RHEED Patterns Calculated for Pt Nano Clusters on TiO$_2$(110) Substrate*

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Platinum nano clusters, which are attractive material for highly activated catalysis, are usually evaluated by scanning tunneling microscopy (STM). Here we challenge to evaluate the structure of Pt nano clusters by reflection high-energy electron diffraction (RHEED) for the first time. The nano cluster models are made of $n = 7$ and $n = 15$ Pt atoms, which are deposited on TiO$_2$(110) substrate. The former has two dimensional (planer) and the latter three dimensional (two layer's) shapes. They are rotated around their [111] axes of Pt crystal, whose axes are also inclined from the substrate surface normal because of the atomically rough substrate surface. The RHEED patterns have been calculated by kinematic diffraction theory. From the calculated patterns for the two types of the clusters ($n = 7$ and $15$), it is found that there is characteristic difference in the radial intensity distributions. The difference is attributed to existence or absence of the higher order reflections which arise from two layers of Pt(111).

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I. INTRODUCTION

The cluster size of catalyst metals has been recently more fined with the aim of the performance enhancement. New technology which forms size selected nano clusters with several numbers of Pt atoms has been developed [1,2]. Simultaneously, structure evaluation of such nano clusters is also required. Of course, though there is scanning tunneling microscopy (STM) observation, it is not useful for the in situ observation of such cluster formation. Then, we advance the challenging research on whether the structure evaluation is possible by reflection high-energy electron diffraction (RHEED) method.

The objective material of this study is size selected nano clusters which consist of 1-15 numbers of Pt atoms formed on a TiO$_2$(110) substrate. From a STM observation [1,2] for this system, it has been confirmed that the cluster structure for the number of Pt atoms, $n \leq 7$, consists of single atomic layer of Pt (two dimensional (2D) cluster), however, two atomic layers of Pt (three dimensional (3D) cluster) for $n \geq 8$. When such size selected Pt clusters on the substrate was tentatively observed by RHEED, the intensity distribution like a Debye-Sherrer ring pattern was very weakly observed. In order to extract the diffraction pattern from the background, energy filter is going to be prepared. Here, prior to the experiment, we present the calculated results of RHEED patterns by kinematic diffraction theory [3,4].

We have ever evaluated a morphology of Ge hut cluster grown on Si(001) substrate by RHEED and low energy electron diffraction (LEED) [3,4]. Whisker like intensity distribution in the vicinity of the diffraction spots for RHEED [4,5] and four-leaf clover like intensity distribution in the vicinity of the diffraction spots for LEED [4] are both well reproduced by kinematic calculation. The bottom edge length of the hut cluster is 10 nm [6] and the number of included Ge atoms is $n = 1750$, however, Pt nano cluster treated in this study is extremely small size. Then this study means challenging one whether RHEED can detect and evaluate such small cluster of Pt.

II. CALCULATION METHOD

Diffraction intensities in RHEED pattern were calculated based on kinematic theory as follows.

$$I = \left| \sum_{i=1}^{n} f_i(\vec{s}) \exp(\vec{s} \cdot \vec{r}_i) \exp(-M) \right|^2$$

where, $f_i(\vec{s})$ is atomic scattering factor [7], $\vec{s}$ scattering vector, $\vec{r}_i$ position vector of atom $i$, and $\exp(-M)$ Debye Waller factor deduce by Debye temperature [8]. Here, the incident beam was set at 10 keV.

Pt nano clusters for 2D ($n = 7$) and 3D ($n = 15$) were treated as typical structure models as shown in Figs. 1(a) and 1(b), respectively. These structures were confirmed by STM observation [1,2], where Pt(111) plane faces to the TiO$_2$(110) substrate surface. The substrate surface of TiO$_2$(110) is not only atomically rough but also has defects practically. Furthermore there exists large misfit between TiO$_2$(110) and Pt(111) lattices. Pt clusters,
which are deposited on the TiO$_2$(110) substrate surface, are considered to be randomly oriented with inclination as shown in Fig. 1(c). Because the substrate oxygen atomic rows along [001] direction of TiO$_2$(110) are arranged with the interval of 6.5 Å and the height of 1.3 Å even in the ideal surface.

III. CALCULATED RESULTS AND DISCUSSIONS

As an example, the calculated RHEED pattern for 3D ($n = 15$) Pt nano cluster of Fig. 1(b) is shown in Fig. 2(a). Here, the Pt([111]) plane is assumed to be parallel to the substrate surface. The incident beam azimuth is [1-1-2] direction of Pt([111]) and the glancing angle 0.5°. The observed streaky and fat spots are attributed to very thin (only two layers) and small Pt nano cluster. In the calculations, surface structure of the substrate TiO$_2$(110) is not taken into account. Because the incident glancing angle is very low, the structure of Pt cluster is dominant in the RHEED pattern. The pattern is rather transmission one than reflection one. The reciprocal lattice of Pt, face centered cubic (fcc) crystal, is shown in Fig. 2(b) with the orientation of the (111) plane parallel to the substrate surface. Scale of the reciprocal space is represented by the inverse of length, where 2π is excluded. The arrow indicates the incident beam direction. Some of the reciprocal lattice spots in the zeroth and the first Laue zone appear in the RHEED pattern as seen in Fig. 2(a).

Rotating the nano cluster through 360° around its [111] axis, RHEED pattern of Fig. 2(a) changes to that of Fig. 2(c). The pattern is obtained by the intensity sum over each rotated pattern with the interval of 1°. The reciprocal lattice becomes a fiber like structure as shown in Fig. 2(d). Then Additional spots appear as seen in Fig. 2(c), for example, such as -111, -222 and their equivalent spots. This pattern is far from Debye-Sherrer ring one.

Since the TiO$_2$(110) substrate surface is atomically rough as shown in Fig. 1(c), Pt clusters are considered to be adsorbed in the manner of tilt and rotation. RHEED patterns have been calculated for two types of 2D ($n = 7$) and 3D ($n = 15$) clusters. Orientations of these clusters are treated as one turn of φ around their [111] axes, whose axes are inclined in the range from θ = 0° to 30°, and simultaneously one turn of φ' around the inclined axes as shown by Figs. 3(a) and 3(c). These rotations and inclination are calculated under the interval of 1°. The intensity distributions in these patterns of 2D and 3D clusters become diffusive as shown in Figs. 3(b) and 3(d), respectively. These patterns show somewhat circular aspect due to the inclination of the clusters. The remarkable feature is seen in the line profiles for these patterns. The intensity profile on A-B line in the pattern of 2D cluster ($n = 7$) is monotonous as shown in the inset of Fig. 3(b), however, that of 3D cluster ($n = 15$) reveals some peaks as shown in the inset of Fig. 3(d). This suggests the possibility of structure evaluation for size selected nano clusters, that is 2D or 3D types.
Bragg reflections. The peak slightly shifts to the lower of Fig. 5(b), the first peak is attributed to 111 and 200 resolution of the diffraction pattern low. For 3D cluster diffraction spots are wide. Such Laue function makes the of extremely small size of clusters than 1 nm, the widths of profiles reveal some peaks as shown in Fig. 5(b). Because as shown in Fig. 5(a), however, for 3D cluster, the line in Fig. 5. For 2D cluster, the line profiles are monotonous of extremely large size of clusters, 

θ = 0^\circ - 60^\circ.

When the inclination angle of [111] axis enlarges as θ = 0^\circ - 60^\circ, RHEED patterns of 2D and 3D clusters become more diffusive and approximate to ring ones as shown in Figs. 4(a) and 4(b), respectively. It is seen that each concentric circular pattern almost agrees with the Debye-Sherrer ring which is notated by fcc plane indices. These RHEED patterns of 2D and 3D clusters are similar to each other, however, the line profiles from A to B as seen in Fig. 3 are rather different.

The line profiles on A-B for the case of θ = 0^\circ - 30^\circ, θ = 0^\circ - 60^\circ, and extremely case of θ = 0^\circ - 90^\circ are shown in Fig. 5. For 2D cluster, the line profiles are monotonous as shown in Fig. 5(a), however, for 3D cluster, the line profiles reveal some peaks as shown in Fig. 5(b). Because of extremely small size of clusters than 1 nm, the widths of diffraction spots are wide. Such Laue function makes the resolution of the diffraction pattern low. For 3D cluster of Fig. 5(b), the first peak is attributed to 111 and 200 Bragg reflections. The peak slightly shifts to the lower angle side due to the rapid gradient of the background intensity profile. The second peak is attributed to three Bragg reflections such as 220, 311 and 222.

IV. CONCLUSION

For the very small nano clusters of Pt on TiO_2(110) substrate, we have examined whether the RHEED method could evaluate their structure. If the Pt nano clusters have not so much interaction with the substrate surface and the substrate surface is atomically flat, the clusters sit on the substrate surface with only rotations around the [111] axis except for their inclinations. In this situation, RHEED pattern indicates the streaky spots as shown in Fig. 2(c). In the practice case, however, atomically rough surface of TiO_2(110) substrate may produce their azimuth rotations accompanied with their inclinations. From the kinematic calculation, it is found that the discrimination between 2D and 3D nano clusters is possible from the intensity distribution in the pattern, for example, the center line profile normal to the shadow edge. The line profile for 2D cluster indicates monotonous, however, that for 3D cluster has some peaks due to the higher order reflections. RHEED may be effective even for low density of clusters. Because the lower the glancing angle of incident beam becomes, the higher the effective density of scattering events becomes. It should be noted that the evalua-
tion of nano clusters by RHEED is usually performed for
the cluster size larger than a few nanometers, for ex-
ample, Au nano clusters on TiO$_2$(110) [9,10], however, the
size of Pt nano clusters in this study is smaller than one
nanometer.

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