Supplementary Information

Pristine, Adherent Ultrathin Gold Nanowires on Substrate and Between Pre-defined Contacts via Wet Chemical Route
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Experimental Section

Growth of Au Nanowires on Substrates: 2 mg of HAuCl₄·xH₂O (Sigma Aldrich) was taken in 5 ml of dry toluene in a clean 25 ml test tube and 40 µl of oleyl amine (Fluka) was added to it. The solution was sonicated for 1 minute to dissolve the salt by formation of the Au(III)-amine complex. A previously cleaned substrate was then placed horizontally in the solution containing the Au(III)-amine complex and was subjected to uniform heating in an oil bath maintained at 95 °C for nucleation of fine Au particles on the substrate. Typically, it takes 35 – 40 minutes to reach this stage. After cooling down to room temperature, the substrate was taken out from the medium and cleaned with ethanol. A fresh gold salt solution was allowed to age for 2-3 hours until a pale pink color develops where fine Au nanoparticles were formed in the medium. It was then allowed to cool down by keeping the test tube in a water bath for 5 mins maintained at 40 °C. The substrate with Au nanoparticles was then dipped in this solution again followed by addition of 8 mg of ascorbic acid (Sigma Aldrich). It was then kept at 40 °C for 45 mins with mild shaking when the solution turns from pale pink to dark magenta color. The solution was cooled to room temperature and the substrate was taken out with a clean tweezer. The substrate was cleaned with ethanol, distilled water and acetone by dipping in each for 1-2 minutes and dried in a vacuum dessicator.

For thickening of the wires the substrate with preformed wires, cleaned with ethanol, was subjected to ascorbic acid treatment again in an aged Au nanoparticles colloid at 40 °C. As this solution contained both Au(0) and Au(+1), it resulted in seed mediated growth by reduction along the width resulting in thickening of the wires. The same solution resulted in lengthening of the wires when the surface was capped.

Control Experiment CE1: A clean SiO₂/Si substrate was subjected to the first step as mentioned above and characterized. After cleaning with ethanol, it was dipped in a solution containing 5 ml toluene and 8 mg ascorbic acid for wire growth at 40 °C for 90 mins. The substrate was finally cleaned with ethanol, water and acetone and characterized.
Control Experiment CE2: Further, the same substrate (in CE1) was dipped in a freshly aged Au nanoparticle solution and treated with ascorbic acid at 40 °C for 90 mins for wire growth.

Control Experiment CE3: A clean Si₃N₄ membrane grid of the same specification (as mentioned in the main text) is subjected to Step 1 as above and characterized. A fresh Au naoparticle solution was prepared in the same way as before and divided into two equal volumes on cooling. The membrane with Au nuclei was subjected to ascorbic acid treatment as before using one half of the aged solution and a blank Si₃N₄ grid was subjected to the same treatment with rest of the aged solution. Ethanol, water and acetone cleaning were done before characterizing.

Microstructural Characterization

Microscopy: Transmission electron microscopy investigations were carried out in Tecnai F30 Microscope at an accelerating voltage of 200 kV. Scanning electron microscopy was done on Zeiss Sigma Scanning Electron Microscope operating at accelerating voltage of 2-3 kV.

Spectroscopy: X-ray photoelectron spectroscopy was carried out using a ThermoScientific Multilab 2000 instrument using Mg X-ray as the source. All data were analysed taking C1s binding energy (284.5 eV) as reference.

Electron beam lithography and device fabrication

For the fabrication of devices with in-situ grown wires, SiO₂/Si substrates were patterned using standard e-beam lithography using PMMA495K/PMMA950K. Gold pads were deposited using sputtering, followed by the growth of wires. Devices were packaged on to a chip using modified wire bonding techniques without any heating.

For two-probe and four-probe measurements on wires contact pads were deposited after the growth. The samples were coated with a PMMA-495K/PMMA-950K and left at room temperature for ≈ 30 mins for curing. E-beam lithography was done using a Zeiss scanning electron microscope integrated with Raith Elphy Quantum. Ti/Au (10nm/50nm) pads were deposited via thermal evaporation. Cooling lines were integrated on to the sample holder to ensure minimal heating during deposition. The fabricated devices were then bonded at room temperature on to a chip and measured subsequently.
**Figure S1.** SEM image of drop cast sample after cleaning on different regions of the SiO₂/Si substrate. Very few intact wires could be located on the substrate as shown in (a). The wires disintegrate and/or aggregate after cleaning with polar solvent like ethanol or acetone as in (b and c). The yield of undamaged wires decreases drastically when subjected to cleaning on the substrate primarily due to their poor adherence to the surface.
Figure S2: Au nanoparticles nucleated on the substrate (marked A) and drop cast on the substrate (marked B). Cleaning results in the removal of the weakly adhering drop-cast particles (marked C) while the nucleated particles are more adherent and are not removed while cleaning.
Figure S3. High resolution TEM image from a portion of wire grown on C-coated Cu grid revealing the presence of twin boundaries (TB) and stacking faults (SF) along the length. This indicates the growth of wire proceeded by oriented attachment of faceted Au particles along the 111 facet.
Figure S4. Bright field TEM image of (a) large particles resulted due to prolonged step 1 at 95 °C, (b) wires that landed ‘by chance’ on Si$_3$N$_4$ membrane grid due to absence of the pre-nucleated Au particles and (c) magnified portion from the wire shown in (b) indicating random branching and interrupted growth of the wires.
Figure S5. XPS data collected after growing Au nanowires on SiO₂/Si substrates. (a) shows the core level N1s spectra from a sample after cleaning with ethanol, water and acetone soon after the synthesis which indicates complete removal of the oleyl amine capping from the wire surface. (b) and (c) shows the core level spectra of N1s and Au4f before and after cleaning of the wires on the same substrate respectively. As the cleaning is done after 24 hours of synthesis, complete removal of capping could not be achieved, however, the relative Au/N intensity ratio increases by a factor of 2.4 after cleaning indicating the removal of amine from the wire surface.
Figure S6. SEM images showing (a) Fine Au nanoparticles along with a few larger ones nucleated after the first step of reaction on Si/SiO$_2$ (doped) substrate; (b) No significant change after the second step of ascorbic acid treatment in the absence of external Au nuclei in the medium. No wires formation takes place in this case (c) Long wires formed on the substrate when the same is subjected to ascorbic acid treatment in presence of aged Au nanoparticles solution. This experiment clearly shows that the wire growth is facilitated by the nanoparticles in the solution phase that attach to existing particles on the substrate.
Figure S7. (a) HRTEM of the thickened wire showing a polycrystalline shell around the original wire obtained by seed mediated growth on the original wire. (b) shows the FFT obtained from the region in (a) which clearly indicates the 111 orientations as marked in the HRTEM. The spot marked by rectangle corresponds to the original wire and the spots encircled are from the shell.