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The templated assembly of highly faceted three-dimensional gold microstructures into periodic arrays

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ABSTRACT

A templated assembly route has been devised which sees the formation of periodic arrays of gold microstructures on oxide substrates. The route, which combines elements of subtractive transfer patterning and templated dewetting, involves the placement of an electroformed nickel mesh in conformal contact with a continuous gold film. When heated, the gold beneath the grid selectively attaches to it due to a surface energy gradient which drives gold from the low surface energy oxide surface to the high surface energy nickel mesh. With this process being confined to areas under and adjacent to the mesh, the underlying gold film eventually ruptures at well-defined locations to form isolated islands of gold which subsequently dewet. Removal of the grid reveals a periodic array of three-dimensional highly-faceted gold microstructures. This templated assembly route is demonstrated for the (100)-, (110)- and (111)-surfaces of MgO and $MgAl_2O_4$ where it is observed that the faceting is strongly influenced by both the substrate and its crystallographic orientation.

1. Introduction

Establishing control over the agglomeration of thin metal films at elevated temperatures provides a straightforward and cost-effective route for obtaining arrays of intricately shaped metal structures with dimensions extending from nanometer to micrometer length-scales. With the understanding that solid state dewetting proceeds via surface diffusion away from edges which extend from the underlying substrate to the surface of the film, numerous groups have induced order into the agglomeration process through the establishment of lithographically patterned edges which, upon heating, retract in an organized manner [1–3]. Using this approach, in combination with epitaxial nickel films, Thompson and coworkers have induced the assembly of intricately shaped micrometer-scale nickel islands where the final shape is dependent on (i) the annealing conditions, (ii) the epitaxial relationship formed and (iii) the orientation of the lithographically-defined edges relative to the substrate crystal structure [4,5]. A second approach relies on the fabrication of a substrate with a periodic surface texture over which a continuous metal film is deposited [6–8]. At elevated temperatures the textured areas with the highest curvature create film weak points at well-defined locations which activate the dewetting phenomenon. While arrays of metal structures have been produced in this manner, the highly-textured nature of the surface creates numerous challenges if these structures are to be incorporated into device architectures.

Numerous unconventional patterning techniques have recently emerged [9,10], but these techniques have been predominantly applied to polymer materials where low processing temperatures are the norm. Broadly speaking, pattern formation can proceed through three different modalities: (i) subtractive processes where material is selectively removed, (ii) additive processes where material is selectively applied or (iii) through the controlled rearrangement of material already present on the surface. Collectively, these techniques have demonstrated the utility of manipulating the dewetting phenomenon from the free surface of the film rather than at the film-substrate interface. Of particular relevance to this work are those processes which rely on capillary forces [11] or the work of adhesion [12] to induce pattern formation. For the former, a continuous uniform film is placed in contact with a mold and heated to the temperatures needed to render it fluid-like, at which point it reorganizes to minimize the total surface energy. Upon cooling, the mold is removed leaving behind a patterned surface. For the latter, a film is confined between a mold and a substrate and the ensuing competition between the adhesive forces present at the film–substrate and mold–substrate interfaces leaves material only in select locations when the mold is removed.

In a previous report, we demonstrated the ability to manipulate the size distribution of dewetted gold nanoparticles by confining them between a platinum foil and the sapphire substrate upon which they formed [13]. With an ascending order of surface energies of sapphire, gold and then platinum [14], there exists a gradient which channels gold atoms from the substrate-based gold structures through a capillary neck to the platinum foil. With time the nanostructures become progressively smaller until finally all gold atoms

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have left the sapphire surface. Here, we demonstrate that the replacement of the continuous foil with a metal mesh leads to the formation of periodic arrays of intricately shaped gold microstructures.

2. Materials and methods

The fabrication route is shown schematically in Fig. 1a. Gold films with a thickness of 160 nm were sputtered (Quorum Technologies Q150T Sputter Coater, 99.99% gold target) at room temperature onto the [001]-, [110]- and [111]-surfaces of MgO and $MgAl_2O_4$. Oxide substrates were used due to their thermal stability and high resistance to gold diffusion at the processing temperatures used. Electroformed nickel mesh TEM grids with 7 μm square cells and a repeat spacing of 12.5 μm were used as the mold. The mesh acts as a rigiflex mold [15], simultaneously offering mechanical strength and flexibility. Conformal contact between the mesh and gold film was obtained by placing a second substrate over the mesh followed by the placement of this sandwich structure into a clamping mechanism (Fig. 1b) that applies a small force throughout the high temperature assembly process. The purpose of the clamp is to prevent the mesh from buckling and is not intended to imprint the gold film.

The loaded clamp was then placed in a Lindberg tube furnace and cycled through a heating regimen which sees the temperature raised to 1065 °C in 23 min, held at that temperature for 5 min, and then cooled to room temperature over a period of 2 h. The procedure was carried out under a 50 sccm argon flow to prevent oxidation of the nickel mesh. Once complete, the sample was removed from the furnace and the nickel mesh was peeled off, leaving behind an array of standalone 3-dimensional faceted gold microstructures. Fig. 1c shows an SEM image of a periodic array of 2.7 μm diameter gold microstructures formed on (100)MgO, a clear demonstration that this assembly method can be used to form large-area defect-free arrays with a high degree of size uniformity. Defects, however, are observed which include cells having multiple or no microstructures and isolated regions of randomly formed structures resulting from a lack of conformal contact between the gold film and mesh.

3. Results and discussion

Fig. 2 shows a series of scanning electron microscopy (SEM) images where the assembly process was interrupted at various stages. Initially, the as-deposited gold film appears black as is expected for a flat and featureless surface imaged in secondary electron mode. As the gold film is heated, contact between it and the nickel mesh leads to the formation of a three-dimensional diffusion field which drives gold from the film surface to the mesh due to the higher surface energy of nickel [14]. As the process continues, gold is selectively removed from the substrate to the nickel for film areas directly below and adjacent to the mesh, leaving the intervening areas relatively unscathed. Above 900 °C, the gold loss to the mesh is so severe that the film ruptures at the periphery of each cell, isolating square islands of gold. At this point, the assembly process proceeds in a manner analogous to other templated dewetting routes [1–8], showing directed surface diffusion away from the gold-substrate interface. The diffusion process continues until a single structure is formed in the center of each cell having a volume equal to approximately 65% of that initially enclosed by the cell. Removal of the mesh reveals a periodic array of highly-faceted microstructures, but where the surface of the substrate shows some scarring due to interactions with nickel [16]. In addition, energy dispersive x-ray spectroscopy (EDS) indicates measurable levels of nickel contamination within the gold microstructures. It is noted that temperatures exceeding the melting point of gold are not required for the assembly of arrays, but does result in the formation of microstructures with pronounced faceting due the melting and subsequent recrystallization which occurs.

Fig. 3(a, b) shows SEM images of the highly-faceted gold microstructures formed on three crystallographic orientations of $MgAl_2O_4$ and MgO, respectively. For the case of $MgAl_2O_4$, the faceting is quite similar for all three structures, but the structure is rotated relative to the substrate due to an altered heteroepitaxial relationship. It has been previously shown that both dewetted gold [17] and copper [18] exhibit a strong tendency to form such a relationship when heated to temperatures in excess of their melting point. The observed faceting is similar to that observed by Curiotto et al. [18] for dewetted copper films deposited on c-plane sapphire substrates, showing (100)-, (110)- and (111)-facets. It is noted that for both cases this is not the predicted equilibrium structure [19].

While there is a strong tendency for the top facet to exhibit the same crystallographic orientation as the underlying substrate, there is a near 20% probability to form a (111) top facet structure on the (100) and (110) substrates as well as the tendency for the structures to show a slight wobble off their expected orientation. The structures formed on MgO show the same general trends, but the contact angle with the substrate is smaller and there is the appearance of additional facets. The contact angle difference is likely attributable to MgO having a higher surface energy than $MgAl_2O_4$. The additional facets are consistent with the formation of (311)- and (210)-surfaces [20]. For both substrates, the microstructure faceting can be influenced by the presence of nickel impurities [18].

4. Conclusion

It is has been demonstrated that the placement of an electroformed nickel mesh on a gold film at elevated temperatures induces

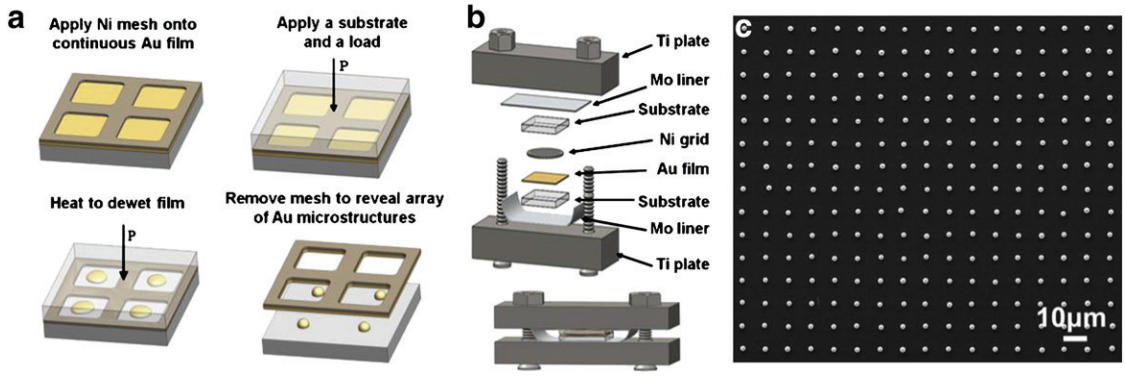

Fig. 1. (a) Schematic of the process used to assemble periodic arrays of intricately shaped gold microstructures. (b) The clamping arrangement used to obtain conformal contact between the gold film and nickel mesh. The molybdenum liner prevented titanium contamination. (c) SEM image of a large-area periodic array of gold microstructures formed on a (100)-MgO substrate.

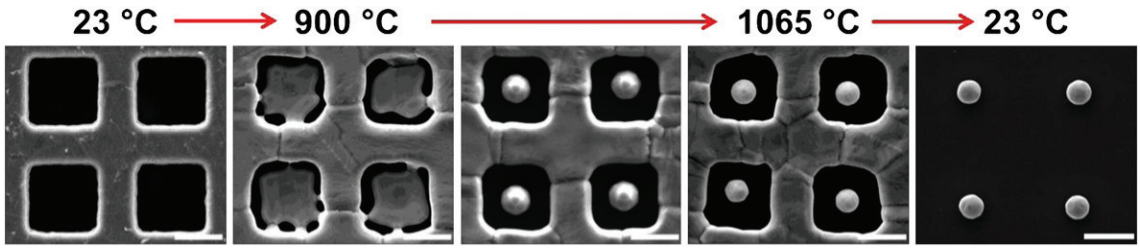

Fig. 2. SEM images showing the high temperature assembly process induced by a nickel mesh (scale bars = 5 μm).

a deterministic assembly process which sees the formation of a periodic array of highly-faceted gold microstructures. With the route likely applicable to other metals, this early stage work presents numerous opportunities in the field of templated assembly.

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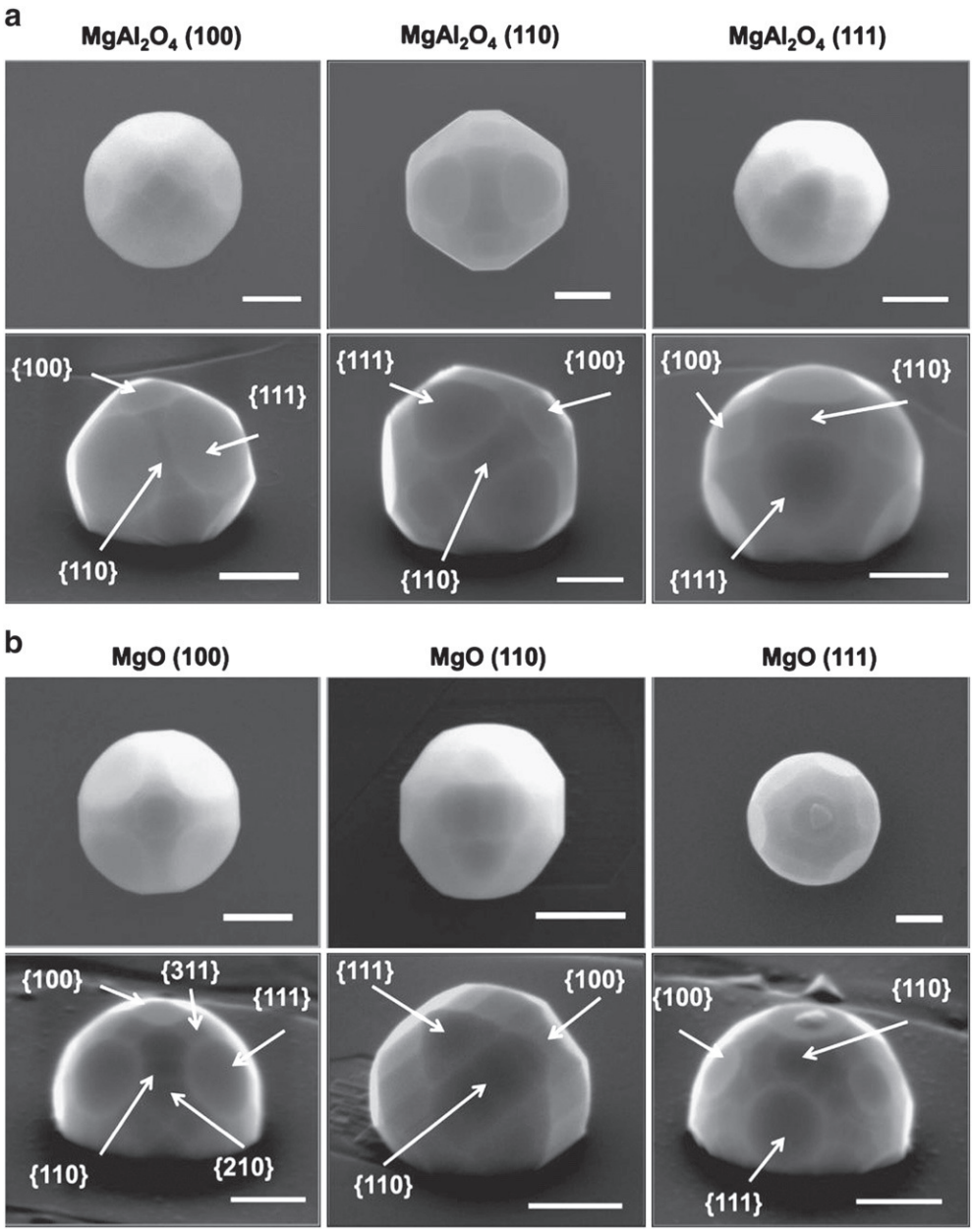

Fig. 3. SEM images of gold microstructures formed in periodic arrays on (a) $MgAl_2O_4$ and (b) MgO substrates of various orientations (scale bar = 1 μm). The labeled facets are based on those observed in face centered cubic materials [20].

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