# Observation of growth and structure of Kr films physisorbed on Ag(111) and Ag(100)

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The structure and growth of two-dimensional crystals of Kr on Ag(111) and Ag(100) have been investigated by means of ellipsometry and eXtremely-low-current Low Energy Electron Diffraction (XLEED) under the quasi-equilibrium condition. The layering growth of a Kr film was observed up to the third layer by ellipsometry while the crystal geometry by XLEED. Kr overlayer on Ag(100) has two types of alignment. In the predominant alignment, one of the unit vectors aligns with <001> of Ag substrate, while in the other alignment with <011>. Kr−Kr spacing in monolayer on Ag is 10% larger than that of bulk.

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## 1. Introduction

The system of rare gas physisorbed on a metal surface has been studied for its interesting structure and phase transition in two-dimension since 1970's. Xe/Ag(111) has been intensively investigated to reveal the structure, the isosteric heat of adsorption and the two-dimensional phase diagram, whereas a few result of a Kr films on a metal surface has been reported.

Roberts and Pritchard observed a Kr monolayer film adsorbed on Ag(111) using low energy electron diffraction (LEED) and revealed that the Kr overlayer has incommensurate hexagonal structure with the substrate [1]. Ungris et al. found the structure and the thermodynamic property of Kr/Ag(111): the phase diagram, the monolayer lattice constant, latent heats of adsorption and isosteric heats [2].

In the case of a Kr film on a metal surface, desorption of Kr atoms by an electron beam is a serious problem in a conventional LEED system whose incident electron current is typically 1 μA. Roberts and Pritchard reported that the diffraction spots disappeared within 10−15 min [1]. Ungris et al. also reported that a Kr monolayer film at 40 K would be completely desorbed by an electron beam in several minutes [2]. Therefore, they either had to make experiments under the constant beam flux of Kr atoms which was sufficient to maintain an adsorbed layer or to measure the diffraction patterns before the coverage decreased due to electronic stimulated desorption (ESD).

The structure and layering growth of rare gas films on metal surfaces are determined by the balance of the adatom-adatom and adatom-surface interaction. The comparison between the same adsorbate on the different substrates and between the different adsorbates on the same substrate is a promising way to reveal how the subtle balance between the lateral and vertical interactions affects the growth and the structure of the overlayer. We have observed the system of Kr and Xe on Ag(111), Ag(110) and Ag(100). In our study, the thickness of the overlayer was observed by ellipsometry and the surface geometry by LEED. Ellipsometry has no restriction on surrounding pressure and does not destroy a physisorbed layer. Our LEED system was prepared to be free from ESD problem as described in Sec. 2.

We present here the results on the growth and the structure of Kr films on Ag(111) and Ag(100) obtained using these two techniques and discuss how the substrate geometry affects the structure of the overlayer. Comparison between the results on Xe/Ag(111), Xe/Ag(100) and Kr/Ag(111), Kr/Ag(100) systems is also made.

## 2. Experimental

Our experimental system makes it possible to observe the surface geometry by XLEED and the film growth by ellipsometry simultaneously [3]. The schematic diagram is shown in Fig. 1. The observation of
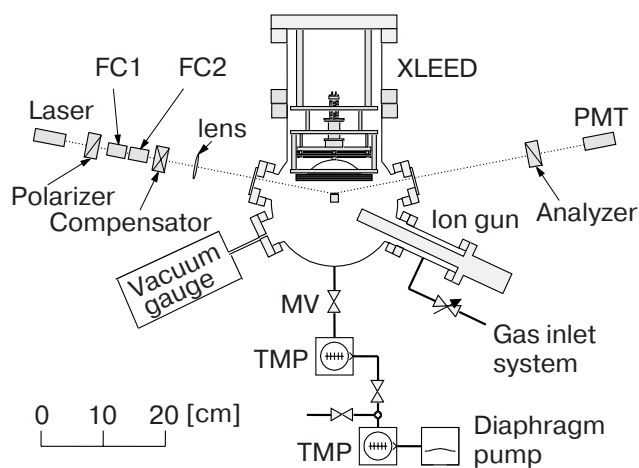
*Fig. 1*. Schematic diagram of our experimental system.

the layer growth can be made under the quasi-equilibrium condition because ellipsometry has no restriction on surrounding pressure.

Our XLEED system utilizes the position sensitive detector using a micro channel-plate (MCP) electron multiplier in a pulse counting mode [3]. The detection area is 75 mm in diameter. The incident electron beam current was about 1 pA which was adjusted so that the total electron counts became $10^5$–$10^6$ over the whole detector area for one minute data accumulation which yielded a sharp diffraction pattern with enough statistics for analysis.

The thickness of an adsorbed film was determined by the ellipsometric parameters; «relative phase shift» $\Delta$ and «amplitude reflectance ratio» $\Psi$. The relative change in $\Delta$, $\delta\Delta = |\Delta - \Delta_0|$, where $\Delta_0$ is the shift for the bare substrate, is proportional to the overlayer coverage and has been used as a monitor of the amount of adsorption in the ellipsometric studies of physisorbed films on metal surfaces [4]. The ellipsometer is a polarizer-compensator-sample-analyzer (PCSA) automatic null system [3].

Silver substrates were prepared by repeated cycles of sputtering by a Kr ion (1 keV, 5–8 μA, 2 min) and annealing (700 K, 3 hours). The base pressure of the main chamber was $10^{-8}$ Pa or lower. The substrates of Ag(111) and Ag(100) are mounted side by side on the sample holder which was cooled by cold He gas.

### 3. Results

#### 3.1. The growth and the structure of Kr/Ag(111)

The diffraction patterns of Kr/Ag(111) are shown in Fig. 2,*a*, which demonstrates a hexagonal structure of the Kr monolayer film whose unit vectors align with those of the substrate. The ellipsometric isotherm
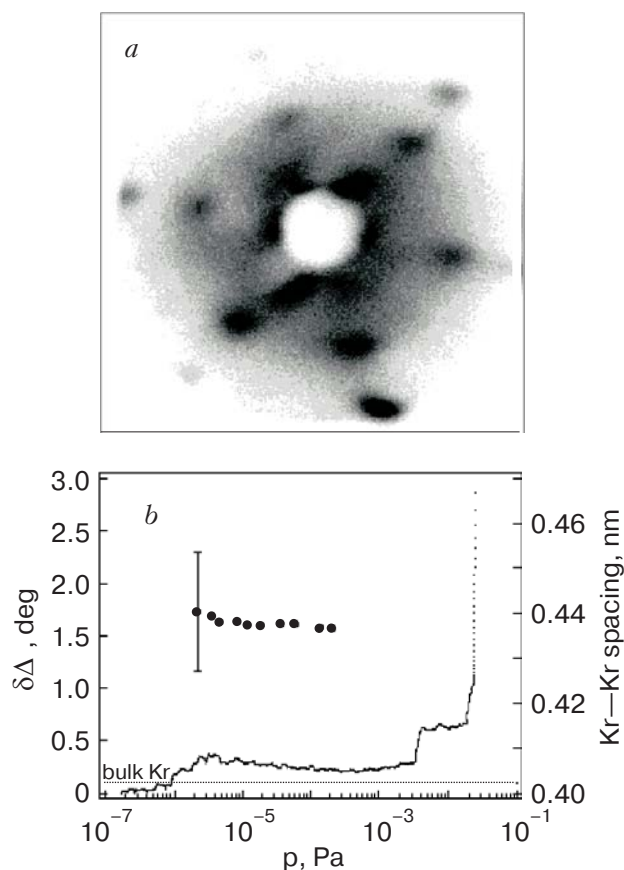


*Fig. 2*. (*a*) XLEED pattern of Kr monolayer on Ag(111). $E_i$ = 104 eV, $P$ = 3·$10^{-5}$ Pa, $T$ = 51.3 K. The incident electron energy was adjusted to the spots both Ag and Kr appeared: outside six-fold spots shows Ag and inside spots Kr. (*b*) Adsorption isotherm of Kr/Ag(111) (stepwise line) and Kr–Kr spacing (solid circle) at 50.5 K.

of Kr/Ag(111) at 50.5 K is shown in Fig. 2,*b*, where the isotherm is represented by the change in relative phase shift $\delta\Delta$ due to adsorption as a function of Kr pressure. The isotherm for Kr on Ag(111) has several steps. Each step is due to a first-order phase condensation where 2D gas and solid coexist and corresponds to the formation of one atomic layer. This isotherm for Kr − Ag(111) at 50.5 K plotted in Fig. 2,*b* shows layer by layer growth up to three atomic layers at least. A Kr–Kr spacing in the monolayer, measured by XLEED simultaneously, is also shown in Fig. 2,*b*. The interatomic distance was calculated using the spot distances in the diffraction pattern, the incident electron energy, the distance between the sample and the MCP, which was determined by the Ag spot distance in the diffraction pattern of bare Ag surfaces. The Kr–Kr spacing is 0.440 nm just after the first layer condensation and 0.436 nm before the second layer condensation; the monolayer compression ratio was less than 1%. The XLEED pattern of the monolayer Kr which has both Ag and Kr spots, as shown in
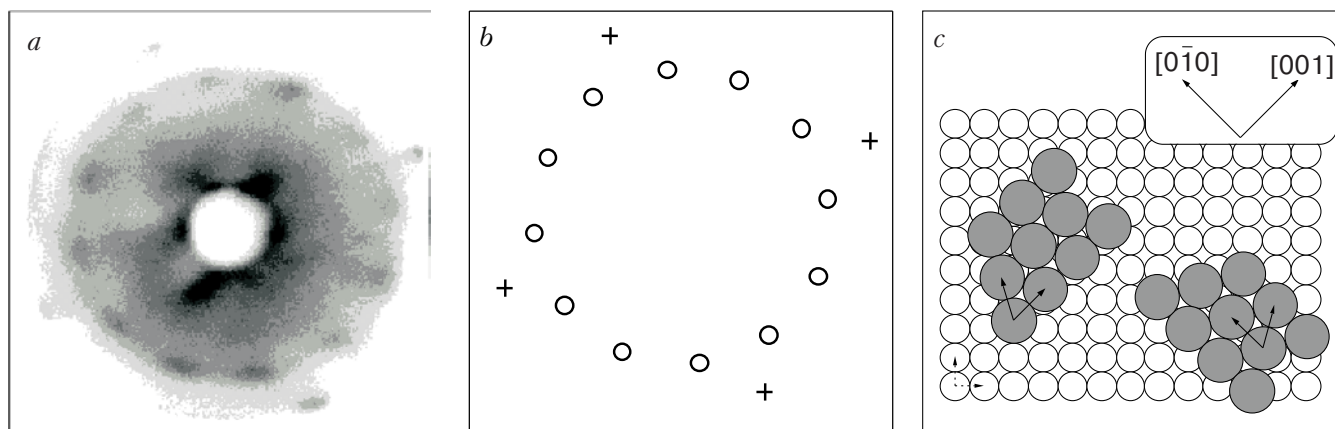
**Fig. 3.** (*a*) XLEED pattern of Kr / Ag(100). $E_i$ = 66.2 eV, $P$ = 3.0·10$^{-5}$ Pa, $T$ = 53.6 K. (*b*) Schematic of diffraction pattern shown in (*a*). Open circles show Kr spots and crosses show the substrate spots. (*c*) The illustration in the real space.

Fig. 2,*a*, was examined to confirm the absolute value of Kr−Kr spacing by direct comparison with Ag interatomic distance of 0.288 nm. It was confirmed that Kr−Kr spacing is about 8−9% larger than Kr bulk value of 0.403 nm [5]. The experimental errors were respectively about 1% for the Ag interatomic distance and 3% for Kr−Kr spacing because the spots of Kr were broader than the spots of the bare Ag.

### 3.2. The structure of Kr / Ag(100)

The structure of Kr films on Ag(100) was observed by XLEED. It was found that the Kr film on Ag(100) has two types of alignment; the corresponding diffraction patterns are shown in Fig. 3,*a* and Fig. 4,*a*. The scheme of the diffraction patterns and the arrangement of the atoms in the real space are shown in Figs. 3,*b,c* and Figs. 4,*b,c*, respectively. As shown in Fig. 3 one of the unit vectors of the Kr film aligns with <001> direction of Ag. We call this type of alignment «along Ag <001> type». On the other

hand, in Fig. 4 one of the unit vectors of the Kr film aligns with <011> of Ag: «along Ag <011> type». The systematic observation by scanning the sample surface with an incident electron beam revealed that the Kr film has both types of alignment but «along Ag <001> type» is predominant.

We observed that Kr−Kr spacing in the «along Ag <001> type» monolayer was 0.450 nm, which is 11% larger than that of bulk, as it was also observed for Kr / Ag(111) case.

## 4. Discussion

### 4.1. Kr−Kr *spacing of* Kr / Ag(111) *and* Kr / Ag(100)

The fact that Kr−Kr spacing is about 10% larger than that of bulk must be a matter of discussion. We obtained the similar results on both Ag(111) and Ag(100). Roberts and Pritchard studied the Kr−Kr
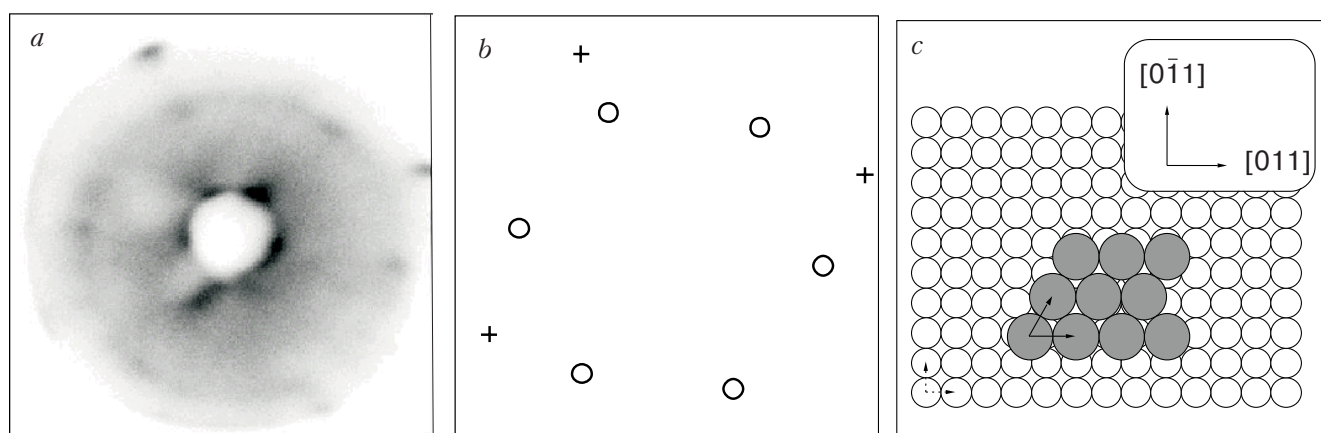


**Fig. 4.** (*a*) XLEED pattern of Kr / Ag(100). $E_i$ = 66.2 eV, $P$ = 3.0·10$^{-5}$ Pa, $T$ = 52.3 K. (*b*) Schematic of diffraction pattern shown in (*a*). Open circles show Kr spots and crosses show the substrate spots. (*c*) The illustration in the real space.

spacing on Ag(111) at 55 K and found that it was 0.419 nm [1]. Ungris et al. investigated Kr–Kr spacing by LEED in the temperature range between 10 and 60 K and obtained value 0.401–0.407 nm [2]. There is a considerable discrepancy in the absolute value of Kr–Kr spacing between our results and those reported by Roberts and Pritchard and by Ungris et al. This discrepancy cannot be attributed only to our experimental error of about 3%.

In the case of Xe/Ag(111), it was observed that Xe–Xe spacing just after the first layer condensation is about 3% larger than that of bulk. Xe–Xe spacing in the monolayer decreases gradually with increasing the pressure or lowering the temperature and reaches the bulk value before the second layer condensation [3]. We observed that in the case of Kr monolayer on Ag the monolayer compression ratio was no more than 1%. This result implies that the Kr film has a structure commensurate with the substrate.

It is known that rare gas films on Ag have structures incommensurate with the substrate. However, if a Kr film on Ag(111) may have Ag(111) 1.5×1.5 commensurate structure, Kr–Kr spacing will be 0.432 nm which is 7% larger than that of bulk Kr. This value is between our result and that of Roberts and Pritchard [1]. However, there is no adequate commensurate structure of Kr/Ag(100).

### 4.2. The structure of Kr/Ag(100)

It is well known that the alignment of a rare gas film on a metal surface is affected by the substrate steps. A Xe film on Ag(111) has incommensurate structure but the unit vectors of the overlayer align with the substrate ones. The reason for this alignment is explained by the inference that the overlayer is pinned by substrate steps and its alignment is determined by the step direction. Leatherman et al. has shown experimentally the effect of the surface steps on the alignment; when a small amount of CO or K is put on the surface to block the steps for rare gas adsorption, the nucleation occurs on a terrace and the overlayer grows in orientation rotated at a non-symmetric angle [6].

In the present study, we found that a Kr film on Ag(100) has two types of alignment and that «along Ag <001> type» is predominant. There are some possible reasons why «along Ag <001> type» is predominant.

The first inference is that most surface steps on Ag(100) are directed along <001> and Kr atoms nucleate at the step edge of the substrate. The second reason is that the steps of Ag(100) are directed along both <011> and <001>, and the step-pinning energy for the Kr film on <001> Ag step edge is larger than that on <011> step. The third circumstance is that Kr atoms

nucleate on the terrace of Ag(100) and its alignment is determined by Novaco and McTague effect [7].

It was also observed that a Xe film on Ag(100) has two types of alignment: «along Ag <001> type» and «along Ag <011> type», and there are, however, no preference between them.

The result that «along Ag <011> type» was observed in the case of Xe/Ag(100) contradicts the supposition that surface steps of Ag(100) are oriented only along <001> direction. The coexistence of two types of alignment can be interpreted by two possible reasons. The first reason is the combination of the step effect and the Novaco and McTague effect [7]: one type of alignment is determined by the step direction and the other by the Novaco and McTague effect. The second one is that the surface steps are along both <001> and <011> direction on Ag(100) and its alignment within the overlayer is determined by the step-pinning energy of overlayer atoms at the step edges.

The one-dimensional structure period of Ag(100) along <001> direction is 0.407 nm which is close to the Kr bulk value. This agreement should have a close relation to the preference of «along Ag <001> type» in the case of Kr/Ag(100). However, the value of 0.407 nm does not accord with our result described in Sec. 3.2. It is considered that, except for the agreement with one-dimensional periodicity, there are more complicated origins of Kr alignment.

Similar bi-structure system was found by Kiguchi et al.: an alkali halide monolayer film on a fcc metal surface. They reported that overlayer on the fcc(100) surface has two types of alignment: one of them is the expected growth and the other is not [8]. They concluded that the alignment is determined by the degree of surface diffusion. When the surface diffusion constant is large, alkali halide atoms diffuse on metal surface and nucleate at the step edges of the substrate, which cause the unexpected growth. They anticipated that the most surface steps of a fcc(100) surface would be along <011> direction of the substrate. However, the direct observation of the surface steps on fcc(100) has not been performed.

### 5. Summary

The structure and layer by layer growth up to the third layer of Kr films were investigated simultaneously by extremely-low-current low energy electron diffraction and ellipsometry. The XLEED pattern showed that a Kr monolayer film on Ag(100) has two types of alignment: «along Ag <001> type» and «along Ag <011> type». In the case of Kr/Ag(100), «along Ag <001> type» is predominant. The existence of two types of alignment was explained by two possible reasons: one is the combination of the step edge ef-

fect and the Novaco and McTague effect and another is the existence of surface steps along both <001> and <011> directions.

1. R.H. Roberts and J. Pritchard, *Surf. Sci.* **54**, 687 (1976).
2. J. Ungris, L.W. Bruch, E.G. Moog, and M.B. Webb, *Surf. Sci.* **109**, 522 (1981).
3. S. Igarashi, Y. Abe, Y. Irie, T. Hirayama, and I. Arakawa, *J. Vac. Sci. Technol.* **A16**, 974 (1998).
4. A. Itakura and I. Arakawa, *J. Vac. Sci. Technol.* **A9**, 1779 (1991).
5. M.L. Klein and J.A. Venables, in: *Rare Gas Solid*, vol. II, Academic Press (1977), p. 783.
6. G.S. Leatherman, R.D. Diehl, M. Karimi, and G. Vidali, *Phys. Rev.* **B56**, 6970 (1977).
7. A.D. Novaco and J.P. McTague, *Phys. Rev. Lett.* **38**, 1286 (1977).
8. M. Kiguchi, S. Entani, K. Saiki, H. Inoue, and A. Koma, *Phys. Rev.* **B**, to be published.