



The kinetics of hollowing of Ag–Au core–shell nanowhiskers controlled by short-circuit diffusion

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Abstract—We have grown single-crystalline Ag nanowhiskers on an inert substrate covered by a thin layer of carbon employing a molecular beam epitaxy deposition technique. Subsequent deposition of Au resulted in single-crystalline core–shell Ag–Au nanowhiskers separated by a nanocrystalline thin Au film. Annealing of the core–shell nanowhiskers at the temperature of 170 °C resulted in their partial hollowing and formation of Au nanotubes. We found that the hollowing process is accompanied by Ag enrichment in the thin Au film in the vicinity of the nanowhisker, and by the increase in grain size in the film with increasing distance from the nanowhisker root. The Ag enrichment on the surface of the Au film, and at the Au–carbon interface in the vicinity of the nanowhisker, was identified with the aid of analytical transmission electron microscopy. We proposed a kinetic model of hollowing based on the competition between the energy decrease driving the hollowing process (formation of Au–Ag solid solution in the grain boundaries) and the energy increase associated with the creation of new surfaces. The model predicted an inverse dependence of the hollowing rate on the inner radius of the nanowhiskers, in good agreement with the experimental data.

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1. Introduction

Hollow metallic nanostructures (hollow nanoparticles, nanoboxes and nanotubes) have attracted a great deal of attention because of their possible applications in various fields of nanotechnology (simultaneous drug delivery and therapy, nanofluidics, catalysis, reinforcing phase in lightweight composite materials, etc.). A number of bottom-up wet chemistry methods of manufacturing hollow metal structures have been proposed, yet these often result in polycrystalline hollow nanostructures with a high concentration of impurities and defects, and the process of pore nucleation and growth is difficult to control [1,2].

An alternative way of manufacturing hollow metallic nanostructures is based on the diffusion processes occurring in core–shell systems. In 2004, Yin et al. demonstrated that the formation of cobalt sulfide on the surface of cobalt nanoparticles exposed to sulfur-containing solution leads to the formation of hollow cobalt sulfide nanoparticles [3]. The nucleation of pores in the interior of the particles was attributed to the Kirkendall porosity: the much faster outward diffusion of Co in the cobalt sulfide shell than the inward diffusion of S toward the center of the cobalt particle leads to an uncompensated vacancy flux toward

the particle center. In bulk systems with abundant vacancy sources/sinks, this flux results in lattice drift [4]. In metals, this drift proceeds by the climb of edge dislocations acting as vacancy sources/sinks [4]. Yet the nanoparticles are often free of dislocations, since any pre-existing dislocation in the interior of a nanoparticle would be attracted to the free surface by the strong image forces and annihilate there. This paucity of vacancy sinks leads to the supersaturation of vacancies in the center of the particle followed by the nucleation of a pore. In addition, the volume effect of the surface reaction causes high mechanical stresses in the particle, which also stimulate the nucleation of internal porosity [5]. Since the work of Yin et al., the diffusion-induced Kirkendall porosity was utilized for the synthesis of hollow nanostructures in a number of systems [1,6,7]. This method is also suitable for the synthesis of nanotubes: nanotubes of ZnAl₂O₄ spinel were produced by employing the reaction of ZnO nanowires with Al₂O₃ coating [8]. The possibility of forming hollow nanoparticles in a binary system with full mutual solubility and without surface reactions (i.e. utilizing the classical Kirkendall effect) has been recently demonstrated [9].

A significant advantage of the Kirkendall-effect-based methods of synthesis of hollow nanostructures over the alternative chemistry-based methods is in the possibility of “fine tuning” the size of the pores. Indeed, since the atomic diffusion in the solid state is relatively slow, the size

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control can be simply achieved by a proper selection of the annealing/reaction time. Yet this method requires relatively high homologous temperatures at which the bulk interdiffusion is active. Since surface diffusion is much faster than bulk diffusion, the morphological stability of complex nanostructures becomes problematic at such high temperatures. Indeed, recent atomistic simulations revealed that the hollow core in a cylindrical nanotube formed by the Kirkendall effect loses its stability and breaks down into an array of nanopores in a process similar to Rayleigh instability of rods [10]. Moreover, a prolonged annealing leads to the closure of the pore and full homogenization of the particle [11].

Recently, Richter proposed a new method of diffusion-assisted synthesis of crystallographically perfect single-crystal Au nanotubes on inert substrates [12]. This method relies on the carbon-mediated synthesis of core–shell metal nanowhiskers employing the molecular beam epitaxy (MBE) technique [13]. For the Ag–Au core–shell nanowhiskers the outer Au layer covers epitaxially the single-crystalline Ag whiskers, but is nanocrystalline on the substrate surface between the whiskers. Annealing of this system at temperatures below 200 °C, at which no bulk interdiffusion between Au and Ag occurs, resulted in the hollowing of the core–shell nanowhiskers and the formation of Au nanotubes [12]. It was suggested that the Ag atoms of the core diffuse along the grain boundaries (GBs) of the polycrystalline Au film, thus hollowing the core of the composite Au/Ag whiskers and leading to the formation of perfect single-crystalline hollow core Au nanotubes. This mechanism proposed by Richter is different from the bulk Kirkendall effect mechanism discussed earlier [3], and bears many similarities with the classical lost-wax metal casting process known for millennia. This method has all the advantages of the methods based on the bulk Kirkendall effect proposed earlier [3] and, in addition, rather than relying on a random pore nucleation process, it allows “sculpturing” the shape, size and morphology of internal porosity by the original “core” nanostructure.

The aims of the present work were studying the kinetics of core–shell nanowhiskers hollowing in the framework of the experimental set-up proposed by Richter [12], developing the kinetic theory of the hollowing process and identifying the atomic processes which control the hollowing kinetics.

2. Experimental

The Ag–Au core–shell nanowhiskers were synthesized in a two-stage process. In the first stage, single-crystal Ag nanowhiskers were grown at 650 °C during MBE deposition of 180 nm thick Ag film (deposition rate $R = 0.05 \text{ nm s}^{-1}$) on a Si/SiO₂/Si₃N₄ substrate coated with a 30 nm thick layer of carbon [13]. During the second stage, the Ag nanowhiskers were coated at room temperature in the same vacuum chamber by Au ($R = 0.01 \text{ nm s}^{-1}$), resulting in the formation of Au/Ag core–shell nanowhiskers and a polycrystalline Au film 50 nm in thickness on the carbon-coated substrate. The selected (nominal) angle of incidence for the Au atoms was 45° relative to the substrate normal [12]. For studying of the kinetics of hollowing, the specimens with core–shell nanowhiskers were annealed at 170 °C in a rapid thermal annealing furnace (RTA;

Ulvac-Riko, Model MILA-5000) for different times in the range of 5–30 min in Ar–10% H₂ gas flow of 150 sccm at 1 atm. The heating and cooling rates were 10 and 4 °C s⁻¹, respectively. Under these annealing conditions the rate of bulk interdiffusion in the Au–Ag system is negligible [14]. The heat treatments of nanowhiskers in the RTA furnace resulted in their full or partial hollowing. After each heat treatment, the dimensions (projected length and diameter) and inclination to the substrate, as well as average local composition of the Au(Ag) hollowed nanowhiskers, were determined by high-resolution scanning electron microscopy (HRSEM; Zeiss Ultra Plus) equipped with an energy-dispersive X-ray spectrometer (EDS) with a take-off angle of 35°. HRSEM micrographs were acquired using either an in-lens secondary electron (SE) detector or a back-scattered electron (BSE) detector, at an acceleration voltage of 4–10 kV. The error in the projected length measurements of the hollow part of the Ag–Au nanowhiskers from the HRSEM images and/or EDS spectra is proportional to the projected length of the hollow part and varied from ±15 to ±150 nm for the 500 nm long and 5000 nm long nanowhiskers, respectively. The error of the nanowhisker diameter measurements with the aid of HRSEM was ±5 nm. Scanning transmission electron microscopy (STEM; FEI Titan 80–300 keV S/TEM) was employed to analyze the sample cross-sections, which were prepared by the lift-out method in a dual beam focused ion beam (FIB; FEI Strata 400-S). The FIB lamellae were cut perpendicular to the projected nanowhisker axis, and positioned on a Ti grid. Final thinning was done by low-kV milling using Ar⁺ ions at an energy of 350 eV (Linda GentleMill3).

3. Experimental results

The HRSEM BSE images of two typical as-grown Ag–Au core–shell nanowhiskers are presented in Fig. 1. The diameters of these nanowhiskers are 180 nm (Fig. 1a) and 260 nm (Fig. 1b). They do not exhibit any compositional contrast along most of their length, and the corresponding Ag content varies in the range of 50–55 at.% Ag (it should be noted that this composition is determined by employing standard EDS procedures and has a qualitative, rather than quantitative, meaning). Annealing of Ag–Au core–shell nanowhiskers at 170 °C for 5–30 min results in their partial hollowing and is accompanied by radial out-diffusion of Ag along the polycrystalline Au thin film away from the nanowhisker root. The HRSEM images of a typical partly hollowed nanowhisker which formed after annealing at 170 °C for 30 min are presented in Fig. 2. The diameter and the inclination angle of this nanowhisker are 265 nm and 43°, respectively. The true length of the hollow part of the nanowhisker is 3.8 μm (see below a description of the method for determining of true length). Fig. 2b demonstrates the locations of EDS measurements of Ag concentration in the Au film. The corresponding concentration profile (Fig. 3) demonstrates that the Ag concentration decreases from ~5 at.% near the nanowhisker root to the background level of ~1 at.% at a distance of 7 μm from the root. According to our estimates, the lateral distribution of the characteristic AgL_{α1} X-ray radiation excited in the Au film at the accelerating voltage of 10 kV can be approximated by a normal distribution function with $\sigma \sim 1 \mu\text{m}$. In this case, a true radius of the Ag-rich zone

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