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LETTER TO THE EDITOR

Potassium-induced restructuring of the Au(001) surface

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Abstract. Low-energy-electron-diffraction patterns on the K-adsorbed Au(001) surface were observed as a function of K coverage at room temperature and at about 100 K. It was found that the hexagonal structure of the clean surface successively changes to a 1×1 and a 1×2 structure with increasing coverage at room temperature. The 1×2 pattern is explained by the reconstruction of the substrate Au(001) surface. The 1×2-reconstructed surface is considered to adopt missing-row-type structure, which is supported by the K-coverage dependence of the work-function change.

Alkali metals are known to induce the missing-row reconstruction on several FCC(110) metal surfaces: Ni(110) [1, 2], Ag(110) [3–5], Cu(110) [6–10], Pd(110) [11], and Au(110) [12]. Some theoretical studies have been carried out for interpreting the mechanism of alkali-metal-induced reconstruction of FCC(110) metal surfaces [13–16]. The higher effective coordination number of the alkali-metal atoms in the troughs formed by the missing rows leads to an additional binding energy compared with chemisorption on the unreconstructed surface [14]. Therefore, a small coverage of alkali-metal atoms can induce a missing-row reconstruction of the FCC(110) surfaces. In this mechanism, the chemical interaction is important for determining whether the adsorption-induced reconstruction occurs or not. Another possible mechanism for adsorption-induced reconstruction is the charge transfer between adsorbate and substrate [13]. In alkali-metal adsorption, the electron transfer occurs from the adsorbate to the substrate and the surface with the higher atomic density appears via restructuring. In this case, the occupied d-state behaves as a repulsive potential and the s, p-state makes a cohesive energy. The increase of the surface electron density for the delocalized s, p-state due to the charge transfer produces an increase in the cohesive energy, which is most effective in the surface of highest atomic density.

Recently, we found a potassium-induced reconstruction of the closer-packed FCC(001) surface of Ag [17, 18]. A missing-row-type structure was proposed as a model of the reconstructed surface, which was supported by the K-coverage dependence of the work-function change and the electron energy loss spectrum. On the other hand, a potassium-induced reconstruction does not occur on Cu(001) [19]. In terms of chemical concepts, the chemical activity of Cu is higher than that of Ag which means that a larger additional binding energy is expected in Cu than Ag. This argument

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contradicts the experimental result. So whether the Au(001) surface will reconstruct into the 1×2-missing-row structure or not is a very interesting problem. We have therefore performed experiments on the K/Au(001) system.

The structure and electronic properties of a clean Au(001) surface have been studied extensively using various experimental techniques [20–26]. The ground state of this surface corresponds to a contracted hexagonal-close-packed overlayer on top of a square lattice. Low energy electron diffraction (LEED) measurements suggested a large $c(26\times68)$ unit cell [21]. A transmission electron microscopy (TEM) study showed the 5×28 unit cell on a thin film [25] and the $5\times n$ ($n=15$–21) unit cell on a bulk single crystal [26]. The Au-surface reconstruction has been successfully explained by Ercolessi *et al* using a 'glue model' [27], and by Dodson using the embedded-atom method [28]. These are simulations with the Au–Au interactions represented by empirical potentials. In a microscopical framework, Takeuchi *et al* performed first-principles total-energy calculations [29] and showed that the calculated ground-state configuration agrees with experimental observation. Such a reconstruction of the clean Au(001) surface seems to be closely related with the adsorption-induced restructuring.

The experiments were performed in an ultrahigh-vacuum chamber with a base pressure of 1×10^{-8} Pa. An Au crystal was mechanically polished and was held on a tantalum wire. A Pt–PtRh(13%) thermocouple was spot-welded on the tantalum wire close to the sample surface. The sample holder was in contact with a liquid N_2 reservoir, so that the sample could be kept at low temperatures during experiments. Final cleaning was achieved by successive cycles of 500 eV argon-ion bombardment and annealing at 650–850 K until no impurities could be detected by Auger electron spectroscopy (AES) and until LEED measurements showed a sharp 5×20 pattern [21, 24]. K atoms were deposited from a commercial SAES getter source. The observation of LEED patterns and the measurements of AES and work-function change ($\Delta\phi$) were carried out by the use of a four-grid LEED optics under the K deposition. The work-function change was determined by the low-energy cut-off of secondary-electron emission from the sample to which a 30 V bias voltage was applied. These measurements were performed with the aid of a computer-controlled system. The absolute value of K coverage, Θ, which is defined as a ratio of the number density of K atoms to that of the Au(001)-1×1 surface atoms, was determined by normalization at $\Theta=0.17$, where the maximum LEED intensity of half-order spots for the 1×2 pattern accompanied with $c(3\times4)$ was observed at room temperature. This determination is adequate upon comparison with the experimental results in the K/Ag(001) system [17, 18].

Successive changes of LEED patterns were observed during K deposition at room temperature (figure 1). A clear 5×20 LEED pattern was observed on the clean Au(001) surface (figure 1(a)). The 5×20 LEED pattern turned into a sharp 1×1 LEED pattern at a low coverage of $\Theta\simeq0.1$ (figure 1(b)). This 1×1 pattern does not originate in the disorder but in the 1×1 order of the first Au layer, since the intensity of the (1 0) spot increases steeply at the same time on the appearance of the 1×1 structure, as shown in figure 2. A sharp and clear 1×2 pattern appeared at $\Theta=0.1$–0.2 (figure 1(c)). The 1×2 pattern was accompanied with a faint $c(3\times4)$ pattern. These 1×2 and 1×2 accompanied with $c(3\times4)$ patterns were also observed in the K/Ag(001) system [17, 18]. The intensity of the (0 1/2) spot takes the maximum intensity at relative coverage $\Theta_{rel}=0.5$, where Θ_{rel} is the ratio of the coverage to the saturation coverage at room temperature. This result is the same as that reported previously [17, 18, 30].
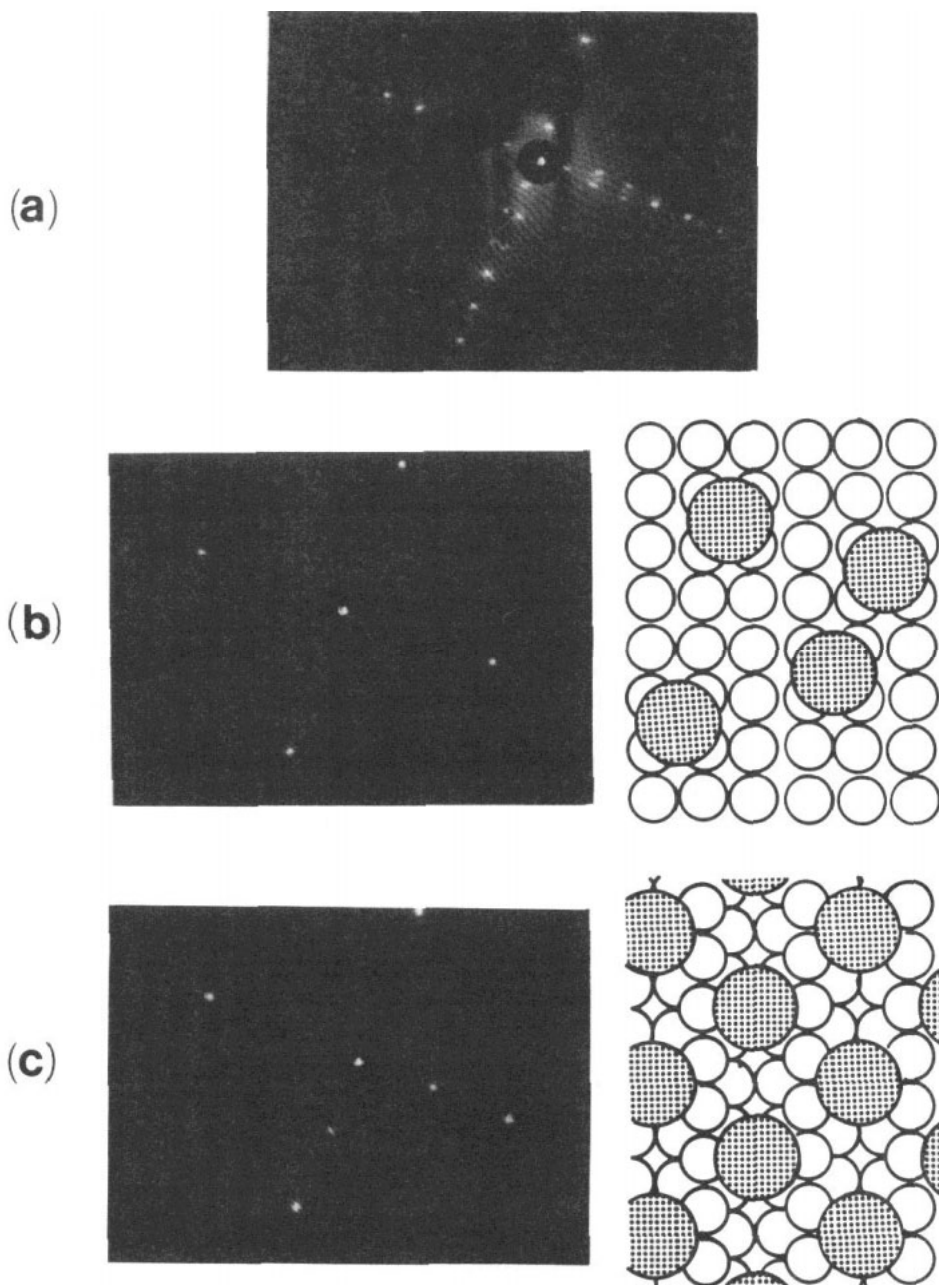
(a)

(b)

(c)

Figure 1. Change of LEED patterns of the K-covered Au(001) surface prepared at room temperature. (*a*) Clean Au(001) surface, primary energy $E_p = 47$ eV; (*b*) $\Theta \simeq 0.1$, 1×1 pattern, $E_p = 47$ eV; (*c*) $\Theta \simeq 0.17$, 1×2 pattern, $E_p = 45$ eV. The figures on the right in (*b*) and (*c*) show corresponding structure models in real space.

At higher K coverages, two $c(8 \times 2)$ and 6×2 patterns were observed, which were not observed in the K/Ag(001) system [17, 18]. The 1×3 pattern observed in the Ag(001)
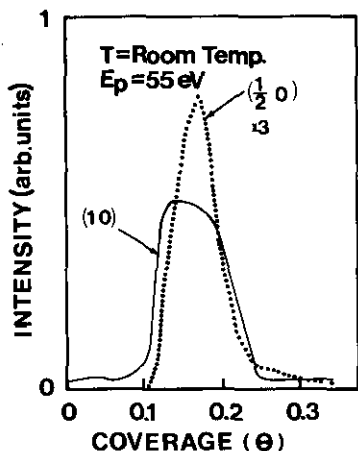
Figure 2. LEED intensity versus coverage curves for (1 0) and (1/2 0) shown by solid and dotted lines, respectively. E_p=55 eV and T=room temperature.

system was not observed in the present K/Au(001) system.

Figure 3 shows the changes of every LEED pattern observed at room temperature and at about 100 K as a function of K coverage. The 5×20 pattern turned into a diffuse 1×1 pattern and no other change of the LEED pattern was observed at about 100 K. Annealing of the K-adsorbed Au(001) surface made at 100 K, which consists of both 5×20 and 1×1 structures, leads to a clear 1×1 and 1×2 structure at about 150 and 190 K, respectively. Moreover, no new LEED pattern appeared when further K atoms were deposited at about 100 K on the surface of the 1×2 structure prepared at room temperature. These observed features are similar to the results in the K/Ag(001) system [17, 18].
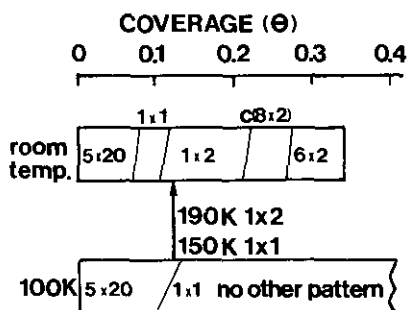

Figure 3. Changes of the LEED pattern of the surfaces prepared at room temperature (upper part) and at about 100 K (lower part) as a function of K coverage.

Let us first discuss a mechanism for the back-reconstruction from a 5×20 to a 1×1 structure. The clean (001) surface reconstructs into two nearly orthogonal domains of dimensions $(5\times n)$ where n ranges between 15 and 21 [26]. The first layer of the reconstructed surface takes a hexagonal-close-packed structure. A good coordination of the surface atom stabilizes the reconstructed surface. Moreover, the reconstructed

structure is locked by a two-dimensional lattice of solitons [27]. The solitons slightly compress the surface atoms between them. The resulting many-body energy gain compensates for the formation energy of the solitons. The surface strain is not uniform but is localized in the soliton-type region. The microscopic driving force of the 5×20 reconstruction is the strong tendency for the top layer to go to a more compact arrangement [29]. This tendency is caused by the bonding and cohesion due to 5d electrons hybridized with the s band.

K atoms sit on the three-fold hollow site when they adsorb on the hexagonal-close-packed surface. The coordination number of a K atom is roughly 3 which is smaller than the 4 occurring for the case of adsorption on the unreconstructed 1×1 surface where K atoms sit on the four-fold hollow site. So, it is possible for the 1×1 surface to be more stable than the 5×20 surface if the chemisorption and dipole energies of a K atom surmount destabilization due to the reduced coordination of the surface gold atom in the structural change from 5×20 to 1×1. Initially, the adsorption of a K atom will locally change the hexagonal-close-packed lattice of surface Au atoms into the 1×1 lattice. The surface strain due to the 5×20 to 1×1 change is transmitted to the soliton-type region and the Au atoms in the soliton-type region are easily pushed off. Since the Au atoms in the soliton-type region are energetically unstable, the 5×20 structure is easily relaxed into the 1×1 structure. The driving force of back-reconstruction to the 1×1 structure is considered to be due to the chemisorption energy of a K atom with the substrate rather than charge donation from a K atom to the substrate, because the 1×1 back-reconstruction was also observed in the Br/Au(001) system [31] in which the charge donation occurs from the substrate to a Br atom.

Next, we discuss the mechanism of the 1×1 to 1×2 reconstruction. The 1×2 structure can be assigned to the missing-row-type reconstruction as well as the 1×2 structure in the K/Ag(001) system, because the features of the 1×2 structure of the Au(001) surface agree with those of the Ag(001) surface. Figure 4 shows the work-function change as a function of K coverage at both room temperature and at about 100 K. This result supports the missing-row-type reconstruction. As the K coverage increases at room temperature, the work function decreases at low coverages and then increases at the coverage level where the 1×1 pattern turns into the 1×2 pattern and takes a nearly constant value up to the 0.17 coverage level at which a half-order spot of the 1×2 pattern takes maximum intensity. At the coverage level where the 1×2 structure was observed, the image dipole moment per K atom at room temperature is smaller than that at about 100 K, as seen in figure 4. The 1×2 structure does not appear at about 100 K. Since K atoms sit in the troughs made in the missing-row-type reconstruction of the Au surface, the distance between a K atom and the image plane is contracted. So, the image dipole moment for each adatom is smaller than that for an adatom which adsorbs on the 1×1 unreconstructed surface. As the K coverage increases, the image dipole moment for an adatom decreases due to the depolarization effect. The atomic density of the top Au layer decreases from 5×20 to 1×1 and again to 1×2, which also contributes to the decrease of the work function. So, the decrease of the image dipole moment due to restructuring is cancelled by both the increase of the K coverage and the decrease of the Au density of the top layer. The work function shows a small increase and then maintains a nearly constant value with developing reconstruction. It was also observed in the FCC(110) surface that the image dipole moment for a Na atom is smaller in the missing-row reconstructed surface than in the unreconstructed surface [2]. Above a coverage of $\Theta = 0.17$, the

work function decreases again at room temperature, since the amount of K atoms adsorbed in the trough increases.
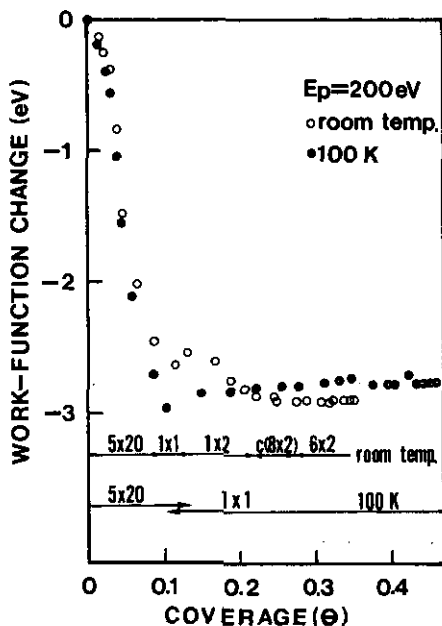

Figure 4. Work-function change as a function of K coverage. Open and closed circles show the data observed at room temperature and at about 100 K, respectively. The sequences of the LEED-pattern change at two different temperature regions are shown in the bottom of the figure.

At low temperatures, the LEED pattern changed from 5×20 to a diffuse 1×1 pattern at $\Theta \simeq 0.1$. This change implies 1×1-island formation on the substrate, since the intensity of the integral spots are clearly enhanced as compared with that of the non-integral spots. Au-1×1-island formation causes a decrease of the surface Au density and then leads to a decrease of the work function. On the other hand, K atoms adsorbed on island edge sites may stabilize the islands. The edge sites of the islands are considered to contribute to the work-function change. The work-function change as a function of K coverage at 100 K is different from those observed on K/Cu(001) [32] and K/Ag(001) at low temperatures [18]. This difference is considered to include the contribution of the island formation.

The 1×2-missing-row-type structure of the FCC(001) surface is considered to be stabilized by the enhancement of the K-chemisorption energy and the dipole-energy difference, which explains the missing-row-type reconstruction of the K/Ag(001) system well, according to the calculation performed by Christensen and Jacobsen [33]. Christensen and Jacobsen calculated missing-row-reconstruction energies for the FCC(001) surfaces of the metals Al, Ni, Pd, Pt, Cu, Ag, and Au. Their calculated result shows that the tendency to reconstruct in the presence of adsorbed K atoms is largest for Ag and that the Au(001) surface is difficult to reconstruct into the missing-row-type 1×2 structure because of its large bulk modulus. Their calculated result is clearly

in contradiction to the present experimental result. In their calculation, the K-dipole-energy difference between the unreconstructed and reconstructed surfaces in the K/Au(001) system is assumed to be equal to that in the K/Ag(001) system. Although the rough estimation excludes the substrate dependence of the dipole energy on the K-adsorption system, this assumption may cause the difference between the calculation and the experimental result. At this stage, however, we cannot comment further on this difference. The adsorption-induced 1×2 reconstruction in the K/Au(001) system can also be considered to be caused by the same origin as the reconstruction of the clean Au(001) surface.

Although $c(8\times2)$ and 6×2 patterns were observed at room temperature, it is not elucidated whether these structures originate in the overlayer or the substrate. These structures were not observed in the K/Ag(001) system; this is considered to be due to the difference in the chemical interaction and the bulk modulus.

In summary, 1×1 back-reconstruction and a reconstruction similar to the K/Ag(001) system were found in the K/Au(001) system. These reconstructions are considered to be caused by the stabilization due to the chemisorption energy and the dipole energy. In contrast to the experimental result, reconstruction in the K/Au(001) system is not expected from the calculation performed by Christensen and Jacobsen [33]. The reconstruction in the K/Au(001) system can be considered to take the same origin as the reconstruction of the clean Au(001) surface.

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