

Gold Nanoparticles Deposited on SiO₂/Si(100): Correlation between Size, Electron Structure, and Activity in CO Oxidation

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Abstract: Nanosize gold particles were prepared by Ar⁺ ion implantation of 10-nm thick gold film deposited onto a SiO₂/Si(100) wafer possessing no catalytic activity in the CO oxidation. Along with size reduction the valence band of the gold particles and the actual size were determined by ultraviolet- and X-ray photoelectron spectroscopy (UPS, XPS) and by transmission electron microscopy (TEM) as well as atomic force microscopy (AFM), respectively. The catalytic activity was determined in the CO oxidation. Energy distribution of the photoelectrons excited from 5d valence band of gold was strongly affected by Ar⁺ implantation. This variation was interpreted by the redistribution of the valence band density of states (DOS). The intrinsic catalytic activity of the gold particles increased with decreasing size. When an Au/FeO_x interface was created by FeO_x deposition on large gold nanoparticles, a significant increase in the rate of the CO oxidation was observed. These data can be regarded as an experimental verification of the correlation between the catalytic activity and valence band density of states of gold.

Introduction

Size dependence of the electronic structure of materials has a central importance in nanoscience. Size reduction of metal particles to nanosize range alters their electronic and atomic structures. The basic chemical properties are determined by the physical behavior of the system. Accordingly, for example, the catalytic properties of a system should be correlated to its electronic structure, consequently, to the size of the metal particles.

About a decade ago in the CO oxidation an exceptional high catalytic activity of the gold nanoparticles deposited onto Fe₂O₃, Co₂O₃, TiO₂ supports was discovered^{1–4} and interpreted by the formation of an active Au/support interface along the perimeter of gold particles.^{5,6} By decreasing the gold particle size the overall activity can be increased by the enlargement of the active interface. However, the size reduction also alters the electronic structure of the Au/support interface. As this interface is a model of a metal–semiconductor or metal–insulator junction; we assume that the interface bears special electronic properties, which could be an essential factor in the formation of high

catalytic activity. Alteration of the valence band density of states of gold may affect the activity of the Au/support interface directly or indirectly by modifying the electronic properties of the Au–Fe₂O₃, Co₂O₃, TiO₂ interfaces.

Neither the electronic properties of the interface nor the valence band of the nanoparticles were separately investigated experimentally; however, a correlation between the electronic structure and the catalytic activity of metal clusters was theoretically predicted.⁷ Furthermore, it has been shown that the valence band of Cu and Ag nanoparticles was changed by the size reduction,^{8,9} and one can suppose a similar effect also for Au nanoparticles, which was shown quite recently.^{10,11}

Using a Au/TiO₂ model system and scanning tunneling spectroscopy (STS) Goodman and co-workers¹² discovered that Au/TiO₂ has an optimum activity in the CO oxidation, when the gold particle size is about 4 nm and the band gap is around 0.4 eV. However, it was not elucidated whether the activity is solely due to the nanometer size of gold nanoparticles or is a result of the Au/TiO₂ interface.

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The dilemma concerning whether the high activity of gold nanoparticles is devoted to the size effect of Au nanoparticles or to the active Au/support interface still exists. To tackle this problem the investigation of electronic structure and catalytic activity of Au nanoparticles ought to be investigated without any supporting material, but it is technically difficult. In our opinion this problem can be studied with nanoparticles deposited onto a noncatalytic inactive substrate. These requirements can be fulfilled by applying a Si(100) wafer covered by native SiO₂.

The aim of the present study is to find a correlation between the CO oxidation rate and the density of states of the Au 5d valence band both measured on gold nanoparticles of varying sizes deposited on SiO₂/Si(100). Starting from a contiguous Au layer on SiO₂/Si(100) that has a bulk-like valence band density of states, the particle size will be altered by means of Ar⁺ ion implantation. The morphology and the electron structure will be determined by TEM, AFM and by UPS, XPS, respectively.

Experimental Section

Gold thin films were deposited by electron-gun evaporation in a VT-460 evaporator under UHV conditions onto Si(100) wafers covered with native SiO₂ of nanometer-thickness range. The Au layer was continuous, and the thickness was around 10 nm. After the Au film was cleaned by Ar⁺ ion bombardment for a few minutes, the valence band of Au film was determined by the measurement of energy distribution of the photoelectrons excited by He(I) using a Kratos ES-300 electron spectrometer. The energy resolution was 0.15 eV. The valence band and the atomic levels were measured by XPS using Al K α excitation in the same photoelectron spectrometer.

To prepare nanosize gold elements (nanoparticles, islands, etc.) the film was ion-implanted with Ar⁺ ions at 40 keV and 10¹⁵ atom/cm² dose.¹⁰ The native SiO₂ oxide layer on the Si(100) substrate served as a barrier against the Si/Au interaction, but it was thin enough to avoid electric charging. UPS and XPS characterized the valence band of gold. The atomic levels of Au 4f and Si 2p were also measured to detect the energy of the atomic level and the average coverage of Au on Si substrate.

The samples were tested in the CO oxidation in an all-glass circulation reactor connected to a QMS-type Hiden. The samples were transferred in He, but the possible surface contamination was removed by treatment in 200 mbar H₂ at 573 K for 60 min. After that the samples were heated to 803 K in a vacuum, and then a mixture of 10 mbar CO + 20 mbar O₂ + 150 mbar He was introduced. The initial rate of CO₂ formation was related to the geometrical surface of the Si(100) single-crystal wafer supporting the contiguous Au film or Au particles produced by Ar⁺ ion implantation. After catalytic tests the photoelectron spectrum of the latter sample was recorded.

The size of the gold nanoparticles in the “as-deposited”, “implanted”, and postreaction states was determined by TEM using Philips CM20 transmission electron microscope operating at 200 kV and atomic force microscopy (AFM) using a Nanoscope III with Multimode AFM-Head. The structure of gold nanoparticles was determined by electron diffraction. The samples for TEM investigation were prepared by extraction replica method using HF etching.

FeO_x was also deposited by laser ablation onto an implanted Au/SiO₂/Si(100) sample after CO oxidation and onto SiO₂/Si(100) as a reference. It was just an effort to model the effect of Au/FeO_x interface in addition to the gold particle size effect.

Results and Discussion

In Figure 1 the size dependence of the valence band density of states (DOS) of Au nanoparticles measured by UPS and XPS, is presented.

The valence band spectra of the sample in “as-deposited” state (see Figure 1, a and c) are identical with that measured for bulk gold.¹³ However, after implantation the valence band 5d states are redistributed indicated by electron spectra obtained by He(I) and Al K α excitations, as well (see Figure 1, b and d). The UPS data shows that the valence bands both at 2–3 eV B.E. and at 6–7 eV B.E. decrease. The valence band structure measured by Al K α excitation fully supports the results measured by He (I) excitation. The Al K α excited valence band peaks, located at 3.6 and 6 eV, are characteristic of gold itself because the peaks in a separate spectrum originating from ion-bombarded SiO₂/Si(100) substrate alone appeared at 2.5 and 9.5 eV.¹⁰ Furthermore, formation of the gold nanoparticles is evidenced by an approximately 1-eV shift of the Au 4f core level binding energy toward higher values (from 83.8 to 84.7 eV, Si 2p 99.2 eV). Gold–silicide formation that could modify the electron spectra after Ar⁺ implantation can be excluded during the treatments (evaporation, ion implantation) of the gold film. After catalytic measurements an agglomeration of the gold particles occurs as indicated by the XPS spectrum, which is similar to that measured for the “as-deposited” film (compare Figure 1, c and e). This is also further evidence for the absence of gold–silicide interaction because it should not yield gold after CO oxidation at 803 K.

Comparing the corresponding TEM pictures (Figure 2) can highlight the morphology change. After implantation the “as-deposited” gold surface (see Figure 2a) is rearranged, showing the formation of elongated islands of 50–100 nm in length and 20–30 nm in width. Spherical particles of 5–10 nm diameter are also visible (see Figure 2b). The TEM images suggest a complex structure of the large islands containing small elements of ca. 10 nm in diameter. The AFM images (Figure 3b) confirm the lateral sizes given by the TEM pictures. According to the AFM data collected on the implanted sample the heights of the elements are 2–7 nm with average roughness of 2.2 nm RMS. The electron diffraction pattern shows that the “as deposited” Au is randomly polycrystalline. After ion implantation the diffraction rings are strongly broadened (compare insets at Figure 2, a and b). It is of importance to note that the observed diffraction rings can be correlated only to Au with the exception of some faint circles that originated from the carbon support. Any diffraction that could be correlated to a gold–silicide can be excluded.

On the other hand, after catalytic reaction the TEM picture displays (Figure 2c) mostly spherical Au nanoparticles of 30–60 nm in diameter, several of them sticking together. The Au grains are partly textured, and the prevailing <111> orientation is perpendicular to the substrate. The particles seem to be more compact than before catalytic reaction. According to the TEM picture the Au coverage of the support is extremely diminished which is in contradiction to the AFM image (Figure 3c) that shows enlarged 200–250 nm × 100–200 nm elements in much higher coverage. The difference between TEM and AFM results could be attributed to the possible loss of a part of the gold particles during the preparation of samples for the TEM study by stripping the Au particles from Si substrate in 10–20% HF solution. Thus the AFM result is more reliable.

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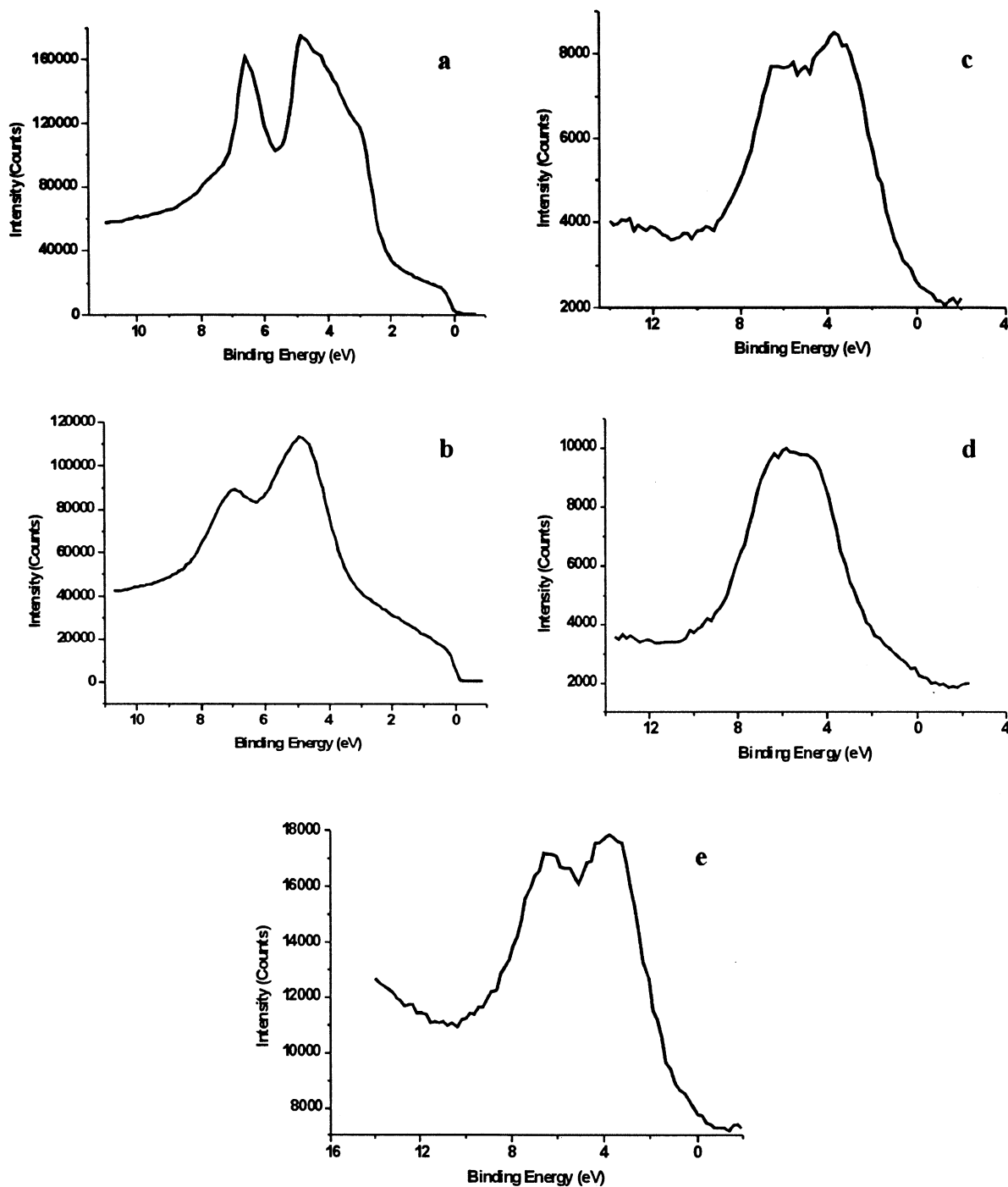


Figure 1. UPS and XPS spectra of the different Au/SiO₂/Si(100) samples. UPS of (a) “as-deposited”, (b) Ar⁺ ion “implanted” state. XPS of (c) “as-deposited”, (d) Ar⁺ ion “implanted”, and (e) “implanted” after catalytic reaction state.

The XPS of the implanted sample after the high-temperature catalytic tests also indicates a valence band characteristic of the bulk gold or of the “as-deposited” state. These results clearly show size dependence of the valence band and of the atomic structure of these gold nanoparticles; however, the size change is relatively small.

In Figure 4 a typical conversion curve is plotted for the CO oxidation to form CO₂ measured on the “as deposited” Au/SiO₂/Si(100) film and on the Au particles formed by Ar⁺ ion implantation. In Table 1 the initial rates (r_0) measured on the various samples and referred to the surface of Si(100) wafer

supporting the Au layer or Au particles, are presented. The catalytic activity of the SiO₂/Si(100) support itself is very low. The “as-deposited” Au film shows a higher activity, which is stable also in a repeated reaction after 1 h treatment in a stream of hydrogen at 573 K. After having the sample implanted by Ar⁺ ions, that is, when the Au particles are formed with size-dependent valence band, the activity significantly increased. The increase in activity is even larger if we relate it to the real Au surface of the sample. According to AFM studies, the total surface area of the two samples is about the same. However, in the “implanted” sample Au covers only around half of the

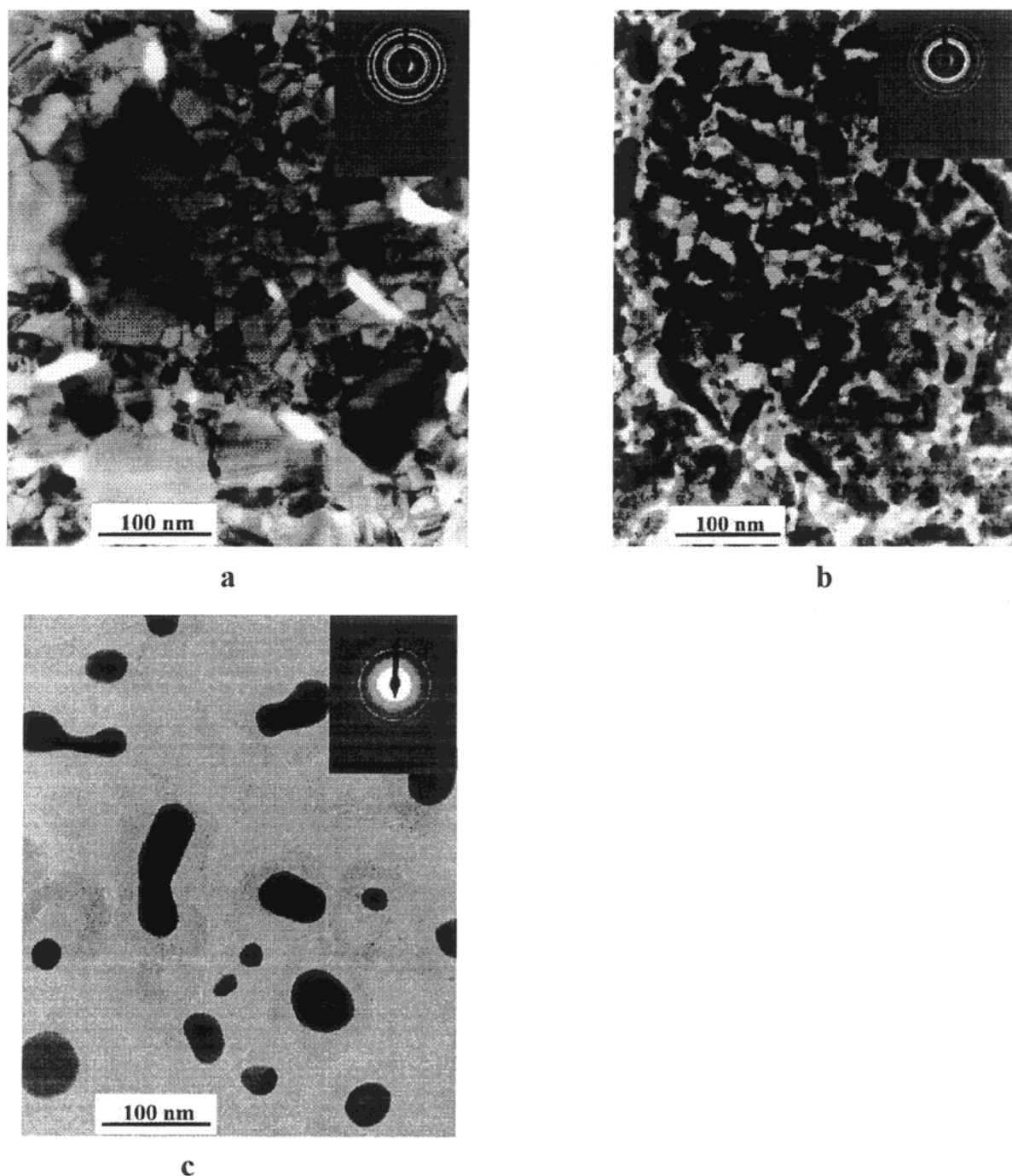


Figure 2. TEM pictures of Au film or Au particles supported on SiO₂/Si(100) (a) in “as-deposited” state, (b) after Ar⁺ ion “implantation”, and (c) after catalytic reaction.

substrate surface, while in the “as-deposited” sample Au covers almost the whole surface. Thus, in the implanted sample the real Au surface must be smaller.

The enhanced activity revealed in the CO oxidation decays in the repeated reaction by an order of magnitude, which further diminishes in the third reaction. The decrease in the catalytic activity is mainly due to the agglomeration of the nanoparticles at the high reaction temperature indicated by the enlarged size of the gold particles and the restored electron structure typical for bulk gold indicated by XPS (see Figure 1e). These results offer a new, straight correlation between the higher activity in

the CO oxidation on the gold nanoparticles and its altered size-dependent electron structure.

We also have to address the problem of the high temperature used in the CO oxidation. This is partly due to the extremely low surface area (the active surface is about 0.5 cm²) as we used small stripes of the sample in the U-shape reactor, and partly to the extremely low activity of the Au/SiO₂ as shown also by other authors.⁶ However, our primary goal was not the development of an extremely active gold catalyst, but the elucidation of the relationship between particle size/electronic structure and catalytic properties.

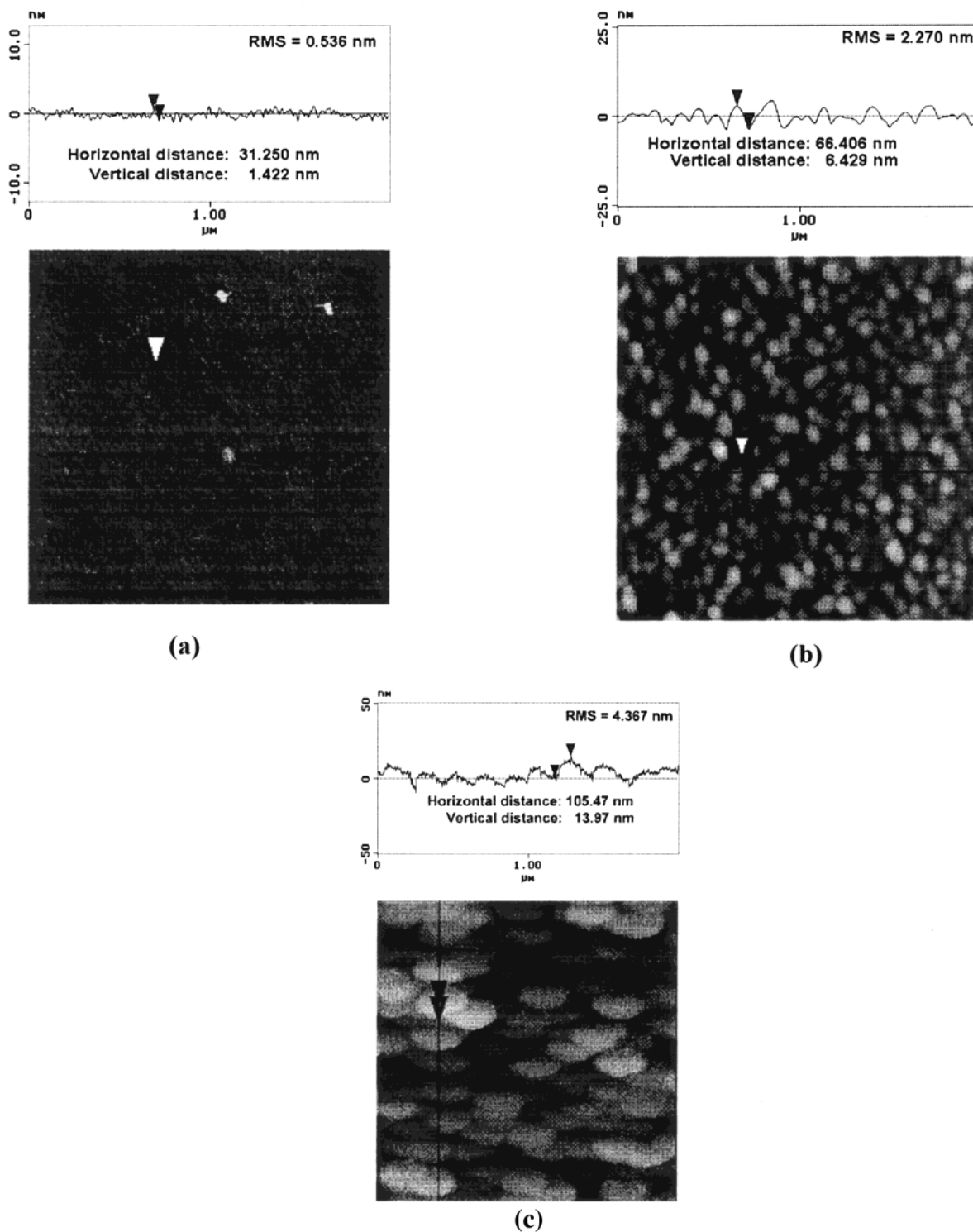


Figure 3. AFM images of Au/SiO₂/Si(100) (a) in “as-deposited” state, (b) after Ar⁺ ion implantation, and (c) after catalytic reaction.

As was mentioned, if transition-metal oxides with various oxidation states form an interface with gold nanoparticles, the catalytic activity is significantly increased at the perimeter of nanoparticles.¹⁴ A comparison between the effect of the change in gold valence band and that of gold/oxide support interface on the catalytic activity becomes possible if an oxide layer is deposited onto gold particles whose activity was previously

measured. Therefore, FeO_x was deposited on the Ar⁺ implanted Au/SiO₂/Si(100) model system that had been used several times in CO oxidation (activity is reported in Table 2). The idea behind this investigation is that if the perimeter is active one should observe an effect similar to that observed earlier on the Au/FeO_x/SiO₂/Si(100) model system.¹⁴

In Table 2 the rate shows about a 4-fold increase in the initial rate of CO oxidation measured on FeO_x/Au/SiO₂/Si(100) as compared with that on FeO_x/SiO₂/Si(100) and about a 60 times

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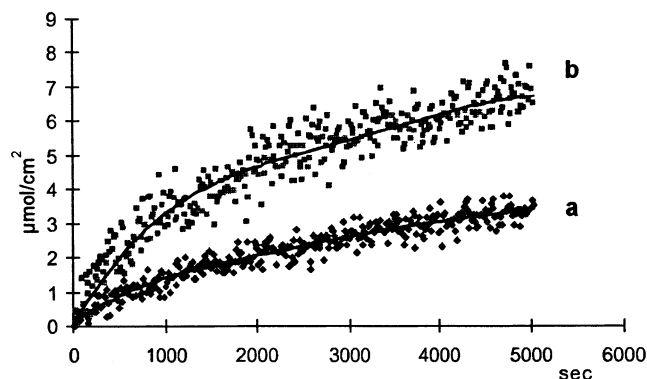


Figure 4. CO oxidation on "as-deposited (a) and on Ar⁺ ion implanted (b) Au/SiO₂/Si(100) samples.

Table 1. Catalytic Activity of Au/SiO₂/Si(100) Samples in CO Oxidation

sample	CO/O ₂ : 13/26 kPa; T = 803 K	initial rate (<i>r</i> ₀) μmol s ⁻¹ cm ⁻²
SiO ₂ /Si(100)	first reaction	4.7 × 10 ⁻⁴
Au/SiO ₂ /Si(100) as deposited	first reaction second reaction preceded by H ₂ treatment at 573 for 1 h	6.7 × 10 ⁻³ 6.7 × 10 ⁻³
Au/SiO ₂ /Si(100) implanted	first reaction second reaction (treatment above) third reaction w/o pretreatment	2.0 × 10 ⁻² 2.0 × 10 ⁻³ 2.7 × 10 ⁻⁴

Table 2. Effect of FeO_x Deposition onto Au Particles on Reaction Rate of CO Oxidation

sample	initial rate (<i>r</i> ₀), μmol s ⁻¹ cm ⁻²
FeO _x /SiO ₂ /Si(100)	2.3 × 10 ⁻²
implanted Au/SiO ₂ /Si(100) used in catalytic reactions	1.5 × 10 ⁻³
implanted Au/SiO ₂ /Si(100) after FeO _x ablation	9.5 × 10 ⁻²

higher initial rate compared to that for the base implanted Au/SiO₂/Si(100) after catalytic reactions. These results indeed indicate that in addition to the sole size effect, the presence of the Au/FeO_x interface significantly influences the CO oxidation. Moreover, this geometry may allow a more detailed investigation of the properties of Au/FeO_x-type systems and their influence on the catalytic activity.

Several theoretical calculations verify the importance of the pure particle size effect as it is experienced also in our case, comparing the activity of the Au layer and Au particles on inert SiO₂/Si(100). Haruta already called our attention to this fact.^{2,15} According to Guzman and Gates¹⁶ Au₆ octahedra is the

geometry of the active gold species. Density functional theory (DFT)^{17,18} and molecular dynamic calculation¹⁹ reveal that the cluster itself in the geometry of Au₁₀ or Au₁₃ preferring to form a three-dimensional compact structure is sufficient to activate CO and oxygen without any support. The DFT calculation indicates that the presence of negatively charged and atomic Au atoms in the cluster causes a stronger interaction with oxygen than that of the neutral Au atoms. However, the negatively charged Au atoms in the presence of a support of changing oxidation state may not exist. Obviously the stability of such small clusters is also a problem, and this is why one cannot anticipate the overwhelming majority of these species without stabilizing them by support.

Conclusions

Gold nanoparticles with sizes of about 50–100 nm × 20–30 nm × 2–7 nm together with spheres of 5–10 nm diameter on SiO₂/Si(100) were created by Ar⁺ ion implantation of a bulk like Au/SiO₂/Si(100) thin film of 10-nm thickness as indicated by AFM and TEM data. During the size reduction the Au 5d valence band redistributed as shown by photoemission spectra, and the catalytic activity in the CO oxidation increased. This is further experimental evidence for the correlation between size and electron structure that has theoretically been predicted.

The size reduction is, therefore, revealed in the activity enhancement of Au nanoparticles in the CO oxidation that can be unambiguously attributed to the changes in the valence band density of states of gold nanoparticles.

During the high-temperature catalytic tests the size and the valence band of the gold nanoparticles was restored to that typical for bulk gold, and the catalytic activity was suppressed. FeO_x deposition on the Au nanoparticles/SiO₂/Si(100) also produces a four times increase in catalytic activity in the CO oxidation, showing the importance of the formation of the Au/FeO_x interface.

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