Thermal stability of uniform silver clusters prepared on oxidized silicon and aluminum surfaces by electron beam lithography in oxidizing and reducing ambients

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100 and 750 nm silver nanoclusters are fabricated on oxidized silicon and aluminum surfaces by electron beam lithography. Silver nanoclusters are characterized by atomic force microscopy, scanning electron microscopy, scanning Auger electron microscopy and high-resolution optical microscopy. The ordered structure of silver nanoclusters facilitates a thermal stability study in both reducing and oxidizing conditions. In reducing conditions, silver clusters are stable on the surfaces up to ~ 700°C before evaporation. The thermal stability of silver clusters is significantly lower in oxidizing conditions. In the presence of oxygen, the silver cluster surface is oxidized and roughened < 300°C. Heating above 350–400°C in oxidizing conditions induces a migration of silver clusters. Micron-size and submicron-size amorphous silver clusters are formed, which spread over the oxide support. On oxidized silicon substrate, annealing treatment at 300°C induces silver silicate formation or spreading of oxidized silicon support onto the silver clusters, causing a buildup of silicon on the silver cluster surface. On the oxidized aluminum surface, by contrast, no spreading or reaction of the oxide substrate with the silver clusters was detected.

Keywords: catalyst stability, silver, cluster, electron beam lithography

1. Introduction

Most industrial catalysts are supported small metal particles prepared through chemical routes (such as impregnation and coprecipitation) from solution. The stability of metal particles deposited on oxide substrates is a fundamental issue in catalysis studies. The optimal catalytic reaction conditions are determined in part by the thermal and chemical stability of supported metal catalysts. Unfortunately, structural changes of conventional industrial catalysts are difficult to investigate, due to a broad distribution of metal particle size and a random distribution of particles on the substrate.

One of the major challenges in catalyst fabrication is to deposit tailored metal clusters with specific structures. A well-defined metal nanocluster array can be fabricated by lithographic technologies, which provide a precise control of the size and spacing of the metal nanoclusters. The uniform nanocluster arrays can be characterized by a variety of surface microscopy techniques. Changes in nanoparticle size, structure, composition and distribution on the supports can be monitored under catalytic reaction conditions, i.e. under high gas pressure (~ 1 atm) of reactants and high temperature (up to 1000°C).

In this paper, we investigate the thermal stability of supported silver catalysts. Silver is an excellent catalyst for a number of industrial catalytic reactions, among which the partial oxidation of ethylene to ethylene oxide is arguably the most important. Ethylene oxide is a primary reactant in the manufacture of a variety of derivatives, including ethyl glycol, surfactants and ethanolamines [1]. About 9.6×106 tons of ethylene oxide were produced in 1994, and silver-based catalysts were involved in virtually all the production. Depending on the source of oxidizing agent, the reaction engineering can be divided into two categories: an air-based process and an oxygen-based process. In either case, the industrial production is carried out at a temperature lower than 300°C.

In order to study the thermal stability of supported silver catalysts, we fabricated an ordered array of nanoscale silver clusters on oxidized silicon and aluminum surfaces by electron beam lithography. Nanoclusters are prepared in two sizes: 100 and 750 nm, which are comparable with particle size in conventional ethylene oxide catalysts. It has been reported that silver catalysts with large particle size (>50 nm) yield optimal catalytic reactivity toward ethylene oxidation reaction [2].

Silica (silicon oxide) and alumina (aluminum oxide) are the two most common oxide substrates in industrial

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catalysts. Unfortunately, the poor electrical conductivity of pure silicon oxide and aluminum oxide samples hampers the application of electron beam lithography and electron-mediated surface analytical instruments. In order to circumvent this problem, we utilize oxidized silicon and aluminum surfaces to mimic silica and alumina supports. The growth of oxide overlayers is confirmed in Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS) studies. The thermal and chemical stability of silver nanoclusters are probed by scanning electron microscopy (SEM), scanning Auger electron microscopy (SAM), atomic force microscopy (AFM) and high-resolution optical microscopy. In oxygen-free gas ambients, silver clusters are stable on the surface up to 700°C before evaporation. In oxygen-containing conditions, the silver nanocluster surface is oxidized and corrugated < 300°C. In addition, on the oxidized silicon support, a thermal treatment at 300°C also induces an accumulation of silicon on the silver catalyst surface. On both oxidized silicon and aluminum surfaces, a further heating to 350–400°C destroys the original periodic arrangement of the nanoclusters, and oxidized silver clusters spread over the oxide surface, with a size range between 10^{-1}–10^{0} micron.

2. Experimental

Silicon wafers (1″ diameter, (100) orientation ±0.5°, Virginia Semiconductor Inc.) are covered by a thin film (1–2 layers) of native oxide, as revealed by Auger electron microscopy. Aluminum wafers (1″ diameter) are cut from amorphous aluminum followed by a mechanical polish. The aluminum surface is cleaned and oxidized in H_2O_2 (30%) and concentrated H_2SO_4 (98%). The growth of amorphous Al_2O_3 overlayer is confirmed in X-ray photoelectron spectroscopy (XPS) studies. Al 2p XPS spectra of the oxidized aluminum surface are shown in figure 1, which are collected at two detection angles of photoelectrons. As well-documented in the literature, the Al 2p binding energy is $\sim$ 73 eV for metallic Al and $\sim$ 76 eV for Al_2O_3 thin film grown on aluminum substrate [3]. With a detection angle of 15° (the detection angle is defined as the angle between the photoelectron ejection direction and the surface), only Al_2O_3 signal is detected, as shown in figure 1 (a). XPS is less surface sensitive with increasing detection angle. At a detection angle of 45°, a small metallic Al signal from the bulk is observed (figure 1 (b)). X-ray energy from a Mg source is adapted in our XPS studies, with an energy $\sim$ 1300 eV. As a result, the Al 2p photoelectrons have a kinetic energy of $\sim$ 1230 eV, with a mean free path of 25 Å in Al_2O_3 overlayer [4]. The surface overlayer thickness can be estimated based on the angular dependence of the bulk signal and the escape length of photoelectrons [5]. Our results are indicative of an oxide thin film of $\sim$ 30 Å thickness on the aluminum surface.

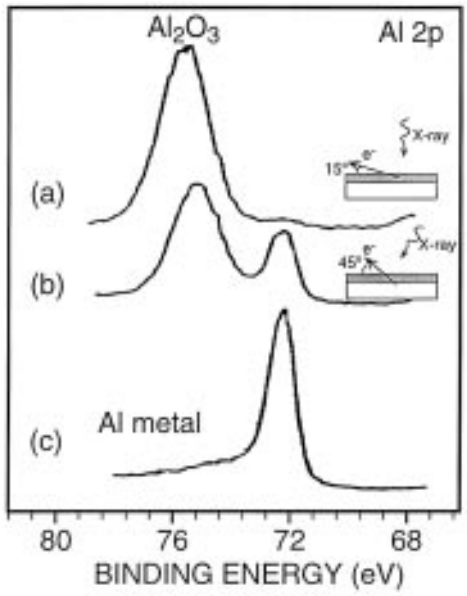


Figure 1. Al 2p X-ray photoelectron spectroscopy (XPS) spectra of oxidized aluminum surface.

Silver clusters are prepared on oxidized silicon and aluminum surfaces by a standard electron beam lithography process, as shown in figure 2. Substrates are first rinsed sequentially by acetone, isopropyl alcohol and deionized water. A polymethyl methacrylate (PMMA) thin film of 100–200 nm thickness is then spin-coated on the substrates. The polymer layer thickness is measured by a Tensor Surface Profiler. Patterns are produced on the polymer layer by a highly collimated electron beam using a modified Joel 6400 scanning electron microscope. The electron-damaged polymer is selectively dis-

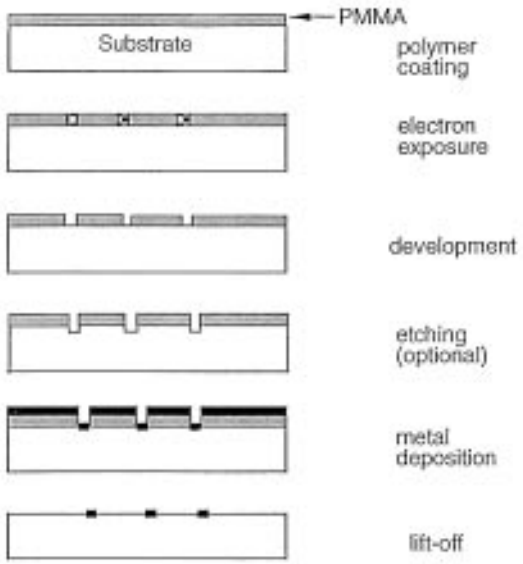


Figure 2. A schematic diagram of sample preparation by electron beam lithography. The optical etching step was skipped in this study.

solved in an isopropyl alcohol/methyl isobutyl ketone solution, while the unexposed portions of polymer layer remain intact on the substrates. In the following step, a silver thin film is evaporated onto the sample. A thermal evaporation process is adapted, with an estimated source temperature of $\sim 1000°C$. The metal deposition is monitored in situ by a quartz microbalance (5 MHz, Inficon Inc.) and the thin film thickness is confirmed by the sample weight difference before and after the silver deposition. The final step is to lift off (dissolve) the remaining polymer on the surface, along with the metal thin film covering the polymer layer. In this fashion, metal particles are produced on the substrate precisely at positions exposed by the electron beam. In addition, the height of metal particles is uniform, which equals to the thin film thickness in the metal evaporation.

Silver clusters are prepared in two sizes. The first pattern contains a pair of 750 nm $\times$ 750 nm squares separated by 250 nm and the feature is repeated in a $\sim 10\ \mu$m periodicity. The silver clusters are 36 nm in height. This pattern is shown in figure 3 and cited in this paper as pattern A. The second pattern is a matrix of 100 nm silver clusters with an inter-particle distance of $\sim 2\ \mu$m and a particle height of ~ 20 nm. Four micron scale markers are deposited around the cluster array. This pattern is shown in figure 4 and cited in the following sections as pattern B.

The silver nanocluster structure is characterized by high-resolution optical microscopy, scanning electron microscopy (SEM), scanning Auger microscopy (SAM) and atomic force microscopy (AFM). Figure 3 presents micrographs of pattern A taken by optical microscopy, SEM and AFM. Optical microscopy was conducted on a Nikon UM-3 Measurescope, with a resolution of ~ 100 nm; SEM spectra were collected on a Joel 6400 scanning electron microscope and an ultimate resolution of ~ 10 nm was obtained with an electron kinetic energy of 15 keV; AFM measurements were performed in air

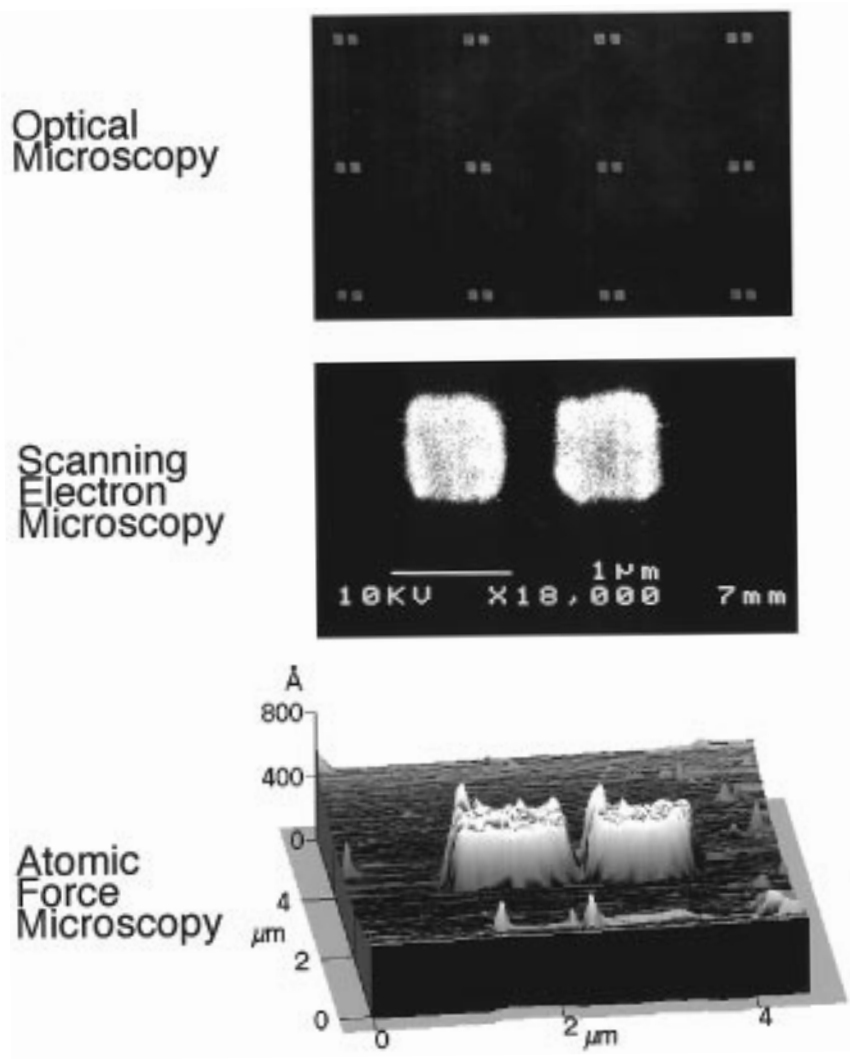
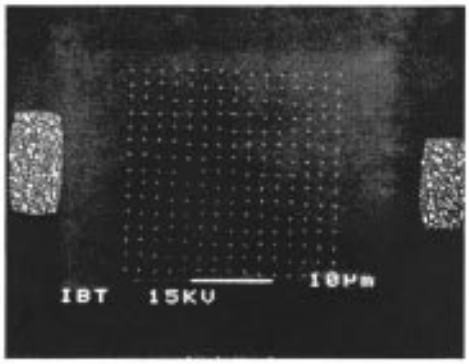
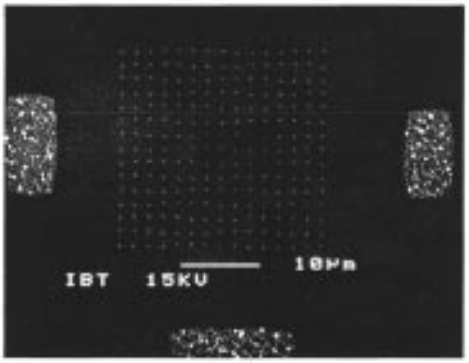


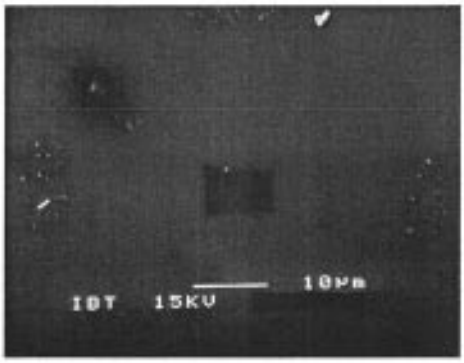
Figure 3. Optical microscopy, scanning electron microscopy (SEM) and atomic force microscopy (AFM) pictures of pattern A deposited on oxidized silicon surface.



350 °C



680 °C



730 °C

Figure 4. Scanning electron microscopy (SEM) micrographs of pattern B deposited on oxidized silicon surface after annealing in hydrogen at the indicated temperature for one hour.

ambient on an Autoprobe system (Park Scientific Instruments), with a resolution better than 1 nm. The edges of silver clusters show a finite slope in the AFM spectrum, which can be attributed to artifacts introduced by the curvature of AFM tip.

Scanning Auger microscopy (SAM) provides spatially-resolved information of surface chemical composition. The SAM spectra were collected by a Perkin-Elmer PHI 660 analytical system. With an electron incident energy of 3 keV, Auger spectra were obtained from a data averaging over one hour.

The annealing of silver nanocluster samples in vacuum was conducted in an ultrahigh-vacuum (UHV) system with a base pressure of 1×10^{-9} Torr. The sample was heated by electron irradiation and the sample temperature was measured by a chromel–alumel thermocouple pressed on the edge of sample. The thermal treatment in gas ambients was carried out in a furnace, with a gas flow rate of $\sim$ 10 ml/min. The gas flows were sustained in the annealing and curing processes. The oxygen/ethylene/nitrogen gases were premixed in the desired proportion.

3. Results

The thermal stability of silver nanoclusters deposited on oxidized silicon surface is discussed in section 3.1. Hydrogen and air are representative reducing and oxidizing agents. The results obtained in these two conditions are first discussed, followed by a summary of the nanocluster stability in other chemical conditions (H_2, N_2, air, C_2H_4, and O_2/C_2H_4 mixture). A comparative study was conducted on silver clusters deposited on oxidized aluminum surface, and its findings are presented in section 3.2.

3.1. Thermal stability of silver clusters fabricated on oxidized silicon surface

3.1.1. Thermal stability in hydrogen

The thermal stability of silver clusters deposited on oxidized silicon is first examined in hydrogen. Figure 4 displays SEM micrographs of pattern B taken after annealing the silver cluster sample in hydrogen at the indicated temperature for one hour. The cluster array remains intact up to 680°C. As shown in figure 4, each individual silver cluster in the matrix is visible in the SEM spectrum collected after the thermal treatment, and no migration of silver clusters is observed. After an annealing at 730°C, the entire cluster array vanishes, along with the micron size markers surrounding the array pattern.

It is most likely that silver evaporation is responsible for the disappearance of silver nanoclusters above 700°C. The vapor pressure of pure silver increases exponentially with temperature, and reaches 3×10^{-6} Torr at

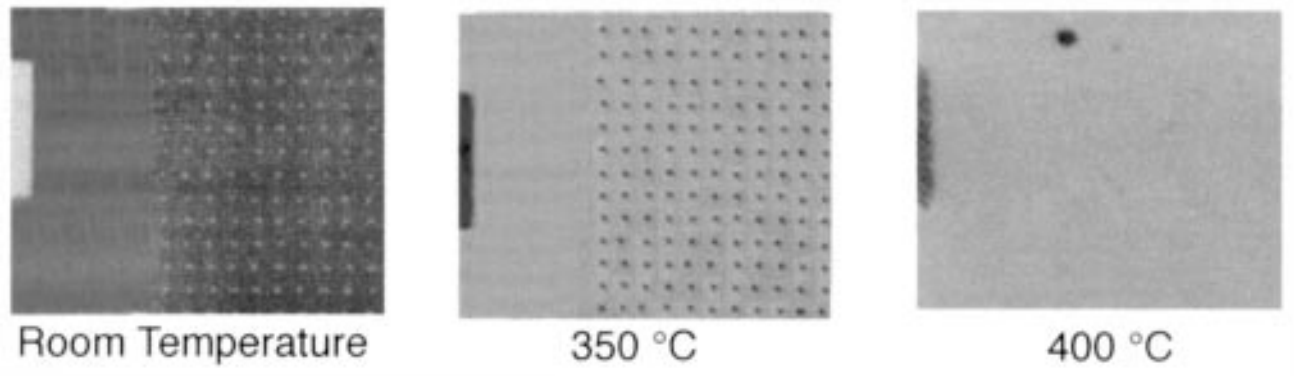


Figure 5. Optical microscopy photographs of pattern B deposited on oxidized silicon surface after annealing in air at the indicated temperatures for one hour. A fraction of silver cluster array is displayed with part of a micron scale marker at left.

$\sim$ 730°C [6]. Based on the vapor pressure, the silver evaporation rate is estimated to be $\sim$ 200 nm/h at this temperature. In comparison, the height of fresh sample is 20 nm for pattern B.

3.1.2. Thermal stability in air and oxygen

Compared with the results in hydrogen, silver nanoclusters have a much lower thermal stability in oxidizing conditions.

Figure 5 presents a series of optical microscopy photographs of pattern B after annealing in an atmospheric pressure of air at indicated temperature for one hour. For the convenience of presentation, only part of the silver cluster array is displayed, along with part of a silver marker deposited around the nanocluster array. The fresh silver clusters deposited at room temperature present a color close to that of pure silver metal, suggesting that silver clusters are in the metallic form. With increasing annealing temperature, the color of the clusters gradually turns dark, which is indicative of an oxidation of the silver cluster surface. Up to a temperature of 350°C, the silver cluster array maintains its periodicity. An annealing at higher temperature causes a migration of the 100 nm silver clusters, and the silver cluster array is erased after annealing at 400°C. The thermal stability of silver clusters is significantly lower in air than in hydrogen, in which ambient the periodic arrangement of silver cluster array remain intact up to $\sim$ 700°C. It is worth noticing that while the matrix of 100 nm silver cluster vanishes at 400°C in air, a trace of micron-scale silver markers is still visible. This implies an increase of thermal stability with increasing silver cluster size. Raising the annealing temperature to 450°C destroys the entire silver pattern. Scattered on the oxidized silicon surface are amorphous silver clusters with a size distribution from 10^{-1} to 10^{0} micron, as shown in figure 6.

The structural change of silver clusters upon annealing is monitored by atomic force microscopy (AFM). Figure 7 presents three-dimensional AFM images of pattern A deposited on the silicon surface. As shown in figure 7a, the uniform silver clusters fabricated at room temperature are 36 nm high with a surface roughness of $\sim$ 2 nm. An annealing in air at 300°C causes notable changes in the surface morphology. As shown in figure 7b, while the overall size of the silver pattern remains approximately constant, the silver cluster surface is corrugated. The height varies from 5 to 90 nm within a single cluster.

A spatially-resolved chemical composition analysis of the sample was conducted by scanning Auger electron microscopy (SAM). SAM scans of pattern A are shown in figure 8, together with corresponding scanning electron microscopy micrographs. As shown in the left panel, for the sample fabricated at room temperature, silicon signal is detected on the substrate (point 1) and silver signal is observed on the silver cluster (point 2).

AFM results presented in figure 7 indicate a roughening of the silver cluster surface upon annealing at 300°C in air for an hour. It is confirmed in the SEM micrograph displayed in the right panel of figure 8. What is more interesting is that the SAM survey reveals a silicon buildup on the silver clusters (point 2), which suggests a spillover of the support onto the silver cluster and/or a silication of silver cluster surfaces.

Since both air and pure oxygen are adapted in the

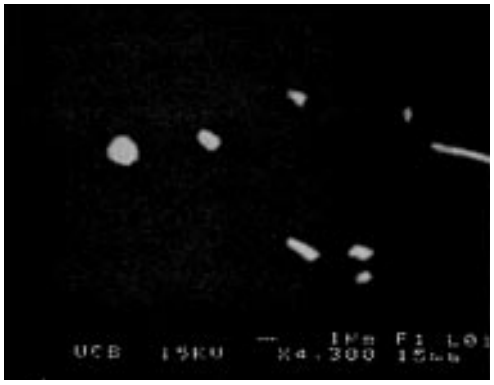


Figure 6. Scanning electron microscopy micrograph of silver clusters on oxidized silicon surface after annealing in air at 450°C.

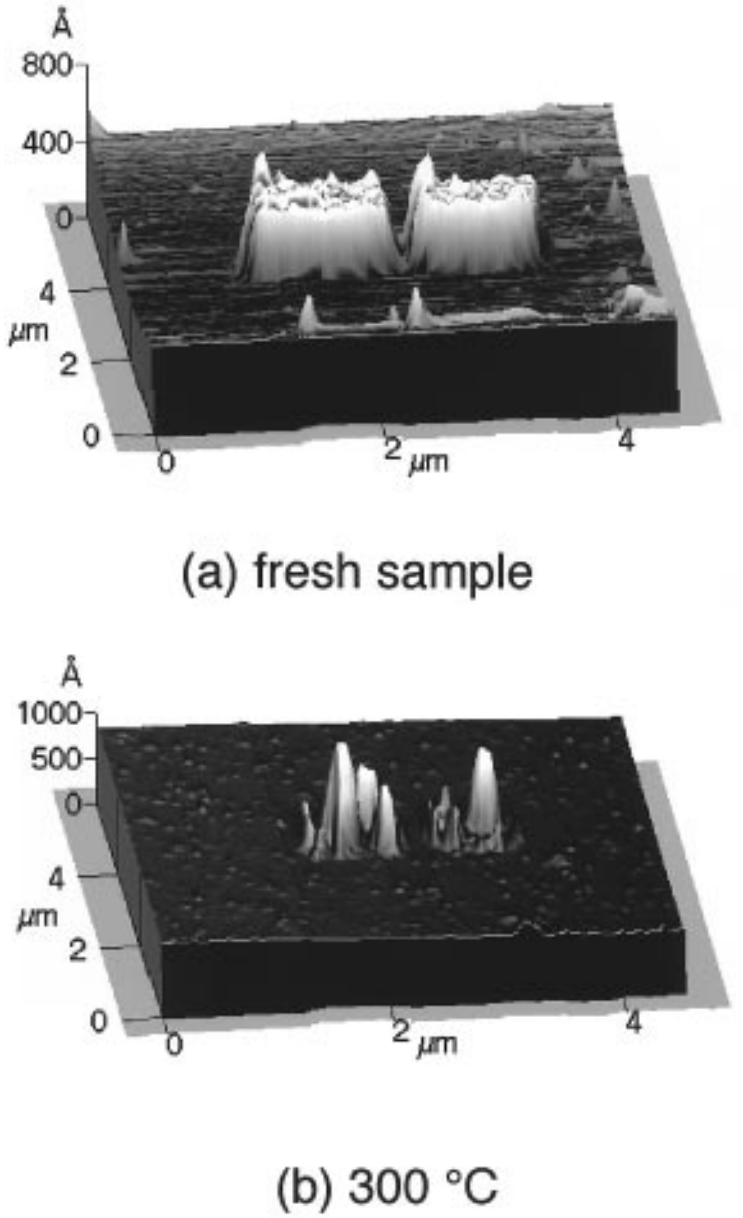


Figure 7. Atomic force microscopy (AFM) images of pattern A deposited on oxidized silicon surface (A) before and (B) after annealing at 300°C in air.

industrial ethylene oxidation process, we also examined the thermal stability of silver nanoclusters in oxygen. Within our experimental uncertainty in annealing temperature (± 10°C), there is no observable difference in silver nanocluster thermal stability in oxygen or air ambients. With increasing annealing temperature in oxygen, silver cluster surface oxidation occurs < 200°C, a presence of silicon on the silver surface takes place < 300°C, followed by a migration and aggregation of silver nanoclusters into micron-size or submicron-size particles > 400°C. The amorphous clusters spread over the oxide surface in a random fashion.

3.1.3. Thermal stability of clusters in other gas ambients

The stability of silver clusters has also been studied in vacuum and other gas ambients, including nitrogen, oxygen and ethylene. In addition, a gas mixture of 10% oxygen and 10% ethylene in nitrogen was employed to mimic the gas composition in industrial ethylene oxidation reactions.

The behavior of silver clusters can be divided into two categories based on the gas composition: the oxygen-free agents (vacuum, N_2 and H_2), and the oxygen-containing agents (O_2, air, $O_2/C_2H_4/N_2$ mixtures). In the absence of oxygen, no migration of silver clusters is observed prior to their evaporation > 700°C. In the presence of oxygen, however, silver clusters are oxidized < 200°C. A transport of silicon onto silver cluster surface is detected after annealing at 300°C. The array of 100 nm silver clusters (pattern B) is stable up to 350–

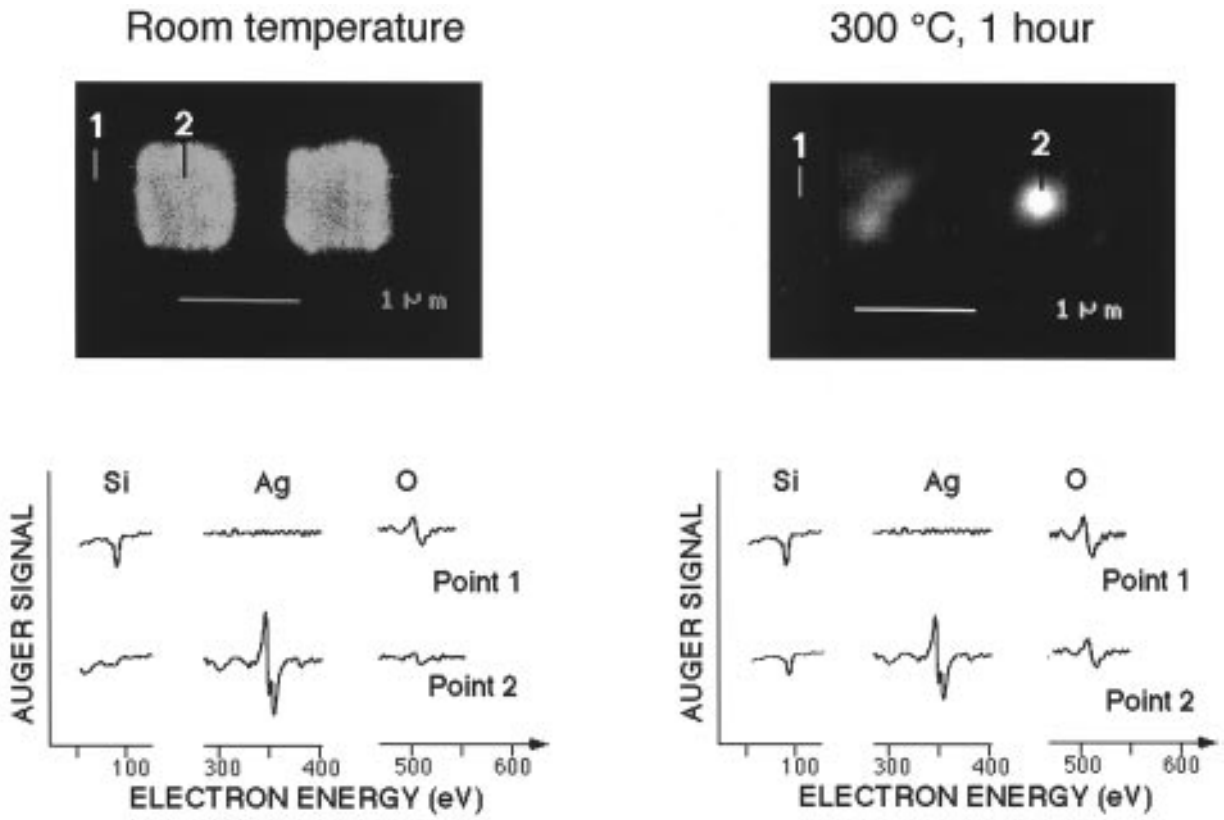


Figure 8. Scanning electron/Auger microscopy analysis of pattern A deposited on oxidized silicon surface. (A) before and (B) after annealing at 300°C in air. SEM micrograph of silver clusters is presented on top and SAM scans collected at indicated positions are shown at the bottom.

400°C before an aggregation into micron-size or submicron-size clusters. The amorphous clusters spread over the oxide surface in a random fashion.

3.2. Thermal stability of silver clusters fabricated on oxidized aluminum

We also fabricated silver clusters on oxidized aluminum surface. As illustrated in the experimental section, the oxidized aluminum surface was characterized by XPS. The sample was adapted to mimic the alumina support in industrial catalysts. The thermal stability of silver nanoclusters was examined in hydrogen and air, which are reducing and oxidizing agents, respectively.

With an atmospheric pressure of hydrogen in the gas phase, the thermal stability of silver clusters is very similar on oxidized silicon and aluminum surfaces. The silver clusters evaporate > 700°C, and no migration of silver clusters is detected prior to the evaporation.

Comparing with the results in hydrogen, the thermal stability of silver nanoparticles is lower in air ambient on both oxidized silicon and aluminum substrates. The silver nanoclusters on the surface are oxidized < 200°C, and conglomerate into micron- or submicron size amorphous clusters > 400°C. A drastic difference, however, exists between oxidized silicon and aluminum supports. As discussed in section 3.1.2, on the oxidized silicon substrate, an annealing at ~ 300°C causes a transport of silicon onto silver cluster surfaces (figure 8). Such a buildup of substrate oxide on metal cluster surface, however, is absent for silver clusters deposited on oxidized aluminum surface. This conclusion is drawn from the surface chemical analysis by scanning Auger electron spectroscopy. SAM surveys of silver clusters on oxidized aluminum surfaces are presented in figure 9. After an annealing at 300°C for an hour, the aluminum signal is not detected on the silver cluster surface (point 2).

4. Discussion

The present thermal stability studies provide some insight into the supported silver catalysts in ethylene oxidation reaction.

Silver cluster surface is oxidized in air ambient < 200°C, as evident from the color change in the high-resolution photographs shown in figure 5. This oxidation process is irrelevant to the nature of oxide support. The silver oxide formation is thermodynamically favored. Heat of formation of silver oxide (Ag_2O) is -7.42 kcal/mol at 25°C and decreases with increasing temperature [7]. It is worth noticing that the industrial catalytic reactions are carried out at a temperature of 250–300°C. Under such reaction conditions, metal catalyst surface is essentially covered by silver oxide, and

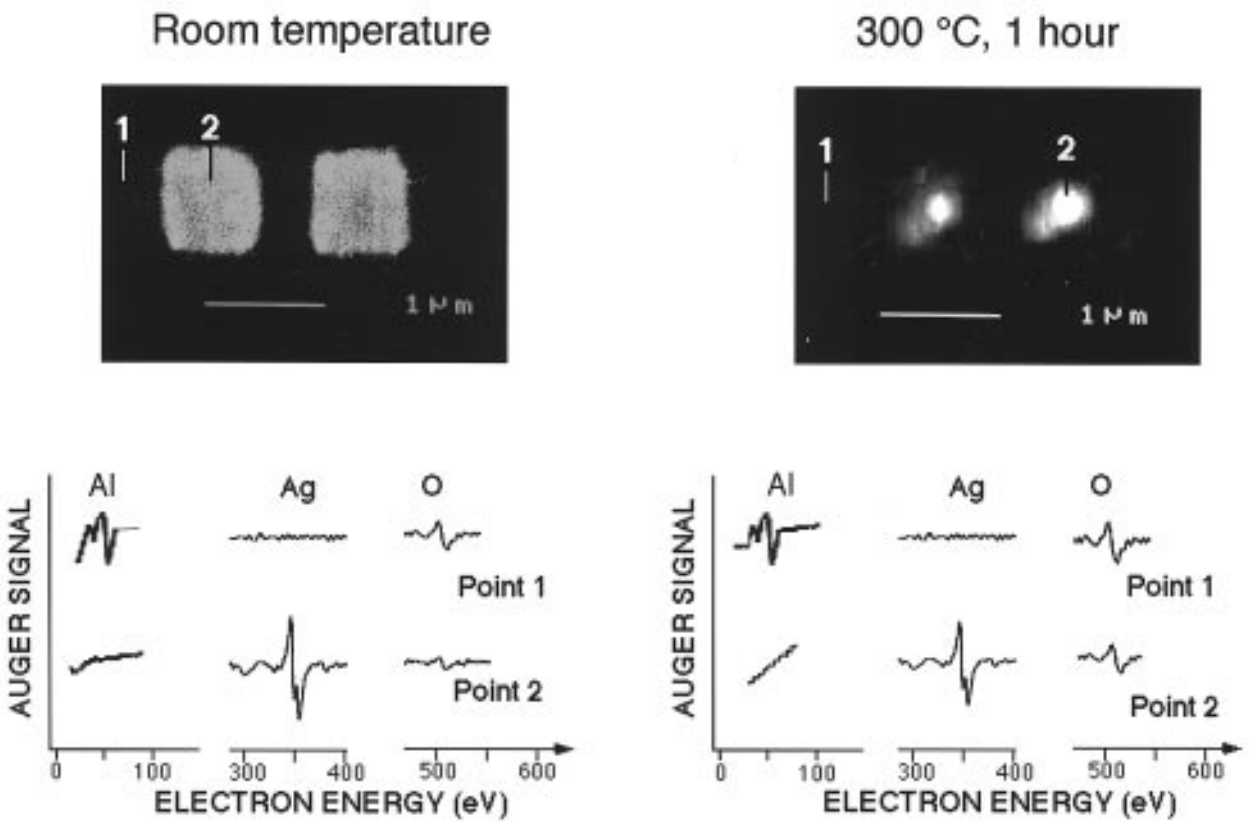


Figure 9. Scanning electron/Auger microscopy analysis of pattern A deposited on oxidized aluminum surface. (A) before and (B) after annealing at 300°C in air. SEM micrograph of silver clusters is presented on top and SAM scans collected at indicated positions are shown at the bottom.

silver oxide rather than silver should be the active catalyst for the ethylene oxidation reaction.

Our study reveals different thermal stabilities of silver nanoclusters in different chemical environments. In the absence of oxygen, silver nanoclusters remain stable on the surface up to 700°C, above which silver evaporation takes place. In the presence of oxygen, however, the silver nanoparticles migrate and conglomerate on the surface above 350–400°C. Amorphous silver clusters spread over the surface, with irregular shape and a size range from 10^{-1} to 10^{0} micron. As a consequence, regardless of the fabrication methods of silver clusters at room temperature, a thermal treatment of supported catalysts at a temperature above 350–400°C in any oxidizing condition will cause a structure change of the catalyst. Although the catalytic reaction for ethylene oxidation is always carried out below 300°C, a high temperature oxidation process can be incorporated in the catalyst preparation and/or regeneration steps.

Even if the oxidation > 400°C is excluded from catalyst preparation in the ethylene oxidation process, we expect an amorphous catalyst structure under the reaction conditions. As mentioned above, industrial ethylene oxidation process is conducted at a temperature near 300°C, and air or oxygen is adapted as oxidizing agent. Our AFM and SEM studies (figures 7 and 8) on 750 nm silver clusters suggest that the surface morphology of uniform silver cluster surface is rough with a heating to 300°C in air or oxygen ambients.

Finally, we report a difference in silicon and aluminum oxide supports. After an annealing at 300°C in oxidizing condition, the surface chemical composition is significantly different for silver clusters deposited on two oxide substrates. On the silicon oxide support, a buildup of silicon is observed on silver cluster surface. Such a spillover of oxide support onto silver cluster surface, however, is absent on aluminum oxide substrate. As a result, it will not be surprising to observe different reactivities for silver clusters deposited on silicon and aluminum oxide supports.

5. Summary

100 and 750 nm silver clusters are fabricated on oxidized silicon and aluminum surfaces by electron beam lithography. Thermal stability of silver nanoclusters is examined in reducing and oxidizing conditions, at a temperature range up to 800°C. Under reducing condition, the silver clusters do not migrate prior to their evaporation > 700°C. Under oxidizing condition, silver cluster surface is oxidized at a temperature < 200°C, and a conglomeration of silver clusters occurs above 350–400°C. In addition,

an annealing above 300°C in air or oxygen ambients induces a buildup of silicon on the silver cluster surface.

Acknowledgement

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