

Fluidic Self-Assembly of Nanowires

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In recent years, the scaling of microelectronic, photonic and micro-electromechanical systems (MEMS) to the 50-500 nm length scale has challenged the capability of conventional micro-fabrication technologies in the cost-effective, mass production of devices and integrated systems [1]. There is an increasing need to develop new nano-fabrication technologies to address the challenges of decreasing dimensions, in order to enable the era of nano-technology [2].

We describe the development of a “bottom-up” strategy to fabricate functional, patterned, metallic nano-wires that can interact with each other, and coalesce in a fluidic medium as a result of the minimization of interfacial free energy, to form well-defined 3D structures. Our strategy utilizes surface tension based self-assembly [3] that involves the modification of the surface energy of components using molecules (hydrophilic / hydrophobic), polymerizable adhesives or high surface energy alloys (solder) and subsequent agitation in a fluidic medium. The agitation causes the components to collide, and if the system is engineered right, there is a driving force for self-assembly due to the minimization of the interfacial free energy of drops of liquid on the surfaces of the components. Since attachment occurs between liquid drops that extend out from the components, interfacial roughness is not a big issue. Surface tension based assembly with polymerizable liquid epoxies and solder result in stable mechanical attachment. Using surface tension based assembly it is possible to design components with favorable (positive) and unfavorable (negative) interactions to fabricate self-assembled structures with different topologies.

We used the strategy of Martin et al [4] to electrodeposit nano-wires in structured, porous alumina templates with a nominal pore size of 200 nm. A seed layer of Ag was evaporated on one side of the membrane to serve as an electrical contact for plating. The length of the wires was restricted by controlling the current density and the duration of electrodeposition. Multicomponent nano-wires composed of a metal (Au or Cu) were formed using an electrolytic solution containing the appropriate metal ions. After electrodeposition, the wires were released into solution by dissolution of the Ag seed layer in nitric acid and the alumina template in dilute NaOH. The schematic diagram is shown in **Figure 1**. The wires were functionalized by immersion in a dilute solution of hexadecane thiol (HDT) for 24 hours that rendered the gold segments very hydrophobic as compared to the nickel segments, due to the formation of a self-assembled monolayer. In order to facilitate

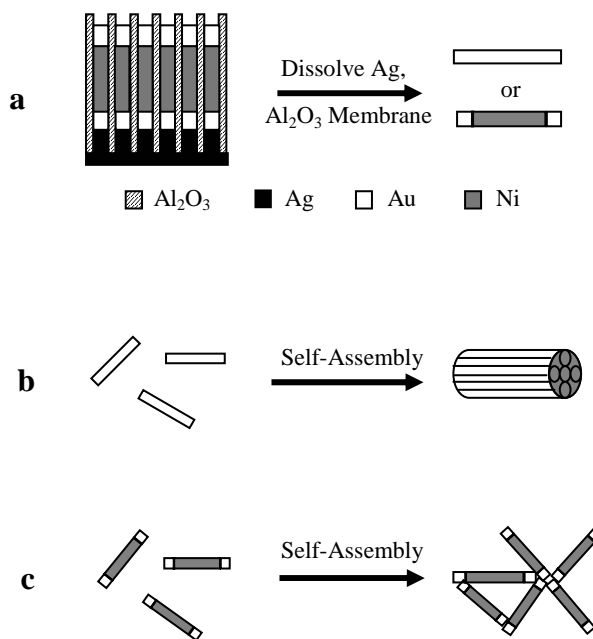


Figure 1 (a) A schematic diagram of the process used to fabricate wires consisting of all Au or Au-Ni-Au segments by electrodeposition in a nano-porous alumina template. (b) Self-assembly of Au wires results in the formation of 3D bundles. (c) Self-assembly of Au-Ni-Au wires results in the formation of 2D networks.

self-assembly, we coated the wires with a curable adhesive. This adhesive comprised a monomer (LM: Lauryl Methacrylate), a crosslinker (HDD: 1,6-Hexanediol Diacrylate) and a polymerization initiator (either a thermal initiator BP: Benzoyl Peroxide or a photo-initiator BIE: Benzoin Isobutyl Ether).

In order to demonstrate the versatility of the methodology, we formed two structures with different topologies, (a) 3D bundles and (b) 2D open networks with end to end connectivity. The self-assembly of 3D bundles necessitated the use of wires composed entirely of Au, so that the whole rod was rendered hydrophobic by HDT. It was also necessary to keep the wires in the bulk during self-assembly, since there was a tendency of the hydrophobic wires to reside at the air-water interface to form 2D rafts. In order to form 2D open networks, we used wires with Au ends separated by a Ni segment. During processing of the wires, the Ni segments were oxidized and the monolayer HDT did not adhere well to these segments. As a consequence, the Au-HDT segments were much more hydrophobic than the Ni-HDT segments. We verified the difference in hydrophilicity of Au and Ni by measuring the contact angle of water on flat Au and Ni coated silicon substrates that were subjected to the same processing conditions as the metallic wires used in the self-assembly. The contact angles were $104^\circ \pm 3^\circ$ for Au and $43^\circ \pm 10^\circ$ for Ni.

In a typical experiment, a small amount of the adhesive solution was added to a few drops of a suspension of wires in ethanol. The glass vial was made hydrophilic by plasma treatment in air. This treatment was necessary to minimize sticking of the hydrophobic wires to the walls of the vial. After adding the adhesive to the wires, the vial was shaken well and allowed to sit for several minutes. Using a syringe, a few drops of water was added to the solution. Since the monomeric adhesive solution was hydrophobic, it precipitated preferentially on the hydrophobic Au-HDT segments on the wires. The adhesive coated wires immediately coalesced to form aggregates; this aggregation was very dramatic and could be observed with the naked eye. The excess ethanol adhesive solution was removed by the addition of an excess of water. The vial was then sealed and agitated to form self-assembled aggregates. After self-assembly, the aggregates were permanently bonded by curing the adhesive. **Figure 2** shows a SEM image of two multi-component wires joined by an adhesive layer. By comparing the image obtained over the same region using two different detectors in the electron microscope, (the back-scatter and secondary electron detector), it was possible to discern the Au, Ni and polymeric adhesive in the bonded structure.

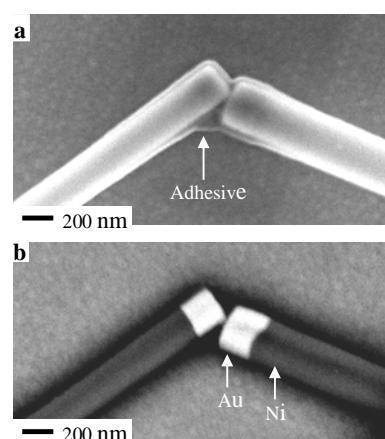


Figure 2 SEM images showing two wires held together by the polymerized adhesive. (a) Secondary electron image showing the polymeric adhesive and the wires (b) Back-scattered electron image (brighter regions correspond to materials with higher atomic numbers), the polymer is not visible, the Au segments appear brighter than the Ni ones.

Figure 3 shows SEM images of 3D polymerized bundles formed using all gold wires and 2D networks formed using Au-Ni-Au wires. The self-assembled aggregates formed on polymerization of the adhesive are mechanically bonded. This conclusion is based on the fact that the 2D networks survived considerable agitation during polymerization when N_2 gas was

blown into the vial. We have also observed that the 3D bundles and 2D network aggregates survive mild sonication. In summary we have demonstrated a methodology for permanently bonding 200 nm scale objects using adhesive joints. This strategy can be extended to other nano-components to form 2D and 3D integrated systems. Since the assembly of 3D bundles occurs because of a thin polymer sheath connecting the wires, it is possible to fabricate insulated electrical wire bundles using this methodology. The attractive feature of this kind of assembly is that it is possible to form mechanically bonded structures that do not break apart easily, this rigidity is crucial in the fabrication of sub-micron and nano- scale 3D electromechanical structures of practical use.

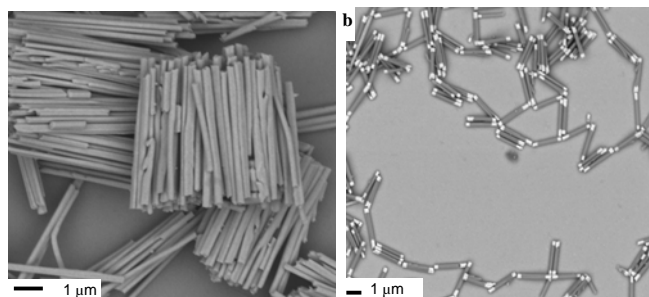


Figure 3 SEM images of self-assembled structures formed, 3D bundles and 2D open networks

We have also obtained preliminary results demonstrating attachment of wires using solder joints. **Figure 4** shows a SEM image of nano-wires bonded together with solder. As can be seen in the figure, the solder reflows to form a sphere that wets the copper tip on the wire. When a concentrated layer of wires was used on the substrate, the solder from adjacent wires flowed into each other to form permanent joints between wires.

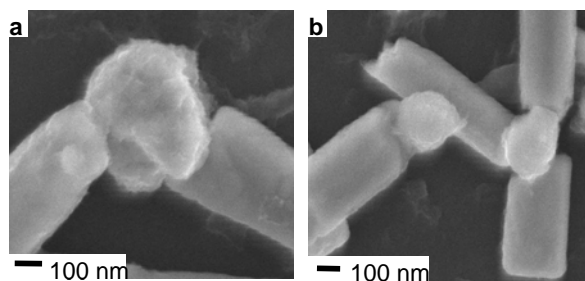


Figure 4 SEM images of Nano-wires bonded together with solder joints

In conclusion, we have demonstrated strategies based on surface tension based fluidic assembly to form permanently bonded structures using nano-wires with different patterns of metal segments. We expect that these strategies can be utilized to bond other nano-components and nano-particles to form 3D nano and sub-micron scale electromechanical structures.

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