Good Control of Spatial and Size Ordering of Fe Nanoparticles by Xe-Gas-Assisted Growth with a Seeding Layer

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Received October 31, 2012; accepted December 20, 2012; published online January 18, 2013

We demonstrate the fabrication of Fe nanoparticles with good spatial and size orderings by Xe-buffer-layer-assisted growth combined with a nanopatterned Au\((111)\) surface. Fe nanoparticles of three atomic layers in height and 2.65 nm in diameter are fabricated by soft landing of Fe atoms on top of the predeposited nucleation seeds with the Xe-buffer-layer-assisted growth. This method is successfully used to control the nucleation toward the surface normal direction, whereby new deposited atoms are stacked on top of the existing ones to form taller nanoparticles, and is applicable to the growth of other nanostructures on various prepatterned surfaces. © 2013 The Japan Society of Applied Physics

The controllable fabrication of nanostructures or nanoparticles with good ordering of size and spatial arrangement is of great importance in basic physical sciences and technologies\textsuperscript{1,2} such as nanocatalysis, nanophotonics, and nanostorage.\textsuperscript{3-6} The development of fabrication techniques to a smaller scale usually leads to a larger exposed surface that enhances the efficiency of catalysis,\textsuperscript{7,8} the Raman scattering,\textsuperscript{9,10} or the impact of surface magnetic anisotropy on those nanoparticles.\textsuperscript{11,12} Advanced control of the size and spatial orderings can significantly change the interparticle interaction and amplify the corresponding collective behavior on the nanoscale without smearing out, realizing fascinating phenomena never yet achieved.\textsuperscript{2,13,14} For example, more active and even selective catalysis can be achieved for the well-controlled nanoparticles than for the larger particles.\textsuperscript{7,8} In the magnetism aspect, the surface/volume magnetic anisotropy was manipulated by good tuning of the particle size for magnetic materials.\textsuperscript{12}

Even though promising applications are expected, controlling the size and aspect ratio of the nanoparticles at will within 10 nm and arranging them in a well-ordered manner remain challenging. One of the reasons is the limitation of the spatial resolution of the existing “top-down” methods, such as lithography with a photon or electron beam, or by scanning probe microscopy (SPM). On the other hand, the success of assembling nanostructures on self-organized nanopatterns might achieve much better resolution.\textsuperscript{10,15-17} These so-called “bottom-up” methods encounter, however, difficulty in enlarging and shaping the individual nanostructures in a controlled way, which may in turn restrict their functionality. Simple deposition on these surface templates mostly extends the lateral size of the nanostructures to become two-dimensional (2D) islands and eventually continuous films.

Herein, we propose a new method for enhancing the vertical assembly of nanoparticles less than 10 nm in size with good spatial ordering, by introducing a seeding layer into Xe-buffer-layer-assisted growth (BLAG).\textsuperscript{18-20} In this way, the size of nanostructures can be extended in the surface normal direction with greatly delayed lateral percolation. Our result indicates that the prenucleated seeds can benefit the spatial ordering and size uniformity of the nanoparticles fabricated by BLAG. This makes the nanostructures readily subject to further decoration by other materials. This method, in the case of a suitable choice of buffer layers, rarely depends on the deposited materials and supporting surfaces, and is thus likely to be applicable to many other materials.\textsuperscript{21}

The proposed method was demonstrated in an ultrahigh vacuum (UHV) system with base pressure better than 4×10\(^{-11}\) Torr for in-situ preparation and characterization.\textsuperscript{16,17} A well-ordered Au\((111)\) herringbone surface was prepared by repeating cycles of 500 eV Ar\(^{+}\) sputtering and subsequent annealing to 1000 K for 5 min. Fe atoms were evaporated with growth rates of (6-9)×10\(^{-4}\) ML s\(^{-1}\), which was kept invariant for all the experiments. The adsorption of Xe, and subsequent deposition of Fe were performed at 33 K. Then, the sample was annealed to 300 K at the rate of 10 K s\(^{-1}\) for the desorption of the Xe buffer layer and the formation of Fe nanostructures.

As is well known, a clean Au\((111)\) surface can be reconstructed into the characteristic “herringbone” pattern with a series of parallel zigzag ridges.\textsuperscript{17,20} The elbows where two ridges join are associated with a surface dislocation, and are distinguished into two different types: the fcc and hcp elbow sites, as respectively indicated by the gray and green arrows in Fig. 1. They are the most active sites on the inert Au surface, and are usually employed as the nucleation centers for the fabrication of well-ordered nanoisland arrays.

At room temperature (RT, 300 K), the deposited Fe atoms land on the herringbone surface and diffuse until they accumulate at the elbow sites, as shown in Fig. 2(a). As the coverage increases, the nucleated islands extend horizontally, keeping the constant height of 1 atomic monolayer (ML) [Figs. 2(a) and 2(b)]. The fact that they do not form 2nd layer islands indicates a high mobility and strong chance for these Fe atoms to descend across the island edge. These islands gradually merge with their nearest neighbors while growing to higher coverage \((\geq 0.5 \pm 0.1\) ML\), as shown in
the inset of Fig. 2(a). Afterward, the grown mode is quasi-layer-by-layer, indicating that Fe tends to grow on Au(111) layer by layer. The deposition at low temperature (LT, 33 K) with subsequent heating to RT shows that the merging of adjacent islands and the formation of bilayer islands both occurred more readily compared with the RT growth, as compiled in Figs. 2(c) and 2(d). The deposited Fe atoms freeze after landing on the cryogenic surface and have little chance to diffuse around to find the most attractive site. The subsequent heating to RT provides the kinetic energy for the landed atoms to diffuse locally and to nucleate with the adjacent atoms. As a result, the nucleated islands are distributed randomly on the surface and are not strongly correlated to the herringbone elbow sites. This is certainly undesirable. However, due to freezing, there is a greater chance for atoms landing on top of previously landed Fe to form large enough 2nd layer aggregations that are immobile even at RT. This will promote growth along the vertical direction. As direct growth at either RT or LT does not produce any well-ordered array of mono-dispersed nanoparticles, buffer-layer-assisted growth shows significantly different growth behavior. As illustrated in Fig. 2(e), xenon gas is introduced to form the buffer layer by cryogenic adsorption (at 33 K) on the substrate surface. Fe atoms are deposited at the same temperature on this buffer layer. During the heating to RT, the deposited Fe atoms aggregate gradually and form the nanoparticles before landing on the substrate surface. The results are compiled in Figs. 2(f) and 2(g). 16 L (1 L = 10^{-6} Torr-s) of Xe was dosed onto the Au(111) surface at 33 K and 0.24 ML Fe atoms were subsequently deposited. Heating to 300 K (heating rate 10 K/s) evaporates the Xe buffer layer. The dewetting, restructuring, or desorption of the Xe buffer layer stimulates the aggregation of Fe atoms into the nanoparticles. At the end of Xe desorption, these Fe nanoparticles softly land on the Au(111) surface. The particle size distribution ranges from 3 nm in width and 0.9 nm in height. It indicates the success of modifying the nucleation behavior from the typical 2D growth mode to 3D stacking and the success of enhancing the size of the nucleated Fe atomic clusters on the Au(111) surface. Note that though these Fe nanoparticles aggregate preferentially on the herringbone elbows, the wide distribution of the nanoparticle sizes and the irregular size distribution in space for the larger nanoparticles (>5 nm in height) are undesirable. To solve these problems, we proposed the idea of performing buffer-layer-assisted nucleation on a well-ordered island array (as the nucleation seeds), as shown in Fig. 3(a). It combines both the advantages of good space-ordering in the RT-grown island array and that of the nanoparticle nucleation in BLAG. The predeposited Fe nucleation seeds before BLAG help to guide the landing of nanoparticles,
leading to the vertical self-assembly and good organization of Fe nanoclusters on the Au(111) herringbone elbows. Firstly, 0.1 ML Fe is deposited on the Au(111) surface at 250 K to form the well-organized nucleation seeds, as shown in Fig. 3(b). Subsequently, the buffer-layer-assisted nucleation process is applied with 0.18 ML of Fe atoms deposited on a 16 L Xe buffer layer at 33 K. In comparison with the BLAG-only results [Fig. 2(f)], the nanoparticles observed in this combined method clearly exhibit the improvement of regularities in size and space [Fig. 3(c)]. The Fe nanoparticles almost nucleate on the nucleation seeds at herringbone elbows with a uniform height distribution. As shown in Fig. 3(d), the nucleation seeds reveal a single-atomic-layer height no matter how large the lateral widths are (green triangles). On the other hand, the combined method (BLAG with seeds) leads to three-atomic-layer height (0.62 ± 0.21 nm, black solid circles) and 2.65 ± 0.76 nm in width with a much narrower lateral distribution than the results by the BLAG-only method, confirming the enhanced vertical assembly behavior.

Compared with the BLAG-only results (empty red squares), the combined method produces Fe nanoparticles with more regular size distributions in both width and height. This means that the predeposited Fe seeds can effectively act as the nucleation centers to guide the landing of the Fe atoms and/or nanoparticles during the desorption process of the Xe buffer layer. The catching probability [Fig. 3(e), defined as the ratio of the nanoparticles landing on the elbows of Au(111) herringbone reconstruction] increase from 65 ± 7% for the BLAG-only process to 95 ± 2% for the combined method with nucleation seeds. Also, the height of the Fe nanoparticles is enhanced from 1 to 3 ML with much narrower distribution [Fig. 3(f)]; the width of them changes from 1.25 nm for the BLAG-only method to 2.65 nm for the combined methods. This confirms that this BLAG-seeds combined technique can achieve the vertical self-assembly needed to fabricate the taller nanoparticles with good ordering in space and size, providing a new route for fabricating nanoparticles of sub-10 nm size by only physical approaches. Also the areal densities of the nanoparticles observed in our study are as high as 10 terabit/in.², which is the same order of magnitude as the current reported values. ²

The capability of the buffer-layer-assisted nucleation on the seeds, such as the dependence of the coverage or the size of the seeds on the catching probability or the spatial regularity, can be further verified by repeating the BLAG process on the existing nanoparticles. Here the existing nanoparticles act as the new and larger nucleation seeds for the subsequent BLAG process, as illustrated in Fig. 4(a). For comparison, the results of repeating BLAG once and 4 times are shown in Figs. 4(b) and 4(c), respectively. Clearly, the assembled nanoparticles stack on the elbows of the Au(111) herringbone structures even after many sophisticated BLAG processes. This indicates that the nucleation mainly occurs on the sites of the existing nanoparticles, enhancing their height to more than 1.05 nm (five atomic layer) after four cycles of the BLAG processes, as shown in Fig. 4(c). Note that the spatial ordering remains nearly invariant during the repeating processes, which shows the capability of keeping the ordering by this “BLAG+seeds” method. Furthermore, the catching probability of nanoparticles for the 4 repeating BLAG processes remains 93 ± 3% which is almost the same as that (95 ± 2%) for the single BLAG process. It suggests that the catching probabilities in the subsequent BLAG processes increase when the particles stack taller owing to the larger and taller nanoparticles as the “nucleation seeds”. For the seeds taller than 1 atomic layer (after first BLAG process), the catching probability must be even as good as 99%. This result is positive for the further application and is also meaningful for how the seeds guide the nucleation of the nanoparticles.

From the fact that larger and taller nucleation seeds conduct the higher catching probability, the morphology...
difference should dominate the nucleation behavior of the Fe nanoparticles in our experiments. Close to the end of the Xe desorption, presumably the Fe seeds was exposed to vacuum earlier than the substrate due to the morphology difference. These predeposited seeds may help to guide the nucleation of the Fe nanoparticles and promote them to stack up. The larger and taller Fe islands thus play a more significant role in guiding the Fe nanoparticles. Most of the vertical assembled nanoparticles form during the desorption of Xe. The Fe atoms landing on the Au(111) surface hardly diffuse to stack on top of the existing Fe nanoparticles. Note that where the Fe nanoparticles land on the surface is a key issue for this combined method, which was hardly taken into account in the typical BLAG-only method.

The statistical comparison of size distributions exhibit that the particle width increases from 2.65 ± 0.76 to 4.30 ± 0.74 nm and the height increases from 0.62 ± 0.21 nm (3 ± 1 atomic height) to 1.05 ± 0.18 nm (5 ± 1 atomic height), as shown in Fig. 4(d). From the simply vertical stacking point of view, the nucleating particles from top of the Xe-buffer layer stack on the prenucleated nanoparticles during the RT-heating procedure in the BLAG. This result indicates that the first BLAG process adds 2 ± 1 atomic height on the single-atomic-layer seeds. Intuitively, the nanoparticles after four repeating cycles of the BLAG process are expected to be ~9 (= 1 + 2 × 4) ML in height, which is higher than our experimental results. It implies that the nanoparticles are not formed by simply direct stacking, but are actually reformed by the thermal heating. Besides, the aspect ratios of the height to width for these nanoparticles, as acquired from Fig. 4(d), are nearly invariant from one and four cycles of the BLAG processes. Both the nanoparticles and the substrate are metallic, which means the electronic structure is relatively continuous, and thus the particle height can be determined precisely. However, the measured particle width is very possibly enlarged by the STM-tip effect. Therefore the real aspect ratio could be even higher than the measured value. This BLAG-seeds combined technique, although doesn’t stack particles without reformation, still can achieve the vertical self-assembly with the invariant, or even higher, aspect ratio.

In conclusion, using the idea of integrating buffer-layer-assisted growth with pre-deposited nucleation seeds, we have demonstrated a method for the vertical assembly of nanostructures to control 3D nucleation with high aspect ratio of height to width. The predeposited Fe seeds can help to guide the landing of nanoparticles during BLAG, leading to the regular and vertical self-assembly of Fe nanoparticles, which are well arranged on the Au(111) herringbone surface. Compared with a typical BLAG-only method, this combined method is shown to assemble the nanoparticles with better regularities in size and space. These regularities can even be kept after repeating the BLAG processes 4 times. This approach opens up a way for detailed size-dependent characterization of many physical or chemical properties for nanoparticles, which can be applied to not only nanoparticle arrays but also various nanostructures with different materials of the deposit/substrate combination.

Acknowledgment This work was financially supported by the National Science Council of Taiwan through grants numbered NSC 96-2112-M-003-015-MY3, NSC 97-2112-M-110-003-MY3, and NSC 100-2112-M-110-005-MY2.

10) S. Nie and S. R. Emory: Science 275 (1997) 1102.