Supporting Information for

Significant Transient Mobility of Platinum Clusters via a Hot Precursor State on the Alumina Surface

Atsushi Beniya,[†] *Hirohito Hirata,*[‡] *and Yoshihide Watanabe*[†]*

[†] Toyota Central R&D Labs, Inc., 41-1 Yokomichi, Nagakute, Aichi 480-1192, Japan

[‡] Toyota Motor Corporation, 1200 Mishuku, Susono, Shizuoka 410-1193, Japan

AUTHOR INFORMATION

Corresponding Author

*Email address: e0827@mosk.tytlabs.co.jp

1. Experimental methods

Experiments were performed in an ultrahigh vacuum chamber ($<1 \times 10^{-8}$ Pa).[1] The NiAl(110) substrate was 10 mm in diameter and oriented to within 0.1° (Surface Preparation Laboratory). The clean NiAl(110) surface was prepared by several cycles of Ar ion sputtering, followed by annealing at 1300 K. The thin Al_2O_3 film was prepared by dosing 1800 L (Langmuir: 1×10^{-6} Torr·s) of O_2 at 600 K, followed by annealing at 1100 K for 5 min.[2] The process was repeated more than three times in order to close open metal patches in the film.

Pt cluster ions were produced by combining a DC magnetron sputtering and gas aggregation cluster source.[1] Size-selected Pt_{15} cluster ions were uniformly deposited on Al_2O_3/NiAl(110) at 300 K using the Lissajous scanning method.[3] The impact energy was tuned to <2 eV/atom (soft-landing condition: average impact energy was ~0.47 eV/atom, see section 3 in supporting information) by adjusting the bias voltage applied to the surface, where the impact energy was estimated using the retarding voltage method. The total amount of Pt deposited was determined by the integrated Pt_{15}^+ neutralization current on the sample.

STM measurements were performed at 78 K using a low-temperature STM (LT–STM, Omicron GmbH) with a Nanonis (SPECS Zurich GmbH) controller and a tungsten tip. The STM images were taken at a positive sample bias (V_s) of 3.5 V and a tunneling current (I_t) of 0.1 nA.

2. Analytical model to estimate cross-section for cluster aggregation

The cluster aggregation probability was calculated using the Poisson distribution.[3] In this model, when only one cluster adsorbs inside a cross-section (σ), that cluster is counted as an isolated cluster. Considering that Pt_n clusters are deposited on the surface of area A, the number of cells, N (of which the area is the cross-section σ), inside area A become

$$N = \mathrm{A}/\sigma \quad (1).$$

The average number of clusters, s_{ave}, inside the cell is calculated to be

$$s_{\mathrm{ave}} = s/N \quad (2),$$

where s is the total number of deposited clusters. The fraction of cells that contain x clusters in the cell obeys the Poisson distribution,

$$\mathrm{P}(x) = s_{\mathrm{ave}}^{x} \times \exp(-s_{\mathrm{ave}})/x! \quad (3).$$

The number of cells that contain x clusters is $N\mathrm{P}(x)$, hence the number of these clusters and atoms are $xN\mathrm{P}(x)$ and $nxN\mathrm{P}(x)$, respectively. Thus, the fraction of these atoms becomes

$$nxN\mathrm{P}(x)/ns = x\mathrm{P}(x)/s_{\mathrm{ave}} = \mathrm{P}(x-1) \quad (4).$$

Therefore, the coverage of these clusters (θ_x: x clusters in the area of cross-section) becomes

$$\theta_x = \theta_{\mathrm{T}}\mathrm{P}(x-1) \quad (5),$$

where θ_T is total coverage. In order to calculate coverage dependence of isolated and aggregated Pt_{15} clusters using eq. (5), coverage dependence of s_{ave} is necessary. Assuming that 1 ML = 1.5×10^{15} atoms/cm^2 = 15 atoms/nm^2 as the Pt(111) surface,

$$\theta_{\mathrm{T}} = \frac{ns/\mathrm{A}}{15} = \frac{15s/\mathrm{A}}{15} = \frac{s}{\mathrm{A}} \quad (6)$$

$$s = \mathrm{A}\theta_{\mathrm{T}} \quad (7).$$

Then, coverage dependence of s_{ave} can be obtained from eqs. (1), (2) and (7) as

$$s_{\mathrm{ave}} = \sigma\theta_{\mathrm{T}} \quad (8).$$

Using eq. (5) and (8), coverage dependence of Pt_{15} monomer (x = 1) becomes

$$\theta_1 = \theta_{\mathrm{T}}\mathrm{P}(0) = \theta_{\mathrm{T}}\exp(-\sigma\theta_{\mathrm{T}}) \quad (9).$$

Coverage dependence of Pt_{15} dimer (x = 2) and trimer (x = 3) become

$$\theta_2 = \sigma\theta_{\mathrm{T}}^2\exp(-\sigma\theta_{\mathrm{T}}) \qquad (10)$$

and

$$\theta_3 = \frac{1}{2}\sigma\theta_{\mathrm{T}}^3\exp(-\sigma\theta_{\mathrm{T}}) \qquad (11),$$

respectively.

3. Coverage estimation of isolated Pt_{15} and its aggregates from histograms of the apparent cluster height

Figure S1a shows the histograms of apparent cluster height as a function of coverage. Fractions of a Pt_{15} monomer, dimer, and trimer were estimated by Gaussian fitting as shown by the red, blue, and green curves, respectively. Using the fitted results, the coverage of Pt_{15} monomer, dimer, and trimer were estimated as shown in Figure 1b. Estimated results were fitted based on the model described above. The coverage of Pt_{15} monomer (θ_m), dimer (θ_d), and trimer (θ_t) are represented by eqs (9)~(11) as

$$\theta_m = \theta_\mathrm{T}\exp(-\sigma\theta_\mathrm{T}),$$

$$\theta_d = \sigma\theta_\mathrm{T}^2\exp(-\sigma\theta_\mathrm{T}),$$

$$\theta_t = \frac{1}{2}\sigma\theta_\mathrm{T}^3\exp(-\sigma\theta_\mathrm{T}),$$

respectively, where θ_T is total deposited Pt_{15} coverage and σ is the cross-section. Estimated θ_m, θ_d, and θ_t were fitted well by these equations as shown in Figure S1b. The cross-section σ was nearly identical for the Pt_{15} monomer (σ = 9.4 nm^2), dimer (σ = 10.8 nm^2), and trimer (σ = 9.4 nm^2).

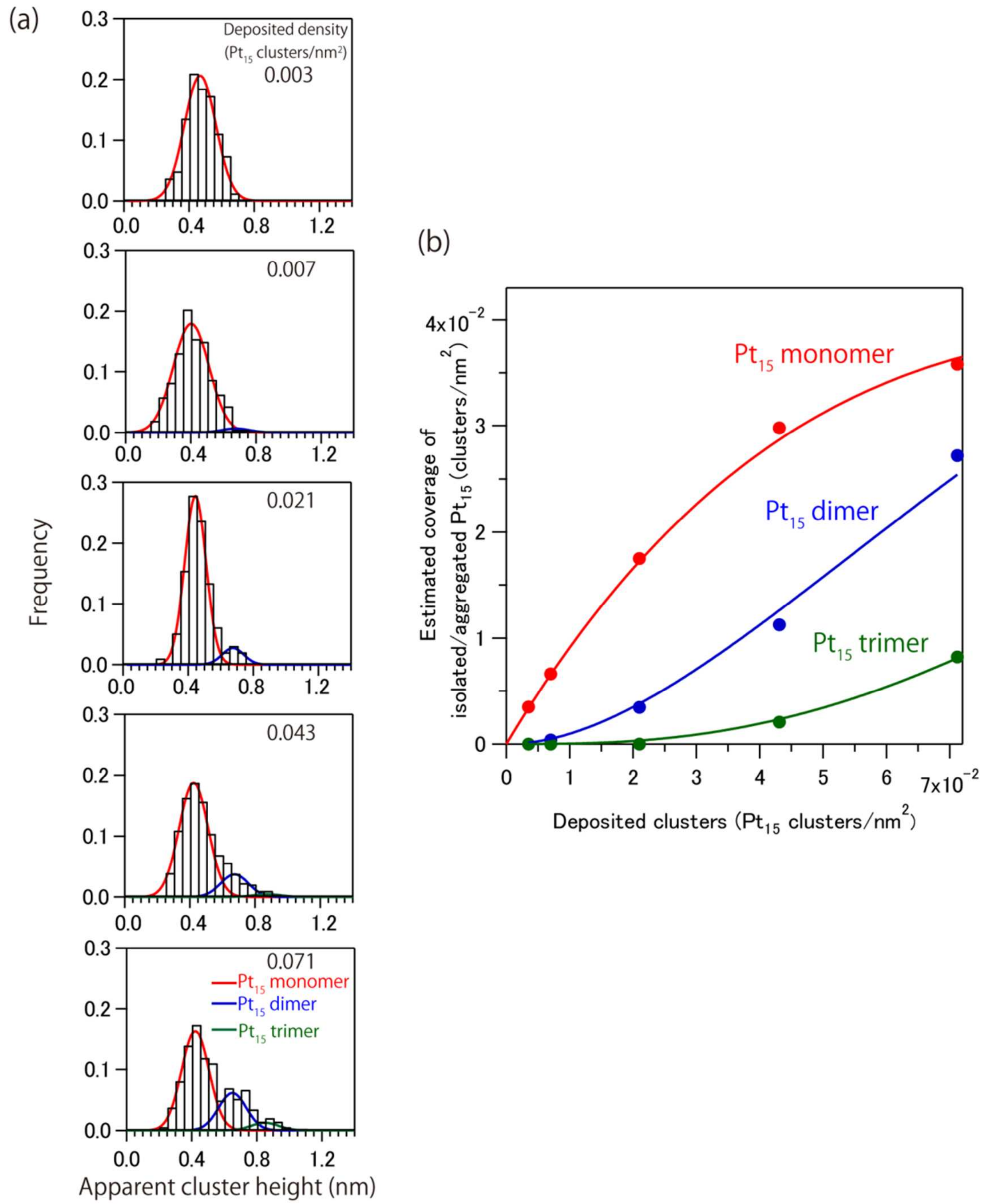

Figure S1. (a) Histograms of apparent cluster height as a function of deposited Pt_{15} coverage. The fractions of Pt_{15} monomer, dimer, and trimer were estimated by the fitting, as shown by red, blue, and green curve, respectively. (b) Estimated coverage of Pt_{15} monomer (red), dimer (blue), and trimer (green) as a function of deposited Pt_{15} coverage. Solid curves are the fitted results.

3. Soft-landing of size-selected Pt_{15} cluster on Al_2O_3/NiAl(110)

Figure S2 shows Pt_{15}^+ ion current and its kinetic energy distribution as a function of bias voltage. The kinetic-energy distribution of the Pt_{15}^+ clusters was measured by the retarding potential method using a metal plate at the sample position. The impact energy was tuned to 0.47 eV/atom (soft-landing condition) by applying a bias voltage of 30 V to the substrate.

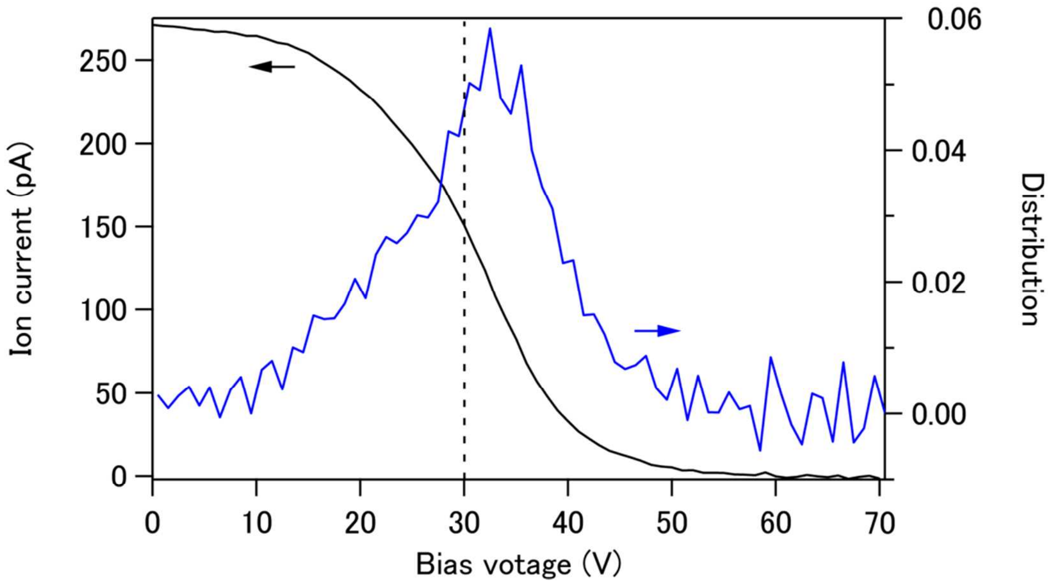

Figure S2. The cluster ion current for Pt_{15}^+ (black curve) and the cluster energy distribution (blue curve) versus bias voltage applied to the metal plate at the sample position. At a bias voltage of 30 V (indicated by a vertical dashed line), clusters reached the sample with an average kinetic energy of 7 eV/cluster (0.47 eV/atom).

REFERENCES

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