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Fabrication of freestanding gold nanotubes

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Ag nanowhiskers were grown on a C-coated Si substrate at 800 °C and subsequently coated with Au by physical vapor deposition. The Au forms a single crystalline, epitaxial layer on the nanowhisker and a polycrystalline Au film on the substrate surface. Annealing at 150 °C for 70 h activates diffusion of Ag into the Au grain boundaries of the polycrystalline film, emptying the Ag nanowhisker core. The remaining epitaxial Au film forms the single crystalline wall of Au(Ag) nanotubes.

Keywords: Physical vapor deposition; Whisker; Diffusion; Nanostructure

Low-dimensional nanostructures are currently the focus of attention in various areas of materials science and applied technology due to their unique mechanical [1–3], optical [4], electronic [5] or magnetic properties [6]. Because of these properties, nanowires and nanotubes could form the building blocks of future nanotechnology. So far, non-metals like carbon, ceramic and semiconductor nanotubes have been synthesized with perfect, defect-free atomic structures in freestanding, one-dimensional configurations [7–9]. The uniqueness of carbon nanotubes stems from their hollow, one-dimensional configuration. Therefore efforts have been made to synthesize, similar to carbon, hollow, high-aspect-ratio nanotubes from semiconductor [8], ceramic [9,10] and metallic materials [11]. While the latter structures have been successfully fabricated in solution, freestanding metallic nanotubes have greater prospects to enable future improvements in catalysis or fuel cells, or to act as drug delivery systems.

Different fabrication routes for nanotubes have been reported: use of templates [12], etching [13], rolling layered materials [10] and the Kirkendall effect [9,14–16]. The latter is a phenomenon based on diffusion processes across the interface of two joining materials and a classical observation from metals science: an unequal opposite diffusional flow of atoms and vacancies across the interface causes characteristic pores, by agglomeration of vacancies, near the interface on the side of the faster diffusing species [17]. Prominent Kirkendall partners are Cu–Zn, SnPb–Cu and Ag–Au for metals [18–20], and ZnO–Al_2O_3 for ceramics [9]. In consequence, hollow zero- and one-dimensional structures were synthesized based on this process [21,22]. The faster diffusing species initially forms the core and the slower diffusing material forms the shell of a core–shell structure. During the diffusion the pores coalesce to form the empty core of the hollow structure, while the wall is made from the two alloyed species. The activated diffusion paths can be tailored by tuning the starting microstructure.

The present study reports the synthesis of metallic, single crystalline and freestanding Au(Ag) nanotubes by a route similar to lost-wax casting processes based on a diffusion-based effect with similarities to the Kirkendall effect.

Ag nanowhiskers were grown via a C-mediated physical vapor deposition (PVD) technique reported previously [3]. Si(1 0 0) wafers were cleaned in acetone and ethanol and subsequently magnetron sputter-coated with 30 nm C at room temperature. Before coating, the wafers were etched by applying an Ar-plasma for 90 s at 100 W and $p_{Ar} = 1 \times 10^{-3}$ mbar. The Ag and Au deposition was carried out in an ultra-high vacuum molecular beam epitaxy system with the pressure never exceeding 2×10^{-10} mbar. In a first process, Ag deposition at a substrate temperature of $T_S = 800$ °C and a deposition rate of $R = 0.05$ nm s^{-1} led to the formation of Ag nanowhiskers [3]. In a second process step, the Ag nanowhiskers were coated by Au ($R = 0.01$ nm s^{-1}) at room temperature to prevent interdiffusion during growth. The selected angle of incidence for the Au atoms is 45°

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relative to the substrate normal, therefore whiskers with inclination angles smaller than 45° are covered by Au on all surface facets. A 10 nm thick Au film on a 100 nm diameter nanowhisker results in an approximate starting composition of Au:Ag $\sim$ 1. Subsequent removal from the PVD system and annealing in air and atmospheric pressure at $T = 150$ °C, $t = 70$ h led in a third step to the formation of Au(Ag) nanotubes. A field emission scanning electron microscope (FESEM) equipped with an energy-dispersive X-ray spectrometer (EDXS) was used for surface microstructure and composition characterization, two different transmission electron microscopes (TEMs) were used for the analysis of single one-dimensional structures lying on polymer coated grid.

Figure 1a shows a FESEM micrograph after formation of the Au–Ag core–shell structures as attached to the Si(1 0 0) substrate. The nominal Ag film thickness was 90 nm, the Au film thickness 15 nm. The structures have a length of up to 15 µm; the typical diameter is $\sim$100 nm. The inclination angle of the whisker axis to the surface normal was typically $\sim$60°. Figure 1b shows a close-up of one Au–Ag core–shell structure and the surrounding Au thin film on the substrate. The Au forms a polycrystalline film on the substrate surface with $\sim$50–100 nm diameter grains. EDXS measurements (Fig. 1c) show that the core–shell structures are formed by Ag and Au; in the Au film on the substrate, no Ag was detectable. The intensity ratio for Au M_α and Ag L_α EDXS spectra is $I_{\mathrm{Au}\,M_\alpha}/I_{\mathrm{Ag}\,L_\alpha} = 0.4$. All EDXS results are summarized in Table 1. Figure 1d shows a conventional TEM micrograph of an Au/Ag nanowhisker after fabrication. By deposition of Au at room temperature, an epitaxial film is formed on the surface facets of the Ag nanowhisker, as expected [23]. Neither grain boundary contrast is seen in the bright-field micrograph, nor contrast from misfit dislocations. Also, dislocations in the bulk of the Ag core or the Au film are not detectable; only bending contours from the TEM specimen preparation and the momentum of the electron beam are visible. The thickness of the Au shell is close to the deposited nominal film thickness of 10 nm. EDXS measurements confirmed the presence of Au and Ag in the nanowhisker. The intensity ratio of the Au M_α and Ag L_α lines is $I_{\mathrm{Au}\,M_\alpha}/I_{\mathrm{Ag}\,L_\alpha} = 0.5$.

Figure 2 shows results from the annealed core–shell nanowhiskers. Figure 2a shows that the structures still have lengths of $\sim$15 µm and typical diameters of $\sim$100 nm. The overall appearance of the core–shell structures therefore seem not to have changed and they are still attached to the surface. In contrast to the as-fabricated specimens, the Au film on the substrate and the whisker root (Fig. 2b) shows pores at grain boundaries.

Table 1. Au M_α and Ag K_α intensity ratios.

	$I_{\mathrm{Au}\,M_\alpha}/I_{\mathrm{Ag}\,L_\alpha}$ as-deposited	$I_{\mathrm{Au}\,M_\alpha}/I_{\mathrm{Ag}\,L_\alpha}$ after annealing
Film SEM	Ag not detectable	11.9 ± 0.5
Whisker SEM	0.4 ± 0.1	12.2 ± 2.8
Whisker TEM	0.5 ± 0.1	13.9 ± 1.3

The results from the quantified EDXS measurements from SEM and TEM are summarized for the as-deposited and after annealing specimens. The SEM measurements were taken from the Au film and from nanowhiskers. Error limits were calculated from spectra taken at different spots.

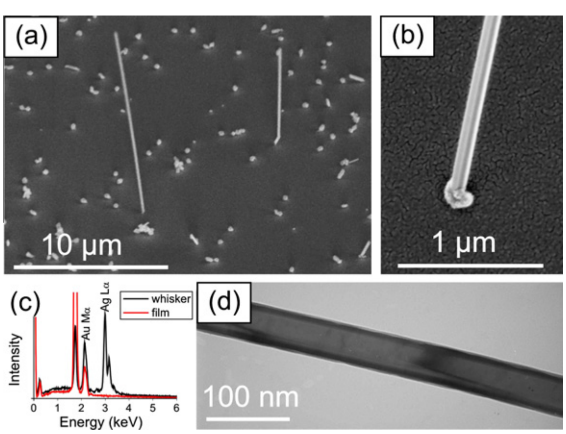

Figure 1. As-grown Au/Ag core–shell nanowhiskers. (a) SEM secondary electron micrograph of as-grown nanowhiskers. The micrograph was taken at an angle of <55° to the surface normal. The whiskers have an apparent length of up to $L \sim 10$ µm and have a diameter of $d \sim 100$ nm. (b) Microstructure of the as-grown Au film microstructure near the root of a nanostructure. (c) EDX spectra from the nanowhisker Ag only detectable in the nanostructure. (d) Conventional TEM picture of an Au/Ag core–shell structure. The projected overall diameter is $d \sim 50$ nm and the Au wall thickness is $t \sim 15$ nm.

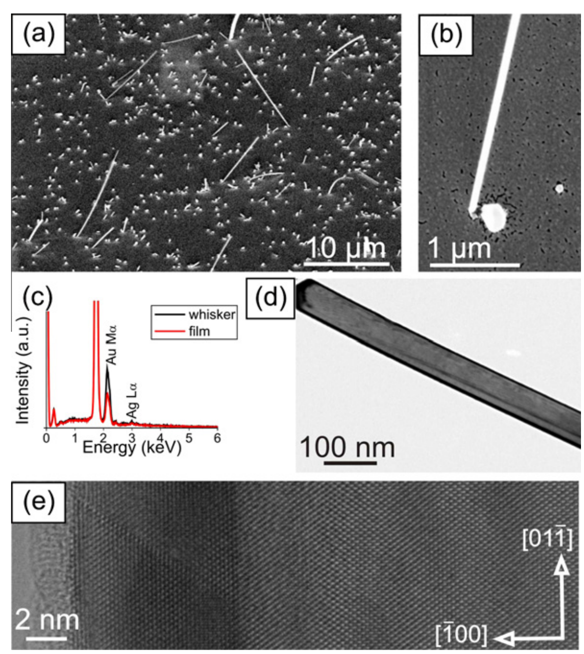

Figure 2. Au(Ag) core–shell nanowhiskers after annealing at 150 °C for 70 h. (a) SEM secondary electron micrograph of nanotubes on the substrate. The micrograph was taken at an angle of <55° to the surface normal. A projected length of up to $L \sim 12$ µm is observed. The tube diameter is still $d \sim 100$ nm. (b) Microstructure of the annealed Au film microstructure near the root of an Au(Ag) nanotube. (c) EDX spectra from nanotube and Au film for the annealed specimen. Ag is depleted in the former core–shell structure and enriched in the Au layer. (d) Conventional TEM image. The projected overall diameter is $d \sim 126$ nm and the Au wall thickness is $t \sim 15$ nm. No defects are visible in the structure. (e) High-resolution TEM micrograph. The wall thickness is 8.5 nm.