Process to grow nanowires controls key properties

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High-quality, compound semiconductor nanowires can be fabricated using metalorganic chemical-vapor deposition with gold nanoparticles as catalysts.

Nanowires have received an explosion of interest in recent years, fueled by advances in fabrication and their impressive potential for future optoelectronic applications. The tiny, wire-shaped structures with diameters less than 100 nanometers and lengths greater than 1 micron are effectively 1D. Yet, they are functional building blocks that can be assembled into more complex devices. With electronics and optoelectronics businesses continually pursuing more compact and powerful systems, nanowire components have emerged as prime candidates to drive these industries into the future.

Nanowires made with III–V compound semiconductors such as gallium arsenide (GaAs) and indium phosphide, which are composed of a 1:1 ratio of group III and V elements of the periodic table, are particularly promising. Aluminum, gallium, and indium are group III elements, while nitrogen, phosphorus, arsenic, and antimony belong to group V. III–V materials are currently of great importance in the electronics and optoelectronics industries because of their unique properties of high electron mobility, direct band gap, and high quantum efficiency that facilitate excellent device performance. The potential of III–V nanowire devices is exemplified by solar cells\(^1\) and lasers.\(^2\) Furthermore, they can be readily integrated with established silicon (Si)-based microelectronics and tailored into unique axial and radial heterostructures (see Figure 1).

Successful development of III–V nanowire-based devices requires fabrication of high-quality nanowires. A number of properties must be tightly controlled, including shape, composition, purity, crystal structure, and optical characteristics. Metalorganic chemical-vapor deposition (MOCVD) using gold (Au) nanoparticles as catalysts is a scalable, flexible, and well-controlled means of growing III–V nanowires. First, Au nanoparticles are deposited onto a semiconductor substrate surface: see Figure 2(a). To initiate growth, vapor-phase group III and V precursor species are provided to the reaction chamber. To grow GaAs nanowires, Ga and As are provided as gas-phase trimethylgallium (TMG) and arsine (AsH\(_3\)), respectively. The Au nanoparticles mix with the group III element to form a liquid or solid alloy such as Au-Ga: see Figure 2(b). The nanoparticles are ideal sinks for group III reaction species supplied from the surrounding vapor. Consequently, deposition of III–V material occurs preferentially at the interface between the nanoparticle and the substrate/nanowire. As deposition continues, the nanoparticles drive highly anisotropic nanowire growth: see Figures 2(c) and 2(d).

Because the precursor species are vapor and the nanowire is solid, the growth process is referred to as a vapor-liquid-solid process when Au forms a liquid eutectic alloy, or a vapor-solid-solid process when it forms a solid alloy. Nanowire growth generally occurs in the most energetically favorable direction. Substrates are often chosen with 111b-type (As-atom-terminated) surfaces, so nanowire growth is normal to the...
Figure 2. Gold (Au)-assisted growth of III–V compound-semiconductor nanowires. (a) Au nanoparticles are deposited onto the substrate. (b) They are ideal sinks for the group III species supplied from vapor and form an Au-group III alloy. (c) III–V material is deposited preferentially at the nanoparticle-substrate interface. (d) Further nanowire growth. The green arrows indicate adsorption and diffusion of reaction species contributing to nanowire growth.

substrate surface (see Figure 2). There are two major contributions to nanowire growth, the group III species impinging directly on the nanoparticle and the group III species adsorbed on the substrate and nanowire sidewalls, which then diffuse down the concentration gradient toward the nanoparticle. These pathways are illustrated by green arrows in Figure 2(d).

In MOCVD, a number of growth parameters can be tailored to achieve optimum nanowire quality. These include the ratio of group V to III precursor flow rates (V/III ratio), growth temperature, and growth rate. A number of techniques can be used to investigate the impact of these growth parameters on quality. Field-emission scanning-electron microscopy can help assess overall nanowire shape and growth orientation. Transmission-electron microscopy reveals the crystal structure. For instance, it enables us to assess whether the nanowire lattice is cubic zinc-blende or hexagonal wurtzite and reveals the presence of planar crystallographic defects such as twins and stacking faults. Photoluminescence measurements probe the optical and electronic properties of nanowires, including the energy band gap, doping and impurities, charge-carrier and spin lifetimes, and quantum efficiency. Terahertz-conductivity spectroscopy is used to measure nanowire conductivity and dielectric response.

For GaAs nanowires, we investigated how growth parameters affect quality. We found that a high V/III ratio reduced both the number of twin-plane crystal defects and the amount of carbon impurities. However, it also introduced nonradiative recombination centers, likely excess-As-related defects such as As-antisite defects, As interstitials, and Ga vacancies. These nonradiative recombination centers reduce the charge-carrier lifetime and hamper the performance of nanowires as optoelectronic components. Furthermore, the increasing V/III ratio raised the degree of nanowire tapering, whereby nanowires featured wide bases and narrow tips. Figure 3(a) illustrates highly tapered nanowires grown with a high V/III ratio of 93. Tapering is undesirable for laser applications, where it compromises the nanowire’s performance as a resonant cavity. Considering the advantages and disadvantages of a high V/III ratio, we have decided that an intermediate V/III ratio is optimal.

We also investigated the effects of growth rate, expecting that a slow rate would increase the nanowire quality, as with planar epitaxy. Very unexpectedly, we found the opposite. With increasing growth rate, nanowire tapering decreases—see Figure 3(b)—carbon contamination decreases, and the density of planar crystal defects decreases. The recombination lifetime was unaffected. A rapid nanowire-growth rate is therefore advantageous for optoelectronic applications.

Finally, we found that a low growth temperature strikingly improves nanowire properties. At 375°C, tapering is minimal—see Figure 3(c)—nanowires feature pure zinc-blende structure without twin defects, and the recombination lifetime is almost intrinsic.

In summary, excellent-quality III–V nanowires can be grown by an Au-assisted MOCVD process using appropriate growth parameters. Key electronic and optoelectronic properties critical to device function, can be controlled very accurately during the nanowire-growth process, making them ideal building blocks for future optoelectronic devices. We plan to further explore radial and axial nanowire heterostructures for opportunities...
to develop nanowire lasers, solar cells, sensors, and single-photon sources. III–V semiconductor nanowires on silicon will open up opportunities to integrate optoelectronics and microelectronics.

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