Reconstruction and growth of Ag on the Si(111)-$\sqrt{3} \times \sqrt{3}$-Ag surface at low temperature

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Surface reconstruction structures and epitaxial growth of Ag on the Si(111)-$\sqrt{3} \times \sqrt{3}$-Ag structure at low temperature (160-K order) have been investigated by reflection high-energy electron diffraction (RHEED). When Ag was deposited on a $\sqrt{3} \times \sqrt{3}$-Ag surface at 160 K, reconstruction structures $\sqrt{21} \times \sqrt{21}$ and 6×6 were observed in addition to the $\sqrt{3} \times \sqrt{3}$ structures. The $\sqrt{3} \times \sqrt{3}$ and $\sqrt{21} \times \sqrt{21}$ structures were observed for a thickness range between 0.19 and 2.6 ML, and the 6×6 structures appeared and coexisted with the $\sqrt{3} \times \sqrt{3}$ and $\sqrt{21} \times \sqrt{21}$ structure between 0.7 and 1.7 ML. From RHEED patterns analysis, a 6×6 model was proposed. Beyond Ag growth of 3 ML, three-dimensional (3D) Ag islands were formed at the temperature range from 160 K to RT. These results imply that the mean free path of Ag atoms on the $\sqrt{3} \times \sqrt{3}$-Ag surface is large enough even at 160 K that 2D nuclei cannot be formed on the terrace in spite of decreasing substrate temperature.

Many studies on surface reconstructions and epitaxial growth of Ag on Si(111) surface have been carried out. It is well known that Ag growth on the Si(111) surface depends greatly upon surface structure[1-3] and substrate temperature. Apparently, the substrate temperature plays an important role in the growth since it greatly affects the atomic diffusion. At room temperature (RT), the epitaxial growth of Ag(111) occurs. This is a typical case since Ag and Si do not form a silicide; in particular, composition change seems to be abrupt. At high temperature, Ag surface reconstruction and three-dimensional (3D) island growth will occur. Until now, however, Ag growth behavior at low temperature is still not understood.

Recently, we systematically studied the epitaxial growth of Ag on Si(111)-7×7 above 120 K by *in situ* reflection high-energy electron diffraction (RHEED) observations and intensity measurements. We did not observe any Ag reconstruction and measured much more RHEED intensity oscillations[4] between room temperature and 120 K. We concluded that Ag grew in the Stranski-Krastanov (SK) growth mode and 2D nuclei were formed on the flat three-dimensional islands of the Ag(111) surface; the growth was not nearly layer-by-layer growth, which was proposed by Jalochowski and Bauer.[1]

When Ag is deposited on a clean Si(111) surface at high temperature, a $\sqrt{3} \times \sqrt{3}$-Ag structure will be formed.[5] The $\sqrt{3} \times \sqrt{3}$-Ag structure has been intensively studied[6-9] since the $\sqrt{3} \times \sqrt{3}$ structure itself appears frequently in metal-adsorption structure on the Si(111) surface. The honeycomb-chained-trimer (HCT) Ag trimers model[10] was proposed for the $\sqrt{3} \times \sqrt{3}$-Ag structure and confirmed as the most reasonable model. This confirmed model can easily lead us to understand Ag growth on the $\sqrt{3} \times \sqrt{3}$-Ag structure.

This paper will describe a study of surface reconstruction and epitaxial growth of Ag on Si(111)-$\sqrt{3} \times \sqrt{3}$-Ag at low temperature by using RHEED. This study was reported partly in a previous paper.[9] Ag atoms deposited on the Si(111)-$\sqrt{3} \times \sqrt{3}$-Ag surface are highly mobile because the desorption energy of the Ag atoms on the $\sqrt{3} \times \sqrt{3}$-Ag structure is 34 kcal/mol, smaller than the

desorption energy 64 kcal/mol of Ag atoms from $\sqrt{3} \times \sqrt{3}$ directly.[11] With decreasing substrate temperature, the mean free path of diffusion of Ag atoms at the surface may become smaller, especially at low temperature. In this study, we carried out *in situ* observations and measured the intensity change of a specular beam during Ag deposition to investigate this diffusion change, because the change of the mean free path affects the intensity oscillation.

We used an ultrahigh vacuum (UHV) chamber equipped with a RHEED system, a sample holder for low temperature, and evaporation sources. The residual gas pressure of the chamber was less than 5×10^{-10} Torr, except during Ag deposition when it was about 2×10^{-9} Torr. The acceleration voltage of the electron beam was set at 15 keV. The substrate is a *p*-type Si(111) wafer with a resistivity of 50 Ω cm and the size was $25 \times 4 \times 0.4$ mm^3. Ag was deposited by using an alumina-coated W basket. Deposition rates were monitored with a quartz-crystal oscillator, and one monolayer (ML) used here corresponds to the number of Si atoms on the Si(111) surface, 7.84×10^{14} cm^{-2}. The Si wafer could be cooled down to low temperature by contacting the block of the sample holder with a liquid-nitrogen vessel. The temperatures were determined by using a Au-Fe thermocouple which was tightly put on the block, so there might exist some temperature difference between the sample surface and the block.

First, a clear 7×7 RHEED pattern was produced by heating the sample at 1200 °C several times. Secondly, a $\sqrt{3} \times \sqrt{3}$-Ag structure was fully formed by deposition of 1 ML Ag on the clean 7×7 surface at 500 °C. Then this sample was cooled down to a temperature between RT and 160 K. Thirdly, after enough sample cooling, Ag was deposited on the $\sqrt{3} \times \sqrt{3}$-Ag structure during RHEED *in situ* observation and intensity measurement. This measurement is a powerful method to help us to distinguish the growth mode, 2D layer, 3D island, or step-flow growth. The intensity of the RHEED specular spot was measured under a small incident angle, below 0.6°, which is between the 111 and 222 Bragg-reflection spots of bulk Si, and corresponds nearly to the out-of-phase
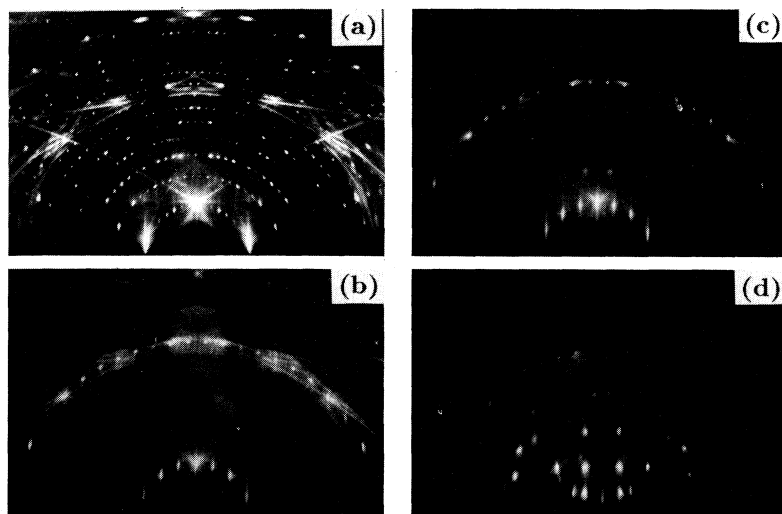
FIG. 1. (a) and (b) are RHEED patterns taken from the 7×7 and the $\sqrt{3}\times\sqrt{3}$-Ag structures at RT, respectively. (c) and (d) are the patterns after the deposition of 3 and 15 ML of Ag on the $\sqrt{3}\times\sqrt{3}$-Ag structure at RT, respectively.

condition (off-Bragg condition), because RHEED intensity oscillation can be observed under the out-of-phase condition[12–14] if 2D nucleation occurs on the surface.

Figures 1(a) and 1(b) show RHEED patterns taken from the 7×7 and the $\sqrt{3}\times\sqrt{3}$-Ag structures, respectively. 1(c) and 1(d) are the patterns after deposition of 3 and 15 ML of Ag on the $\sqrt{3}\times\sqrt{3}$-Ag structure at room temperature, respectively. In 1(c), the reflection spots of 3D Ag particles appear together with the $\sqrt{3}\times\sqrt{3}$-Ag spots. We also observed that with increasing deposited Ag thickness the $\sqrt{3}\times\sqrt{3}$-Ag spots gradually disappeared and the spots from 3D Ag particles became strong.

When Ag was deposited on the $\sqrt{3}\times\sqrt{3}$-Ag surface at 160 K, some different structures were observed as shown in Fig. 2. Figure 2(a) shows the $\sqrt{3}\times\sqrt{3}$-Ag pattern before growth. Figures 2(b), 2(c), and 2(d) are the patterns after Ag deposition at 160 K, with the thicknesses of 0.2, 0.5, and 4.0 ML, respectively. Figure 2(b) shows strong $\sqrt{21}\times\sqrt{21}$ and weak $\sqrt{3}\times\sqrt{3}$ structures. This pattern was observed for the range of Ag coverage from 0.19 to 2.6 ML at a variety of deposition rates. In Fig. 2(c), a 6×6 structure appears in addition to the $\sqrt{21}\times\sqrt{21}$ and $\sqrt{3}\times\sqrt{3}$ structures. This pattern was observed from 0.7 to 1.7 ML. Figure 3 shows their reciprocal lattice, which includes the $\sqrt{3}\times\sqrt{3}$, the $\sqrt{21}\times\sqrt{21}$ and the 6×6 structures. We observed that the 6×6 structure was stable at 160 K; this structure, however, disappeared when the substrate temperature became higher than 250 K. Thus we only observed the $\sqrt{3}\times\sqrt{3}$ and $\sqrt{21}\times\sqrt{21}$ structures above 250 K. For thicker deposition than 2.6 ML, the $\sqrt{3}\times\sqrt{3}$-Ag spots faded and Ag island spots appear as shown in Fig. 2(d). These reconstruction structures for the Ag/Si(111) system were also observed at various deposition rates, from 0.4 to 20 ML/min when the substrate temperature was kept at 160 K. But these reconstructions were not observed when the substrate was at RT.

We measured the changes of RHEED intensity during Ag deposition on the $\sqrt{3}\times\sqrt{3}$-Ag structure at RT and 160 K.[9] In each case, the RHEED intensity decreased rapidly at first, and then showed nearly a constant value. This nonoscillation growth suggests that in terms of atomic diffusion the mean free path of Ag atoms is large enough that 2D nucleation on the terrace cannot occur, even at 160 K. Apparently, the Ag growth on the 7×7 structure at 160 K is quite different, where streaks from Ag thin crystals appeared in RHEED patterns and much more RHEED intensity oscillations were observed in our measurements.[4]

In this experiment, the reconstruction structures $\sqrt{21}\times\sqrt{21}$ and 6×6 are observed at low temperature. The reconstruction is induced by the change of mean free path.

In the case of Ag growth on $\sqrt{3}\times\sqrt{3}$-Ag at temperatures from RT to 160 K, the RHEED patterns showed 3D diffraction spots at 3 ML growth which means Ag growth is by 3D island formation. We could not observe intensity oscillations for the Ag growth. In contrast, in the case of Ag growth on the 7×7 structure,[4] we observed more than ten oscillation peaks at 160 K. These results imply definitely that the mean free path of Ag atoms on the $\sqrt{3}\times\sqrt{3}$-Ag structure is larger than on the 7×7 structure, even at 160 K. The smaller mean free path for the 7×7 surface can be understood partly by considering dangling bonds, as seen in the dimer-adatom–stacking fault (DAS) model.[15] With the formation of the $\sqrt{3}\times\sqrt{3}$-Ag structure, the dangling bonds disappear and Si atoms form covalent bonds with the Ag atoms which was shown by ultraviolet photoelectron spectroscopy (UPS).[16] In the HCT model[10] of the $\sqrt{3}\times\sqrt{3}$-Ag structure, the dangling bonds do not exist. Thus the bonding energy between deposited Ag atoms and the $\sqrt{3}\times\sqrt{3}$-Ag structure may be considerably reduced, resulting in the increase of the mean free path.

At the first stage of Ag growth, the reconstructions $\sqrt{21}\times\sqrt{21}$-Ag and 6×6-Ag were observed at low temperature 160 K in addition to 3D islands which were the only observed structure at RT. These reconstructions are caused by the slightly reduced mobility of Ag at low temperatures and the kinetic barrier to the agglomeration of all deposited Ag into the 3D islands. In addition, the

structure formation may also be related to the $\sqrt{3}\times\sqrt{3}$-Ag trimer structure which from scanning tunneling microscopy (STM) images (see later) seems easily to be as a hollow site to locate atoms, and thus surface reconstruction will possibly occur under suitable conditions such as reduced mobility at low temperature. From RHEED *in situ* observations, we did not observe reconstruction in addition to Ag(111) epitaxial growth whenever Ag was deposited on the 7×7 structure at low temperature. The growth of Ag(111) is nearly consistent with that at room temperature. This is due to the dangling bonds existing on the surface as mentioned above. STM images by Neddermeyer[17] showed that Ag trimers would rapidly cover the adatom positions on the 7×7 surface after $\frac{1}{3}$ ML Ag deposition. Consequently, Si-Ag bonds will be
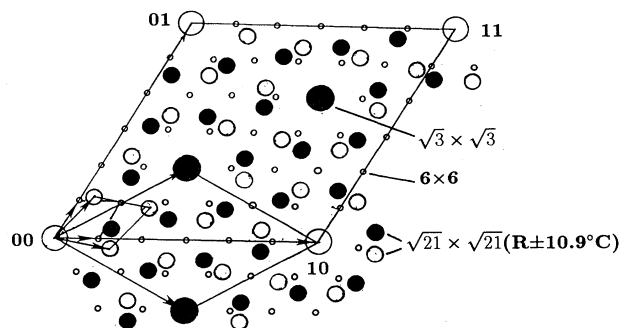
FIG. 3. A reciprocal lattice deduced from the RHEED pattern shown in Fig. 2(c).

formed and Ag is condensed nearly in a close-packed arrangement with the radius of the Ag metallic state and Ag(111) will be formed at large coverage. These Si-Ag bonds may not change greatly at low temperature since the growth is still in the Ag(111) surface. This analysis can be supported further from In growth on Si(111).[7] In the case of In on Si(111)-$\sqrt{3}\times\sqrt{3}$-In, 2×2 and $\sqrt{7}\times\sqrt{3}$ reconstructions can be formed within 3 ML deposition even at room temperature but only In epitaxial growth on Si(111)-7×7, is like the Ag behavior at 160 K.

On the other hand, the $\sqrt{21}\times\sqrt{21}$-Au or -Cu structure was observed when Au (Ref. 18) or Cu (Ref. 19) was
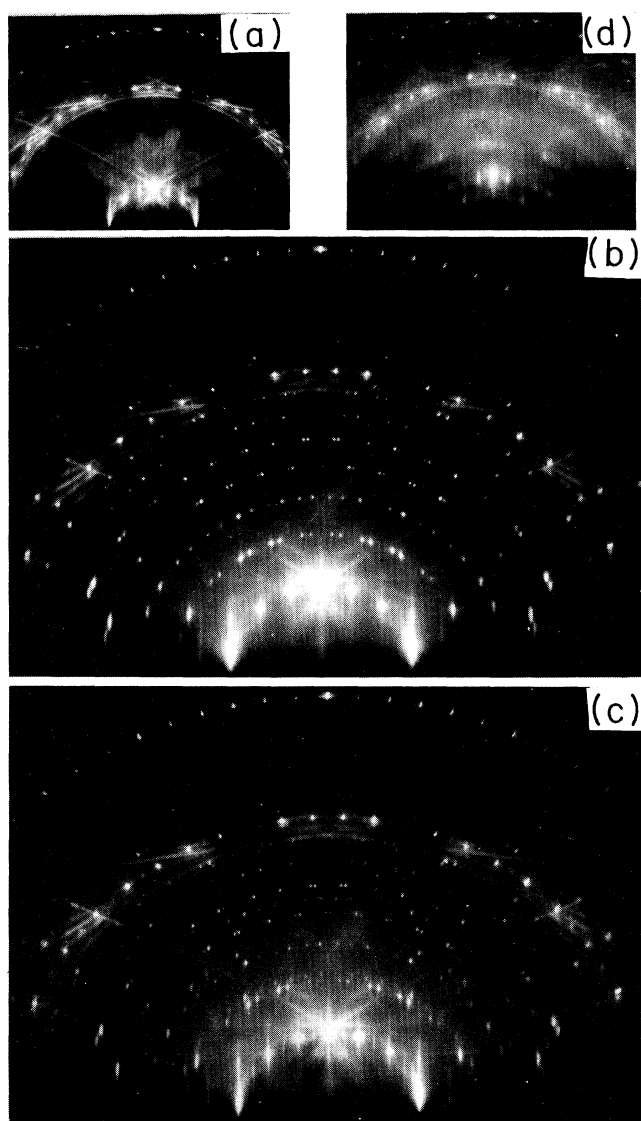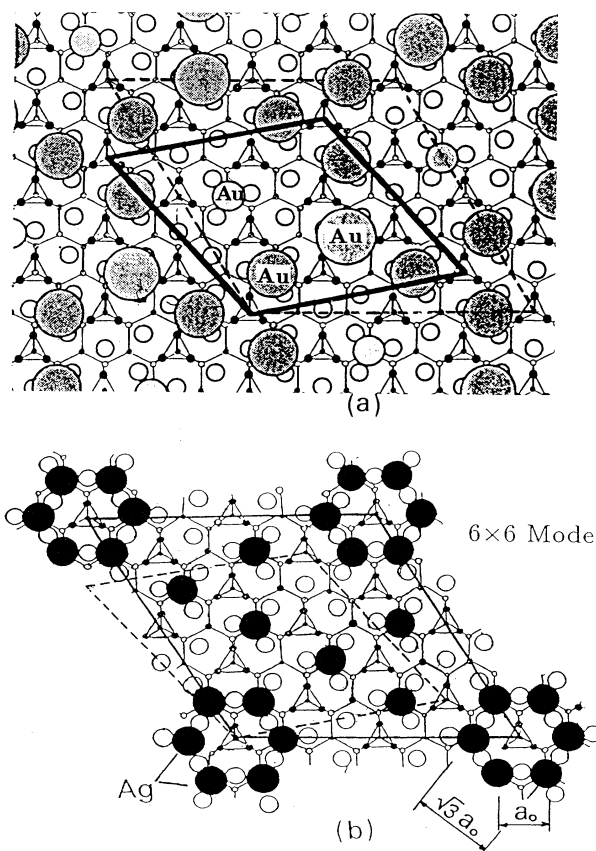
FIG. 2. (a) shows the $\sqrt{3}\times\sqrt{3}$-Ag pattern before the Ag deposition at 160 K. (b), (c), and (d) are the patterns after deposition of Ag at 160 K, with the thickness of 0.2, 0.5, and 4.0 ML, respectively. (b) shows a strong $\sqrt{21}\times\sqrt{21}$ structure in addition to the weak $\sqrt{3}\times\sqrt{3}$. (c) shows a weak 6×6 structure in addition to strong $\sqrt{21}\times\sqrt{21}$ and $\sqrt{3}\times\sqrt{3}$.

FIG. 4. (a) A model for the $\sqrt{21}\times\sqrt{21}$-Au($R\pm10.9\,°C$) structure by Nogami, Wan, and Lin (Ref. 18). (b) A proposed model for the 6×6 structure observed in this experiment.

deposited on the $\sqrt{3} \times \sqrt{3}$-Ag structure at RT. By using STM, Nogami, Wan, and Lin[18] observed the $\sqrt{21} \times \sqrt{21}$-Au structure, and proposed a model, as shown in Fig. 4(a). The unit mesh of $\sqrt{21} \times \sqrt{21}$-Au is drawn using solid lines. This model consists of an arrangement of three clustered Au adatoms which are located on top of the $\sqrt{3} \times \sqrt{3}$-Ag trimers. The coverage of Au for this model is $\frac{5}{21} = 0.24$ ML. This critical coverage corresponds nearly to Ichimiya et al.'s model[20] proposed from RHEED and STM results, which suggested a coverage of 0.19 ML, four additional atoms per $\sqrt{21} \times \sqrt{21}$-Au unit cell. These two coverage values (0.24 and 0.19 ML) agree well with the coverage of 0.19 ML in our observation for the $\sqrt{3} \times \sqrt{3}$-Ag structure. This may imply that both surface structures, the $\sqrt{21} \times \sqrt{21}$-Au and the $\sqrt{21} \times \sqrt{21}$-Ag, are identical.

We found furthermore the 6×6 structure between 0.7 and 1.7 ML together with the $\sqrt{21} \times \sqrt{21}$ structure. For the 6×6 structure, we propose a model derived from a Patterson function calculation, the symmetry, and the measured critical coverage of the 6×6 structure, as shown in Fig. 4(b). For comparison the 6×6 unit cell is drawn using a dashed line in Fig. 4(a). The black circles are adsorbed Ag atoms. The model has three characteristic points. (1) Using the intensity distributions of the 6×6 structure in the RHEED pattern, we calculated a Patterson function,[21] which predicted clearly four abnormal scattering centers with a hexagonal cluster existing in the corner of the unit cell. The Ag density of formed hexagonal clusters is $\frac{6}{36} = 0.17$ ML, which is smaller than expected, since the $\sqrt{21} \times \sqrt{21}$ and the 6×6 structures appeared at 0.24 and 0.7 ML, respectively. This means additional atoms in the unit cell have to be considered in the model. Therefore, as a reasonable model, there are two triangle clusters within the unit cell to be included but with asymmetry between the different six-member clusters. This triangle cluster also appeared in the $\sqrt{21} \times \sqrt{21}$-Au structure of Ref. 18. (2) The deposited Ag atoms are located on the Ag trimers of the $\sqrt{3} \times \sqrt{3}$-Ag structure, as proposed by Nogami et al. for the $\sqrt{21} \times \sqrt{21}$-Au structure. (3) The coverage of Ag in Fig. 4(b) is $\frac{12}{36} = 0.33$ ML, smaller than critical coverage. The observed range of the coverage for the 6×6 structure is from 0.7 to 1.7 ML. This discrepancy may arise from coexistence with the $\sqrt{21} \times \sqrt{21}$ structure and cluster formation. As seen in Figs. 1(c), 1(d), and 2(d), the deposited Ag atoms on the $\sqrt{3} \times \sqrt{3}$-Ag surface have high mobility and form clusters. In Figs. 2(b) and 2(c), although the RHEED spots from the Ag clusters could not be recognized, there is no doubt that small 3D clusters are formed on the $\sqrt{3} \times \sqrt{3}$-Ag structure.

In the corner of the model, each Ag atom combines with two Ag atoms, forming the hexagonal Ag cluster. These clusters and two triangle clusters within the unit cell form the 6×6 structure which seems to be relatively stable. In particular, the distance of two Ag atoms in the hexagonal cluster is a_0 (Si lattice constant), smaller than $\sqrt{3} a_0$ of $\sqrt{21} \times \sqrt{21}$-Au structure. This fact means that a shorter Ag atomic distance may become stable with decrease of substrate temperature. This analysis can be supported from our experimental observation for lower temperatures than 250 K, where the 6×6 structure could not be observed in addition to the $\sqrt{21} \times \sqrt{21}$-Ag structure. This analysis can also be understood much better from Ag growth after 3 ML on the $\sqrt{3} \times \sqrt{3}$-Ag structure. After 3 ML, Ag cluster growth was confirmed from the RHEED pattern in which 3D Ag spots could be observed. Due to the formation of Ag clusters during Ag growth at the substrate temperature of RT and 160 K, the RHEED intensity during the appearance of the $\sqrt{21} \times \sqrt{21}$ and 6×6 structures did not oscillate. The Ag atom during growth on the $\sqrt{3} \times \sqrt{3}$-Ag structure tends to form Ag clusters.

In a word, Ag surface reconstruction occurs not only at high temperature but also at low temperature.

The obtained results are summarized as follows.

(1) The following reconstructions are observed: the $\sqrt{21} \times \sqrt{21}$-Ag and the $\sqrt{3} \times \sqrt{3}$-Ag structures between 0.19 and 2.6 ML, and the $\sqrt{3} \times \sqrt{3}$, the $\sqrt{21} \times \sqrt{21}$, and the 6×6 structures between 0.7 and 1.7 ML.

(2) Through a Patterson function analysis of the RHEED intensity distribution, a model for the 6×6 reconstruction on the $\sqrt{3} \times \sqrt{3}$ surface was proposed.

(3) In the case of Ag growth on $\sqrt{3} \times \sqrt{3}$-Ag at RT and 160 K, RHEED intensity decreased quickly at first, followed by a nearly constant value.

(4) The mean free path length of Ag atoms on the $\sqrt{3} \times \sqrt{3}$ reconstruction is so large that the RHEED intensity oscillations could not appear, even at 160 K.

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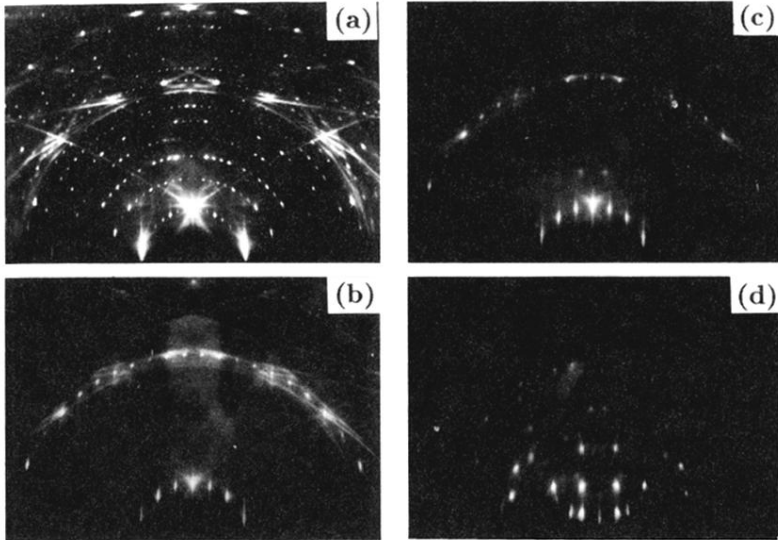[21] S. Ino, Jpn. J. Appl. Phys. 19, 1277 (1980).

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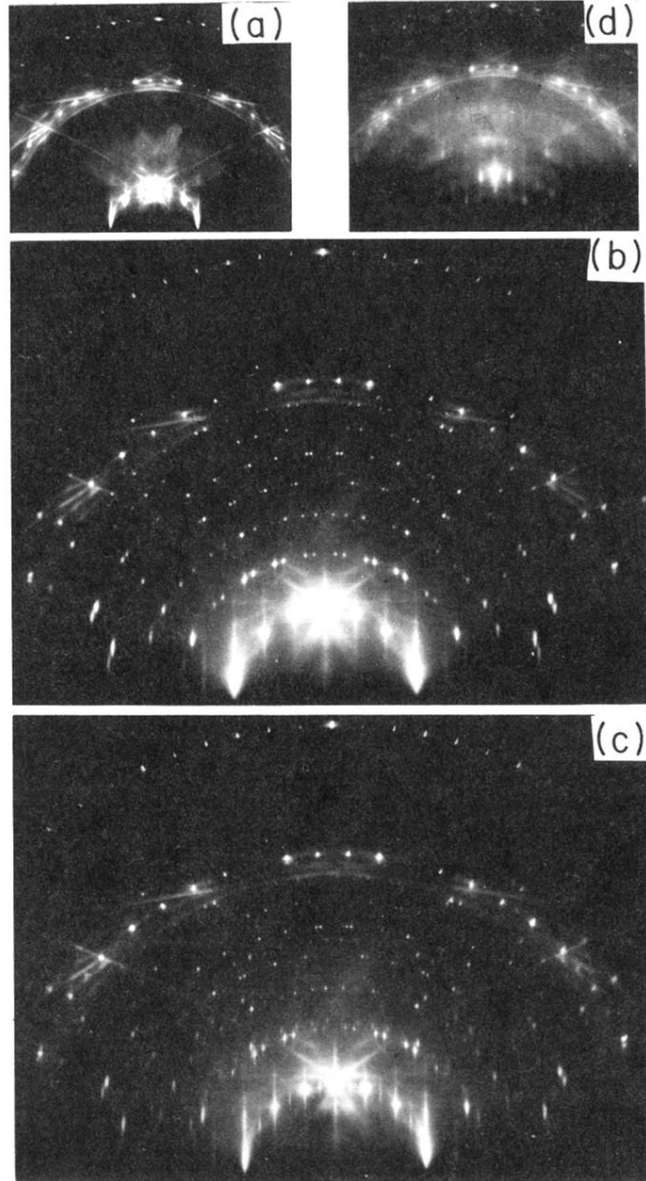
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