Rotational Epitaxy of Chemisorbed K Monolayers on Cu(001)

Tetsuya Aruga, Hiroshi Tochihara, and Yoshitada Murata
The Institute for Solid State Physics, The University of Tokyo, Roppongi, Minato-ku, Tokyo 106, Japan
(Received 30 January 1984)

The structure change of incommensurate potassium monolayers on low-dislocation-density copper (001) has been observed at 330 K by low-energy electron diffraction. The orientation angle was found to increase uniformly from 3.3° to 6.0° when the potassium interatomic spacing was varied from 4.72 to 4.57 Å. The existence of rotational epitaxy, observed previously for physisorbed rare-gas monolayers, has been demonstrated for an alkali-metal monolayer on a metal surface.

PACS numbers: 68.20.+t, 61.14.Hg

Rotational epitaxy of incommensurate monolayers in physically adsorbed rare-gas films was first predicted theoretically by Novaco and McTague (NM)[1] and then observed by low-energy electron diffraction (LEED).[2-4] The theory has been worked out for the static distortion waves in a monolayer induced by the lateral periodic potential of a rigid substrate.[1,5] The orientation angle, ϕ, between the monolayer lattice and the surface lattice varies with the mean overlayer interatomic spacing, d. The observed relationship between ϕ and d agreed with calculations of NM[1,5] and Shiba.[6]

A number of incommensurate structures in chemisorbed layers have been studied,[7] and rotated structures have also been reported for a few systems, such as Ag on mica,[8] Pb on Au(111),[9,10] Pb on Ag(111),[10] and Mn on Al(111).[11] In the case of Ag on mica, however, the rotated structure was caused either by edge effects[12] or by dislocation-induced lattice coincidences.[13] Since no observation has been made on the variations in the orientation angle with the lattice parameters,[8,10] it is hard to decide whether the observed rotated structures are caused by the NM-type effects or by other factors such as impurities, surface steps, and dislocations; these factors might lock an incommensurate overlayer into a certain orientation.

In the present Letter we report on LEED measurements of ϕ and d for an incommensurate potassium monolayer chemisorbed on Cu(001) at 330 K. The results demonstrate clearly the rotational epitaxy predicted by NM in a chemisorbed potassium monolayer.

The experiments were performed in a magnetic-field-free vacuum system with a base pressure of 7×10^{-9} Pa. It was equipped with a four-grid LEED optics system, which was also used for a retarding-field analyzer for Auger-electron spectroscopy (AES). The Cu sample was cut by a wire saw from a single crystal of low-dislocation-density and oxygen-free high-purity copper made by the Czochralski method after orienting the sample to within 0.3° of the (001) plane. The surface was polished mechanically with diamond paste and then electrolytically in nitric acid–methanol (1:1) solution at 233 K. This scheme of moderate sample preparation is considered to minimize surface defects and strains. The crystal was then mounted on a specimen holder; in order to avoid strain, small holes were bored by spark erosion near the four corners of the crystal, and this sample was suspended with thin copper wires. Final cleaning was achieved by successive cycles of argon-ion bombardment and annealing to $\sim$800 K until AES exhibited no impurities and LEED showed very sharp and well-contrasted patterns. The LEED observation or AES measurements were performed under deposition of potassium. Potassium atoms were deposited by using a SAES dispenser (from S.A.E.S. Getters), which was mounted close to the front of the copper sample with much caution not to disturb the electron flux. The amount of adsorbed potassium was monitored by recording the *LMM* Auger peak (250 eV) of potassium as a function of the deposition time, with a constant potassium flux at a substrate temperature of 330 K. The peak-to-peak height of the K Auger spectrum increased linearly with the deposition time until a saturation coverage, which corresponds to monolayer completion, was attained. The pressure during the experiments was maintained below 1×10^{-8} Pa. No Auger signal of oxygen impurity was detected even an hour after the potassium deposition.

The LEED pattern clearly shows that the potassium overlayer undergoes three sequential transitions with increasing coverage[14]: short-range order to long-range order (commensurate), commensurate to commensurate, and commensurate to incommensurate. The LEED pattern first exhibited halos at a lower coverage ($0.15 < \theta < 0.3$); this implies

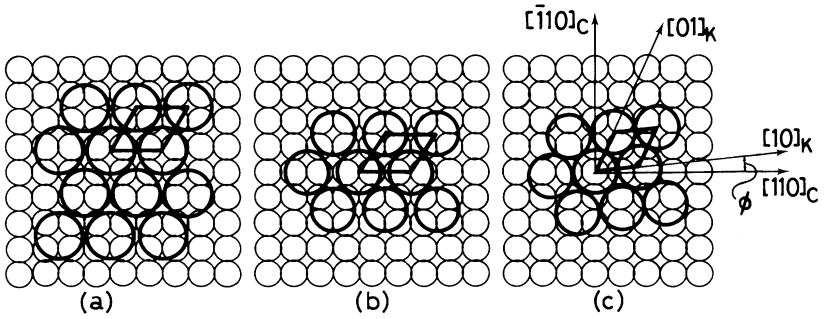

FIG. 1. Models for potassium monolayers (large circles) adsorbed on copper (001) surface (small circles): (a) the C-1 structure, whose unit mesh is $\begin{pmatrix}2&3\\0&5\end{pmatrix}$; (b) the C-2 structure, whose unit mesh is $\begin{pmatrix}2&2\\0&3\end{pmatrix}$; (c) the incommensurate structure. The [10] and [01] axes of the potassium monolayer are denoted by $[10]_K$ and $[01]_K$, and the [110] and $[\bar{1}10]$ axes of copper by $[110]_C$ and $[\bar{1}10]_C$.

that K adatoms are ordered in a rather short range. The mean interatomic spacing was estimated from a radius of the halo to be about 5.8 Å. Models for the two commensurate structures (C-1 and C-2) and the incommensurate structure are shown in Fig. 1. The C-1 phase appeared at $\theta = 0.29$ following the short-range–order phase. The unit mesh of the C-1 structure is an oblique lattice [Fig. 1(a)] distorted slightly from a hexagonal one and is commensurate with the substrate square lattice. The C-1 structure was further distorted to another oblique lattice, the C-2 structure [Fig. 1(b)], at $\theta \geq 0.3$. At $\theta = 0.33$ the potassium monolayer underwent a commensurate-incommensurate transition and became a nonregistered hexagonal lattice [Fig. 1(c)]. Details of these transitions will be discussed in a separate paper,[14] since the present Letter is mainly concerned with the characteristic behavior of an incommensurate potassium monolayer.

A typical LEED pattern of an incommensurate structure at $\theta = 0.37$ and for an incident electron energy of 53 eV is shown in Fig. 2; its schematic representation is shown in Fig. 3. Twelve pairs of superlattice spots located on a circle correspond to four equiprobable hcp domains rotated by $\pm\phi$ from either the [110] or the $[\bar{1}10]$ axis of the Cu substrate. A model for one of the domains is shown in Fig. 1(c). The unit mesh is a hexagonal lattice with its [10] axis rotated by ϕ from the [110] axis of the Cu(001) surface. A diffuse spot between each pair of these spots is also seen in Fig. 2. These diffuse spots originate from patches of overlayers which are registered by some surface defects. Besides these first-order diffraction beams there are several extra spots, which can be accounted for by double diffrac-

FIG. 2. LEED pattern of a potassium monolayer on copper (001) for $\theta = 0.37$, at incident electron energy of 53 eV, and substrate temperature of 330 K.

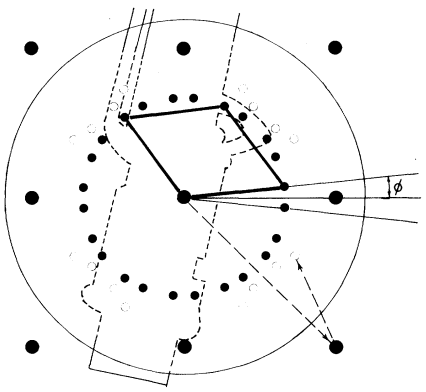

FIG. 3. Schematic representation of the observed LEED pattern for the incommensurate structure. The large and small filled circles represent the copper fundamental spots and the potassium superstructure spots, respectively. The spots denoted by the open circles are due to double diffraction, whose typical process is shown by broken arrows. Faint spots from nonrotated domains are not shown. The area surrounded by the broken lines is shaded by the specimen holder shown in Fig. 2.

tion by both the substrate lattice and the overlayer superlattice.

As shown in Fig. 4, ϕ decreases nearly linearly with increasing d. This result is similar to those for rare-gas monolayers on graphite[2-4] despite the very different properties of these adsorption systems. In the present case, where alkali-metal atoms are chemisorbed on a metal substrate, the adatom-adatom interaction and the adatom-substrate interaction are entangled with each other in contrast with the case of rare-gas atoms on graphite, in which case the interactions are simply pairwise additions of the atom-atom van der Waals interactions.

The electronic properties of alkali-metal atoms adsorbed on solid surfaces can be considered as follows. At a lower coverage the alkali-metal adsorption can be described in terms of the atomic valence level,[15] where an extensive charge transfer from the adatoms to the substrate occurs and the interaction between the cationic adatoms can be expressed by both the direct electrostatic repulsion and the interaction through the substrate. On the contrary, at a higher coverage where the adatom-adatom overlap becomes more extensive, the alkali-metal atom overlayers are well characterized by a two-dimensional metal[16] whose cohesive energy surpasses the interaction with the substrate. This picture is supported by our recent electron spectroscopic and thermal desorption studies.[14,17,18]

According to the above argument, a potassium monolayer chemisorbed on copper near the saturation coverage can be approximated as a two-dimensional elastic body lying on a lateral periodic potential. Thus the general equations of NM[5] and Shiba[6] are applicable to the present system, although it is difficult to evaluate each energy with accuracy comparable with the experimental results.

Static distortion of potassium monolayers can, in principle, produce satellite spots.[5] While a part of them overlap with double-diffraction spots, others are expected to appear separately. However, we have not observed any of these satellites, as in the case of rare-gas monolayers.[2-4] There still remains the possibility that a periodic distortion in the substrate lattice is caused by the lateral potential of the K monolayers. This possibility has been disregarded by NM and Shiba in their rigid-substrate models, since these authors discuss physisorption systems only. As yet we have not confirmed the modulation of the substrate lattice, since all the satellites produced by the modulation of the substrate lattice coincide with the double-diffraction spots.

When we used a copper substrate of rather high defect density which was prepared by the Bridgman method, the rotation of K monolayers was not observed in the whole incommensurate phase. The existence of nonrotated incommensurate states has also been reported in Cs on Cu(001)[19] and in several other chemisorption systems.[7] These systems should be reexamined by use of substrates with low enough defect density so as not to affect monolayer dynamics. We believe that rotational epitaxy, which was first predicted for physisorbed rare-gas monolayers, does exist in a wider range of adsorption systems.

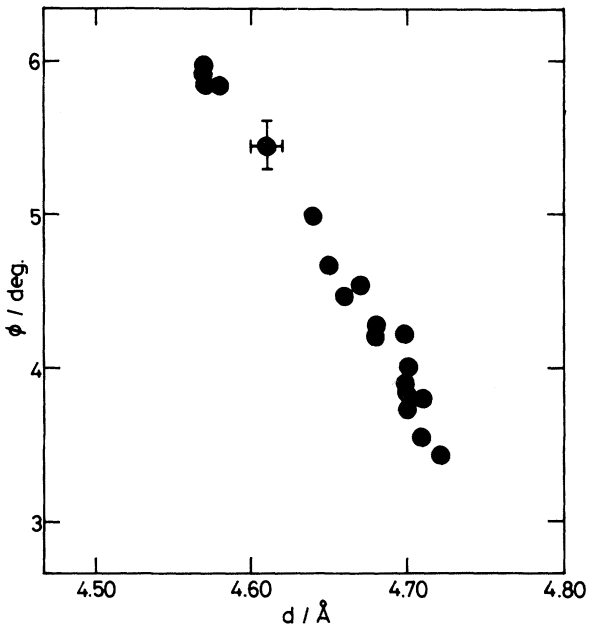

FIG. 4. Orientation angle ϕ vs potassium interatomic spacing d. Error bars estimated from random errors in measuring ϕ and d are shown.

We thank Professor S. Takeuchi for kindly supplying a copper single crystal and Professor K. Kuchitsu for critically reading the manuscript. This work was supported by a Grant in Aid for Scientific Research from the Ministry of Education, Science, and Culture.

[1]A. D. Novaco and J. P. McTague, Phys. Rev. Lett. **38**, 1286 (1977).

[2]C. G. Shaw, S. C. Fain, Jr., and M. D. Chinn, Phys. Rev. Lett. **41**, 955 (1978).

[3]S. C. Fain, Jr., M. O. Chinn, and M. D. Diehl, Phys. Rev. B **21**, 4170 (1980).

[4]S. Calisti and J. Suzanne, Surf. Sci. **105**, L255 (1981).

[5]J. P. McTague and A. D. Novaco, Phys. Rev. B **19**, 5299 (1979).

[6]H. Shiba, J. Phys. Soc. Jpn. **46**, 1852 (1979).

[7]See, for instance, J. P. Biberian and G. A. Somorjai, J. Vac. Sci. Technol. **16**, 2073 (1979).

[8]G. A. Basset, in *Proceedings of the European Regional Conference on Electron Microscopy,* edited by A. L. Howink and B. J. Spit (de Nederlandse Vereniging Voor Electronenmikroskopie, Delft, The Netherlands, 1960).

[9]J. Perdereau, J. P. Biberian, and G. E. Rhead, J. Phys. F **4**, 798 (1974).

[10]K. Takayanagi and H. Kanamori, in Proceedings of the Fifth European Conference on Surface Science, Gent, Belgium, August 1982 (unpublished).

[11]I. A. S. Edwards and H. R. Thirsk, Surf. Sci. **39**, 245 (1973).

[12]H. Reiss, J. Appl. Phys. **39**, 5045 (1968).

[13]J. W. Mattews, in *Epitaxial Growth,* edited by J. W. Mattews (Academic, New York, 1976).

[14]T. Aruga, H. Tochihara, and Y. Murata, to be published.

[15]J. P. Muscat and D. M. Newns, Prog. Surf. Sci. **9**, 1 (1978).

[16]E. Wimmer, Surf. Sci. **134**, L487 (1983).

[17]H. Tochihara, Surf. Sci. **126**, 523 (1983).

[18]H. Tochihara, M. Kubota, T. Aruga, Y. Murata, and M. Miyao, Jpn. J. Appl. Phys. (to be published).

[19]C. A. Papageorgopoulos, Phys. Rev. B **25**, 3740 (1982).

FIG. 2. LEED pattern of a potassium monolayer on copper (001) for $\theta = 0.37$, at incident electron energy of 53 eV, and substrate temperature of 330 K.