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Deposition of Size-Selected Metal-Cluster on Solid Surface and Individual STM Observation

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We developed an apparatus for investigating the physical and chemical properties of a size-selected single cluster deposited on a sold surface by use of a scanning tunneling microscope (STM). The apparatus consists of an intense cluster-ion source, a quadrupole mass-filter, a deposition stage and an STM. Metal atoms and ions produced in a magnetron were aggregated into cluster ions in helium and argon atmosphere at 77 K. Size-selected cluster ions passing through the quadrupole mass-filter were deposited on a solid surface at a given collision energy (10-250 eV) and observed in STM. Platinum, silver and copper cluster cations of a given size (less than 50) having a typical current of 500 pA were deposited on a cleaved graphite surface and at a temperature of 300 K and at a pressure of 10^{-6} Pa. STM images of platinum and silver clusters with the size of 4, 10 and 20 were successfully observed with an atomic resolution. The clusters were found to be deposited firmly to the surface, so that the STM images did not cha nge by scanning of an STM tip as well as exposing to air.

Key words: cluster, deposition, surface, STM, graphite, magnetron

1. INTRODUCTION

Physical and chemical properties of a cluster deposited on a solid surface vary characteristically with interaction between the cluster and the surface [1], and with the cluster size [2]. In such studies, we should, therefore, deal with the local geometrical and electronic structures of the surface and the cluster, because the interaction between the cluster and the surface is determined by these structures. Physical properties of the cluster are then derived from the measurements of these quantities. On the other hand, chemical properties such as the reactivity of the cluster can be elucidated by observing the entities after the reaction is completed.

We developed an apparatus to perform the experimental studies of this kind. At the first place, an intense cluster-ion source equipped with a magnetron plasma-generator and a gas-aggregation chamber was constructed, and was joined to a scanning-tunneling microscope (STM), which characterizes individual size-selected clusters deposited on a solid surface [3-5]. Platinum clusters with the sizes less than ~30 and silver clusters with the sizes less than ~50 were prepared and deposited on a graphite surface with a sufficient amount for several minutes or more. The STM images of these clusters were observed at an atomic resolution.

2. EXPERIMENTAL

Figure 1 shows a schematic view of an apparatus, which consists of a cluster-ion source, ion optics consisting of octopole ion-guides and ion-focusing lenses, a quadrupole mass-filter, a cluster-deposition equipment, devices for treatment of a sample and an STM tip, an STM and a load-lock system for introduction of the sample and tip.

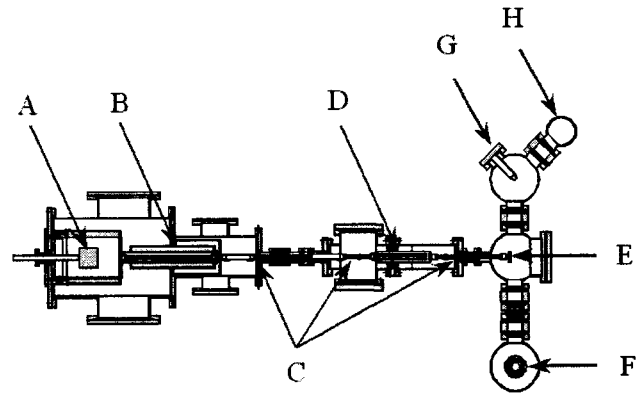

Figure 1. Schematic view of apparatus for cluster deposition and STM observation. The apparatus consists of (A) a magnetron-type cluster ion source, (B) a cooling jacket, (C) octopole ion-guides, (D) a quadrupole mass-filter, (E) a deposition equipment, (F) an STM, (G) a sample-treatment room, and (H) a load-lock room.

2.1 Cluster-ion source

Cluster ions were produced in a gas-aggregation chamber equipped with a magnetron sputter-source (Kurt J. Lester TRS-2CV MM was modified for the cluster-ion production) [6]. Argon gas was introduced in front of a sample plate as thick as 3.2 mm with 50.8 mm in diameter, which was placed in the magnetron, while helium gas was introduced separately into the gas-aggregation chamber. The flow rate of each gas (typically 20-200 cm^3/min) was controlled independently by a mass-flow controller (Kofloc 3650). A pressure in the gas-aggregation chamber was increased from $4x10^{-6}$ Pa to 10-100 Pa in operation. Discharge was made in argon gas in front of the sample plate by applying a DC bias voltage (Advanced Energy MDX-1K, 200-500 V, 20-150 W) to the target. Argon cations produced in the plasma were allowed to sputter the sample plate, and resulting metal atoms and ions were aggregated into clusters and cluster ions by colliding with the argon and helium gases. These gases were cooled by filling liquid nitrogen in a jacket surrounding the gas-aggregation chamber.

The source chamber was evacuated by a turbo-molecular pump (2200 ls^{-1}) backed by a mechanical booster pump (78 ls^{-1}) together with a rotary pump (10 $lmin^{-1}$).

2.2 Mass selection of cluster ion

The cluster ions thus produced were admitted into the first octopole ion guide [7] placed in a cooling jacket through an aperture (5 mm in diameter) mounted at the exit of the gas-aggregation chamber, which was biased by a DC voltage. An rf voltage (3.6 MHz, 10 W) from a radio transceiver (ICOM IC-706 MKIIG) was applied to the octopole ion guide, the center of which was biased by a DC voltage. In this ion guide, the cluster ions were cooled by collision with helium and argon gases cooled by liquid nitrogen filled in the jacket. A typical transmittance of the first ion-guide was measured to be 20%; this low transmittance is ascribable to escape of ions from the ion guide by scattering with the ambient gas having a pressure of 1-10 Pa.

The cluster ions thus produced were allowed to pass through two other octopole ion-guides with more than 90% transmittance. The cluster ions were focused at the entrance of the quadrupole mass-filter by three aperture lenses. A cluster ion with a given size was selected in the quadrupole mass filter (ABB Extrel MEXM-9000, maximum mass is 9000 amu).

2.3 Deposition of cluster ion and intensity measurement

The size-selected cluster ion was admitted into the final octopole ion guide, and deposited on a sample surface at a given collision energy and at a pressure of $1x10^{-7}$ Pa or less, where the base pressure of $2x10^{-8}$ Pa was attained by evacuating a turbo-molecular pump (500 ls^{-1}). Two sheets of aperture lens were placed in front of the target. The collision energy was varied in a range of 1-250 eV by changing a bias voltage applied to the surface. The surface can be cooled at 77 K. The current of the cluster ion was measured by a pico-ammeter (Keithley 487).

The sample surface was mounted on a holder made of molybdenum and tantalum, and was cleaned by resistive heating at $3x10^{-8}$ Pa. Typically, 20-A current was sufficient to heat the sample at 1500 K.

2.4 STM

The sample surface was transported onto an STM (Unisoku STM was modified) at $3x10^{-8}$ Pa, and STM images were observed at a temperature of 6-300 K and at a pressure of $4x10^{-9}$ Pa.

The STM tip was made of tungsten or platinum-iridium alloy. The latter was made by mechanical processing on an alloy rod (0.5 mm in diameter), while the former is made by electrical etching of a tungsten rod (0.3 mm in diameter) in a aqueous solution of potassium hydroxide. The STM tip was cleaned at 1500 K by electron bombardment (350 eV, 30 mA) at a pressure of 10^{-8} Pa.

The STM chamber was located on a table with four pneumatic legs for vibrational isolation. Further vibrational isolation was attained by hanging the STM head with three coil springs having a resonance frequency of ~3 Hz. The vibration of the STM was damped by three sets of magnets (Eddy-current dampers) and cupper-mesh.

During the STM observation, the STM chamber was evacuated by a titanium sublimation pump (800 ls^{-1}) and an ion pump (60 ls^{-1}) to avoid additional vibration due to pumping.

3. RESULTS AND DISCUSSION

3.1 Mass spectra of cluster ions

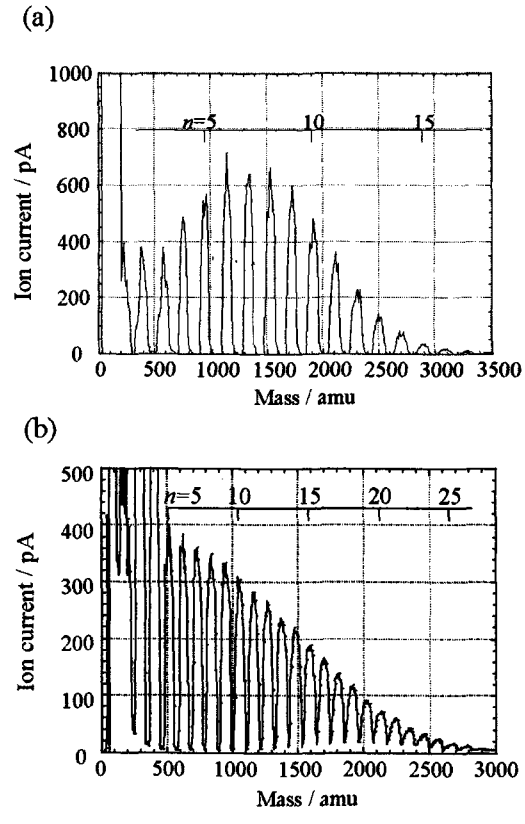

Figure 2. Mass spectra of (a) platinum and (b) silver cluster cations. The assignment of the cluster size, *n*, is shown in the figure.

Figure 2 shows mass spectra of platinum and silver cluster cations, $(Pt)_n^+$ and $(Ag)_n^+$. Typical currents of $(Pt)_{10}^+$ and $(Ag)_{10}^+$ were 500 pA and 300 pA, respectively. The largest sizes of these cluster ions produced with practical currents were 30 and 50 for $(Pt)_n^+$ and $(Ag)_n^+$, respectively. Copper cluster cations, $(Cu)_n^+$, were also produced with currents of 300 pA in the size range of n<~45.

3.2 Translational-energy distribution of cluster ions

A retarding potential method was employed to measure the translational energy of the cluster cations. Figure 3 shows the currents measured at the entrance and the exit of the mass filter as a function of the retarding bias-voltage applied to the detector plate, where the current measured at the entrance and the exit are those for $(Pt)_n^+$ (n=1-15) and $(Pt)_4^+$, respectively. The full widths at half maximum (FWHM) of the translational-energy distribution were determined to be 0.8 eV and 8 eV for $(Pt)_n^+$ and $(Pt)_4^+$, respectively, by use of an error function for the determination of each FWHM. The translational-energy distribution of $(Pt)_n^+$ can be widened because of the rf field applied in the mass filter. The increase of the FWHM with the cluster size is attributed to this effect; the FWHM of $(Pt)_{10}^+$ was 10.5 eV.

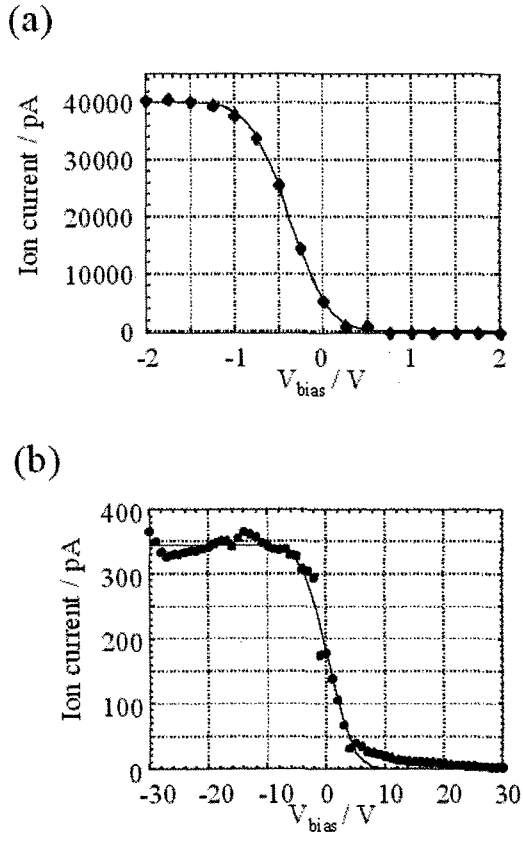

Figure 3. Translational-energy distributions of the platinum cluster cations observed (a) before and (b) after the mass filter as a function of the retarding bias voltage, V_{bias}, applied to the detector. The solid circles show the measured distribution, while the solid curves the calculated one obtained by fitting with an error function.

3.3 Profile of cluster-ion beam

A profile of the cluster-ion beam was measured by a phosphor screen attached behind a tandem micro-channel plate (MCP). The profile was well reproduced by a two-dimensional Gaussian with the standard deviation of 2 mm at the translational energy of 50 eV. Figure 4 shows a one-dimensional distribution of the beam profile along a line perpendicular to the axis of the cluster-ion beam at the energy of 50 eV. The beam diameter slightly increased with decreasing in the translational energy of the cluster ions; the standard deviation was 3.5 mm at the energy of ~1 eV.

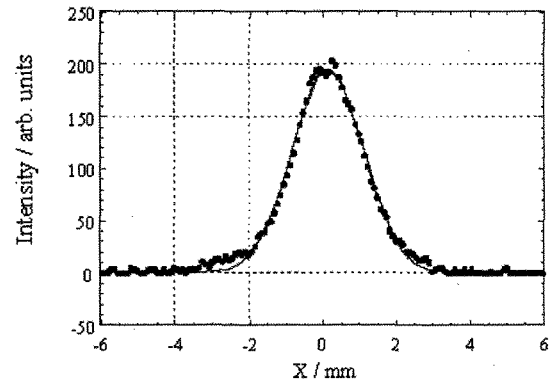

Figure 4. Beam profile of $(Pt)_4^+$ along a line (x direction) perpendicular to the beam axis at the translational energy of 50 eV. The solid circles show the observed distribution, while the solid curve the calculated one by fitting with a Gaussian.

3.4 Cluster deposition and STM observation

Size-selected platinum and silver cluster ions with a typical current of 10-250 pA were deposited for 5-30 min at 300 K and at 10^{-6} Pa on a graphite (0001) surface prepared by cleaving in air and without any further treatment.

Figure 5 shows STM images of $(Pt)_{10}$, $(Pt)_4$ and $(Ag)_4$ on the graphite surface observed at 300 K and at $1x10^{-5}$ Pa by use of a platinum-iridium tip in a constant height mode (current imaging), where the collision energy for the deposition was 30 eV for $(Pt)_{10}$ and $(Pt)_4$, and 10 eV for $(Ag)_4$. A typical bias voltage applied to the surface and the tunneling current were +0.05 V and 500 pA, respectively. The STM images of the clusters were observed with an atomic resolution.

As shown in Figure 5(a), the STM images of the clusters have comparable diameters. This indicates that the clusters remain intact at and after the collision. The STM images were not influenced both by scanning and by exposure of the surface to air. These findings indicate that the clusters are held firmly on the graphite surface, probably because of forming Pt-C chemical bonds during instantaneous heating by the cluster impact [8,9].

The STM images $(Pt)_{10}^{+}$ have an average diameter of 1.5 nm, while that for $(Pt)_{10}$ is calculated to be 0.6 nm on the basis of a bond length of a platinum bulk metal. It seems that electron cloud of $(Pt)_{10}$ extends to the outside of the actual region of $(Pt)_{10}$ and a finite size of the STM tip gives the larger diameter [10].

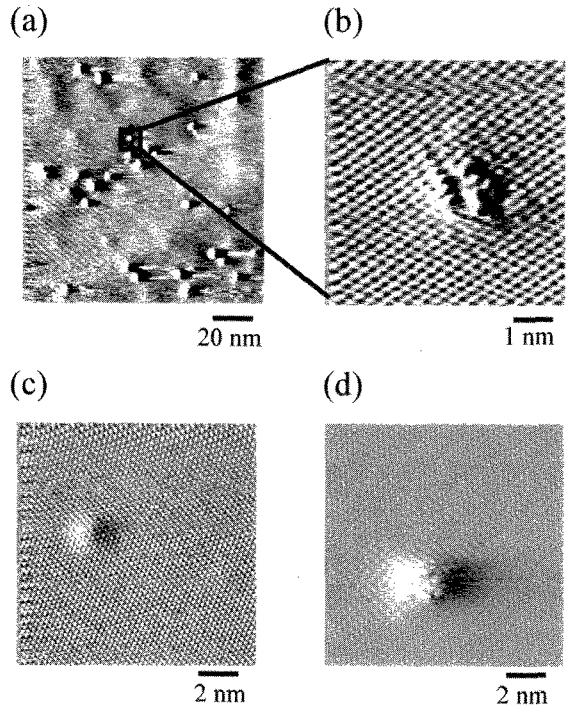

Figure 5. STM images of (a), (b) $(Pt)_{10}$, (c) $(Pt)_4$ and (d) $(Ag)_4$ deposited on a graphite(0001) surface at the collision energy of 30 eV for $(Pt)_{10}$ and $(Pt)_4$ and 10 eV for $(Ag)_4$. Image (b) was a magnified view of (b) by 20 times. All were measured at 300 K and at 10^{-5} Pa with a platinum-iridium tip in a constant height mode (current imaging). The scales are shown in the figure.

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