

# Size-selected Au clusters deposited on SiO<sub>2</sub>/Si: Stability of clusters under ambient pressure and elevated temperatures

Dong Chan Lim<sup>a</sup>, Rainer Dietsche<sup>b</sup>, Gerd Ganteför<sup>b</sup>, Young Dok Kim<sup>c,\*</sup>

<sup>a</sup> Department of Surface Technology, Korea Institute of Materials Science, Changwon 641-010, Republic of Korea

<sup>b</sup> Department of Physics, University of Konstanz, D-78457 Konstanz, Germany

<sup>c</sup> Department of Chemistry, Sungkyunkwan University, 440-746 Cheoncheon-dong, Jangan-gu, Suwon, Gyeonggi-do, Republic of Korea

## ABSTRACT

This study examined the oxidation and reduction behavior of mass-selected Au clusters consisting of 2–13 atoms deposited on silica. An atomic oxygen environment was used for the oxidation of Au. X-ray photoelectron spectroscopy (XPS) was used to identify Au(III) and Au(O). Au<sub>5</sub>, Au<sub>7</sub> and Au<sub>13</sub> clusters deposited on the as-prepared SiO<sub>2</sub>/Si substrates were highly inert towards oxidation, whereas the other clusters could be oxidized, i.e. the chemical property drastically changed with the number of atoms in a cluster. The size-selectivity in chemical reactivity remained unchanged upon air-exposure. The chemical properties of the deposited Au clusters were unchanged after annealing at 250 °C. Annealing at higher temperatures caused structural changes to the surface, as determined by the oxidation behavior. XPS of the deposited Au clusters upon annealing indicated charge transfer from Au to silica.

## Keywords:

Au  
SiO<sub>2</sub>  
Mass-selected clusters  
Oxidation

The catalytic activity of supported nanoparticles can be tuned by changing the particle size on the nanometer scale [1–6]. Quantum-confinement effects, geometric structures and metal-support interactions are related to the size-effect in heterogeneous catalysis [2,3,5]. Various techniques have been used to control the particle size. In particular, the deposition of size-selected clusters has attracted considerable attention because this method can be used to control the cluster size precisely on an atom-by-atom basis.

The pioneering work of Heiz and co-workers found that Au clusters consisting of 8–20 atoms supported on MgO are active towards CO-oxidation [7]. The catalytic activity of supported Pd and Pt clusters has also been studied [8,9]. These studies demonstrated that chemical reactivity is affected significantly by the cluster size on an atom-by-atom basis, suggesting that the clusters survive as individual entities after being deposited on a surface without fragmentation or agglomeration. The electronic structures of Au clusters supported on silica were examined by cavity ring down spectroscopy. The results showed that the Au clusters preferentially occupy the defect sites of the surface [10].

Recently, it was reported that the oxidation reactivity of silica-supported Au clusters is strongly dependent on the cluster size [11]. Some odd-numbered Au clusters, such as Au<sub>5</sub> and Au<sub>7</sub>, were inert to atomic oxygen, while the other clusters could be oxidized. Moreover, the oxidation behavior of Au clusters varies consider-

ably with the number of atoms in a cluster, suggesting only minor agglomeration or fragmentation of the deposited clusters with most size-selected clusters surviving as individual entities with their atomic size on the surface maintained. On the other hand, the Au clusters deposited on graphite had completely different oxidation behaviors to those on silica. This suggests that the metal-support interaction plays an important role in the chemical properties of these small deposited clusters [12].

Most studies on size-selected clusters deposited on the surface have been carried out under ultrahigh-vacuum conditions and at room temperature. It is unclear if these small clusters can survive under the more realistic conditions associated with heterogeneous catalysis. Therefore, one can study the size-selectivity in catalytic activity on an atom-by-atom basis under more realistic conditions. The present study examined the stability of these clusters under air and elevated temperatures under vacuum. Under air, the Au clusters on silica maintained their unique size-dependent chemical properties, suggesting that the clusters still maintain their original size and structure under ambient conditions [13]. Upon annealing at 250 °C, there was no change in the chemical properties of Au<sub>7</sub>. On the other hand, higher temperature annealing caused a change in cluster properties, most likely due to the effect of cluster sintering. Changes in the Au 4f and Si 2p spectra were observed after annealing at 500 °C. These results shed light on the electronic properties of Au clusters on silica.

All measurements were carried out under ultrahigh-vacuum (UHV) conditions [11–13]. X-ray photoelectron spectroscopy (XPS) was performed using a concentric hemispherical analyzer (CHA)

\* Corresponding author. Tel.: +82 31 299 4564; fax: +82 31 290 7075.

E-mail address: ydkim91@skku.edu (Y.D. Kim).

and an X-ray source with an Al target ( $K\alpha$ , photon energy = 1486.6 eV). One hour was required to acquire each Au 4f spectrum. Si wafers were chemically etched using a mixed aqueous solution of  $H_3PO_4$ ,  $HNO_3$ ,  $CH_3COOH$ , and  $H_2O$  at a volume ratio of 3:3:23:1. Chemical etching was necessary to increase the number of defect sites on the silica surface, thereby reducing the diffusion of the clusters over the surface, which can cause agglomerations. For the oxidation experiments, the backsides of the samples were exposed to a hot Pt-filament. At the same time, the chamber was backfilled with  $O_2$  ( $8 \times 10^{-5}$  mbar), which is known to create atomic or excited molecular oxygen [14]. Using this method, metal surfaces that do not react with  $O_2$  can be oxidized. After these atomic oxygen treatments, no Pt was detected by XPS. The exposure time to atomic oxygen was 30 min for each experiment.

A magnetron-sputtering source was used to produce Au cluster anions [15]. After extracting the ion beam into a vacuum, the cluster anions were accelerated to 1 kV. Mass separation was performed using a  $30^\circ$  sector magnet with a resolution of  $m/\Delta m = 20$ . In front of the sample, the clusters were decelerated to the desired deposition energy by applying the corresponding voltage to the sample. The number of clusters deposited on the surface was determined by measuring the sample current during deposition. All the clusters soft-landed on the surface with a kinetic energy  $<0.6$  eV per atom was used (most of the clusters had a kinetic energy  $<0.2$  eV per atom during deposition). The deposition time for the Au cluster anions on the substrate was  $\sim 30$  min. The measured sample current was approximately 0.4 nA during deposition.  $2 \times 10^{12}$  clusters were deposited on each sample. The estimated cluster density on a total area of deposition 3 mm was approximately  $3 \times 10^{13}$  clusters/cm<sup>2</sup>, which corresponds to  $<10\%$  of a monolayer equivalent.

Fig. 1 shows the XPS Au 4f level spectra of the Au clusters containing 2–13 atoms deposited on silica, which were collected after 30 min of atomic oxygen exposure [11]. In the Au 4f spectrum, the oxidation of Au was discriminated by a chemical shift of  $\sim 1.5$  eV. Additional shoulders corresponding to the oxidized Au species could be identified for most clusters. No Au-oxide formation was found on  $Au_5$ ,  $Au_7$  and  $Au_{13}$ , indicating that these clusters are highly inert and chemically stable. Generally, odd-numbered clusters tended to show lower reactivity towards oxidation than the even-numbered neighbors. The only exception was  $Au_{11}$ , which was more reactive than  $Au_{12}$  and  $Au_{10}$ . In contrast to silica, on graphite,  $Au_8$  was shown to be the only reactive species towards oxidation, indicating that the metal-support interaction changes the chemical properties of a cluster significantly [12].

Further studies will be needed to determine the origin of this size-selectivity of the oxidation behaviors, particularly theoretical calculations. From the experimental data, it was concluded that the size-selected clusters maintained their size upon deposition. If there would be sintering or fragmentation of the deposited clusters, pronounced size-selectivity in chemical properties should not be observed experimentally.

In order to shed light on the stability of these clusters in air, samples of the deposited clusters were exposed to air and then exposed to an atomic oxygen environment. Fig. 2 shows the XPS spectra of  $Au_5$  and  $Au_8$  clusters deposited on silica after these treatments. In Fig. 1,  $Au_5$  was shown to be inert towards oxidation, whereas  $Au_8$  was active. The  $Au_5$ -sample was still not oxidized after the air and atomic oxygen treatments, whereas,  $Au_8$  formed an Au-oxide. The chemical properties of these clusters remained unchanged after air-exposure. In contrast to silica,  $Au_8$  on graphite, which readily formed Au-oxide, could not be oxidized after air-exposure, suggesting that there is either a change in cluster structure upon air-exposure, or the formation of carbonate species by a reaction between oxygen and carbon, which poisons the Au surface (Fig. 3). It was reported that Ag nanoparticles supported on

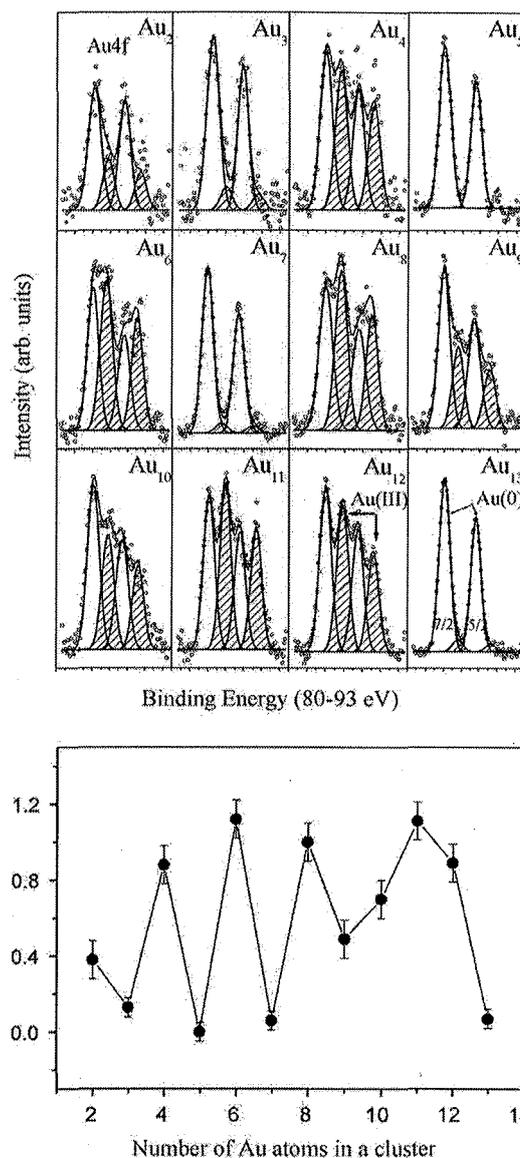


Fig. 1. XPS Au 4f level spectra of soft-landed Au clusters after atomic oxygen exposure. The bottom figure shows the change in the ratio of the Au(III) and Au(O) intensity as a function of the number of atoms in a cluster.

defective graphite can be deactivated chemically under oxidizing conditions, due to the formation of carbonate species on the Ag surface [16]. This suggests that silica can be a suitable substrate for examining the unique size-selective catalytic activity of Au under ambient conditions, whereas graphite is not.

Fig. 4 shows the Au 4f level spectra of the  $Au_7$  clusters on silica after a thermal treatment followed by atomic oxygen exposure. Soft-landed  $Au_7$  clusters were quite inert towards oxidation (Fig. 1), which was maintained upon annealing at 250 °C. It should be noted that no Au-oxide state appeared after annealing at 250 °C followed by the atomic oxygen treatment (Fig. 4). In contrast to annealing at 250 °C, the  $Au_7$  clusters deposited on silica could form Au-oxide upon exposure to atomic oxygen after annealing at 500 °C. It was reported that Au clusters deposited on oxide surfaces were mobile and tended to agglomerate at temperatures as high as 500 °C [17]. This suggests that Au clusters agglomerated upon annealing at 500 °C to form larger Au particles.

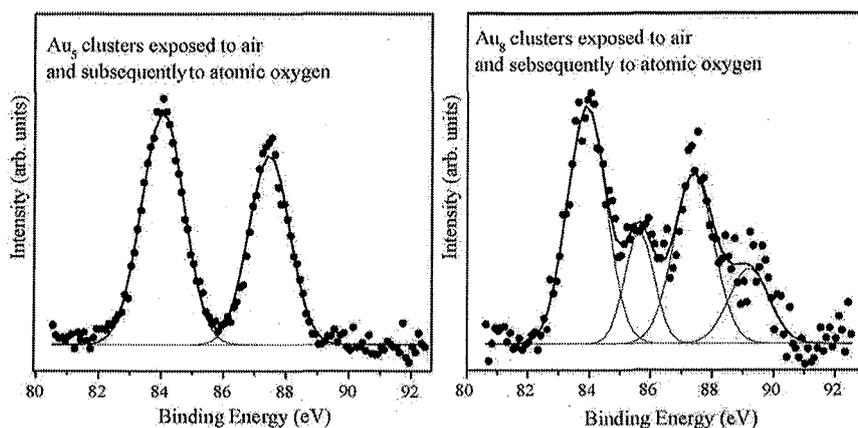


Fig. 2. XPS spectra of the Au 4f level of  $Au_5$  and  $Au_8$  clusters on silica obtained after air-exposure and a subsequent atomic oxygen treatment.

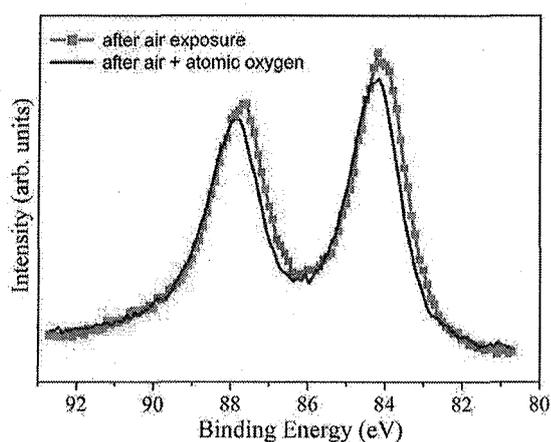


Fig. 3. Au 4f level spectra of  $Au_8$  clusters deposited on defective graphite. After exposing the sample to the air, the Au 4f level spectrum was obtained (line). After a subsequent atomic oxygen treatment, another Au 4f level spectrum was obtained (symbol + line).

Fig. 5 shows the XPS spectra of Au 4f, O1s and Si 2p levels acquired before and after the thermal treatment at 500 °C. Upon annealing, Au 4f level showed a new state at a lower binding energy. The Si 2p and O 1s peaks showed a positive shift after annealing. Upon agglomeration of Au clusters during annealing, number of Au atoms directly bound to  $SiO_2$  should decrease,

whereas number of Au–Au bonds should increase. The new state at the lower binding energy regime in the Au 4f level should correspond to the Au atoms coordinated to Au and not to  $SiO_2$ . The Au atoms directly bound to  $SiO_2$  should have a higher binding of the Au 4f level than that of Au atoms neighbored only by Au. Our results imply that Au atoms at the Au/ $SiO_2$  interface should be more positively charged than other Au atoms. The shift in the Si(IV) state upon annealing was more pronounced than that of Si(O), i.e. annealing resulted in a larger change in the surface electronic structure than that of the deeper layers of the substrate. It should be noted that a native silicon oxide layer exists on the Si surface. Recently, the electronic structures of Au nanoparticles on silica were examined in detail using synchrotron radiation photoemission spectroscopy, and there was a positive and negative core level shift for Au 4f and Si 2p levels, respectively as a consequence of the Au to silica charge transfer [18]. Similar to the result of the present study, a larger shift of the Si(IV) state than Si(O) was found [18]. The positive and negative shifts of the Si 2p and Au 4f levels in Fig. 5 suggest charge transfer from Au to  $SiO_2$ , resulting in a partially positively charged Au, and the influence of charge transfer in the core level shift was reduced upon thermal treatment due to sintering.

The formation of positively charged clusters can partially explain some of the odd-numbered Au clusters being highly inert and chemically stable. Within the electronic shell model, even-numbered cluster neutrals should show closed electronic shell configurations, and be chemically more inert than their odd-numbered neighbors. If one Au atom of a cluster attached directly to

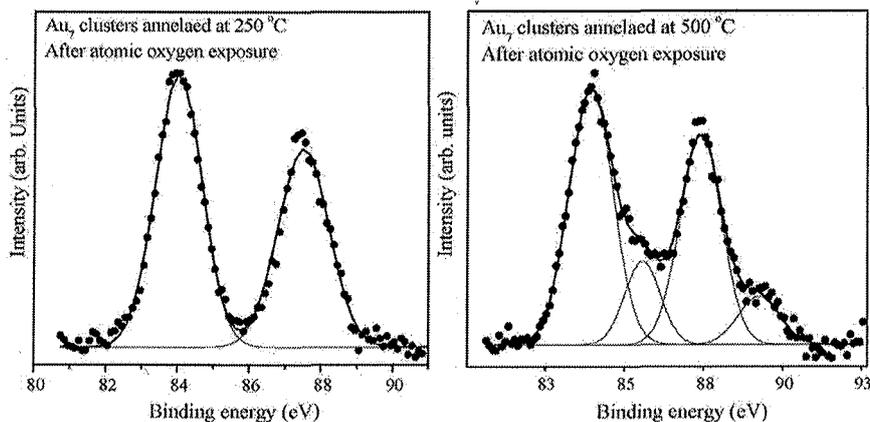


Fig. 4. Au 4f level spectra of  $Au_7$  on silica obtained after annealing followed by atomic oxygen exposure. The annealing temperatures and times are given in the figure.

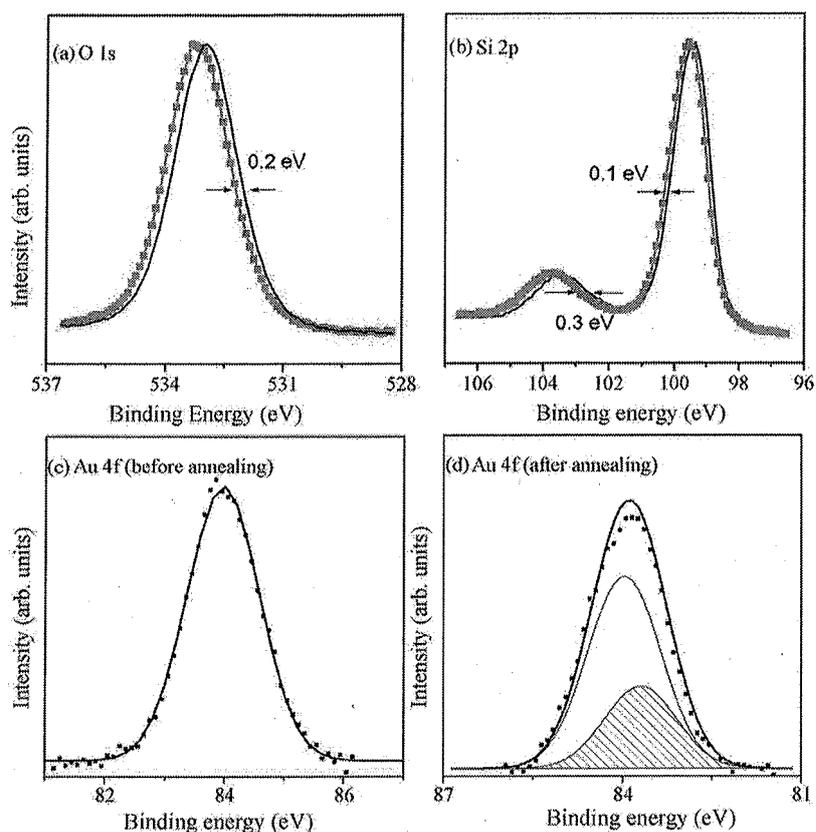


Fig. 5. (a) O 1s and (b) Si 2p spectra of Au<sub>7</sub> clusters on silica before (line) and after annealing (scatter + line). (c) and (d) Au 4f level spectra before and after annealing, respectively. A new state at a lower binding energy can be found after annealing.

the substrate is positively charged, then the number of valence electrons of the odd-numbered clusters should become even, i.e. odd-numbered clusters on silica could show a closed electronic shell configuration. Charge transfer from Au to silica can provide a reasonable explanation for the appearance of some odd magic numbers for Au clusters supported on silica, and further theoretical studies may provide a better insight into this issue. The only exception in this even-odd relationship is Au<sub>11</sub>, which is an odd-numbered reactive cluster. In the gas-phase studies, one can also find some exceptional cases, e.g. even-numbered Au cluster anions are more reactive with oxygen than other odd-numbered neighbors; however, Au<sub>16</sub> cluster anions are inert towards oxygen chemisorptions [19]. For a complete understanding of the size-selectivity of chemical properties, a simplified electron shell model is not enough, and geometric and electronic structures should be fully considered.

In conclusion, the oxidation behavior of Au clusters deposited on silica showed strong size-selectivity, suggesting that the size-selected clusters survive as individual entities upon deposition with only minor agglomeration. Au clusters on silica maintained their cluster properties upon exposure to air, whereas the chemical properties of Au on graphite were changed. Au<sub>7</sub>/silica samples did not undergo structural transformation upon annealing at 250 °C. This suggests that size-selected Au clusters deposited on silica can be used for catalytic reactions under the conditions used in real catalysis.

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