Nanoconstruction by welding individual metallic nanowires together using nanoscale solder

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Abstract. This work presents a new bottom-up nanowelding technique enabling building blocks to be assembled and welded together into complex 3D nanostructures using nanovolumes of metal solder. The building blocks of gold nanowires, (Co72Pt28/Pt)n multilayer nanowires, and nanosolder Sn99Au1 alloy nanowires were successfully fabricated by a template technique. Individual metallic nanowires were picked up and assembled together. Conductive nanocircuits were then welded together using similar or dissimilar nanosolder material. At the weld sites, nanoscale volumes of a chosen metal are deposited using nanosolder of a sacrificial nanowire, which ensures that the nanoobjects to be bonded retain their structural integrity. The whole nanowelding process is clean, controllable and reliable, and ensures both mechanically strong and electrically conductive contacts.

1. Introduction
Individual building blocks used in bottom-up techniques, such as nanoparticles, nanowires and nanotubes, can now be routinely fabricated. Scanning probe technologies, such as the latest robotics nanomanipulators, make the manipulation and assembly of nanoscale building blocks into nanocircuits available to researchers around the world [1-6]. However, there is a major difference between simply bringing nano-objects into contact (formation of an interface), and integrating two nano-objects together (interfacing through a functional junction). The practical applications of nanocircuits and nanodevices require secure, functional and long-lasting bonds between their individual building blocks. Here we describe a new nanoscale electrical welding technique which radically improves the spatial resolution, flexibility and controllability of welds between individual bottom-up building blocks.

2. Fabrication of nanowires
Anodic aluminium oxide (AAO) templates with about 55nm pore diameter were fabricated by anodising 99.999% Al sheets (Goodfellow) in 0.6M oxalic acid electrolyte for three hours at room temperature with continuous stirring. The detailed fabrication method of gold nanowires and (Co72Pt28/Pt)n multilayer nanowires has been detailed in our previous work [1-3,7]. The nanosolder Sn99Au1 alloy nanowires were electrodeposited into a polycarbonate (PC) template with 80 nm pore diameter using an electrolyte composed of 0.5 M SnCl2 (Alfa Aesar, 98.0-103.0%), 5g/l AuCl4 (Aldrich, 99.99%), 0.01 M HCl (Aldrich, 99.5+) and 5g/l L-Ascorbic (Alfa Aesar, 99+) at -0.08V DC signal was applied between the PC template and a 5mm diameter tin rod anode (Goodfellow,
99.75%). The typical total deposition time for each specimen was set up to 30 minutes, and the electrolyte was continuously agitated throughout by a magnetic stirrer.

The morphology and chemistry of the electrodeposited multilayer nanowires were analysed using a scanning electron microscope (SEM) (JEOL 6500F, Japan), and a high-resolution transmission electron microscope (TEM) (JEOL 2010F, Japan) equipped with energy-dispersive X-ray analysis (EDX, Oxford Instrument INCA). SEM samples were prepared by dissolving the AAO templates using 0.2M sodium hydroxide solution and rinsing with distilled water, and by dissolving the PC template and rinsing with chloroform (Fisher Scientific, 99.9+%). Nanowires completely dissolved out of the templates were dispersed on holey carbon film coated grids for TEM and EDX analysis and on a SiO₂(100nm)/Si wafer for nanomanipulation, nanoassembly, electrical nanowelding and testing. The electrical nanowelding and testing was carried out using two in-situ SEM nanomanipulators (Kleindiek Nanotechnik, Germany) equipped with a Keithley 6487 picoampermeter. The data acquisition was automated using a dedicated multi-functional programme.

3. Nanowire morphology

Figures 1(a) – (c) show three representative TEM images of gold nanowires, (Co₇₂Pt₂₈/Pt)ₙ multilayer nanowires, and nanosolder Sn₉₉Au₁ alloy nanowires from which the AAO and PC templates have been completely dissolved. The gold nanowires are uniform in diameter and length, indicating a good quality deposition. The average size of these gold nanowires is about 55nm in diameter and 10 μm in length. Selected-area electron diffraction (SAED) analysis confirms that the gold nanowires are polycrystalline with the fcc structure.

![Figure 1](image)

**Figure 1.** TEM images of (a) gold nanowires, (b) (Co₇₂Pt₂₈/Pt)ₙ multilayer nanowires and (c) nanosolder Sn₉₉Au₁ alloy nanowires. (d) EDX spectrum of Sn₉₉Au₁ alloy nanowires.

Figure 1(b) clearly shows that each individual multilayer nanowire has a regular periodic structure like bamboo. The dark contrast layers are Pt (significant electron scattering) and the grey contrast layers mainly cobalt (lower electron scattering). The Pt layers grew to the full width of the AAO template, however the cobalt-rich layers in each nanowire did not fully fill the template pores during growth, resulting in a repeatably oscillating nanowire diameter. The chemical composition of multilayer nanowires was measured to be (Co₇₂Pt₂₈/Pt)ₙ by EDX. Both the Co₇₂Pt₂₈ and Pt layers were polycrystalline, consisting of fcc nanocrystals <5nm in size. More detailed microstructure and chemical characterisation of both building block nanowires have been reported in our previous work [2, 3, 7].

The nanosolder SnₙAuₓ alloy nanowires are found to be uniform in length. The top ends of all SnₙAuₓ alloy nanowires are about 80nm, consistent with the commercially quoted PC template pore diameter, whilst the bottom diameter is about 150nm. This reveals that the channels of the commercial
PC templates have a cone shape rather than cylinder. Figure 1(d) shows a typical EDX spectrum of the Sn$_{99}$Au$_1$ nanowires, revealing that Sn and Au have been successfully co-electrodeposited. Cu and C (and minor Cr and Fe peaks) come from carbon coated copper grids, which was confirmed by EDX of an empty carbon coated copper grid. The O peak indicates that the surface of Sn$_x$Au$_y$ alloy nanowires has been partly oxidised after they have been released from PC templates for two weeks. Quantitative analysis of EDX spectra indicates a 99:1 atomic ratio of Sn:Au, inferring a Sn$_{99}$Au$_1$ composition. SAED and TEM characterisation shows that individual 80nm Sn$_{99}$Au$_1$ alloy nanowires are polycrystalline with tetragonal $\beta$Sn structure.

4. The bottom-up assembly of nanostructures

![Figure 2](image.png)

**Figure 2.** Bottom-up assembly of nanostructures using gold nanowires building blocks. (a) placement of gold nanowires; (b) assembly of the third nanowire; (c) complete assembly of letter “A”.

The gold nanowires, (Co$_{72}$Pt$_{28}$/Pt)$_n$ multilayer nanowires, and nanosolder nanowires were dispersed on a SiO$_2$(100nm)/Si wafer for the bottom-up assembly of nanoconstruction. Figure 2 shows an example in which individual gold nanowires were assembled into a complex pattern by mechanical manipulation using nanomanipulators within a SEM. First the nanowires were released from the strong bonding to the substrate wafer by a mild mechanical push from a SEM nanomanipulator. The chosen nanowire is then lifted from the substrate using Van der Waals force, followed by precise release at the desired location adjacent to another nanowire (Figure 2(b)). The whole SEM mechanical manipulation process is clean, simple, quick and reliable. It also avoids the increased time, expense and contamination of methods involving nano-object pick-up via e-beam and ion-beam gas deposition [3, 8]. By means of this clean manipulation method, complex structures, like letter “A” (Figure 2(c)) and heterojunctions composed of dissimilar building blocks, can be easily assembled.

5. Electrical nanowelding of the assembled nanostructure

Once nanowire building blocks have been positioned into a required design, the goal is to securely join them together ensuring mechanically strong and electrically conducting junctions. Electrical currents can be directly and controllably applied to individual nanosolder nanowires, and through sections of nanowire circuits, using two SEM nanomanipulators (Figure 3(b) and Figure 3(e)). High quality welded nanojunctions can be achieved using nanosolder material. The solder can be the same, or different to the materials being welded. Figure 3 shows examples using similar nanosolder (gold nanowires) and dissimilar nanosolder (Sn$_{99}$Au$_1$ alloy nanowires). It is found that Joule heating of a sacrificial nanowire can dramatically improve the controllability, reproducibility and reliability of the nanowelding procedure. Explicitly, a $\sim$ 70% maximum current density $J_{\text{max}}$ (4.94$\times$10$^8$A/cm$^2$) is applied to the sacrificial nanosolder for 1–2 minutes before a weld process. The high current density (typically about 3.5$\times$10$^8$A/cm$^2$ or 8mA) causes a softening of the solder nanowire due to Joule-heating, and induces the first join to the patterned nanowires (Figure 3(b) and 3(e)). In some cases, if the solder nanowire remains attached to the junction after welding (Figure 3(f)), mechanical force can be applied to separate them by pulling the probe away. Furthermore, if any unwanted residues of solder nanoparticles and rods exist, which are conductive and therefore dangerous and potential short-circuit sites for real nanoelectronics devices, the nanomanipulators can easily and precisely mechanically remove the welding residues.
Once formed the welds joining two nanowires are strong and very conductive. An immediate check of nanoweld quality can be done in-situ directly after welding which is essential for practical nanoconstruction. Nanoscale weld resistances of just 20Ω are achieved by using Sn₉₉Au₁ alloy solder [1].

![Figure 3. Electrical nanowelding of the assembled nanostructures. (a) - (c) Nanowelding nanowire structures using similar nanosolder, using 55nm Au nanowires as an example: (a) Placement of nanowires; (b) Pre-weld softening of the solder nanowire. The current flows from the right tip to the left tip via the nanowire; (c) Nanowelding nanowires together by a rectangular voltage pulse through the solder nanowire, inset showing a magnified view of the welded nanojunction. (d) – (f) Welding Chinese character “人” using a sacrificial 200nm diameter Sn₉₉Au₁ solder nanowire.](image)

6. Summary
In conclusion, a high spatial resolution nanowelding method has been presented in this work, which provides a controllable and reliable approach for manipulating, assembling and welding <100nm diameter metallic nanowire building blocks into complex structures by means of SEM nanomanipulators. The key advance is to avoid detrimental current flow though the nanobjects to be joined, and instead to locally deposit nanoscale volumes of a chosen metal at the weld site by Joule heating a sacrificial nanowire. Precise engineering of nanowelds by this technique, including the chemical flexibility of the nanowire solder, and high spatial resolution of the nanowelding method, should result in research applications including fabrication of nanosensors and nanoelectronics constructed from a small number of nanobjects, and repair of interconnects and failed nanoscale electronics. This technique provides a promising way to conquer the challenge of the integration of nanocomponents for bottom-up nanotechnology.

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References
[1] Peng Y, Cullis A G and Inkson B J 2009 Nano Lett. 9 91
[2] Peng Y, Cullis A G and Inkson B J 2008 Appl. Phys. Lett. 93 183112
[3] Peng Y, Luxmoore I, Forster M D, Cullis A G and Inkson B J 2007 J. Phys. Conf. Ser. 126 012031
[4] Cui Y and Lieber C 2001 Science 291 851
[5] Dong L, Tao X, Zhang L, Zhang X and Nelson B 2007 Nano Lett. 7 58
[6] Cumings J and Zettl A 2000 Science 289 602
[7] Peng Y, Cullis A G, Moebus G, Xu X J and Inkson B J 2007 Nanotechnology 18 485704
[8] Matsui S, Kaito T, Fujita J, Komuro M, Kanda K, Haruyama Y 2000 J. Vac. Sci. Technol. B 18, 3181