Structure and Stability of Ultrathin Au/ Alloy Nanowires

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A detailed study of structure and stability of ultrathin, single crystalline Au nanowires (~2 nm in diameter) is desired both from fundamental and application point of view. Many fundamental aspects including structure, stability and properties get modified as Au is synthesized in the nanowire form. While bulk Au has the FCC structure, structural relaxation in ultrathin Au wires due to anisotropic surface stresses leads to the formation of intriguing structures where the close-packed planes along the growth direction undergo wrinkling. In addition, these wires show insulating behavior for electrical transport.

Although nanowires exhibit several interesting properties, their extreme fragility has hampered their use in potential applications. There are multiple ways to improve their stability. Some of which we could achieve are to grow them on supports, alloying with other metals and coating with a suitable material that can still provide access to the surface of the nanowires. The surfactant (Oleyl amine) that is already present on nanowires imparts stability to some extent. But for realizing applications like sensing, catalysis and plasmonic a clean interface is desired. But extreme fragility of the wires on polar solvent cleaning in solution for the removal of surfactant, limit its use. Here we have shown a method by which these nanowires can be directly grown on a variety of substrates by an in-situ functionalization technique. Detailed mechanistic investigation using SEM, TEM, AFM, XPS and FTIR reveals that Oleylamine bilayer plays the crucial role in anchoring the nanowires onto substrates which otherwise had a high interfacial energy with Au. The anchored nanowires show enhanced stability on cleaning with polar solvents like ethanol, water and acetone.

Poor thermal stability of the ultrathin Au nanowires is impediment for high temperature applications. Role of supports in imparting stability and Rayleigh instability effects were studied on directly grown and drop casted wires on TEM grid as support. Higher stability of wires that are closer to the support is evident from both ex-situ and in-situ TEM heating experiments. We have attempted to synthesize ultrathin bimetallic alloy nanowires using Au nanowires template. Alloying enhances the properties and stability of the Au nanowires. Ex situ heating of the Au based alloy nanowires have shown stability till at least 200°C whereas Au nanowires are stable only up to 60°C. We have also developed a technique to coat these nanowires with mesoporous SiO_2. The SiO_2 layer thickness could be controlled very easily by varying the reaction time. In-situ TEM thermal stability study has been carried out. A comparison of thermal stability of coated and uncoated nanowires show that uncoated nanowires disintegrate at temperature ~140°C whereas the coated nanowires become segmented at that temperature but the segments show remarkable stability till at least ~550°C.

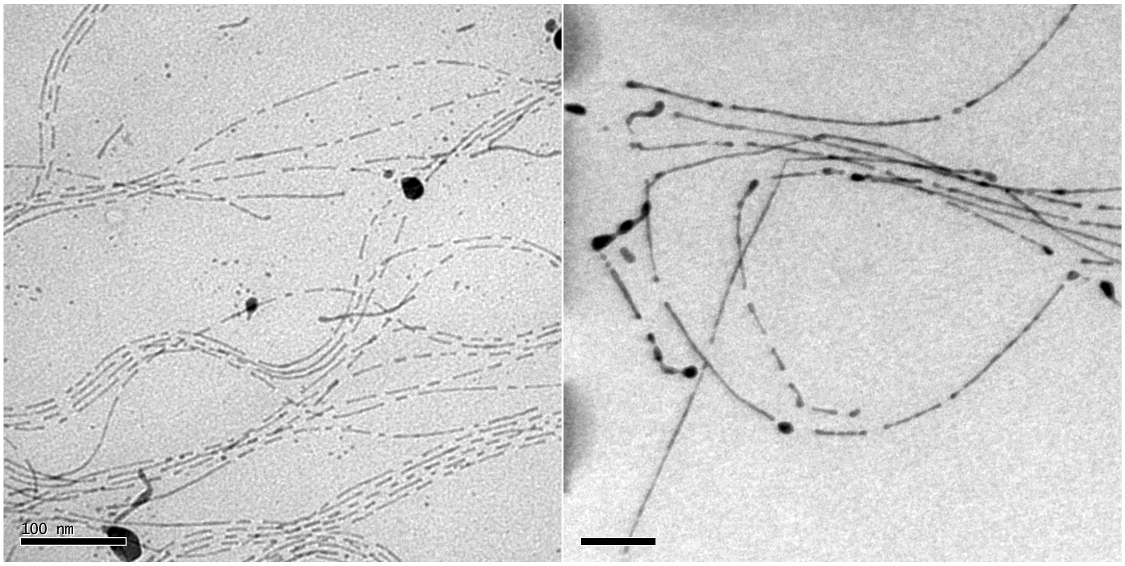

Figure: Transmission Electron Micrographs of (a) Au nanowires heated to 60 °C and (b) AuPd nanowires heated to 200°C which show that alloying increases the thermal stability of Au nanowires.

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References:

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