

RHEED Patterns Calculated for Pt Nano Clusters on TiO₂(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 TiO₂(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). [DOI: 10.1380/ejsnt.2015.125]

Keywords: RHEED; Nano-particles; Platinum

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 TiO₂(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.

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

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 TiO₂(110) substrate surface. The substrate surface of TiO₂(110) is not only atomically rough but also has defects practically. Furthermore there exists large misfit between TiO₂(110) and Pt(111) lattices. Pt clusters,

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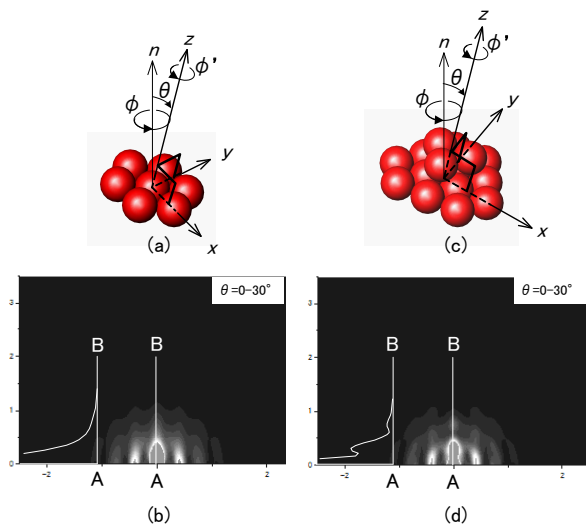


FIG. 3. (a) and (c) are 2D cluster ($n = 7$) and 3D one ($n = 15$), respectively, with the notations of rotation angles ϕ and ϕ' , and inclination angle θ . (b) and (d) are calculated RHEED patterns for 2D and 3D clusters, respectively, on the condition of rotation ranges of $\phi = 0^\circ - 360^\circ$, $\phi' = 0^\circ - 360^\circ$ and inclination range of $\theta = 0^\circ - 30^\circ$. The insets show the line profiles on A-B in the patterns.

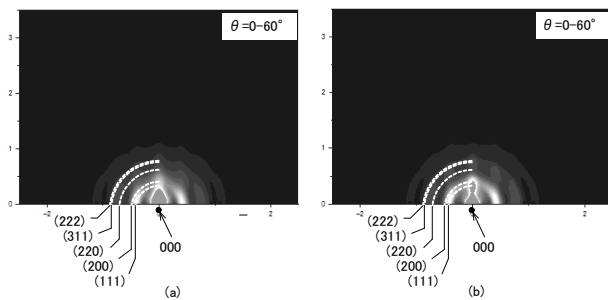


FIG. 4. (a) and (b) are calculated RHEED patterns for 2D cluster ($n = 7$) and 3D one ($n = 15$), respectively. These clusters are rotated similarly to Fig. 3, but inclination range is $\theta = 0^\circ - 60^\circ$.

When the inclination angle of $[111]$ axis enlarges as $\theta = 0^\circ - 60^\circ$, 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-Scherrer 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 $\theta = 0^\circ - 30^\circ$, $\theta = 0^\circ - 60^\circ$, and extremely case of $\theta = 0^\circ - 90^\circ$ 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

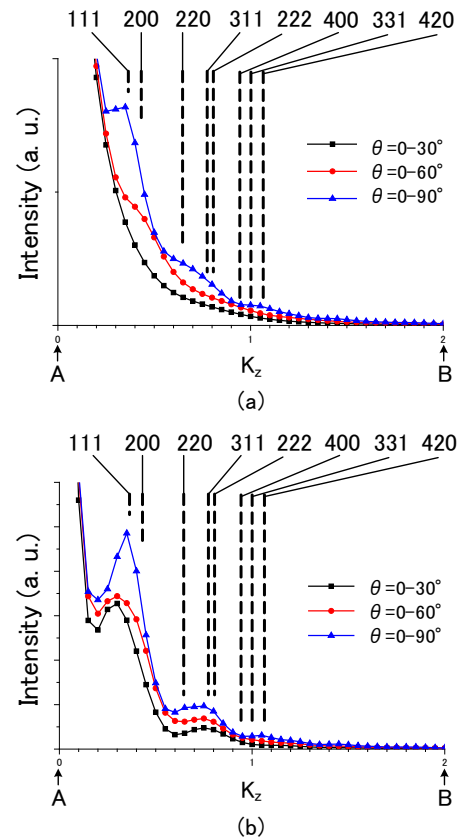


FIG. 5. (a) and (b) are line profiles for 2D cluster ($n = 7$) and 3D one ($n = 15$), respectively. These clusters are rotated similarly to Fig. 3, but the inclination range is changed as $\theta = 0^\circ - 30^\circ$, $\theta = 0^\circ - 60^\circ$ and $\theta = 0^\circ - 90^\circ$.

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 $\text{TiO}_2(110)$ 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 $\text{TiO}_2(110)$ 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 example, Au nano clusters on $\text{TiO}_2(110)$ [9,10], however, the size of Pt nano clusters in this study is smaller than one nanometer.

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