Surface Science 157 (1985) L367–L372
North-Holland, Amsterdam

SURFACE SCIENCE LETTERS

DIRECT ATOMIC IMAGING OF SOLID SURFACES
IV. Dislocations on Au(100)

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Received 30 October 1984; accepted for publication 12 February 1985

Direct observation of the metastable gold (100) 1×1 surface by high resolution electron microscopy provides evidence for surface Shockley partial dislocations. This result is correlated with the known 5×20 reconstruction to a hexagonal overlayer since the dislocations possess a pseudo-hexagonal core structure. This implies a dislocation mechanism for the phase transformation from 1×1 to 5×20. It is proposed that pipe diffusion along the dislocation cores or mass transport via dislocation glide or climb could explain the rapid atomic migration required during the phase transition from 1×1 to hexagonal.

Among the various reconstructed metal surfaces that have been studied to date, the fcc (100) surface is probably the one where the basic structural unit is best known. Either when prepared, or after minimal heating (to about 373 K for gold, [1]) the metastable 1 × 1 surface reconstructs with the first layer transforming to a hexagonal structure (e.g. see ref. [2] and the references therein). A number of different models for the detailed structure of this hexagonal overlayer and its precise registry and commensurate nature have been proposed, e.g. ref. [2], with only minor variations between different metals. One slightly awkward problem remains unanswered – how does the necessary mass transport occur during the phase transformation; for a given number of atoms, there is approximately a 13% reduction in surface area.

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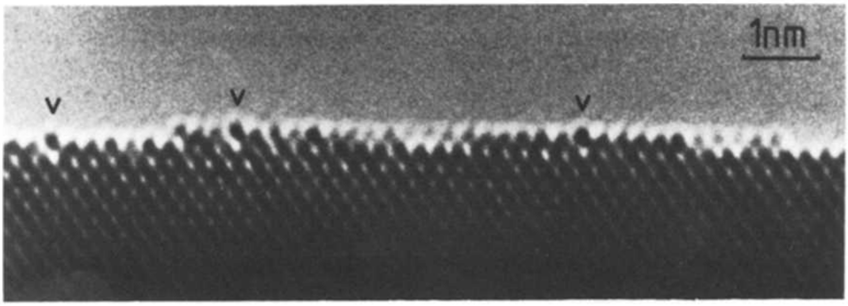

Fig. 1. High resolution electron micrograph of an extensive area of gold (100) 1×1 surface with surface defects arrowed. The small normal displacements can best be seen by viewing along the surface from one side.

We have recently been studying gold surfaces at the atomic level by direct imaging in a high resolution electron microscope [3–9]. (Details of the technique and the specimen preparation and cleaning procedures are given in these references and are not repeated herein.) In this letter we report observations of the metastable gold (100) surface which we find to contain surface Shockley partial dislocations. This result can immediately be correlated with the hexagonal superlayer and implies that the mass transport is accomplished via either or both pipe diffusion or dislocation movement.

The important experimental result is given in fig. 1. This shows a gold (100) 1×1 surface viewed down an [011] zone axis under electron-optical conditions where the atomic columns are black. (These samples were cleaned and examined at room temperature which is too low for the phase transition to the hexagonal 5×20 structure.) As established previously, this image is a faithful representation of the surface on the atomic scale, except for a 5% artificial expansion of the surface layer due to the imaging system at this particular lens defocus [7].

The in-plane periodicity was exceedingly good (better than the 3% accuracy with which it could be digitally measured) except for a number of surface defects (arrowed in the figure, and discussed below). There was some evidence of inhomogeneous relaxations normal to the plane, both expansions and contractions, of magnitude less than 10%. These often appeared to be correlated into waves along the surface which could be interpreted as weak charge density waves. However, we should caution that our specimens are not bulk samples, and it is possible that boundary effects and artifacts from other surfaces not grazing to the beam, and hence not resolved, will influence the image appearance. For example, these waves could be due to small stresses from nearby (111) surfaces. (Refs. [6] and [8] describe observations of large elastic and plastic deformations on the gold (111) surface.) These results were experimentally reproducible, and the surface showed little indication of changing with time (either during or after surface cleaning) except for the location of the surface defects.

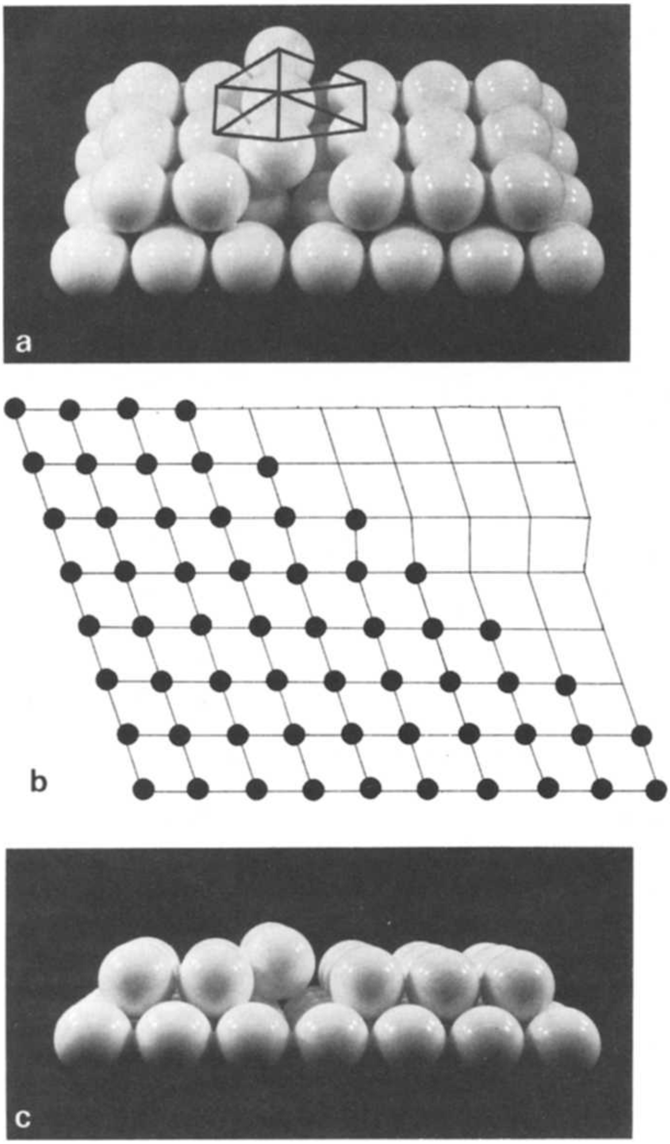

Fig. 2. The proposed Shockley partial dislocation structure in (a) sphere model at an angle, (b) in terms of a cut bulk partial dislocation and (c) the sphere model viewed along the electron beam direction. The pseudo-hexagonal core structure of the dislocation is indicated in (a). In (b), the large discs correspond to the atomic columns retained after the surface cut.

These surface defects were initially a surprising and unexpected observation: it appeared that one whole column of atoms had been shifted substantially both away from the surface and across to one side. One original hypothesis was that the effect was due to some form of residual carbonaceous contaminant. However, in order to explain the strong contrast (and its variation with defocus which for brevity is not included here) it would be necessary to consider a very dense material such as a carbene. Under reactive conditions where carbon is being etched, this seems unreasonable.

A simple model of these defects, which fits exceedingly well with the experimental observations, is a surface Shockley partial dislocation as shown in fig. 2. We use here the definition of a surface dislocation as a bulk dislocation with the surface "cut" passing through the dislocation core (see fig. 2b). These dislocations were extremely mobile, often moving between micrographs (i.e. within about 10 s). These and other observations of atomic rearrangements on gold surfaces are described elsewhere [9].

The observation of Shockley partials on the gold (100) surface provides an important clue to the actual mechanism of the phase transition. When viewed from above, the core structure of the dislocation is almost hexagonal in symmetry (see fig. 2). A representation of the hexagonal layer reconstruction is a 50% coverage of these dislocations (with a compression and some other small displacements), and the phase transition from 1×1 to hexagonal can then be viewed as an aggregation of these dislocations, as shown schematically in fig. 3. Since mass transport by dislocation is substantially faster in general than single atom diffusion (in the bulk), it is to be expected that surface diffusion involving surface dislocations would also be a faster process than single atom processes. Two mechanisms are possible, either pipe diffusion along the

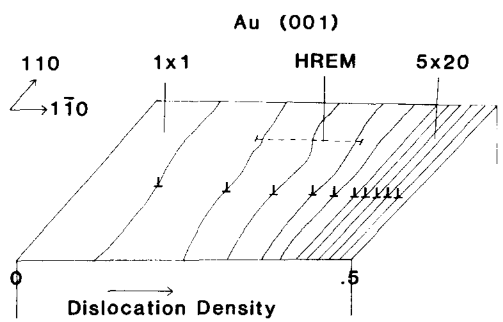

Fig. 3. Schematic diagram of the gold (100) surface in terms of surface dislocations. To the left, the pure 1×1 surface contains no dislocations whilst the 5×20 hexagonal reconstruction can be represented as a 50% dislocation coverage. The experimentally observed surfaces are between the two extremes as indicated.

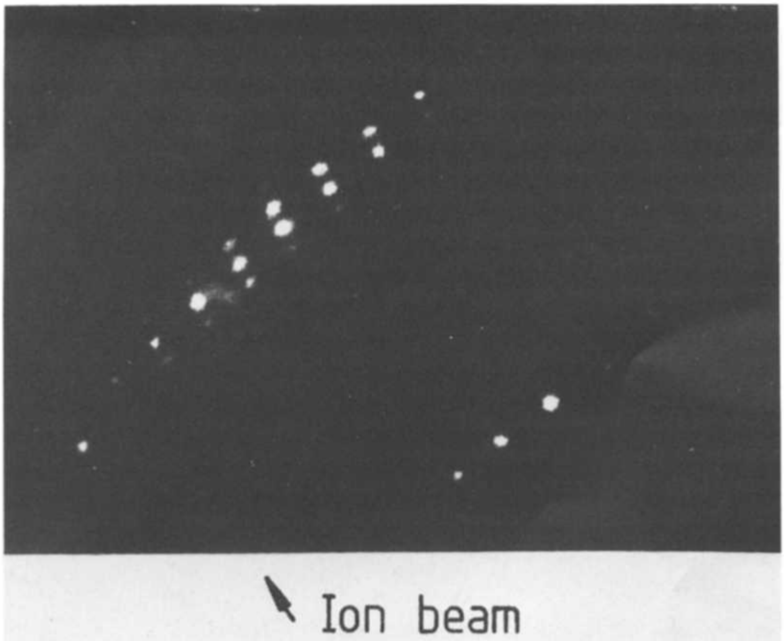

Fig. 4. LEED diffraction pattern of the reconstructed Pt(100) surface following ion bombardment at a grazing angle along [011], courtesy of R.C. Stair [10]. Only one domain of the reconstruction occurs.

dislocation core or a glide/climb mechanism involving some variant of the observed dislocation. Some estimates of surface-dislocation-aided diffusion rates by theoretical methods and experimental measurements of the activation energy for the phase transition should provide further information, although both may prove to be somewhat intractable problems.

Additional evidence for the importance of dislocations in the phase transition comes from the work of Stair [10]. He found that, following ion beam cleaning with a normal incidence bombardment of the Pt(100) surface, two domains at 90° to each other occurred, but only one was observed when the sample was bombarded at grazing incidence along an [011] direction, as shown in fig. 4. (The occurrence of two rather than four domains at normal incidence was attributed to faceting arising from a small miscut of the crystal.) Since grazing angle bombardment will tend to produce defect lines, Stair suggested that these defects may be determining the domain structure. From our work, these defects will be surface Shockley partials and these would produce precisely the ordering observed by Stair.

As a final point, it should be mentioned that LEED analyses are often worst for integral order (bulk) diffraction spots, e.g. ref. [2]. This may be due to a rough, only partially ordered, reconstruction. Hence, it is plausible that the hexagonal overlayer may be a high concentration of surface Shockley partials, almost a surface melting, rather than a completely ordered structure.

We are indebted to Professor Stair for his information on the Pt(100) surface and for allowing us to include some of his data. We would like to acknowledge the SERC, UK, for support of this work, and L.D. Marks also acknowledges funding on Department of Energy (USA) Grant No. DE-AC02-76ER02995.

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