Gallium-driven assembly of gold nanowire networks

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Nanowire networks of Au–Ga alloy are fabricated at temperatures between 220 and 300 °C by application of small drops of liquid gallium to 10- to 100-nm-thick gold films. As the liquid gallium drop spreads and reacts with the gold film, lamellar segregation of gold-rich and gallium-rich regions form fractal-like networks of Au–Ga nanowires connected between gold-rich islands in specific zones concentric to the gallium droplet. The wires are subsequently suspended by wet chemical etching that undercuts the ~10-nm-thick chromium adhesion layer and the silicon substrate. Suspended nanowires as long as 6 μm and as narrow as 35 nm diameter have been produced using this method. © *2004 American Institute of Physics*. [DOI: 10.1063/1.1787938]

There is a growing interest in nanowire structures in studies ranging from catalysis to fundamental structural characterization.[1–3] Nanowire growth methods often produce mats of wires that either lie in the plane of the substrate or that are connected at one end to the substrate forming free-standing wires.[1,2] It is far less frequent that nanowire growth methods result in nanowires connected on two ends spanning an air gap, e.g., where nanowires are grown between pillars or between catalysts on two sides of a recess.[4,5] Prefabricated nanowires have also been selectively adhered, or otherwise positioned and manipulated, to bridge recesses on substrates.[6] Here it is shown that an Au thin film interacting with Ga at a range of temperatures above the Ga melting point self-assembles Au–Ga nanowires that can then be released, undercut, and suspended by standard wet chemical etching recipes.

The Au–Ga nanowires are self-assembled on silicon substrates [(110) oriented *p*-type with 1–10 Ω cm resistivity onto which is sputter-deposited a chromium adhesion layer (~10 nm thick) and Au (10 to 100 nm thick)]. A small probe (e.g., a tungsten STM tip) is dipped into liquid Ga and removed, leaving a small drop of Ga attached to the tip. With the substrate heated to between 220 and 300 °C (with 270 °C preferred, as described in the following) the tip is lightly tapped on the Au sample surface. A nearly hemispherical Ga drop (around 50 μm diameter or 33 pl volume) adheres to the Au from which spreads a 10- to 100-nm-thick wave front of material. The front spreads at a typical rate of 50–100 μm/min with speeds of up to 1 mm/min for larger drop sizes on thinner Au films. Less than 0.8 pl (~2% of the volume of the original Ga droplet) actually spreads, with the maximum volume spread corresponding to the thickest, 100 nm Ga front.

After the Ga has spread, various morphologies (labeled zones 1–4 in Fig. 1) are evident in scanning electron microscope (SEM) images taken with a LEO 1430 SEM. Zone 1 is a smooth region of mostly Cr. Zone 2 shows extended networks of Au–Ga wires with lengths reaching up to 3 μm and widths as large as 300 nm.[7] Zone 3 consists of clusters or "islands" of a few microns diameter that are interconnected by Au–Ga nanowires. In zone 4 there are Au–Ga islands within the original Au thin film, which is slightly modified by incorporation of less than 10 at. % Ga.

Observation of the spreading under a video microscope (0.55 NA, 50X objective) shows that the zone 4 morphology expands in radius over time, until a maximum radius is reached (~1–5 mm within 5–10 min) and the spreading stops. During the spreading, zone 4 is trailed by a thin annular wake of zone 3 morphology. Zone 2 increases in radius and area over time, while zone 1 stays fixed in radius. Under the higher magnification in Fig. 1, the islands in zone 4 are seen to form and segregate into interconnected islands in zone 3. In zone 2 the islands completely erode away, leaving behind a network of Au–Ga wires on the Cr adhesion layer. The original location of each island has been transformed into an intersection point of two to four wires.

Figure 2 shows SEM close-ups of the boundary between zones 2 and 3, where the islands have nearly eroded away leaving mostly wires. The contrast of the image from the backscatter detector [BS, Fig. 2(b)] indicates that the more dense material (Au-rich) is closer to the centers of the islands and wires than near their edges.

Analysis by energy dispersive spectroscopy (EDS) in a JEOL 2000 transmission electron microscope (TEM with ~2 nm lateral resolution) has been used to determine the composition and spatial distribution of materials in the nanowires and the islands. The sample is easily transferred to

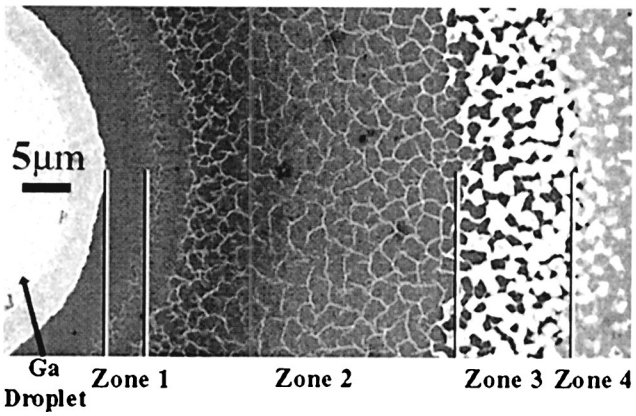

FIG. 1. Morphologies produced by the spreading of a gallium droplet on a 35 nm Au film at 300 °C (SEM Image)—Ref. 7.

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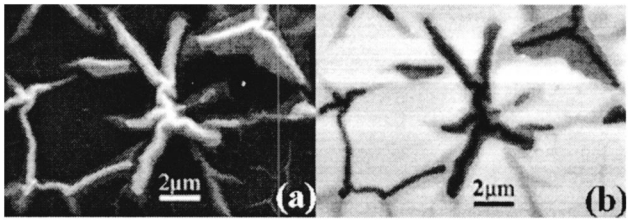

FIG. 2. Wire-island structures due to gallium spreading on 35 nm Au at 300°C. (a) Secondary electron and (b) backscattered electron SEM images at the boundary between zones 2 and 3. In (b) the image contrast has been inverted such that the dark regions correspond to the more dense Au-rich lamellae that are surrounded by and segregated from the lighter contrast Ga-rich lamellae.

a TEM grid by flaking the Cr adhesion layer from the various zones off of the silicon substrate. The EDS compositional analysis is summarized in Table I. In zone 1 mostly Cr is present with some Au and Ga. A ~3:1 Au:Ga atomic ratio is found for the center of the wires in zone 2 and the interior of the islands in zone 3. At the peripheries of both the islands in zone 3 and the edges of the wires in zones 2 and 3 the Au:Ga atomic ratio decreases to 1.35:1. Between the wires in zone 2 and the wire-island networks in zone 3 Cr, Au, and Ga are found in the same proportion (within a few percent) as in zone 1; i.e., the regions between the islands are mostly Cr with some residual Ga and Au left from the spreading process.

In comparing the BS SEM image in Fig. 2(b) with the spatially resolved EDS data, the most-dense material is Au-rich alloy that is segregated from the less-dense Ga-rich alloy surrounding the island and wire structures. This type of lamellar segregation in alloys has been predicted and observed for many binary alloys during isothermal eutectic growth.[8] It should be noted that after zone 1 has formed, the Ga front is no longer connected to the original droplet. The Ga front continues to spread and become depleted leading to the incomplete dissolution of Au, and finally termination of Ga spreading altogether.

A two-step etching process is used to suspend the nanowires. First the Cr is etched for 15 min at room temperature in chromium etchant (Microchrome Technology Inc. Reno, NV) followed by a light (~1 min) hydrofluoric acid (HF, 100:1 H_2O:HF) oxide etch. Second, the Si substrate is etched at 80°C for 1 min in tetramethyl-ammonium hydroxide (TMAH, Alfa Aesar premixed at 45% wt. H_2O and diluted to 83% TMAH to 17% isopropanol). This releases the nanowires without completely undercutting the island structures. The samples are transferred to water and then dried in air. We have also dried samples by immersing them in acetone and performing critical point drying in CO_2 following the etching in TMAH, and have found no substantial difference in the number of suspended nanowires in zone 3.

TABLE I. Compositions of zones by EDS after Ga spreading.

Zone No.	Au(at. %)	Ga(at. %)	Cr(at. %)
1	13.10	20.91	65.99
2,3 (interior island /wires)	69.30	22.51	8.19
2,3 (periphery island /wires)	26.80	19.84	53.35
4	55.88	44.12	0

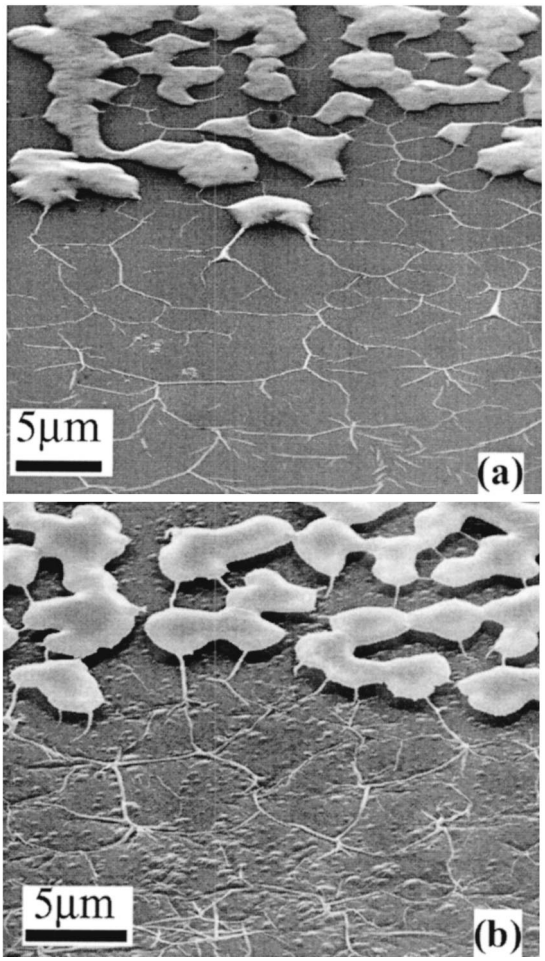

FIG. 3. Au–Ga structures in zones 2 and 3 (a) before and (b) after etching. The Ga was spread on 20 nm Au at 270°C. The SEM images are taken at 45° sample tilt. After etching the wires are released and are found suspended between the islands. Away from the islands, networks of nanowires are adhered to the substrate.

Figure 3 shows SEM images from zones 2 and 3 of two identically prepared samples (20 nm Au at 270°C, dried in air) before and after the etching process. Apparent in both images are the wire network structures in the foregrounds and the island/wire networks in the backgrounds. Multiple wires are seen suspended between the raised island structures in the middle and background of Fig. 3(b). The wire-net structures are still apparent in Fig. 3(b), but some appear to have separated from the now exposed Si surface and stuck to one another, as seen at the bottom of the image. At the boundary between zones 2 and 3 several wires are suspended on one end by islands and on the other end to the nanowire networks on the substrate.

SEM close-ups of suspended nanowires are shown in Fig. 4. Diameters as small as 35 nm are observed with values ranging from 35 to 110 nm. Figure 4(a) shows four separate suspended wires and Fig. 4(b) includes a triple-point suspended wire. Prior to etching, the above-mentioned EDS analysis showed that the wires had ~3:1 Au:Ga atomic ratio. After the Cr etch there is little change of Au:Ga content. However, after the Si etch, EDS of a single, suspended, nanowire (separated from the sample surface and placed on a TEM grid) shows that the wire is now composed of a 6:1 Au:Ga atomic ratio. At the TMAH etching temperature (which exceeds the melting point of Ga, 29.8°C) the Ga tends to ball-up and separate from the Au.

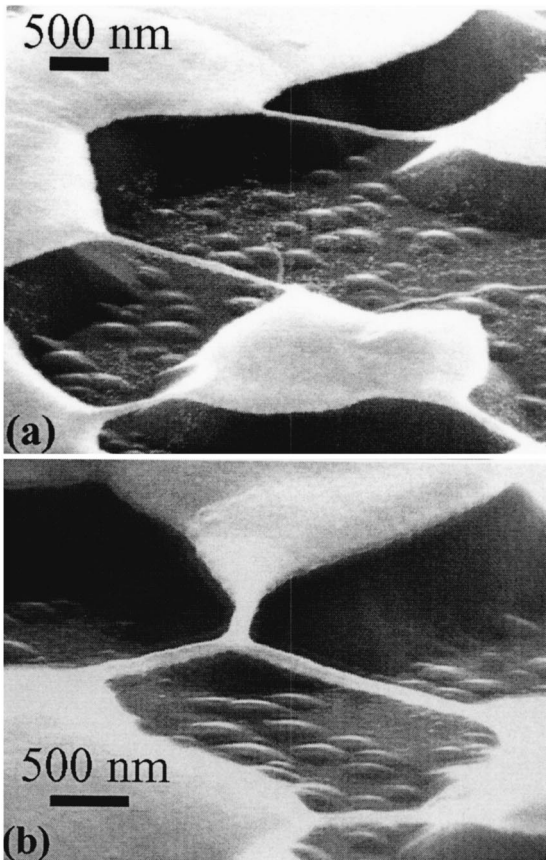

FIG. 4. Suspended Au–Ga nanowires in zone 3. (a) Four suspended wires. The diameter of the wire at the top of the image varies from 35 nm (left end) to 85 nm (right side). (b) A triple-wire structure with average width of 130 nm. The Ga was spread on 20 nm Au at 270°C.

Most of the suspended wires in zone 3 appear to have a ribbon-like cross section [e.g., in Fig. 4(b)]. Atomic force microscope (AFM) scans (prior to etching) show that these wires have the same thickness as the original Au film. In zone 2 the AFM scans show that the thickness of these wires are often half, or even less, the thickness of the original gold film.

The Au–Ga binary phase diagram shows that $AuGa_2$, AuGa, and Au_7Ga_3 are stable, congruently melting compounds that can form as Ga and Au mix in equilibrium.[9,10] In fact, for temperatures ranging from −15 to 150°C (i.e., even for temperatures below the bulk melting point) we have observed that Ga spreads and forms crystallites of $AuGa_2$ (composed of 20 to 150 nm size crystallites suspended in Ga). However, at the higher temperatures of the experiments presented here, little evidence has been found for crystallite formation. It appears that at the elevated temperatures used in these experiments, the continual depletion of the Ga as it spreads precludes the attainment of equilibrium necessary to form these stable compounds.

The temperature window required to form Au–Ga nanowires is narrow. In the range 220–240°C the morphologies appear identical to those shown in Fig. 1 except for zone 3, which does not form. From temperatures of 240–270°C a gradual transition occurs where the width of zone 3 increases to a maximum at 270–280°C. In this temperature range, the nanowires also are smallest in diameter. At temperatures above these values the wires in zone 2 increase in diameter and there are fewer wires. The Cr adhesion layer also plays an important role in the spreading/alloying process. Without the Cr layer, the Ga–Au reaction is confined to a small region (~10 μm wide), apparently because neither Ga nor Au appreciably wet Si, causing the spreading to be minimal.[9]

In conclusion, a Ga drop on a Au thin film with an underlying Cr layer, will rapidly spread out and alloy with the Au at temperatures from 220 to 300°C. Near the Ga droplet, filamentary, fractal-like structures composed of lamellae of Ga-rich and Au-rich regions are formed. Subsequent etching of the Cr layer followed by anisotropic etching of the underlying Si releases Au–Ga nanowires suspended between Au-rich islands. Most of the remaining Ga-rich material from the wire and island-wire networks is lost during the second etching step. This relatively simple process has produced suspended wires of widths as small as 35 nm and lengths of up to 6 μm.

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