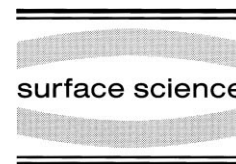




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## Unreconstructed Au(100) monolayers on a Au<sub>3</sub>Pd(100) single-crystal surface

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### Abstract

The Au<sub>3</sub>Pd(100) single-crystal surface was studied with ion scattering methods, low-energy electron diffraction (LEED) and scanning tunneling microscopy. The crystal is covered at room temperature with a pure, (100)-ordered gold layer. Palladium is found in the second layer only. The lattice constant of the gold surface as evaluated by ion scattering and a tensor low-energy electron diffraction (TLEED) analysis is equal to the bulk lattice constant of 4.017 Å as evaluated by X-ray analysis. The surface lattice constant of the gold layer on the alloy surface is 0.08 Å smaller than that of bulk gold. © 1998 Elsevier Science B.V. All rights reserved.

*Keywords:* Gold alloys; Low-energy ion scattering (LEIS); Scanning tunneling microscopy (STM); Single-crystal surfaces; Surface structure

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Metal alloy surfaces are of increasing interest owing to their applications in different fields of technology and catalysis [1,2]. So far, AuPd alloy surfaces have rarely been studied by modern surface-physics analytical techniques. We have reported a study of Au<sub>3</sub>Pd(113) [3] using ion scattering as the main analytical tool. The surface is covered by a segregated gold layer after the usual cleaning and preparation procedures. Segregation is a common effect on metal alloy surfaces [4,5]. The (113) surface is, however, not a very simple system – for example, it naturally

has many steps – and so any findings may not be generalized. In the present work we use a (100) surface as the sample, and as an example of one of the three low-index surfaces of an fcc metal. The main results are the first determination of the bulk lattice constant of  $4.017 \pm 0.001$  Å of Au<sub>3</sub>Pd and confirmation of the ordered structure of the alloy at that concentration [6], and the finding of a segregated gold surface layer which adapts the bulk lattice constant. Since the experimental value at the surface is  $4.00 \pm 0.01$  Å, the gold layer is compressed by 2.5% in comparison with the bulk gold lattice constant of 4.08 Å. Both the surface lattice constant and the bulk lattice constant are smaller than the lattice constant expected for the

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solid solution, of 4.03 Å. Although it is common for ordered binary alloys to have lattice constants different from that of the solid solution, this has not been discussed in the surface science literature. Furthermore, it is not trivial, obviously, that a segregated layer is truly epitaxial, especially in a case where the respective bulk lattice constants are so different. These observations may have an influence on the growth of thin films. A hint for such effects may be an early observation that it was not possible to grow gold epitaxially on Pd(111) [7].

The experiments on Au<sub>3</sub>Pd were performed in Osnabrück, Vienna and Stuttgart. The techniques applied were ISS, NISS, AES, STM and LEED. ISS is the acronym for low-energy ion-scattering spectrometry in the mode for surface chemical composition analysis [8]; NISS is the acronym for neutral impact ISS [8]; AES is Auger electron spectroscopy; STM is scanning tunneling microscopy; and LEED is low-energy electron diffraction. The NISS technique makes use of the shadow cone effect of classical particle scattering. A parallel beam of ions scatters from a chain of atoms in the forward direction only, if the grazing angle of incidence is smaller than a certain critical angle. When approaching the critical angle the intensity backscattered into a large scattering angle (here 165°) increases and reaches a maximum. The maximum is due to the enhancement of ion flux at the edge of the shadow cone. Evaluation of the intensity versus angle of incidence measurements affords the determination of surface lattice constants. The collaborative STM and ISS experiments in Vienna served the purpose of searching for palladium in the topmost layer of the surface, since the STM operating in Vienna has shown the capability of “chemical” contrast. In Vienna also, LEED *I-V* curves were measured. In Stuttgart the bulk concentration analysis and the bulk lattice constant measurements were done. The crystal was obtained from Mateck, Jülich, Germany. It was cut into a disk with a diameter of approximately 5 mm and a thickness of 2 mm. It had a ring etched into the perimeter for clamping the crystal onto the ultrahigh vacuum (UHV) manipulators and the STM holders. This way of holding the crystal is thought to minimize possible strain effects on such single crystals. The crystal was mechani-

cally polished (0.03 μm diamond). In the UHV systems the crystal was prepared by the usual round of sputter and anneal cycles leading to a clean surface and a satisfying LEED pattern. The annealing temperature was kept below the phase transition temperature of 1123 K of the bulk crystal [6].

The bulk analysis results can be summarized by the finding of a gold concentration measured by an electron microprobe of 71 ± 1 at%, slightly below the nominal 75%. X-ray diffraction (XRD) analyses show that the crystal is ordered with the correct fcc structure and the bulk lattice constant is 4.017 ± 0.001 Å. The X-ray data give weak evidence for some tetragonal distortion or a mixture with some tetragonal phase, which could be the AuPd phase [9].

The ISS data obtained in Osnabrück and Vienna show a strong segregation of gold to the surface. The STM shows a well-ordered (100) surface structure (Fig. 1(a), Vienna). There is no evidence for more than one atomic species on the surface. Only after sputtering at elevated temperatures, that is not followed by a prolonged annealing period, is evidence for palladium on the surface visible (Fig. 1(b), Vienna). Under that condition the ISS spectra show a palladium peak which supports the STM evidence. That is, the well annealed and clean Au<sub>3</sub>Pd(100) surface is covered by a clean, flat gold layer. The same observation was made on the (113) surface previously [3]; i.e., complete coverage of the surface by a well-ordered gold layer.

The NISS analysis (Fig. 2) affords the surface lattice constant evaluation. The example is the ion intensity versus angle of incidence data for the [001] direction. The experimental points represent time-of-flight spectra taken in steps of 1° of the angle of incidence. The spectra show in general a gold and a palladium peak, where the gold peak is from the first- and second-layer scattering whereas the palladium peak is from second-layer scattering only. The data in Fig. 2 are for the gold scattering only. The line fitted to the data is calculated from a “two-atom” scattering model. The scattering potential used is the ZBL potential [8]. The result is a surface lattice constant of 4.00 ± 0.01 Å, and a surface Debye temperature of 129 ± 4 K. In fact, the surface lattice constant

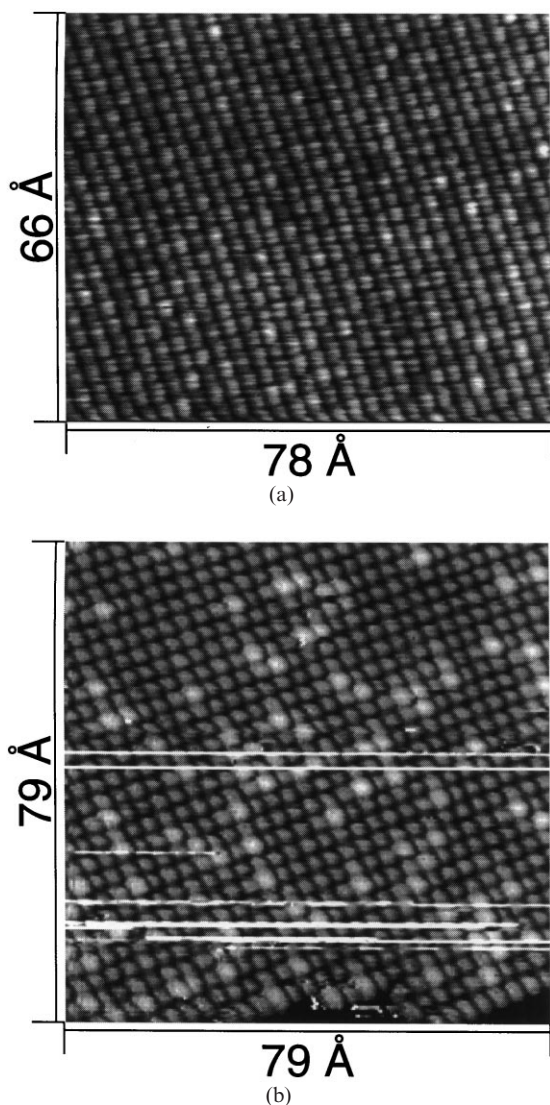


Fig. 1. (a) Topography of the  $\text{Au}_3\text{Pd}(100)$  surface by STM after argon sputtering and annealing for 80 min at 875 K. Imaging conditions:  $U = -0.4$  mV,  $I = 2.22$  nA. (b) Topography of the  $\text{Au}_3\text{Pd}(100)$  surface by STM after argon sputtering at 625 K without annealing. “White” atoms are palladium. Imaging conditions (at room temperature):  $U = -0.4$  mV,  $I = 4.44$  nA.

determined by NICISS was the first number obtained during the work on the  $\text{Au}_3\text{Pd}$  problem. Since it deviates so much from the gold bulk value of 4.08 Å and also from the bulk value expected for the  $\text{Au}_3\text{Pd}$  alloy as a solid solution of 4.03 Å [6], it led us to the other studies described here.

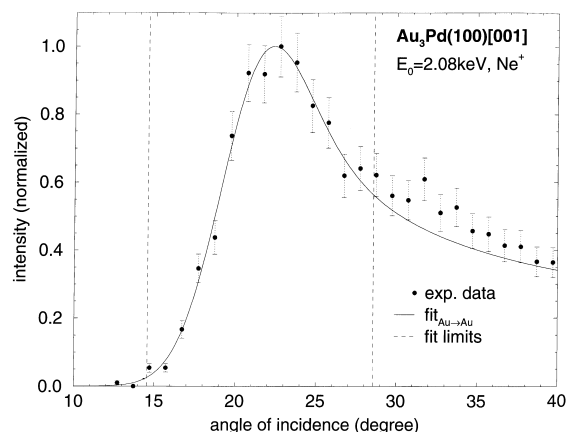


Fig. 2. NICISS of the  $\text{Au}_3\text{Pd}(100)$  surface along the [001] surface direction with 2.08 keV neon at a laboratory scattering angle of 165°. Only Au–Au collisions have to be taken into account. The solid line is the calculation of the two-atom model fitted to the experimental data within the vertical dashed lines (fit limits).

The LEED  $I(V)$  analysis was done using a bulk terminated fcc structure as the reference structure. Seven sets of non-equivalent beams in normal incidence have been measured, covering a total energy range of 1670 eV. The variable structural parameters were the first three interlayer spacings. A grid of compositions for the first three layers has been calculated by using the average  $t$ -matrix approximation [10,11], described in more detail in [12]. With the optimized composition further refinement was achieved when the lattice parameter was varied. Table 1 shows the results corresponding to the lattice parameter for a solid solution model,  $a_{\text{oss}} = 4.03$  Å, and the lattice parameter yielding the best Pendry  $R$ -factor,  $a_{\text{ofit}} = 3.99$  Å. The optimum composition for the first layer was 100 at% Au in both cases, in perfect agreement

Table 1

Structural data from the TLEED analysis of the  $\text{Au}_3\text{Pd}(110)$  surface lattice constants, i.e., the lattice constant of the solid solution and the constant resulting from the fit (first column). The interlayer spacings are  $d_{12}$  etc. for the planar distance between the first and second layer, etc.  $R_p$  is the Pendry  $R$ -factor

$a_0$ (Å)	$d_{12}$ (Å)	$d_{23}$ (Å)	$d_{34}$ (Å)	$R_p$
4.03 (solid solution)	$2.00 \pm 0.02$	$2.01 \pm 0.02$	$2.01 \pm 0.02$	0.24
$3.99 \pm 0.02$ (fit)	$1.99 \pm 0.02$	$1.99 \pm 0.02$	$2.00 \pm 0.02$	0.17

with ISS, NCISS and chemically resolved STM. The deeper layers taken into account have gold concentrations of 75% independent of the lattice constant under consideration. The error bars for the structural parameters have been estimated from the variance of the Pendry *R*-factor [13]. Within the error limits the same interlayer spacings have been found for both lattice constants. Significantly, the LEED analysis confirms the results obtained by NCISS and XRD.

Another aspect of the results obtained here is the comparison with the Au(100) surface of pure gold. It is well known that the Au(100) surface on gold is unstable and reconstructs. The surface unit cell is approximately ( $5 \times 1$ ), incommensurate, corrugated and quasi-hexagonal (see [14,15] and references therein). The driving force for the reconstruction is generally believed to be stress, which relieved by an approximate compression of the top-layer atom density of 20%. Since the reconstructed surface is “buckled” the corresponding lattice distances are difficult to evaluate. In an earlier work an “average” value was reported. The surface lattice constant of the “hex”-reconstructed surface is reduced by approximately 3.5% [16] (the values in the literature vary around this number), which results in a lattice constant of 3.94 Å. So, from the point of view of pure gold, the Au<sub>3</sub>Pd(100) seems to provide the substrate that allows growth of a stress-free monolayer of Au(100), since there is no evidence for any reconstruction in our STM and LEED data. Another possible cause for the “hex” reconstruction, besides the generally accepted stress relief, is from a bond breaking argument developed for the case of Pt<sub>x</sub>Ni<sub>1-x</sub>(100) [17]. The pseudohexagonal reconstruction on that surface has been shown not to be caused by surface stress. Transferring the bond breaking argument to the unreconstructed Au(100) layer on Au<sub>3</sub>Pd(100) implies the stabilization of the structure by Au–Pd bonds, which are energetically more favorable than Au–Au bonds.

In summary, we have measured the structure and bulk lattice constant of Au<sub>3</sub>Pd which has not been reported so far [6]. We find a lattice constant of  $4.017 \pm 0.001$  Å, considerably lower than that calculated from Vegard's rule for a solid solution of 4.03 Å. Comparable effects have been found for other metal alloy systems too, e.g., in Au<sub>3</sub>Pt but

not in Au<sub>3</sub>Ni and Au<sub>3</sub>Cu [6]. The segregated gold layer on Au<sub>3</sub>Pd(100) behaves like an epitaxially grown layer. For surface structure evaluations the result has two aspects: (1) ordered phases may have a lattice constant differing from the disordered phase of the same chemical composition and (2) segregated layers may have lattice constants deviating strongly from their respective bulk value. This effect must lead to some problems when trying to grow thicker layers on such surfaces.

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