

Surface Science Letters

Intermixing and two-dimensional alloy formation in the Na/Au(111) system

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Received 2 March 1993, accepted for publication 6 April 1993

The adsorption of Na on Au(111) has been studied by scanning tunneling microscopy (STM) and low-energy electron diffraction (LEED). Upon thermal activation ordered structures are formed which consist of intermixed Na–Au layers. A thermodynamically stable hexagonal NaAu₂ layer with a lattice constant of $\sim 5.4 \text{ \AA}$ is identified, which can be regarded as a two-dimensional alloy.

Alkali metal adsorption on metal surfaces was extensively studied in the last decade [1,2]. The adsorption behavior is dominated by the dipole–dipole repulsion between the positively charged alkali adatoms. These interactions cause ordered quasi-hexagonal alkali overlayers to be formed [2,3]. The adsorbed alkali atoms are generally assumed to reside *on* the underlying substrate. The only exceptions known so far were the alkali-induced missing-row reconstructions on 3d and 4d fcc (110) transition metal surfaces [4]. For the K/Au(110)-system even a mixed K–Au surface layer was predicted theoretically [5] and experimentally verified by ion scattering [6] and STM [7]. Recently the alkali-induced reconstruction of a close-packed metal surface was reported. Surface-extended X-ray adsorption fine-structure data and *ab initio* density functional calculations showed that at 300 K in the Na on Al(111) system Na atoms displace Al surface atoms and occupy sixfold coordinated holes in a $(\sqrt{3} \times \sqrt{3})R30^\circ$ geometry [8]. In this paper we

present first results of a combined STM, LEED, Auger electron spectroscopy (AES), and thermal desorption spectroscopy (TDS) study on the interaction of Na with a Au(111) single crystal surface. This chemisorption system exhibits a similar tendency to form mixed overlayers, where Au–Au bonds are replaced by Au–Na bonds. A thermodynamically stable hexagonal NaAu₂ compound layer is characterized, which can be understood as a two-dimensional analogue to the well known NaAu₂ bulk alloy [9,10]. The data presented here provide the first atomic scale observation of the initial stage of alloy formation between a free-electron and a d-band metal.

The experiments were performed with a pocket size STM [11], incorporated in a standard ultra-high vacuum chamber (base pressure $\sim 10^{-10}$ Torr) containing LEED, AES, TDS, and standard facilities for sample preparation. Surface preparation followed the procedure outlined in ref. [12]. Sodium was evaporated from a commercial SAES getter source.

Upon deposition at 85 K adsorbed Na orders spontaneously at coverages between 0.2 and 0.6 ML (1 monolayer (ML) corresponds to 1 Na atom per substrate atom in the unreconstructed surface). A sequence of quasi-hexagonal structures is formed with increasing coverage, as evidenced by LEED. Because of their easy formation and their similarity with alkali overlayer structures on Pt(111) [13] and Ru(001) [14] these structures are associated with ordered overlayers. They are used for coverage calibration in the subsequent experiments. Both integral order beams and Na adlayer beams exhibit weak satellites, similar to the LEED pattern of the clean surface, indicating that under these conditions the reconstruction of the clean Au(111) surface is maintained. If the Na-covered sample is heated to 300 K, the hexagonal low-temperature structures transform irreversibly. At $\theta \approx 0.5$ ML a sharp LEED pattern of a well ordered $c(4 \times 2)$ structure appears. The absence of satellite spots indicates a removal of the reconstruction. Further heating to ~ 600 K leads to the formation of a new LEED satellite pattern, where the central high-intensity spots do not lie on the Au lattice positions. The resulting reciprocal lattice is contracted and rotated by 30° and can best be described by a $(1.08\sqrt{3} \times 1.08\sqrt{3})R30^\circ$ structure. The satellite peaks, which are oriented along the Au(111) lattice directions, span approximately a (13×13) unit cell. The fact that both the $c(4 \times 2)$ and the expanded $(1.08\sqrt{3} \times 1.08\sqrt{3})R30^\circ$ structure require thermal activation signals that a rearrangement of surface Au atoms is involved in the formation of these structures.

STM data (recorded at 300 K) give further insight into the adsorption system. We will concentrate on the 0.5 ML coverage regime. The overview image presented in fig. 1 reveals a significant restructuring of the surface after Na deposition at 300 K. Irregularly shaped islands with ~ 50 – 500 \AA diameter are formed, which are randomly distributed over larger terraces on the surface. Island size and shape do not change with time on a time scale of ~ 30 min. Considering the generally repulsive dipole–dipole interactions between adsorbed alkali atoms and their high mobility at 300 K [15] it is impossible that these islands are formed by condensed alkali atoms



Fig. 1 Large-scale STM topography image ($2000 \times 2000 \text{ \AA}^2$) of a Au(111) surface after deposition of 0.5 ML Na at 300 K.

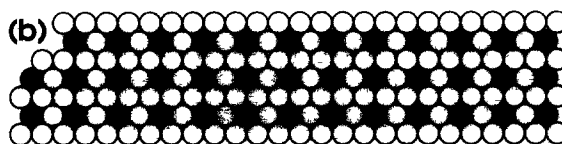


Fig. 2 (a) Atomic resolution image ($210 \times 210 \text{ \AA}^2$) of the $c(4 \times 2)$ structure in the lower terrace and the protruding islands. The 120° rotational domains of the $c(4 \times 2)$ are marked A, B and C. (b) Model of the $c(4 \times 2)$ structure (open circles Au atoms, shaded circles Na atoms substituting Au surface atoms).

The islands cover approximately 40% of the surface on the large terraces. This is much more than the about 0.05 ML of Au atoms which would be set free from the topmost Au layer upon a Na-induced removal of the Au(111) reconstruction. Therefore, we assume these islands to consist of a mixed adlayer of both Au and Na atoms. The islands exhibit an irregular structure of elevated lines, about 1 Å high and 10–20 Å wide. These lines are not present on the lower terrace level, instead there is a series of ~ 10 Å deep holes. The height difference of ~ 1.4 Å between island and terrace level and their different structural characteristics indicate that different structures are present.

High-resolution STM data resolve that a large fraction of the lower level areas is covered by islands, 30–300 Å in diameter, which exhibit a periodic structure (see fig 2a). A rectangular unit cell with $2a$ and $a\sqrt{3}$ lattice constants and a corrugation amplitude of about 0.4 Å are found, corresponding to a $(2 \times \sqrt{3})$ rect., or, equivalently, a $c(4 \times 2)$ structure, as observed before with LEED. This phase can exist in three 120° orientational domains, all of which are present in the image. Also this phase is assumed to consist of a mixed topmost layer. In the atomic model shown in fig 2b the depressions in the STM image are associated with Na atoms substituting every fourth Au atom in the (1×1) surface layer. This structural assignment will be discussed below. In the protruding islands a hexagonal lattice with a corrugation amplitude of ~ 0.2 Å is resolved (cf fig 2a). The image reveals that the elevated lines on the islands coincide with domain boundaries of the hexagonal structure. In contrast to the $c(4 \times 2)$ islands the hexagonally structured areas show an additional long-range height modulation of 0.5 Å, which, however, is not very regular. This is a first hint that the topmost layer atoms do not reside on identical adsorption sites. By comparison with the $c(4 \times 2)$ structure we find that the hexagonal pattern of the protruding islands is oriented along $[11\bar{2}]$. The lattice constant amounts to ~ 5.4 Å and thus differs from the Au lattice. Lattice parameter and orientation agree well, however, with that of the $(1.08\sqrt{3} \times 1.08\sqrt{3})R30^\circ$ structure derived from the LEED pattern observed after \sim

600 K annealing. The ~ 1 Å deep holes in the lower terrace level mentioned above often exhibit a characteristic, network-like structure, similar to the elevated lines in the upper level islands. The height difference from the bottom of these holes to the hexagonal island areas amounts to ~ 2.4 Å, equivalent to a Au(111) layer height. Therefore, we conclude that the surface layer in these holes consists of a similar type albeit poorly ordered structure as that found in the elevated islands.

Structure and topography of the surface changed drastically after the sample is flashed to ~ 600 K, as seen in the STM image reproduced in fig 3a. The flat $c(4 \times 2)$ areas have disappeared, in agreement with LEED observations. Though the surface still exhibits a characteristic two-level terrace island topography, it is entirely covered now by a well ordered hexagonal structure with a periodicity of ~ 38 Å. The height difference between the two levels has increased to ~ 2.4 Å. The formation of a two-level system is attributed to the limited mass transport during the short period of annealing. After longer annealing flat terraces with the same structural characteristics are formed. Elevated lines are found, similar to those formed at 300 K on the protruding islands, indicating a similar nature of both structures. The atomic structure of this phase is resolved in the image in fig 3b. It is of the same hexagonal type as that of the protruding islands in fig 2, with a periodicity of ~ 5.4 Å $\approx 1.08a\sqrt{3}$. The long-range corrugation pattern is oriented along the bulk Au lattice directions. The characteristics of this corrugation pattern do not depend on the tunneling parameters. Therefore, we conclude that this pattern is not due to an electronic effect but rather reflects the topography of the surface. It is identified as a moiré structure caused by the lattice mismatch of substrate and surface layer. Both interatomic distances and lattice orientations agree with the $(1.08\sqrt{3} \times 1.08\sqrt{3})R30^\circ$ LEED satellite pattern, where the LEED satellite spots result from the long-range periodicity of the moiré structure. The chemical composition of the topmost atomic layer can be derived from the terrace topography of the surface. The formation of islands is attributed

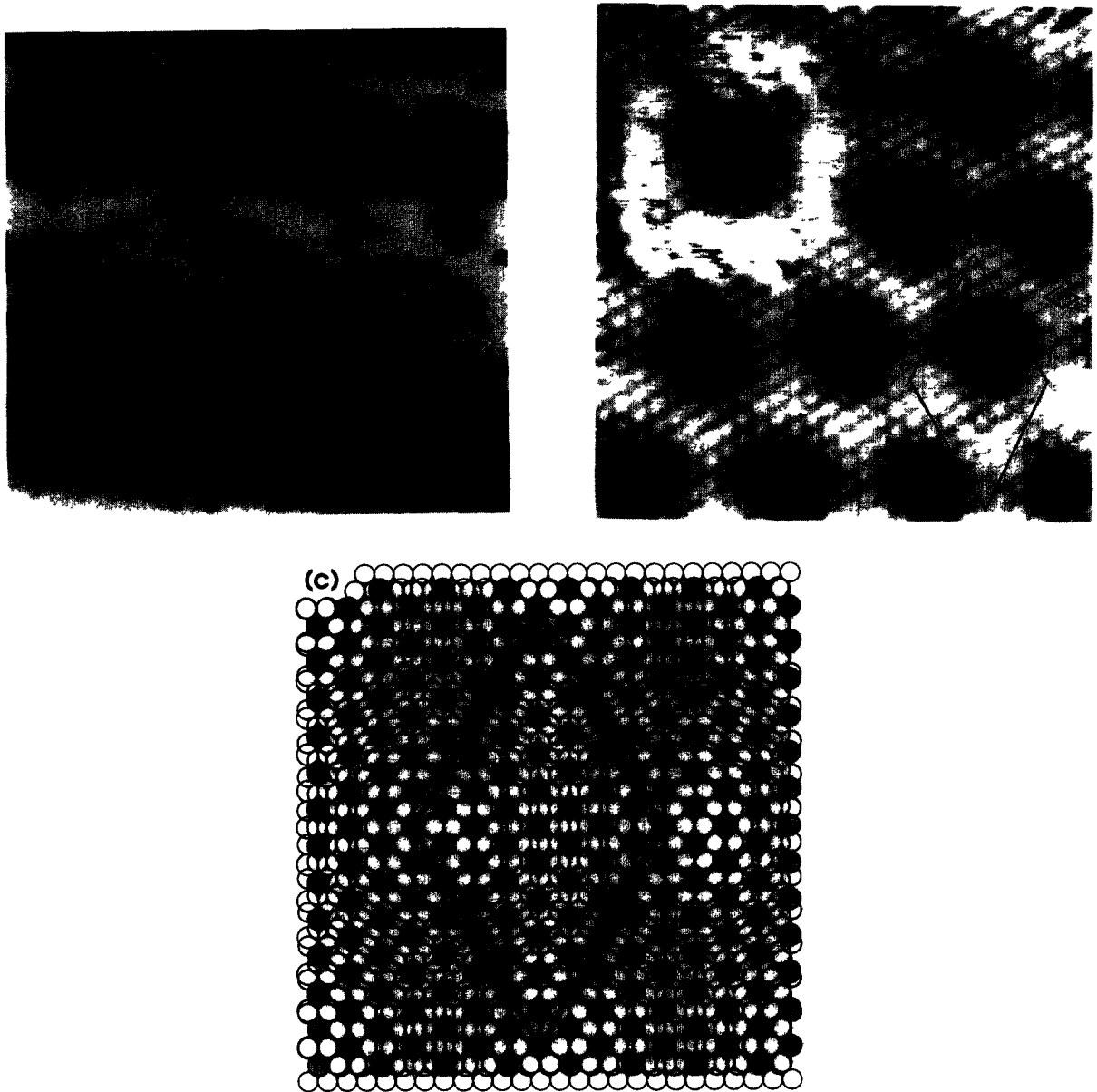


Fig 3 (a) Large-scale STM topography image ($2000 \times 2000 \text{ \AA}^2$) of a 0.5 ML Na-covered Au(111) after flash annealing to $\sim 600 \text{ K}$. (b) Atomic resolution image ($120 \times 130 \text{ \AA}^2$) of the moiré structure with a domain boundary, the (13×13) and $(1.08\sqrt{3} \times 1.08\sqrt{3})R30^\circ$ unit cells are marked by a rhombus. (c) Model of the mixed NaAu_2 layer (open circles first- and second-layer Au atoms, shaded circles substitutional Na atoms, the (13×13) and the $(1.08\sqrt{3} \times 1.08\sqrt{3})R30^\circ$ cells are marked)

to a lower density of Au atoms in the mixed surface layer. Assuming that during the formation of the new phase the excess Au atoms cluster in monolayer islands and that the second layer re-

tains its bulk symmetry we can estimate the density of Au surface atoms from geometrical arguments. These assumptions are plausible if we take the central parts of large terraces for evalua-

tion only. On the large terrace in fig 3a the islands cover about 55% of the total area, a value also found in other flash annealing experiments. Taking into account that the density of surface Au atoms on the clean reconstructed Au(111) surface amounts to 1.05 ML, the density of Au atoms in the mixed hexagonal surface layer approximately amounts to $1.05 - 0.55 = 0.5$ ML.

The low density of Au atoms in this layer, the moiré pattern and its $(1.08\sqrt{3} \times 1.08\sqrt{3})R30^\circ$ atomic structure are explained by a mixed surface layer of NaAu₂ composition. A schematic model of this structure is depicted in fig 3c. The Au top layer atoms form a honeycomb lattice with a nearest-neighbor atomic distance of $1.08a$. The density of Au atoms in this layer amounts to 0.57 ML. Within the limits of accuracy this is identical with the density of surface Au atoms estimated from STM data. The sixfold coordinated central sites of the honeycomb lattice are occupied by Na atoms. By comparing the model with the STM image in fig 3b we see that these Na atoms form the hexagonal lattice with an n - n distance of ~ 5.4 Å resolved there. The in-plane Na–Au distance in the NaAu₂ surface layer, $1.08a = 3.1$ Å is very close to the Na–Au atomic distance in the NaAu₂ alloy of 3.23 Å [9]. The mixed surface layer can be regarded as a two-dimensional analogue to the NaAu₂ bulk alloy, representing the first stage of bulk alloy formation between Na and Au. LEED and TDS data show that with increasing coverage the Na and Au atoms form a similar structure also in the deeper lying layers. This indicates that Na and Au atoms in the mixed layers are approximately located in one plane. The steric structure of the NaAu₂ monolayer as well as the compound multilayers, however, is not of a MgCu₂-type lattice, which is the bulk NaAu₂ structure [9]. The expansion of the top layer means that 12 surface layer atoms reside on 13 atom sites of the second (111)Au layer along the $[\bar{1}\bar{1}0]$ directions. This corresponds to a $13a \times 13a = 37.5 \times 37.5$ Å² unit cell of the moiré pattern, in agreement with LEED and STM data. Depending on their position in the unit cell the surface atoms occupy different adsorption sites on the second layer which leads to a modulation of the vertical position of the topmost layer atoms. The

STM corrugation amplitude of ~ 0.5 Å agrees well with recent findings for modulated metal structures, e.g., for the reconstructed Au(001) [16] and Au(111) [12] surfaces. An analysis of large-scale atomic resolution STM data shows that small deviations from the 12 on 13 scheme of the surface layer occur, indicating that, in fact, an incommensurate overlayer rather than a coincidence lattice is formed. We also found that, in particular after longer annealing, the NaAu₂ surface layer can be slightly rotated with respect to the second layer.

With the interpretation of the moiré structure the $c(4 \times 2)$ phase can be rationalized. The islands created upon Na deposition at 300 K cover about 40% of the surface area in the large terraces. Taking into account that the Au density in these islands amounts to ~ 0.57 ML (where the influence of defects is neglected for simplicity) it follows that the average density of Au in the surrounding areas equals $\sim [1.05 - (1 + 0.57)0.4]/0.6 = 0.7$ ML. This shows that our previous interpretation of a mixed topmost layer with Na atoms substituting every fourth of the Au surface atoms was correct.

The densities of Na atoms in the mixed moiré layer and in the $c(4 \times 2)$ structure amount to 0.28 and 0.25 ML, respectively. Hence, none of these phases can accommodate the 0.5 ML Na adatoms which were deposited on the surface. Since AES and TDS data showed that no significant desorption or bulk diffusion of Na atoms occurs during the formation of these structures these species must still be present on the surface. Consequently the mixed Na–Au layers are covered by a dilute Na adlayer with an average coverage of ~ 0.2 ML. A similar observation was made for the CsAu system. CsAu alloy thin films are always covered by a chemisorbed Cs layer, as verified by Penning spectroscopy [17]. The presence of a mobile Na adlayer does not contrast the STM observations of the ordered structures. It is well known that mobile adsorbates are in general transparent in STM images and that in these cases the underlying substrate can be resolved [18].

The data presented here lead to the following scenario for the reconstructive Na adsorption on

Au(111) upon deposition at low temperature (85 K) Na is adsorbed on the reconstructed Au surface, forming ordered quasi-hexagonal overlayers. These phases are thermodynamically unstable and at a coverage of ~ 0.5 ML a metastable $c(4 \times 2)$ structure upon annealing to 300 K is formed. During this transition the reconstruction of the Au(111) surface is removed and every fourth Au atom is replaced by a Na atom. The excess Au atoms released from the topmost Au layer condense together with additional Na atoms into poorly ordered monolayer islands on bulk-like previous surface areas. The ordered areas of these islands arrange into a hexagonal lattice with a $(1.08\sqrt{3} \times 1.08\sqrt{3})R30^\circ$ geometry. This structure is a precursor to the stable phase, and upon annealing to ~ 600 K the entire surface transforms irreversibly to this structure. The lattice misfit between surface and second layer leads to a regular hexagonal moiré pattern of ~ 38 Å length and ~ 0.5 Å corrugation. The surface layer consists of a mixed NaAu_2 monolayer where the Au atoms form a honeycomb lattice with the interstitial sites occupied by Na atoms. This phase can be regarded as a two-dimensional surface alloy.

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