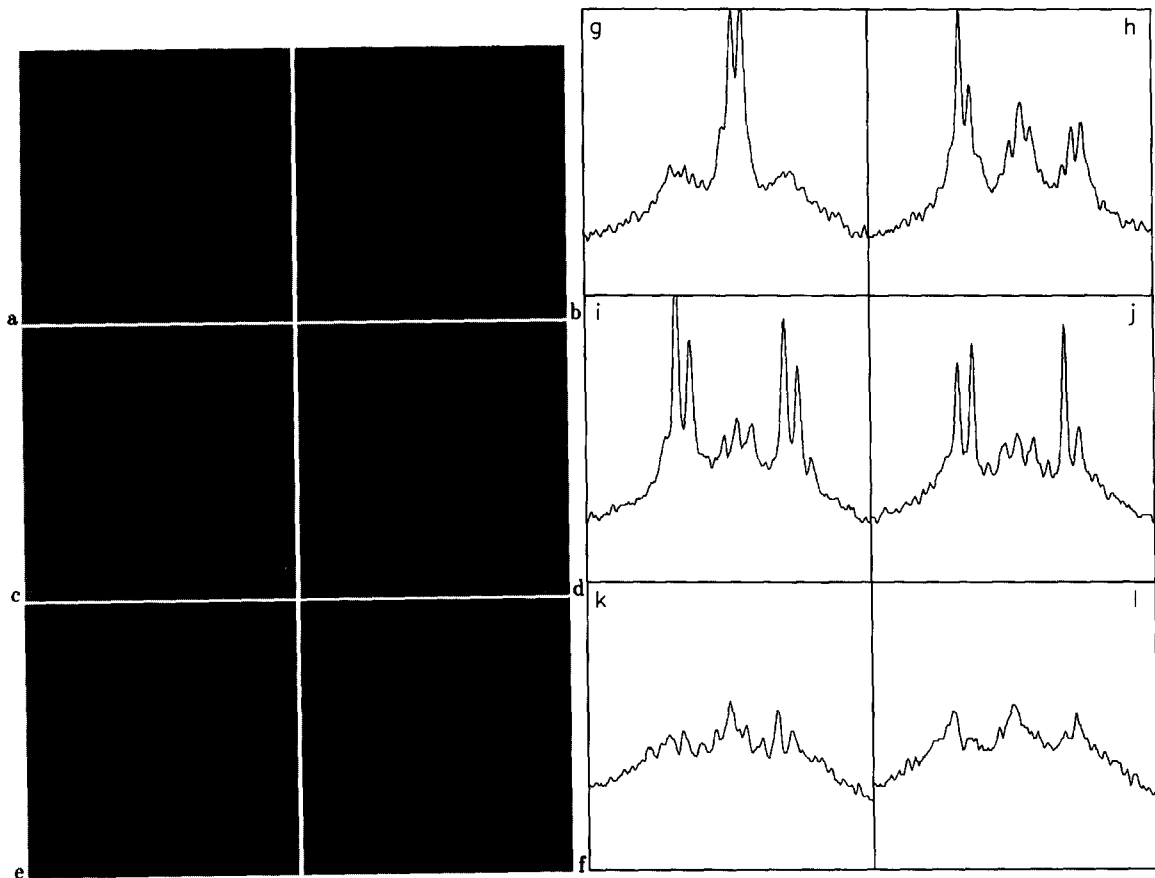
Fig. 6. RHEED analysis of an annealing procedure of a sputtered Au(110)-surface. The left hand panels show the diffraction spots, the right hand panels intensity line scans. Beam along ⟨1̄10⟩; $E = 12$ keV. (a), (g) 1 h after sputtering (~room temperature), rough, disordered, weak evidence for (1 × 3). (b), (h) 14 min, 400 K, disordered, evidence for (1 × 3). (c), (i) 24 min, 500 K, ordered (1 × 2). (d), (j) 34 min, 530 K, ordered (1 × 2). (e), (k) 43 min, 660 K, evidence for disorder (1 × 2). (f), (l) 48 min, 685 K, disordered (1 × 1).

ing. Also based on ion scattering results we discussed the "random" model [32] for the (110) surface above the 650 K transition temperature [33]. "Randomness" was achieved by distributing the top half monolayer at random on available lattice sites on the 2nd (1 × 1) layer. The positioning on lattice sites is a must in view of high energy scattering experiments [33]. The agreement of the experimental results with calculated results based on that model was not satisfactory. The reasons are probably the neglect of disorder in the second layer [3] and the neglect of the rather lengthy ⟨1̄10⟩ chains found here (Fig. 2). These chains are longer than those obtained from a random model. The "stability" of ⟨1̄10⟩ chains on Au(110) is a

new experimental result from our present work. In molecular dynamics calculations evidence for longer chains than predicted from random distributions have been found [35]. It implies that an element of short range order may survive above the order–disorder transition temperature. The data exclude the necessity of any longer range mass transport [15] during the (1 × 1)→(1 × 2) reconstruction process.

The existence of the chains above T_c is certainly questionable, since from Fig. 2 it is obvious, that the length of the chains changes continuously at room temperature. Another structural element of Fig. 2 is the arrangement of "islands" and "clearing" in a quasi "checkerboard" pattern. This struc-

ture is relatively stable and room temperature. The annealing process of this structure may be similar to that of a sputtered surface [36] as suggested also by the annealing process followed by RHEED (Fig. 6), even though not as many layers are in play here as in case of sputtering. As noted above the RHEED patterns of the sputtered and the rapidly cooled surface are not equal. Further work to analyse the RHEED patterns is under way. The comparison of the RHEED pattern at 685 K with that of an rapidly cooled surface (Figs. 6l and 6f) shows that some ordering into (1 × 2) and (1 × 3) structures occurs during the rapid cooling, simply because at 685 K all higher order spots are washed out. There is no order within the transfer length of RHEED, but short range order may exist within the length scale of a few lattice distances probed by ion scattering [33].

Another new finding is the preference of (1 × 3) related distances on the rapidly cooled surface.

Even though the long range order is poor, as shown by STM and RHEED, there is an obvious activation barrier between the disordered state and the "final" fish scale (1 × 2), structure. From the experimental time scales obtained from the high temperature annealing and the room temperature experiments an activation energy of 0.25 ± 0.10 eV can be estimated by assuming 2 exponentials with the same activation energy. Part of the energy puzzle of the arrangement into the fish scale pattern is the necessity for atoms travelling over distances of the dimension of the terraces (100 Å and more). Another energetic aspect is the interplay between steps and the fish scale pattern. This consideration has been discussed previously [27–29], we give here a more detailed account (Fig. 7) based on the results of the calculations of Bernasconi and Tosatti [3]. The basic finding is that a single island shaped like a "scale" on a terrace of a (1 × 2) reconstructed surface has to be bordered by a (111) type step on
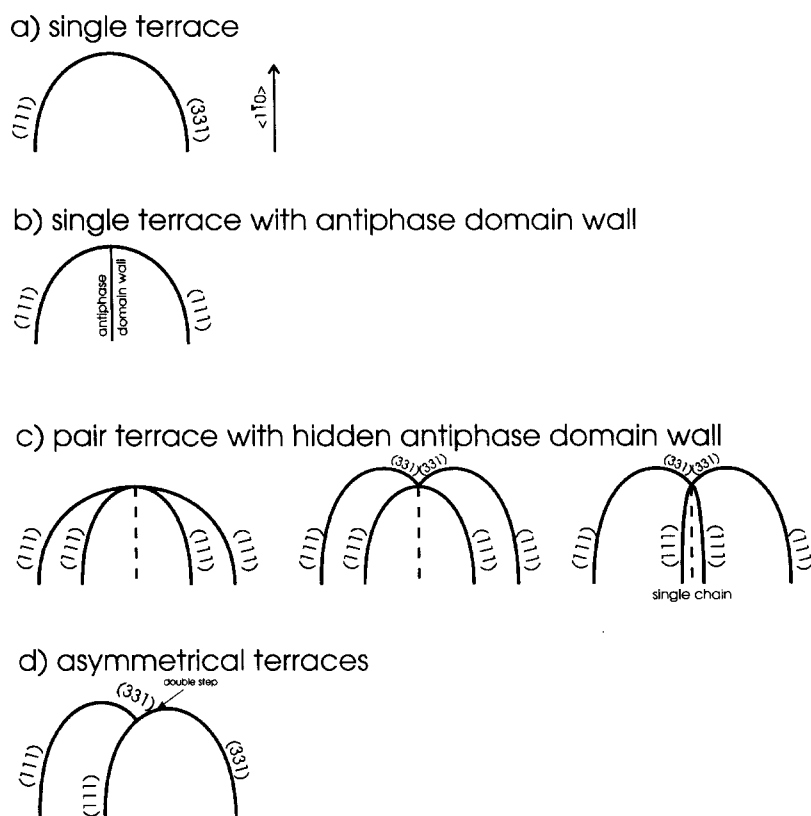

Fig. 7. Schematic diagrams of the structural elements of the fish scale structure of Au(110).

one side and by a (331) type step on the other side. The energy/atom of these steps are 86 meV and 151 meV respectively. Therefore there is a driving force, an energy difference of 65 meV/atom, to reduce the number of (331) steps and increase the number (111) steps. The actual numbers of the energy/atom of any given step depend on the potential used in the calculation [3], but the ratios do not depend on the potential, i.e. the energy of the (331) type steps is in all cases higher than the energy of the (111) type steps. As shown in Fig. 7 the energy minimization can be achieved by several means, antiphase domain walls in single terraces, pair terraces with hidden antiphase domain walls, asymmetrical and symmetrical terraces. The latter two are the most abundant on the "final" fish scale patterns, in qualitative agreement with the energetic estimates.

In this paper we have also addressed the problem of the evaluation of STM results beyond "looking at it". The statistics obtained in real space is not clearly objective, since it is only possible to evaluate lattice distance by eye or by computer when the atoms or the atomic positions are clearly defined. Fourier analysis on the other hand may overemphasize periodic structures so it may be more useful to combine STM with either a diffraction technique or with an "averaging" real space technique like ion scattering.

Acknowledgement

References

[1] J. Villain and I. Vilfan, Surf. Sci. 199 (1988) 165.
[2] M. Bienfait, Surf. Sci. 272 (1992) 1.
[3] M. Bernasconi and E. Tosatti, Surf. Sci. Rep. 17 (1993) 363.
[4] D.G. Fedak and N.A. Gjostein, Surf. Sci. 8 (1967) 77.
[5] J.R. Noonan and H.L. Davis, J. Vac. Sci. Technol. 16 (1979) 587.
[6] W. Moritz and D. Wolf, Surf. Sci. 88 (1979) L29; 163 (1985) L655.
[7] K.H. Rieder, T. Engel and N. Garcia, Proc. Int. Conf. Solid Surfaces, Cannes (1980) p. 861.
[8] N. Müller, M. Erbudak and G. Wolf, Solid State Commun. 39 (1981) 1247.
[9] S.H. Overbury, W. Heiland, D.M. Zehner, S. Datz and R.S. Thoe, Surf. Sci. 109 (1981) 239; H. Derks, H. Hemme, W. Heiland and S.H. Overbury, Nucl. Instrum. Methods. B 23 (1987) 374.
[10] H.P. Bonzel and S. Ferrer, Surf. Sci. 118 (1982) L263.
[11] G. Binnig, H. Rohrer, Ch. Gerber and E. Weibel, Surf. Sci. 131 (1983) 2379.
[12] I.K. Robinson, Phys. Rev. Lett. 50 (1983) 1000; I.K. Robinson, Y. Kuk and L.C. Feldman, Phys. Rev. B 29 (1984) 4762.
[13] L.D. Marks, Surf. Sci. 139 (1984) 281.
[14] M. Copel and T. Gustafsson, Phys. Rev. Lett. 57 (1986) 723.
[15] J.C. Campuzzano, M.S. Foster, G. Jannings, R.F. Willis and W. Uertl, Phys. Rev. Lett. 54 (1985) 2684; J.C. Campuzzano, A.M. Lahee and G. Jennings, Surf. Sci. 152/153 (1985) 68.
[16] S.P. Withrow, J.H. Barret and J.R. Culbertson, Surf. Sci. 161 (1985) 584.
[17] J. Möller, H. Niehus and W. Heiland, Surf. Sci. 166 (1986) L111.
[18] T. Engel and J.H. Weare, Surf. Sci. 164 (1985) 403.
[19] J. Möller, W. Heiland, K.J. Snowdon and H. Niehus, Surf. Sci. 178 (1986) 475.
[20] E. van de Riet, H. Derks and W. Heiland, Surf. Sci. 234 (1990) 53.
[21] J. Spröer, B. Salanon and J. Lapujoulade, Europhys. Lett. 16 (1991) 283.
[22] D. Cvetko, A. Lausi, A. Morgante, F. Tommasini and K.C. Rince, Surf. Sci. 269/270 (1992) 68.
[23] L. Kuipers, M.S. Hoogeman and J.W. Frenken, Phys. Rev. Lett. 71 (1993) 3517; J.W.M. Frenken, L. Kuipers and J.B. Sanders, Faraday Discuss. 95 (1993) 27.
[24] M. den Nijs, Phys. Rev. Lett. 64 (1990) 435.
[25] J. Lapujoulade, Surf. Sci. Rep. 20 (1994) 191.
[26] S. Speller, S. Molitor, C. Röthig, J. Bömermann and W. Heiland, Surf. Sci. 312 (1994) L748.
[27] C. Röthig, Thesis, Universität Osnabrück, 1995.
[28] T. Gritsch, D. Coulman, R.J. Behm and G. Ertl, Surf. Sci. 257 (1991) 297.
[29] J.K. Gimzewski, R. Berndt and R.R. Schlittler, Surf. Sci. 247 (1991) 327; Phys. Rev. B... (1992) 6844.
[30] D. Häberle, P. Fenter and T. Gustafsson, Phys. Rev. B 39 (1989) 5810.
[31] B.M. Ocko, G. Helgesen, B. Schardt, J. Wang and A. Hamelin, Phys. Rev. Lett. 69 (1992) 3350.
[32] C.B. Duke and A. Liebsch, Phys. Rev. B 9 (1975) 1126 and 1150.
[33] H. Derks, J. Möller and W. Heiland, The Structure of Surfaces II, Springer Series in Surf. Sci., Vol. 11 (1988) 496.
[34] D.P. Jackson, T.E. Jackmann, J.A. Davies, W.N. Unertl and P.R. Norton, Surf. Sci. 126 (1983) 226.
[35] M.S. Daw and S.M. Foiles, Springer Series in Surf. Sci., Vol. 11 (1988) 125.
[36] T. Michely and G. Comsa, Surf. Sci. 256 (1991) 217.