Oxidation of deposited Au_n ($n = 2-13$) on SiO₂/Si: Influence of the NaOH(aq) treatment

Dong Chan Lim^a, Rainer Dietsche^b, Gerd Ganteför^b, Young Dok Kim^{c,*}

^aDepartment of Surface Technology, Korea Institute of Materials Science, Changwon 641-010, Republic of Korea

^bDepartment of Physics, University of Konstanz, D-78457 Konstanz, Germany

^cDepartment of Chemistry, Sungkyunkwan University, 440-746 Cheoncheon-dong, Jangnan-gu, Suwon, Gyeonggi-do, Republic of Korea

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ABSTRACT

Au cluster anions consisting of 2–13 atoms were soft-landed on native-oxide-covered Si wafers. Reaction of soft-landed clusters with an atomic oxygen atmosphere was studied using X-ray photoelectron spectroscopy (XPS). Au₅, Au₇, and Au₁₃ turned out to show pronounced inertness for Au-oxide formation. When the samples with deposited Au clusters were treated with aqueous NaOH, the inert Au₅, Au₇, and Au₁₃ clusters became reactive towards Au-oxide formation, whereas the other originally reactive clusters became inert. This result can be interpreted in terms of electronic modification of Au clusters by Na, which was also evidenced by Au 4f and Na 1s core level shifts.

1. Introduction

Size-dependent changes of the properties of transition metal particles have attracted much attention due to the appearance of unique chemical and physical properties at certain sizes [1–4]. In order to shed light on the size-selectivity on the atom-by-atom basis, size-selected clusters have been studied. In the gas phase, mass of free clusters can be precisely selected using mass-spectrometry, and therefore, size-dependent changes of the physical and chemical properties of materials can be studied in detail [5–7]. More recently, not only free, but also deposited size-selected clusters have been studied, which can provide a deeper insight into the alteration of the cluster properties by the cluster-substrate interactions [8–11].

Mass-selected Au clusters deposited on oxide surfaces have been of particular interest due to their interesting activity in heterogeneous catalysis. Au clusters with certain sizes are reactive for heterogeneously-catalyzed reactions such as CO-oxidation. Au clusters consisting of 8–20 atoms on MgO turned out to be reactive for CO-oxidation, whereas smaller cluster are not [8]. It was suggested that the charge transfer between the Au and F centers on MgO should be crucial for enhancement of catalytic activity [8]. On TiO₂, Au₃ and Au₇ turned out to be reactive towards CO-oxidation [9]. On silica surfaces, pronounced inertness towards Au-oxide formation for some odd-numbered Au clusters such as Au₅ and Au₇ were shown [10]. Using cavity ring down spectroscopy (CRDS), it

was suggested that Au is bound to non-bridging oxygen sites of silica surfaces, which may change the charge state of Au, thereby influencing its chemical properties [11].

In the present work, Au clusters consisting of 2–13 atoms were deposited on native-oxide-covered Si wafers, and their chemical properties studied by investigating the oxidation/reduction behaviors. For Au clusters smaller than Au₉, an even-odd behavior can be found, whereby the odd-numbered clusters are generally more inert than the even-numbered neighbors when they are exposed to an atomic oxygen environment [10]. Among the odd-numbered clusters, 5 and 7 are the magic numbers with a pronounced inertness towards oxidation; however, this even-odd pattern was absent for larger clusters. For the Au clusters consisting of more than 8 atoms, Au₁₃ was the only inert species. Upon NaOH solution treatment, clusters inert towards oxidation became more reactive, whereas the other originally reactive neighbors became less reactive. This result can be interpreted in terms of electronic modification of the Au clusters by Na, which was also evidenced by Au 4f and Na 1s core level shifts.

2. Experimental

All the measurements were performed under ultrahigh vacuum (UHV) conditions [10,12]. For X-ray photoelectron spectroscopy (XPS), a concentric hemispherical analyzer (CHA) and an X-ray source with an Al target ($K\alpha$, photon energy = 1486.6 eV) were used. For acquisition of each Au 4f spectrum, 1 h was required. Si wafers were chemically etched using a mixture of three different acids and water (H₃PO₄, HNO₃, CH₃COOH, and H₂O with a volume

* Corresponding author. Tel.: +82 31 299 4564; fax: +82 31 290 7075.
E-mail address: ydkim91@skku.edu (Y.D. Kim).

ratio of 3:3:23:1). The chemical etching was done in order to increase the number of defect sites of the silica surface, thereby reducing the diffusion of the clusters on the surface, which can cause their agglomeration. For the oxidation experiments, the backsides of the samples were exposed to a hot Pt-filament and, at the same time, the chamber was filled with molecular oxygen (8×10^{-5} mbar), which is known to create atomic or excited molecular oxygen [13]. Using this method, metal surfaces, which do not react with molecular oxygen, can be oxidized. After these atomic oxygen treatments, no Pt could be detected using XPS. The exposure time of each sample to atomic oxygen was 30 min.

For the creation of Au cluster anions, a magnetron-sputter-source, originally designed by Prof. Haberland's group at the University of Freiburg, Germany, was used [14]. After extracting the ion beam into a vacuum, the cluster anions were accelerated to 1 kV. Mass separation was done by means of a 30° 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 can be counted by measuring the sample current during deposition. All the clusters were soft-landed on the surface in which a kinetic energy of less than 0.6 eV per atom was used (most of the clusters had a kinetic energy less than 0.2 eV per atom during deposition). For deposition of the Au cluster anions on the substrate, ~ 30 min were required. The measured sample current was about 0.4 nA during deposition. 2×10^{12} clusters were deposited on each sample. Considering that the diameter of the area of the cluster deposition is estimated to be 3 mm, the cluster density is suggested to be roughly 3×10^{13} clusters/cm². This corresponds to less than 10% of a monolayer equivalent [10,12].

After the clusters had been deposited on the surface, the samples were immersed into distilled water or aqueous 0.1 M NaOH (purity: 99%) for 10 min [15]. After these treatments, the samples were immediately inserted into the vacuum system and oxidation/reduction experiments and XPS-analyses performed. For reduction, the surfaces were exposed to 10,000 Langmuir ($L = 1 \times 10^{-6}$ torr $\times$ 1 s) of CO at room temperature.

Fig. 1. Au 4f level spectra of deposited Au clusters consisting of 2–13 atoms after atomic oxygen exposure are summarized. The shadowed regions correspond to the Au(III) species.

3. Results and discussion

Mass-selected Au cluster anions consisting of 2–13 atoms were soft-landed on native-oxide-covered Si wafer surfaces. Subsequently, the samples were exposed to atomic oxygen environments. Fig. 1 shows the Au 4f level spectra obtained after atomic oxygen treatment of each sample. The peaks of the doublet structure of Au(0) were centered at 84 and 87 eV, respectively, as in bulk Au, whereas the Au(III) species showed a positive core level shift of 1.5 eV with respect to the Au(0) state.

With increasing the number of Au atoms in a cluster, the ratio between Au(III) and Au(0) strongly varied (Fig. 2). For $n = 2-9$, an even-odd alteration could be found where the even-numbered clusters showed higher intensities of Au(III) peaks with respect to the Au(0) peaks than in the case of the odd-numbered neighbors. In particular, an even-odd variation was pronounced for $n = 4-9$, where Au_5 and Au_7 showed an extraordinarily high inertness towards Au-oxide formation. For Au clusters consisting of more than 9 atoms, the even-odd behavior disappeared. Oxidation of Au_{11} was more facile than that of other directly neighboring clusters. In contrast to Au_{11} , Au_{13} was absolutely inert towards oxidation under our experimental conditions. For the samples with complete inertness of Au towards oxidation (Au_5 , Au_7 and Au_{13}), one can suggest that Au clusters survived as individual cluster after deposition with only minor fragmentation and sintering, since the chemical properties of these clusters are unique and different from those of other neighbors. For other clusters, it is not clear from the result in Fig. 1, whether deposited clusters partially underwent fragmentation and sintering, or not.

The samples prepared in the same way as those in Fig. 1 were immersed into aqueous 0.1 M NaOH and reinserted into the UHV system. Subsequently, the samples were exposed to the atomic oxygen environments (Figs. 3 and 4). Fig. 3 shows the Au 4f level spectra acquired after the atomic oxygen treatment of the NaOH(aq)-treated samples. We focused on those Au clusters, showing pronounced inertness in Fig. 1 (Au_5 , Au_7 and Au_{13}), warranting survival of individual clusters upon deposition, and their direct neighbors. One can conclude that the originally inert Au_5 , Au_7 , and Au_{13} became more reactive because these clusters showed higher relative intensity of the Au(III) peak compared to the case prior to NaOH(aq) treatment. In contrast, the other originally reactive clusters became less reactive towards Au-oxide formation.

Au 4f spectra of the deposited Au clusters exhibited negative core level shifts upon NaOH-treatment by 0.2–0.5 eV (Fig. 5). The core level shift was small, but could be found for all clusters studied here. The Na 1s spectra of the Au_8 -deposited sample with the NaOH-treatment are compared with the Na 1s spectrum of a Si wafer without NaOH(aq)-treated Au (Fig. 6). When Au was absent on

Fig. 2. Relative intensity ratio of Au(III) and Au(0) for each cluster is summarized.

the surface, Na showed a peak centered at about 1072 eV. When the Au-deposited sample was treated with NaOH, an additional shoulder at a higher binding energy could be identified in the Na 1s spectrum, possibly indicating Na atoms directly attached to Au. Change in Na 1s signal is rather small, since only a part of the surface was covered by Au, whereas Na covered whole the surface. Our XPS spot was larger than the Au cluster spot. The change in the Na 1s spectrum by Au is small, but reproducible in repeated experiments. Coexistence of Na and Au resulted in a positive and a negative Na 1s and Au 4f level shift, respectively. From these results of the core level shifts, one can suggest that interactions between Na and Au result in a charge transfer from Na to Au.

Considering electronic structure, a closed-shell electronic configuration with an even number of valence shell electrons can be magic [5–7]. Depending on preparation methods, both electronic and geometric magic numbers can appear. In the gas phase studies,

Fig. 3. Au 4f level spectra of originally inert clusters and non-inert neighbors are compared, which were taken after the NaOH(aq) treatment and subsequent atomic oxygen exposure.

Fig. 4. Relative intensity ratio of Au(III) and Au(0) for atomic-oxygen-treated Au_5 , Au_6 , Au_7 , Au_8 , Au_{12} , and Au_{13} , with and without NaOH(aq) treatment, is summarized.

Fig. 5. Au 4f level spectra before and after the NaOH(aq) treatment are compared, in which negative core level shifts upon NaOH-treatment are apparent.

odd-numbered Au cluster anions were shown to be less reactive than other even-numbered neighbors towards reactivity of molecular oxygen adsorption, due to lower electron affinity of odd-numbered cluster neutrals [5–7]. This result demonstrates that cluster reactivity is governed by electronic structures. Considering that addition of NaOH can electronically modify Au clusters, thereby changing the cluster reactivity, it can be proposed that the reactivity of the soft-landed clusters in our study is governed more by the electronic properties of Au clusters. For wet-chemically prepared

Au clusters, in contrast, Au₅₅ with a closed-shell geometry was shown to be the only inert species towards Au-oxide formation; however, for Au_n with $n < 14$, it has been demonstrated that the cluster geometry does not correspond to a closed-shell structure [16–18]. Our results mentioned above suggest that the chemical activity of deposited clusters is greatly influenced by electronic modification, implying an importance of electronic structure for determining chemical activity of deposited clusters. It is still not completely clear why the odd-numbered clusters are generally more reactive than even-numbered clusters towards Au-oxide formation. The Si wafer is kept at deposition potential during deposi-

Fig. 6. Na 1s spectrum collected from a Au₈-covered Si wafer after NaOH(aq) treatment (black) is compared with that of a pristine Si wafer after the same NaOH-treatment (gray).

Fig. 7. Au 4f level spectra of the samples in Fig. 3 collected after CO exposures.

tion, and additional charge of the deposited cluster flows to ground. This electron flow is measured in order to estimate the number of Au clusters deposited. It can be tentatively suggested that the deposited Au clusters are not charged, and thus, in a simple electronic model, even-numbered clusters with closed shell configurations should be more inert than odd-numbered clusters. One may argue that the Au clusters on the surface are either negatively or positively charged due to the metal-support interaction. Considering that Na renders Au more negatively charged, it is less likely that Au is already partially negatively charged on the Si wafer without Na. A positive charging of Au clusters on silica is not supported by our XPS results. Theoretical studies about interaction between Si, Au clusters and Na may further shed light on this issue.

When the oxidized Au clusters in Fig. 3 were exposed to CO, reduction of the Au-oxide could be found; however, large amounts of oxygen still remained un-reacted (Fig. 7). The un-reacted Au-oxide species are attributed to the species existing in the subsurface regime. When Au was oxidized, not only the surface topmost layer, but also the deeper layers, could be partially oxidized. Upon CO exposure, the Au-oxide at the deeper layers could remain unreacted.

4. Conclusion

Au clusters consisting of 2–13 atoms were deposited on silica and their electronic and chemical properties studied using XPS. Some odd-numbered clusters were highly inert towards reaction with the atomic oxygen atmosphere. Upon NaOH(aq) treatment, the inert clusters became more reactive, whereas the other neighboring clusters became less reactive. This result could be interpreted in terms of modification of the electronic structures of the Au clusters by Na, which could also be evidenced by the Au 4f and Na 1s level shifts.

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