Controlling the Structure and Size of Au Nanocrystals by Annealing and Ion Sputtering

Weixing Li,^{†,‡,§} Yanbin Chen,[‡] Jiaming Zhang,[§] Lumin Wang,^{†,‡} and Rodney C. Ewing^{*,†,‡,§}

[†]Department of Materials Science and Engineering, [‡]Department of Nuclear Engineering and Radiological Sciences, and [§]Department of Earth and Environmental Sciences, University of Michigan, Ann Arbor, Michigan 48109, United States

S Supporting Information

ABSTRACT: In situ thermal annealing was used for the first time to observe directly that Au nanoparticles, which were originally fully embedded in the near-surface region of TiO₂, can be tailored into hemispheres exposed at the surface at elevated temperature. Precise control of the size of the Au hemispheres was achieved by subsequent low-energy ion sputtering. This method can be used to control the structure and size of a wide variety of nanoparticles in a matrix where surface structure and particle size are required to obtain specific material properties.

I. INTRODUCTION

Highly dispersed nanocrystals in a matrix have attracted increasing interest because of their potential use in a wide range of catalytic reactions^{1–6} as well as in biomedical, magnetic, and optical applications.^{7–11} However, the performance of these nanocomposites depends strongly on the size and structure of the nanocrystals. For example, bulk gold is chemically inert and a poor catalyst. However, when gold particles are smaller than 10 nm in diameter and deposited on selected oxides, they exhibit remarkable catalytic activity² that strongly depends on the particle size.¹² Because catalytic reactions occur at the interfaces around the perimeter of Au particles,¹³ it is important that the nanoparticles are exposed but also retain a strong contact with the surface (e.g., hemispherical Au nanoparticles deposited on TiO₂).¹³ Similarly, TiO_x nanoparticles grown on a Au(111) substrate, as inverse catalysts, exhibit high performance in the water–gas shift reaction because of cooperative effects at the oxide–metal interface.¹ For biomedical applications, Fe₃O₄ nanoparticles embedded in polystyrene nanospheres exhibit strong fluorescence emission in the visible range of the electromagnetic spectrum.¹⁰ The particle size must be controlled for these applications because it strongly affects the superparamagnetic state of the Fe₃O₄ nanoparticles.^{10,14} An obvious improvement in photocatalytic efficiency has also been reported in rutile TiO₂ with Ag nanoparticles implanted near the surface.⁵ Therefore, the synthesis of nanocomposites for different applications requires the creation of nanoparticles with precise control of the particle size and strong, favorable contact with the supporting matrix.

As a widely used technique for the synthesis of nanocomposite materials, ion implantation has the main advantage that it can be used to exceed the equilibrium solubility limit for the metal in the dielectric matrix,^{15,16} as compared to that of

other methods.^{12,17–21} Essentially any element in the periodic table can be implanted into the near surface region in most host materials.^{11,22–25} However, the change in the morphological and chemical properties of the oxide support can be very limited, especially when thermal treatment is performed after implantation. The surface treatment of powders by negative-ion implantation has also been reported.^{26,27} There are intense studies on controlling the precipitation location of the nanoparticles by tuning implantation parameters such as the ion energy, beam current, annealing temperature, and the use of negative ions or an electron-beam resist mask.^{11,22,23} Recent studies show that thermal annealing likely causes the formation of nanocrystals on the surface of the supporting matrix,²⁸ which strongly favors many catalytic reactions. However, as a result of the thermally induced growth and coalescence, the average size of these particles is much larger than 10 nm, making them less than ideal for this application. Furthermore, there have been no in situ observations of the thermal annealing behavior, despite the importance of this process to the understanding of the formation and growth of nanoparticles in a matrix. In this letter, we have directly observed the growth of half-embedded Au nanocrystals on the surface of crystalline TiO₂ during the in situ thermal annealing of an implanted (260 keV Au⁺ ions) specimen with a TEM. The size of the Au nanocrystals has been precisely controlled by the sputtering of low-energy Ga⁺ ions (5 keV) as compared to those for a typical ion implantation with higher energies (several tens to hundreds of keV). The mechanisms for the formation, growth, and size control of Au nanocrystals on TiO₂ have been discussed.

Received: October 13, 2011

Revised: November 23, 2011

Published: December 5, 2011

II. EXPERIMENTAL METHODS

The 260 keV Au⁺ ions were implanted into the (001) plane of rutile TiO₂ single crystals at room temperature using a Danfysik ion implanter. The ion fluence was 5×10^{16} Au⁺/cm² with a beam current density of ~ 2.0 μ A/cm². Two types of thermal annealing experiments on the implanted specimens were performed. Cross-sectional thin foils of implanted specimens, prepared by a standard polishing method for TEM analysis, were used for in situ thermal annealing experiments in a JEOL 3011 TEM equipped with a Gatan double-tilt hot-stage specimen holder heated to 800 °C. In parallel, ex situ thermal annealing of bulk specimens was performed in a muffle furnace at 800 °C for 1 h. The externally annealed specimens were further investigated by TEM, atomic force microscopy (AFM), and scanning electron microscope (SEM) in order to study the distribution and contact structure of Au nanoparticles on TiO₂ after annealing. AFM experiments were performed in tapping mode with a Nanoscope IIIa AFM. To control the particle size, the externally annealed specimens were sputtered by 5 keV Ga⁺ ions with a beam current of 0.12 nA and a modified area of ~ 150 μ m² in a FEI Nova NanoLab focused ion beam (FIB) operated in a vacuum of 2×10^{-7} mbar at room temperature. The FIB angle of incidence was set close to the normal direction of the specimen. The gradual decrease in the size of Au nanoparticles was recorded in situ by an SEM attached to the FIB between the intervals of ion sputtering. The simulation was performed by SRIM,²⁹ which is a widely used code for ion–matter interaction, with the densities of Au and TiO₂ set as 19.32 and 4.25 g/cm³, respectively.

III. RESULTS AND DISCUSSION

In situ thermal annealing has been previously utilized to observe the very different thermal annealing behavior of latent fission tracks in apatite and zircon directly.^{30,31} In this study, after implanting 260 keV Au⁺ ions into TiO₂, we performed in situ thermal annealing by using cross-sectional thin foils of the implanted specimens in a TEM hot-stage holder at 800 °C in order to observe the thermally induced nucleation and growth of Au particles in TiO₂ directly (Figure 1). The implanted gold nanoparticles were fully embedded in the near-surface regions of TiO₂ before thermal treatment (Figure 1a). Generally, the morphology of large gold nanoparticles is close to that of a sphere with an average diameter of ~ 20 nm, but some faceted features can be seen in the deeper portions of the large particles, confirming the crystalline nature of the nanoparticles. High-resolution TEM (HRTEM) images show that there are small particles embedded in the amorphous TiO₂ layer with a diameter of 1 to 2 nm (not shown), which can be easily distinguished from the large particles. Once the temperature of the hot-stage stabilized at 800 °C for 9 min, the growth of gold nanoparticles is clear as the average size of large particles increases to ~ 27 nm (Figure 1b). The large nanoparticles do not move, as directly observed during the in situ annealing. This contrasts with the higher mobility of the smaller particles. As a gold cluster absorbs the nearby gold atoms, its size gradually increases, which significantly hinders its mobility within the TiO₂ crystalline matrix. The nanoparticles, which were fully embedded in the host before annealing, become half-embedded as they grow upward preferentially along the [111] directions of TiO₂ by merging with the smaller and closest particles (or Au atoms), making the faceted features more obvious. After annealing times in excess of 21 min, the growth rate of large particles decreases and the average size saturates at ~ 29 nm (Figure 1c). After thermal annealing, the contrast of the implanted TiO₂ layer is significantly enhanced, suggesting the recrystallization of the damaged layer.

Figure 1. Cross-sectional TEM micrographs showing the in situ annealing of 260 keV Au⁺ ion-implanted TiO₂ in a TEM hot stage at 800 °C. (a) Before heating and after (b) 9 and (c) 21 min. As marked by the arrows, the Au clusters, which were initially fully embedded in TiO₂, grow and become exposed on the surface.

The compositional and structural changes in the Au ions implanted TiO₂ after in situ thermal annealing were compared to those after ex situ thermal annealing, where a bulk specimen was heated in a furnace at 800 °C for 1 h. After ex situ thermal annealing, the large particles originally embedded below the surface grow into half-embedded Au nanocrystals (average size ~ 24 nm) on the surface of TiO₂ (Figure 2a). Similar to that observed in in situ thermal annealing, the crystallization of the implanted TiO₂ host is evident from the enhanced contrast of the implanted layer after ex situ thermal annealing (Figure 2a). HRTEM images further confirm that both the gold particles and TiO₂ host are crystalline (Figure 2b). A representative HRTEM image (Figure 2b) shows a faceted Au nanocrystal half-embedded on the crystalline TiO₂ surface with orientation relationships of Au[111]||TiO₂ [110] and Au(−220)||TiO₂(1−11), similar to a previous TEM observation of Au/TiO₂ prepared by the sol–gel technique.¹⁷ The morphologies and distribution of Au nanoparticles on the surface of TiO₂ were investigated by AFM (Figure 2c). The density of nanoparticles on the surface was estimated to be 1.38×10^{10} /cm², indicating the average spacing between two particles to be ~ 85 nm. The average height of half-embedded Au particles is ~ 10 nm, consistent with that observed by TEM.

The formation of half-embedded Au particles is not due to the motion of the large particles toward the surface but is due to the absorption of small particles (or Au atoms) locally^{32,33} and the preferential growth of the large particles upward, as observed by TEM. The formation of a gold-depleted zone around the large particles (Figure 2a) is attributed to the highly localized absorption of small particles around the large particles. This highly localized absorption also results in a direct correlation between the distribution of nanoscale particles as observed by TEM and the Au concentration profile as calculated by SRIM.²⁹ Further discussion of the highly localized absorption is shown in the Supporting Information.

Figure 2. Structure and distribution of Au particles in the TiO_2 host after the Au^+ ion implantation and subsequent ex situ thermal annealing at 800°C for 1 h in a furnace. (a) Low-magnification cross-sectional TEM micrograph. (b) HRTEM image showing a gold hemisphere. (c) AFM image.

The irradiation by low-energy ions has a very limited ion mixture in the host³⁴ (e.g., the irradiation with 5 keV Ga^+ has a peak Ga concentration of only 2 atom %).³⁵ In this study, the preferential sputtering of Au over TiO_2 by the low-energy 5 keV Ga^+ ions was utilized to decrease the size of the Au hemispheres continuously (Figure 3a–f). The sputtering yield of Au under the irradiation of 5 keV Ga^+ ions can be calculated to be 10.0 atoms/ion, which is significantly larger than that for TiO_2 (0.7 for Ti, 3.0 for O). This situation is similar to the sputtering effect during the implantation by high-energy ions (e.g., 40.0 (Au) vs 2.9 (Ti) and 8.6 (O) atoms/ion for 260 keV Au^+ ions). The average diameter of the large Au particles was measured and plotted at different sputtering times (Figure 3g). The average diameter before sputtering is 25 nm (with a standard deviation 3.4 nm), consistent with the observations by TEM. The particle density measured by SEM is $1.21 \times 10^{10}/\text{cm}^2$, close to that of the measurements obtained by AFM. As the irradiation time increases, the average diameter of Au particles decreases. At 100 s, the average diameter decreases to 7 nm with a standard deviation of 1.1 nm, suggesting that the large particles maintain good uniformity in size during the sputtering. Because of the resolution limit of the SEM, it is difficult to measure a particle size below 7 nm, although it should be possible to have smaller sizes with longer irradiation times. Although the particle size decreases, the particle density (or the interval between large particles) remains constant during sputtering. This further confirms that it is the Ga^+ irradiation that causes the gradual decrease in the size of the nanoparticles on the surface. Because of the significant difference in sputtering yields, Ga^+ irradiation results in a rapid decrease in the size of Au particles but there is no apparent change in the thickness of the TiO_2 host.

Figure 3. SEM images showing the size-change sequence of Au nanoparticles half-embedded on the TiO_2 surface (a) before and after Ga^+ sputtering at (b) 8, (c) 25, (d) 50, (e) 75, and (f) 100 s in Nova FIB operated at 5 kV with a current of 0.12 nA. (g) The average diameters of large Au nanoparticles and the corresponding standard deviation at different sputtering times. The implanted specimen was thermally annealed in a furnace before ion sputtering.

Upon the irradiation of energetic ions, the knocked-out atoms from the embedded metal nanoclusters can diffuse over a distance in the oxide and form satellite nanoparticles around the original nanoclusters.^{36,37} The atom loss in the nanoclusters results in the size decrease of the center nanoclusters.³⁸ As compared to the fully embedded Au particles, the sputtering effect of the exposed Au hemispheres should be more intense. Furthermore, the nuclear contribution of the energy loss (S_n) for 5 keV Ga^+ is significantly larger than the electronic contribution (S_e) within the entire penetration range of ~ 7 nm. The high ratio S_n/S_e (~ 5) would also significantly contribute to the sputtering and size decrease of the Au hemispheres.³⁷ However, the sizes of satellites are smaller upon irradiation with a reduced S_n at a lower energy of ions.³⁹ As a result, the sizes of the satellites for the Ga^+ of only 5 keV would be too small to be detected by the SEM if the satellites could form during the sputtering. The SEM images in Figure 3 have provided some information on the morphological changes in Au particles after the Ga sputtering. To confirm the compositional and morphological changes after the sputtering, cross-sectional TEM images similar to those in Figure 2a would be interesting. Unfortunately, the size of the modified region after the Ga sputtering in a FIB is only several tens of micrometers, which is too small to make a cross-sectional sample. Similarly, for many applications of the nanocomposites it requires a large modified area. However, current ion implanters, usually capable of handling a broad range of ion types and energies, provide a promising means of synthesizing nanocrystals of a specific size on oxides over a large area by combining high-energy ion implantation and low-energy sputtering.

In situ studies of the thermally induced formation and growth mechanism of Au nanocrystals in TiO_2 provide a perspective by which one may understand the fundamental processes that occur during ion implantation and ion sputtering (Figure 4). During the high-energy ion implantation, the

Figure 4. Fabrication of Au nanocrystals with controlled structure and particle size. (a) Implantation with high-energy ions. (b) Thermal annealing. (c) Preferential sputtering of Au over TiO₂ by low-energy ions.

positive Au⁺ ions tend to form neutrally charged Au⁰ as the negative electron coming from the conductive base of the ion implanter. The coarsening of Au clusters due to irradiation-enhanced diffusion competes with the decreasing particle size caused by the surface sputtering, resulting in the formation of Au clusters that are fully embedded in the region near the top surface of TiO₂ (Figure 4a). Without the sputtering, the thermally enhanced diffusion during annealing causes the formation of half-embedded Au nanocrystals on the surface because of the preferential growth of Au particles toward the top surface (Figure 4b). The preferential sputtering of Au over TiO₂ by low-energy ions causes the decreasing size of the half-embedded Au nanocrystals (Figure 4c). The Supporting Information provides detailed explanations of these processes. With the ion implantation and subsequent thermal processing or further ion sputtering, the important properties of the nanocomposite can be optimized for a particular application by controlling the location and average size of the precipitates.

IV. CONCLUSIONS

In situ thermal annealing was used to observe Au nanoparticles directly, which were initially fully embedded in TiO₂, grew, and become exposed at the surface as a result of the localized absorption of nearby smaller particles and the preferential growth of Au particles toward the surface. The precise control of the size of the half-embedded Au nanoparticles from 25 to 7 nm was achieved by the preferential sputtering of Au over the TiO₂ host by low-energy ions. This method can be used to control the structure and size of a wide variety of nanoparticles in a matrix where the surface structure and particle size are required to obtain specific material properties.

■ ASSOCIATED CONTENT

Supporting Information

Highly localized absorption and formation of a gold-depleted zone. Fundamental processes that occur during ion implantation, thermal annealing, and ion sputtering. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: rodewing@umich.edu. Fax: +1 734 647 5706. Tel: +1 734 763 9295.

■ ACKNOWLEDGMENTS

The funding for this study was provided by the Office of Basic Energy Sciences of the U.S. DOE (DE-FG02-97ER45656).

■ REFERENCES

- (1) Rodriguez, J. A.; Ma, S.; Liu, P.; Hrbek, J.; Evans, J.; Perez, M. *Science* **2007**, *318*, 1757–1760.
- (2) Haruta, M.; Yamada, N.; Kobayashi, T.; Iijima, S. *J. Catal.* **1989**, *115*, 301–309.
- (3) Bamwenda, G. R.; Tsubota, S.; Nakamura, T.; Haruta, M. *Catal. Lett.* **1997**, *44*, 83–87.
- (4) Subramanian, V.; Wolf, E. E.; Kamat, P. V. *Langmuir* **2003**, *19*, 469–474.
- (5) Tsuji, H.; Sugahara, H.; Gotoh, Y.; Ishikawa, J. *Nucl. Instrum. Methods Phys. Res., Sect. B* **2003**, *206*, 249–253.
- (6) Campbell, C. T. *Science* **2004**, *306*, 234–235.
- (7) Heitmann, J.; Muller, F.; Zacharias, M.; Gosele, U. *Adv. Mater.* **2005**, *17*, 795–803.
- (8) Honda, S.; Modine, F. A.; Meldrum, A.; Budai, J. D.; Haynes, T. E.; Boatner, L. A. *Appl. Phys. Lett.* **2000**, *77*, 711.
- (9) Shi, D. L.; Lian, J.; Wang, W.; Liu, G. K.; He, P.; Dong, Z. Y.; Wang, L. M.; Ewing, R. C. *Adv. Mater.* **2006**, *18*, 189.
- (10) Shi, D. L.; Cho, H. S.; Chen, Y.; Xu, H.; Gu, H.; Lian, J.; Wang, W.; Liu, G.; Huth, C.; Wang, L. M.; Ewing, R. C.; Budko, S.; Pauletti, G. M.; Dong, Z. *Adv. Mater.* **2009**, *21*, 2170–2173.
- (11) Meldrum, A.; Haglund, R. F.; Boatner, L. A.; White, C. W. *Adv. Mater.* **2001**, *13*, 1431–1444.
- (12) Haruta, M.; Tsubota, S.; Kobayashi, T.; Kageyama, H.; Genet, M. J.; Delmon, B. *J. Catal.* **1993**, *144*, 175–192.
- (13) Haruta, M. *CATTECH* **2002**, *6*, 102–115.
- (14) Michalek, X.; Pinaud, F. F.; Bentolila, L. A.; Tsay, J. M.; Dooze, S.; Li, J. J.; Sundaresan, G.; Wu, A. M.; Gambhir, S. S.; Weiss, S. *Science* **2005**, *307*, 538.
- (15) Stepanov, A. L.; Popok, V. N. *Surf. Sci.* **2004**, *566–568*, 1250–1254.
- (16) Meldrum, A.; White, C. W.; Boatner, L. A.; Anderson, I. M.; Zuhur, R. A.; Sonder, E.; Budai, J. D.; Henderson, D. O. *Nucl. Instrum. Methods Phys. Res., Sect. B* **1999**, *148*, 957.
- (17) Bokhimi, X.; Zanella, R. J. *Phys. Chem. C* **2007**, *111*, 2525–2532.
- (18) Cuenat, A.; George, H. B.; Chang, K. C.; Blakely, J. M.; Aziz, M. J. *Adv. Mater.* **2005**, *17*, 2845.
- (19) Lian, J.; Wang, L. M.; Sun, X.; Yu, Q.; Ewing, R. C. *Nano Lett.* **2006**, *6*, 2637.
- (20) Wei, Q.; Lian, J.; Lu, W.; Wang, L. M. *Phys. Rev. Lett.* **2008**, *100*, 076103.
- (21) Tom, R. T.; Nair, A. S.; Singh, N.; Aslam, M.; Nagendra, C. L.; Philip, R.; Vijayamohanan, K.; Pradeep, T. *Langmuir* **2003**, *19*, 3439–3445.
- (22) Fromknecht, R.; Linker, G.; Wang, L. M.; Zhu, S.; Sun, K.; Veen, A. v.; Huis, M. v.; Niemeyer, J.; Weimann, T.; Wang, J. *Surf. Interface Anal.* **2004**, *36*, 193–194.
- (23) Kishimoto, N.; Umeda, N.; Takeda, Y.; Gritsyna, V. T.; Renk, T. J.; Thompson, M. O. *Vacuum* **2000**, *58*, 60–78.
- (24) Ramaswamy, V.; Haynes, T. E.; White, C. W.; MoberlyChan, W. J.; Roorda, S.; Aziz, M. J. *Nano Lett.* **2005**, *5*, 373.
- (25) White, C. W.; Budai, J. D.; Zhu, J. G.; Withrow, S. P.; Aziz, M. J. *Appl. Phys. Lett.* **1996**, *68*, 2389.
- (26) Tsuji, H.; Ishikawa, J.; Itoh, H.; Toyota, Y.; Gotoh, Y. *Appl. Surf. Sci.* **1996**, *100–101*, 342–346.
- (27) Tsuji, H.; Kido, S.; Sasaki, H.; Gotoh, Y.; Ishikawa, J. *Rev. Sci. Instrum.* **2000**, *71*, 804.
- (28) Zhu, S.; Sun, K.; Wang, L. M.; Ewing, R. C.; Fromknecht, R. *Nucl. Instrum. Methods Phys. Res., Sect. B* **2006**, *242*, 152–156.
- (29) SRIM 2011, <http://www.srim.org/SRIM/SRIM2011.htm>.
- (30) Li, W. X.; Wang, L. M.; Lang, M.; Trautmann, C.; Ewing, R. C. *Earth Planet. Sci. Lett.* **2011**, *302*, 227–235.
- (31) Li, W. X.; Wang, L. M.; Sun, K.; Lang, M.; Trautmann, C.; Ewing, R. C. *Phys. Rev. B* **2010**, *82*, 144109.
- (32) Budai, J. D.; White, C. W.; Withrow, S. P.; Chisholm, M. F.; Zhu, J.; Zuhur, R. A. *Nature* **1997**, *390*, 384–386.
- (33) Voorhees, P. W. *Annu. Rev. Mater. Sci.* **1992**, *22*, 197–215.
- (34) Mayer, J.; Giannuzzi, L. A.; Kamino, T.; Michael, J. *MRS Bull.* **2007**, *32*, 400–407.

- (35) Thompson, K.; Gorman, B.; Larson, D. J.; van Leer, B.; Hong, L. *Microsc. Microanal.* **2006**, *12*, 1736–1737.
- (36) Cesca, T.; Pellegrini, G.; Bello, V.; Scian, C.; Mazzoldi, P.; Calvelli, P.; Battaglin, G.; Mattei, G. *Nucl. Instrum. Methods Phys. Res., Sect. B* **2010**, *268*, 3227–3230.
- (37) Mattei, G.; De Marchi, G.; Maurizio, C.; Mazzoldi, P.; Sada, C.; Bello, V.; Battaglin, G. *Phys. Rev. Lett.* **2003**, *90*, 085502.
- (38) Rizza, G.; Cheverry, H.; Gacoin, T.; Lamasson, A.; Henry, S. J. *Appl. Phys.* **2007**, *101*, 014321.
- (39) Mattei, G.; Battaglin, G.; Bello, V.; De Marchi, G.; Maurizio, C.; Mazzoldi, P.; Parolin, M.; Sada, C. *J. Non-Cryst. Solids* **2003**, *322*, 17–21.