Directed Self Assembly of Mixed Nanowire Populations via Lithographic Microwells

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Introduction:
Vertical nanowire arrays can be used for both energy harvesting and storage. Using assembly to create such arrays allows two populations to be mixed together, while standard fabrication limits the product to a single material. However, in the absence of applied fields [1] or controlled drying conditions [2], nanowires typically assemble parallel to the surface, forming horizontal arrays. The Keating group has worked with anisotropic particles, called partially etched nanowires, which form arrays where up to 70% of wires were vertically oriented on a planar surface when their internal asymmetry was tuned to optimize van der Waals and electrostatic interactions [3]. Array quality was increased to nearly 100% standing when microwells were used to direct assembly [4].

A similar approach was used for this work to generate vertical arrays of single component nanowires that lacked the material anisotropy used previously. Wire-wire interactions, such as van der Waals forces, which depend on the composition of the nanowire, were also studied by mixing wires of two different compositions.

Understanding these assemblies could help with design of reconfigurable materials.

Experimental Fabrication:
Nanowires were made by templated electrodeposition [5] in porous alumina membranes. Silver (Ag, 300 nm) was evaporated on to the membrane (Whatman). Plating solutions of silver cyless R, orotemp 24, and pallasspeed VHS_RTU (Technic inc.) were used to make palladium and gold wires with diameters around 300 µm, as determined using transmission electron microscopy.

The evaporated Ag layer, which served as a working electrode, was dissolved in nitric acid, and the alumina template was dissolved in sodium hydroxide, freeing the wires into suspension.

Figure 1, top: Assembled nanowires after one hour. (A) shows 4 µm wires in a 4.5 µm well which have a low standing percentage. (B) shows 5.5 µm wires in a similar well which have a high standing percentage.

Figure 2, bottom: Standing percentage for different particle lengths in different sized wells. At least 480 wells were counted for each data point.

Figure 3, top: Standing percentages for nanowires assembled in microwells of different depths. At least 900 wells were counted for each data point.

Figure 4, bottom: Optical micrograph of a binary nanowire assembly. Images are an overlay of reflectivity information collected at wavelengths of 488, 514, and 543 nm. A ratio of the intensities was used to determine the assignments as labeled in the right image.
Nanowires were cleaned by repeated centrifugation in sodium hydroxide or ethanol, and were ultimately suspended in deionized water. Particles were coated with a silica shell using a modified Stober process [3]. Wire concentration was determined using a hemocytometer. Microwells were made using SPR 955 photoresist (Microchem).

**Assembly:**

An assembly chamber was created by isolating a selection of microwells using a polydimethylsiloxane spacer (DOW Corning). Enough particles to form a single monolayer of standing wires were rinsed in deionized water. The suspension was sonicated and added to the assembly chamber, where it was allowed to settle for one hour before imaging. Standing percentage was determined using previously published methods in which image analysis software distinguished standing from laying down wires [3]. In binary mixture experiments, the wire material was determined by comparing the reflected light intensity for 488, 514, and 543 nm light.

**Results:**

Wire length affected standing percentage when well size was constant for palladium nanowires assembled into microwells. Longer wires in general had higher standing percentages (Figure 1). Palladium wires 4 µm in length assembled in 4.5 µm wells had 20 percentage points lower standing than 5.5 µm wires (Figure 2). Gravity drove the wires into the wells, where the longer wires were unable to fit in the horizontal conformation, and thus form vertical arrays. Microwell size also affected standing percentage. When 4 µm wires were assembled in 4.5 µm wells, standing percentage was higher than when the same wires were assembled in 3.5 µm wells (Figure 2). Deeper wells could support the wires along the entire length of the 4 µm wires, as well as a larger fraction of the 5.5 µm wires. This extra support raises the standing percentage in the wells regardless of nanowire length.

After vertical array quality had been optimized, binary nanowire mixtures were assembled. For these experiments, gold wires 4 µm in length were mixed with 5.5 µm palladium wires. These wires had the potential to exhibit interesting physical behavior due slight differences in their Hamaker constants (i.e. van der Waals interactions). Here we successfully assembled mixtures of these particles into vertical arrays and using optical microscopy we were able to distinguish the two populations via their differing reflectivities. Further study is needed to explore potential phase behavior.

**Conclusions and Future Directions:**

Nanowires were assembled vertically in microwells by controlling the particle and microwell dimensions. Mixtures of two types of wires were placed in the wells and identified by the differing reflectivities of the metals. As more samples are examined, it will be possible to study the phase behavior caused by the differences in inter-wire interactions, allowing generation of phase diagrams to describe the system. Understanding the mixing and demixing of vertical nanowire arrays will allow for the development of reconfigurable materials.

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**References:**