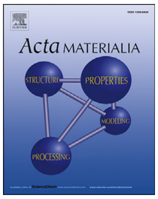
Acta Materialia 117 (2016) 188–196

Contents lists available at ScienceDirect

Acta Materialia

journal homepage: www.elsevier.com/locate/actamat



Full length article

Formation of hollow gold-silver nanoparticles through the surface diffusion induced bulk intermixing

N. Gazit [a], L. Klinger [a], G. Richter [b], E. Rabkin [a, *]

[a] Department of Materials Science and Engineering, Technion – Israel Institute of Technology, 32000 Haifa, Israel
[b] Max Planck Institute for Intelligent Systems, Heisenbergstr. 3, 70569 Stuttgart, Germany

A R T I C L E I N F O

Article history:
Received 6 April 2016
Received in revised form
3 July 2016
Accepted 3 July 2016

Keywords:
Nanoparticles
Surface
Diffusion
Nanovoid
Solid state dewetting

A B S T R A C T

Hollow nanoparticles with size-controlled internal cavities can be synthesized through a novel mechanism of surface diffusion induced bulk intermixing in a thin polycrystalline film between the particles. Starting with single crystalline silver nanoparticles on sapphire substrate produced by solid state dewetting technique, we show that subsequent deposition of the thin gold layer, followed by annealing at a low homological temperature leads to the outdiffusion of silver into the film and formation of hollow nanoparticles with a single internal cavity. We built a kinetic model of hollowing which identified the surface diffusion induced bulk intermixing as a dominating atomistic mechanism, and provided an excellent fit to experimental data without any adjustable parameters. This process allows sculpturing of internal porosity of the nanoparticles and provides a general route to the synthesis of ordered arrays of hollow nanostructures attached to the substrate.

1. Introduction

Hollow metallic nanostructures attract a great deal of attention due to their various possible applications in drug delivery [1], nanofluidics, catalysis [2], and plasmonic devices [3]. Several wet chemistry methods of their synthesis have been proposed [4], yet these methods result in high concentration of defects and impurities. Another essential drawback of these methods is the difficulty in controlling the pores nucleation and growth processes [5].

In 2004, Yin et al. [6] proposed an alternative synthesis method of hollow metallic nanostructures based on diffusion processes. This method relies on the nucleation of pores inside the core-shell structures due to the nanoscale Kirkendall effect [6,7]: a much faster outward diffusion of the core component than the inward diffusion of the shell component results in uncompensated vacancy flux toward the center of the core-shell system, and concomitant supersaturation of the core material with the vacancies. The latter promotes nucleation of internal porosity and formation of the hollow nanostructure. Later, González et al. [8] proposed a hybrid method for synthesis of double-walled gold nanoboxes combining the galvanic replacement reaction and the nanoscale Kirkendall effect.

The nanoscale Kirkendall effect holds significant advantages over more traditional chemical methods, namely the ability to produce fully closed porosity, and to fine tune the size of the pores by a proper selection of the process parameters. However, the Kirkendall effect requires relatively high bulk diffusivities (which can be achieved either at high homological temperatures [9], or due to high concentration of defects [8]), resulting in morphological instability of the nanostructures [10], closing of the pores [9,11,12], and Rayleigh instability-related phenomena in nanotubes. Moreover, because of highly defective microstructure of the nanostructures produced by wet chemistry methods the atomistic mechanisms of Kirkendall hollowing in them are still uncertain. Bulk interdiffusion enhanced by point defects [6,8], grain boundary diffusion [6,7], stress-assisted nucleation and growth [13,14], and interface diffusion [15] were discussed as possible dominant hollowing mechanisms.

In this study we report on the synthesis of hollow Au-Ag nanoparticles (NPs) at low homological temperatures at which bulk interdiffusion does not occur. Our method provides higher microstructure stability of the hollow structure than the nanoscale Kirkendall effect, and allows "sculpturing" of the size and shape of internal pore. A similar method for the synthesis of metal nanotubes was firstly proposed by Richter [16] and later studied in more details by Baylan et al. [17], whereas in this work we demonstrate

---

* Corresponding author.
E-mail address: erabkin@tx.technion.ac.il (E. Rabkin).

http://dx.doi.org/10.1016/j.actamat.2016.07.009
1359-6454/

the method generality, extend it to metal NPs, and uncover the microscopic mechanisms of hollowing. In short, Richter has deposited a thin Au overlayer on an array of single crystalline Ag nanowhiskers attached to the substrate [16]. Au coating was heteroepitaxial on the Ag nanowhiskers, and nanocrystalline on the substrate. Annealing at 170 °C resulted in outdiffusion of Ag from the core of Ag-Au core-shell nanowhiskers into the grain boundaries of the nearby nanocrystalline Au film, and formation of hollow Au nanotubes. Later it was shown that Ag diffusion and segregation on the surface of Au film also play a role in the process [17], yet the relative importance of various diffusion paths, and the detailed atomistic mechanisms of the process were not determined.

2. Experimental

2.1. Sample preparation

Ag films of 25 nm in thickness were deposited using thermal evaporator (VINCI E-PVD4) on *c*-plane oriented sapphire substrates. The substrates were 2″ in diameter and 430 μm in thickness with a miscut of 0.2° toward the *m*-plane. The deposition was performed at room temperature with a base pressure of 2×10^{-6} Torr and with deposition rate of ≈ 1 Å s^{-1}. Firstly, the samples were annealed at the temperature of 700 °C in a quartz tube resistance furnace in ambient air. Most annealings were performed for 5 h, which resulted in equiaxed, equilibrated Ag particles. Annealing for longer times resulted in particles coarsening. All results shown below refer to the samples annealed for 5 h, unless stated otherwise. After the first high-temperature annealing, the Au film of 15 nm in thickness was deposited on the samples with Ag particles using electron beam deposition (Airco Temescal FC 1800). The deposition was performed at room temperature, with a base pressure of 2.5×10^{-7} Torr and with deposition rate of 0.5 Å s^{-1}. The ratio of thicknesses of the Ag and Au films corresponds to a nominal composition of Au-62 at.% Ag. After the deposition, the second annealing of the samples was performed in a Rapid Thermal Annealing furnace (ULVAC-RIKO MILA 5000 P-N) in air at the temperature of 170 °C for 15, 22, 30, 40, 60 and 90 min. The heating rate was 10 °C s^{-1} and the cooling was performed by switching off the heating system.

2.2. Characterization methods

The high resolution scanning electron microscopy (HRSEM, Zeiss Ultra-Plus) micrographs were acquired using a secondary electron detector (SE) at the acceleration voltage of 4 keV. The cross-section samples (of about 70 nm in thickness) were prepared by a dual-beam focused ion beam (FIB, FEI Strata 400-S) by employing the lift-out method. A final low-kV thinning was performed using Ar+ ions with the energy of 500 eV (Linda Gentle Mill 3). High resolution transmission electron microscopy (FEI Titan 80–300 KeV S/TEM) was used for examining the cross-section samples. Energy filtered transmission electron microscopy was used for acquiring the Ag maps around the M-edge of silver (390 eV) with pre edge values of 55 eV and 60 eV, post edge value of 35 eV, and with a slit width of 20 eV. The atomic force microscopy (AFM, XE-70 of Park Inc.) was performed in tapping mode employing NSG30 Si probes supplied by NT-MDT, with an average nominal value of resonant frequency of 270 kHz, and an average nominal radius of curvature at the apex of <25 nm.

3. Results

The formation of Ag NPs during the first high-temperature annealing is the final result of the solid state dewetting process, in which the initial layer transforms into array of isolated particles (similar to water on hydrophobic surface) in order to decrease the energy of all surfaces and interfaces in the system. The HRSEM micrographs of the Ag particles with as-deposited 15 nm-thick Au layer prior and after the second, low-temperature annealing are shown in Fig. 1A and B, respectively. The average particles radius after the Au deposition was 160 ± 37 nm (assuming spherical shape). This size did not change after the second annealing at 170 °C (see Supplementary material). Energy dispersive X ray spectroscopy (EDS) measurements in HRSEM at acceleration voltage of 6 keV were performed prior and after the second heat treatment (Fig. 1C, D). The EDS spectra show no traces of Ag in the areas between the particles after the deposition of Au layer (Fig. 1C, E). However, after the second (hollowing) thermal treatment Ag traces appear both in the particles and in the Au film (Fig. 1D, F).

In order to study the morphology of the particles and the pores, cross sections of the NPs were prepared. The transmission electron microscopy (TEM) micrographs of a focused ion beam (FIB)-prepared cross-section of the Ag particles after deposition of Au layer are shown in Fig. 2. No pores within the Ag particle, or at the Ag-sapphire interface can be observed (near-interface black spots in Fig. 2B, C represent the defects of FIB cross-section preparation). After the second annealing treatment most particles exhibited a well-defined single pore located at the Ag-sapphire interface (Fig. 3). The pores exhibit smooth internal surface and the shape close to that of spherical dome, indicating an important role played by surface diffusion. Energy filtered transmission electron microscopy (EFTEM) indicated that diffusion processes did occur during the hollowing and, in particular, that the free surface of the Au film and the grain boundaries in it were enriched in Ag, and the Au-Ag solid solution was formed (Fig. 4). Quantitative chemical analysis was performed on the cross sectioned samples. Traces of Ag were found in the polycrystalline Au shell. A relatively thick Ag-rich layer (of Au − 46 ± 6 at.% Ag composition within the layer of 10–15 nm in thickness) was found on the surface of the Au film. It was found that both the Au shell and the Au film between the particles are polycrystalline, like in the as-deposited state. In addition, it was found that the thickness of the Au(Ag) film between the particles increased from 16 nm to about 31 nm after annealing for 1 h (Fig. 5).

The kinetics of the film thickening and of the pore growth are shown in Fig. 6. The radii of the pores, and the thickness of the as-deposited Au film, and of the film after the longest (1 h) hollowing heat treatment were determined on the cross-sectional TEM micrographs. The film thickness after hollowing annealing for 30 min was determined with the aid of AFM. The surface of the sample was scratched by a scalpel. Then the sample was scanned using an AFM in tapping mode. The height difference between the exposed substrate and the Au layer was measured in several positions.

In order to exclude the possible role of Ag oxidation during hollowing [18] we performed a control hollowing annealing at 170 °C for 60 min in vacuum of 10^{-2} mbar, and also in a molecular beam epitaxy (MBE) system in ultra-high vacuum. The hollowing was also observed, albeit the shape of the pores changed from the rounded to the faceted one (see Fig. 7). The change of the pore morphology is most likely associated with the dependence of surface energy anisotropy on annealing ambient.

4. Discussion

In this study, we observed the hollowing process at relatively low homological temperature ($\approx 0.33T_m$, where T_m is the melting point of Au). At this temperature, a concentrated Ag-Au solid solution layer of the thickness exceeding 10 nm was formed and covered the entire area between the particles (the average interparticle distance is about 1 μm). While the lateral spreading of Ag