

Room Temperature Growth of Single Intermetallic Nanostructures on Nanoprobes

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ABSTRACT

Many metals readily alloy with gallium at room temperature to form intermetallic crystals. The process is directed to grow single crystals directly on nanoprobes, such as atomic force microscope (AFM) probes, tungsten needles and nanotapered glass pipettes. To date we have grown single Ag_2Ga nanoneedles and PtGa_6 nanoplates/blades from supersaturated melts of Ga on AFM tips. Several other alloy crystallites have been identified in bulk, but not yet grown individually on probe tips. For selective growth of the nanostructures, metal films from 30-150 nm thick are sputtered onto AFM probes (that are first flashed with a 10 nm Cr adhesion layer). The probes are placed in a nanomanipulator and inserted into a Ga droplet while observing the crystal formation under a scanning electron microscope. So far, Ag_2Ga wires are the most easily grown with a success rate of around 80 %. Single nanowires up to 70 microns long have been grown in this way. Ga_5Pt plates have been grown in this same way, but with a much lower success rate. In mechanical tests we have observed that the nanostructures are very strongly attached to the AFM probe. The Ag_2Ga needles are very flexible and difficult to break or detach from AFM probes.

Keywords: Self-assembly, nanostructures, nanomanipulation, AFM, NEMS

1 INTRODUCTION

In the past decade many efforts have been devoted to the synthesis of metallic nanostructured materials in the forms of nanowires, nanorods and nanobelts for their preferred electrical, optical, mechanical, magnetic and catalytic properties. In the majority of the previously published fabrication methods, synthesis of nanomaterials usually requires expensive precursors and bulky gas fixturing. Also, the particular fabrication method normally can only be used for synthesis of nanostructures with specific morphologies. Alternatively, lithographic fabrication of freestanding nanostructures requires the use of electron-beam lithography, which has high cost and low throughput.

In this paper we demonstrate a fast and simple method of fabricating metal nanostructures at room temperature. Our method is based on direct self-assembly of gallium-metal (Ga-M) alloys, where gallium is used as a solvent that is

incorporated into the final product of synthesis. Depending on the chemical nature of precursors, the nanostructure shapes can be 1-D (nanorods, nanobars), 2-D (nanoplates), or 3-D (cubooctahedrons and icosahedrons). The method of growing a single nanostructure on a single probe appears capable of being performed in parallel, making it suitable for mass production of unique probes, as well as integrated nano-electro-mechanical systems (NEMS).

The general method for developing a metal-tipped probe consists of a first exploratory phase in which the nanocrystals from Ga-M alloys are grown in bulk, followed by a second directed self-assembly phase in which the growth of a single individual crystal is localized to the tip of an AFM cantilever, or similar probe; e.g., a tipless cantilever, a tapered tungsten STM probe, a tapered glass pipette, or any other suitably prepared solid surface.

2 CRYSTALLIZATION AND GROWTH OF NANOSTRUCTURES ON THIN FILMS

Nanostructures readily form at room temperature at the interface between liquid Ga and a solid metal. This is demonstrated by placing 2 μm to 1 mm diameter drops of Ga (99.9 % purity from Alfa Aesar), in contact with sputter deposited metal thin films or foils of Pd (99.9 %), Ag (99.998 %), Pt (99.99 %), Fe (99.95 %), and Co (99.95 % purity) all from Alfa Aesar. The thin films are between 20 nm and 350 nm and the foils are between 25 μm and 125 μm in thickness. Ga is left in contact with the foil from 10 minutes to 24 hours. In some cases, the Ga is not completely reacted with the film. The excess Ga is removed by etching the sample in 1 N HCL at 60 $^\circ\text{C}$ for 5 to 10 minutes.

Figure 1 shows the crystals that result from the reaction of Ga with different metal foils. Each material combination produces unique crystal morphologies and in each experiment, structures of nanoscale dimensions are formed. As shown in Figure 1 these structures are hexagonal rods (Ag_2Ga , CoGa_3), square bars (FeGa_3), cubooctahedrons and icosahedrons (Ga_5Pd) and thin rectangular plates (Ga_6Pt , FeGa_3). The plates are frequently less than 10 nm thick, as well as being electron transparent. Note also the occasional tubular needle (Figure 1e) which we believe is templated on the growth of a cluster of nanoneedles, which then grows together to form plate-like sidewalls.

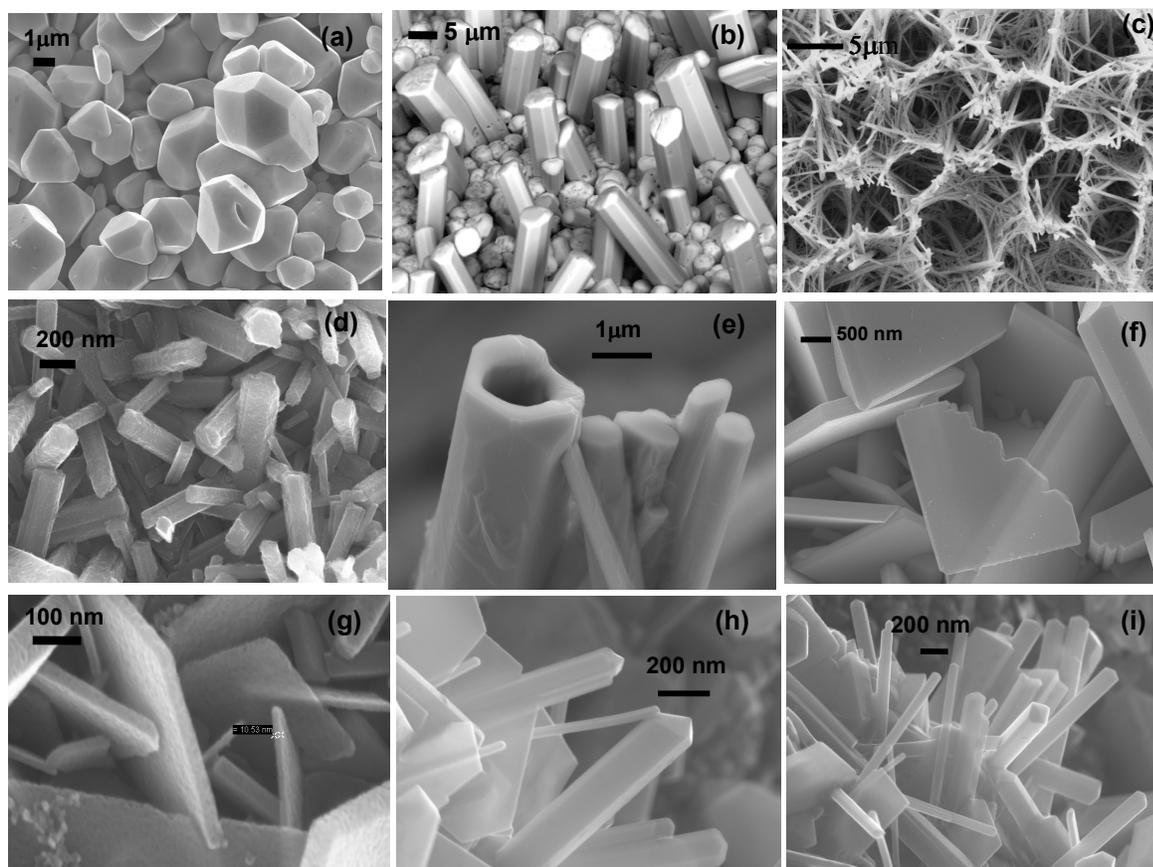


Figure 1. Ga-M crystals that form at the interface between a Ga droplet and a metal foil for foils of M= (a) Pd (b, c, e) Ag, (d) Co, (f, g) Pt, and (h, i) Fe. The reactions were performed at 25° C, except in (b) at 200° C and in (f) at 160° C.

The Ga-M crystallites are associated with *ordered phases* (i.e., Ga and M display a near-periodic atomic arrangement with a high degree of short and long range order) on their Ga-M binary phase diagrams [1,2]. We have confirmed by X-ray diffraction (XRD), energy dispersive spectroscopy (EDS), selective area diffraction (SAD) and high resolution transmission electron microscopy (HRTEM) that most of crystals are ordered phases. For instance, EDS shows that the rods in Figure 1b and c are 32-33 at % Ga which corresponds to the ordered Ag_2Ga phase.

Figures 1b and c show SEM images of Ag_2Ga crystalline needles that grew at 200 °C and room temperature respectively. The larger diameter of the needles in Figure 1b than in Figure 1c corresponds to the increased value of the diffusion constant at the higher temperature [1]. Again, Ga-Pt at 160 °C (Figure 1f) produces larger plates of Pt_6Ga that at room temperature (Figure 1g).

The temperature dependence suggests that growth is nucleated. For the growth of Ga-Pd (Figure 1a) the growth is roughly isotropic, with differences related to the surface free energy of the lower energy low order crystal planes. More precisely, the grains take on the shapes of cubo-

octahedrons and icosahedrons [3-9]. The surface energies corresponding to different crystallographic facets typically increase in order of $\{111\} < \{100\} < \{110\}$. Therefore, the metallic crystals nucleate and grow into quasi-spheres enclosed by mix of both $\{111\}$ and $\{100\}$ facets to minimize the total surface free energy.

However, for different metals, Ga-M growth can become highly directional. Probably nuclei grow similar to those found in Ga-Pd followed by strongly preferential growth upon reaching a critical size. Initially, a seed of Ag_2Ga takes the shape of the plate bound by $\{111\}$ planes from the top and the bottom, and the six side facets by $\{111\}$ and $\{100\}$ planes. These lower energy surfaces become much less wetting to Ga (contact angle 90 degrees or more), resulting in strongly enhanced growth at the end of the needle, where there are a great number of incomplete planes and higher surface free energy. Therefore growth becomes highly directional with the incoherent liquid-solid interface growing and continuing to extend the low-energy coherent crystalline facets in its wake, without increasing the needle diameter further. Formation of nanostructures in the form of hexagonal nanorods is also observed in the case of reaction of gallium with silver and cobalt (Figure 1b-d).

3 DIRECTED SELF-ASSEMBLY OF NANOSTRUCTURES ON AFM PROBES

The most interesting application of the crystallization of Ga-M alloys is the possibility for directed self-assembly of individual nanostructures at selected locations and orientations on probes (Figure 2). The method of selective growth presented here, not only can be performed at room temperature, but it produces strongly adhered nanostructures that are positioned both at arbitrarily desired locations and with specified orientations.

First the fabrication process of individual nanostructure on an AFM tip will be described for a Ag_2Ga nanorod [1]. The AFM tips are sputter-coated with ~ 10 nm Cr film followed by a 50 to 200 nm Ag film with a preferred thickness of 100 nm. Small Ga spherical droplets are formed on a Si substrate. First, a small amount of Ga (less than 1 mm diameter) is placed on the Si surface using a tungsten tip. Then the tip is scratched on the Si substrate until several micron wide lines of Ga are formed. Next the sample is dipped in 1 N HCl at 60 °C for 1 minute. This operation removes any surface gallium oxide and causes the gallium lines to dewet into spheres that are usually less than 20 μm in diameter. The sample is then blown dry with nitrogen and immediately transferred into a SEM chamber.

In the SEM the AFM tips are manipulated using a Zyvex nanomanipulator. Coarse mode manipulation is used to position the cantilever close to the Ga droplet and fine mode manipulation (5 nm resolution) is used to dip the tip into and withdraw it from the droplet.

The silver coated AFM tip is dipped into the liquid Ga droplet and partially retracted from the droplet forming a meniscus between the cantilever and the droplet. Ga reacts with and dissolves the silver film, followed by nanoneedle growth. Before the needle formation is complete, the cantilever is pulled further to narrow the meniscus. The needle continues to grow within the meniscus and towards the center of the Ga droplet. As the needle grows the contact angle of the meniscus increases to at least 90 degrees, greatly reducing the force required to withdraw the needle from the Ga. The total time of needle formation on the AFM tip ranges from 5 seconds to 10 minutes, depending largely on the time required for the onset of adequate supersaturation needed to overcome the barrier to nucleated growth, as well as the length of the needle grown.

Another example of directed self-assembly is a Ga_6Pt nanoplate, synthesized on the AFM probe (Figure 2a, b). This fabrication technique is very similar to the fabrication of nanoplates, and includes the same phases of interaction between the AFM-tip and gallium droplet. However, Pt-Ga reaction is significantly slower than Ag-Ga reaction. Initially, the surface of Pt shows a contact angle greater than 90 degrees in liquid gallium. Instant removal of the tip from the Ga droplet shows no plates synthesized. However, in 30-40 minutes after the immersion of the tip into Ga the reaction increases the wetting of the Pt and the contact angle reduces to less than 90 degrees. When the tip is removed from the droplet after 40 minutes, the synthesized nanoplates from 0.2-5 μm in size and ~ 10 nm thick are found extending past the tip. This slow reaction rate was also observed with the non-selective growth of Ga-Pt on foils of Pt.

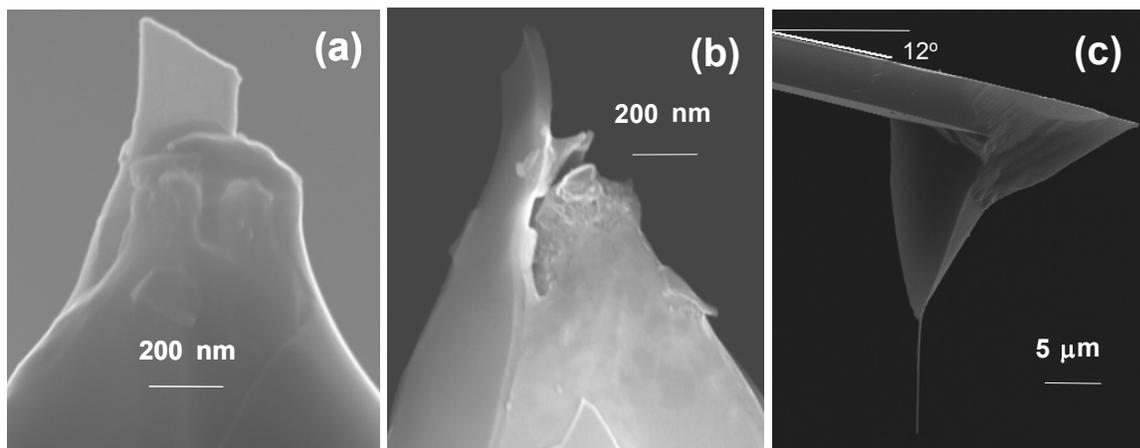


Figure 2. Ga-M nanostructures synthesized on the tips of AFM-probes. (a, b) front and side-view of Ga_6Pt nanoplate, (c) Ag_2Ga nanoneedle.

In contrast, the Ag coated AFM tips initially wet easily and become less wetting on the sidewalls of the Ag₂Ga which causes the needles to grow mostly in length over width. The end of the needles often are rounded incoherent growth fronts, which can more easily accommodate growth than the coherent sidewalls. These features seem to account for the needles being of constant diameter over tens of microns in length (Figure 2c).

4 CONCLUSIONS

A two step procedure for growing metal nanostructures at room temperature on AFM and other nanoprobe was presented. The first step identifies the possible structures for a specific metal in liquid Ga, and the second step uses a Ga meniscus to localize the growth and orientation of the nanostructure with respect to the supporting probe. It was shown that Ga-M alloys can grow in several different crystal morphologies. Prior to this report only Ag₂Ga nanoneedles had been demonstrated [1]. This report shows that Ga₆Pt can be similarly grown. While the other nanostructures containing Fe and Co have not yet been selectively grown, issues related to wetting and reactivity (as observed with Pt) certainly need to be considered further in refining this technique. The unusual shapes and metal nature of these modified AFM-tips recommend them for assorted applications, e.g. as we have recently reported [1,10].

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