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Static lattice distortions and the structure of Au/Si(111)-(5×1): An x-ray-diffraction study

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Grazing-incidence x-ray diffraction has been used to determine the atomic arrangement in the 5×1 structure of Au on Si(111). The main features of this structure are partially occupied rows of gold atoms in low-symmetry sites. The density of Au atoms is highly asymmetric in the direction perpendicular to the rows. The substrate atoms in the top double layer are shifted up to 1 Å from their bulk position. The structure has a disordered 5×2 periodicity due to the variation of the interatomic Au-Au distances within a row in the $[0\bar{1}1]$ direction. The model is consistent with recent scanning-tunneling-microscopy topographs.

Metal-semiconductor interfaces have been frequently studied because of their technological importance. It is a surprising fact that minute amounts of metals adsorbed on semiconductor surfaces induce a variety of reconstructions. Furthermore, the structures change with increasing coverage and eventually alloys may be formed. The Au/Si interface has been studied extensively with several different techniques,[1] but there are still a number of unsolved problems. The solid solubility of Au in Si is very small and there are no intermetallic compounds found. In the monolayer (ML) range, however, there are strong interactions found between Au and Si.[1] Three different ordered structures are induced by depositing different amounts of Au on a clean Si(111) 7×7 surface. A 5×1 reconstruction has been reported for a Au coverage in the range 0.2–0.8 ML. Between 0.5 and 1.0 ML a $\sqrt{3}\times\sqrt{3}$ structure is observed coexisting with the 5×1 structure up to about 0.8 ML, and above 1 ML a 6×6 structure appears.[2] 1 ML corresponds to 1 atom per 1×1 unit cell. Up to now there is neither consensus of the atomic geometry in any of these structures, nor about the corresponding coverages. In this paper we report the results of x-ray-diffraction studies of the 5×1 structure.

A possible structure model was proposed by Le Lay,[3] assuming that the Au atoms are ordered in rows along $[0\bar{1}1]$ direction, alternatively separated by two and three bulk lattice constants in $[\bar{1}10]$ direction. The adsorption site has been assumed above the topmost Si layer[3] or embedded below the Si surface.[4] We present here a model with shorter Au-Au distances which differ from the Si bulk lattice vectors. Preliminary results have been presented previously.[5,6] The present analysis carried out using the PROMETHEUS program for structure refinement[7] includes partial occupation and static displacements of both Au and substrate atoms. The results show the tendency of Au to form small clusters and explain the observed disorder in the adsorbate layer. The structure model agrees well with recent scanning-tunneling-microscopy (STM) topographs[8,9] and is consistent with x-ray-standing wave measurements[10] in so far as only low-symmetry adsorption sites are occupied, but our results differ from Le Lay's model.

The Au was deposited at a rate of 0.3 ML/min from an effusion cell held at 1450 K. The substrate temperature during Au deposition was 670 K, the x-ray measurements were performed at room temperature. In the analysis 52 in-plane, fractional-order structure factors were used, obtained from an x-ray-diffraction experiment at the Hamburg Synchrotron Radiation Laboratory (HASYLAB). A wavelength of 1.3 Å was used. Experimental details have been described previously.[5,6] Low-energy-electron diffraction (LEED) patterns observed by Lipson and Singer[11] showed diffuse streaks halfway between the 5×1 spots. The occurrence of these streaks, which were also observed in our x-ray-diffraction experiment,[6] suggest a disordered sequence of rows of 5×2 unit cells. Such disorder is also supported by recent STM topographs.[8] Therefore, a disordered 5×2 structure should be assumed, although the analysis presented here is based exclusively on the sharp 5×1 diffraction spots.

In Fig. 1(a) the primitive and the centered configuration of the 5×1 unit cell are shown. In the following analysis we use the centered unit cell and assume one set of mirror planes within each domain. Three rotational domains maintain the threefold symmetry of the diffraction pattern.[11] A loss of the mirror planes and correspondingly, six domains has not been considered. The contour map of the Patterson function[12] is shown in Fig. 1(b). It shows four intense maxima (labeled *A*, *C*, *D*, *F*) within the irreducible unit and is, therefore, in contradic-

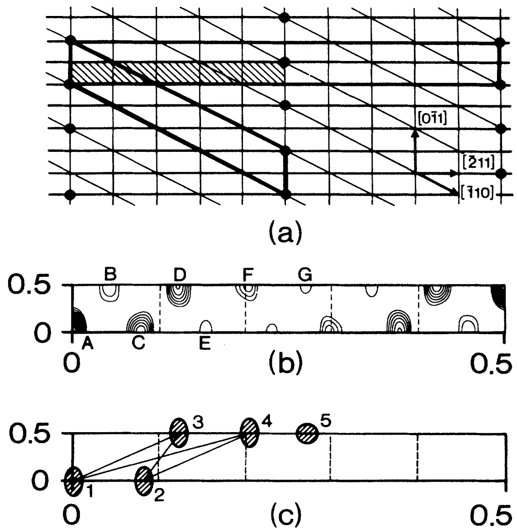

FIG. 1. (a) The primitive 5×1 unit cell and the equivalent centered unit cell. The lattice constants are 19.2 and 3.84 Å for the primitive cell and 33.24 and 3.84 Å for the centered cell. The hatched area corresponds to the asymmetric unit displayed in 1(b), 1(c), and Fig. 2. (b) Contour plot of the Patterson function for the asymmetric unit, and (c) a corresponding arrangement of five Au atoms. Only the positive peaks can be interpreted as interatomic vectors. Therefore the negative peaks are omitted for clarity (Ref. 21).

tion with Le Lay's two atom model which would only show three peaks. The positions of the peaks show that the interatomic distances are not the bulk interatomic vectors. Hence, the Au atoms must occupy low-symmetry sites. The peaks are also significantly elongated in the $[0\bar{1}1]$ direction, indicating the presence of disorder in the $[0\bar{1}1]$ direction. Assuming four Au sites within the irreducible unit, Au atoms must be situated on the corners of the parallelogram [Fig. 1(c)]. The weak maxima E and G are due to a fifth Au site.

In a preliminary study[5,6] a model, based on difference Fourier maps, having four fully and three partially occupied Au sites was proposed. This model is shown in Fig. 2(a). It has 12 free parameters (including one scale factor) and the structure refinement results in a χ^2 of 3.9 and an unweighted R value of 31%, where

$$\chi^2 = 1/[N-p]\sum_{h,k}[(|F_{hk}^{\rm obs}|^2 - |F_{hk}^{\rm calc}|^2)^2/\sigma_{hk}^2]$$

and

$$R_u = \sum_{h,k}(|F_{hk}^{\rm obs}|^2 - |F_{hk}^{\rm calc}|^2)/\sum |F_{hk}^{\rm obs}|^2 .$$

N is the number of observed structure factor intensities, p the number of free parameters, and σ_{hk} the standard deviations of $|F_{hk}^{\rm obs}|$. An anisotropic temperature factor was used for the atoms 1–3. Its large component in the $[0\bar{1}1]$ direction expresses a static disordering of these atoms. In the structure refinement presented here, we neglect Au site 7, since STM topographs of Baski, Nogami, and Quate[8] give no indication of its presence. The Au site 6 is also not visible in the STM images, but leaving out this site or assuming full occupation with Si instead of partial occupation with Au resulted in significantly higher χ^2 values. We introduced four split positions instead of anisotropic temperature factors and refined the occupation factors of five Au sites [see Fig. 2(b)]. For this model (18 parameters) a χ^2 of 4.0 was found. χ^2 dropped to 2.4 when 27 parameters including 10 Si positions were optimized. B_3 and B_5, the temperature factors of the atoms 3 and 5, were refined independently from an overall temperature factor and were found to be 0.68 and 0.64 Å^2. However, large error bars indicate a low significance of these parameters. Therefore, we fixed B_3 and B_5 to 0.56 Å^2, the bulk temperature factor of Au.[13] In the final refinement 25 parameters were refined (Table I) leading to a χ^2 of 1.7 and an unweighted R value of 14%. The relation of 25 free parameters to 52 structure factors is fairly low. A ratio of 3 is frequently considered as sufficient,[14] but a ratio of 2 is still acceptable, provided the data are precise enough. The large drop of the R factor and the χ^2 value by introducing more parameters indicate the significance of the result. Difference Fourier maps show a far better agreement for the refined model with 25 parameters than for the 7 atom model with 12 parameters.

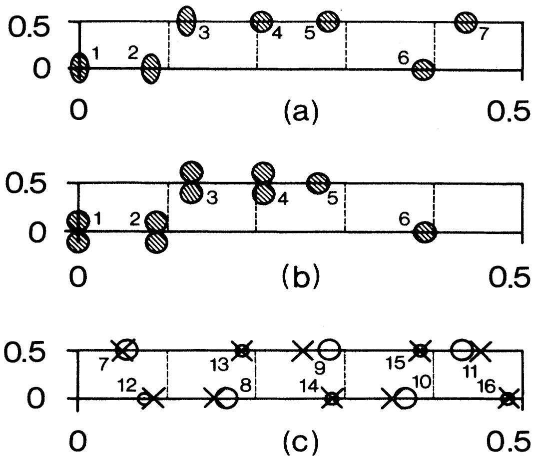

FIG. 2. Asymmetric units of the models: (a) The seven atom model and the model taking account of (b) 6 Au and (c) 10 Si sites. Si sites in the first layer are indicated by large circles, Si sites in the second layer by small circles, and the positions of an undistorted Si double layer by crosses.

The Au-Au distance in $[\bar{2}11]$ direction of 2.89 Å between sites 1 and 2 is close to the nearest-neighbor distance in bulk Au (2.88 Å). The split positions correspond to the superposition of the 5×2 unit cell into a single 5×1 unit cell. Two Au-Au distances of 3.10 and 4.58 Å, occur along the $[0\bar{1}1]$ direction. Au atom 3 must be located beneath or above its neighbors, because all its nearest-neighbor distances are much smaller than 2.9 Å. In the surface of bulk Au a contraction of bond lengths has been found.[15] The bond lengths in the small clusters found here on the Si(111) surface cannot be directly determined because only the projection of the structure is seen. The small in-plane distance of 2.3 Å between the Au atoms 4 and 5 precludes simultaneous occupation of both sites unless large height differences occur. The small occupation

TABLE I. Structure parameters of Au atoms and Si in the top double layer. The overall temperature factor of Au and Si atoms was found to be $B = 1.3(4)$ Å^2. However, B_3 and B_5 were fixed to the bulk temperature factor of Au (0.56 Å^2) (Ref. 13). The temperature factor is defined as $B = 8\pi\langle u^2\rangle$ where $\langle u^2\rangle$ is the root-mean square displacement of the atom. Occupation factors of split positions refer to one asymmetric site. $\chi^2 = 1.7$.

Atom	x	y	Occupation factor
1	0.000	0.097(3)	0.5 (×2)
2	0.087(1)	0.097(3)	0.38(5) (×2)
3	0.127(1)	0.572(8)	0.24(2) (×2)
4	0.207(1)	0.54(1)	0.33(5) (×2)
5	0.270(1)	0.5	0.22(6)
6	0.389(2)	0.0	0.27(3)
7	0.055(2)	0.5	1.0
8	0.168(3)	0.0	1.0
9	0.283(3)	0.5	1.0
10	0.368(3)	0.0	1.0
11	0.433(3)	0.5	1.0
12	0.076(5)	0.0	1.0
13	0.185(6)	0.5	1.0
14	0.286(4)	0.0	1.0
15	0.385(5)	0.5	1.0
16	0.483(5)	0.0	1.0

factor of site 5 (22%) as compared to that of site 4 (66%) would allow alternate occupation. The splitting of the interatomic distances along the first two rows corresponds to the tendency of Au atoms to adsorb in metallic clusters. A chain of Au atoms with short distances is achieved if the atoms 1 and 2 are alternately shifted in the [0$\bar{1}$1] direction in every second 5×1 unit cell, leading to a 5×2 reconstruction (see Fig. 3).

In Fig. 2(c) we show the positions of the Si atoms in the first double layer. Large shifts from bulk positions should correspond to the weaker bonds which are most likely associated with the outermost atoms of the top double layer. Because stacking faults may occur between the top Si double layer and the deeper substrate layers the registry to the bulk is still uncertain. Au sites 1–4 are close to distorted threefold hollow sites of the first Si layer. We assume that two mechanisms influence the adsorption: Au atoms prefer symmetric hollow adsorption sites, but tend to approach a bond length close to the Au bulk value. The fact that Au atoms leave the high-symmetry sites in order to reduce the bond length means that Au-Au bonding predominates over the interaction between substrate and adsorbate.

The temperature factors B_3 and B_5 were found to be significantly smaller than those of the other atoms. This suggests that the Au atoms 3 and 5 are more tightly bound. Since Au atom 3 is located at the apex of a tetrahedral configuration, the three next Au neighbors explain the tight bonding. The small temperature factor B_5 makes an atop position of atom 5 unlikely. It seems more probable that part of the Si atoms 9 are substituted by Au. The refinement of the overall temperature factor may cause systematic errors in the determination of the Au occupation factors, because both parameters are strongly correlated. Neither occupancies nor separate temperature factors were refined for the Si sites in order to limit the number of free parameters.

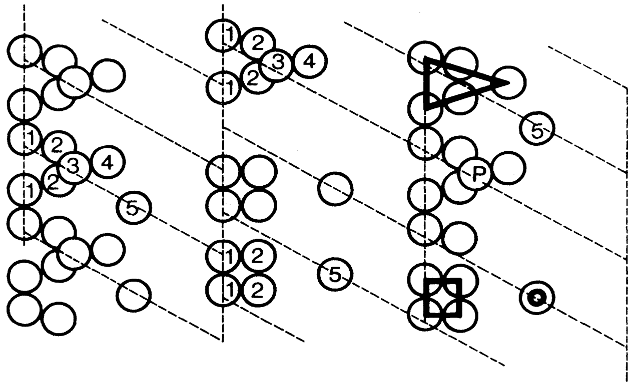

FIG. 3. Possible local atomic arrangements according to the splitting and the partial occupation of the Au sites 1–5 (Table I). Different configurations agree with round, rectangular, triangular units, and protrusions observed by STM topographs (Ref. 8). Dashed lines indicate the primitive 5×2 unit cell. Adjacent rows of 5×2 cells may be shifted according to the one-dimensional disordering in the [$\bar{2}$11] direction (Ref. 11).

The structure model described above can be compared with STM topographs by Baski, Nogami, and Quate.[8] The authors report the formation of rows along the direction [0$\bar{1}$1] and a five unit-cell spacing along the [$\bar{2}$11] direction. An irregular occurrence of topographic protrusions above these rows is observed. However, the protrusions are spaced at multiples of twice the bulk lattice constant. Apart from the protrusions, round, rectangular, and triangular patterns are also seen. On the basis of our data (Table I) the topographic protrusions correspond to Au atom 3 [Fig. 2(b)] situated above its neighbors. Triangular and rectangular units could consist of atoms 1, 2, and 4, as schematically shown in Fig. 3. Since the STM images indicate triangular units mainly between closely situated protrusions, atom 3 is most likely adsorbed above the triangular unit. We assume that atom 5 corresponds to the round unit. Our data suggest that sites 4 and 5 are not occupied simultaneously and indeed the STM images do not show the occurrence of round and triangular units in the same unit cell.

The x-ray and LEED diffraction pattern exhibits streaks in [$\bar{2}$11] direction.[6,11] This is consistent with the STM images which show that adjacent rows of protrusions do not remain in phase. From the STM image follows further that disorder occurs also along the [0$\bar{1}$1] direction showing an irregular sequence of structural elements as discussed above. This would cause distortions of the substrate atoms leading to an increased temperature factor of the Si atoms.

Different Au coverages for the formation of the 5×1 structure have been reported. According to Auger electron spectroscopy (AES) examination by Le Lay and coworkers[2] the 5×1 structure is completed at the coverage of 0.5 ML, followed by coexistence of the 5×1 and $\sqrt{3}\times\sqrt{3}$ phases. The pure $\sqrt{3}\times\sqrt{3}$ phase is reported to appear between 0.8 and 1.0 ML. Measurements using a quartz oscillator microbalance confirmed these results.[4] However, scanning electron microscopy (SEM) and reflection high-energy electron diffraction (RHEED) observations[16,17] revealed a coverage of 0.75 ML for the pure 5×1 structure supported by coverage estimates from the evaporation rate.[18] From the x-ray data the coverage with Au atoms cannot be determined directly. The occupation factors given in Table I refer to relative values keeping the occupation of Au atom 1 fixed. The overall Au coverage follows from the occupation ratio of Au to Si. If the Si occupation factors were kept fixed, refinement was not possible. Table I gives the ratio of the number of Au atoms to Si top layer atoms as 0.7. Note however, that the Au coverage is lowered correspondingly, if Si sites are not fully occupied. The SEM measurements[19,20] showed that the density of the Si atoms in the 5×1 structure is about 40% smaller than that in the unreconstructed surface. From the Au/Si ratio of 0.7 a coverage of 0.4 ML is obtained in agreement with the phase diagram of Le Lay and co-workers.[2] The occupation of different Au sites, as given in Table I, agrees qualitatively with the asymmetric density distribution found by STM pictures. Baski, Nogami, and Quate reported an average occurrence of the protrusion in 16% of all 5×1 cells. Taking account of the lowered Si density in the top layer the occupation factor of Au site 3 drops to 29%. We assume that the Au atom 3 produces protrusions only in specific configuration with its neighboring Au atoms.

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