Synthesis of Inorganic Nanowires and Nanotubes

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1. INTRODUCTION

The relentless pursuit to achieve faster computation speeds has driven the miniaturization of electronic devices to date. Further reduction in the electronic device size requires the creation of nanometer-scale structures [1]. However, the current optical lithography based technology is fast reaching its physical and processing limitations, and will eventually fail to yield nanostructures smaller than 50 nm. This has necessitated the exploration of new routes for creation of bulk amounts of molecular and nanoscale materials, to directly yield individual device components with sizes less than 50 nm. In this regard, two- and three-dimensional rational assemblies of bulk-synthesized nanostructures could present a new route for increasing the packing densities. Similar strategies could be applied to build 3D assemblies for engineering photonic crystals and crystalline and porous matrices for catalysts and sensors.

The nanowires, also known as quasi-1D structures, become interesting in terms of their properties when their diameter is reduced below a certain length scale characterized by the Bohr exciton size, when the separation distance between electron–hole pair reduces and electronic confinement takes place. This is also referred to as quantum confinement, and is of great interest in studying the excitonic behavior of low-dimensional solids for its effect on electron transport, band structure, and optical properties. In fact, the electronic and optical properties of these low-dimensional solids differ from those at macroscopic scale [2–4]. For example, Si in bulk is an indirect energy bandgap material. When its size is reduced below 5 nm, the non-radiative recombination rate reduces due to quantum confinement, enabling Si to emit visible luminescence at room temperature [2]. Theoretical computations predicted that Si exhibits a direct energy bandgap at nanoscale and the energy bandgap increases with an inverse relationship with the nanocluster size (\(\propto d^{1.3}\) for wires) [3]. This quantum confinement effect was predicted to be the strongest for the wire shape compared to films and dots [3].

In addition, the structure of inorganic solids at nanometer scale could be different from its bulk structure. For example, carbon exhibits fullerene, and silicon is predicted to exhibit stable clathrate type structure at nanoscale. Similar existence of new phases (or structures) for several other inorganic materials cannot be ruled out and is still unknown. Systematic efforts to discover these phases for inorganic solids have led to materials synthesis efforts at nanoscale, followed by thorough structural investigations. In the past, the synthesis efforts for micron-scale whiskers were motivated by superior mechanical properties and applications in composites [5, 6]. However, these techniques were never focused on tight size control. The current motivation in determining the size-constraint effects on both structure and properties for a variety of inorganic materials at nanometer scale has prompted intense research in bulk synthesis methodologies over the last few years. In this chapter, we have tried to provide a comprehensive review on synthesis methods for one-dimensional nanostructures (less than 100 nm in diameter) of various elements and inorganic compounds, along with a historical perspective on synthesis of
the respective micron-scale whiskers. This review intentionally avoids the vast amount of literature that is available on carbon nanotube structures and their synthesis methods, lithography, and template-based techniques for inorganic nanowires. This chapter also discusses the popular mechanisms used to explain the one-dimensional growth of elements that can be extended to compounds in general. Considering the vast, at times redundant, literature on synthesis of various inorganic nanowires and nanotubes, we have summarized and compiled only the notable reports for synthesis of nanowires and nanotubes and the resulting characteristics in Table 1.

2. ELEMENTAL WHISKER SYNTHESIS—HISTORY

The growth of one-dimensional crystals, termed whiskers, was of great interest as early as 1948 [7], due to their better mechanical characteristics compared to the bulk materials [4, 5]. In the 1940s, Frank and his co-workers introduced a spiral growth mechanism to explain enhanced growth rates on certain facets, which were otherwise unexplainable with experimentally attainable vapor-phase solute supersaturation [8]. In this mechanism, the spiral resulting from screw dislocations on certain facets of crystals perpetually generates new layers without the need for new step nucleation events. The enhanced growth in this direction typically leads to the formation of elongated crystals. The basic steps in this vapor-solid (VS) mechanism for one-dimensional growth of crystals, as shown in Figure 1a are (1) adsorption of gas-phase species on the side faces, (2) appearance of screw dislocations at the growing end of the crystal, resulting in perpetual generation of growth steps in the plane perpendicular to the growth direction of the crystal, (3) rapid surface diffusion of the growth species followed by attachment at the whisker tip. Whisker growth of several materials was explained based on this model [8–14]. The growth of mercury whiskers in a field emission tube by an evaporative technique was explained on the basis of this growth model [13]. The spiral growth mechanism is also typically observed in chemical vapor deposition of diamond, and leads to elongated crystals as shown in Figure 1b. This growth mode seems to be active in micron-scale whiskers, and to date no reports exist on clear demonstration of any phenomena in nanowire growth of any material. However, one cannot yet reliably reproduce screw dislocations to yield micron-scale whiskers in bulk quantities.

Throughout the 1950s and early 1960s, experimentally observed growth of whiskers was primarily explained by the above VS mechanism. Carbon filaments were grown using catalytic thermal decomposition of carbonaceous gases such as methane, benzene, cyclohexane, acetylene, and carbon monoxide over Fe, Co, and Ni catalyst particles [15–21]. Iron clusters at tips of the filaments were also observed in one report [15]. Hofer et al. also observed the growth of sub-micron-scale carbon filaments during decomposition of carbon monoxide over Ni catalyst particles [19]. It was contemplated that the one-dimensional growth took place due to preferential deposition of carbon on the (111) planes of the Ni catalyst particles. All of these studies failed to recognize the role of catalyst particle for growth of 1D carbon structure.

The first report on the synthesis of true semiconductor whiskers appeared in 1949. Lyon et al. [22] synthesized 250-µm-thick silicon fibers using reduction of SiCl4 with Zn vapor at 950 °C. The resulting Si fibers were pure and were 1 cm long and 0.25 mm thick. Using a similar reaction, but with diluted SiCl4 in Ar or H2, Johnson and Amick [23] reported synthesis of thinner (1 µm), single-crystalline silicon whiskers. The reaction was carried out in a tube furnace, and the products were collected at the downstream end. Authors contemplated the reason for 1D growth to be spiral dislocations in the whiskers. In 1961, Greiner et al. [24] reported synthesis of silicon ribbons by a chemical vapor transport technique. Silicon pellets were reacted with iodine and hydrogen at 950 °C, and the resulting vapors were transported to the cooler portion of a sealed quartz tube. The growth direction was observed to be (111). One-dimensional growth was attributed to the presence of structural defects such as twins along the whisker axis. From the reports of whisker growth using catalytic metals, it became apparent that Frank’s dislocation-mediated growth mechanism did not hold in all cases.

Wagner and Ellis [25], in a breakthrough report in 1964, identified the vapor-liquid-solid (VLS) growth mechanism for single-crystal whisker growth (Au particle on (111) Si, 950 °C, SiCl4/H2) and provided clear demonstration of one-dimensional crystal growth due to size confinement of the catalytic cluster solvent medium. In this mechanism, as shown in Figure 2, an impurity forms a molten alloy for selective and preferential deposition from the vapor phase. Silicon and germanium whiskers were grown using this mechanism [26–29]. The VLS type growth was also found to be responsible for whiskers found on the lunar surface [30] and in volcanic eruptions [31].

3. VLS AND RELATED MECHANISMS

The VLS mechanism using transition metal clusters [32–34] consists of four steps: (1) diffusion in vapor phase, (2) chemical reaction at the vapor-liquid interface, (3) diffusion in the liquid phase, and (4) crystallization at the solid-liquid interface. The rate-limiting step could be either chemical reaction at the V-L interface [32] or crystallization [34]. The nature of the limiting step could vary depending upon the temperature and the catalytic nature of the liquid alloy. Wang and Fischman [35] also considered surface diffusion of the adsorbed species on the molten alloy droplet at the whisker tip. They concluded that surface diffusion becomes more important for decreasing whisker diameters, decreasing the solubility of the growth species in the liquid phase, and the increasing ratio of surface diffusion coefficient to bulk diffusion coefficient. The conclusion that can be derived from these empirical studies is that the molten metal cluster at the whisker tip acts in two ways: (1) it reduces the activation energy of the chemical reaction taking place at the vapor-liquid interface, and (2) it enhances the sticking coefficient through dissolution [32].
## Table 1. Brief experimental conditions for various nanowires and nanotubes synthesized to date and the resulting nanowire/nanotube characteristics.

<table>
<thead>
<tr>
<th>Inorganic material</th>
<th>Synthesis method with experimental parameters and Ref.</th>
<th>Resulting wire/tube features</th>
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<tbody>
<tr>
<td><strong>Nanowires</strong></td>
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<tr>
<td>Si</td>
<td>Thermal chemical vapor deposition (CVD): 320–600 °C, SiH₄/He, 0.1–1 Torr, Au film on (111) Si substrates; [36–38]</td>
<td>10–25 nm diam, 0.5–5 μm long, (111) growth direction, bends and kinks</td>
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<td></td>
<td>Thermal CVD: 640–670 °C, SiH₄/SiH₄Cl₂, Ti islands on (100) and (111) Si substrates; [42]</td>
<td>25 nm mean diam, ~1 μm long</td>
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<tr>
<td></td>
<td>Laser ablation: Si₆₋₇Fe₀.₁ target, Nd-YAG laser, 1200 °C; [39]</td>
<td>6–20 nm diam, 1–30 μm long, (111) growth direction, 1.5–2.5 nm oxide sheath</td>
</tr>
<tr>
<td></td>
<td>Physical evaporation: Si₆₋₇Fe₀.₁ pellet, 1200 °C, 20 h, 100 Torr, flowing Ar; [40]</td>
<td>12–18 nm diam, 10–100 μm long, crystalline, 2 nm oxide sheath</td>
</tr>
<tr>
<td></td>
<td>Laser ablation and physical evaporation: Si/SiO₂ mixture: 930–1200 °C, 12 h, 500 Torr, Ar atmosphere; [47–49]</td>
<td>15–20 nm diam, &gt;10 μm long, (112) growth direction, &gt;2 nm oxide sheath, stacking faults and micro-twins</td>
</tr>
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<td></td>
<td>Supercritical solvent (SCS)-based synthesis: diphenylsilane and alkane-thiol stabilized gold catalyst nanoclusters dissolved into the supercritical hexane, 500 °C, 200–270 bar; [45]</td>
<td>4–5 nm diam, &gt;1 μm long, (110) and (100) growth directions, 4 nm thick sheath of carbon and oxygen</td>
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<td>Low-melting metal mediated bulk nucleation: large pools of Ga exposed to a SiH₄/H₂ microwave (MW) plasma, 15 min.–3 h, 10–60 Torr, 400–1100 MW power, 300–600 °C; [73]</td>
<td>10–60 nm diam, 10–100 μm long, (100) growth direction, 0.1–5 nm oxide sheath</td>
</tr>
<tr>
<td>Ge</td>
<td>Laser ablation: Ge₆₋₇Fe₀.₁ target, Nd-YAG laser, 820 °C; [39]</td>
<td>3–9 nm diam, twinned nanowires</td>
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<td></td>
<td>Solution-based synthesis: reduction of GeCl₄ and phenyl-GeCl₄ by Na in alkane solvent, 275 °C, 2–8 days, 100 atm; [44]</td>
<td>7–30 nm diam, up to 10 μm in length, (110) growth direction, stacking faults</td>
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<td></td>
<td>Laser ablation: Ge/GeO₂ mixture: 830 °C target temperature, 500 Torr, Ar atmosphere; [48]</td>
<td>16–500 nm diam, &gt;10 μm long, [211] growth direction, &gt;3 nm oxide sheath</td>
</tr>
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<td></td>
<td>SCS-based synthesis: diphenylgermane and triethylgermane, alkane-thiol stabilized gold catalyst nanoclusters dissolved into the supercritical cyclohexane, 300–450 °C, 30 MPa; [46]</td>
<td>10–150 nm diam, &gt;1 μm long, (110) and (111) growth directions</td>
</tr>
<tr>
<td><strong>Indium tin oxide (ITO)</strong></td>
<td>Electron shower/evaporation: 1 × 10⁻⁵ Torr, ITO pellet source; [120, 123]</td>
<td>30 nm diam, 600 nm long</td>
</tr>
<tr>
<td>α-Al₂O₃</td>
<td>Evaporation: SiO₂/Al source, 1300–1500 °C, 2–4 h, flowing Ar; [122]</td>
<td>100 nm to 10 μm diam, &gt;100 μm long, crystalline</td>
</tr>
<tr>
<td>GeO₂</td>
<td>Physical evaporation: Ge/Fe source, 820 °C, 200 Torr, flowing Ar; [124]</td>
<td>15–80 nm diam, &gt;10 μm long, crystalline</td>
</tr>
<tr>
<td>TiO₂</td>
<td>Carbothermal reduction: GeO₂/active carbon mixture, 840 °C, flowing N₂, 3.5 h; [126]</td>
<td>50–120 nm diam, &gt;100 μm long, crystalline</td>
</tr>
<tr>
<td>Ga₂O₅</td>
<td>Thermal annealing: Ti(OH)₄/NaCl mixture, 730–780 °C, 2 h; [152]</td>
<td>10–50 nm diam, &gt;1 μm long, [001] growth direction</td>
</tr>
<tr>
<td></td>
<td>Physical evaporation: Ga source, 300 °C, 100 Torr, flowing H₂/Ar, 24 h; [138]</td>
<td>10–150 nm diam, &gt;100 μm long, twinned nanowires</td>
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<tr>
<td></td>
<td>Carbothermal reduction: Ga₂O₅/C mixture source, 980 °C, 2 h, flowing N₂; [139]</td>
<td>60 nm mean diam, &gt;100 μm long, crystalline</td>
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<td></td>
<td>Arc-discharge: GaN and Ni/C or Ni/Cu/Y mixture pressed into a hole in a graphite anode, 500 Torr, O₂/Ar atmosphere; [142]</td>
<td>33 nm mean diam, &gt;100 μm long, [100] growth direction, rough step edges</td>
</tr>
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<td>Heating a mixture of Ga, SiO₂, and Fe₂O₃ in flowing Ar, 1.2 atm, 1200 °C, 2 h; [140]</td>
<td>20–60 nm diam, &gt;1 μm long, crystalline</td>
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<td></td>
<td>Thermal evaporation: GaN powder, 1100 °C, 2 h, 300 Torr, flowing Ar; [141]</td>
<td>Nanobelts 50–300 nm wide, 20–60 nm thick, &gt;1 μm long, [001] or [010] growth direction</td>
</tr>
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<td></td>
<td>Direct reaction of oxygen and hydrogen plasma with molten gallium: Microwave power of 600–1200 W, 30–60 Torr, 1–12 h, O₂/H₂; mixtures, 400–600 °C; [65]</td>
<td>10–100 nm diam, &gt;100 μm long, [110] growth direction</td>
</tr>
<tr>
<td>Sb₂O₃ and Sb₂O₅</td>
<td>Thermal annealing: Sb₂O₃ powder generated by hydrolysis of SbCl₅, 350 °C, 1 h, ambient atmosphere; [153]</td>
<td>Sb₂O₃ nanowires 10–100 nm in diam and 5–15 μm long; Sb₂O₅ nanowires 10–50 nm in diam and 5–25 μm long</td>
</tr>
</tbody>
</table>

*continued*
## Table 1. Continued

<table>
<thead>
<tr>
<th>Inorganic material</th>
<th>Synthesis method with experimental parameters and Ref.</th>
<th>Resulting wire/tube features</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO</td>
<td>Heating MgCl₂ powder at 750 °C for 1.5 h in flowing mixture of H₂/Ar; [135] Heating MgB₂ powder at 800–900 °C in flowing H₂/Ar atmosphere; [137]</td>
<td>15–50 nm diam, 1–3 μm long, (111) growth direction</td>
</tr>
<tr>
<td></td>
<td>Heating a mixture of ZnO and graphite to 900–925 °C under flowing argon atmosphere, with Au-coated silicon substrates in the vicinity; [130]</td>
<td>15–20 nm diam, ~30 μm long, (001) growth direction</td>
</tr>
<tr>
<td></td>
<td>Heating a mixture of Zn and Se at 1100 °C for 10 h, flowing H₂/O₂/Ar atmosphere, 100 Torr; [132]</td>
<td>40–70 nm diam, 10–20 μm long, (001) growth direction</td>
</tr>
<tr>
<td></td>
<td>Thermal evaporation: ZnO powder at 1400 °C for 2 h, 300 Torr, flowing Ar; [133]</td>
<td>30–100 nm diam, &gt;1 μm long, crystalline</td>
</tr>
<tr>
<td>SnO₂</td>
<td>Thermal evaporation: SnO₂ powder at 1350 °C or SnO powder at 1000 °C, 2 h, 300 Torr, flowing Ar; [133]</td>
<td>Nanobelts 50–300 nm wide, 10–30 nm thick, &gt;100 μm long, [0001] and [01–10] growth directions</td>
</tr>
<tr>
<td></td>
<td>Thermal evaporation: In₂O₃ powder at 1400 °C, 2 h, 300 Torr, flowing Ar; [133]</td>
<td>Nanobelts 50–200 nm wide, width-thickness ratios of 5–10, &gt;1 mm long, [101] growth direction</td>
</tr>
<tr>
<td></td>
<td>A crystalline InP substrate coated with Au film heated under a flowing O₂/Ar atmosphere, 1080 °C, 1.5 h; [143]</td>
<td>Nanobelts 50–150 nm wide, &gt;100 μm long, (100) growth direction</td>
</tr>
<tr>
<td>CdO</td>
<td>Thermal evaporation: CdO powder at 1000 °C, 2 h, 300 Torr, flowing Ar; [126]</td>
<td>15–150 nm diam, &gt;10 μm long, [100] growth direction</td>
</tr>
<tr>
<td>Cu₂O</td>
<td>Direct oxidation of CdTe film: 450 °C, O₂/Ar, 2 h; [149]</td>
<td>Nanobelts 100–500 nm wide, width-thickness ratios greater than 10, &gt;10 μm long, [100] growth direction</td>
</tr>
<tr>
<td></td>
<td>Reduction of copper hydroxide: hydrazine hydrate was used as a reducing agent for Cu(OH)₂; [162]</td>
<td>40–60 nm diam, &gt;10 μm long, [111] growth direction</td>
</tr>
<tr>
<td>β-PbO₂</td>
<td>Thermal evaporation: PbO powder at 950 °C, 1 h, 300 Torr, flowing Ar; [144]</td>
<td>8 nm mean diam, 10–20 μm long, crystalline</td>
</tr>
<tr>
<td>α and β-MnO₂</td>
<td>Hydrothermal reaction: chemical reaction between MnSO₄ and (NH₄)₂SO₄ at 120 °C, 12 h, adding (NH₄)₂SO₄ to the systems caused α phase to form; [146]</td>
<td>Nanobelts 50–300 nm wide, 10–30 nm thick, 10–200 μm long, [010] growth direction</td>
</tr>
<tr>
<td>Mn₃O₄</td>
<td>Solid-state reaction between MnCO₃ and NaCl at 850 °C, 2 h; [147]</td>
<td>α phase nanowires 5–20 nm in diam, 5–10 μm long, with growth direction along [110]; β phase nanowires 40–100 nm in diam, 2.5–4 μm long, with growth direction along [110]</td>
</tr>
<tr>
<td>NiO</td>
<td>Solid-state reaction between NiCO₃ and NaCl at 900 °C, 2 h; [148]</td>
<td>40–80 nm diam, up to 150 μm long, (211) growth direction</td>
</tr>
<tr>
<td>Vanadium oxide</td>
<td>Hydrothermal reaction: reaction of HNO₃ and NH₄VO₃ aqueous solution followed by heating at 180 °C for 5 h; [150]</td>
<td>30–80 nm diam, &gt;10 μm long, (110) growth direction</td>
</tr>
<tr>
<td>Cu(OH)₂</td>
<td>Chemical reaction between CuSO₄ and NH₄OH followed by reaction with NaOH; [154]</td>
<td>Mixture of V₂O₅ - 0.3H₂O, V₂O₅ - xH₂O(O.3&lt; x&lt; 1.7) and V₂O₅ phases, 20–85 nm wide, 10–80 μm long, [010] growth direction</td>
</tr>
<tr>
<td>GaN</td>
<td>Laser ablation: GaN/Fe target, 250 Torr, NH₃, 900 °C; [82]</td>
<td>8 nm mean diam, &gt;100 μm long, crystalline</td>
</tr>
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<td></td>
<td>HFCVD: Ga₂O₃/C powder, NH₃, 200 Torr, 900 °C, 1 h; [83]</td>
<td>~10 nm diam, &gt;1 μm long, [100] growth direction</td>
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<td></td>
<td>Direct reaction of Ga with NH₃: 825–925 °C, 15 Torr, 3–4 h; [84]</td>
<td>5–12 nm diam, &gt;1 μm long, single crystalline</td>
</tr>
<tr>
<td>AIN</td>
<td>Co-heating Al and AIN: 850–950 °C, 0.1 MPa N₂, 1 h; [86]</td>
<td>20–150 nm diam, 500 μm long, [2-1-10] growth direction</td>
</tr>
<tr>
<td>Si₃N₄</td>
<td>Heating a Si/SiO₂ powder with/without Fe/Ni, N₂/NH₃/Ar, 1200 °C, 1 h; [85]</td>
<td>10–50 nm diam, up to 500 μm long</td>
</tr>
<tr>
<td>InN</td>
<td>Ammonothermal reduction of Azido[bis-(3-methylaminopropyl)indium] at 400–550 °C, 15 min, 8 mTorr; [68]</td>
<td>10–70 nm diam, &gt;10 μm long, single crystalline</td>
</tr>
<tr>
<td>GaAs</td>
<td>Laser ablation: GaAs power and Ga₂O₃, Si substrate, 800 °C, 300 Torr; [39]</td>
<td>10–200 nm diam, 10–100 μm long, crystalline</td>
</tr>
<tr>
<td></td>
<td>Laser ablation: (GaAs)₅Au₃(Au)₃ target, Si substrate, 800–1000 °C, 100–500 Torr; [93]</td>
<td>10–120 nm core diam, 2–10 nm outer sheath, up to 10 μm long, [11-1] growth direction</td>
</tr>
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<td></td>
<td>Metalorganic chemical vapor deposition (MOCVD): TMG and AsH₃ in H₂, 150 Torr, 500 °C, SiO₂ patterned, Au-covered GaAs substrate; [91]</td>
<td>19 nm mean diam, up to 10 μm long, (111) growth direction</td>
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<td></td>
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<td>10–50 nm diam, (111) growth direction</td>
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Table 1. Continued

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<thead>
<tr>
<th>Inorganic material</th>
<th>Synthesis method with experimental parameters and Ref.</th>
<th>Resulting wire/tube features</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cds</td>
<td>Organometallic reactions: 111 °C, hydrocarbon solvent, (t-Bu)$_3$M(M = In, Ga) and EH$_3$(E = As, P) precursors; MeOH, PhSH, Et$_3$NH, and PhCO$_2$H catalysts; [96]</td>
<td>10-100 nm diam, up to 1 µm long, kinked polycrystalline fibers, [111] growth direction</td>
</tr>
<tr>
<td>ZnS</td>
<td>Physical evaporation: Cds powder produced from CdSO$_4$ and Na$_2$S, Ar atmosphere, 1000 °C; [95]</td>
<td>50 nm diam, several µm long, hexagonal Cds wires grown along [101]; 100 nm diam and tens of µm long, fish-bones shape cubic Cds wires grown along [111]</td>
</tr>
<tr>
<td>CdE (E = S, Se, Te)</td>
<td>Physical evaporation: ZnS powder, Au-coated Si substrate, Ar atmosphere, 900 °C; [94]</td>
<td>30-60 nm diam, several µm long, (110) growth direction</td>
</tr>
<tr>
<td>CuFeS$_2$</td>
<td>Solvothermal method: CdCl$_2$ or Cd + thiosemicarbamide, mixture was ground and put into autoclave filled with Et$_3$NH$_2$(Ethylenediamine), 170 °C for 14 h; [97]</td>
<td>20-50 nm diam, 200-1300 nm long</td>
</tr>
<tr>
<td>ZnTe</td>
<td>Hydrothermal: CuCl$_2$, FeCl$_2$, 6H$_2$O (NH$_4$)$_2$S, 200-250 °C for 10 h; [98]</td>
<td>20-40 nm diam, several µm long</td>
</tr>
<tr>
<td>Mn(S,Se)$_2$ (M = Cu, Ag)</td>
<td>Solvothermal method: elements or M(S$_2$CNE$_2$)$_x$, 195 °C, Et$_3$NH$_2$(Ethylenediamine) as solvent; [100]</td>
<td>30-100 nm diam, 500-1200 nm long</td>
</tr>
<tr>
<td>NiTe$_2$ (E = Se, Te)</td>
<td>Solvothermal method: NOCl$_2$ + Se/Te, 160-180 °C, ethylenediamine as solvent; [101]</td>
<td>3-50 nm diam, 80-450 nm long</td>
</tr>
<tr>
<td>Sn$_2$P$_3$</td>
<td>Solvothermal method: SnCl$_2$ + Na$_2$P, 120-140 °C, Et$_3$NH$_2$(Ethylenediamine) as solvent; [102]</td>
<td>20-35 nm diam, 90-120 nm long</td>
</tr>
<tr>
<td>SbS</td>
<td>Hydrothermal method: SbCl$_5$ + (NH$_3$)$_2$CS + I$_2$, 180-190 °C in water for 8-10 h; [103]</td>
<td>~20 nm diam, up to 400 nm long</td>
</tr>
<tr>
<td>CdWO$_4$</td>
<td>Hydrothermal method: CdCl$_2$ + NaWO$_4$, 130 °C; [104]</td>
<td>20-50 nm diam, up to several microns long</td>
</tr>
<tr>
<td>Bi$_2$S$_3$</td>
<td>Hydrothermal method: Bi(NO)$_3$ + 5H$_2$O + Na$_2$S, 9H$_2$O, 100-170 °C for 2-24 h; [105]</td>
<td>20-40 nm diam, 80-280 nm long</td>
</tr>
<tr>
<td>β-SiC</td>
<td>Hot filament CVD: powder of Si containing Ni, Cr, Fe impurities and graphite source, filament temperature of 2200 °C, 2 h; [164]</td>
<td>10-50 nm diam, 1-5 µm long, [220] growth direction</td>
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<td></td>
<td>Laser ablation: SiC target, KF excimer laser, 300 Torr, 1100 °C, a graphite substrate dipped in saturated iron nitrate was used at the cooler end of the furnace; [166]</td>
<td>10-30 nm diam, &lt;1 µm in length, (100) growth direction</td>
</tr>
<tr>
<td></td>
<td>Heating graphite substrate, Si$_2$SiC$_x$-CH$_2$-H$_2$-Ar, 1030 °C, Co impurity; [173]</td>
<td>80 nm mean diam, with an amorphous SiO$_2$ shell, &gt;10 µm long, (100) growth direction</td>
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<td>Reaction using SiCl$_4$, CCl$_4$ and Na as a metal co-reductant, 9 MPa, 400 °C; [181]</td>
<td>0.1-1 µm diam, &gt;50 µm long, crystalline</td>
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<td>Arc-Discharge: SiC rod containing Fe impurity as anode and graphite plate as cathode; [182]</td>
<td>25 cm mean diam, several µm long, crystalline</td>
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<td>MWVCD: Fe film on a Si substrate, CH$_4$/H$_2$, 40 Torr, 420-550 W MW power; [183]</td>
<td>20-60 nm diam, with 5-20 nm inner core of SiC and SiO$_2$ outer core, &gt;1 µm long (111) growth direction</td>
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<td>Carbothermal reduction: sol-gel derived silica xerogel containing carbon nanoparticles, 1650 °C, 2.5 h; [187]</td>
<td>15 nm mean diam, 1.5-2.1 µm long, [111] growth direction</td>
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<td>Heating SiO$_2$/graphite mixture, 1500 °C, 12 h; [188]</td>
<td>20-70 nm diam, a central core of 10-30 nm of SiC and an amorphous SiO$_2$ sheath, (111) growth direction</td>
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<td>CVD: Fe-catalyzed decomposition of CH$_4$ on Si substrate, 1100 °C; [189]</td>
<td>50-80 nm diam SiC-silica biaxial ([211] and [311] growth directions) and coaxial ([111] growth direction) nanowires</td>
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<td>Multiwalled, 25–35 nm ID, 50–70 nm OD, up to 2 μm long, nominal composition of VO\textsubscript{2}(C\textsubscript{6}H\textsubscript{5}H\textsubscript{3}NH\textsubscript{3})\textsubscript{0.54} Multiwalled, 10–50 nm OD, 1 nm wall thickness, &lt;1 μm long</td>
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<td>6–8 nm ID, 65–95 nm OD, 0.2–1.5 μm long</td>
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<td></td>
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<tr>
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<tr>
<td>LaC</td>
<td>DC arc evaporation: lanthanum metal-loaded graphite rod in He atmosphere, 20–30 V, 200 A; [254]</td>
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for laser ablation and evaporation laboratory setups, respectively. The physical evaporation system and the vapor transport systems essentially consist of a tube furnace that has a programmed temperature gradient along the length. In most cases, the generated clusters were finally supported on a substrate. In another approach, uniform-sized, molten gold clusters were dispersed in a supercritical fluid medium for increasing the control of size distribution.

Lieber and his co-workers, in a series of papers [39], developed the laser ablation technique with the target composed of a catalyst metal and the material of interest. His group demonstrated the use of catalyst-containing target material for producing nanowires of several inorganic materials including Si, Ge, GaAs, InP, InAs, GaP, and GaN. As shown in Figure 3a (a representation of the typical laser ablation experimental setup), the Si-Fe targets (1) were ablated using a Nd-YAG laser (2) at 1200 °C and the nanowires were deposited downstream on a cold-finger (7). The variables in this method include ablation power, target composition, gas-phase composition, and cold-finger conditions/geometry. The resulting silicon nanowires were found to contain a minimum oxide sheath thickness of 1.5–2.5 nm.

Almost concurrent to the laser ablation method, several groups employed physical evaporation as a way to reduce the catalyst cluster size for synthesizing nanowires. For example, Yu et al. [40] reported silicon nanowire synthesis using physical evaporation of a Si-Fe target (1200 °C, 4 hr, 100 Torr, Ar). The nanowire mass was deposited on the inner walls of the quartz tube. Silicon whiskers were also grown using Au-mediated VLS method vertically on (111) Si substrates for use as atomic force microscopy (AFM) tips [41]. Transition metals other than Fe and Au have also been investigated. Titanium clusters upon reaction with silicon formed titanium silicides that acted as the catalyst for dissolution and subsequent precipitation of silicon in a nanowire form [42]. Ni nanoclusters were used to dissolve Si from underlying silicon substrate to grow amorphous silicon nanowires in a mechanism termed solid-liquid-solid [43].

Both laser ablation and evaporation-based techniques typically work under vacuum and primarily utilize gas-phase precursors. Heath and LeGoues demonstrated a liquid solution-based synthesis method [44] for single-crystalline Ge nanowires using sodium in an alkane solvent to reduce GeCl4 and phenyl-GeCl3 at elevated temperatures and pressures (275 °C, 2–8 days, 100 atm). The resulting nanowires were 7–30 nm in diameter and up to 10 μm in length. However, a mechanism for one-dimensional crystal growth and the role of sodium were not elaborated. Korgel and his co-workers [45] used supercritical hexane to disperse both the solute material of interest and uniform-sized, alkanethiol stabilized gold catalyst nanoclusters. Figure 3c shows a simplified schematic of the high-pressure reactor used by Korgel’s group. For silicon nanowire synthesis, they used silicon precursor, diphenylsilane, dissolved into the supercritical hexane at 500 °C and 200–270 bar pressure. At these temperatures, diphenylsilane decomposes and dissolves into gold clusters to yield silicon nanowires. In another report, Hanrath and Korgel [46] reported synthesis of Ge nanowires using a similar experimental setup at temperatures of 300–500 °C (Fig. 4). Nanowires grown at slightly different temperatures had different growth directions.
Figure 3. Simplified reactor schematics popularly used for nanowire and nanotubes synthesis using (a) Laser ablation. (b) evaporation: Typically, the nanowire products are collected near the downstream end of the tube furnace, without a specific need for the cold finger. In some cases, nanowires were obtained from the quartz tube inner walls. (c) Supercritical fluids. Courtesy: B. A. Korgel and T. Hanrath, University of Texas, Austin, TX. (d) Activated vapor and low-melting metals: The molten metal film thickness can be arbitrary, ranging from micron to millimeter. (e) Fluidized bed. Courtesy: R. Tenne, Weizmann Institute, Israel.

(110) or (111). The growth mechanism is exactly similar to that in the previous VLS techniques except for the fact that the dissolution into molten metal cluster happens from the solution phase rather than the vapor phase, thus giving the name, the solution-liquid-solid (SLS) method. The supercritical fluid environment offers rapid mass transport of the solute, thus giving much more control on the solution chemistry for the dissolution kinetics and the nanowire growth kinetics. It is not surprising that this method yielded different growth directions for silicon nanowires by changing the reaction pressure and temperature.

In addition to using catalyst metal particles, micron-scale whiskers were also synthesized using evaporative techniques that used vapor-phase suboxide species as the growth precursors. These reports attributed 1D growth to be according to Frank's screw dislocation based model. Recently, S. T. Lee and his co-workers recognized the oxide cluster-assisted 1D growth. They reported [47] synthesis of silicon...
The stable configuration of the solid-liquid interface
determines the growth direction of the precipitating solid
phase [53]. In all the VLS techniques using transition metal
clusters, the growth direction for silicon nanowires has been
primarily in the (111) direction. On the other hand, the
supercritical SolLS method yielded different growth direc-
tions for nanowires such as (111), (110), and (100) direc-
tions depending upon the reaction pressure. In the oxide
cluster and sheath-assisted techniques, the growth direction
was primarily (211) due to the presence of twins.

A common aspect of all the above techniques is that
the nanowire diameter is directly controlled by the clus-
ter size generated either prior to or during the nanowire
growth process. This is expected as the transition-metal cat-
alyst clusters or other type of confinement such as subox-
ide clusters form eutectics with solute material of interest
at high concentrations. As an example, Au-Si phase dia-
gram shown in Figure 5a illustrates the eutectic composition
of 18.6 at.% Si at 363 °C. The eutectic temperatures limit
the minimum temperature for nanowire synthesis using
the mentioned processes. In addition, the high eutectic com-
position expands the molten alloy cluster at higher tem-
peratures, thus making the size of the resulting nanowire
larger than the cluster size unevenly depending upon par-
ticular conditions. Also, the high eutectic composition of
the transition-metal solute alloy limits the maximum solute

Figure 4. (a) Mass of Ge nanowires synthesized using supercritical
fluid-based technique. (b) High-resolution TEM image of a 7-nm-thick
Ge nanowire grown along the [110] direction. Micrographs courtesy of
B. A. Korgel and T. Hanrath, University of Texas, Austin, TX.

nanowires using a mixture of Si and SiO₂ powder (500 Torr,
Ar, 930–1200 °C) and germanium nanowires using a mix-
ture of Ge and GeO₂ [48]. As shown in the schematic
in Figure 3b, a quartz chamber with an axial temperature
gradient was used to evaporate the source material. The
nanowires were deposited either on the inside walls or at
the downstream end of the quartz chamber. The genera-
tion of gas-phase SiO species and the preferential depo-
sition at the tip due to thick oxide sheath around the
growing nanowire were hypothesized to be the main rea-
sons for observed nanowire growth. The resulting nanowires
contained substantial oxide sheath and also stacking errors
[49, 50]. In addition, in this mechanism, where initial nuclei
form upon condensation from the vapor phase, control over
the nanowire diameter and diameter distribution is very dif-
ficult. Silicon nanoribbons were synthesized using a similar
oxide-assisted technique [51], by evaporating SiO powder
at 1150 °C, and carrying it to a cooler, downstream end
of a tube furnace in 5% H₂/Ar (900 °C) at a total pres-
sure of 0.5 torr. The authors attributed the ribbon growth
to lower temperatures and pressures. Pan et al. reported
synthesis of semiconducting oxide nanobelts by an evapo-
ration technique [52]. In this technique, evaporation and
subsequent chemical vapor transport of metal oxide species
from powders resulted in the growth of oxide nanobelts. This
technique has been well demonstrated for zinc, tin, indium,
cadmium, and gallium oxides. Even though the resulting
beltlike morphology is interesting, the growth mechanism is
unclear at this time. At the same time, nanobelt morphol-
ogy is not entirely surprising because similar morphology,
that is, micron-scale ribbons, had been reported in whisker
literature using a similar technique [24].

Figure 5. Binary phase diagrams for (a) Au-Si and (b) Ga-Si systems.
supersaturation, necessitating precise control over metal cluster diameter for the uniform diameter distribution of nanowires. There are certain other disadvantages in using high-solubility eutectic systems. For example, nanowires will be extremely useful if electronic device components can be incorporated directly into individual nanowires. In this regard, attempts have been made to synthesize nanowire superlattices by switching the gas-phase composition during growth using transition metals. These attempts have so far been futile in achieving atomically abrupt junctions along individual nanowires [54–56]. This is expected because of the high retention of solute in the eutectic liquid alloy. In addition, there are no recent attempts or prior reports on metallic nanowire growth using transition-metal catalyst cluster-based VLS synthesis techniques. Recently, core-shell/multishell heterostructures have been generated in nanowires towards building versatile devices [57].

5. MULTIPLE NANO-METER-SCALE NUCLEI FORMATION

The Gibbs’ free energy change associated with creation of a spherical nucleus of radius \( r \) in a molten metal solvent can be written as

\[
\Delta G_T = \Delta G_V \cdot \frac{4}{3} \pi r^3 + \Delta G_s \cdot 4 \pi r^2
\]

For the critical nucleus size

\[
\frac{\partial}{\partial r} \Delta G_T = 0
\]

Therefore

\[
r^* = -\frac{2\sigma}{\Delta G_V}
\]

where \( r^* \) is the critical nucleus radius, \( \sigma \) is the interfacial energy, \( \Delta G_V \) is the volume free energy driving force (assuming an ideal solution) given by [58]

\[
\Delta G_V = -RT \ln \left( \frac{C}{C^*} \right)
\]

where \( \Omega \), \( C \), and \( C^* \) represent molar volume, activity coefficients, solute concentration within the liquid alloy and equilibrium concentration, respectively.

Thus, the critical nucleus diameter, \( d_c \), is given by

\[
d_c = \frac{4\sigma \Omega}{RT \ln \left( \frac{C^*}{C} \right)}
\]

As shown in Figure 5a, in order to isothermally nucleate Si from Au-Si solution, one needs to proceed along the path ABC. Until point B, the dissolved silicon concentration remains less than the equilibrium solubility, making super-saturation, \( C/C^* \), less than unity. A supersaturation of less than 1 will cause the nuclei to dissolve back into the solution. As the Si concentration is further increased along BC, the supersaturation exceeds unity and stable nuclei begin to form. In order to reduce the nuclei size, one needs to achieve increased supersaturation values. In the case of transition-metal–Si systems, such as Au-Si, greater than 40 at. % Si will be needed in an Au pool in order to reduce the nuclei diameters to less than 100 nm (Fig. 6). Multiple micron-thick silicon whiskers have indeed been grown from a large pool of Au [32]. However, there must be a maximum achievable supersaturation value that could be achieved in the molten metal in order to keep the ideal solution approximation valid. A similar maximum limit has been reported for undercooling in molten melts [59]. In order to satisfy such a requirement of dilute solutions, for modest dissolved Si supersaturations near unity, the nuclei diameter exceeds the molten Au-Si eutectic droplet size at typical conditions [60], causing one nanowire to grow from one Au cluster. The critical nucleus size can be reduced if the solute supersaturation can be increased, which will be possible for metals that form low solubility eutectics with other elements. Gallium, for example [61], forms a eutectic with silicon at about 29 °C with an extremely low silicon fraction of about \( 10^{-9} \) (Fig. 5b). At 1000 K, with an arbitrary dissolved silicon concentration of less than 3 at. % in gallium, Eq. (1) yields the critical nucleus diameter to be 10 nm. Figure 6 shows the variation of critical nuclei diameter as a function of dissolved silicon concentration. As can be seen, less than 10 at. % dissolved silicon at 1000 K will result in 5-nm nuclei. These multiple 5-nm nuclei can form in a large pool of gallium, and due to the low solubility and miscibility, can grow out in one dimension. Recently, the authors have demonstrated that the use of low-melting metal melts allows for formation of multiple nanometer-scale nuclei of the solute that gets dissolved from either the vapor phase or from the solid/liquid phases [62–66]. The authors exposed pools of molten metals to activated gas-phase species in a vacuum chamber in order to demonstrate this approach (see Fig. 3d). Since the nanowire diameter is not limited by the metal droplet size, the authors’ synthesis technique eliminates the absolute need for creation of nanosized droplets.

In the past, the use of low-melting metals for thermally activated silicon and germanium halides at temperatures below 900 °C was unsuccessful for Si and Ge whiskers [32]. In fact, this study noted that the use of low-melting metals required much higher temperatures than those used for transition-metal catalyst clusters, probably due to the necessary requirement of higher thermal energy for dissociation at V-L interface towards dissolution. These studies pointed out the extreme low solubility as the reason for failure.
In reality, the above results could be explained simply with low or no catalytic activity of the low-melting metals with dehydrogenation or dechlorination reactions at the vapor-liquid interface, but present as the necessary liquid solvent medium. This brings up an interesting question, that is, does one need “true” catalytic action of molten metal alloy for enhancing the dissolution?

The authors’ work on low-melting metals and plasma chemistry at temperatures lower than 500 °C illustrates that the gas-phase chemistry could directly be used for influencing dissolution kinetics at V-L interface selectively. However, due to the low solubility, the nucleation could occur spontaneously forming polycrystalline crusts on top of the metal melt [66, 67]. However, the authors found that if appropriate gas-phase composition is used to disturb the crust formation, then the spontaneity of nucleation could be contained [65]. In this case, the nanometer-scale nuclei surface-out and would grow vertically in one dimension. The surface dynamics of nanometer-scale nuclei could determine the final morphology of one-dimensional structures as illustrated by a schematic in Figure 7. Figure 8a shows a SEM image of the resulting micron-scale gallium oxide tubes. Figure 8b shows a SEM image of the base of a gallium oxide tube. A spiral pattern is clearly seen, indicating unique nuclei agglomeration. Similar results were obtained with addition of hydrogen to nitrogen plasma chemistry for direct synthesis of gallium nitride nanowires and tubes (Fig. 9).

The overall approach in utilizing the noncatalytic, low-solubility eutectics is as follows: (1) vapor-phase decomposition of gas-phase solutes at the vapor-liquid interface using activated gas-phase chemistry, (2) solute dissolution, and (3) phase segregation via nucleation. The authors have demonstrated this approach using gallium-melt with solutes such as nitrogen for the direct synthesis of nitrides, oxygen for the direct synthesis of oxides, and other elements such as silicon and oxygen for the synthesis of silica, crystalline silicon, and amorphous silicon nitride (Fig. 10) [68]. In the case of silicon, the experiments using either solid silicon in contact with a gallium melt or chemical vapor transport of silyl radicals produced nanowires [62]. Silicon nanowires synthesized using molten gallium and silane plasma produced single-crystalline nanowires with no or minimal oxide sheath (Fig. 11). However, the use of silane in hydrogen-rich gas phase with a microwave plasma activation produced a blanket deposition. Another set of experiments using chlorine along with silane in the hydrogen-rich gas phase increased the selective growth of nanowires (Fig. 10c) [68]. The plasma chemistry for radicals seems to mediate the dissolution and re-dissolution kinetics at V-L interface, thus giving a good selectivity. Also, the radical-based gas-phase chemistry seems to reduce the need for catalytic action by the liquid metal alloy cluster. This is essential if one were to take advantage of the class of low-melting metals such as Ga, In, Sn, Bi, and Al and develop a rational foundation for a new class of VLS based techniques, with much more direct control of nanostructure characteristics using gas-phase chemistry. However, this technique is in the beginning stages of development with no or few specific studies either in nanowire or whisker literature. Nevertheless, the whisker literature along with studies on nanowires are discussed in Section 6, which is divided by various groups of inorganic materials.

6. SYNTHESIS OF WHISKERS AND NANOWIRES OF INORGANIC COMPOUNDS

The composition of solid phases that precipitate from molten alloy mixtures could be predicted if pertinent liquidus-solidus phase diagrams are available for the materials of interest. The binary phase diagrams involving metals
and silicon or germanium are readily available, such as those shown in Figure 5. However, the ternary phase diagrams for a variety of inorganic compounds with the metals are not readily available and precipitation of one phase cannot be reliably predicted. In this regard, the experimental evidence for synthesizing several inorganic compounds using either transition-metal catalyst clusters or oxide clusters is necessary and is reviewed in the following sections.

Figure 9. (a) Bulk amounts of GaN nanowires synthesized by exposing a molten gallium pool to a mixture of nitrogen and hydrogen plasma. (b) A high-resolution TEM image of a 60-nm-thick, single-crystalline GaN nanowire grown along the [100] direction. (c) Micron-scale tubes of GaN with hexagonal cross section, synthesized using gallium pool and H₂/N₂ plasma.

Figure 10. (a) and (b) Crop of Si nanowires synthesized from a pool of molten gallium placed on a silicon substrate and exposed to a diluted hydrogen plasma. (c) Multiple silica nanowires synthesized by providing both silicon and oxygen solutes into molten gallium. (d) Silicon nanowires synthesized using a pool of molten gallium and silane plasma. (e) Silicon nanowires synthesized by modifying the gas-phase chemistry in order to inhibit blanket deposition. Finely ground solid NaCl powder was placed in the vicinity of the gallium pool. (f) Amorphous silicon nitride nanowires grown using molten gallium and a microwave plasma containing silane and nitrogen. Figures (c), (e), and (f) courtesy of the authors' laboratory.

6.1. Nitrides and Other Compound Semiconductors

The synthesis of metal nitride whiskers was reported as early as 1956 [69] and was carried out by either carbothermic reduction or halide reduction followed by reaction with nitrogen. The metal nitrides such as AlN [70], BN [71], HfN [72], InN [73], NbN [74], SiN [75], and TiN [76, 77] were grown using VLS type mechanism. In some of these stated metal nitrides such as InN, the respective molten metal component (In) acted as the molten impurity.

Whiskers of III-V [78–80] and II-VI [81] compound semiconductors had been studied since the first report of the VLS mechanism [25]. Barns and Ellis reported growth of micron-size rectangular blades and ribbons of GaAs and GaP by vapor transport using Au as a catalyst [78]. Curved whiskers [80] had also been observed and the reason for bending was proposed. However, all these studies about
whiskers had no control over the morphology, width, or length, and no properties were reported.

Nanowires of group-III nitrides were obtained by providing catalyst clusters such as gold and iron using laser ablation [82]. Direct reaction of Ga$_2$O$_3$ in NH$_3$ in a hot filament reactor also resulted in GaN nanowires but with a thick oxide sheath [83]. In this case, the oxide phase assisted in preserving the GaN nuclei by preferentially allowing the reduction of the \{10-11\} plane of the GaN nuclei. Similarly, the direct reaction of Ga in NH$_3$ has been demonstrated to result in GaN nanowires [84]. Similar scheme using thermal activation at high temperatures produced Si$_3$N$_4$ nanowires using Si or Si/SiO$_2$ powder in the ammonia environment [85]. The authors have also reported direct synthesis of GaN nanowires using molten gallium and nitrogen plasma [66]. Recently, AlN nanowires were synthesized by heating a mixture of Al and AlN under nitrogen atmosphere at 750–850 °C [86].

GaAs quantum wires had been fabricated by ion beam lithography [87], ion etching [88], MBE [89], and MOVPE [90] since the 1980s. But all these structures were anchored on a substrate. Hiruma et al. [91] grew 10- to 50-nm-thick GaAs needle-shaped nanowiskers on Au-coated SiO$_2$ patterned GaAs substrate using metalorganic chemical vapor deposition, but the sizes of the nanowiskers were still not controllable.

GaAs nanowiskers were synthesized by laser ablation targeting a target composed of gold and gallium arsenide (GaAs) target [39]. Similar results were obtained when oxide-containing GaAs target was ablated using a laser [92, 93]. Nanowiskers were also synthesized by evaporating the source materials at high temperature in the absence of any transition metals or oxides [94, 95]. The growth method is somewhat similar to the authors’ nitride growth technique in which arsenic gets dissolved at high temperatures directly and grows from the basal front. The solution-phase chemistry using either organic [96, 97] or aquatic environments [98–105] has also been used to synthesize III-V and II-VI compound semiconductor nanostructures.

6.2. Oxides

In 1957, Webb and Forceng reported the synthesis of microns-thick sapphire (alpha-alumina) whiskers by oxidation of molten aluminum at 1300–1450 °C in hydrogen atmosphere [106]. The resulting whiskers were alpha-Al$_2$O$_3$, and had hexagonal cross section. Globules were observed at the growing tips of the whiskers. The authors attributed the formation of the globules to the growth of the oxide-assisted growth mechanism. BeO whiskers were synthesized [107] by direct reaction of molten Be and water vapor. The authors contemplated that oxygen from the vapor phase diffuses through an oxide-coated Be globule and reacts to form BeO, which eventually diffuses to the whisker-Be interface. Following these early reports, several authors reported synthesis of other metal oxide whiskers, such as ZnO [108, 109], SnO$_2$ [110], titania [111], and copper oxide [112]. ZnO whisker growth was attributed to screw dislocation-based spiral growth model.

Following discovery of the VLS mechanism by Wagner and Ellis in 1964, there were several reports with VLS-based synthesis of oxide nanowiskers and nanowiskers. The increased realization of VLS-type whisker growth can also be attributed to timely improvement in analytical techniques such as electron microscopes, etc. Growth of tungsten oxide [113], NiO [114], cadmium oxide [115, 116], SnO$_2$ [117], alumina [118], and Cr$_2$O$_3$ [119] whiskers was attributed to VLS-type mechanism. The fact that in these reports, the droplet was not always a catalytic impurity, demands detailed investigation of the exact role of a molten droplet at the whiskers tips in enabling 1D growth.

First reports of the synthesis of truly nanoscale oxide whiskers appeared in 1996. Yumoto et al. synthesized ITO whiskers using an e-beam evaporative technique [120].
A predominantly Sn globule at the whisker tips indicated the growth mechanism to be VLS type. Amorphous silica nanowires were synthesized [121] using gas-phase SiO with cobalt as the catalyst in Ar/CO environment at 1500 °C. Since these reports, a variety of oxides have been grown in the nanoscale regime by nonequilibrium processing techniques such as laser ablation and physical vapor deposition according to either VS or molten impurity-assisted VLS mechanism. These oxides include Al₂O₃ [122], ITO [123], GeO₂ [124–126], tungsten oxide [127, 128], ZnO [129–136], MgO [135–137], gallium oxide [138–142], In₂O₃ [143], β-PbO₂ [144], Cu₂O [145], MnO₂ [146], Mn₂O₃ [147], NiO [148], CdO [149], vanadium oxide [150], and Sb₂O₃ [151]. Additionally, nanowires of TiO₂ [152], Sb₂O₃, and Sb₂O₅ [153] have been synthesized using a microemulsion method. In this method, the structure of the microemulsion defined the growth in one dimension. In a method similar to that reported for synthesis of Cu₂O nanowires [145], Cu(OH)₂ nanowires were synthesized using chemical reaction between CuSO₄ and NH₃·H₂O and NaOH [154]. Recently, the authors have demonstrated bulk synthesis of gallium oxide and silica nanostructures. These studies showed that direct reaction of oxygen and hydrogen plasma with molten gallium enabled multiple nucleation and growth of gallium oxide nanostructures [65]. Similarly, silyl and oxygen plasma over molten gallium pool resulted in multiple nucleation and growth of silica nanowires (Fig. 10c) [68].

6.3. Carbides

Carbides in general are hard, lightweight, high-temperature refractory materials with high thermal conductivity. Whiskers of carbides are interesting due to their use as reinforcing phase in ceramic or metal matrix composites.

6.3.1. Silicon Carbide

Particularly, β-SiC with zinc-blende cubic structure is the most attractive form due to its mechanical and thermal properties. Hexagonal silicon carbide (α-SiC) has also been interesting for applications in high-temperature and high-power electronics. α-SiC whiskers were first synthesized [155, 156] by accident in 1958, using vapor-phase species containing Si and C in the presence of hydrogen onto the walls of a furnace. Similarly, the hydrogen reduction of methyltrichlorosilane [157] and SiO₂–C–H₂ system at high temperatures between 1200 and 1800 °C yielded whiskers containing mixture of α-SiC and β-SiC phases [158].

Following these reports, much of the work has been focused on obtaining control over the growth of SiC whiskers for yield and phase, by using different gas-phase chemistries and different types of transition-metal or other types of catalysts. The popular chemistries for producing α-SiC whiskers included hydrogen reduction of methyltrichlorosilane [159–161]. It was established that the conditions for the formation of α-SiC were very stringent (1400–1450 °C), close to the melting point of silicon; hence molten silicon could have a role in the growth of one-dimensional α-structures. Later studies using carbothermal reduction of silicon dioxide in the presence of transition-metal catalyst clusters illustrated that SiC whisker growth follows that of VLS mechanism. Using the same reactants, β-SiC was easily synthesized in a broad range of temperature and reactant conditions. β-SiC has been synthesized by carbothermal reduction of silicon dioxide using a range of molten impurities such as Fe [162–166], Ni [167, 168], and Al [169]. In the carbothermal reduction of SiO₂, the partial pressures of SiO₂ and CO₂ were found to be important to control the morphology of the SiC whiskers produced. This prompted a number of modifications to the gas-phase composition: usage of SiO₂–CO₂ systems [170], methane [163, 171, 172] and gas-phase sources such as SiCl₄ and Si₂Cl₆ with H₂, CH₄ [173], and economical silica source materials such as agricultural wastes [174–179]. To minimize catalyst contamination in the whiskers, catalyst-free methods such as vapor-solid-assisted growth via molten fluorosilicate [180] and low-temperature self-catalyzed method for using Na as a co-reductant [181] with SiCl₄ and CCl₄ were also proposed.

The progress in SiC nanowire synthesis followed much of the whisker synthesis routes except for reducing the catalyst metal cluster sizes using laser ablation [166], arc-discharge [182], dissolving silicon into iron which remains at the base of the nanowhiskers [183], confined reactions with carbon nanotubes [184–187]. Biaxial SiC–SiO₂ nanowires [188] and co-axial helical SiC–SiO₂ nanowires [189] have also been synthesized. The β-SiC whiskers and nanowires seemed to grow preferentially in (111) direction with either transition-metal catalyst driven or oxide-assisted growth methods [190–194]. Because of this growth direction, as expected, the nanowires and whiskers contain high densities of defects such as twins.

6.3.2. Other Carbides

Other carbides of interest include boron carbide and refractory metal carbides such as ZrC, TiC, GeC, TaC, and NbC. Boron carbide filaments and whiskers were synthesized using boron trichloride, carbon tetrachloride, and metallic impurities at high temperatures (>1400 °C) on graphite substrates [195–199]. A similar gas-phase reaction of YCl₃ (Y = Zr, Ti) with hydrocarbon gas (CH₄ or C₂H₂) and H₂ was used in an argon atmosphere with Ni catalyst to obtain whiskers of ZrC and TiC [200–206] and ZrC fibers [207]. Another common mechanism used in carbides was the carbothermal reduction of oxides at temperatures of about 1500 °C using catalyst and NaCl. This method was used for whiskers of B₄C [208], NbC [209, 210], and TaC [211, 212]. Germanium carbide whiskers were reported to be synthesized from CH₃(GeH₃)₂ by forming Ge-C films on (100) Si [213].

Carbothermal reduction in absence of any catalyst by thermal evaporation of B₂O₃/C powder under argon atmosphere was used to grow crystalline nanowires of boron carbide [214]. Lithium-assisted synthesis of Al₄C₃ nanowires using solid-state reaction of Al/CLi powder at 780 °C was reported [215]. Plasma decomposition of 1,2-dicarbododecaborane (C₁₂B₁₈H₁₈) at lesser temperatures (<1200 °C) using iron clusters produced nanowires with diameters ranging from 18 to 150 nm. The tip consisted primarily of Fe₃B alloy [216]. The same method also produced amorphous B₄C nanosprings [217]. The growth of this nanospring seemed to follow a similar mechanism as that of helical growth of graphite [218]. Also, unlike nanowires, in which the catalyst diameter is larger than the diameter of
the nanowire, in this case, the catalyst diameter was smaller than the nanospring.

The synthesis of series metallic/nonmetallic carbide nanorods like TiC, NbC, Fe₃C, BCₓ, apart from SiC was demonstrated using the reaction of carbon nanotubes with gas-phase species (e.g., B₂O₃ for BCₓ) [185]. The diameter of the boron carbide nanowire was defined by the diameter of the carbon nanotubes. Other similar work was also reported for NbC, TaC, and TiC [219, 220].

7. SYNTHESIS OF METAL WHISKERS AND NANOWIRES

The vapor-phase schemes primarily involving halide reduction similar to silicon were also applied to metallic whiskers [221] as early as 1956. However, the studies are only a few with no understanding of the growth mechanism, and have primarily been confined to micron-scale whisker growth. Commonly, a metal salt was heated in a tube furnace and transported to colder regions of the furnace in a reducing environment to form whiskers. This technique has been demonstrated for whiskers of Cd [222], Cu [223, 224], Fe [225, 226], Ni [227], Sn [228], In [228], W [229], and Co-Fe [230] alloys systems. In almost all the cases, the whiskers contained a cluster of impurity elements at their tips. However, the detailed information on these clusters at the tips is missing in all the previous reports. The general consensus seems to be that these metallic whiskers grew with the help of another metallic cluster at the tip similar to the traditional VLS mechanism. Only in the case of cadmium, it was conclusively determined that Sn cluster at tip helped the growth. No reports exist on any type of demonstrations or attempts to grow metallic nanowires using the previous reports on whiskers, possibly due to lack of understanding of the growth mechanisms involved. However, Ag nanowires have been synthesized using a solution-based method [231]. A solid-liquid phase arc-discharge was used to generate a colloidal Ag solution that upon aging resulted in short Ag nanowires.

8. SYNTHESIS OF INORGANIC NANOTUBES

The graphitic sheets, when reduced to sizes of a few nanometers, fold to form both cage compounds and tubular structures. This phenomenon does not seem to be limited to carbon. Inorganic materials, both 2D layered and 3D, started to exhibit tubular and closed-shell structures when sizes are restricted to several nanometers or less [232]. However, this is not a universal phenomenon holding true for all 3D inorganic compounds; that is, nanowires of nitrides and oxides have been synthesized to sizes less than 10 nm without forming tubular structures. The nanotubular structures in these materials provide uniform surface throughout and present sites for active functionalization compared to inert surface that carbon nanotubes present in the absence of kinks or defects. In addition, the nanotubular and micro-tubular structures have an increased surface area.

The synthesis procedures for producing nanotubes can be classified into four main groups: (a) reactions with inorganic nanowires such as sulfidization during oxide nanowire growth, (b) coating or doping of carbon nanotubes either after or during growth and then removing of carbon nanotube by oxidation, (c) templating via creation of mesoporous material followed by ionic exchange, and (d) vapor-liquid-solid methods similar to those used in the production of nanowires and carbon nanotubes, that is, metallic or metal-containing compounds aiding the tip growth of nanotubes with vapor-phase precursors.

The tubular and closed-shell structures of 2D layered compounds such as disulfides of tungsten and molybdenum were reported immediately after the discovery of carbon nanotubes. The tungsten disulfide nanotubular structures were obtained by carrying out sulfidization using hydrogen disulfide during the growth of nanoscale tungsten oxide particles. The growth mechanism involves, initially, the formation of tungsten disulfide monolayer on the tungsten dioxide particle, thus forming a shell. The shell formation helps in avoiding the particle coalescence and enables 1D growth through the tip. The competing sulfidization on the shell and the tungsten oxide growth at the tip determine the length of the resulting nanotubes. This technique has been successfully applied to other sulfides [233–236] such as MoS₂. This technique primarily produced multiwalled nanotubes (Fig. 12a) but was extremely amenable for bulk manufacturing (see the reactor schematic in Fig. 3e). Similar studies of layered metal halides (NiCl₂, CdCl₂) such as nickel chloride by dehydration of the respective hydrated compounds in inert gases at different temperatures resulted in particles with fullerene-like structures [237]. Recently, the chemical transport of MoS₂ powder, with iodine as transport agent, and CₓHᵧ as growth promoter over several days in a closed ampule at 1010 K with 50 K as temperature gradient resulted in single-walled MoS₂ nanotubes, which were stabilized by intercalation of iodine in between the nanotubes [238].

The stability of BN nanotubes was first predicted [239] in 1994 and was first successfully demonstrated [240] in 1995 using an arc-discharge method. Hot pressed BN powder packed into hollow W rod served as the anode and cooled pure Cu rod served as the cathode. The tip of BN nanotube contained tungsten with boron and nitrogen, suggesting traditional VLS mechanism. Following this, several metal boride anode sources, such as HfB₂ [241], LaB₆ [242], YB₆ [243], and ZrB₂ [244] have been demonstrated for the growth of BN nanotubes. Another variation involved packing BN/B₂O₃ powder along with a small amount of transition-metal catalyst, such as Ni, Co [245], V₂O₅, MoO₃ [246], and Fe [247] along with carbon into anode or using B₂O₃, N-containing compounds reacting with NiB clusters at high temperature [248]. Boron reacts with nitrogen at the tip of the nanotube to form a sheet of BN around the catalyst. Using this method, both single-walled and multiwalled boron nitride nanotubes were obtained. The synthesis of B₄CₓNₓ nanotubes was first achieved by doping carbon nanotubes with boron and nitrogen during arc-discharge synthesis of carbon nanotubes [249]. This method has been extended by directly reacting boron oxide powder and carbon nanotubes at 1523–1623 K under a nitrogen atmosphere.
composited of surfactant and hydrolyzed vanadium oxide. The treatment of this hydrolysis product under hydrothermal conditions yielded a product of \( \text{VO}_2(\text{C}_{16}\text{H}_{21}\text{NH}_2)_{0.34} \).

Recently, gallium oxide nanotubular structures have been synthesized in the authors’ laboratory without the use of catalysts or preformed templates using multiple nucleation out of tiny gallium droplets (less than 100 nm in size) exposed to hydrogen and oxygen plasma system at temperature less than 800 °C (Fig. 12b, c). The tube walls seemed to be composed of \( \text{Ga}_2\text{O}_3 \) with layer spacing of 0.367 nm. The tubes were microns in length and the outer diameters ranged from 5 to 15 nm with inner diameters varying from 2.5 to 5 nm. In some cases, the bamboo styled folding of layers was seen. The details of growth mechanism are yet to be understood [258].

Hollow, microtubular crystals of aluminum borate have been synthesized using direct reaction of alumina with boric acid in the presence of nickel chloride [259]. Also, millimeter-long microtubular crystals of \( \beta\)-Ag\textsubscript{2}Se have been synthesized using hydrothermal reaction of silver chloride with selenium in the presence of sodium hydroxide at 155 °C for several hours [260]. However, the formation mechanism for hollow crystals is not entirely clear at this time. Nickel as a catalyst might have played a role in the formation of aluminum borate micron-scale tubular crystals. In the second case, the formation of sodium selenide needles followed by their reaction with silver might have produced the silver selenide hollow crystals.

Direct reaction of nitrogen and hydrogen plasmas with molten gallium produced hollow, tubular crystals of wurtzitic gallium nitride shown in Figure 9, in a similar fashion to gallium oxide tubular structures, shown in Figure 8. Figure 8b shows the base of a gallium oxide tube that was unanchored from the molten gallium pool. A spiral pattern represents unique manipulation of the nuclei agglomeration using activated gas-phase chemistry. Electron cyclotron resonance plasma containing hydrogen and nitrogen [261] was used at 50 mTorr and 900 °C. The external faceting of tubes varied from hexagonal to star-hexagonal (not shown). Though there have been theoretical studies that predict the possibility of GaN nanotubes [262], it has not yet been experimentally demonstrated.

9. SUMMARY

The interest in one-dimensional, nanoscale materials such as nanowires and nanotubes has led in the recent past to intense research towards developing various synthesis methods for producing bulk amounts of these materials. The prior work on whisker technology has provided a rich amount of literature on various inorganic materials synthesis at micron scale. The synthesis methods used for whiskers seemed to be divided into two types of mechanism, that is, transition-metal cluster catalyzed VLS and oxide-assisted growth methods. These two techniques have been primarily used for micron-scale whisker synthesis of several inorganic materials, including elemental semiconductors, metals, and compounds. The whisker size in both these techniques is controlled by the size of the cluster that could be transition-metal cluster or vapor condensed suboxide cluster. The clusters of sizes greater than 0.2 μm are thermodynamically
easier to form and control. In order to produce nanoscale wires, several research groups focused their efforts on how to create nanoscale clusters and disperse them on a support. The most notable techniques have been laser ablation, evaporation, and supercritical fluid processing.

Recently, another technique was demonstrated with nucleation and growth of multiple nanowires from pools and thin films of low-melting metals. In this technique, gas-phase chemistry directly controlled the solute dissolution at the V-L interface, and eliminated the need for creation of nanosized clusters. This is a relatively unexplored technique and holds promise towards synthesis of nanostructures with diameters below 5 nm, which is necessary for exploring new phases in several inorganic materials. For example, the synthesis of 1D nanostructures at extremely small scales has allowed discovery of new phases for several inorganic compounds.

At this time, the availability of inorganic nanostructures is limited to only a few laboratories. This has hindered our understanding of the commercial applicability of these nanostructures. Thus, obtaining precise control over the size, size distribution, and morphology of the nanostructures is necessary for scale-up into bulk manufacturing.

GLOSSARY

Catalyst An impurity confined to nanometer-scale dimensions to selectively enhance the growth of material, thus providing one-dimensionality to the growing structure.

Critical nuclei A nucleus is defined as a thermodynamically stable cluster of molecules. The aggregates smaller than the critical nucleus size will redissolve, and the aggregates larger than the critical nucleus will continue to grow.

Eutectic A eutectic alloy is a mixture of substances having a minimum melting point. For a binary system, the eutectic temperature is lower than the melting points of either of the components.

Nanometer A unit of spatial measurement that is one-billionth of a meter (10⁻⁹ m).

Nanotube A hollow structure with lengths exceeding the diameter by at least a factor of 100 with the diameters smaller than 100 nm. The walls of the tubular structure may consist of multiple layers of the comprising material.

Nanowire A solid structure with lengths exceeding the diameter by at least a factor of 100 with the diameters smaller than 100 nm.

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Synthesis of Inorganic Nanowires and Nanotubes


