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Parallel deposition of size-selected clusters: a novel technique for studying size-selectivity on the atomic scale

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Abstract

A new size-selected cluster deposition technique referred to as "parallel-deposition" is presented. An ion beam of multi-sized Au_n clusters was spatially separated into individual cluster sizes by utilizing a Wien filter and the clusters spatially separated based on their atomic sizes were simultaneously deposited on a SiO_2/Si(100) substrate. Parallel-deposited Au_n clusters (n = 6, 7, and 8) on the SiO_2/Si(100) showed even-odd oxidation behaviour by an exposure to atomic oxygen atmosphere, demonstrating the potential of this new technique to study the size-dependent properties of deposited clusters in various research fields.

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The size-selectivity of transition metal nanoparticles has been extensively studied in many different research fields over the past few decades due to its importance in fundamental science as well as applications in energy and environmental sciences.[1-13]

Clusters are entities consisting of only several hundreds of atoms. In this very small size regime, changes of various physical and chemical properties as a function of the atoms in a cluster can be not only strongly size-dependent but also non-scalable.[14-18] Only even-numbered anionic Au clusters consisting of less than 21 atoms in the gas phase react with molecular oxygen whereas the odd-numbered neighbors are inert, representing only one of the many recent examples of non-scalable changes of the properties of clusters as a function of the number of atoms in a cluster.[18-23] It is worth noting that mass-selection of clusters on the atomic scale should be achieved for studying the size-selectivity of clusters, which can only be done with the aid of mass spectrometry. After the generation of variously sized clusters in the gas phase, the clusters are guided to pass through a mass spectrometer, in which clusters are timely or spatially separated by their cluster masses.[24-26] The size-dependence of properties of free gas-phase clusters can be measured. In addition, size-selected clusters can be deposited on the surface and these deposited clusters can be used for investigating not only size-selectivity of various properties, but also cluster-substrate interactions.[14-23]

In most previous studies of mass-selected clusters deposited on surfaces, clusters with only one specific size could be deposited at once.[18-23] The preparation of samples with different cluster sizes is time-consuming and the conditions of each experiment must be strictly controlled to properly study the chemical and physical properties of deposited clusters with various sizes. Here, we present a new parallel-deposition technique utilizing a Wien velocity filter, which enables deposition of clusters on a substrate with lateral separation based on their sizes. Using this technique, clusters with neighboring atomic sizes can be deposited on different places on a substrate at once, which can allow faster screening of size-selectivity of deposited clusters in diverse research fields. As an example, the parallel-deposition of Au_n^+ (n= 6, 7, and 8) clusters on a SiO_2/Si(100) surface was carried out. Among the clusters with

2-13 atoms, these series of Au_n (n= 6, 7, and 8) clusters have been demonstrated to show pronounced even-odd alteration of oxidation behaviors on a SiO_2/Si(100) surface.[21,23] This previously-reported the size-selectivity on oxidation behaviors of Au clusters was re-demonstrated with the parallel-deposited Au_n (n= 6, 7, and 8) clusters on silica surface, proving the practicability of this new parallel-deposition technique for size-dependent property study of mass-selected clusters.

The clusters were produced by Ar-sputtering of a gold (99%) target with a magnetron sputter source.[26] (+)-charged Au clusters were extracted and accelerated by a 90° quadrupole deflector with a guiding tube (U_o = -1 kV, as a guiding voltage). The cluster beam was focused using Einzel lenses and its direction was corrected using electrostatic deflectors (see ESI†, Fig. S1). This focused (+)-charged cluster ion beam entered the Wien velocity filter[25, 27, 28] and split into several cluster ion beams with various charge to mass (q/m) ratios (Fig. 1).

In Fig. 1, the experimental set-up used to investigate the spatial resolution of split cluster beams and their parallel deposition is schematically described. A cylinder-shaped guiding tube (U_o = 1 kV, diameter of 24 mm) covered by a nickel mesh (74 microns) was placed in front of the Wien filter (~0 mm distance along the X-axis) in order to reduce possible broadening of the (+)-charged cluster beam by an inhomogeneous electric field between the Wien filter and detector. The cross-section of the spread beams was checked by scanning the channeltron detector with a pin hole aperture of ~0.1 mm along the Z-axis using a linear motion feedthrough with a step motor at a scanning speed of 0.1 mm/s.

The cross-section of the beam along the Z-axis shown in Fig. 2 was obtained with fixed electric and magnetic fields of the Wien filter of 80 V across the Wien filter electrodes and 200 mT, respectively. These values of the electric and magnetic fields correspond to the maximum intensity position of the Au_7^+ clusters in the mass spectrum (see ESI†, Fig. S2). A sudden drop of the cluster signal from the channeltron detector was observed when its Z position went beyond the size of the guiding tube (below ~-12 mm and above ~12 mm). The beam cross-section shown in Fig. 2 obtained by the channeltron scanning mode showed that each cluster ion beam (Au_6^+, Au_7^+, and Au_8^+) was well spatially separated along the Z-axis by

the Wien filter. In the spatial cluster profile shown in Fig. 2, a peak corresponding to the Au_7^+ cluster beam was centered at the '0' Z-axis position and the relative intensity of each Au_n^+ cluster peak (n=6, 7, and 8) decreased with increasing number of Au atoms, which agrees with the mass spectrum shown in the ESI† (Fig. S2). The distance between the maximum intensities of adjacent cluster peaks was around 11 mm.

Au_6^+, Au_7^+, and Au_8^+ spatially separated by the Wien filter were deposited on a Si wafer (SiO_2/Si (100), 25 x 15 mm) by positioning a Si wafer in front of the channeltron detector at the center of the guiding tube (Fig. 1). The Si wafer was chemically etched with an acidic solution containing H_3PO_4, HNO_3, CH_3COOH, and H_2O at a volume ratio of 3:3:23:1 before deposition to immobilize the deposited Au clusters.[21, 23] Size-selected Au_n^+ clusters were soft-landed on the SiO_2/Si surface with a kinetic energy of less than ~0.2 eV per atom by applying a de-acceleration voltage on the substrate. Clusters were deposited on the Si wafer with a cluster current of ~0.7 nA for 40 min and the estimated coverage of the Au clusters on the Si wafer was ~10^{13} clusters/cm^2 (10% of a monolayer).

Then, the sample with deposited clusters was transferred from the deposition chamber to the XPS analysis chamber (see ESI†, Fig. S3) in order to evaluate the lateral separation of deposited clusters on the surface. The spatial resolution of our XPS system was checked with Au foil with a lateral size of 2 x 20 mm and was found to be less than ~3 mm (see ESI†, Fig. S4). XPS spectra at different Z-positions were obtained in order to check the position of each cluster spot and spatial separation between neighboring spots (Fig. 3).

The intensity of the Au4f core-level XPS spectra increased and decreased when the sample was laterally scanned along the Z-axis, showing three discrete spots of Au clusters (Au_6, Au_7, and Au_8 clusters at ~9, 0, and -8 mm, respectively). Fig. 3 shows the intensity ratio of the Au4f to Si 2p core-level XPS spectra recorded at 5 different positions along the Z-axis, corresponding to the center of Au_6, between Au_6 and $_7$, the center of Au_7, between Au_7 and Au $_8$, and the center of Au_8 (from top to bottom). Each $Au4f_{7/2}$ peak (Au_6, Au_7, and Au_8) was centered at ~84 eV, corresponding to Au(0).[21]

The exact positions of each spot of the Au_n clusters (n= 6, 7, and 8) along the Z-axis probed

by XPS after deposition shown in Fig. 3 were not exactly the same as those determined by channeltron scanning shown in Fig. 2. This is probably due to differences of the experimental conditions where the drift distance of cluster beams along the X-axis from the end of the guiding tube to the substrate was shorter than that for the detector (Fig. 1). Also, an additional de-acceleration voltage was applied on the substrate only during deposition for soft-landing.

Concerning the limitations of the technique, the spatial resolution would in principle correspond to the mass resolution of the Wien filter. In this case, the upper limit of the Au cluster size which can be parallel deposited with a spatial separation with neighboring clusters would be ~ n=20. However, when we measured the spot size on the sample using XPS and compared it to the diameter of the ion beam for a single mass, we found a spot size of 5 mm for deposited Au_6^-, while the diameter of the ion beam was 3 mm. Hence, there is a broadening caused by the soft landing process, which reduces the mass resolution for the deposited clusters down to 10. If there would be more space for the ion beam in the Wien filter, a larger spread between the different beams corresponding to different masses would be found, making parallel deposition of larger clusters with spatial separation possible.

Spatial separation of adjacent cluster spots was observed after the cluster deposition and more importantly, size-dependent behaviors of parallel-deposited Au_n (n= 6, 7, and 8) clusters were also observed, which will be presented in the below.

Oxidation behaviours of parallel-deposited Au_n (n= 6-8) clusters on a SiO_2/Si surface were evaluated using an *in situ* XPS set-up in order to prove the feasibility of the parallel-deposition technique to study size-dependent properties (see ESI†, Fig. S3). These particular series of Au clusters were chosen, since their even-odd oxidation behaviors have been already well established by previous works.[21,23] The sample surface of parallel-deposited Au_n clusters (n=6, 7, and 8) was exposed to oxygen (8.0×10^{-5} torr) activated by a hot Pt filament (4.5 A) for 1 hr in the preparation chamber. Then, the sample was subsequently exposed to a CO atmosphere (6000 Langmuir) in the preparation chamber. After exposure to each gas, XPS spectra were recorded in the main chamber at different Z positions corresponding to the Au_6, Au_7, and Au_8 clusters. No changes of the lateral separation on the SiO_2/Si surface were

observed even after 6 hr of O_2 exposure.

In Fig. 4, the Au4f core-level spectra before gas exposure, after O_2 exposure, and after CO exposure at each Z position for the Au_6, Au_7, and Au_8 clusters are displayed after Si satellite subtraction. Each Au 4f peak was deconvoluted using linearly-mixed Gaussian-Lorentzian functions with a fixed binding energy and full-width at half-maximum.

Oxidized Au states (Au(III)) appeared in the Au 4f XPS spectra of the even-numbered Au_n clusters (n=6 and 8) upon O_2 exposure, whereas odd-numbered Au_7 did not show any discernable change under the same conditions. The oxidized states at the Au_6 and Au_8 clusters were reduced by subsequent CO exposure (6000 Langmuir) at room temperature. The previously reported even-odd oxidation pattern of Au_n (n= 6-8) on a silica surface[21, 23] was reproduced by our experimental results, where unique properties of Au_6, Au_7, and Au_8 can be found on different places in one sample. It is also worth mentioning that the even-odd oxidation behaviors of Au_n clusters (n=6, 7, and 8) parallel-deposited on a silica surface were seen even with Pt contamination (~1.5 at.%) during oxygen exposure.

In summary, we present a new parallel-deposition technique, in which clusters can be spatially separated by their masses and simultaneously deposited on one substrate. By utilizing a Wien velocity filter, the spatial separation of differently sized clusters from non-size-selected cluster ion beams was achieved. The cross-section of the spread beams after passing the Wien filter was investigated by scanning a channeltron detector and the spatial resolution of the deposited clusters was also confirmed by XPS analysis. The previously reported even-odd oxidation pattern of Au clusters was reproduced with parallel-deposited Au_n clusters (n=6, 7, and 8) on a silica surface, demonstrating the potential of this new parallel-deposition technique for studying various size-dependent properties of clusters.

Associated Content

Supporting Information. Experimental set-up for the generation of the (+)-charged cluster ion beam is schematically shown. Wien filter mass spectrum of Au_n^+ clusters obtained by scanning the magnetic field with a fixed electric field of 100 V is shown. The in-situ XPS

set-up used to determine the spatial separation of clusters spots after the parallel-deposition of Au_n clusters (n=6, 7, and 8) on SiO_2/Si surface is schematically shown. The experimental scheme used to determine the spatial resolution of X-ray photoelectron spectroscopy (XPS) with Au foil is displayed along with XPS spectra obtained at different Z positions.

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Notes and references

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† Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/c000000x/

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Figure captions

Figure 1. The splitting of the (+)-charged cluster beam by a Wien velocity filter is schematically described with an experimental set-up of the parallel-deposition chamber. Here, the incoming cluster beam into the Wien filter with only X-axis velocity is assumed to consist

of three different cluster sizes (n+1, n, n-1) (zero Z-axis and Y-axis velocities). The center of the guiding tube (or Wien filter) is at the zero position of the Z-axis. Experimental set-up for the generation of the (+)-charged cluster ion beam is schematically shown.

Figure 2. The cross-section of the beam of Au_n^+ clusters (n=6, 7, and 8) after the Wien filter obtained by a channeltron detector scan along the Z-axis is displayed.

Figure 3. a) Au $4f_{7/2}$ core-level spectra at different Z-axis positions are displayed. b) The intensity ratio of Au $4f_{7/2}$ with respect to the Si 2p core-level XPS spectra at each Z-axis position is shown.

Figure 4. a) Au 4f core-level XPS spectra of the as-prepared sample recorded at different Z-axis positions, corresponding to the centers of the three spots of the Au_6, Au_7, and Au_8 clusters are shown. b) Au 4f core-level XPS spectra of the sample after O_2 exposure (8.0×10^{-5} torr O_2 for 1 hr with a hot Pt filament) are shown. c) The Au 4f core-level XPS spectra of the sample after subsequent CO (6000 L) exposure at room temperature are shown. Each spectrum was normalized by the intensity of each Au(0) state for comparison.

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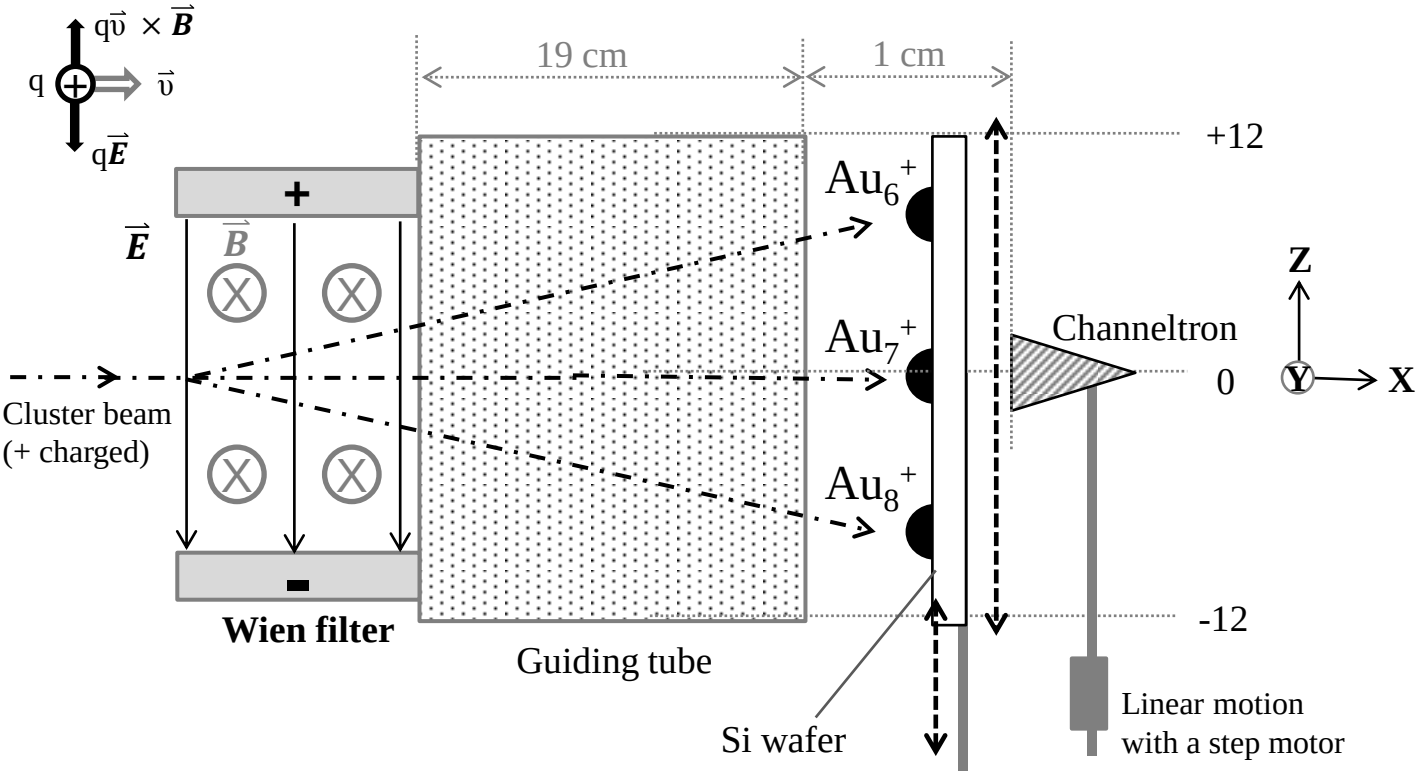

qυ × B
q
υ
qE
19 cm
1 cm
+12
0
-12
+
-
E
B
Au6+
Au7+
Au8+
Channeltron
Z
Y
X
Cluster beam
(+ charged)
Wien filter
Guiding tube
Si wafer
Linear motion
with a step motor

Figure 1

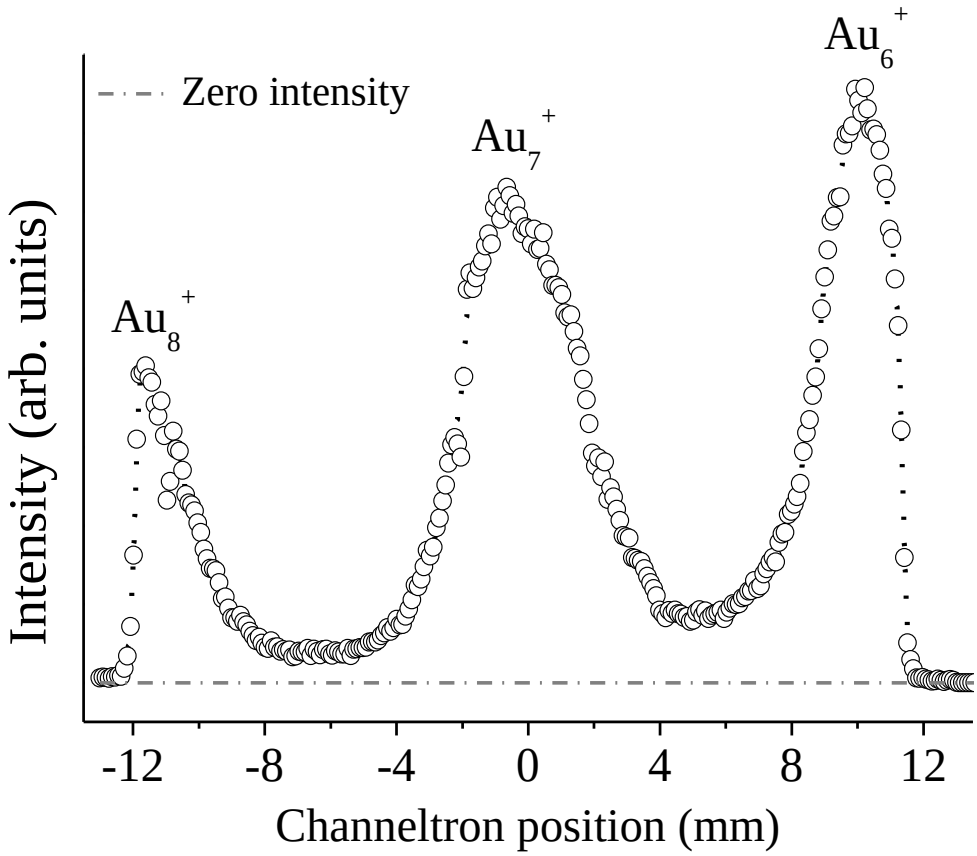

Zero intensity
Au8+
Au7+
Au6+
Intensity (arb. units)
-12
-8
-4
0
4
8
12
Channeltron position (mm)

Figure 2

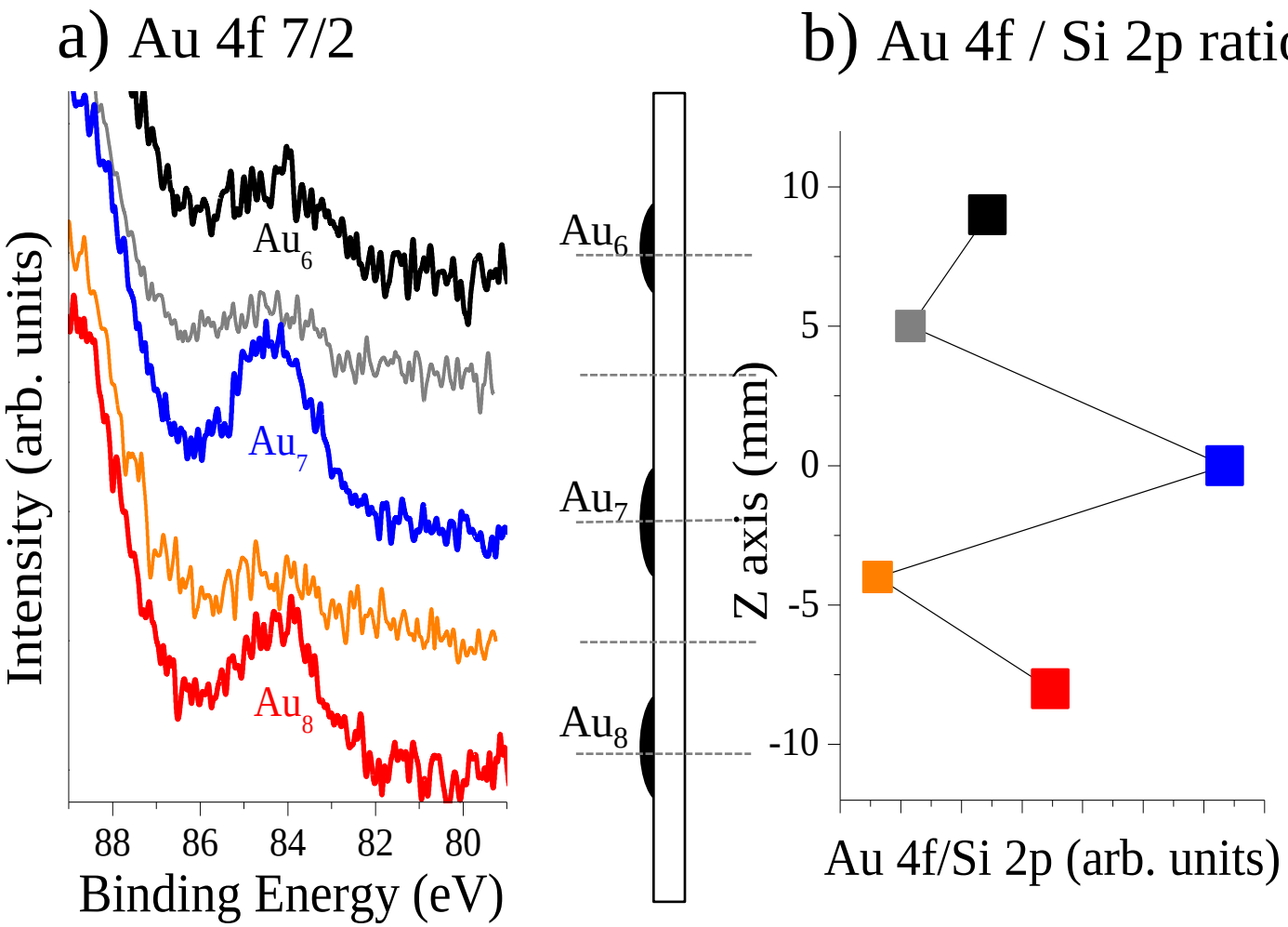

a) Au 4f 7/2
Intensity (arb. units)
Au6
Au7
Au8
88
86
84
82
80
Binding Energy (eV)
Au6
Au7
Au8
Z axis (mm)
b) Au 4f / Si 2p ratio
10
5
0
-5
-10
Au 4f/Si 2p (arb. units)

Figure 3

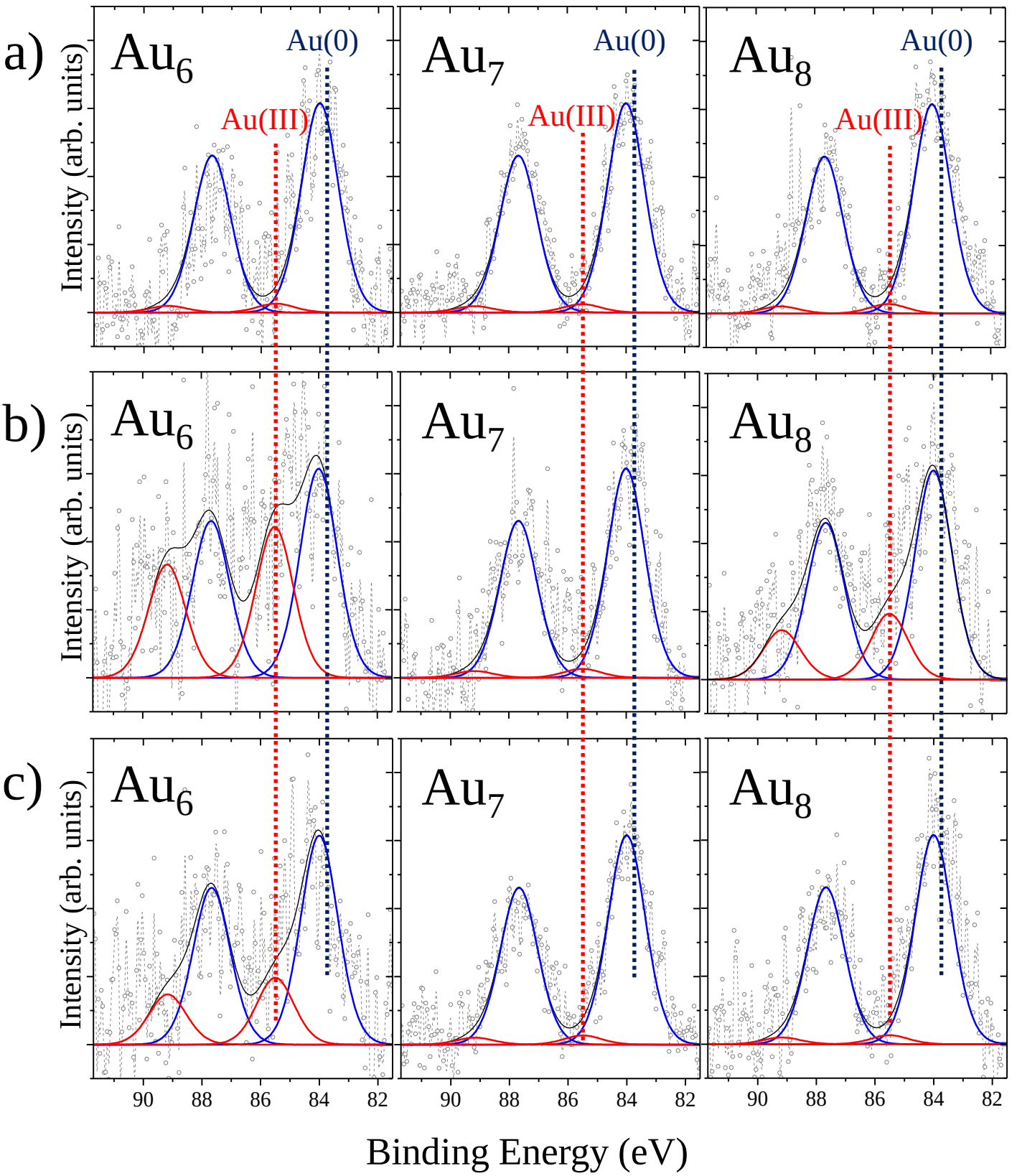
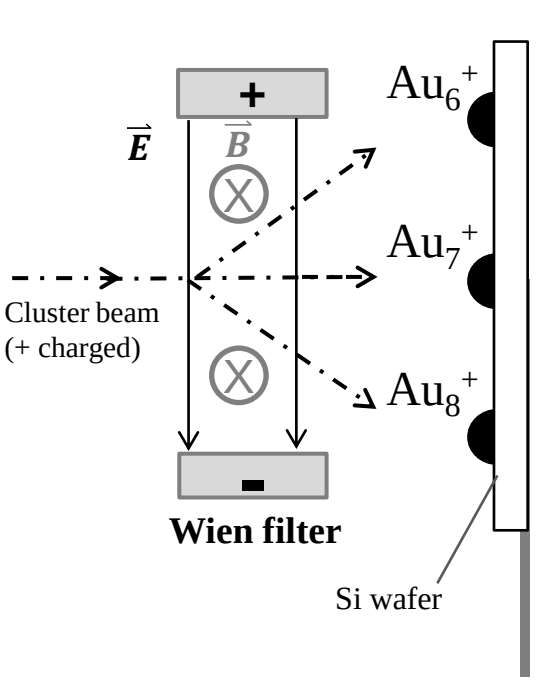
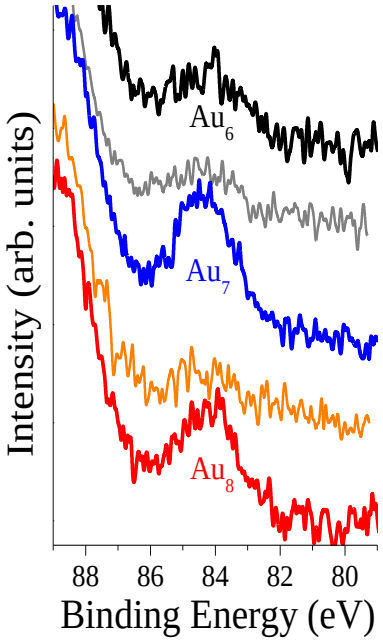

a)
b)
c)
Au6
Au7
Au8
Au(0)
Au(III)
Intensity (arb. units)
90
88
86
84
82
Binding Energy (eV)

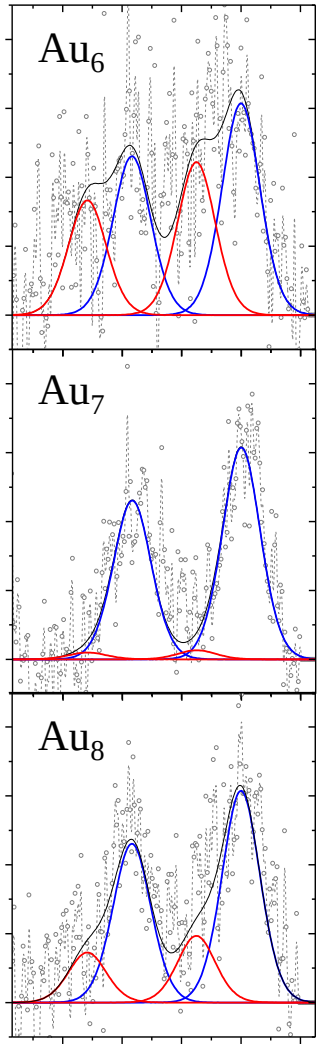
Figure 4

Parallel deposition of Au_n clusters





O_2 exposure



Oxidized

Non-oxidized

Oxidized