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X-Ray Photoelectron Diffraction (XPED) Studies of Platinum on Titanium Dioxide (110) Surface

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X-Ray photoelectron diffraction patterns from platinum atoms deposited on TiO_2 (110) surface were measured, and the structural analysis was made by means of the single scattering calculation. It is found that the structural model of platinum particles based on the (111) surface of fcc crystal explains the experimental results very well.

The small metal particles have been the subject of much recent interest in the field of chemistry and physics.$^{1)}$ Especially, the structure and the chemical state of the noble metal particles on the metal oxides are of great importance in connection with the supported metal catalysts.$^{2,3)}$

X-Ray photoelectron diffraction (XPED) has been shown to be a new promising method for surface structural and chemical state analysis.$^{4,5)}$ The advantages of XPED measurement compared with other surface analytical methods are summarized as follows: 1) the charging of the sample does not prevent obtaining explicit diffraction patterns; 2) long-range ordering is not necessary to obtain structural information; 3) the contribution from each component can be distinguished. From these features, XPED measurement is considered to be a more desirable method to analyze the metal particles deposited on insulating materials like metal oxides than other conventional methods.

In this study, the XPED patterns for platinum atoms deposited on TiO_2 (110) surface were obtained, and the structure of the platinum particles was analyzed by means of the single scattering calculation.

All experiments were performed with an angle-resolved X-ray photoelectron spectrometer. AlKα radiation was used to excite photoelectrons. The base pressure of the system was less than 2.7×10^{-8} Pa. A (110) oriented TiO_2 rutile single crystal, obtained from Nakazumi Crystal Laboratory, was aligned to within ±0.5° of the desired orientation, and was mechanically polished, and chemically etched. Before measurements, the sample was cleaned by Ar^+-ion bombardment (700 eV) and annealing (1010 K) cycles. The cleanliness of the surface was checked by X-ray photoelectron spectroscopy, and no carbon nor other impurities were detected. Platinum was evaporated in vacuum from a pure platinum ribbon onto the titanium

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dioxide. The deposition rate of platinum was approximately 0.08 Å/min. To eliminate the apparent shift caused by the charging of the sample, the binding energy of platinum was calibrated by using the $Ti2p_{3/2}$ peak (458.8 eV).

The azimuthal dependences of Ti2p emission from TiO_2 (110) at polar angle θ=50° relative to surface normal are shown in Fig.1(a). The XPED pattern exhibits many fine structures, which indicates that the crystal regularity is sufficiently restored after annealing treatment. The XPED pattern is mirror symmetric about the azimuthal angle φ=0° ([1$\bar{1}$0] direction of TiO_2) and 90° ([001] direction), which reflects that the crystal structure is two-fold symmetry.

Figure 2 shows the XPS signal intensity (a) and the binding energy (b) of the Pt4f level as a function of the metal coverage. It is evident from this result that the binding energy of $Pt4f_{7/2}$ level decreases as the metal coverage increases. The decrease of the binding energy is caused mainly by the change of the degree of the screening of the

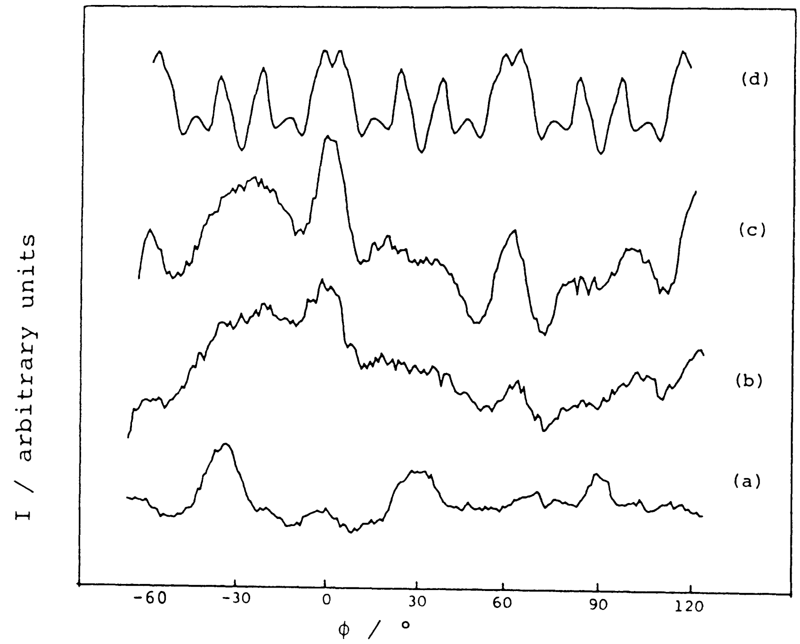

Fig.1. (a) Azimuthal pattern of Ti2p at θ=50° from TiO_2(110). (b) Azimuthal pattern of Pt4f at θ=53° deposited on TiO_2(110) to a thickness of about 15.8 Å. (c) Azimuthal pattern of Pt4f at θ=53° after annealing at 823 K for 30 min. (d) Calculated pattern of Pt4f at θ=53°.
φ : Azimuthal angle.
I : Intensity.

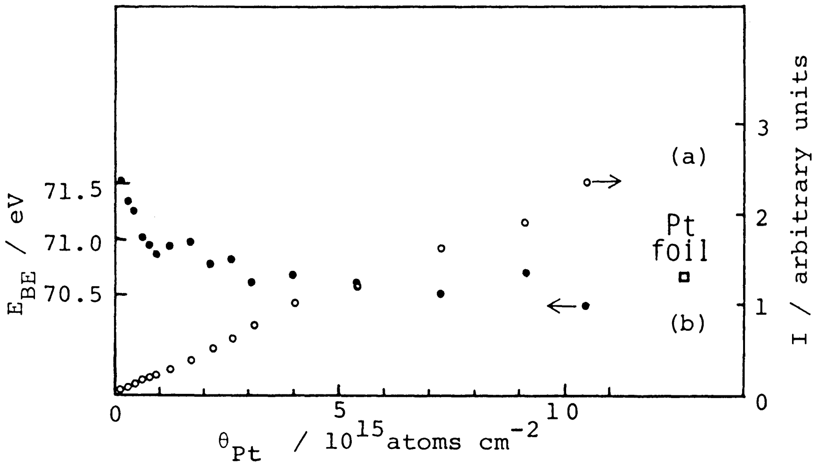

Fig.2. (a) XPS signal intensity of Pt4f. (b) Binding Energy of $Pt4f_{7/2}$ as a function of Pt coverage.
θ_{Pt} : Pt coverage.
E_{BE} : Binding energy.

core-hole by the electrons of neighbouring atoms.[3)] In the larger particles, as there are more neighbouring electrons, the screening is more effective than in the smaller particles, and the binding energy lowers. After the final step of the deposition, the thickness of the platinum layer is approximately 15.8 Å equivalent, which is determined from the XPS signal intensity ratio of Pt4f peak to Ti2p and O1s peaks, and the platinum atoms become metallic.

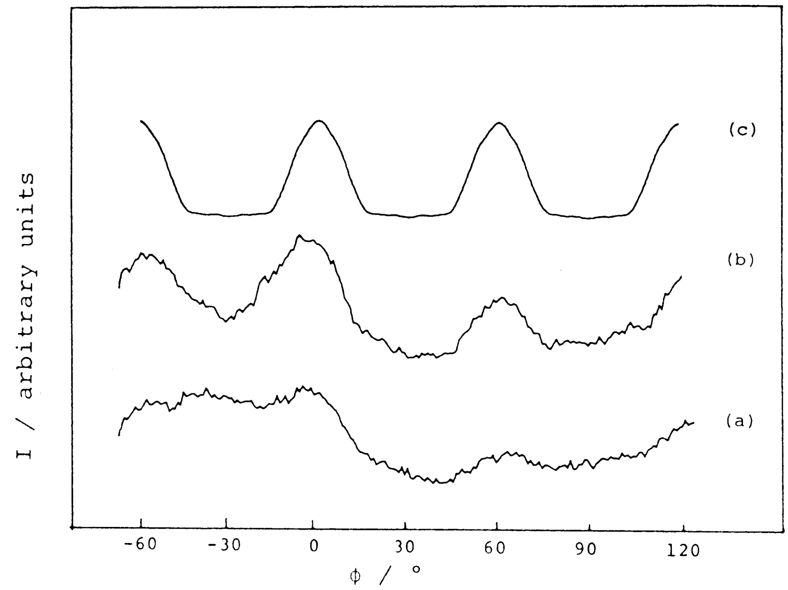

Fig.3. (a) Azimuthal pattern of Pt4f at θ=33° deposited on TiO_2(110) to a thickness of about 15.8 Å. (b) Azimuthal pattern of Pt4f at θ=33° after annealing at 823 K for 30 min. (c) Calculated pattern of Pt4f at θ=33°.

The azimuthal dependences of Pt4f emission at polar angle θ=53° (Fig.1(b)) and θ=33° (Fig.3(a)) just after deposition are shown. As can be seen in these XPED patterns, the photoelectron intensity maxima are already observed at ϕ=0°, ±60°, 120°, which indicates that the platinum clusters already have structural regularity to some degree.

After annealing at 823 K for 30 min, the relative XPS intensity from the substrate atom increased. This result shows that the platinum particles coalesce and become larger by heat treatment. On the other hand, the fine structures of the azimuthal patterns of platinum atoms at θ=53° (Fig.1(c)) and θ=33° (Fig.3(b)) become clear, which indicates that the degree of crystallization of platinum increases. Contrary to the pattern from titanium atom(Fig.1(a)), these patterns can be regarded as six-fold symmetry rather than two-fold symmetry.

It is known that the detailed analysis of the surface structure is possible by use of the theoretical calculations based on the single scattering model.[6,7)] The detail of the calculation is seen elsewhere.[7)] The elastic scattering amplitudes were used from tabular form data.[8)] The cluster of atoms used in this calculation consists of the hemispherical platinum cluster with radius 15 Å and the substrate cluster whose atoms are within 10 Å to the emitter atom. Considering that the six-fold symmetry of the experimental results is explained by the multiple of two fold-symmetry of the substrate and three-fold symmetry of the overlayer, it is sufficient to consider only the structure model based on the (111) plane of the fcc platinum crystal. In order to elucidate above model, two cluster models No.1 and No.2 are assumed. The cluster model No.1 is expressed as follows; viz. (111) plane of platinum is parallel to the (110) surface of titanium dioxide and [$\bar{2}$11] direction of the former is parallel to $[1\bar{1}0]$ direction of the latter. The cluster model No.2 is mirror symmetric with the model No.1 about the $(1\bar{1}0)$ plane of the substrate. These two models are equivalent from the standpoint of the structural relationships between substrate and overlayer. When two clusters exist with the equal probability on the surface of titanium dioxide, which is called the symmetric type,[9] the corresponding pattern are obtained as shown in Fig.1(d) and Fig.3(c). From the comparison, it is found that the calculated pattern at $\theta=33°$ agreed very well with the experimental pattern. For the fine structure in the pattern at $\theta=53°$, the agreement with the experimental pattern is not sufficient, possibly because this calculation considers only single scattering. For the other experimental results, which are obtained by the different angular scans, this model also explains the experimental results very well.

Considering that the XPED pattern is very sensitive to the crystal structure, it is concluded from the XPED analysis that after the platinum deposition the two types of clusters based on the (111) surface of the fcc crystal exist with the equal probability on $TiO_2(110)$ surface. Furthermore, the XPED analysis is proved to be a useful technique for structural analysis of the dispersed metal particles on the metal oxide, which are very difficult to be analyzed by other technique.

References

1) W. D. Knight, K. Clemenger, W. A. de Heer, W. A. Sounders, M. Y. Chou, and M. L. Cohen, Phys. Rev. Lett., 52, 2141 (1984); I. Katakuse, T. Ichihara, Y. Fujita, T. Matsuo, T. Sakurai, and H. Matsuda, Int. J. Mass Spectrom. Ion Phys., 67, 229 (1985).
2) R. T. K. Baker, E. B. Prestridge, and R. L. Garten, J. Catal., 56, 390 (1979); T. Wang, C. Lee, and L. D. Schmidt, Surf. Sci., 163, 181 (1985).
3) T. Huizinga, H. F. J. Vant' Blik, J. C. Vis, and R. Prins, Surf. Sci., 135, 580 (1983).
4) Y. Nihei, M. Owari, M. Kudo, and H. Kamada, Jpn. J. Appl. Phys., 20, L420 (1981); N. Koshizaki, M. Kudo, M. Owari, Y. Nihei, and H. Kamada, ibid., 19, L349 (1980); M. Kudo, N. Koshizaki, M. Owari, Y. Nihei, and H. Kamada, Hyoumen Kagaku, 1, 48 (1980); M. Kudo, Pei-Xun Jien, M. Owari, N. Koshizaki, H. Kamada, and Y. Nihei, Nippon Kagaku Kaishi, 1985, 1223.
5) K. Tamura, M. Owari, M. Kudo, and Y. Nihei, Bull. Chem. Soc. Jpn., 58, 1873 (1985).
6) L. McDonnell, D. P. Woodruff, and B. W. Holland, Surf. Sci. 51, 249 (1975); S. Kono, S. M. Goldberg, N. F. T. Hall, and C. S. Fadley, Phys. Rev. Lett., 25, 1831 (1978).
7) M. Owari, M. Kudo, Y. Nihei, and H. Kamada, J. Electron Spectrsc. Rela. Phenom., 34, 215 (1984).
8) M. Fink and A. C. Yates, At. Data, 1, 385 (1970); M. Fink and J. Ingram, At. Data, 4, 129 (1972); D. Gregory and M. Fink, At. Data Nucl. Data Tables, 14, 39 (1974).
9) Y. Kainuma, J. Phys. Soc. Jpn., 6, 135 (1951).

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