

# Nanotechnology

First version of the PDF edition of the Opensource Handbook of Nanoscience and Nanotechnology  
Containing only the more than 25% finished sections.

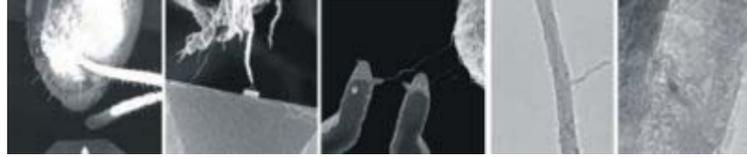
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## The Opensource Handbook of Nanoscience and Nanotechnology

Nanotechnology and nanoscience is about controlling and understanding matter on the sub-micrometer and atomic scale.



This wikibook on nanoscience and nanotechnology gathers information about the various tools, methods and systems to provide students, researchers and everyone else an open-source handbook and overview guide to this vast interdisciplinary and expanding field - a book that can be adjusted as new things appear and improved by you!

- [Google Search in this book](http://www.google.com/custom?sa=Google+Search&domains=en.wikibooks.org/wiki/Nanotechnology&sitesearch=en.wikibooks.org/wiki/Nanotechnology) (<http://www.google.com/custom?sa=Google+Search&domains=en.wikibooks.org/wiki/Nanotechnology&sitesearch=en.wikibooks.org/wiki/Nanotechnology>)
- There is a related Opensource Handbook on Microtechnology
- Nanotechnology Demonstration Experiments in the Wikibook on Science Shows
- [Wikimedia Commons Nanotechnology](#) with files for this book
- Latest major additions in: AFM and Electron microscopy
  
- This book is under construction - hope you will join the effort to create it!

### Brief introductions to the parts

to give a quick overview

### Detailed descriptions

(■-icons are individual web pages; Numbers are sub-sections)

#### Part 1: INTRODUCTION

Why is nanotechnology such a 'hot' subject - and is it more hype than substance? This part gives a brief introduction to the visions of nanotechnology and why so many people are working on it around the world. To help set a perspective there are overview tables with timelines, length scales and information resources.

■ Perspective	■ Overviews	■ About the Book	■ Reaching Out
<ol style="list-style-type: none"> <li>1. A perspective on Nanotechnology</li> <li>2. Nanocomponents, Tools, and Methods</li> <li>3. Hot and hyped</li> </ol>	<ol style="list-style-type: none"> <li>1. Internet Resources</li> <li>2. Journals</li> <li>3. Nanotech Products</li> <li>4. A nano-timeline</li> <li>5. A nano-scale overview</li> </ol>	<ol style="list-style-type: none"> <li>1. Vision</li> <li>2. How to contribute</li> <li>3. History</li> <li>4. Authors and Editors</li> <li>5. Support and Acknowledgments</li> <li>6. How to Reference this Book</li> </ol>	<ol style="list-style-type: none"> <li>1. Teaching Nanotechnology</li> <li>2. Outreach projects</li> <li>3. Demonstration experiments</li> </ol>

#### Part 2: SEEING 'NANO'

Microscopes allows us to probe the structure of matter with high spatial resolution, making it possible to see for instance individual atoms with tools such as the scanning tunneling microscope, the atomic force microscope, and the transmission electron microscope. With the related spectroscopic methods, we can study the energy levels in nanosystems. This part gives an overview of the tools and methods used in microscopy and spectroscopy of nanostructures.

■ Optical Methods	■ Electron Microscopy	■ Scanning probe microscopy	■ Additional methods
<ol style="list-style-type: none"> <li>1. Optical Microscopy</li> <li>2. Confocal Microscopy</li> <li>3. X-ray Microscopy</li> <li>4. UV/VIS Spectrometry</li> <li>5. Infrared Spectrometry (FTIR)</li> <li>6. Terahertz Spectroscopy (THz)</li> <li>7. Raman Spectroscopy</li> <li>8. Surface Enhanced Raman Spectroscopy (SERS)</li> </ol>	<ol style="list-style-type: none"> <li>1. Scanning electron microscopy (SEM)</li> <li>2. Transmission electron microscopy (TEM)</li> <li>3. Electron energy loss spectroscopy (EELS)</li> <li>4. Electron Probe Micro Analysis or Energy Dispersive X-ray spectroscopy (EDS/EDX)</li> <li>5. Electron diffraction</li> <li>6. Electron Holography</li> <li>7. Electron Tomography</li> </ol>	<ol style="list-style-type: none"> <li style="color: red;">■ Atomic force microscope (AFM)</li> <li style="color: red;">■ Scanning tunneling microscopy (STM)</li> <li style="color: red;">■ Scanning Near-field optical microscopy (SNOM)</li> </ol>	<ol style="list-style-type: none"> <li>1. Low energy electron diffraction (LEED)</li> <li>2. Reflection High Energy Electron diffraction (RHEED)</li> <li>3. X-ray Spectroscopy and diffraction</li> <li>4. Nuclear Magnetic Resonance (NMR)</li> <li>5. Electron Paramagnetic Resonance (EPR /ESR)</li> <li>6. Auger electron spectroscopy (AES)</li> <li>7. Mössbauer spectroscopy</li> </ol>

#### Part 3: PHYSICS -ON THE NANOSCALE

On the nanoscale force that we in everyday life do not consider strong, such as contact adhesion, become much more important. In addition, many things behave in a quantum mechanical way. This chapter looks into the scaling of the forces and fundamental dynamics of matter on the nanoscale.

■ Intro to Nanophysics	■ Modelling Nanosystems	■ Physical Chemistry of Surfaces	■ Background material
<ol style="list-style-type: none"> <li>1. Scaling laws</li> <li>2. Quantized Nano Systems</li> <li>3. Bulk matter and the end of bulk: surfaces</li> </ol>	<ol style="list-style-type: none"> <li>1. The Schrödinger equation</li> <li>2. Hartree-Fock (HF) or self-consistent field (SCF)</li> <li>3. Density Functional Theory (DFT)</li> <li>4. Transport phenomena</li> </ol>	<ol style="list-style-type: none"> <li>1. Hydrophobic and hydrophilic surfaces</li> <li>2. Surface Energy</li> <li>3. Surface Diffusion</li> <li>4. Mass transport in 1, 2, and 3D</li> </ol>	<ol style="list-style-type: none"> <li>1. Dispersion relations</li> </ol>

#### Part 4: NANOMATERIALS

Many unique nanostructured materials have been made, such as carbon nanotubes that can be mechanically stronger than diamond. This part provides an overview of nanoscale materials such as carbon nanotubes, nanowires, quantum dots and nanoparticles, their unique properties and fabrication methods.

■ Overview of Production methods	■ Semiconducting Nanostructures	■ Metallic Nanostructures	■ Organic Nanomaterials
<ol style="list-style-type: none"> <li>1. Commercial suppliers of nanomaterials</li> </ol>	<ol style="list-style-type: none"> <li>1. Buckyballs - carbon 60</li> <li>2. Carbon nanotubes</li> <li>3. Semiconducting nanowires</li> <li>4. Semiconducting nanoparticles</li> </ol>		

## Part 5: NANOSYSTEMS

To understand the novel possibilities in nanotechnology, this part gives an overview of some typical nanoscale systems - simple experimental devices that show unique nanoscale behavior useful in for instance electronics.

▣ **Nanoelectronics**

1. Diffusive and Ballistic Electron Transport
2. Double barrier systems
3. Moletronics

▣ **Nano-optics**▣ **Nanomechanics**

1. Mechanics of beams and cantilevers
2. The harmonic oscillator

▣ **Nanofluidics**

## Part 6: NANOENGINEERING

Combining nanodevices into functional units for real life application is a daunting task because making controlled structures with molecularly sized components requires extreme precision and control. Here we look at ways to assemble nanosystems into functional units or working devices with top-down or bottom-up approaches.

See also the Wikibook on Microtechnology which contains information about many fabrication and processing details.

▣ **Top-down and bottom-up approaches**

1. Microfabrication made smaller

▣ **Self assembly**

1. Selfassembled monolayers
2. Bottom-up chemistry
3. Molecular engineering

▣ **Lithography**

1. Electron beam lithography (EBL)
2. Nano imprint lithography (NIL)
3. Focused Ion Beam (FIB)

▣ **Nanomanipulation**

1. AFM manipulation
2. STM manipulation
3. In-situ SEM manipulation
4. In-situ TEM manipulation

▣ Electron Beam Induced Deposition (EBID or EBD)

## Part 7: NANO-BIO PRIMER

Your body is based on a fantastic amount a biological nanotechnology happening right now in each of your body's cells, that has evolved to an awesome level of complexity. Much of nanotechnology is aimed at bio-applications, such as bio-sensors and biologically active nanoparticles for medical therapy or targeting cancer. This part is an introduction to this cross-disciplinary field.

▣ **Nano-bio Primer**

1. Biological building blocks
2. Lengths and masses
3. Cells
4. Virus
5. Bacteria
6. The body

▣ **Biosensors**

1. Typical applications and Analytes
2. Sensor principles

▣ **Targeting Diseases**

1. Magnetic Resonance Imaging (MRI)
2. Cancer

## Part 8: ENVIRONMENTAL NANOTECHNOLOGY

In the beginning researchers were very enthusiastic about the visions of nanotechnology, but in the public there was a natural worry about the environmental issues of nanotechnology. This area is being increasingly brought into focus.

▣ **Health effects of nanoparticles**

1. Particles around us
2. Characterizing Particles
3. Biodistribution
4. Particles in nature
5. Sooth
6. Asbestos
7. Silicate particles

▣ **Environmental Impact**

1. Ecological Footprints
2. Nanostructure Lifecycles

▣ **Nano and Society**

1. The Nano-hype
2. The Nano-scare
3. Funding, science and the political aspects



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# Nanotechnology/Introduction

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## 1 Introduction to Nanotechnology

Nanotechnology encompasses numerous fields of the natural sciences - broadly speaking anything with a dimension under 100nm can be termed 'nanostructured' and these days it also seems that anything that fit that definition *will* be termed nanostructured.

The vision of nanotechnology to control matter on the atomic scale both provides hopes for huge technological advances providing cures for diseases and high increases in the performance of the technology we use around us - and on the other hand scares us with still rather unknown health effects of many new types of nanoparticles and science fiction style 'Nanites' that will reproduce and take over the world. 'Nanites' seems a very distant possibility - and before anyone would even come close to create anything 'nano' that could reproduce in a very controlled environment, technology itself will probably have started moving in quite a new direction for a new 'aera'.

This opensource handbook on nanoscience and nanotechnology is divided into sections that each deal with a 'field' of nanotechnology and describes this in greater detail as you go into subsections.

- **Part 1: INTRODUCTION** - giving a general overview
- **Part 2: SEEING 'NANO'** - how to observe what is going on on the nanoscale
- **Part 3: PHYSICS -ON THE NANOSCALE** - how do things move and what are the important forces on the nanoscale
- **Part 4: NANOMATERIALS** - the typical nanostructures and their functionality
- **Part 5: NANOSYSTEMS** - fundamental electronic, optical, mechanical, and fluidic systems that can be made with nanostructures.
- **Part 6: NANOENGINEERING** - how to make nanostructures integrated into useful devices.
- **Part 7: NANO-BIO PRIMER** - an important part of nanotechnology is to interface with living organisms.
- **Part 8: ENVIRONMENTAL NANOTECHNOLOGY** - and should we worry about nanotechnology? Used wisely it can help improve our lives and the environment, and used ignorantly it can very likey cause damage as all other technologies.

Each part contains a brief introduction and overview, and numerous chapters with detailed information that each can become a whole book on their subject. We hope to be able to span a wide range of readers, so anyone who would like to know more about nanotechnology can use the book and dive deeper into the detail as they wish.

## 2 References

See also notes on editing this book [Nanotechnology/About#How\\_to\\_contribute](#).

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Category: Science

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# Nanotechnology/Perspective

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## 1 A perspective on Nanotechnology

### A Vision

In his famous speech *There's Plenty of Room at the Bottom* (<http://www.zyvex.com/nanotech/feynman.html>) in 1959, Richard Feynman discussed the possibility of manipulating and controlling things on a molecular scale in order to achieve electronic and mechanical systems with atomic sized components. He concluded that the development of technologies to construct such small systems would be interdisciplinary, combining fields such as physics, chemistry and biology, and would offer a new world of possibilities that could radically change the technology around us.

### Miniaturization

A few years later, in 1965, Moore noted that the number of transistors on a chip had roughly doubled every other year since 1959, and predicted that the trend was likely to hold as each new generation of microsystems would help to develop the next generation at lower prices and with smaller components. To date, the semiconductor industry has been able to fulfill Moore's Law.

### Technological development and limits

The impact on society and our lives of the continuous downscaling of systems is profound, and continues to open up new frontiers and possibilities. However, no exponential growth can continue forever, and the semiconductor industry will eventually reach the atomic limit for downsizing the transistor.

### New ways

Today, as that limit still seems to be some 20 years in the future, the growth is beginning to take new directions, indicating that the atomic limit might not be the limiting factor for technological development in the future, because systems are becoming more diverse and because new effects appear when the systems become so small that quantum effects dominate. The semiconductor devices show an increased diversification, dividing for instance processors into very different systems such as those for cheap disposable chips, low power consumption portable devices, or high processing power devices. Microfabrication is also merging with other branches of science to include for instance chemical and optical micro systems. In addition, microbiology and biochemistry is becoming important for applications of all the developing methods. This diversity seems to be increasing on all levels in technology and many of these cross-disciplinary developments are linked to nanotechnology.

### Diversification

As the components become so small that quantum effects become important, the diversity will probably further increase as completely new devices and possibilities begin to open up that are not possible with the bulk materials of today's technology.

### The nanorevolution?

The visions of Feynman are today shared by many others: when nanotechnology is seen as a general cross disciplinary technology, it has the potential to create a coming "industrial" revolution that will have a major impact on society and everyday life, comparable or exceeding the impact of electricity and information technology.

## 2 Nanocomponents, Tools, and Methods

### A positive spiral

As an emerging technology, the methods and components of nanotechnology are under continuous development and each generation is providing a better foundation for the following.

### Seeing 'nano'

With regards to the methods, the Scanning tunneling microscope (STM) and Atomic Force Microscope (AFM) were developed in the 1980's and opened up completely new ways to investigate nanoscale materials. An important aspect was the novel possibility to directly manipulate nanoscale objects. Transmission and scanning electron microscopes (TEM and SEM) had been available since the 30's, and offered the possibility to image as well as create nanodevices by electron beam lithography.

### New nanomaterials

Several unique nanoscale structures were also discovered around 1990: the Carbon-60 molecule and later the carbon nanotubes. In recent years, more complex nanostructures such as semiconductor nanowire heterostructures have also proven to be useful building blocks or components in nanodevices.

### So what can I use this 'nano' for?

The applications of such nanocomponents span all aspects of technology: Electronics, optics/photonics, medical, and biochemical, as well as better and smarter materials. But to date few real products are available with nanoscale components, apart from traditional nanoscale products, such as paint with nanoparticles or catalytic particles for chemical reactors.

Prototype devices have been created from individual nanocomponents, but actual production is still on the verge. As when integrated electronics were developed, nanotechnology is currently in the phase where component production methods, characterization methods, tools for manipulation and integration are evolving by mutual support and convergence.

### Difficult nanointegration

A main problem is reliable integration of the nanoscale components into microsystems, since the production methods are often not compatible. For fabrication of devices with integrated nanocomponents, the optimal manipulation technique is of course to have the individual components self-assembling or growing into the required complex systems. Self assembly of devices in liquids is an expanding field within nanotechnology but usually requires the components to be covered in various surfactants, which usually also influence the component properties. To avoid surface treatments, nanotubes and whiskers/wires can be grown on chips and microsystems directly from prepatterned catalytic particles. Although promising for future large scale production of devices, few working devices have been made by the method to date.

The prevailing integration technique for nanowire/tube systems seems to be Electron beam lithography (EBL) of metal structures onto substrates with randomly positioned nanowires deposited from liquid dispersions. By using flow alignment or electrical fields, the wire deposition from liquids can be controlled to some extent. The EBL method has allowed for systematic investigations of nanowires' and tubes' electrical properties, and creation of high performance electronic components such as field-effect transistors and chemical sensors. These proof of principle devices are some of the few but important demonstrations of devices nanotechnology might offer. In addition nanomechanical structures have also recently been demonstrated, such as a rotational actuator with a carbon nanotube axis built by Fennimore et al

(<http://www.physics.berkeley.edu/research/zettl/pdf/285.Nat424fennimore.pdf#search=%22Fennimore%20rotational%20actuator%22>).

A more active approach to creating nanowire structures is to use Scanning probe microscopy (SPM) to push, slide and roll the nanostructures across surfaces. SPM manipulation has been used to create and study nanotube junctions and properties. The ability to manipulate individual nanoscale objects has hence proven very useful for building proof-of-principle devices and prototypes, as well as for characterizing and testing components.

The **bottom-up self-assembly** method may be important for future large scale production as well as many of the different approaches to improve the top-down lithographical processes. Such techniques could hence become important factors in the self-sustaining development of nanotechnology.

## 3 Hot and hyped

### Suddenly everything is 'nano'

There's no question that the field of nanotechnology has quite a sense of hype to it - many universities have created new nanotech departments and courses. But there is also a vision behind the hype and emerging results - which are truly very few in industrial production - but nevertheless hold promises of a bright future. In the hype, many things that were once chemistry, microtechnology, optics, mesoscopic or cluster physics, have been reborn as nanotechnology.

### Nanotech is old

You can find nanotechnology in the sunscreen you use in the summer, and some paints and coatings can also be called nanotech since they all contain nanoparticles with unique optical properties. In a way nanoparticles have been known in optics for hundreds of years if you like to take a broad perspective on things, since they have been used to stain and colour glasses etc. for centuries.

Catalysis is a major industrial process, without which not much of the materials we have around us today would be possible to make, and catalysis is often highly dependent on nanoscale catalytic particles. In this way thousands of tons of nanotechnology has been used with great benefit for years.

Nanoscale wires and tubes have only recently really been given attention with the advent of carbon nanotubes and semiconductor nanowires, while nanoscale films are ever present in antireflection coatings on your glasses and binoculars, and thin metal films have been used for sensitive detection with surface plasmons for decades. Surface plasmons are excitations of the charges at a surface. Nanowires actually were observed in the middle ages - well, they did not have the means to observe them, but saw whiskers grow from melted metals.

The better control over the nanostructure of materials has led to optimization of all these phenomena - and the emergence of many new methods and possibilities.

### An example

Take for instance nano-optics: The surface plasmons turn out to be very efficient at enhancing local electrical fields and work as a local amplifier for optical fields, making a laser seem much more powerful to atoms in the vicinity of the surface plasmon. From this comes the surface enhanced raman spectroscopy which is increasingly used today because it makes it possible to do sensitive raman spectroscopy on the large majority of samples that would otherwise be impossible to make such spectra on. In addition, photonic crystals, fancy new quantum light sources that can make single photons on demand and other non-classical photon states are being developed, based on nanotechnology.

### The future

There is definitely future scientific applications and commercial potential of all these new methods to handle light, use it for extremely sensitive detection and control its interaction with matter - and so it seems nanotechnology, being about making smaller versions of existing technology as well as new technology, seems to be worth a bit of hype :-)

## 4 References

This is an example reference <sup>[1]</sup>. See also notes on editing this book Nanotechnology/About#How\_to\_contribute. .

- <sup>↑</sup> Martin GS, Mannino DM, Eaton S, Moss M. The epidemiology of sepsis in the United States from 1979 through 2000. *N Engl J Med.* 2003 Apr 17;348(16):1546-54. PMID 12700374 ([http://www.ncbi.nlm.nih.gov/entrez/query.fcgi?cmd=Retrieve&db=pubmed&dopt=Abstract&list\\_uids=12700374](http://www.ncbi.nlm.nih.gov/entrez/query.fcgi?cmd=Retrieve&db=pubmed&dopt=Abstract&list_uids=12700374)) Full Text (<http://content.nejm.org/cgi/content/abstract/348/16/1546>).

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# Nanotechnology/Overviews

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## 1 Internet Resources

### 1.1 Handbooks and Encyclopedias

These are only accessible for subscribers (which is one reason this wikibook on Nanotechnology was started):

- Encyclopedia of Nanoscience and Nanotechnology (<http://www.ingentaconnect.com/content/asp/enn>)
- Springer Handbook of Nanotechnology (<http://www.knovel.com/knovel2/Toc.jsp?BookID=1121>)

### 1.2 Websites and newsletters

- Virtual journal of nanotechnology (<http://www.vjnano.org/nano>) compiles nanorelated papers in peer reviewed journals that do not specialize solely in nanotechnology.
- Nanotechweb.org (<http://www.nanotechweb.org/>)
- Nanoforum (<http://www.nanoforum.org/>)
- Physorg.com (<http://physorg.com/>)
- Foresight institute (<http://www.foresight.org/>)
- A-Z of nanotechology (<http://www.azonano.com/>)
- Google Directory - Nanotechnology (<http://www.google.com/Top/Science/Technology/Nanotechnology>) (sourced from the Open Directory Project (<http://dmoz.org/Science/Technology/Nanotechnology>))
- Scientific American Nanotechnology Page (<http://www.sciam.com/nanotech/>)
- Join the Wikireason: Nanotechnology debate

### 1.3 Search engines

There are many ways to find information in scientific literature and some that even specialize in nanotechnology. Apart from the free search engines and useful tools such as Google scholar (<http://scholar.google.com/>) and Google Desktop (<http://desktop.google.com/>), there are several more dedicated commercial services:

- ISI - Web of Science Database (<http://isi3.isiknowledge.com/portal.cgi/wos>) contains peer reviewed journals, their references and citations. It also has very useful tools such as 'find related papers' that searches for papers sharing the same

references as the entry you're looking at. This is the database behind the compilation of the journal citation factors.

- Knovel - Online Handbook Collection and Database (<http://www.knovel.com/knovel2/library/default.jsp>) is an extensive collection of handbooks and tables.
- PROLA - the Physical Review Online Archive (<http://prola.aps.org/>) searches Physical Review journals.
- Rubber Bible Online (<http://www.hbcernetbase.com/>) is a physical chemistry handbook which contains tables of physical and chemical data.
- Spin AIP Scitation (<http://scitation.aip.org/>) searches related journals.
- Web of Science by ISI (<http://scientific.thomson.com/products/wos/>) generates the impact factors (see journals below).
- Virtual Journal of Nanotechnology (<http://www.vjnano.org/nano/>) collects nanotech related papers from non-nano specialized journals.
- Derwent Patent database (<http://scientific.thomson.com/ts/derwent>)

## 2 Peer reviewed Journals

Overview of the nanotechnology related journals and their impact factors (Aug. 2006 values)

Nanotechnology Related Journals

Name	Impact Factor	Comments
Advanced Functional Materials ( <a href="http://www3.interscience.wiley.com/cgi-bin/jhome/77003362">http://www3.interscience.wiley.com/cgi-bin/jhome/77003362</a> )	<b>6.8</b>	?
Advanced Materials ( <a href="http://www3.interscience.wiley.com/cgi-bin/jhome/10008336/">http://www3.interscience.wiley.com/cgi-bin/jhome/10008336/</a> )	<b>9.1</b>	?
The Journal of Physical Chemistry C ( <a href="http://pubs.acs.org/journals/jpcckc">http://pubs.acs.org/journals/jpcckc</a> )	<b>wait</b>	Nanomaterials and Interfaces, Nanoparticles and Nanostructures, Surfaces, Interfaces, Catalysis, Electron Transport, Optical and Electronic Devices, Energy Conversion and Storage
American Journal of Physics (AJP) ( <a href="http://scitation.aip.org/ajp/">http://scitation.aip.org/ajp/</a> )	<b>0.82</b>	?
Applied physics A ( <a href="http://www.springer.com/east/home/physics?SGWID=5-10100-70-1048382-0">http://www.springer.com/east/home/physics?SGWID=5-10100-70-1048382-0</a> )	<b>2.0</b>	?
Applied physics letters (APL) ( <a href="http://apl.aip.org/apl/top.jsp">http://apl.aip.org/apl/top.jsp</a> )	<b>4.1</b>	?
Chemical Reviews ( <a href="http://pubs.acs.org/journals/chcreay">http://pubs.acs.org/journals/chcreay</a> )	<b>20.9</b>	?
Journal of Applied Physics ( <a href="http://jap.aip.org/">http://jap.aip.org/</a> )	<b>2.5</b>	?
Journal of Micromechanics and Microengineering ( <a href="http://www.iop.org/EJ/journal/0960-1317/1">http://www.iop.org/EJ/journal/0960-1317/1</a> )	<b>2.5</b>	?
Journal of the American Chemical Society (JACS) ( <a href="http://pubs.acs.org/journals/jacsat/">http://pubs.acs.org/journals/jacsat/</a> )	<b>7.4</b>	Multidisciplinary chemistry journal
Japanese Journal of Applied Physics ( <a href="http://www.ipap.jp/jjap/online/index.htm">http://www.ipap.jp/jjap/online/index.htm</a> )	<b>1.1</b>	?
Journal of physical chemistry - A & B ( <a href="http://acsinfo.acs.org/journals/jpchax/">http://acsinfo.acs.org/journals/jpchax/</a> )	<b>~4</b>	?
Journal of nanoscience and nanotechnology ( <a href="http://www.aspbs.com/jnn/">http://www.aspbs.com/jnn/</a> )	<b>1.9</b>	Nanotech in general
Journal of Vacuum Science and Technology A (JVSTA) ( <a href="http://scitation.aip.org/jvsta/">http://scitation.aip.org/jvsta/</a> )	<b>1.4</b>	Vacuum, Surfaces, Films
Journal of Vacuum Science and Technology B (JVSTB) ( <a href="http://scitation.aip.org/jvstb/">http://scitation.aip.org/jvstb/</a> )	<b>1.6</b>	Microelectronics and Nanometer Structures: Processing, Measurement, and Phenomena
Langmuir ( <a href="http://pubs.acs.org/journals/langd5/index.html">http://pubs.acs.org/journals/langd5/index.html</a> )	<b>3.7</b>	Research in the fields of colloids, surfaces, and interfaces

Micron - Journal for microscopy ( <a href="http://www.dlno.nl/wps/product/cws_home/475">http://www.dlno.nl/wps/product/cws_home/475</a> )	<b>1.3</b>	?
Microscopy Research and Technique ( <a href="http://www3.interscience.wiley.com/cgi-bin/jhome/38527">http://www3.interscience.wiley.com/cgi-bin/jhome/38527</a> )	<b>2.3</b>	?
Nano Letters ( <a href="http://pubs.acs.org/journals/nalefd/index.html">http://pubs.acs.org/journals/nalefd/index.html</a> )	<b>9.8</b>	The highest impact nanotechnology journal
Nanotechnology ( <a href="http://www.iop.org/EJ/journal/0957-4484">http://www.iop.org/EJ/journal/0957-4484</a> )	<b>3</b>	Journal specializing in nanotechnology
Nature ( <a href="http://www.nature.com/nature/">http://www.nature.com/nature/</a> )	<b>29.3</b>	One of the major journals in science
Nature Biotechnology ( <a href="http://www.nature.com/nbt/index.html">http://www.nature.com/nbt/index.html</a> )	<b>22.7</b>	?
Nature Materials ( <a href="http://www.nature.com/nmat/">http://www.nature.com/nmat/</a> )	<b>15.7</b>	?
Nature Nanoetchnology ( <a href="http://www.nature.com/nnano/">http://www.nature.com/nnano/</a> )	<b>wait</b>	New nanotech journal
Proceedings of the National Academy of Sciences (PNAS) ( <a href="http://www.pnas.org/">http://www.pnas.org/</a> )	<b>10.2</b>	?
Physical Review Letters (PRL) ( <a href="http://scitation.aip.org/prl/help.jsp">http://scitation.aip.org/prl/help.jsp</a> )	<b>7.5</b>	One of the top physics journals
Science ( <a href="http://www.sciencemag.org/">http://www.sciencemag.org/</a> )	<b>30.9</b>	One of the major journals in science
Small Journal ( <a href="http://www3.interscience.wiley.com/cgi-bin/jhome/107640323">http://www3.interscience.wiley.com/cgi-bin/jhome/107640323</a> )	<b>wait</b>	New nanotech journal
Journal of Solid-state electronics ( <a href="http://www.elsevier.com/wps/find/journaldescription.cws_home/103/description#description">http://www.elsevier.com/wps/find/journaldescription.cws_home/103/description#description</a> )	<b>1.2</b>	?
Thin solid films ( <a href="http://authors.elsevier.com/journal/tsf">http://authors.elsevier.com/journal/tsf</a> )	<b>1.6</b>	?
Ultramicroscopy ( <a href="http://www.sciencedirect.com/science/journal/03043991">http://www.sciencedirect.com/science/journal/03043991</a> )	<b>2.5</b>	Microscopy related research.
Virtual Journal of Nanotechnology ( <a href="http://www.vjnano.org/nano/">http://www.vjnano.org/nano/</a> )	<b>none</b>	Collecting nanotech related papers from non-nano spcialized journals

- Impact factors are only guides to how much a papers is referenced in the years just after publication.
- Please add comments about the journals and update impact factors!

## 3 Nanotech Products

Please add more products, comments and more info about the products if you have any!

See also the List of nanotechnology applications in wikipedia

### 3.1 Emerging products

- Batteries are increasingly incorporating nanostructures.
- Flexible, cheaper, or more luminous Flat screen displays

### 3.2 Available in 2005

- Molybdenum disulfide catalytic nanoparticles in Brimm catalysts[1] (<http://ing.dk/article/20051118/FORSKNING/111180046/-1/arkivugensavis>) made by Haldor Topsøe (<http://www.topsoe.com/>)
- Forbes top ten nanoproducts in 2005[2] ([http://www.forbes.com/2006/01/10/apple-nano-in\\_jw\\_0109soapbox.inl.html?boxes=popstories&boxes=custom](http://www.forbes.com/2006/01/10/apple-nano-in_jw_0109soapbox.inl.html?boxes=popstories&boxes=custom))
  - Apples iPod with sub 100nm elements in its memory chips
  - Choleterol reducing nanoencapsulated oil,Shemen Industries Canola Active.
  - Nanocrystals improve the consistency of chocolate[3] (<http://www.olalafoods.com/>)
  - Zelen Fullerene C-60 Day Cream [4] (<http://www.zelens.com/>)

- Easton Stealth CNT baseball bat
- Nanotex textiles once again
- ArcticShield polyester socks from ARC Outdoors with 19nm silver particles that kill fungi to reduce odor.
- NanoGuard developed by Behr Process for improved paint hardness.
- Pilkingtons self-cleaning 'Activ Glass'.
- NanoBreeze Air Purifier from NanoTwin Technologies, where the UV light from a fluorescent tube cleans the air by photochemical reactions in nanoparticles.

### 3.3 Available in 2004

- Cold cathode carbon nanotube emitters for X-ray analysis by Oxford instruments[5] ([http://www.smalltimes.com/Articles/Article\\_Display.cfm?ARTICLE\\_ID=267960&p=109](http://www.smalltimes.com/Articles/Article_Display.cfm?ARTICLE_ID=267960&p=109))[]
- Forbes has an overview in 2004 of what they consider the top ten nanotech products ([http://www.forbes.com/investmentnewsletters/2005/01/12/cz\\_jw\\_0112soapbox.html](http://www.forbes.com/investmentnewsletters/2005/01/12/cz_jw_0112soapbox.html)):
  - Footwarmers with nanoporous aerogel for 3-20 times lighter than comparable insulating materials used in shoes (produced by Aspen Aerogels).
  - Mattress covers with nanotex fibres that can be washed (Simmons bedding company).
  - Better golf drivers with carbon nanotube enforced metal composites (produced by Maruman & Co) and nanocomposite containing golf balls (produced by NanoDynamics)
  - The company 'Bionova' apparently adds some nanoproducts to their 'personalized product line'.
  - EnviroSystems make a nanoemulsive disinfectant cleaner, called EcoTru, that is EPA Tox category 4 registered (meaning very safe to use)
  - EnviroSystems also make a spray-on version of this product.
  - BASF makes a nanoparticle coating for building materials called Mincor, that reduces their wettability.
  - A nanostructured coating produced by Valley View, called Clarity Defender, improves visibility through windscreens in rain. Another company, Nano-Film, makes a similar coating on sunglasses.
  - Flex-Power makes a gel containing nanoscale liposomes for soothing aching muscles
  - 3M espe Dental adhesive with silica nanoparticle filler.

### 3.4 Available in 2003

- Forbes 2003 top ten nanoproduct [6] ([http://www.forbes.com/investmentnewsletters/2003/12/29/cz\\_jw\\_1229soapbox.html](http://www.forbes.com/investmentnewsletters/2003/12/29/cz_jw_1229soapbox.html)) includes:
  - High performance ski wax, Cerax Nanowax [7] (<http://www.ceraxusa.com/>).
  - Nanotex textiles in ski jackets from Ziener[8] (<http://www.ziener.de/>)
  - Nanotex (<http://www.nano-tex.com/>) textiles
  - Plenitude Revitalift antiwrinkle cream by L'Oréal contains nanocapsules with vitamin A [9] (<http://www.lorealparis.co.uk/>)
  - organic light-emitting diodes (OLEDs) in Sony camera flat screen display
  - Nanofilm coatings for anti-reflection and scratch resistance [10] (<http://www.nanofilm.cc/>)
  - Zinc oxide nanoparticles in Sunscreen by BASF [11] (<http://www.nucelle.com/>)
  - carbon nanotube enforced tennis rackets [12] (<http://www.babolat.com/>) and nanopolymer enforced tennis balls [13] (<http://www.wilson.com/>)

### 3.5 Available in 2000

Nanotex (<http://www.nano-tex.com/>) makes textiles where the clothing fibres have been coating in nanoscale fibres to change the textile wettability. This makes the textile much more stain resistant.

## 3.6 Companies making nanotech research equipment

- Veeco (<http://veeco.com/>) AFM and related equipment
- Zyvex (<http://zyvex.com/>) nanomanipulation equipment
- Nanofactory (<http://nanofactory.se/>) in-situ TEM manipulation equipment
- SmarAct (<http://www.smaract.de/>) nanomanipulators
- Capres (<http://capres.com/>) micro four point conductance measurement probes
- ImageMetrology (<http://www.imagemet.com/>) SPIP software for SPM analysis
- Atomistix (<http://www.atomistix.com/>) software for simulating nanosystems

## 3.7 Products that have been nanostructured for decades

- Catalysts

- Haldor Topsøe (<http://www.topsoe.com/>)
- Computer processors are increasingly made of nanoscale systems
  - Intel (<http://intel.com/>)

### 3.8 Non-nanotech products and a warning

Not everything that says nano is nano - and given the hype surrounding nanotechnology you will see an increasing number of 'nano' products that have nothing to do with it. It is worrying when sometimes problems arise with non-nano products and this adds to the 'scare' that is present in the public, fuelled by the newspapers where they are just waiting for a nice scandal... an example was the product Magic Nano from a German company that made a number of users sick when inhaling the aerosol cleaning product - which in the end turned out to have nothing 'nano' in it. There is good reason to be very alert to such issues. Not all countries have legislation in place to secure the consumers against the possible dangers present in nanoparticles and some products could end being marketed before having been tested well enough. Though this example turned out to be 'non-nano', we will probably meet new cases shortly that are truly 'nano'. On this background environmental and health aspects will be an important part of this book.

## 4 Suppliers

Nanomaterials

- Sigma-Aldrich (<http://www.sigma-aldrich.com/>)
- Zyvex (<http://www.zyvex.com/>)

Nanolithography

- NIL Technology (<http://www.nilt.com/>) sells stamps for nanoimprint lithography (NIL) and provides imprint services.

Quantum Dots

- Evident technologies (<http://www.evidenttech.com/>)

## 5 A nano-timeline

Overview of some important events in nanotechnology

See also History of Nanotechnology in Wikipedia

A Nanotechnology Timeline

Year	Development
<b>Medieval</b>	Observation of metal whisker growth and nanoparticles used for staining glass
<b>1900</b>	Max Planck proposes energy quantization.
<b>1905-30</b>	Development of quantum mechanics
<b>1927</b>	Heisenberg formulated his uncertainty principle
<b>1933</b>	The first First electron microscope was built by Ernst Ruska
<b>1953</b>	DNA structure discovered by James D. Watson and Francis Crick
<b>1959</b>	Feynmans talk There is plenty of room at the bottom
<b>1965</b>	Proposal of Moores Law
<b>1981</b>	Invention of STM by Gerd Binnig and Heinrich Rohrer
<b>1985</b>	Invention of AFM by Binnig, Quate and Gerber
<b>1988</b>	Buckyball discovery by Kroto, Curl, and Smalley
<b>1991</b>	Discovery of carbon nanotubes by Sumio Iijima

# 6 A nano-scale overview

Just to get a sense of proportion

A Nano-scale overview

Scale	typical elements
<b>1 m</b>	1 m is 1.000.000.000 nanometers ( $10^9$ nm )
<b>200 <math>\mu</math>m</b>	About the size of the smallest letters you can write with a very very sharp pencil and a very very steady hand.
<b>100 <math>\mu</math>m</b>	Typical thick hair
<b>10-1000 <math>\mu</math>m</b>	Cells in living organisms can have many sizes, and neurons can be much longer. In frog embryos (Tadpoles) the initial embryo cells can be up to 1000 $\mu$ m.
<b>8 <math>\mu</math>m</b>	Red blood cell
<b>1 <math>\mu</math>m</b>	Bacteria
<b>100 nm</b>	Virus
<b>5-100 nm</b>	The range for nanotechnology systems built from atomic/molecular components (quantum dots, nanoparticles, diameter of nanotubes and nanowires, lipid membranes, nanopores...).
<b>10 nm</b>	Size of typical Antibody molecules in living organisms immune defence
<b>6-10 nm</b>	Thickness of a cell membrane, and typical pore size in membrane.
<b>2.5 nm</b>	The width of DNA (but it depends on the conditions)
<b>1 nm</b>	The size of a C60 buckyball molecule or glucose molecule.
<b>0.3 nm</b>	The size of a water molecule.
<b>1 <math>\text{Å}</math> = 0.1 nm</b>	Roughly the size of hydrogen atom.
<b>0.7 <math>\text{Å}</math> = 70 pm</b>	The best resolution in AFM achieved so far where they managed to image individual orbitals in an atom.

- Distances between objects can be measured with sub  $\text{Å}$  precision with STM, laser interferometry and its even done continuously in a standard airbag acceleration sensor chip that costs a few dollars and senses the vibrations of a micro-inertial mass element with femtometer precision ( $10^{-15}$  m).

## 7 References

See also notes on editing this book [Nanotechnology/About#How\\_to\\_contribute](#).

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# Nanotechnology/About

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## 1 Vision

We hope to use the wikibooks format to make an Opensource Wikibook on Nanoscience and Nanotechnology, freely accessible for everyone, that can be updated continuously.

Discussion about the content of the book can be found on the main talk page talk:Nanotechnology

## 2 How to contribute

Please make any corrections and additions you like.

### 2.1 Editing hints

#### 2.1.1 References in wikibooks

Add references whenever possible, with reference lists at the end of each page. Please try to make links to the articles with the DOI (digital object identifier) because that gives a uniform and structured access for everyone to the papers.

All papers get a DOI - a unique number like a bar code in a supermarket. All DOIs are registered by [www.doi.org](http://www.doi.org) (<http://www.doi.org/>) and in the reference list you can add links like <http://dx.doi.org/10.1039/b504435a> so people will be able to find it no matter how the homepage of the journal or their own library changes.

The References section has an example reference.

Add links to the wikipedia whenever possible - and for the beginning I will rely extensively on wikipedia's pages on the subjects, simply referring to these. This textbook could be simply a gathering of wikipedia pages, but an encyclopedia entry is brief, and for a handbook it is preferable to have more in-depth material with examples and the necessary formulas. So, some information in this textbook will be very much like the wikipedia entries and we might not need to write it in the book but can simply refer to wikipedia, but the hope is that this will be more a text book as is the intention with wikibooks.

Multiple references, see [w:Help:Footnotes](http://en.wikibooks.org/wiki/Help:Footnotes)

#### 2.1.2 Links

There's a shorthand way to make links to wikipedia from wikibooks: `[[w:Quantum_tunneling|Wikipedia on Quantum`

Tunneling]] gives the link Wikipedia on Quantum Tunneling.

### 2.1.3 Media

Wikimedia Commons has media related to:  
*Nanotechnology*



## 3 History

The book was started by Kristian Molhave (<http://kristian.molhave.dk/>) (wiki user page) 13. Apr. 2006. Initially it was named Nanowiki, and later changed to Nanotechnology. Kristian is currently slowly uploading material to the book and looking for people who would like to contribute that can and substantial material to specific sections under the GNU license. I hope we can make an 'editorial panel' of people each keeping an eye on and updating specific sections.

## 4 Authors and Editors

- The Opensource Handbook on Nanoscience and Nanotechnology was started by Kristian Molhave (<http://kristian.molhave.dk/>)(wiki user page)

### 4.1 Editors

- An editorial board is currently being organized.

## 5 Support and Acknowledgments

Writing this book is supported by the Danish Agency for Science, Technology and Innovation ([http://forsk.dk/portal/page/pr04/FIST/FORSIDE/DIVERSE\\_SIDER/DANISH\\_RESEARCH\\_AGENCY](http://forsk.dk/portal/page/pr04/FIST/FORSIDE/DIVERSE_SIDER/DANISH_RESEARCH_AGENCY)) through Kristian Mølhave's talent project 'NAMIC (<http://kristian.molhave.dk/namic>)' No. 26-04-0258.

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- 2) Reference the book with a specific page and date - the previous versions of the pages are all available in the history pane and can easily be accessed by future users.
- 3) Reference the PDF version and its version number. Once the book achieves a reasonable level, PDF versions will become available for download and they will have a unique version number and can be retrieved.

Other suggestions are most welcome!

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# Nanotechnology/Reaching Out

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## 1 Teaching Nanotechnology

Teachers' Toolbox is a Wikibook on teaching methods and ways to improve teaching. The toolbox is intended to give you an overview of methods you can use when teaching in general.

If you know of places that have teaching material available on the net, please add a link to the list below:

- Nanotechnology ([http://nano.ece.uci.edu/nano\\_05.htm](http://nano.ece.uci.edu/nano_05.htm))
- Nano-to-Macro Transport Processes, Fall 2004 (<http://ocw.mit.edu/OcwWeb/Mechanical-Engineering/2-57Fall-2004/LectureNotes/index.htm>)
- nanostructured materials and interfaces (<http://www.chem.wisc.edu/courses/801/Spring00/index.html>)

## 2 Outreach projects

There are several nanotechnology related outreach projects. Here are some examples to give ideas:

- Nanoscale Science Education (<http://www.cs.unc.edu/Research/nano/ed/index.html>)
- Citizens school of nanotechnology (<http://nsts.nano.sc.edu/outreach.html>)
- Webcast outreach lecture ([http://streamer.cit.utexas.edu:16080/esi/webcast.php?redir=archive\\_barbara.html](http://streamer.cit.utexas.edu:16080/esi/webcast.php?redir=archive_barbara.html))
- Exploring the nanoworld (<http://mrsec.wisc.edu/Edetc/>)
- K-14 outreach (<http://www.engr.ucr.edu/osp/cnse/activities/index.html>)
- Cornell Museum (<http://www.news.cornell.edu/stories/Feb06/AAAS.Waldron.ws.html>)

## 3 Demonstration experiments

There is a dedicated section for nanotechnology in the Wikibook on Science Show, which is a cross disciplinary collection of demonstration experiments. The is growing steadily and we will begin to add to the English version soon. Please add to these books with any demonstration experiments and ideas you have!

There are others available on the net:

- Nano-Tex: Testing New Nano Fabrics (<http://mrsec.wisc.edu/Edetc/IPSE/educators/activities/nanoTex.html>)
- Nano kits (<http://mrsec.wisc.edu/Edetc/supplies/index.html>) and for instance the exercise moving a wall (<http://mrsec.wisc.edu/Edetc/cineplex/STM/STM3.html>)

## 4 References

See also notes on editing this book about how to add references [Nanotechnology/About#How\\_to\\_contribute](#).

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# Nanotechnology/Seeing Nano

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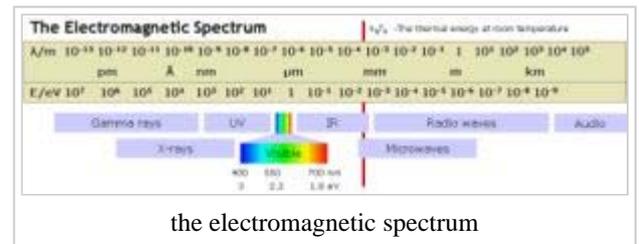
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>>> Next Part: Physics - on the nanoscale

## 1 The eyes in nanotech

Without being able to 'see' the nanoscale objects nanotechnology would be very difficult. In this part the different microscope techniques are reviewed and various spectroscopic and diffraction methods that can tell us more about the nanoscale structure of matter.

Visible light is only a part of the electromagnetic spectrum and useful information about different physical interactions in nanostructures can be acquired from the different parts of the electromagnetic spectrum.

Seeing 'nano' can be done in different ways, but not with the naked eye which normally cannot see things much smaller than  $100\mu\text{m}$  (though a single atom can be seen if it lights up in a dark room). Instead of our eyes we use various instruments to 'see' for us, and they 'see' different things depending on how they are made:



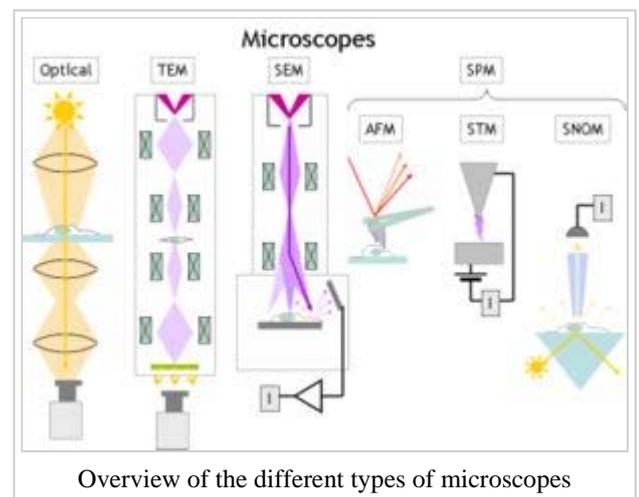
## 2 Microscopy

Microscopy uses microscopes to create an image of the specimen. The image is rarely an image as you see it with your eyes, but rather how some physical probe interacts differently with the specimen as function of position on it. The physical probe can be an AFM cantilever, a beam of light or electrons, or something completely different.

### 2.1 Overview of Microscopes

**Optical:** The beam from a light source is focused onto a sample and either the transmitted or scattered light is collected by an objective lens and the image is magnified onto a camera or to the observers eye. The resolution can be down-to about 200 nm, and the microscopes can be fairly cheap, small and easy to use.

**Transmission Electron Microscope (TEM):** Electrons from a very bright electron source are focused onto a very thin sample that is transparent to the high energy electrons (100-300 keV) and the electron beam is then magnified by electro magnetic lenses and sent onto a fluorescent screen or a camera to observe the image. The resolution can be less than 0.1nm on expensive high-end instruments where even individual atoms can be imaged. The samples must be very thin (typically less than 200 nm) and the whole system must be under high



vacuum.

**Scanning Electron Microscope (SEM):** A focused electron beam is scanned over a sample and the scattered electrons are detected. The detector current is used to give an image depending on the electron beam position on the sample. The resolution can be down-to about 5 nm and the sample can be much larger than in the TEM because the electrons do not have to pass through the sample.

**Scanning Probe Microscopes (SPM)** move a very sharp probe across a sample in a raster pattern while recording how the probe interacts with the sample. The typical SPMs are the AFM, STM and SNOM:

**Atomic Force Microscope (AFM):** An almost atomically sharp tip is protruding from a cantilever and is scanned over the sample. When the cantilever deflects, a laser beam reflected off the backside of the cantilever will change directions and this will be measured by a photodetector. The laser position can be used to control the force between the tip and the sample, and the AFM is often used to measure both topography and forces on the nanoscale. The resolution is normally down-to about 1 nm, but even subatomic resolution is possible. The AFM can work with both dry and wet, conducting and isolating samples.

**Scanning Tunneling Microscope (STM):** An atomically sharp tip is moved within atomic distance of a sample that has a voltage applied to it. When the tip-sample distance becomes so small that the electron clouds of the tip and sample touch, electrons can much more easily tunnel between the two and this gives rise to a tip-sample current (often a few pA at a 1V bias voltage). This current can be used to maintain a fixed tip-sample distance when the tip is scanned over the sample, and this can give images of conducting surfaces with atomic resolution.

**Scanning Near-field Optical Microscope (SNOM):** As electrons can tunnel between electrical conductors in the STM, photons can tunnel between optical guiding structures. The SNOM uses a narrow light guide to measure how the optical electromagnetic field changes as the guide is moved across the sample. For instance, light can be sent from below the sample and then scattered into the scanning light guide above it. The resolution can be much smaller than the wavelength of light.

## 3 Spectroscopy

Spectroscopy uses spectrometers to tell how radiation interacts with the specimen as function of the energy/wavelength of the radiation

## 4 Diffraction

Diffraction uses radiation to observe how it is scattered in different directions from the specimen. This can be used to tell about the order of the atoms in the sample.

## 5 Surface analysis

Many of these methods are used for 'macroscopic' surface analysis where the outmost nanometers of a material is being studied over larger areas. The methods can be combined with microscopes to give spectrometrical information from a well defined location on the sample - for instance when doing diffraction measurements in a TEM or level spectroscopy in an STM on a single atom.

## 6 References

See also notes on editing this book about how to add references [Nanotechnology/About#How\\_to\\_contribute](#).

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# Nanotechnology/Optical Methods

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## 1 Optical Microscopy

### 1.1 The Abbe diffraction limit

Observation of sub-wavelength structures with microscopes is difficult because of the Abbe diffraction limit. Ernst Abbe found in 1873 that light with wavelength  $\lambda$ , travelling in a medium with refractive index  $n$  and converging to a spot with angle  $\phi$  will make a spot with radius

$$d = \frac{0.61\lambda}{n\sin\phi}$$

The denominator  $n\sin\phi$  is called the numerical aperture (NA) and can reach about 1.4 in modern optics, hence the Abbe limit is roughly  $d=\lambda/2$ . With green light around 500nm the Abbe limit is 250nm which is large compared to most nanostructures or biological cells with sizes on the order of  $1\mu\text{m}$  and their internal organelles being much smaller. To increase the resolution, shorter wavelengths can be used such as UV and X-ray microscopes. These techniques offer splendid resolution but are expensive, suffer from lack of contrast in biological samples, and also tend to damage the sample

### 1.2 The optical microscope

The Microscope

#### 1.2.1 Bright Field

The light is sent to the sample in the same directions as you are looking - most things will look bright unless they absorb the light.

#### 1.2.2 Dark Field

Light is sent towards the sample at an angle to your viewing direction and you only see light that is scattered. This makes most images appear dark and only edges and curved surfaces will light up.

### 1.2.3 Polarized Light

### 1.2.4 DIC vs H

## 2 Laser Scanning Confocal Microscopy (LSCM)

Confocal laser scanning microscopy is a technique that allows a much better resolution from optical microscopes.

Using a high NA objective also gives a very shallow depth of focus and hence the image will be blurred by structures above or below the focus point in a classical microscope. A way to circumvent this problem is the confocal microscope, or even better the Laser Scanning Confocal Mikroscope (LSCM). Using a laser as the light source gives better control of the illumination, especially when using fluorescent markers in the sample. The theoretical resolution using a 1.4 NA objective can reach 140nm laterally and 230nm vertically <sup>[1]</sup> while the resolution quoted in ref <sup>[2]</sup> is  $0.5 \times 0.5 \times 1 \mu\text{m}$ . The image in the LSCM is made by scanning the sample in 2D or 3D and recording the signal for each point in space on a PC which then generates the image.

## 3 X-ray microscopy

X-ray microscopy uses X-rays with much shorter wavelength than optical light, and hence a much better resolution. The systems are unfortunately rather large, expensive and X-rays do have the nice quality to pass rather unhindered through your body, and hence also give rather poor contrast in many of the biological samples you would like to observe with the x-ray microscope. Despite the drawbacks, X-ray microscopy is an interesting technique and do give very nice results.

A presentation of x-ray microscopy can be found at [1] (<http://www.isa.au.dk/SR/XRM/xrm.html>)

## 4 UV/VIS spectrometry

UV/VIS spectroscopy

## 5 Infrared spectrometry (FTIR)

FTIR

## 6 Terahertz Spectroscopy

Terahertz radiation

## 7 Raman Spectroscopy

- Raman spectroscopy
- Raman scattering
- Resonance Raman spectroscopy

### 7.1 Surface Enhanced Raman Spectroscopy (SERS)

- Surface Enhanced Raman Spectroscopy (SERS)

## 8 References

See also notes on editing this book [Nanotechnology/About#How\\_to\\_contribute](#).

1. ↑ Confocal laser scanning microscopy, Paddock SW, Biotechniques , vol. 27 (5): 992 NOV 1999
2. ↑ A new UV-visible confocal laser scanning microspectrofluorometer designed for spectral cellular imaging, Favard C, Valisa P, Egret-Charlier M, Sharonov S, Herben C, Manfait M, Da Silva E, Vigny P, Biospectroscopy , vol. 5 (2): 101-115 1999

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# Nanotechnology/Electron microscopy

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## 1 Electron microscopy

An overview:

Electron microscopes use electrons instead of photons, because electrons have a much shorter wavelength than photons and so allow you to observe matter with atomic resolution.

There are two general types of electron microscopes: the Scanning Electron Microscope (SEM) that scans an electron beam over the surface of an object and measures how many electrons are scattered back, and the Transmission Electron Microscope (TEM) that shoots electrons through the sample and measures how the electron beam changes because it is scattered in the sample.

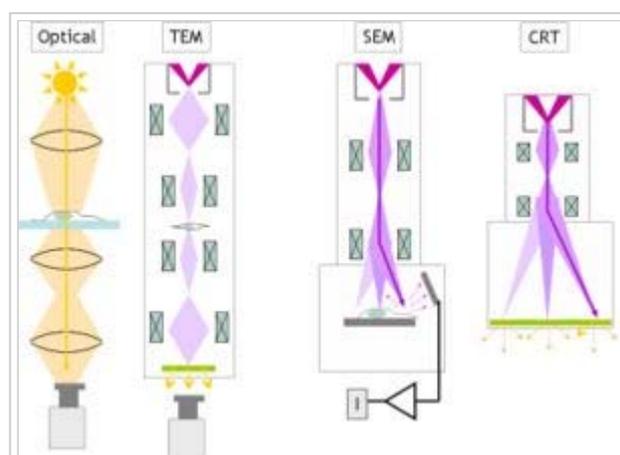
Using electron beams however requires working in a vacuum environment, and this makes the instruments considerably larger and expensive. All electron microscope work under at least low pressures and usually in high vacuum chambers to avoid scattering the electrons in the gas. In environmental electron microscopes, differential pumping systems are used to actually have gasses present by the sample together with the electron beam.

### 1.1 Additional resources on electron microscopy

- What are Electron Microscopes? (<http://www.unl.edu/CMRAcfem/em.htm>)
- wikipedia: Electron microscope

### 1.2 Introduction to Electron Microscopy

For imaging of nanoscale objects, optical microscopy has limited resolution since the objects are often much smaller than the wavelength of visible light. The achievable resolution for a wavelength  $\lambda$  is often given by the diffraction limit  $d$  as



A very simple sketch of a Transmission Electron Microscope (TEM) and Scanning Electron Microscope (SEM) compared to an optical transmission microscope and a cathode ray tube (CRT) TV screen - both systems have many things in common with the electron microscope. The optical microscope uses lenses to control the light's pathway through the system and is in many ways built up like a TEM - only the TEM uses electromagnetic lenses to direct the beam of electrons. The CRT uses electromagnetic lenses as the TEM and

$$d = 0.61 \frac{\lambda}{(NA)} \text{ (Eq. Diffraction limit)}$$

SEM to control the electron beam, and generates an image for the viewer by scanning the beam over a fluorescent screen - in the same way the a SEM generates an image by scanning the electron beam over a small sample.

with numerical aperture  $NA$ , which can be approximated by the largest angle of incidence  $\alpha$  of the wavefront towards the sample,  $NA \approx \alpha$ .

Since  $\alpha \ll 1$  for the present purposes, we can approximate  $\sin(\alpha) \approx \tan(\alpha) \approx \alpha$  and hence  $NA \approx \alpha \approx r_a / r_{wd}$  where  $r_a$  is the radius of the objective lens aperture and  $r_{wd}$  the working distance.

Optical microscopes can often reach a resolution of about  $d = 200\text{nm}$ . For nanoscale resolution this is unfortunately not sufficient to distinguish for instance a single nanotube from two adhering to each other, since they have diameters of less than 100 nm.

The figure below gives an overview typical magnifications achievable by the different electron microscopes compared to a light microscope.

Electron optical systems use electrical and magnetic fields to control the electron beam. Although the law of refraction in optics is exchanged with the Lorentz force in electrodynamics, the electron optical system has similar diffraction limits as optical systems, since they depend on the wave nature of the electron beam.

One can achieve a considerable improvement in resolution with instruments such as the transmission electron microscope and the scanning electron microscope that use electrons with De Broglie wavelength much smaller than that of visible light. The De Broglie wavelength  $\lambda$  of an electron with momentum  $p$  is

$$\lambda = \frac{h}{p} = \frac{h}{\sqrt{2m_e E_b}}, \text{ (Eq. De Broglie wavelength)}$$

where  $h$  is Plancks constant. The electron has rest mass  $m_e$  and energy  $E_e = m_e c^2 = 511\text{keV}$ .

If an electron with charge  $q_e$  is accelerated from rest by an electrical potential  $U$ , to the electron beam energy  $E_b = q_e U$ , it will have a wavelength of 1 nm at 1 eV decreasing to 1 pm at 100 keV where it will be travelling with 50% the speed of light.

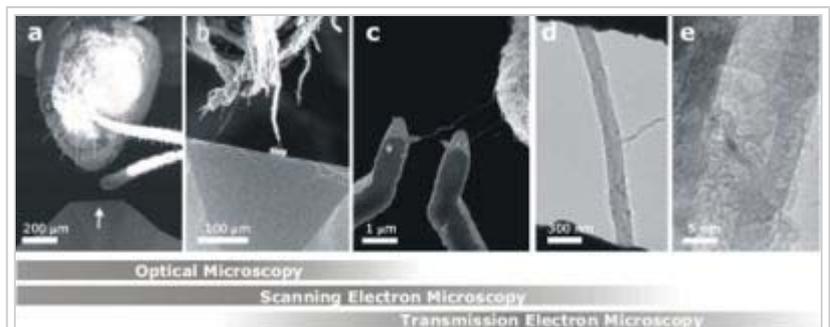
This chapter will briefly review fundamental issues for electron microscopy that are similar for SEM and TEM: the limitations imposed by the electron optical beam system in the microscope column; the interaction of the electron beam with the sample; the standard image formation method in SEM and TEM. These issues are essential to understand the results and limitations reached in SEM and TEM microscopy.

For further details, please refer to reviews of electron microscopes and their applications, such as Goldstein et al. <sup>[1]</sup> that contains a thorough review of SEM, while Goodhew and Humphreys <sup>[2]</sup> is a more general introduction to both SEM and TEM.

## 2 The Electron Optical System

For high resolution imaging, a well focused beam is required, just as in optical microscopy. Due to the short wavelength of electron beams with keV energies, as given by the #Eq de Broglie wavelength, the properties of the electron optical system and the electron emitter mainly defines the limits on the achievable beam diameter. The current density in the electron beam can be approximated by a Gaussian distribution of current density  $j$  [A/m<sup>2</sup>] as function of radius,  $r$ , from the beam center

$$j(r) = j_0 e^{-((r/(r_0))^2)},$$



The different methods for microscopy cover a range of magnification roughly indicated by the bars in the figure. The resolution of optical microscopy is limited to about 200 nm. a) SEM image of the head of an ant facing a microfabricated chip with a pair of microfabricated grippers. The grippers are barely visibly at the tip of the arrow. b) SEM image of a gripper approaching a large bundle of carbon nanotubes. c) Closeup in SEM of the gripper and nanotubes. d) TEM image of a carbon nanotube suspended between two grippers. e) TEM closeup of the shells of carbon atoms in a carbon nantoube. On the nanometer scale this particular carbon nanotube does not show a well defined carbon shell structure.

with radius determined by  $r_0$ , giving a the full width half maximum  $FWHM = 2\sqrt{\ln 2}r_0$ . Integrating  $I_b = \int \int j(r)rdrd\theta$  gives the total beam current

$$I_b = j_0\pi r_0^2.$$

The electron optics impose a limit on the achievable beam current density and radius by the brightness of the electron emitter  $\beta_e$ , which is conserved throughout the system [3].

Brightness,  $\beta$ , is a measure of the current per area normal to the beam direction and per element of solid angle [4]. At the center of the Gaussian beam,

$$\beta = (j_0 / (\pi a^2)) \quad \text{eqSEMcurrentdensity}$$

and the brightness is related to the current density in Eq. eq SEM gaussian beam profile. The emitter brightness  $\beta_e$  is determined by the type of electron emitter and the beam energy  $E_b$  [5]

$$\beta_e = (j_e E_b) / (p^2 E)$$

with emission current density for W-filament sources about  $j_e \approx 3$  A/cm<sup>2</sup>, for LaB6 sources about 100 A/cm<sup>2</sup>, while field emission guns (FEG) can reach 10<sup>5</sup>A/cm<sup>2</sup>. The energy spread of the electrons from the sources are about  $\Delta E \sim 1$  eV and slightly lower for FEGs. Due to conservation of the brightness in the system, the beam diameter depends on current as

$$r_0 = (1/p)((r_{wd}/r_a)\sqrt{(I_b/\beta_e)}).$$

The ideal beam probe size determined by the conservation of brightness cannot be obtained in a real system. Effects such as aberration will make the minimum achievable beam diameter larger. Equation #eq SEM beam diameter however seem to adequately describe the beam diameter for the present discussion. Apart from the additional beam widening contributions, the image detection method imposes limits on useful values for the parameters in Eq. #eq SEM beam diameter which differ for SEM and TEM.

### 3 Electron Range

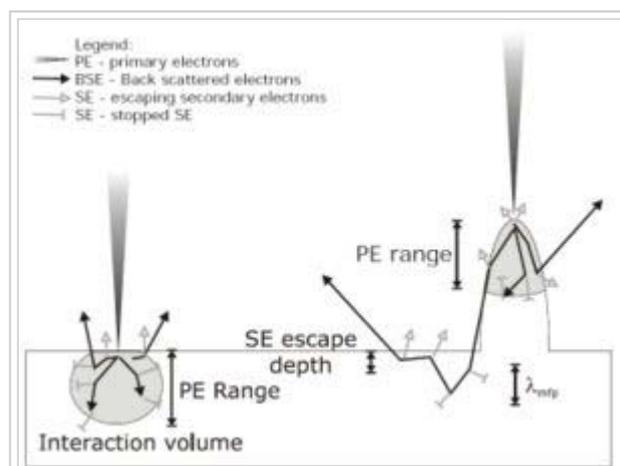
The electron optical system sets limitations to the achievable primary beam current and radius. The expected image resolution set by the primary beam cannot be reached if the signal detected for imaging is caused by electrons scattered far in the sample. The trajectory of an electron penetrating a bulk solid is a complex trajectory due to multiple elastic and inelastic collision events. As the primary electron (PE) penetrates into the sample it will gradually change direction and loose energy in collisions. The mean free path due to elastic and inelastic collisions,  $\lambda_{mfp}$ , depends on the atomic number of the material and the PE energy. At 100 keV  $\lambda_{mfp} = 150nm$  for carbon and 5 nm for gold [6]. For samples thinner than  $\lambda_{mfp}$  the main part of the PE will pass relatively unaffected through the sample, which is the basis for TEM.

SEM can be used for thicker specimens. The electrons that escape from the sample in a new direction compared to the PE due to elastic collisions are called backscattered electrons (BSE).

For samples thicker than  $\lambda_{mfp}$ , the volume interacting with the scattered PE defines the range of the electrons in the material, and this is considerably larger than the minimum achievable primary beam diameters.

The electron range is about 1  $\mu m$  at 10 keV for carbon, decreasing with higher atomic number for the material. Both the high energy PE and BSE generate secondary electrons (SE) by inelastic scattering events. The SE are generally defined as having energy below 50 eV while the BSE have energies up to the PE energy. The range of SE is typically 1 nm for metals and about 10 nm for insulators [7].

The short range of the SE make the yield of SE highly dependent on the



Overview of electron electron scattering processes in bulk and tip-shaped specimens. The PE are scattered

energy lost by the PE within the SE range from the surface, and this makes high Z substances efficient generators of SE. The main emission of SE takes place in the region where the PE strikes the surface and within the SE escape depth from this region.

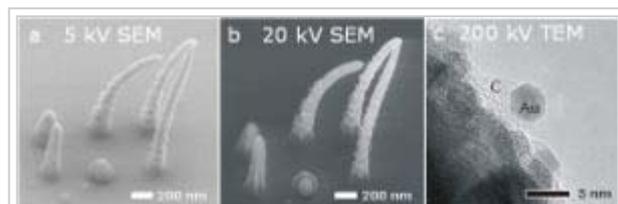
within the interaction volume, defined the electron range in the material. The range is longer than the mean free path  $\lambda_{mfp}$ . The SE have a very short range, and only those created within that range from the surface can escape the material. This defines the SE escape depth.

## 4 Scanning electron microscopy (SEM)

- Wikipedia: Scanning electron microscopy (SEM)

In a scanning electron microscope a beam is scanned over the sample surface in a raster pattern while a signal is recorded from electron detectors for SE or BSE. The PE energy is kept relatively low (1-30 keV) to limit the interaction volume in the specimen that will contribute to the detected signal. Especially low energy PE will provide high sensitivity to surface composition as they cannot penetrate far into the sample.

The figure above showed the effect of PE penetration depth of a carbonaceous nanostructure with a gold core, where only the surface is visible at low PE energies, while the carbon becomes increasingly transparent and the core visible at high PE energies.



The electron range increases with beam energy. The internal structure of the EEBD deposits can be examined at high electron beam energies in SEM. At 5 kV with shallow penetration depth, the surface of the tips is clearly visible while at higher energies a core of more dense material becomes increasingly visible. At 100 keV and above, TEM images can achieve atomic resolution where the lattice planes in nanocrystals such as the gold nanocrystal in (c). The gold crystal is embedded in amorphous carbon with no clear lattice pattern.

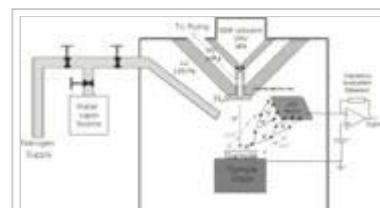
The low energy SE can easily be attracted and collected by a positively charged detector and are hence an efficient source for an image signal. The standard SE detector is an Everhart-Thornley (ET) detector where a positively charged grid attracts the SE and accelerates them to sufficiently high energies to create a light pulse when striking a scintillator. The light pulse is then amplified by a photomultiplier. Despite the complex construction, the ET detector is remarkably efficient, but requires large  $r_{wd}$  for effective collection of the SE by the charged grid.

Another SEM detector is the in-lens detector, where SE passing through the column aperture are accelerated towards a solid state detector. The in-lens detector complements the ET by being more efficient at short  $r_{wd}$ .

### 4.1 Environmental SEM (ESEM)

The ESEM makes it possible to use various gasses in the sample chamber of the microscope since there are narrow apertures between the sample chamber and the gun column, and a region in between that is connected to a differential pumping system. Pressures up to about 10 Torr are normally possible in the sample chamber.

The standard Everly-Thornhart SE detector would not work under such conditions since it would create a discharge in the low pressure gas. Instead a "gaseous secondary electron detector (GSD)" is used, as shown in the figure below. The GSD measures the current of a weak cascade discharge in the gas, which is seeded by the emission of electrons from the sample.



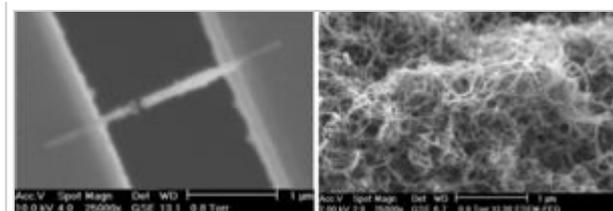
Simple sketch of an Environmental Scanning Electron Microscope (ESEM), where a differential pumping system with two pressure limiting apertures between the ultra high vacuum SEM column and the low vacuum sample chamber allows high pressures up to 10 hPa around the sample. This is enough to have liquid water at moderate cooling of 5 deg. C.

In the ESEM one can work with for instance water vapour or argon as the environmental gas, and it is possible to have liquid samples in the

chamber if the sample stage is cooled sufficiently to condense water.

## 5 Transmission electron microscopy (TEM)

- Transmission electron microscopy (TEM)
- High Resolution Transmission electron microscopy (HRTEM)



Two examples of images from an ESEM. Taken with a Philips XL-30 FEG. The first shows a electron beam deposited nanowire between two microelectrodes that has burnt after sustaining a high bias current. The other shows a multiwall carbon nanotube sample. Shorter working distances often improves image quality and so does a low beam current but it also increases the image acquisition time

When the specimen thickness is about the mean free path,  $\lambda_{mfp}$ , TEM can be used to achieve high resolution images such as the image above where the atomic lattice of a gold nanocrystal is visible. Since the detected electrons are transmitted PE where the energy can be in the 100 keV range, the resolution is not limited by the issues regarding secondary electrons. The electron beam optics can be optimized for higher current densities (Eq. #eq SEM current density) at higher energies compared to SEM.

To achieve optimal imaging conditions for the thin TEM samples, the working distance has been made short. In most TEMs, the space for the sample holder is only about (5 mm)<sup>3</sup> between the two objective lenses for the incoming and transmitted beam. Before reaching a CCD camera, the transmitted beam is sent through several magnification lenses to achieve the high magnification (500.000X is not unusual).



A Philips EM 430 TEM

The image formation in TEM can be based on several principles, but practically all images used in this work were made by phase contrast imaging, here called High Resolution TEM or HRTEM. At sufficiently high brightness, electron sources can produce coherent electron beams due to the point-like emitter surface area and small energy spread<sup>[8]</sup>. The coherent electron beam can be considered as a spherical wave propagating from the emitter and out through the electron optical system, much like a laser beam would propagate through an optical system.

The HRTEM images are often based on the interference of the electron wavefront after it has passed through the sample and reaches a CCD detector to give a phase contrast image of the sample. The image will have a resolution determined of course by the wavelength of the electrons (Eq. #eq SEM de broglie wavelength) but mainly by the imperfections of the electron optics which also perturbs the wavefront. The optimal imaging condition is for a sample thickness about  $\lambda_{mfp}$ , where the wavefront is only slightly perturbed by passing through the sample. TEM instruments are normally easily capable of resolving individual shells of a carbon nanotubes. The fine-tuning of the electron optical system to the required resolution can be achieved in about 30 min for many microscopes.

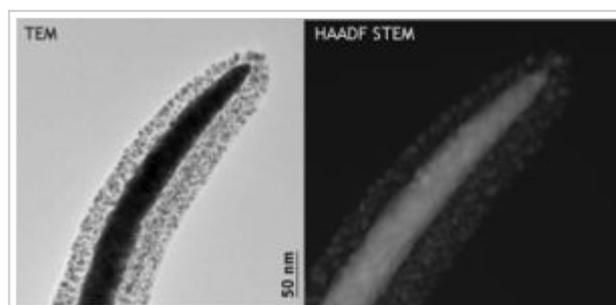
### 5.1 Environmental TEM (ETEM)

## 6 Electron energy loss spectroscopy (EELS)

- Electron energy loss spectroscopy

## 7 Electron Probe Micro Analysis or Energy Dispersive X-ray spectroscopy (EDS/EDX)

- Energy Dispersive X-ray spectroscopy



TEM images of the same nanostructure using standard 'bright field' TEM vs HAADF STEM. The sample is a gold nanoparticle containing environmental electron beam deposited rod.

## 8 Electron Diffraction

- Electron diffraction

## 9 Electron Holography

In special TEM microscopes, the diffracted beam can be combined with a part of the original electron beam from the electron gun, and the image that is recorded is an interference pattern that depends on how much the phase of the diffracted beam was changed. By recording such images, one can measure how the electron wave function changes as it passes through or nearby a nanostructure - and this allows you to measure the electric and magnetic fields surrounding nanostructures.

## 10 Electron Tomography

By recording numerous TEM images of an object at many different angles, these images can in a computer be combined to create a three-dimensional model of the object. The technique is time consuming but allows you to see nanostructures in 3D.

## 11 References

See also notes on editing this book about how to add references [Nanotechnology/About#How\\_to\\_contribute](#).

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# Nanotechnology/Scanning probe microscopy

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## 1 Scanning probe microscopy

Scanning probe microscopy covers the methods where a sharp tip is scanned over a surface in a raster pattern and the interaction with the surface is recorded in each pixel to form an image of the interaction. There are a multitude of methods and interactions in SPM. Broadly speaking, there are three main categories:

- In scanning tunneling microscopy (STM), one uses an atomically sharp metallic tip and records the minute tunneling current between the tip and the surface, when the tip is hovering so close to the surface that electrons can move between the surface and the tip.
- In Atomic force microscopy (AFM), a cantilever with a sharp tip - somewhat like the needle of an old record player - is scanned over the surface and the topography or surface softness can be recorded.
- In Scanning near-field optical microscopy (SNOM) a probe with a small aperture is scanned over the surface collecting the light coming from regions much smaller than the wavelength of the light used.

### 1.1 Atomic force microscope (AFM)

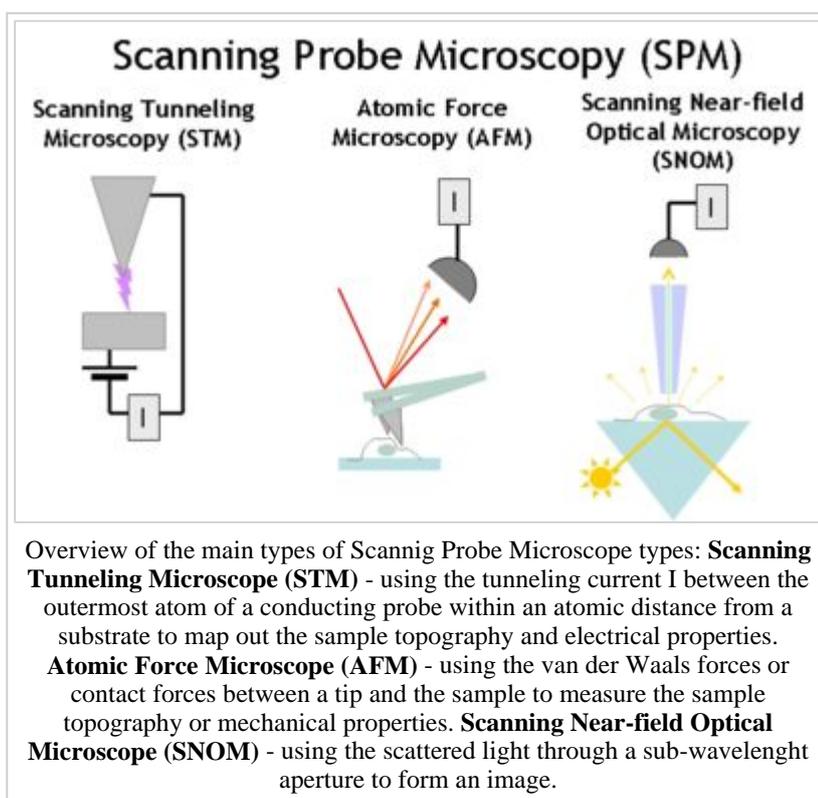
- Upcoming page in this wiki book on AFM
- Atomic force microscope (AFM)
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- Magnetic resonance force microscope
- Lateral force microscopy

### 1.2 Scanning tunneling microscopy (STM)

- Upcoming page in this wiki book on STM
- Scanning tunneling microscopy (STM)

### 1.3 Scanning Near-field optical microscopy (SNOM)

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Wiki links:

- Scanning Near-field optical microscopy (SNOM)
- Evanescent wave coupling

## 2 References

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# Nanotechnology/EBID

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# 1 Electron Beam Induced Deposition (EBID or EBD)

## 1.1 EBID Background

It was apparent with the first electron microscopes in the 50's, that the presence of an electron beam slowly coated the sample with a carbonaceous substance <sup>[1]</sup>.

Even earlier, it was observed that electron radiation decomposed organic vapors present in the vacuum chamber, such as oil vapors unavoidable in diffusion pumped vacuum systems or outgassing from the sample itself <sup>[2][3]</sup>.

When the background gas is decomposed by irradiation through various ionization and dissociation processes, the gas turns partly into volatile compounds re-emitted into the chamber and partly into solid amorphous carbon. The material properties range from diamond-like-carbon (DLC) to polymers depending on the exact deposition conditions <sup>[4]</sup>.

The reactions taking place during EBD are not well characterized. Both ionization and dissociation are expected to contribute <sup>[5]</sup>. The cross-section for both dissociation and ionization are peaked at low electron energies (<50 eV), indicating that secondary electrons are likely to be the main cause of deposition rather than the primary electrons (PE).

By focusing the PE beam in a fixed spot, a thin needle-shaped deposit will grow up towards the electron beam. The tip width can be considerably wider than the PE beam diameter and typically of the order 100 nm. The width is determined by the scattering of the PE in the tip structure which in turn also creates SE escaping through the tip apex and sidewalls causing a wider deposit <sup>[5]</sup>.

With many potential applications in micro- and nanotechnology, the EBD technique has received increasing attention since the 80's as a method for creating submicron structures. Comparing EBD to electron beam lithography (EBL), the EBD process must be considered "slow" while EBL is "fast" since the required irradiation dose is many orders of magnitude smaller for EBL.

The use of EBD in commercial production of nanostructures is today limited to "supertips" for AFM cantilevers with extreme aspect ratios that cannot readily be achieved by other methods <sup>[6]</sup>.

For research purposes, where high throughput is not a requirement, the technique appears convenient in several applications. Apart from depositing structures, it has also been used to solder nanocomponents. Both single and multiwalled carbon nanotubes (SWNT and MWNT) have been soldered to AFM cantilevers for stress-strain measurements <sup>[7][8]</sup> and to micromechanical actuators for electrical and mechanical tests <sup>[9] [10]</sup>

## 1.2 Metal deposition by EBID

A large fraction of the EBD publications have been focussing on the use of metal containing precursor gasses. Koops et al. <sup>[11]</sup>

and Matsui et al. <sup>[12]</sup> pioneered the extensive use of metal containing source gasses to make deposits with high metal contents. They also began scanning the beam in patterns to make three-dimensional structures. Complex three-dimensional structures can be made by EBD with both carbonaceous and metal-containing EBD. Another intriguing possibility is to use EBD to make catalyst particles for subsequent growth of nanowires and tubes <sup>[13]</sup>.

Compared to the planar and resist-based EBL, the EBD method is slow and difficult to scale to large productions, but on the other hand offers the possibility to create elaborate three-dimensional structures, which cannot readily be made by EBL. The EBD method appears to be a versatile tool capable of constructing nanodevies, contacting nanostructures to create composite electronic nanostructures, and soldering nanostructures such as carbon nanotubes to microelectrodes.

For electronic applications one would like to achieve as high a conductivity as possible of the deposited material. Metal-containing EBD materials usually contain metallic nanocrystals in an amorphous carbon matrix with a conductance considerably lower than that of the pure metal. The metal content and conductivity of the EBD material can be increased to approach that of bulk metals by several methods:

1: Heating the substrate has been shown to increase the metal content of the deposit. Koops et al. <sup>[14]</sup> have observed an increase from 40 wt. % at room temperature to 80 wt.% at 100°C. Others, for example Botman et al. <sup>[15]</sup> have shown the link between deposit composition and conductivity as a function of post-treatment in heated gases.

2: Using a carbon free precursor gas, such as  $PF_3AuCl$ , Hoffman et al. <sup>[16]</sup> made gold deposits with a conductivity of 22  $\mu\Omega\text{cm}$  which is only 10 times the bulk value of Gold.

3: Introducing an additional gas such as water vapor while using an environmental scanning electron microscope (ESEM)<sup>[17]</sup>. It is even possible to create desposits with a solid gold core under controlled deposition conditions <sup>[10]</sup>.

## 2 Resources

- Review paper: Focused, Nanoscale Electron-Beam-Induced Deposition and Etching by Randolph et al. <sup>[18]</sup>
- [<http://www.febip.info/> Focused Electron Beam Induced Processes

(FEBIP)]

## 3 A Simple Model of EBD

To accurately model the EBD process, one has to resort to Monte Carlo simulations that can incorporate the different scattering effects taking place during the process. Extensive work done has been done on models for the deposition of amorphous carbon tips <sup>[5]</sup>. Generally there is very little available knowledge on:

- The radiation induced chemistry of the metal containing precursor gas. A wealth of reactions are possible, but limited data is available for the conditions and substances used for EBD.
- The chemical content of the produced amorphous carbon in the deposit.
- The current density in the electron beam is rarely well characterized.

Not knowing the chemical details of the deposition process, the exact product of the deposition, or the electron beam, a simple analytical model will also provide insight to the essential parameters. A simple model is reviewed below to provide an understanding of the basic requirements and limitations for the EBD process.

### 3.1 The Rate Equation Model

Electron beam deposition of planar layers on surfaces can be reasonably described by a simple rate equation model <sup>[19]</sup>.

The model shows the fundamental limitations for growth rate and its dependence on beam current and precursor gas flow. The model calculations and most experiments in this thesis, are based on the precursor gas dimethyl gold acetylacetonate, here abbreviated to DGAA. The vapor pressure of the precursor gas determines the flux of precursor molecules to the surface. The flux rate of molecules  $F$  [ $\text{m}^2\text{s}^{-1}$ ] of an ideal gas at rest is

$$F = \frac{P}{\sqrt{2\pi mk_B T}}$$

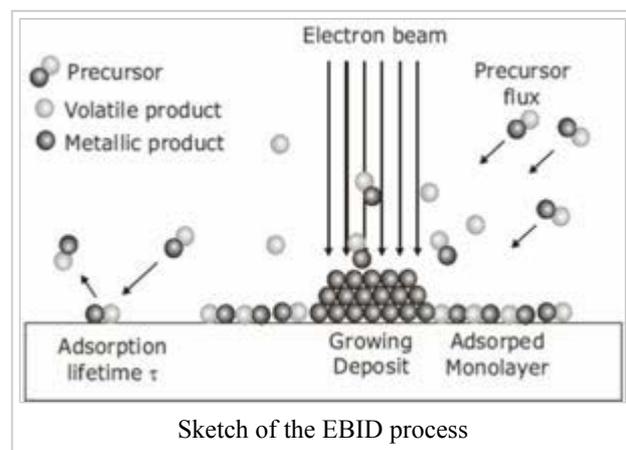
with pressure  $P$ , atomic weight  $m$ , Boltzmann constant  $k_B$  and temperature  $T$ . For DGAA which has a vapor pressure of 1.3 Pa at 25 °C, this gives a flux rate  $F = 10^{18} \text{ cm}^{-2} \text{ s}^{-1}$

The cross-sections for electron beam induced ionization and dissociation of the precursor gas to form the deposits are generally not known. Cross-sections are usually of the order  $\text{\AA}^2$  and peak at low energies, corresponding to the low energy of the secondary electrons which are probably the main cause of the deposition.

The adsorption of molecules on the target surface and highest density of SE near the surface make it reasonable to assume that the deposition rate  $dN_{\text{dep}}/dt$  depends on the surface density of adsorbed precursor molecules  $N_{\text{pre}}$ , the beam current density  $J$ , and the effective cross section  $\sigma_0$  as

$$\frac{dN_{\text{dep}}}{dt} = N_{\text{pre}} \sigma_0 \frac{J}{q_e}$$

The surface density  $N_{\text{pre}}$  of the adsorbed precursor molecules in Eq. #eq EBD dep surface rate is the source for the deposited material and depends on both the deposition, ad- and desorption processes as sketched in the figure.



With maximum surface density  $N_0$  (e.g. one monolayer, since generally more than one monolayer cannot be expected unless the target is cooled compared to the source, to give condensation of the source gas. Then adsorption probability  $a$  and lifetime  $\tau$  (s), a rate equation can be written for the precursor surface density as <sup>[20]</sup>

$$\frac{dN_{\text{dep}}}{dt} = aF(1 - (N_{\text{pre}}/N_0)) - \sigma_0 J N_{\text{pre}}/t - N_{\text{pre}}/q_e$$

The steady state adsorbate density,  $N_{\text{pre}}$ , is then

$$N_{\text{pre}} = \frac{aF}{aF/N_0 + 1/\tau + \sigma_0 J/q_e}$$

If each deposition event on average results in a cubic unit cell of deposited material with volume  $V$ , the vertical growth rate  $R$  [nm/s] is

$$R = N_{\text{pre}} V \sigma_0 J / q_e$$

$$= V \frac{aF}{q_e \frac{\tau aF/N_0 + 1}{\sigma_0 J t} + 1}$$

The dependence on precursor flux falls into two cases:

- $\tau aF > N_0$  when a monolayer is always present and increasing the flux rate  $F$  has little effect on the growth rate  $R$ , since the surface is saturated
- $\tau aF < N_0$  when less than a monolayer is present, and increasing  $F$  will increase the growth rate  $R$ .

Increasing the electron beam current will in this model always increase the deposition rate. The rate increases relatively linearly with the electron flux, until it begins to saturate when the source gas flux becomes the limiting factor for the growth rate.

Scheuer et al. <sup>[21]</sup> have measured the EBD deposition cross section of  $\text{Ru}_3(\text{CO})_{12}$  to be of the order  $\sigma_0 = 0.2 \text{ \AA}^2$  and  $\tau = 1 \text{ s}$ . Using these values, a rough estimate of the growth rate can be calculated. For the estimate, we assume a monolayer is present ( $\tau aF = N_0$ ); a sticking efficiency of  $a=100\%$ ; the vapor pressure flux of DGAA; an electron beam diameter of 20 nm; a total

beam current of 0.2 nA; and finally that the unit cell volume  $V$  for deposition is that of gold. With this set of values, the deposition rate becomes  $R = 100$  nm/s.

The used values make  $\sigma_0 J / q_e \gg \tau a F / N_0$  so the deposition is not limited by the electron beam current but by the gas flux which would have to be 10 times higher to reach saturation. The beam radius will have to be increased to  $r = 0.5$   $\mu\text{m}$  to reach the electron flux limited region and this radius is much larger than the observed resolution in most experiments. It is important to secure as high as possible flux of precursor gas in the experiments, since this is the main limiting factor in the model whereas the focus of the electron beam is expected to be less important due to the high current density.

## 3.2 Limitations to the model

The rate model is suited for describing deposition of planar layers, but for the case of deposition of tip structures in a real system, several other effects influence the deposition rate:

Scattering of primary electrons in the deposited structure. BSE and SE are emitted through the sidewalls and apex of the structure in a non-uniform way, and the PE/BSE scattering make SE generation take place in a larger region than the PE beam radius, which considerably limits the minimal radius for tip structures.

The figure above illustrate these effects. Simulations are needed to make proper estimates of the influence of scattering, but qualitatively it should cause a lower vertical growth rate as less electrons must be expected to emerge through the upper surface of the structure.

The PE beam is not uniform as considered in the model. In an ESEM, a Gaussian distribution of the PE beam can be expected, and the scattering of the electron beam in the environmental gas creates an low current density "electron skirt" around the PE beam. This should be considered both for the possible contamination in the larger region irradiated with low current density, but also for reducing the current in the primary beam and thus the growth rate.

It was assumed that the source supply precursor gas with the vapor pressure gas flux rate. The rate could be considerably lower if the source material does not have enough surface area to sustain the gas flow or the distance to the source is too large. The fact that many organometallic compounds decompose in contact with water in the case of EEED could also reduce the source gas flow.

Not all irradiation induced events will result in deposition of material. Substantial amounts of material could be volatile or negatively ionized and carried away, especially in an the ESEM environment. Electron attachment is also taking place in the ESEM and is known to influence the detection of secondary electrons <sup>[22]</sup>. This could reduce the supply of precursor gas and hence the deposition rate.

Surface diffusion of the precursor gas will influence the supply rate. When depositing in only a small area, surface diffusion of adsorbed molecules from the surrounding area can considerably increase the supply of precursor molecules. This is usually the explanation given why many EBD experiments observe that the tip deposition is faster in the beginning; for then to decrease to a steady state growth rate, when a tip structure is formed which limits the supply by surface diffusion. This could increase the rate at the very beginning of the deposition.

The predicted vertical growth rate from the model must be an upper estimate on the achievable rate, since most unaccounted effects will work to reduce the steady state growth rate.

## 3.3 Summary

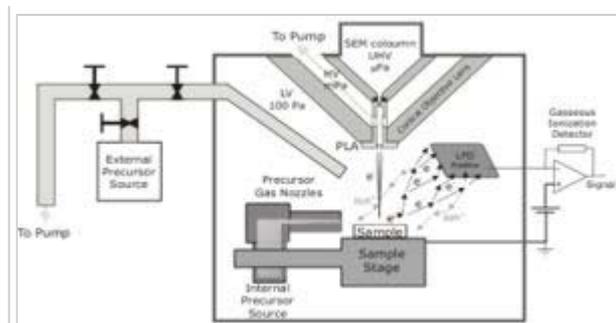
Little data is available on the precursor gasses for EBD. A simple rate equation model gives an estimated deposition vertical growth rate of 100 nm/s for the typical precursor gasses. This estimated growth rate is expected to be an upper limit. Especially the flow rate of precursor gas should be as high as possible in the experiment since this is the limiting factor for the deposition rate.

# 4 Environmental Electron Beam Deposition (EEBD)

The ESEM makes it possible to use various gasses in the sample chamber of the microscope since there are narrow apertures between the sample chamber and the gun column, and a region in between that is connected to a differential pumping system. Pressures

up to about 10 Torr are normally possible in the sample chamber.

The standard Everly-Thornhart SE detector would not work under such conditions since it would create a discharge in the low pressure gas. Instead a "gaseous secondary electron detector (GSD)" is used, as shown in the figure below. The GSD measures the current of a weak cascade discharge in the gas, which is seeded by the emission of electrons from the sample.



The experimental setup for environmental electron beam deposition (EEBD) with a precursor gas supply either mounted on the sample stage or via an external gas feed system.

In the ESEM one can work with for instance water vapour or argon as the environmental gas, and it is possible to have liquid samples in the chamber if the sample stage is cooled sufficiently to condense water.

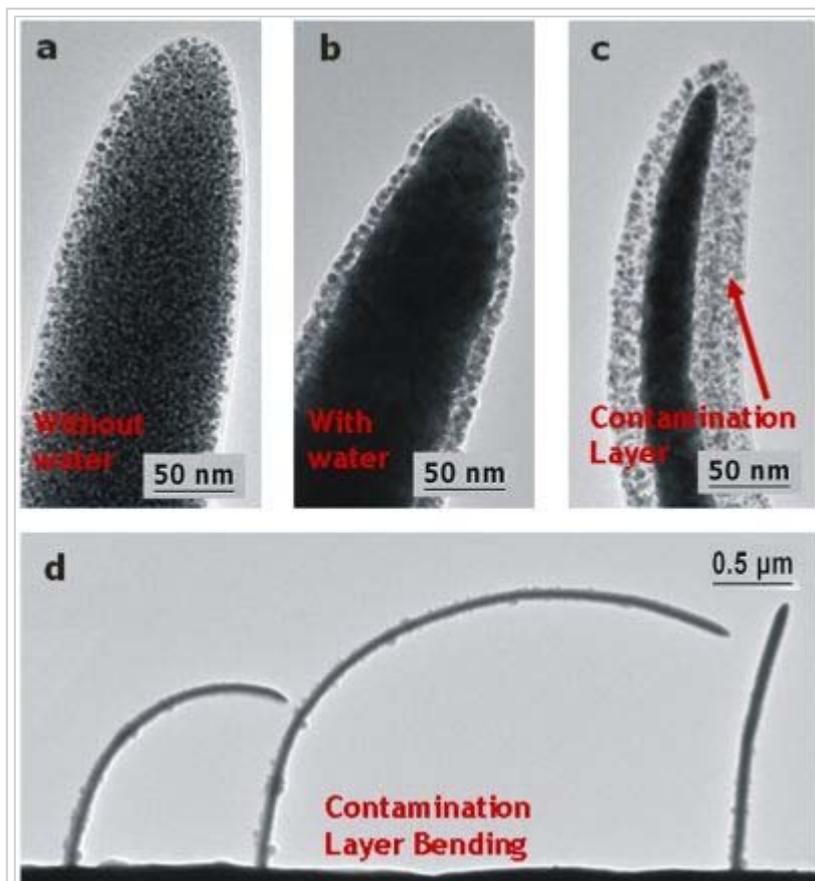
Without precursor gas present in the chamber, the EBD deposition rate is normally negligible in the high vacuum mode as well as in the gas mode of the ESEM.

In environmental electron beam deposition (EEBD), the deposited tips have a shell structure and consist of different material layers each characterized by a certain range of gold/carbon content ratio. Above a certain threshold of water vapor pressure and a certain threshold of electron beam current, the deposited tips contain a solid polycrystalline gold core <sup>[10]</sup>.

## 5 Acknowledgement

This page was started based on the material in:

- Kristian Mølhave's PhD thesis chapter 4



TEM images illustrating how the morphology of EEBD tips using DGAA as precursor depends on the deposition conditions. (a) Apart from water vapor, all other tested environmental gasses (N<sub>2</sub>; O<sub>2</sub>/Ar; H<sub>2</sub>/He) have resulted in tips containing gold particles embedded in an amorphous carbon containing matrix. (b) When using water vapor as environmental gas, a dense gold core becomes increasingly pronounced as the vapor pressure and beam current is increased. (c) A contamination layer almost void of gold can be deposited on the tip by scanning the beam while imaging. So-called proximity contamination can also occur if depositions are done later within a range of a few μm from the tip. The contamination layer is thicker on the side facing later depositions. (d) Electron irradiation in SEM or TEM causes the contaminated tips to bend irreversibly towards the side with the thickest contamination layer. The tips were deposited from left to right and thus bent towards the last deposition. More information in <sup>[10]</sup> and <sup>[9]</sup>.

(<http://www.molhave.dk/kristian/thesis/phd/MolhavePhDThesis.pdf>) and accompanying papers <sup>[10]</sup> and <sup>[9]</sup>.

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See also notes on editing this book about how to add references Nanotechnology/About#How\_to\_contribute.

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