

## Potassium-induced reconstruction of Ag(001)

Michio Okada, Hiroshi Tochihara,\* and Yoshitada Murata

*Institute for Solid State Physics, The University of Tokyo, 7-22-1, Roppongi, Minato-ku, Tokyo 106, Japan*

(Received 2 April 1990; revised manuscript received 7 September 1990)

Low-energy-electron-diffraction patterns on the K-adsorbed Ag(001) surface were observed as a function of K coverage at two different temperature ranges of 315–335 and 125–150 K and remarkably different changes in the surface structure were found, which are explained by the reconstruction of the substrate Ag(001) surface at higher temperatures. The K-induced reconstruction occurs above 190 K and is given by a model of the missing-row type.

The interaction of atoms and molecules with surfaces has been investigated extensively for a few decades. Alkali-metal adsorption on metal surfaces is one of the most typical systems for the studies of such interaction, since an alkali-metal atom has only one valence electron and adsorbs with a weak chemical interaction. It is of importance for various applications that both the properties of alkali-metal overlayers and the influence of alkali-metal adsorption on substrates are elucidated.

Alkali-metal adsorption on Ag surfaces has been studied by several experimental methods.<sup>1–11</sup> In the study of the Li/Ag(111) system, Parker reported that Auger-electron spectroscopy (AES) and work-function measurements indicate the monolayer formation but the growth mechanism of the overlayer is complicated by slow diffusion into the bulk and more rapid diffusion at coverages beyond monolayer.<sup>1</sup> No new low-energy-electron-diffraction (LEED) patterns were observed during Li deposition. For Na on Ag(111) and Ag(110), Marbow and Lambert observed a distinct sharpening of the LEED beams from the substrate during the monolayer growth and implied that the ordering of the surface atoms is enhanced.<sup>2</sup> In the alkali-metal/Ag(110) system, the adsorption-induced reconstruction of the substrate was observed.<sup>3–5</sup> On the other hand, only a few studies of alkali metals on Ag(001) have been reported. Kitson and Lambert<sup>6</sup> and Bowker *et al.*<sup>7</sup> did not detect any ordered structures for K adsorption on Ag(001) and explained by diffusion into the substrate. It was also reported that Na atoms penetrate into the subsurface of Ag(001).<sup>8</sup>

In the present paper, we report the surface structure changes as a function of K coverage on the K/Ag(001) system at two different temperature ranges of 315–335 and 125–155 K. Very anomalous features at 315–335 K were found as compared with those of other K/fcc(001) metal systems; Ni(001),<sup>12</sup> Cu(001),<sup>13</sup> Ir(001),<sup>14</sup> Al(001),<sup>15</sup> and Pd(001).<sup>16</sup> On the other hand, the results at 125–150 K were similar to those of other systems. The 2×1 and 3×1 patterns for K/Ag(001) observed at 315–335 K can be assigned to the missing-row-type reconstruction of the substrate Ag(001) surface. The present result is clearly different from those reported by Kitson and Lambert<sup>6</sup> and Bowker *et al.*<sup>7</sup> However, their results suggest that an alkali-metal atom can induce a stress on the surface

region and moves away from the substrate surface atoms on Ag(001). It has been observed that alkali-metal-induced reconstruction takes place on the fcc(001) metal surface, although the alkali-metal-induced reconstruction was observed on several fcc(110) metal surfaces; Ni(110),<sup>17</sup> Ag(110),<sup>3–5</sup> Cu(110),<sup>18</sup> Pd(110),<sup>19</sup> and Au(110).<sup>20</sup> Some theoretical studies were carried out for interpreting the mechanism of alkali-metal-induced reconstruction of fcc(110) metal surfaces.<sup>21–24</sup>

The experiments were performed in an ultrahigh-vacuum chamber with a base pressure of  $1 \times 10^{-8}$  Pa. A Ag crystal was polished mechanically and was held on a tantalum foil. A Pt-PtRh(13%) thermocouple was inserted between the sample and the tantalum foil. The sample holder was in contact with a liquid N<sub>2</sub> (or liquid He) 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 to 530–600 K until no impurities could be detected by AES and until LEED showed a sharp 1×1 pattern. K atoms were deposited from a commercial SAES getter source. The observation of LEED patterns and the measurement of AES were carried out by the use of four-grid LEED optics under the K deposition. The absolute value of K coverage  $\Theta$ , which is defined as a ratio of the number density of K atoms to that of the Ag(001) surface atoms, was determined by normalization at  $\Theta=0.25$ , where the maximum LEED intensity of the  $c(4 \times 2)$  pattern was observed at low temperatures.

Four types of LEED patterns were observed during K deposition at 315–335 K (Fig. 1). A sharp 2×1 LEED pattern appeared at a low coverage of  $\Theta \approx 0.1$  [Fig. 1(b)]. The 2×1 pattern was accompanied with a very faint  $c(4 \times 3)$  pattern. The faint  $c(4 \times 3)$  pattern became clearer when the sample at  $\Theta \approx 0.19$  was cooled to about 150 K [Fig. 1(c)]. At a higher K coverage, the 2×1 pattern accompanied with the faint  $c(4 \times 3)$  pattern turned into a 3×1 pattern [Fig. 1(d)]. The 3×1 pattern was not observed during K deposition at higher temperatures (375–395 K); only the 2×1 pattern was observed. Moreover, the 3×1 pattern changed into the 2×1 pattern gradually after the K source was turned off. These facts show that the 3×1 pattern is equilibrated at K coverages higher than a stable coverage without K flux.

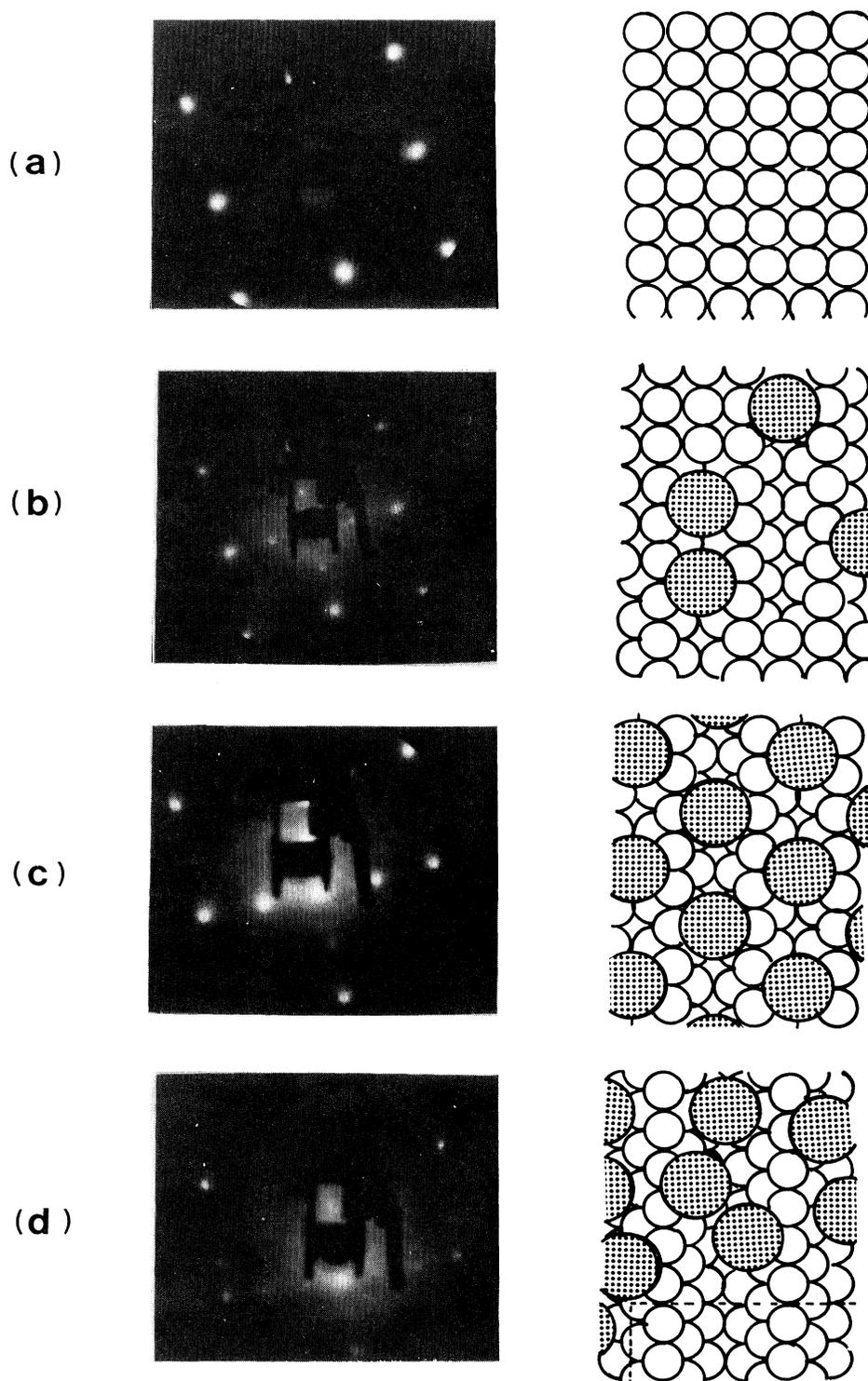


FIG. 1. Change of LEED patterns of the K-covered Ag(001) surface prepared at 315–335 K. (a) Clean Ag(001) surface, primary energy  $E_p = 60$  eV; (b)  $\Theta \approx 0.1$ ,  $2 \times 1$  pattern,  $E_p = 58$  eV; (c)  $\Theta \approx 0.19$ ,  $2 \times 1$  pattern accompanied with a faint  $c(4 \times 3)$  pattern observed at  $\sim 150$  K,  $E_p = 53$  eV; and (d)  $3 \times 1$  pattern,  $E_p = 53$  eV. Right-side pictures show corresponding structure models in real space.

The change of the LEED intensity as a function of K coverage is shown for three spots of  $(\frac{1}{2}0)$ ,  $(\frac{2}{3}\frac{1}{4})$ , and  $(\frac{1}{3}0)$  in Fig. 2. We divided the sequence of the surface structure change into four regions: I, II, III, and IV. In region I, the K overlayer takes the disordered structure. In region II, the  $2\times 1$  and faint  $c(4\times 3)$  structures develop, but the " $c(4\times 3)$ " pattern is so faint that we could not assign the pattern exactly. The  $2\times 1$  pattern emerges before the  $c(4\times 3)$  pattern appears. The  $(\frac{1}{2}0)$  spot of the  $2\times 1$  and the  $(\frac{2}{3}\frac{1}{4})$  spot of the  $c(4\times 3)$  pattern have the maximum intensity at the same K coverage. In region III, the  $2\times 1$  and faint  $c(4\times 3)$  structures change into the  $3\times 1$  structure and the  $3\times 1$  structure develops, as the intensity of the  $2\times 1$  LEED pattern decreases. In region IV, only the  $3\times 1$  structure appears. The spot intensity of the  $3\times 1$  LEED pattern does not change, although K coverage increases.

The LEED pattern found at 125–150 K showed a quite different pattern change from that found at 315–335 K. Figure 3 shows the changes of the LEED pattern observed at 315–335 K and at 125–150 K as a function of K coverage. The change at 125–150 K is similar to that in other K-absorbed fcc(001) metal systems.<sup>12,13,15</sup> When the surface showing the streak pattern of  $\Theta \approx 0.18$  prepared at low temperatures was heated, the LEED pattern changed into the  $2\times 1$  structure at about 190 K.

At first, we discuss the surface structure model speculated from the LEED patterns observed at 315–335 K, as compared with those observed at 125–150 K and those in other K/fcc(001) metal systems.<sup>12–16</sup> Usually, the LEED pattern change is caused by the K-overlayer structure change. If the  $2\times 1$  structure observed at 315–335 K is also formed by a K-overlayer arrangement, the K coverage should be 0.5 and the LEED pattern observed

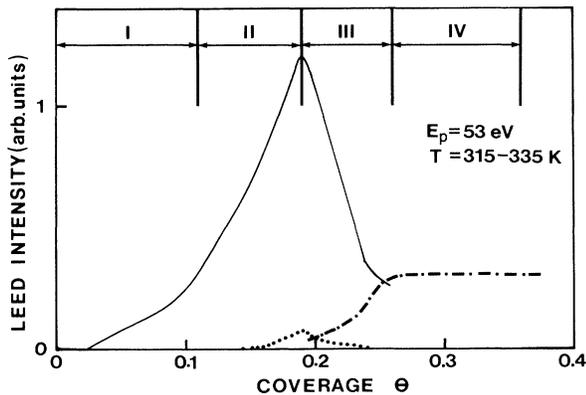


FIG. 2. LEED-intensity-vs-coverage curves for  $(\frac{1}{2}0)$ ,  $(\frac{2}{3}\frac{1}{4})$ , and  $(\frac{1}{3}0)$  spots are expressed by solid, dotted, and dot-dashed lines, respectively.  $E_p = 53$  eV and  $T = 315\text{--}335$  K. The sequence of the change is divided into four regions: I, II, III, and IV.

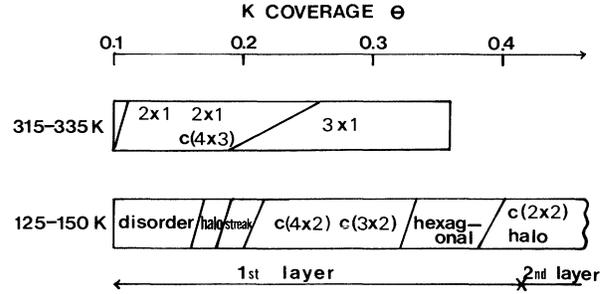


FIG. 3. Changes of the LEED pattern of the surfaces prepared at 315–335 K (upper part) and at 125–150 K (lower part) as a function of K coverage.

at lower temperature is expected to indicate a change similar to that observed at 315–335 K. However, the present experimental results are quite different. Moreover, considering the atomic radius of a K atom, it is very difficult for the K overlayer to take the  $2\times 1$  commensurate structure with the coverage of 0.5. So, this  $2\times 1$  structure is considered to be given by the substrate reconstruction. This consideration is supported by the following observations. The streak pattern obtained by K deposition at 125–150 K changed irreversibly into the  $2\times 1$  pattern without K desorption at 190 K, when the sample was heated up. When more K atoms were deposited at

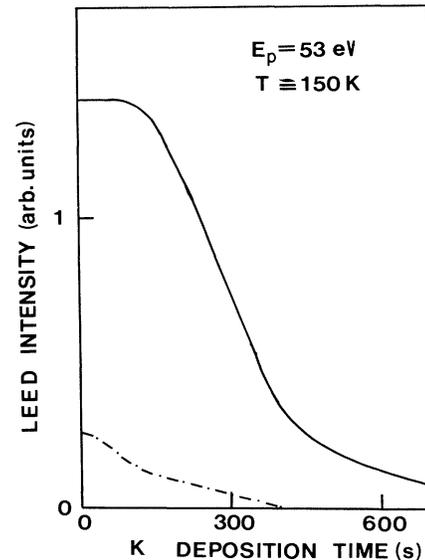


FIG. 4. LEED-intensity-vs-deposition-time curves for  $(\frac{1}{2}0)$  and  $(\frac{2}{3}\frac{1}{4})$  spots are shown by solid and dot-dashed lines, respectively. The surface was prepared by K deposition at  $\sim 330$  K with the maximum intensity of these two spots. K deposition was carried out at 150 K.

about 150 K on the surface of the  $2 \times 1$  and the faint  $c(4 \times 3)$  structure prepared by K deposition at  $\sim 320$  K, no new structure appeared but the intensity of LEED spots changed, as shown in Fig. 4. The  $2 \times 1$  pattern did not disappear even when 1.5 monolayers of K atoms were deposited. The fact that the  $3 \times 1$  structure was not induced in the above experiment supports the structure model that the  $3 \times 1$  pattern is also made by the substrate reconstruction.

The  $3 \times 1$  structure should be closely correlated with the  $2 \times 1$  structure, since the  $3 \times 1$  pattern developed as the  $2 \times 1$  pattern declined in region III, as shown in Fig. 2. The LEED pattern in region III was accompanied with a faint streak along the [10] direction. So, the  $3 \times 1$  pattern is considered to originate in the structure of the Ag substrate. The transition from  $2 \times 1$  to  $3 \times 1$  structure on the substrate surface occurs in region III and is completed at the end of this region. The  $(\frac{1}{3}0)$  intensity was constant in spite of K coverage increase in region IV, as shown in Fig. 2. If the  $3 \times 1$  structure were a K overlayer structure, the LEED intensity would increase with increasing K coverage. In region IV, the disordered K overlayer grows and is equilibrated with the impinging K flux.

Several models of the substrate reconstruction are considered for the  $2 \times 1$  structure; the missing-row, paired-row, saw-tooth, and buckled-surface models. It is most probable to assign the  $2 \times 1$  structure to the missing-row model from the insight based on the fcc(110) results [Fig. 1(c)],<sup>3-5,17-20</sup> and moreover, Heine and Marks presented in their paper<sup>21</sup> the possibility of the existence of alkali-metal-induced reconstruction on Ag(001). We can also assign the  $3 \times 1$  structure to the missing-row model similarly [Fig. 1(d)].

The  $c(4 \times 3)$  pattern originates from the K-overlayer structure, since the intensity of the  $c(4 \times 3)$  pattern decreased more rapidly than that of the  $2 \times 1$  pattern with increasing coverage. The maximum intensities of the  $(\frac{1}{2}0)$  and  $(\frac{2}{3}\frac{1}{4})$  spots were observed at the same coverage, as shown in Fig. 2, but the intensity of the  $(\frac{2}{3}\frac{1}{4})$  spot is much weaker than that of the  $(\frac{1}{2}0)$  spot. When the sample was cooled down to 150 K without more K deposition, the intensity of the spots originating in the  $c(4 \times 3)$  structure increased more effectively than the intensity of the half-order spots, as seen in the comparison between Figs. 2 and 4. These results show that the disordered part of the K overlayer is dominant at  $\sim 320$  K and the ordered domain of the  $c(4 \times 3)$  structure takes wider area at low temperatures. That is, the order-disorder transition occurs on the K overlayer. Then, we propose a structure model shown in Fig. 1(c) for the  $(2 \times 1) + c(4 \times 3)$  structure.

This model is supported by the data concerning the work-function change and low-resolution electron-energy-loss spectroscopy, which were also measured by the use of four-grid LEED optics under the K deposition with the aid of a computer-controlled system.<sup>25</sup>

Next, we discuss the reconstruction mechanism. Theoretical studies have been carried out for the alkali-metal-induced reconstruction of fcc(110) metal. Heine

and Marks suggested the mechanism of the attractive force from *sp* electrons.<sup>21</sup> The donation of an electron from alkali-metal atom to the noble metal increases the electron density in the surface. The flow of more mobile *sp* electrons into the attractive outer edge of the core leads to the instability at surface regions; the normal expansive and tangential contractive force at flat surface regions and the expansive force at the surface step regions. From this consideration, they predicted that alkali metals will probably also induce Ag(001) to reconstruction. The reconstruction is considered to take place initially at surface-step regions. The missing-row-type reconstruction will be stabilized by contractive force due to *sp* electrons.

Jacobsen and Nørscov calculated the chemisorption energy and equilibrium configuration for K/Cu(110) by the effective-medium theory.<sup>22</sup> They reported that the alkali-metal-induced reconstruction was attributed to local adsorbate-substrate bonding effects. Namely, the adsorbed K atom gets a larger effective Cu coordination number on the reconstructed surface than the unreconstructed surface and stabilizes the Cu atoms on the ridge of the missing-row structure. So, the missing-row reconstruction is stabilized. In the present K/Ag(001) case, the Ag coordination number of the K atom adsorbed on the missing-row-reconstructed surface is 6, which is larger than 4 in the case of K adsorption on the unreconstructed surface. Then, the K chemisorption energy may surpass the substrate instability energy, and the missing-row reconstruction can be stabilized. Fu and Ho investigated the effect of external fields on the structural and electronic properties of Ag(110) using the local-density-functional method<sup>24</sup> supported by the theory of Ho and Bohnen.<sup>23</sup> They included all effects of charge transfer in the calculation, and concluded that the mechanism of the missing-row reconstruction induced by alkali-metal-atom adsorption is a combination of the unique fcc(110) surface geometry and the tendency for spreading out of *sp* electron kinetic energy.

In the case of K/Ag(001), the  $2 \times 1$  structure does not have as large a surface facet area as in K/Ag(110). However, the *sp*-like induced charge distribution is considered to be smoother than that of the  $1 \times 1$  structure. The lowering in electron kinetic energy and the enhanced K chemisorption energy are expected to overcome the rise in the surface potential energy even in Ag(001) [fcc(001)], when substrate atoms in the row are removed due to K adsorption. Fu and Ho also showed that the charged surface undergoes a structural transformation from  $1 \times 1$  to  $2 \times 1$  as the number of induced electrons reaches a value of  $q_c \approx 0.05e/(\text{surface atom})$ . Since the potassium-induced reconstruction of Ag(001) was observed at  $\Theta \geq 0.1$ , the present result is  $q_c \geq 0.1 e/(\text{surface atom})$  and larger than the calculated value for Ag(110). This argument shows that the enhancement of the surface potential in the reconstruction of Ag(001) is larger than that of Ag(110). The driving force of the  $3 \times 1$  reconstruction is similarly the lowering in the induced electron kinetic energy.

The origin of potassium-induced reconstruction of

Ag(001) is considered to be the same as that of alkali-metal-induced reconstruction of fcc(110) surfaces. So the present study will be very helpful in elucidating the mechanism of alkali-metal-induced reconstruction of metal surfaces. Few experimental studies of the electronic structures and properties are available, though such information is needed to elucidate the mechanism of alkali-metal-induced reconstruction of metal surfaces. So the experimental studies of electronic structures and

properties are expected to be done in a future study. Additionally, for the present K/Ag(001) system, the structural determination by LEED or ion-scattering spectroscopy will be desired for more exact discussion.

This work is supported by the Grant-in-Aid for the Scientific Research from the Ministry of Education, Science, and Culture.

---

\*Present address: Catalysis Research Center, Hokkaido University, Kita-ku, Sapporo 060, Japan.

<sup>1</sup>S. D. Parker, *Surf. Sci.* **157**, 261 (1985).

<sup>2</sup>R. A. Marbow and R. M. Lambert, *Surf. Sci.* **61**, 329 (1976).

<sup>3</sup>B. E. Haydan, K. C. Prince, P. J. Davie, G. Paolucci, and A. M. Bradshaw, *Solid State Commun.* **48**, 325 (1983).

<sup>4</sup>J. M. Frenken, R. L. Krans, J. F. van der Veen, E. Houlb-Krappe, and K. Horn, *Phys. Rev. Lett.* **59**, 2307 (1987).

<sup>5</sup>C. J. Barnes, M. Lindroos, D. J. Holmes, and D. A. King, *Surf. Sci.* **219**, 1438 (1989).

<sup>6</sup>M. Kitson and R. M. Lambert, *Surf. Sci.* **109**, 60 (1981).

<sup>7</sup>M. Bowker, B. Wolfendale, D. A. King, and G. Lamble, *Surf. Sci.* **192**, 95 (1987).

<sup>8</sup>E. L. Garfunkel, X. Ding, G. Dong, S. Yang, X. Hou, and X. Wang, *Surf. Sci.* **164**, 511 (1985).

<sup>9</sup>G. M. Lamble, R. S. Brooks, D. A. King, and D. Norman, *Phys. Rev. Lett.* **61**, 1112 (1988).

<sup>10</sup>A. Fäldt, *Surf. Sci.* **114**, 311 (1982).

<sup>11</sup>P. M. Blass, X. L. Zhou, and J. M. White, *Surf. Sci.* **215**, 74 (1989).

<sup>12</sup>S. Anderson and U. Jostell, *Solid State Commun.* **13**, 829

(1973).

<sup>13</sup>T. Aruga and Y. Murata, *Prog. Surf. Sci.* **31**, 61 (1986).

<sup>14</sup>K. Heinz, H. Hertrich, L. Hammer, and K. Müller, *Surf. Sci.* **152/153**, 303 (1985).

<sup>15</sup>M. Okada, H. Tochiyama, and Y. Murata (unpublished).

<sup>16</sup>A. Bercko and F. Solymosi, *Surf. Sci.* **187**, 359 (1987).

<sup>17</sup>R. J. Behm, D. K. Flynn, K. D. Jamison, G. Ertl, and P. A. Thiel, *Phys. Rev. B* **36**, 9267 (1987).

<sup>18</sup>M. Copel, W. R. Graham, T. Gustafsson, and S. Yalisove, *Solid State Commun.* **54**, 695 (1985).

<sup>19</sup>C. J. Barnes, M. Lindroos, and D. A. King, *Surf. Sci.* **201**, 108 (1988).

<sup>20</sup>P. Haberle, P. Fenter, and T. Gustafsson, *Phys. Rev. B* **39**, 5810 (1989).

<sup>21</sup>V. Heine and L. D. Marks, *Surf. Sci.* **165**, 65 (1986).

<sup>22</sup>K. W. Jacobsen and J. K. Nørskov, *Phys. Rev. Lett.* **60**, 2496 (1988).

<sup>23</sup>K. M. Ho and K. P. Bohnen, *Phys. Rev. Lett.* **59**, 1833 (1987).

<sup>24</sup>C. L. Fu and K. M. Ho, *Phys. Rev. Lett.* **63**, 1617 (1989).

<sup>25</sup>M. Okada, H. Tochiyama, and Y. Murata, *Surf. Sci.* (to be published).

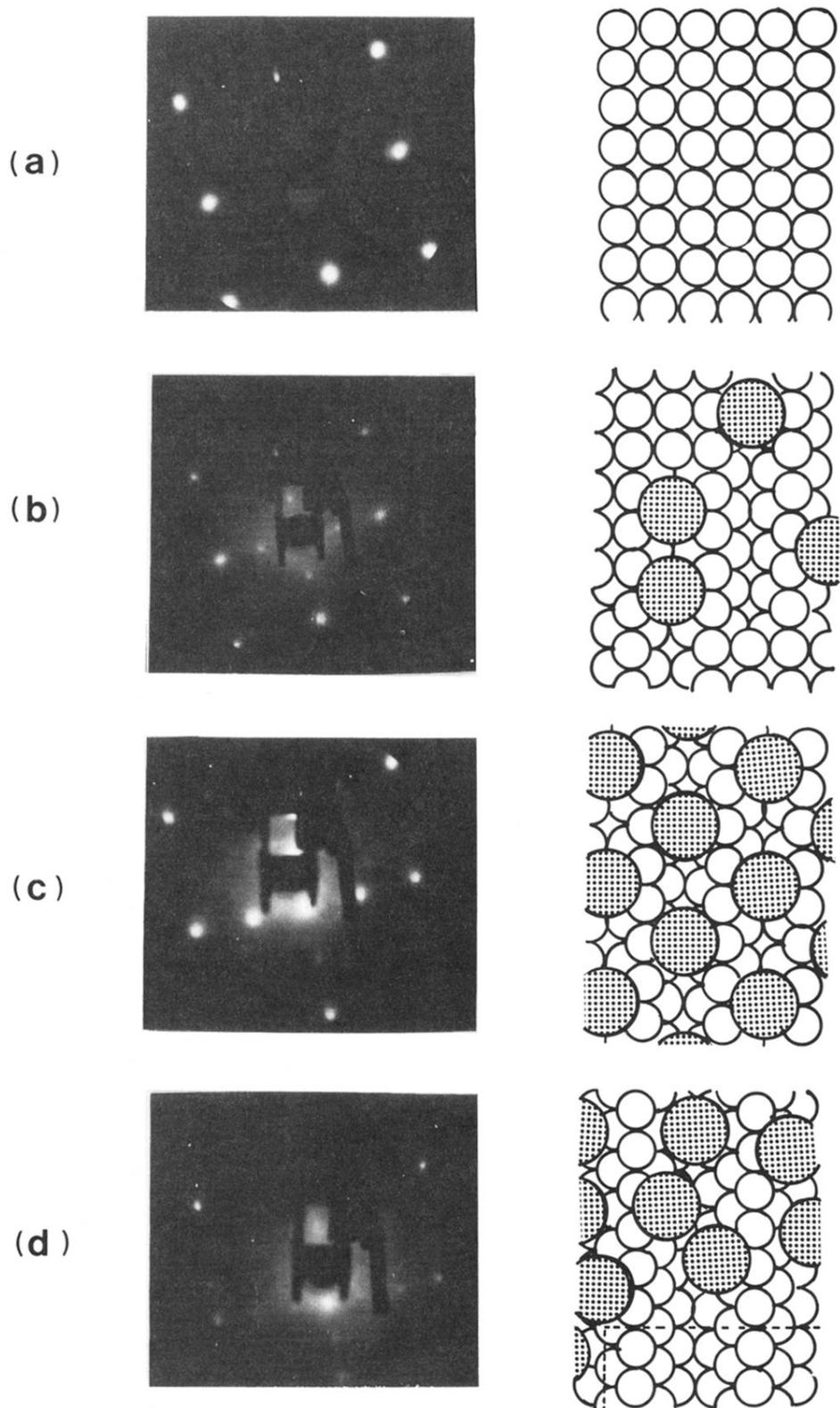


FIG. 1. Change of LEED patterns of the K-covered Ag(001) surface prepared at 315–335 K. (a) Clean Ag(001) surface, primary energy  $E_p = 60$  eV; (b)  $\Theta \approx 0.1$ ,  $2 \times 1$  pattern,  $E_p = 58$  eV; (c)  $\Theta \approx 0.19$ ,  $2 \times 1$  pattern accompanied with a faint  $c(4 \times 3)$  pattern observed at  $\sim 150$  K,  $E_p = 53$  eV; and (d)  $3 \times 1$  pattern,  $E_p = 53$  eV. Right-side pictures show corresponding structure models in real space.