

## Manipulating the size distribution of supported gold nanostructures

A. Sundar,<sup>1</sup> R. A. Hughes,<sup>1</sup> P. Farzinpour,<sup>1</sup> K. D. Gilroy,<sup>1</sup> G. A. Devenyi,<sup>2,3</sup> J. S. Preston,<sup>2,3</sup> and S. Neretina<sup>1,a)</sup>

<sup>1</sup>*Department of Mechanical Engineering, Temple University, Philadelphia, Pennsylvania 19122, USA*

<sup>2</sup>*Brockhouse Institute for Material Research, McMaster University, Hamilton, Ontario L8S 4M1, Canada*

<sup>3</sup>*Department of Engineering Physics, McMaster University, Hamilton, Ontario L8S 4L7, Canada*

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Gold nanostructures, with a wide size distribution, are confined between a metal foil and the oxide substrate upon which they were formed. When heated the surface energy gradient between the oxide and foil results in a net migration of gold atoms from the nanostructure to the foil. With time, the nanostructures show a size reduction and a narrowed size distribution. The narrowing results from the formation of foil contact points with only the largest nanostructures, a characteristic which leaves small nanostructures intact while consuming larger ones. Also demonstrated is the size reduction of arrayed gold structures to nanoscale dimensions. © 2012 American Institute of Physics. [doi:10.1063/1.3675569]

While the vast majority of noble metal nanostructures has been produced using solution-based synthetic protocols, a significant number of potential applications require that the nanostructures be supported by a substrate in a manner which renders them immobile. Numerous routes have been devised for the fabrication of supported nanostructures including the attachment of functionalized solution-based nanoparticles to the surface,<sup>1</sup> growth off surfaces seeded with linked nanoparticles,<sup>2</sup> lithographically patterning continuous thin films,<sup>3</sup> thermal dewetting,<sup>4</sup> spinodal dewetting,<sup>5</sup> microwave plasma-induced dewetting,<sup>6</sup> vapor phase epitaxy,<sup>7</sup> and nanosphere lithography.<sup>8</sup> These routes can be categorized into (1) technically demanding, cost-prohibitive methods yielding well-ordered periodic arrays of nearly identical nanostructures over small areas and (2) cost-effective procedures yielding randomly spaced nanostructures with a considerable size distribution over large areas. Synthesis routes which close the gap between these two extremes are of technological significance.

The most straightforward method for obtaining supported gold nanostructures is through the room temperature deposition of a continuous ultrathin gold film followed by its subsequent dewetting and agglomeration into droplets at elevated temperatures. This thermal dewetting procedure requires that the substrate has a lower surface energy than gold, a property which, from a thermodynamic perspective, favors the formation of nanoscale droplets with a substrate contact angle defined by Young's equation. A metastable continuous film typically forms at room temperature because the evaporated gold adatoms arriving at the substrate surface lack the kinetic energy required to reach the thermodynamically favored state. Upon heating, the gold layer becomes unstable to the nucleation of holes which extend through the film to the substrate surface. The nucleation of these holes and the subsequent dewetting phenomenon is quite complex<sup>9</sup> and is driven by Rayleigh instabilities,<sup>10</sup> fingering instabilities,<sup>11</sup> grain boundaries,<sup>12</sup> and substrate surface texture.<sup>13</sup> It

typically occurs in the solid state at temperatures well below the melting point and is initiated at defects associated with film granularity.<sup>12</sup> Thinner films dewet at lower temperatures and give rise to droplets which are smaller and more numerous.<sup>14</sup> Once formed, the gold droplets are subject to Ostwald ripening, where there is an exchange of atoms along the substrate surface with larger droplets growing at the expense of smaller ones.<sup>15,16</sup> At higher temperatures, gold sublimation (or evaporation) from the structures also plays a significant role.<sup>14</sup>

In a previous report, we described a high temperature synthesis route where an ultrathin gold film dewets, liquefies, and then slowly self-assembles on various orientations of a lattice-matched oxide substrate.<sup>17</sup> The supported nanostructures formed were intricately shaped, crystalline, and epitaxially aligned. The report, as well as a more recent study by Yoo *et al.*,<sup>18</sup> demonstrates the significance of forming gold nanostructures in this previously unexplored high temperature regime (i.e.,  $\geq 1000^\circ\text{C}$ ). For this regime, oxide substrates provide an ideal platform for gold nanostructure formation due to their chemical and thermal stability, crystallographic perfection, high resistance to gold interdiffusion, and significantly lower surface free energy.

The main drawbacks of gold nanostructure fabrication via thermal dewetting are the substantial size distributions realized and the lack of control over nanostructure placement. Efforts to control this process have focused on exploiting substrate surface textures obtained either through lithographic means<sup>9</sup> or the step-terrace morphologies resulting from vicinal substrates.<sup>13</sup> The intent of these patterns is to create weak points which activate the dewetting phenomenon in well-defined locations. While some degree of progress has been reported, control over nanostructure size and placement is far from ideal. Unconventional nanopatterning techniques directed toward polymer films have also demonstrated the utility of manipulating the dewetting phenomenon from the free surface of the film rather than at the film-substrate interface.<sup>19</sup> Here, we describe the effectiveness of placing a metal foil in contact with a gold film as it dewets on the surface of an oxide substrate. It is observed that the

<sup>a)</sup>Author to whom correspondence should be addressed. Electronic mail: neretina@temple.edu. Tel.: 215-204-6326. FAX: 215-204-4956.

foil, due to its high surface energy, preferentially removes gold from the larger nanostructures while leaving smaller nanostructures intact. The net result is a much improved nanostructure size distribution.

The experimental procedure used to manipulate the gold nanostructure size distribution is shown schematically in Fig. 1. Gold films with a thickness of 12 nm were sputtered (Quorum Technologies Q150T Sputter Coater, 99.99% gold target) at room temperature onto (0001)-oriented  $\text{Al}_2\text{O}_3$  substrates (i.e., c-plane sapphire). Platinum foil (0.025 mm thick, 99.9% purity) was then laid overtop the gold film, covering approximately 50% of its area. The thermal dewetting process proceeded by placing the combination into an alumina crucible and then cycling it through a heating regimen which sees the temperature raised to 1065 °C in 23 min, held at that temperature for a set time interval (0, 5, 10, 15, and 20 min), and then cooled to room temperature over a period of 2 h. The procedure was carried out in a tube furnace under a 50 sccm argon flow. The foil was then removed from the sample, exposing a clear boundary between those areas covered by the foil and those adjacent to it. The foil itself offered little resistance to removal, often sliding off when merely tilting the sample. The resulting nanostructures were characterized using scanning electron microscopy (SEM) in both secondary electron and backscattering modes, tapping mode atomic force microscopy (AFM) energy dispersive x-ray spectroscopy (EDS), and x-ray diffraction (XRD).

Figure 2(a) shows an SEM image of the nanostructures formed by the dewetting of a 12 nm gold film in the absence of platinum foil. While film agglomeration initially occurs near 600 °C, a further increase in the substrate temperature to 1065 °C results in gold nanostructures with (1) an aspect ratio consistently near unity, (2) a high degree of faceting, (3) a preferential [111]-orientation normal to the substrate surface, and (4) adhesion to the substrate surface strong enough to withstand sonication. The high temperature regime, however, adversely influences the nanostructure size distribution through Ostwald ripening, a process where there is an exchange of atoms along the substrate surface with larger structures growing at the expense of smaller ones.<sup>15</sup>

Figure 2 also shows an SEM image (Fig. 2(b)) and the gold nanoparticle size distributions (Fig. 2(c)) obtained when identical gold films are confined between a platinum foil and the oxide substrate upon which they were formed. All sam-

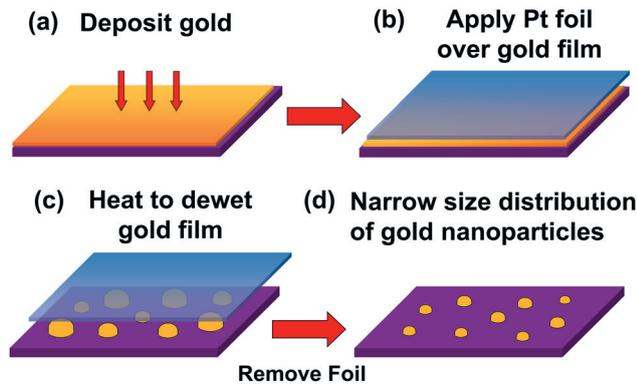


FIG. 1. (Color online) Schematic of the thermal dewetting procedure used to manipulate the nanoparticle size distribution.

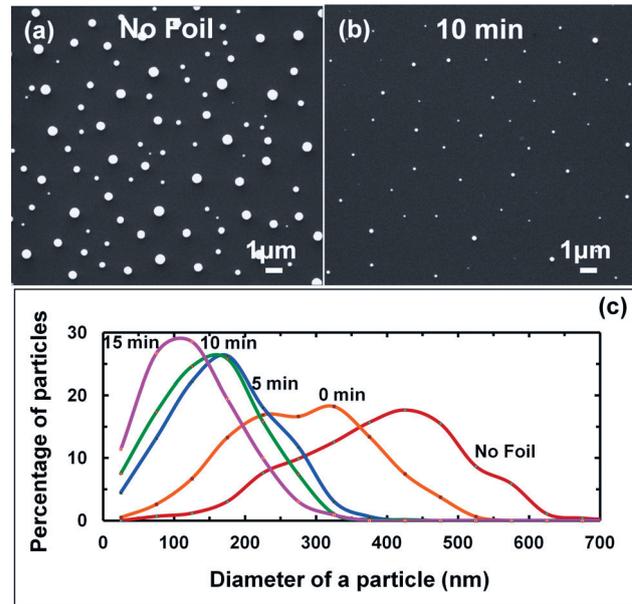


FIG. 2. (Color online) Evolution in the gold nanoparticle size distribution occurring when a platinum foil is placed over a dewetting film at 1065 °C for various time intervals. The evolution is illustrated through SEM images at time intervals: (a) 0 min and (b) 10 min and (c) through the measured size distributions where each is obtained from 1000 nanoparticles binned into 50 nm increments. The line between points is a guide for the eye. Only a small number of nanoparticles were observed for the 20 min time interval.

ples were exposed to a similar heating regimen with the only difference being the time interval for which they remained at the maximum temperature of 1065 °C. The progression shows a systematic reduction in the size of the nanostructures which proceeds to the point of nanoparticle extinction. EDS measurements indicate that the structures are indeed gold, with a platinum content below the level of detectability. Also noteworthy is the fact that experiments using nickel or palladium foils show a similar progression, but where there exists a significant transfer of atoms from the foil to the gold nanostructures.

The observed results can be attributed to an interplay between the various surface energies, nanoparticle curvatures and binary phase diagrams involved. The migration of gold from the nanostructure to the foil proceeds via nanoscale contact points which likely take the form of a capillary bridge.<sup>20</sup> With an ascending order of surface energies of sapphire, gold, and then platinum,<sup>21</sup> there exists a surface energy gradient able to drive gold diffusion towards the platinum foil. Verification that diffusion along these nanoscale point contacts is vital to the observed results, stems from experiments which eliminate gold loss to the foil through the placement of 20  $\mu\text{m}$  yttria stabilized zirconia (YSZ) ceramic spacers between the foil and gold film. The high curvature of the gold surface also leads to an increased chemical potential (i.e., the Gibbs-Thompson effect) which further drives gold migration and likely accounts for the fact that platinum diffusion into the structure is negligible despite the Au-Pt binary phase diagram suggesting a significant platinum solubility at the processing temperature. With the understanding that the foil is only in contact with the largest diameter nanostructures, it follows that gold is preferentially depleted from them. With time, the largest structures shrink

in size, bringing the foil into contact with progressively smaller structures; this process continues until all gold is lost to the foil. Of significance, is the fact that this process is in opposition to Ostwald ripening which promotes the growth of large nanostructures at the expense of smaller ones, and hence, a broadening of the size distribution. It is noted that the ripening process is not eliminated by the presence of the foil, but instead plays a considerably diminished role in determining the overall size distribution. As the sample is cooled to room temperature, the degree of bonding between the platinum foil and gold nanostructures is likely mitigated by shear forces originating from differences in the thermal expansion coefficients between the foil ( $9 \times 10^{-6}/\text{K}$ ) and the substrate ( $7 \times 10^{-6}/\text{K}$ ), the result of which is a foil that is easily removed. Palladium and nickel foils show much the same behavior except for complications which arise from the interdiffusion of atoms into the gold nanostructures. The fact that palladium foils are more prone to interdiffusion is not surprising due to complete miscibility with gold and a vapor pressure large enough to support the limited transfer of atoms directly to the substrate surface.<sup>22</sup> The Ni-Au binary phase diagram also shows miscibility at the processing temperature where, for a range of alloy compositions, there exists a liquid phase field which, if entered, would further accelerate kinetically driven processes.

The ability to sink material from one surface to an adjacent surface connected via nanoscale point contacts also yields opportunities in terms of reducing the size of identical gold particles formed in periodic arrays. The formation of such arrays becomes technically challenging on nanometer length-scales (i.e., for diameters  $< 100$  nm), but is quite straightforward on larger length-scales. By first producing these larger structures and then placing them in contact with the platinum foil, we have demonstrated that it is possible to reduce their size to nanoscale dimensions. Figure 3 shows AFM images of a gold nanoparticle array where each particle initially had a diameter near 350 nm (Fig. 3(a)), but was then reduced in size to 22 nm (Fig. 3(b)). This corresponds to a

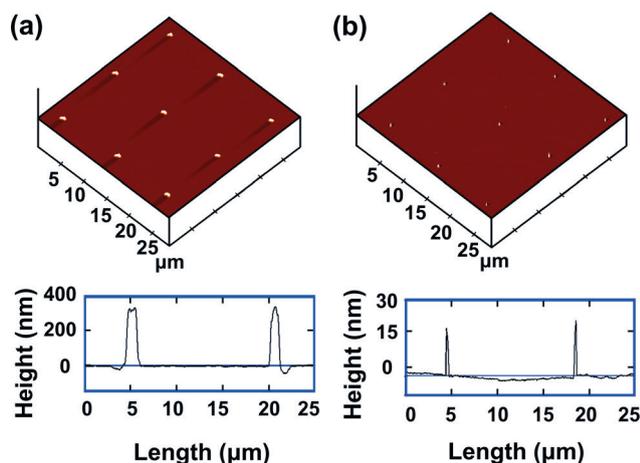


FIG. 3. (Color online) AFM images and cross-sections for (a) a gold particle array with a  $12.5 \mu\text{m}$  periodicity and particle radius of 350 nm and (b) an identical array after being exposed to a platinum foil at  $1065 \text{ }^\circ\text{C}$  for 2.5 min. Note the dramatic size reduction (350–22 nm) apparent from a comparison of the cross-sections across two adjacent structures.

94% reduction in particle diameter and a 99.97% reduction in volume.

From the standpoint of applications, the use of surface energy gradients to manipulate the dewetting process presents both immediate and future possibilities. Obtaining gold nanostructures with a narrow size distribution using the dewetting phenomenon is of technological relevance to plasmonic applications where the resonant frequency is determined by finite size effects<sup>23</sup> and in obtaining nanowire homogeneity via the vapor-liquid-solid growth mode.<sup>24</sup> The utilization of such gradients could also extend beyond the present results, where global manipulations in nanostructure size distribution is achieved, to those where local manipulations are induced by selectively making contact with only discrete areas. Furthermore, the discovery has applications to the field of nanoalloys<sup>25</sup> as the replacement of the platinum foil with either nickel or palladium has resulted in similar manipulations to the gold nanostructure size distribution but where measurable quantities of nickel (or palladium) have been incorporated into the nanostructures. This ability to both locally source and sink material between two adjacent surfaces connected via nanoscale point contacts could also facilitate new growth pathways and allow for diffusion-based combinatorial synthesis routes achieved by sourcing different elements at specific contact points.

To summarize, we have devised a straightforward procedure for manipulating the size distribution of supported nanostructures derived from the dewetting of thin gold films. The discovery advances the application of the dewetting phenomenon to applications where size uniformity is beneficial. The procedure also demonstrates the utility of sinking or sourcing material between nanoscale conduits linking surfaces with dissimilar surface energies, a result which provides a mechanism by which local three-dimensional surface diffusion fields can be utilized for nanoscale patterning, alloying or combinatorial synthesis.

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