# Nanowire Research and Development: A Survey of Selected Research from 2001 to 2005

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#### Overview

This paper presents an overview of recent and current nanowire research efforts worldwide. We examine methods of nanowire synthesis, types of materials used, and applications associated with nanowire research. A brief survey of global activity in nanowire research is presented, as well.

For the purposes of this survey, a nanowire may be defined as a structure with a diameter/width on the nanometer scale and a high aspect ratio. This means that the diameter can range from tenths of nanometers to several hundred nanometers, where a nanometer is  $10^{-9}$  meters (approximately 10 atomic diameters), and the aspect ratio (ratio of the length to the width/diameter) is on the order of 10 or more.

Data for this survey was collected through a review of scientific literature that appeared from 2001-2005 in publications such as IEEE journals, Nature and Science, and publications from the American Institute of Physics. Due to the extraordinarily large number of research papers containing the keyword "nanowire," only selected search results were included. The papers included in this survey were selected to highlight the diversity of R&D in nanowire synthesis, materials, and applications. The papers are intended to be qualitatively, but not necessarily quantitatively, representative of the level of activity in any particular area.

The selected research papers, in combination with a search of the Delphion patent database, were the basis of the brief survey of global nanowire research which concludes this report.

#### **Nanowire Synthesis**

Many of the papers included in this survey concentrated on methods or materials used to synthesize nanowires. Most nanowire synthesis occurs via Vapor-Liquid-Solid (VLS) processes. VLS processes use a liquid catalyst to draw components out of a vapor phase and deposit them in a solid phase. While terms such as "laser ablation" and "chemical vapor deposition" may often be used to describe the synthesis technique used in a particular experiment, this commonly refers only to the means by which the vapor phase is produced or transported. For example, laser ablation uses a laser to vaporize a source material, forming the vapor phase that is absorbed and later deposited by the catalyst droplet as the nanowire grows.

Silicon nanowires often are synthesized through VLS processes [1-3]. Specifically, a substrate is coated with gold nanoparticles and then heated until the gold melts and forms tiny droplets. A silicon-containing vapor, typically silane, or SiH<sub>4</sub>, is then passed over the substrate. At the vapor-gold interface, silicon atoms are stripped from the silane and are absorbed into the nanoparticles. When the saturation limit of silicon in gold has been reached, the silicon precipitates out of the droplet onto the substrate. This precipitate builds up and lifts the catalyst away from the substrate, giving rise to a vertical, wire-like growth. The diameter of the growth is directly related to the diameter of the catalyst droplet.

The second most common method of nanowire synthesis can be classified as a template growth process. Template growth simply means that nanowires are grown within or on top of another nanometer-scale structure. A vapor or liquid phase is introduced and, through a chemical reaction or cooling process, solidified, with the solid phase assuming the physical size and shape of the surrounding or underlying material. The substrate is often etched away following deposition, leaving behind only the nanowires. Electrochemical deposition [4-7] and injection of a molten phase under pressure [8-11] are two commonly used template growth methods.

Anodic alumina is commonly used as a substrate material in template growth [12-14], both because it is relatively inert and because the size, shape, and distribution of its pores can be well controlled, thus controlling the size of the nanowires. Ion-track-etched polymer membranes also can be used as substrate materials [15-17]. Nanowires have been formed, as well, by coating or filling nanotubes [18-20] and other nanometer-scale fibers [21]. It should be noted that template growth and VLS growth are not mutually exclusive; catalytic nanoparticles can be introduced into a porous template to combine the two processes [22], but this is not common.

Some template growth techniques use topographical features such as ridges or trenches to expose specific areas of the substrate to nanowire growth. Some nanowire materials show a preference for formation along exposed "steps" in the atomic structure of a substrate [23, 24]. Another technique uses trenches in conjunction with low-angle deposition processes (such as sputtering and evaporation) to form dense arrays of fine, highly-organized nanowires [25]. These techniques are noteworthy in that they combine fabrication with organization, eliminating the need to manipulate individual nanowires.

Beyond VLS and template growth processes, nanowires can be synthesized through solution chemistry [20, 26], lithography [27-29], or even extruded or drawn [30, 31]. Many of the synthesis processes, including VLS and template growth, build up the nanowires atom-by-atom, often resulting in nanowires with well-defined crystallographic structures and preferred growth directions [22, 32-34].

#### Nanowire Physical Characteristics and Material Composition

The smallest reported nanowires found in this survey were silver nanowires of 0.4 nanometer (nm) diameter with lengths of approximately 750 nm [20]. These nanowires were synthesized by filling a calyx[4]hydroquinone nanotube array template in a solution-based electrochemical deposition process. Nanowires of 0.5 nm diameter have been synthesized from silicon [35], and 10,12-nonacosadiynoic acid has been polymerized through electrical stimulation with a scanning-tunneling-microscope (STM) tip to produce wire-like structures of 1 nm width. Most nanowire research appears to focus on nanowires from 10 to 100 nm in diameter.

In order to determine which nanowire materials are being investigated, literature searches were performed using two online resources, the American Institute of Physics Scitation, http://scitation.aip.org, and the ISI Web of Knowledge, http://www.isiknowledge.com. The searches were performed using the term "\* nanowire," where "\*" was the material or element of interest. Search results were limited to papers published between 2001 and 2005 for Scitation, and within the last 5 years for Web of Knowledge (WOK). "Nanowire" alone returned 834 and 1958 hits with Scitation and WOK, respectively, while silicon was the most popular material with 84 and 79 hits. Gold nanowires produced 47/36 hits, while silver (18/24), copper (22/13), and nickel (17/12) were also popular nanowire materials. Further generalizing search terms to metallic and semiconducting nanowires produced 81/58 and 152/32 references, respectively. The full list of materials and search terms can be found in Table 1 in the Appendix.

#### Applications

In addition to variations in size and material, nanowire research also spans a wide range of application areas. Many researchers have investigated the optical properties of

nanowires and nanowire arrays, with studies ranging from the infrared absorption of bismuth nanowires [36] to green light emission from ZnSe nanowires [37]. Nanowire lasers have been demonstrated [38, 39], as have subwavelength optical waveguides using nanoribbons (nanowires with rectangular cross sections). Silver nanowires have been used to create a material that exhibits negative index of refraction-like properties in the near-infrared [40].

The electrical properties of nanowires also are heavily studied. Their small size and often their high electrical conductivity make nanowires very attractive for applications in nanoelectronics [41], where nanowire transistors [42-46] of various materials have been demonstrated by a number of research groups. The thermoelectric properties of a range of nanowire materials, including bismuth alloys [8, 47-48] and skutterudites [26, 49], also have undergone intensive research. Some nanowires and nanowire composites even exhibit superconducting properties [17, 50, 51].

Sensing is yet another area in which the application of nanowires is likely to have a great impact. Nanowire sensors have been demonstrated that can detect the presence of many gases, including oxygen [52], hydrogen [53], NO<sub>2</sub> [54], and ammonia [55], at very low concentrations. Nanowires also have been used to detect ultraviolet light [56], changes in pH [57], and the presence of low-density lipoprotein cholesterol [58]. These sensors generally function by measuring changes in the electrical or physical properties of the nanowires in the presence of the target analyte. The sensing capabilities of nanowires may be enabled by selective doping or by surface modifications that enhance their affinities for certain substances.

A major hurdle facing the developers of integrated nanowire systems is that of organizing, manipulating, or otherwise controlling the placement of large numbers of nanowires. This problem has been addressed by research groups that can grow nanowires in precisely controlled locations, either by using tiny resistive heating elements to stimulate local nanowire growth [59] or by providing energetically-favorable growth locations [60]. Other research groups have turned to post-synthesis manipulation using alternating electrical fields [61] or physical confinement [62].

Some purely theoretical research was also represented in the papers surveyed. This research included topics such as predicting the physical and electrical properties of

nanowires [63-65] and determining the thermodynamic limit to the smallest diameter nanowire that can be grown through VLS processes [66].

#### **Global Research Trends**

Based on the papers selected for this review, the United States appears to have the most well-developed nanowire research efforts, accounting for roughly 100 of the 190 papers reviewed. Among the Asian countries, China had approximately 30 papers, followed by Korea and Japan with just under 10 papers each. Belgian research efforts were on par with the Japanese, and scattered papers were found from a number of other countries. This information is summarized in Table 2 in the Appendix. For papers in which the authors were from multiple countries, the country of the first listed author was used.

A separate search was conducted, using Thomson Scientific's Delphion patent database, for patents concerning nanowires. Specifically, the INternational PAtent DOCumentation Center (INPADOC) was searched for nanowire patents and the countries where those patents were held. Corresponding to its lead in number of research papers, the United States also leads in nanowire-related patents, with 177 patents within the INPADOC database. Japan is in second place, credited with 28 nanowire-related patents. More complete country and patent data can be found in Table 3 in the Appendix.

#### Summary

There is great interest, both in the United States and abroad, in research into nanowires and their applications. Over the past few years significant progress has been made in investigations into the synthesis of nanowires of various materials, as well as their application to nanometer-scale electronics, optical devices and sensing systems. The next few years should see the transition from nanowire synthesis to nanowire production and incorporation into nano-enabled devices and systems.

## Appendix

### Table 1: Nanowire materials as found through AIP Scitation

## and ISI Web of Knowledge

	"* nanowire" search hits	
	American	
	Institute of	ISI Web of
''*'' = Material	Physics, Scitation	Knowledge
Nanowire	834	1958
Silicon	89	79
Gold	47	36
Copper	22	13
Silver	18	24
Nickel	17	12
Cobalt	15	6
Bismuth	10	10
Platinum	9	6
Iron	9	3
Germanium	8	3
Boron	6	8
Silica	6	7
Lead	4	4
Indium	3	2
Aluminum	3	1
Diamond	2	6
Palladium	2	4
Tellurium	2	3
Tin	2	1
Zinc	2	1
Gallium	2	0
Selenium	0	1
Tungsten	0	0
Cadmium	0	0
Molybdenum	0	0
Potassium	0	0
Erbium	0	0
Vanadium	0	0
Semiconduct*	152	32
Metal*	81	58

	No popor	No. papers found
	No. papers	
<b>a</b>	reviewed (see	Knowledge
Country	spreadsheet)	address search
USA	98	678
China	28	578
Korea	9	108
Belgium	8	17
Japan	8	225
Germany	6	114
Spain	4	24
Australia	3	10
France	3	56
Switzerland	3	13
Ireland	2	31
Russia	2	15
Sweden	2	36
Argentina	1	3
Austria	1	5
Brazil	1	20
Canada	1	36
The Netherlands	1	16
India	1	34
Israel	1	9
Italy	1	24
Moldova	1	6
Singapore	1	29
Slovenia	1	5
Taiwan	1	54
Mexico	0	10
No Country Listed	2	
Total	190	2156

Table 2: Nanowire research, by country.

**Note:** This table presents two views of the worldwide distribution of nanowire research publications. The center column sorts the publications reviewed for this paper by country of origin. The right-most column presents the results of a search performed through the ISI Web of Knowledge website by using the search term "nanowire" and putting the country in the "Address" field. The total number of papers found by searching the ISI site by country is more than the number of papers found by searching for "nanowire," but each paper may have multiple authors from more than one country.

Table 3: Nanowire-related patents, by country.

As Found in INPADOC\* Using the Delphion Patent Database

Country	No. Nanowire Patents
United States	177
Japan	28
China	14
Canada	8
Korea	7
Germany	6
Taiwan	3
United Kingdom	1
Russia	1
Total	245

**Note:** INPADOC = The INternational PAtent DOCumentation Center, produced by the European Patent Office (EPO), which contains patent data of 71 organizations, including the EPO and World Intellectual Property Organization (WIPO)

#### References

[1] Qi, J., Belcher, A., & White J. (2003). Spectroscopy of individual silicon nanowires. *Applied Physics Letters*, *82*(16), 2616-2618.

[2] Englander, O., Christiansen, D., & Lin L. (2003). Local synthesis of silicon nanowires and carbon nanotubes on microbridges. *Applied Physics Letters*, *82*(26), 4797-4799.

[3] Sunkara, M., Sharma, S., & Miranda R. (2001). Bulk synthesis of silicon nanowires using a low-temperature vapor-liquid-solid method. *Applied Physics Letters*, 79(10), 1546-1548.

[4] Vila, L. et al. (2002). Transport and magnetic properties of isolated cobalt nanowires. *IEEE Transactions on Magnetics*, *38*(5), 2577-2579.

[5] Guittienne, P. et al. (2001). Switching time measurements of current-induced magnetization reversal. *IEEE Transactions on Magnetics*, *37*(4), 2126-2128.

[6] Nielsch, K. et al. (2002). Switching behavior of single nanowires inside dense nickel nanowire arrays. *IEEE Transactions on Magnetics*, *38*(5), 2571-2573.

[7] Tian, M. et al. (2003). Synthesis and characterization of superconducting singlecrystal Sn nanowires. *Applied Physics Letters*, *83*(8), 1620-1622.

[8] Lin, Y. et al. (2002). "Experimental investigation of thermoelectric properties of Bi<sub>1-x</sub>Sb<sub>x</sub> nanowire arrays." 21st International Conference on Thermoelectronics.

[9] Cronin, S. et al. (2002). "Thermoelectric transport properties of single bismuth nanowires." 21st International Conference on Thermoelectronics.

[10] Cao, H. et al. (2003). Room-temperature ultraviolet-emitting  $In_2O_3$  nanowires. *Applied Physics Letters*, 83(4), 761-763.

[11] Vedernikov, M. et al. (2001). "Experimental study of thermoelectric properties of InSb nanowires." 20th International Conference on Thermoelectronics.

[12] Black, M. et al. (2002). Infrared absorption of bismuth nanowires resulting from quantum confinement. *Physical Review B*, 65,195417-1.

[13] Nielsch, K. et al. (2001). Hexagonally ordered 100 nm period nickel nanowire arrays. *Applied Physics Letters*, *79*(9), 1360-1362.

[14] Lei, Y., & Zhang, L. D. (2001). Fabrication, characterization, and photoluminescence properties of highly ordered TiO<sub>2</sub> nanowire arrays. *J. Mater. Res.*, *16*(4), 1138-1144.

[15] Molares, M. E. et al. (2003). Electrical characterization of electrochemically grown single copper nanowires. *Applied Physics Letters*, *82*(13), 2139-2141.

[16] Yu, S. et al. (2003). Nano wheat fields prepared by plasma-etching gold nanowirecontaining membranes. *Nano Letters*, *3*(6), 815-818.

[17] Tian, M. et al. (2003). Synthesis and characterization of superconducting singlecrystal Sn nanowires. *Applied Physics Letters*, *83*(8), 1620-1622.

[18] Mickelson, W. et al. (2003). Packing  $C_{60}$  in boron nitride nanotubes. *Science*, 300, 467-469.

[19] Yin, L. W., Bando Y., Zhu Y. C., & Li, M. S. (2004). Controlled carbon nanotube sheathing on ultrafine InP nanowires. *Applied Physics Letters*, *84*(26), 5314-5316.

[20] Hong, B. et al. (2001). Ultrathin single-crystalline silver nanowire arrays formed in an ambient solution phase. *Science*, *294*, 348-351.

[21] Kumzerov, Y. (2002). "Transport properties of nanostructures within porous materials." 21st International Conference on Thermoelectronics.

[22] Zhang, J. et al. (2001). Fabrication and photoluminescence of ordered GaN nanowire arrays. *Journal of Chemical Physics*, *115*(13), 5714-5717.

[23] Li, J. et al. (2001). Spontaneous formation of ordered indium nanowire array on Si(001). *Applied Physics Letters*, *79*(17), 2826-2828.

[24] Gurlu, O. et al. (2003). Self-organized, one-dimensional Pt nanowires on Ge(001). *Applied Physics Letters*, *83*(22), 4610-4612.

[25] Melosh, N. et al. (2003). Ultrahigh-density nanowire lattices and circuits. *Science*, *300*, 112-115.

[26] Hu, X. et al. (2001). "Synthesis and growth mechanism of NaFe<sub>4</sub>P<sub>12</sub> nanowires."20th International Conference on Thermoelectronics.

[27] Nielsch, K. et al. (2003). "Nickel nanowire arrays based on imprint lithography." Magnetics Conference.

[28] Matsukawa, T. et al. (2001). "Silicon nanowire memory using surface charging and its operation analysis by scanning Maxwell-stress microcopy (SMM)." International Semiconductor Device Research Symposium.

[29] Doherty, L., Hongbing, L., & Milanovic, V. (2003). "Application of MEMS technologies to nanodevices." Proceedings of the 2003 International Symposium on Circuits and Systems.

[30] Cheng, Y. et al. (2002). Stress-induced growth of bismuth nanowires. *Applied Physics Letters*, *81*(17), 3248-3250.

[31] Tong, L. et al. (2003). Subwavelength-diameter silica wires for low-loss optical wave guiding. *Nature*, *426*, 816-819.

[32] Duan, X. et al. (2003). Single-nanowire electrically driven lasers. *Nature*, *421*, 241-245.

[33] Molares, M. E. et al. (2003). Electrical characterization of electrochemically grown single copper nanowires. *Applied Physics Letters*, *82*(13), 2139-2141.

[34] Zhang, D. et al. (2003). Electronic transport studies of single-crystalline  $In_2O_3$  nanowires. *Applied Physics Letters*, 82(1), 112-114.

[35] Ma, D. et al. (2003). Small-diameter silicon nanowire surfaces. *Science*, 299, 1874-1877.

[36] Black, M. et al. (2002). Infrared absorption in bismuth nanowires resulting from quantum confinement. *Physical Review B*, *65*(195417-1).

[37] Xiang, B. et al. (2003). Green-light-emitting ZnSe nanowires fabricated via vapor phase growth. *Applied Physics Letters*, *82*(19), 3330-3332.

[38] Johnson, J. et al. (2002). Single gallium nitride nanowire lasers. *Nature Materials*, *1*, 106-110.

[39] Kong, Y. C. et al. (2001). Ultraviolet-emitting ZnO nanowires synthesized by a physical vapor deposition approach. *Applied Physics Letters*, *78*(4), 407-409.

[40] Hu, X., & Chan, C. T. (2004). Photonic crystals with silver nanowires as a near-infrared superlens. *Applied Physics Letters*, *85*(9), 1520-1522.

[41] Cui, Y., & Lieber, C. (2001). Functional nanoscale electronic devices assembled using silicon nanowire building blocks. *Science*, *291*, 851-853.

[42] Kang, D. & Park, W. (2004). "Change in electrical characteristics of gallium phosphide nanowire transistors under different environments." 4th IEEE Conference on Nanotechnology.

[43] Chen, J., Klaumunzer, S., Lux-Steiner, M. C., & Konenkamp, R. (2004). Vertical nanowire transistors with low leakage current. *Applied Physics Letters*, 85(8), 1401-1403. [44] Wang, D. et al. (2003). Germanium nanowire field-effect transistors with SiO<sub>2</sub> and high- $\kappa$  HfO<sub>2</sub> gate dielectrics. *Applied Physics Letters*, 83(12), 2432-2434.

[45] Cui, Y. et al. (2003). High performance silicon nanowire field effect transistors. *Nano Letters*, *3*(2), 149-152.

[46] Duan, X. et al. (2003). High-performance thin-film transistors using semiconductor nanowires and nanoribbons. *Nature*, *425*, 274-278.

[47] Li, D. et al. (2002). "Measurements of Bi<sub>2</sub>Te<sub>3</sub> nanowire thermal conductivity and Seebeck coefficient." 21st International Conference on Thermoelectronics.

[48] Huber, T., Constant, P. & Celestine, K. (2001). "Magnetoresistance and thermopower of ultrafine bismuth nanowire arrays." 20th International Conference on Thermoelectronics.

[49] Wang, J. et al. (2001). "Progress in skutterudite-based thermoelectric materials." 20th International Conference on Thermoelectronics.

[50] Michotte, S., Matefi-Tempfli, S., & Piraux, L. (2003). Current-voltage characteristics of Pb and Sn granular superconducting nanowires. *Applied Physics Letters*, *82*(23), 4119-4121.

[51] de Horne, F., Piraux, L., & Michotte, S. (2005). Fabrication and physical properties of Pb/Cu multilayers superconducting nanowires. *Applied Physics Letters*, 86(152510-1).
[52] Li, Q. H. et al. (2004). Oxygen sensing characteristics of individual ZnO nanowire transistors. *Applied Physics Letters*, 85(26), 6389-6391.

[53] Yun, M. (2004). Electrochemically grown single nanowire sensors. *Proceedings of the SPIE*, 5593, 200-206.

[54] Zhang, D. et al. (2003). "Gas sensing properties of single-crystalline indium oxide nanowires." Third IEEE Conference on Nanotechnology.

[55] Zhang, D. et al. (2003). Doping dependent NH<sub>3</sub> sensing of indium oxide nanowires. *Applied Physics Letters*, *83*(9), 1845-1847.

[56] Kind, H. (2002). Nanowire ultraviolet photodetectors and optical switches. *Advanced Materials*, *14*(2), 158-160.

[57] Cui, Y., Wei Q., Park, H., & Lieber, C. (2001). Nanowire nanosensors for highly sensitive and selective detection of biological and chemical species. *Science*, *293*, 1289-1292.

[58] Li, C. et al. (2003). "Detection of biomolecules using  $In_2O_3$  nanowires." Third IEEE Conference on Nanotechnology,

[59] Englander, O., Christiansen, D., & Lin L. (2003). Local synthesis of silicon nanowires and carbon nanotubes on microbridges. *Applied Physics Letters*, 82(26), 4797-4799.

[60] Alaca, B. E., Sehitoglu, H., & Saif, T. (2004). Guided self-assembly of metallic nanowires and channels. *Applied Physics Letters*, *84*(23), 4669-4671.

[61] Razavi, B. et al. (2001). "Electric field assisted nanoparticle assembly." International Semiconductor Device Research Symposium.

[62] Whang, D., Jin S., Wu, Y., & Lieber, C. (2003). Large-scale hierarchical organization of nanowire arrays for integrated nanosystems. *Nano Letters*, *3*(9), 1255-1259.

[63] Barnard, A., Russo S., & Snook L. (2003). Ab initio modeling of diamond nanowire structures. *Nano Letters*, *3*(10), 1323-1328.

[64] Wang, J., Polizzi, E., & Lundstrom, M. (2003). "A computational study of ballistic silicon nanowire transistors." IEEE International Electron Devices Meeting.

[65] Guo, J. et al. (2003). Electrostatics of nanowire transistors. *IEEE Transactions on Nanotechnology*, 2(4), 329-334.

[66] Tan, T., Li, N., & Gosele U. (2003). Is there a thermodynamic size limit of nanowires grown by the vapor-liquid-solid process?. *Applied Physics Letters*, *83*(6), 1199-1201.