

for tomorrow

PROFESSORIAL INAUGURAL LECTURE

PROFESSOR JR BOTHA

29 MAY 2013

17:30

Faculty of Sciences

Topic: "Of Science and Small Things: Recollections from the past twenty(-)odd years"

Of Science and Small Things Inaugural Lecture: JR Botha Department of Physics 29 May 2013

Acting Vice-Chancellor, Deans, colleagues, family, friends

It is an honour for me to be here. I would like to express my sincere gratitude towards the NMMU for its recognition of my small contribution to the institution over the years. I can assure you that the pursuit of accolades and personal gain is not foremost in my mind when performing my daily tasks as an academic. Having said that, it is human nature to enjoy recognition for one's efforts and my promotion to Professor of Physics last year was definitely one of the highlights of my career.

Before launching into the formal part of my presentation, I would like to acknowledge several people who have played a role in my development as an academic over the years. I also need to point out that the development of an academic depends to some extent on a parasitic relationship with others in the system. I would be the first to concede that my progression through the ranks of academia cannot be ascribed solely to my own efforts, but that there have been substantial contributions from colleagues and post graduate students through the years.

In no specific order then, I would like to thank the following:

Professor Japie Engelbrecht for his support during his term as Head of the Physics Department. My former promoters, Andrew Leitch and Jan Neethling, for starting me on a research path. A special thanks to Andrew for his mentoring role during the early part of my career at the former UPE. To Pearl Berndt, a former colleague who married an internet friend and moved to the USA some years ago – thanks for teaching me patience. To my present colleagues Andre Venter and Magnus Wagener, with whom I collaborate closely in the field of semiconductor development: thanks for your contributions during the past several years. I hope I can count on your continued support and friendship in years to come. My friends Jano Jonker and Deon Raubenheimer: thanks for the many interesting discussions and debates (often of a non-academic nature) – one needs a little balance in life after all.

Mrs Linda Kritzinger and Jualine Ferreira – I am truly grateful for your administrative assistance through the years. Jualine, I have never come across a person as selfless as you are. No matter how mundane the task, you always perform it with a smile on your face.

Johan Wessels, Dan O'Connor (who sadly passed away in 2011), Len Compton, Marius Claassen – many thanks for your technical assistance. Uncle Len – your exceptional skills as a fine instrument maker will be sorely missed when you retire.

I am indebted to several colleagues and friends from the rest of the country as well as overseas who have made a contribution to our research over the years. I will not read out names, but simply list

them here. Not only have I benefitted academically from interacting with these people over the years, but also some of my colleagues, students and post-doctoral fellows.

I also need to acknowledge the valued contributions of the various post-doctoral fellows active in our group over the years, as well as those of the post graduate students whom I have been involved with. Some of them made my life more difficult than others, but in the end they all made me proud.

Last, but not least, I need to tank my family for all the sacrifices they have made through the years. My wife Nanette, my apologies for all the times you have had to fulfil the role of father while I was at a conference or on a research visit. I also apologise for my poor choice of career, specifically considering the poor salaries that academics earn.....

Of Science and small things

When I submitted a title for this lecture, I had not quite decided what the content of the presentation would be. I was in two minds whether to bore you with our own research activities over the years, or to present an overview of international efforts in nanoscience and technology in recent decades. In the end I decided to err on the safe side and focus on a topic of more general scientific interest, and to keep our own modest efforts in the blossoming field of nansocience to a minimum. Since senate requires of me to submit a written version of the presentation, I decided to read this lecture tonight in order to ensure that the content is shared accurately, in the correct order and that nothing gets left out.

I will start, therefore, with an overview of achievements in a "new" field of endeavour, a science of small things, popularly called nanoscience, and its spin-off called nanotechnology. I will present a brief history, look at the approaches that have been followed by scientists and engineers to develop and understand small things, and summarise some of the benefits to society in terms of new materials and processes, energy storage and generation, electronics, environmental applications, medicine and transportation. Since our own research focuses on the development on semiconductors, I will conclude the scientific part of the presentation by considering the contribution of semiconductors to the development of nanotechnology and highlight a few examples from our own research during the past two decades on the development of nano-scale semiconductor structures, like nanorods, quantum wells and superlattices.

What is Nanotechnology?

A survey of available scientific and science policy literature reveals numerous definitions for nanotechnology. They all agree on the length scales of interest: between 1 and 100 nm.

Two examples:

In the 2007 Strategic Plan of the US National Nanotechnology Initiative Nanotechnology is defined as follows:

• "Nanotechnology is the understanding and control of matter at dimensions of roughly 1 to 100 nanometers, where unique phenomena enable novel applications."

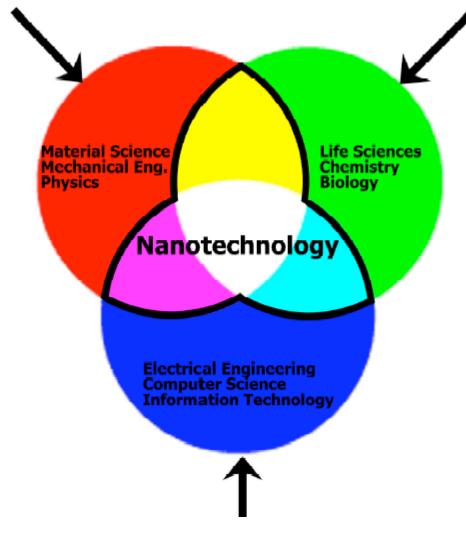
• "Encompassing nanoscale science, engineering and technology, nanotechnology involves imaging, measuring, modeling, and manipulating matter at this length scale."

From the July 2004 issue of Nanoscience and Nanotechnologies, published by the Royal Society and the Royal Academy of Engineering, the following distinction between nanoSCIENCE and nanoTECHNOLOGY:

We define nanoscience as the study of phenomena and manipulation of materials at atomic, molecular and macromolecular scales, where properties differ significantly from those at a larger scale; and nanotechnologies as the design, characterisation, production and application of structures, devices and systems by controlling shape and size at the nanometre scale.

I will loosely refer to both components (the scientific and the technological) as nanotechnology, although it is understood that nanoscience refers to all endeavours aimed at understanding the behaviour of matter on the nanoscale, while nanotechnology refers to the manipulation, application, and use of nanometer-sized objects and matter for a specific function, or for specific technologies and applications.

Nanotechnology is inherently multidisciplinary: it spans Physics, Chemistry, Biological Sciences, Engineering and Medicine. A Google search combining these two terms (nanotech and multidisciplinary) will return close to a million hits. Although often stated or accepted as fact, the multi-disciplinary nature stems mainly from the fact that all these disciplines operate on the nano-scale and use the same instrumentation in their research. At least, this is the status at present. Nanotechnology requires (demands is perhaps a better term) scientists to cut across discipline boundaries to unite the isolated islands of innovation, since



it appears to be node/intersection of all the sciences.

Is it a new Science?

The answer is simple: NO. It is evolutionary, yes, in the sense that the same science developed over the past hundred years can describe the phenomena occurring on the nanoscale. Through advancements in technology, however, matter can now be manipulated at the nanoscale, creating new building blocks that produce material with specific desired properties and phenomena not experimentally observed before.

How small is a nanometer?

Just how small is "nano?" In the International System of Units, the prefix "nano" means onebillionth, or 10⁻⁹; therefore one nanometer is one-billionth of a meter. It's difficult to imagine just how small that is, and some examples I have come across are not all that useful:

- A finger nail grows 1 nm in 1 second I have never been able to observe my finger nail growing, which either shows how bad my eyesight is, or that a nanometer is indeed very small. I can check the accuracy of this statement, however, since I know that 1 mm is 10⁻³ m which means that there are 1 million nm in 1 mm. So, in a period of 1 million seconds, my fingernails will grow by 1 mm. Now, 1 million seconds is ~11 ½ days that checks out, because I have to trim my nails by approximately 1 mm every two weeks.
- Another dumb one: Imagine ten hydrogen atoms lined up side by side this is roughly one nanometer. OK, this means 1 hydrogen atom is 1/10th of a nanometer. I have never observed a hydrogen atom!

Perhaps these will help to bring home the concept:



- A sheet of paper is about 100,000 nanometers thick
- There are 25,400,000 nanometers in one inch
- A human hair is approximately 80,000- 100,000 nanometers wide

What makes it special?

Nanoscale particles are not new in either nature or science. However, progress in areas such as microscopy have given scientists new tools to understand and take advantage of phenomena that occur naturally when matter is organized at the nanoscale. In essence, these phenomena are based on "quantum effects" and other simple physical effects such as expanded surface area (more on these below). In addition, the fact that a majority of biological processes occur at the nanoscale gives scientists models and templates to imagine and construct new processes that can enhance their work.

• Quantum effects dominate material properties at this scale

When particles are created with dimensions of about 1–100 nanometers (this is the regime where they can be "seen" only with very special microscopes), their properties change significantly from those at larger scales. This is the size scale where so-called quantum effects rule the behavior and properties of particles. I will return to quantum effects later. The properties of materials (like their melting point, light emission, electrical and magnetic behaviour, chemical reactivity) become size dependent in this scale range.

Nanoscale gold is a good example. Nanosized gold particles are not the yellow color with which we are familiar; they can appear red or purple. Their size and optical properties can be put to practical use: nanoscale gold particles selectively accumulate in tumors, where they can enable both precise imaging and targeted laser destruction of the tumor by means that avoid harming healthy cells.

• Biology occurs at this scale

Over thousands of years, nature has perfected the art of biology at the nanoscale. Many of the inner workings of cells naturally occur at the nanoscale. For example, hemoglobin, the protein that carries oxygen through the body, is 5.5 nanometers in diameter. A strand of DNA, one of the building blocks of human life, is only about 2 nanometers in diameter.

Many medical researchers are working on designing tools, treatments, and therapies that are more precise and personalized than conventional ones—and that can be applied earlier in the course of a disease and lead to fewer side-effects. As an example, "recognition" particles and DNA "amplifiers" can be attached to gold nanoparticles, for a prostate cancer biomarker. The growing understanding of nanoscale biomolecular structures is impacting other fields than medicine. Some scientists are looking at ways to use nanoscale biological principles of molecular self-assembly, self-organization, and quantum mechanics to create novel computing platforms. Other researchers have discovered that in photosynthesis, the energy that plants harvest from sunlight is nearly instantly transferred to plant "reaction centers" by quantum mechanical processes with nearly 100% efficiency (little energy wasted as heat). They are investigating photosynthesis as a model for "green energy" nanosystems for inexpensive production and storage of nonpolluting solar power.

• Surfaces and interfaces dominate at this scale

Nanoscale materials have far larger surface areas than similar masses of larger-scale materials. Thus, a greater amount of the material can come into contact with surrounding materials, increasing the reactivity.

Let's consider a solid cube of some material with sides of 1cm. The volume of the cube is 1 cm^3 and the total surface area will be 6 square centimeters, about equal to one side of your pinkie. I this cube were filled with smaller cubes, say 1 mm on a side, there would be 1,000 millimeter-sized cubes (10 x 10 x 10), each one of which has a surface area of 6 square millimeters, for a total surface area of 6000 square mm or then 60 square centimeters (remember a square of 1 cm x 1 cm is the same as 10 mm x 10 mm, meaning there are 100 square mm in 1 square cm). You can see what is happening here: every time I reduce the size of the building blocks by a factor 10, the total area goes up by a factor 10. If the building blocks have sides 1 nm (10⁷ times smaller than a cm) the total area increases 10⁷ times (10 million times). Thus the total surface area of cubes with sides 1 nm making up the original cube will be 10 million times 6 cm² or then 6 000 m². You can check the maths later, but this means that a single cubic centimeter of cubic nanoparticles has a total surface area one-third larger than a rugby field!

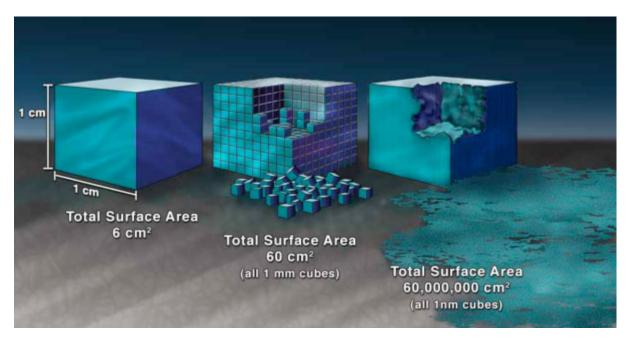


Illustration demonstrating the effect of the increased surface area provided by nanostructured materials

The impact of the vast increase in surface area on the reactivity of the material is extreme. As an example, consider a simple aluminium Coke can. If you take the inert aluminium metal in that can and grind it down into a powder of 20-30nm particles, it will spontaneously explode in air. It becomes a rocket fuel catalyst!

We shall return to the implications and benefits of the above-mentioned effects later.

Timeline

I will now mention a few of the examples, discoveries and milestones in nanotechnology,

both from the pre-modern era and from the modern era.

Pre-modern Era

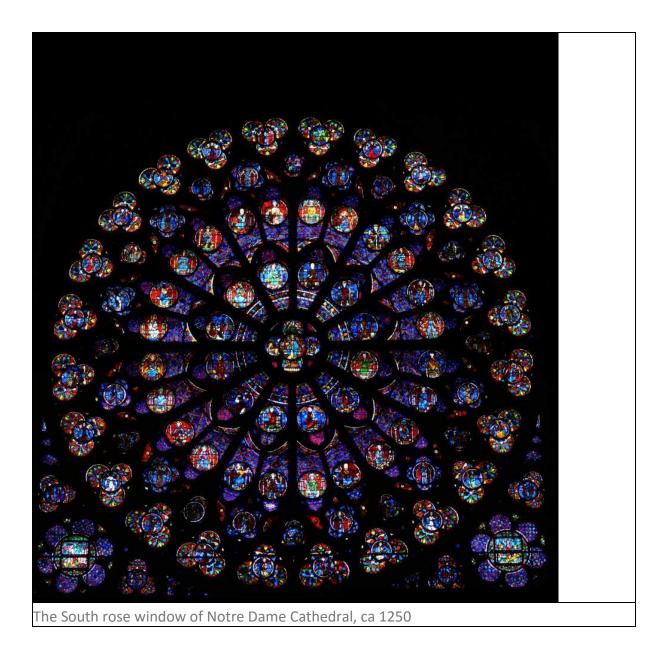
Nanotechnology has been around for more than a millennium. Early examples of nanostructured materials were based on craftsmen's empirical understanding and manipulation of materials, and certainly not on their understanding of the physical and other properties of materials on the nanoscale. The use of high temperatures was one common step in their processes to produce these materials with novel properties.



The Lycurgus Cup at the British Museum, lit from the outside (*left*) and from the inside (*right*)

4th Century: The Lycurgus Cup (dating back to the 4th Century and used in the Roman Empire) is an example of **dichroic glass (from the Greek DIKHROOS, meaning two colours), which transmits and reflects different colours. C**olloidal gold and silver layers in the glass with thickness similar to the wavelength of visible light allow it to look opaque green when lit from outside (i.e. green light is reflected) but translucent red when light shines through the inside (i.e. red light is transmitted). This is an example of thin film interference, something taught at first year level.

6th-15th Centuries: The vibrant **stained glass windows** in European cathedrals constructed during the 6th to 15th centuries owed their rich colors to nanoparticles of gold chloride and other metal oxides and chlorides. The colour arises from the preferential scattering of visible light from particles with diameters similar to the wavelength of light (Mie scattering).



The Modern Era

More recent discoveries and ideas are based on an increasingly sophisticated scientific understanding of the nano-world and highly sophisticated instrumentation, as well as experimentation.



"Ruby" gold colloid (Gold Bulletin 2007 40,4, p. 267)

1857: Michael Faraday discovered **colloidal "ruby" gold**, demonstrating that nanostructured gold under certain lighting conditions produces different-colored solutions.

1936: Erwin Müller, working at Siemens Research Laboratory, invented the **field emission microscope**, allowing near-atomic-resolution images of materials.

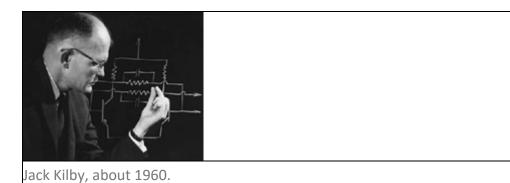
1947: Bardeen, Shockley and Brattain at Bell Labs discovered the **semiconductor transistor** which laid the foundation for electronic devices and the Information Age. I will come back to



1947 transistor, Bell Labs

the role of semiconductor materials in the development of nanotechnology shortly.

1951: Erwin Müller pioneered the **field ion microscope**, with which the arrangement of atoms at the surface of a sharp metal tip could be viewed.



1958: Jack Kilby of Texas Instruments proposed, designed and built the first integrated

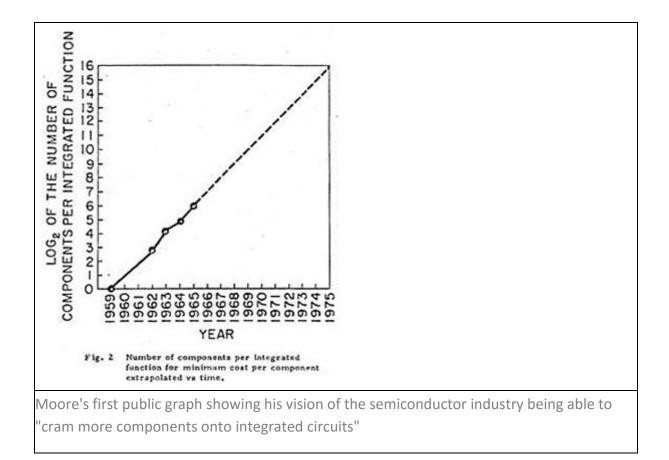


circuit, for which he received the Nobel Prize in 2000.

1959: At the California Institute of Technology the brilliant physicist and Nobel laureate Richard Feynman presented what is considered to be the first lecture on technology and engineering at the atomic scale, entitled "**There's Plenty of Room at the Bottom**". This rather casual effort was delivered as an after-dinner speech at an American Physical Society meeting. The ideas he proposed for a future technology based on atomic scale manipulation were truly remarkable, The world has traveled far toward what Feynman saw, and has far still to go.

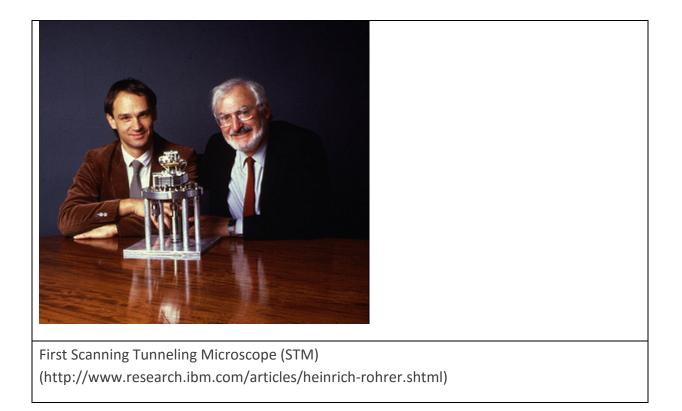
Feynman proposed shrinking computing devices toward their physical limits, where "wires should be 10 or 100 atoms in diameter". Bear in mind that in those days a computer still filled an entire room. In 2012, Samsung announced large-scale production of mobile memory devices built with 30 nanometer technology, while Intel's revolutionary 22 nm technology for producing microprocessors reached the production stage. This is to say, these technologies operate at Feynman's 100-atom scale.

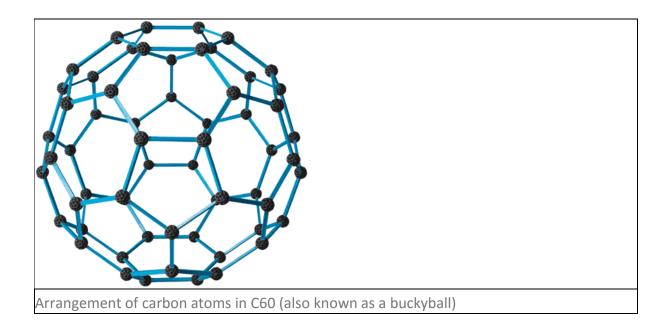
The talk held much more than that: Feynman suggested that focused electron beams could write nanoscale features on a surface; this is now called "electron-beam lithography". He suggested that electron microscopes with less symmetric lenses could image atoms; this is the idea behind the new generation of aberration-corrected microscopes, and they do image atoms. He pointed to complex, active, nanoscale biological mechanisms as an inspiration for nanoscale technology; these have become the basis of what is called "biotechnology", which has delivered what are in some ways the most advanced nanotechnologies developed to date.



1965: Intel co-founder Gordon Moore described in *Electronics* magazine several trends he foresaw in the field of electronics. One trend now known as "**Moore's Law**," described the density of transistors on an integrated chip (IC) doubling every 12 months (this was later amended to every 2 years). Moore also saw chip sizes and costs shrinking with their growing functionality—with a transformational effect on the ways people live and work. That the basic trend Moore envisioned has continued for 50 years is to a large extent due to the semiconductor industry's increasing reliance on nanotechnology as ICs and transistors have approached atomic dimensions.

1981: Gerd Binnig and Heinrich Rohrer at IBM's Zurich lab invented the **scanning tunneling microscope**, allowing scientists to create direct spatial images of individual atoms for the first time. They won the Nobel Prize for this discovery in 1986.





1985: Rice University researchers Kroto, O'Brien, Curl, and Smalley discovered the **Buckminsterfullerene**, also known as the **buckyball**, which is a molecule containing 60 carbon atoms and which resembles a soccer ball in shape. The team received the 1996 Nobel Prize in Chemistry for their roles in this discovery.

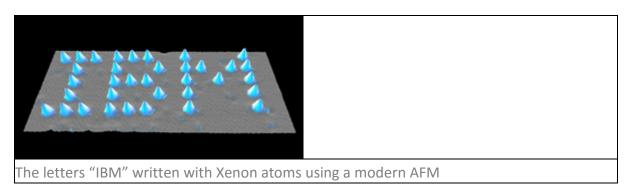
1985: Bell Labs's Louis Brus discovered **colloidal semiconductor nanocrystals (quantum dots)**, for which he shared the 2008 Kavli Prize in Nanotechnology.

1985: Gerd Binnig, Calvin Quate, and Christoph Gerber invented the **atomic force microscope**, which has the capability to view, measure, and manipulate materials down to fractions of a nanometer in size, including measurement of various forces intrinsic to nanomaterials.



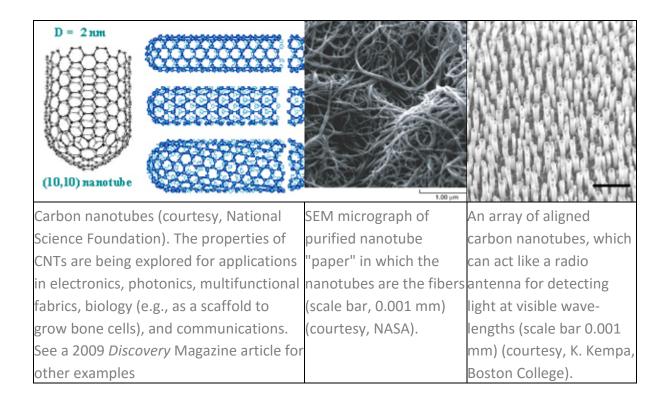
1989: Don Eigler and Erhard Schweizer at IBM's Almaden Research Center **manipulated 35 individual xenon atoms to spell out the IBM logo**. This demonstration of the ability to precisely

manipulate atoms ushered in the applied use of nanotechnology.

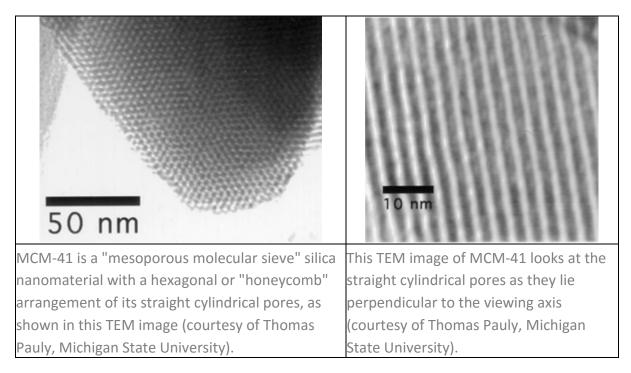


1990s: Early nanotechnology companies began to operate.

1991: Sumio Iijima of NEC is credited with discovering the **carbon nanotube (CNT)**. CNTs, like buckyballs, are entirely composed of carbon, but in a tubular shape. They exhibit extraordinary properties in terms of strength, and electrical and thermal conductivity.



1992: C.T. Kresge and colleagues at Mobil Oil discovered the **nanostructured catalytic materials MCM-41 and MCM-48**, now used heavily in refining crude oil.

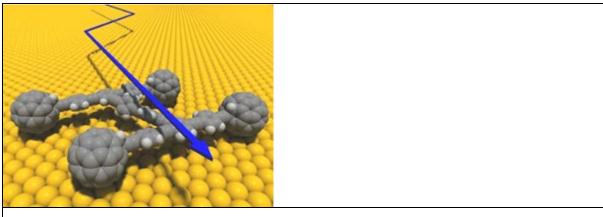


1999–early 2000's: Consumer products using nanotechnology started appearing in the marketplace.

2000: President Clinton launched the National Nanotechnology Initiative (NNI), while the US Congress funded the NNI for the first time in FY2001.

2003: Scientists at Rice University developed gold nanoshells, which when "tuned" in size to absorb near-infrared light, serve as a platform for the discovery, diagnosis, and treatment of breast cancer without invasive biopsies, surgery, or systemically destructive radiation.

2004: The European Commission followed in the footsteps of the Americans and adopted the Communication "Towards a European Strategy for Nanotechnology".



Nanocar with turning buckyball wheels (credit: RSC, 29 March 2006).

2006: James Tour and colleagues at Rice University built a **nanoscale car** with frame made of OPE (an abbreviation for molecules with the unpronounceable name oligo(phenylene ethynylene) and four spherical buckyball wheels. In response to increases in temperature, this nanocar moved about on a gold surface as a result of the buckyball wheels turning, as in a conventional car. At temperatures above 300°C it moved around too fast for the chemists to keep track of it!

2006: South Africa launched its National Nanotechnology Strategy with the objective to support long-term nanoscience research, to develop human capital and to develop supporting infrastructure. One of the key interventions was the establishing of two national nanotechnology innovation centers, one at the CSIR in Pretoria and the other at Mintek, Johannesburg. It also resulted in establishing a Center for High Resolution Electron Microscopy at NMMU in 2011.

2012: A new structured degree in Nanoscience was offered for the first time at four SA universities: NMMU, UFS, UWC, UJ. Students may specialize in Nanophysics, Nanobiotechnology or Nanochemistry, but are exposed to introductory level modules in all three sub-disciplines.

Seeing/Observing at the nanoscale

How do scientists see what's going on in the extremely small world of nanotechnology? The optical microscopes that are typically used in high school and in undergrad courses simply won't do the job.

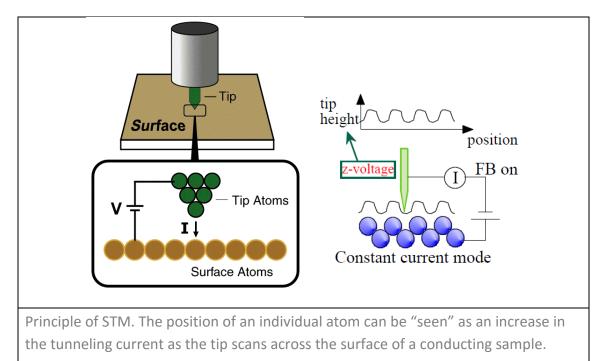
As early as the 1930s, scientists were able to see at the nanoscale using instruments such as the scanning electron microscope, the transmission electron microscope, and the field ion microscope. The most significant tools developed in recent years are the scanning tunneling microscope and the atomic force microscope.

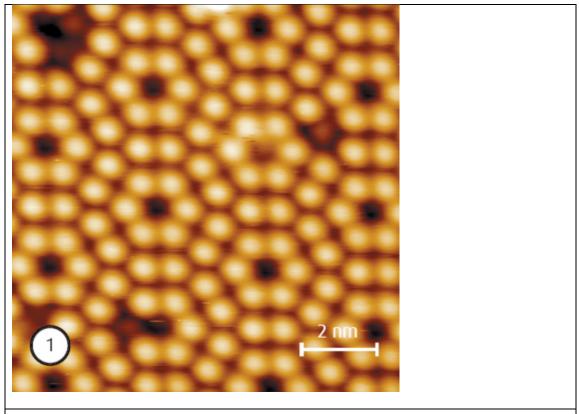
The electron microscope, first developed by German engineers Ernst Ruska and Max Knoll in the 1930s, uses a beam of electrons to illuminate a specimen and create a highly magnified image. Electron microscopes yield much greater resolution and can obtain magnifications of up to 1 million times, while the best light microscopes can magnify an image only about 1,500 times.



The scanning tunneling microscope (STM) is among a number of instruments that allows scientists to view and manipulate nanoscale particles, atoms, and small molecules. I want to spend some time on this, for the simple reason that I recently applied successfully to the National Research Foundation (NRF) for funding to purchase a state-of-the-art Scanning Probe Microscope, valued at ~R7 million. The application was supported by several Eastern Cape academics from various disciplines and will contribute significantly to nantechnology research activities in the Eastern Cape. The NRF has approved 2/3 of the price of the instrument and I am keenly awaiting a commitment from the NMMU for the other 1/3. Also, in preparing for this presentation, I could not help to remember one of the questions I was asked during my interview for the position of lecturer at the former UPE in 1996. I will refrain from mentioning the name of the panel member, but the essence of the question was whether I think it is necessary for a scientist to have access to first class instruments to conduct new research. I remember that my opinion differed strongly from that of the panel member, who thought that a few pieces of wire, a pair of pliers and perhaps some other off-the-shelf tools are sufficient for innovation. When thinking of the level of sophistication of today's instruments and the profound impact they have had on advances in science and technology, it would be my pleasure to tell that person "I told you so".

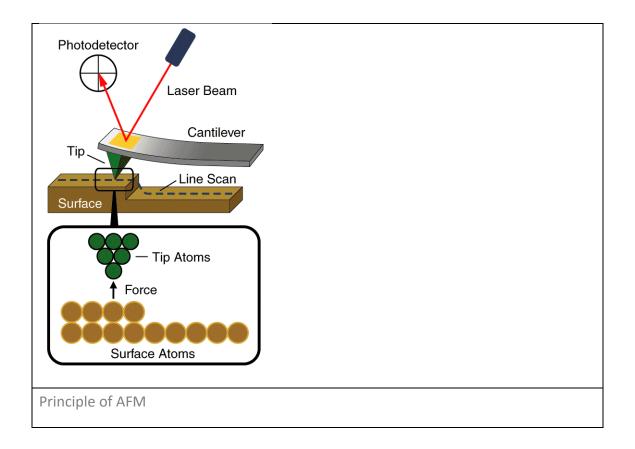
Let's return to the STM. In one mode of STM, a fine metallic tip is held very close to (<1 nm) and scanned across the surface of a conductive sample, to which a voltage is applied. The tunneling current (which results from the wave nature of electrons) flowing between the tip and sample depends exponentially on the sample-tip separation. By some clever feedback electronics, the sample-tip separation can be varied in order to keep the tunneling current constant. Adjustments made to the tip height yield information on the electron density on the sample surface, and hence on the positions of atoms on the surface.

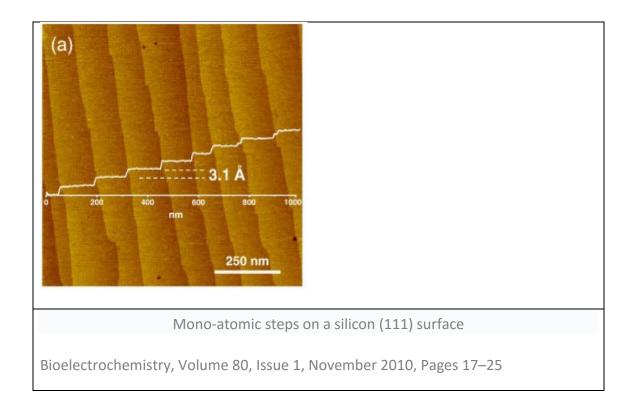




Reconstructed Si(111) surface (with a few vacancies/missing atoms) www.omicron.de

While a STM measures a tunnelling current between a sharp tip and the surface atoms of a conducting sample, the AFM monitors the force between the sample surface and a fine probe tip attached to a cantilever. The cantilever acts as a soft spring. The interaction between probe tip and sample surface could be repulsive or attractive, depending on the probe-tip distance, the chemical nature of the surface, etc. In the simplest mode of operation, the tip is maintained in close contact with the sample surface. Vertical deflections of the probe cantilever as the tip scans the sample, is monitored optically and compensated for by a feedback mechanism, which adjusts the the sample height in order to maintain a constant deflection of the cantilever. In this way the force between the sample surface and the tip remains the same as it scans over the surface, and the movement of the sample to maintain the same sample-tip distance is taken to be the sample topography. Vertical and lateral resolutions of 0.01 nm and 1 nm, respectively, can be achieved.





Since the invention the first STM and AFM, scientists and engineers have developed a number of different scanning modes. Today, Scanning Probe Microscopes which incorporate both STM and AFM are commercially available. These can be operated in various ways, providing far more information than just the atomic arrangement or topography of a surface. Nanometer scale information can be obtained on the conductivity, capacitance, surface potential, magnetic properties, elastic properties, etc. The comprehensive systems of today have been designed for measurements on hard and soft materials, as well as biological samples. Samples can be studied under vacuum, in air or even in a fluid, and at scan speeds previously unprecedented, allowing real time studies of biological processes occurring on timescales down to a few seconds.

Manufacturing approaches

There are two design approaches in nanotechnology known as top-down and bottom-up.

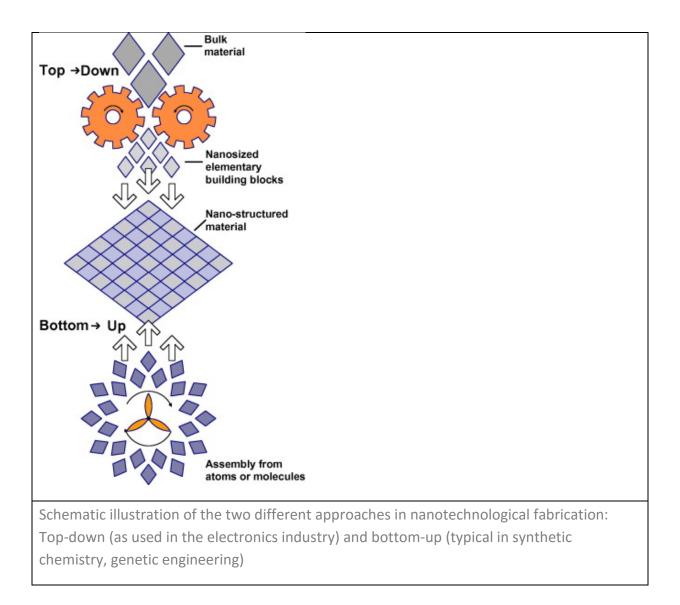
Top-down Approach

In a top-down approach, nano-scale objects are made by manipulating materials down to the nanoscale through lithography, cutting, etching and grinding techniques. The starting materials in these fabrications are relatively large structures such as silicon crystals. Lithography is the technology which has enabled making such tiny chips and there are many types of them, such as photo, electron beam and ion beam lithography.

In some applications larger scale materials are grinded to the nanometer scale to increase the surface area to volume aspect ratio for more reactivity. Nano gold, nano silver and nano titanium dioxide are such nanomaterials used in different applications.

Bottom-up Approach

The "bottom-up" approach, instead, creates new materials at the nanoscale, for example through chemical synthesis, self-assembly and positional assembly. It can involve the controlled self-assembly of molecules and their macrostructures, based on the manipulation of individual atoms, and also draws on biotechnology. The top-down approach is currently more common, especially owing to its applications in the electronics industry. The bottom-up approach still faces many bottlenecks, especially when considering the cost-efficient scaling of some of the techniques, for industrial use.



Benefits of Nanotech

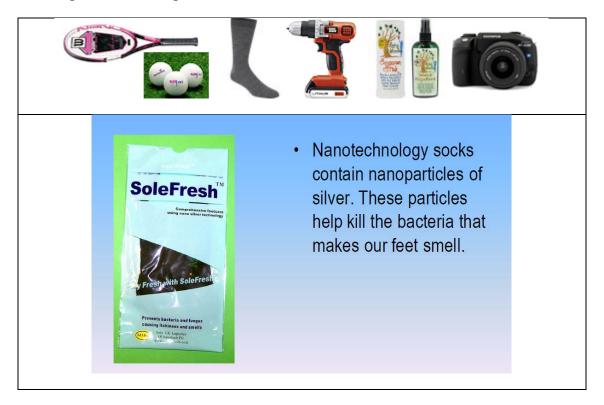
After more than 20 years of basic research, the applications of nanotechnology are starting to deliver in both expected and unexpected ways on nanotechnology's promise to benefit society.

• Everyday Materials and Processes

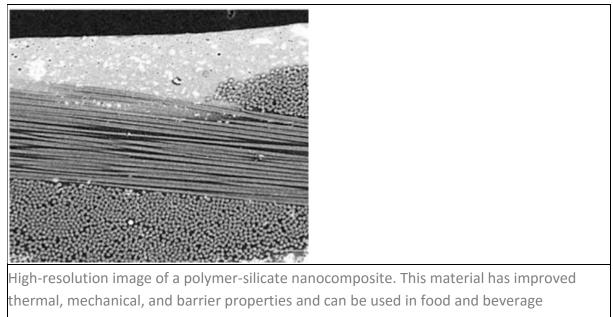
Most benefits of nanotechnology depend on the fact that it is possible to tailor the essential structures of materials at the nanoscale for specific properties. Materials can made stronger, lighter, more durable, more reactive, more sieve-like, or better electrical

conductors, to name a few. More than 800 commercial products already rely on nanosized materials and processes. A few examples:

- Nanoscale additives in polymer composite materials for baseball bats, tennis rackets, helmets, automobile bumpers, luggage, etc. can make them simultaneously lightweight, stiff, durable, and resilient.
- Nanoscale additives to or surface treatments of fabrics help them resist wrinkling, staining, and bacterial growth.



- Nanoscale thin films on eyeglasses, computer and camera displays, windows, and other surfaces can make them water-repellent, antireflective, self-cleaning, resistant to ultraviolet or infrared light, antifog, antimicrobial, scratch-resistant, or electrically conductive.
- Nano-engineered materials in the food industry include nanocomposites in food containers to minimize carbon dioxide leakage out of carbonated beverages, and to reduce oxygen inflow, moisture outflow, and bacteria growth.



containers, fuel storage tanks for aircraft and automobiles, and in aerospace components. (Image courtesy of NASA.)

- Nano-engineered materials in automotive products include high-power rechargeable battery systems; thermoelectric materials for temperature control; lower-rollingresistance tires; high-efficiency/low-cost sensors and electronics; thin-film smart solar panels; and fuel additives and improved catalytic converters for cleaner exhaust and extended range.
- Nanostructured ceramic coatings exhibit much greater toughness than conventional wear-resistant coatings for machine parts. In 2000, the U.S. Navy qualified such a coating for use on gears of air-conditioning units for its ships, saving \$20 million in maintenance costs over 10 years.

• Electronics and IT Applications

Nanotechnology is already in use in many computing, communications, and other electronics applications to provide faster, smaller, and more portable systems that can manage and store larger and larger amounts of information. These continuously evolving applications include:

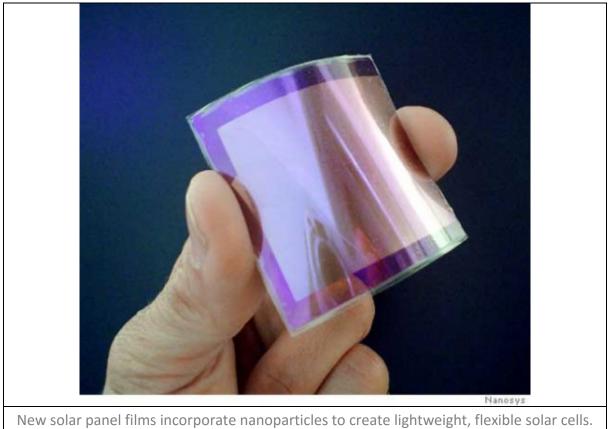
• Nanoscale transistors that are faster, more powerful, and increasingly energyefficient; soon your computer's entire memory may be stored on a single tiny chip.

- Magnetic random access memory (MRAM) enabled by nanometer-scale magnetic tunnel junctions that can quickly and effectively save even encrypted data during a system shutdown or crash, enable resume-play features.
- Displays for many new TVs, laptop computers, cell phones, digital cameras, and other devices incorporate nanostructured polymer films known as organic light-emitting diodes, which offer brighter screens and images in a flat format, wider viewing angles, lighter weight, better resolution, lower power consumption, and longer lifetimes.
- Other computing and electronic products include Flash memory chips for iPod nanos; ultra-responsive hearing aids; antimicrobial coatings on mouse/keyboard/cell phone casings; and flexible displays for e-book readers.

• Sustainable Energy Applications

The difficulty of meeting the world's energy demand is compounded by the growing need to protect our environment. Many scientists are trying to develop clean, affordable, and renewable energy sources, along with the means to reduce energy consumption and lessen toxicity burdens on the environment.

 Prototype solar panels incorporating nanotechnology are more efficient than standard designs in converting sunlight to electricity, promising inexpensive solar power in the future. Nanostructured solar cells already are cheaper to manufacture and easier to install, since they can use print-like manufacturing processes and can be made in flexible rolls rather than discrete panels.



(Image courtesy of Nanosys)

- Nanotechnology is improving the efficiency of fuel production from normal and lowgrade raw petroleum materials through better catalysis, as well as fuel consumption efficiency in vehicles and power plants through higher-efficiency combustion and decreased friction.
- Nano-bioengineering of enzymes is aiming to enable the conversion of cellulose into ethanol for fuel.
- Nanotechnology is already used in new kinds of batteries that are less flammable, quicker-charging, more efficient, and lighter weight. One new lithium-ion battery type uses a common, nontoxic virus in an environmentally benign production process.
- Nanostructured materials are being pursued to greatly improve hydrogen membrane and storage materials and the catalysts needed to realize fuel cells for alternative transportation technologies at reduced cost.
- An epoxy containing carbon nanotubes is being used to make windmill blades that are longer, stronger, and lighter-weight than other blades to increase the amount of electricity that windmills can generate.

- Researchers are developing wires containing carbon nanotubes to have much lower resistance than the high-tension wires currently used in the electric grid and thus reduce transmission power loss.
- More efficient lighting systems, like solid state lighting, use light emitting diodes to generate white light. These devices have low power consumption, more efficient conversion of electricity into light, and much longer lifetimes compared to fluorescent and incandescent lamps.

• Environmental applications

There are many eco-friendly applications for nanotechnology, such as materials that provide clean water from polluted sources in both large-scale and portable applications, and ones that detect and clean up environmental contaminants.

 Nanotechnology could help meet the need for affordable, clean drinking water through rapid, low-cost detection of impurities in and filtration and purification of water. For example, researchers have discovered unexpected magnetic interactions between ultrasmall specks of rust, which can help remove arsenic or carbon tetrachloride from water.



Nanorust cleans arsenic from drinking water. (Image courtesy of Rice University)

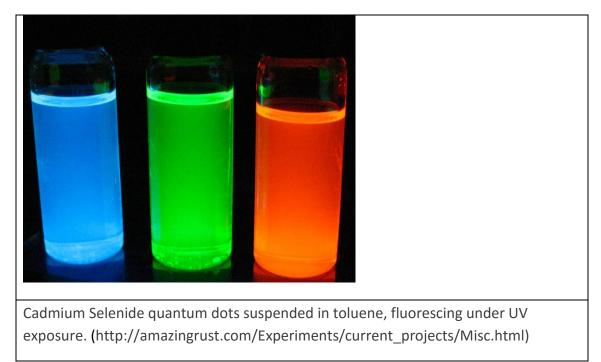
- Researchers have developed a nanofabric "paper towel," woven from tiny wires of potassium manganese oxide that can absorb 20 times its weight in oil for cleanup applications.
- Many airplane cabin and other types of air filters are nanotechnology-based filters that allow "mechanical filtration," in which the fiber material creates nanoscale pores that trap particles larger than the size of the pores.
- New sensors and solutions may one day be able to detect, identify, and filter out harmful chemical or biological agents in the air and soil with much higher sensitivity

than is possible today. Researchers around the world are investigating carbon nanotube "scrubbers" and membranes to separate carbon dioxide from power plant exhaust.

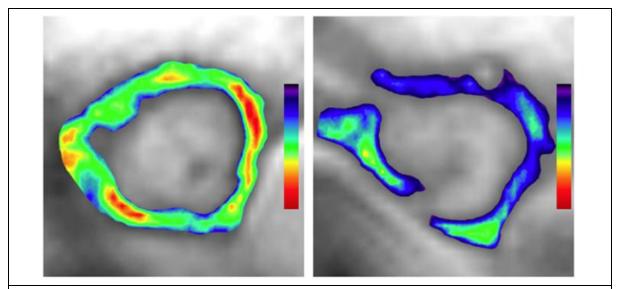
Nanobiosystems, Medical and Health Applications

Nanotechnology has the real potential to revolutionize a wide array of medical and biotechnology tools and procedures so that they are more personalized, portable, cheaper, safer, and easier to administer. Some examples of are:

 Quantum dots (tiny semiconducting nanocrystals) that can enhance biological imaging for medical diagnostics. When illuminated with ultraviolet light, they emit a wide spectrum of bright colors that can be used to locate and identify specific kinds of cells and biological activities.



• Nanotechnology has been used in the early diagnosis of the buildup of plaque in arteries. Researchers have developed an imaging technology to measure the amount of an antibody-nanoparticle complex that accumulates specifically in plaque.



Before (left) and after (right) picture of atherosclerotic plaque in a mouse artery. Plaque accumulation is shown in this image by the increasing intensity of color, from blue to yellow and red. (Image courtesy of M. Nahrendorf, MGH Center for Systems Biology, Harvard Medical School)

- Gold nanoparticles can be used to detect early-stage Alzheimer's disease.
- Research is underway to use nanotechnology to spur the growth of nerve cells, e.g., in damaged spinal cord or brain cells.

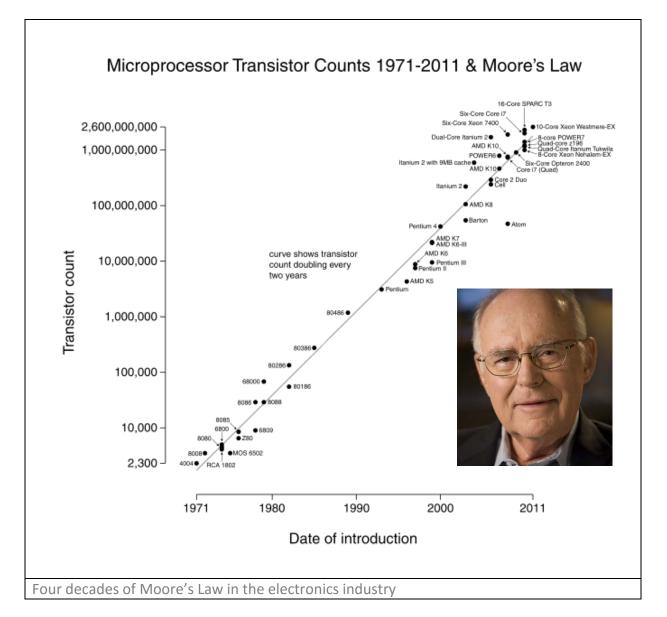
• Future Transport Applications

In addition to lighter, smarter, more efficient, and "greener" vehicles, aircraft, and ships, nanotechnology offers various means to improve the transportation infrastructure:

- Nano-engineering of steel, concrete, asphalt, and other cement-like materials offers great promise in terms of improving the performance, resilience, and longevity of highway and transportation infrastructure components.
- Nanoscale sensors and devices may provide cost-effective continuous structural monitoring of the condition and performance of transport infrastructure, and may also support an enhanced transportation infrastructure that can communicate with vehicle-based systems to help drivers maintain lane position, avoid collisions and traffic congestion, etc.

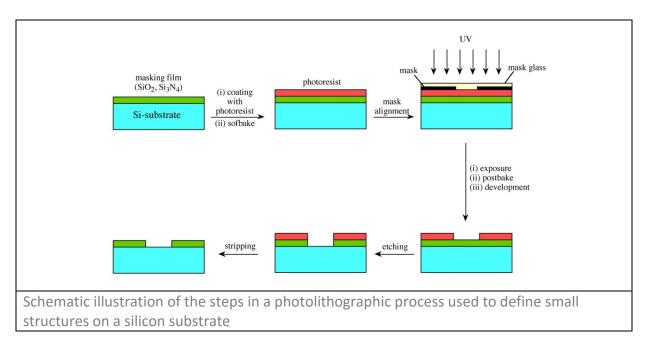
Of semiconductors and small things

I will move to the second part of this presentation now (perhaps a drinks break would have been nice at this point?). It deals with a topic that is much closer to home, namely semiconductors, its role in the development of nanotechnology and some examples from our own research.



• Moore's Law as driver for Nanotechnology

Let's return to Moore's Law. Moore's Law is not a Physical Law. It is merely an observation on what engineers can achieve with silicon. For more than 40 years, it has been the major driver of developments in the electronics (read "semiconductor") industry, and has been used as a guiding principle by the leading computer components manufacturers in the world. The reduction in size of the components on an integrated circuit, which is an example of a top-down manufacturing approach, has led to many technological innovations, specifically in terms of lithographic and etching processes, and certainly in terms of the diagnostic tools required to analyze materials and structures on the nano scale (like scanning probe microscopy). Lithography refers to a process in which small patterns are defined on a resist, which can then be transferred onto a substrate, normally by etching. Traditionally, ultraviolet light is used, but the smallest feature size that can be defined is limited by the diffraction of the light source. Because of the much shorter wavelength of particles, patterns can also be defined/written directly onto a resist coated substrate, without the draw-back of diffraction, using a beam of ions or electrons scanning over the substrate. These are called ion beam and electron beam lithography. The current standard in the electronics industry is deep ultraviolet lithography, using a laser wavelength of 193 nm, with extreme ultraviolet lithography, using an expected wavelength of 13.5 nm, probably the next serious contender. Efficient, coherent light sources operating at this short wavelength, however, need further development.



Gordon Moore recently admitted that Moore's Law, in its current form, will probably run out of steam in 2017. In order to keep it alive, the inherently bottom-up processes dominating in the biological world and in chemical engineering, will have to be incorporated into the manufacturing process. This will usher in a new era of molecular electronics. How far away that is, I do not know, however.

I found the following remark (with reference to the electronics industry) by Gordon Moore so illuminating that I had to share it with you:

"This is a unique industry.....



If the automotive industry had advanced as rapidly as the semiconductor industry we'd all be driving a Rolls Royce, It would do half a million miles to the gallon and it would be cheaper to throw away than to park"

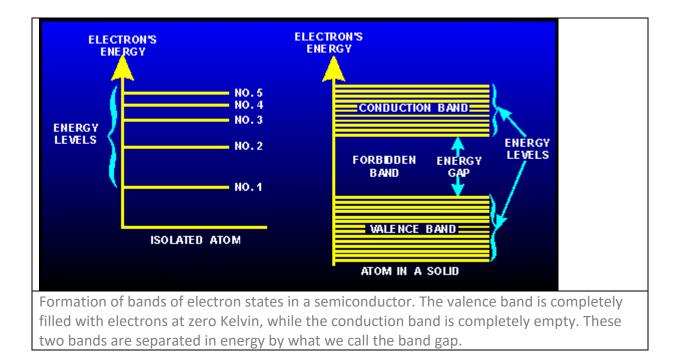
Gordon Moore

• Semiconductor heterostructures as driver for nanotechnology

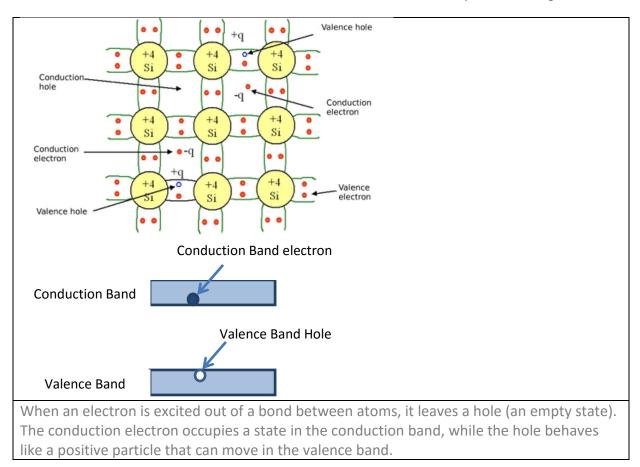
Very few discoveries/milestones in the history of semiconductors have had such a profound effect on the development of this type of material as the demonstration of the ability to produce highly coherent interfaces between two different semiconductors. This has led to the development of a variety of device architectures, including so-called low-dimensional structures. I'll return to these in a few moments.

What is a semiconductor?

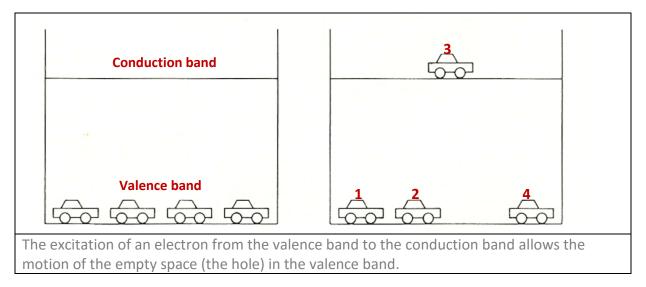
Before launching into some of the fascinating advantages of semiconductor heterostructures, I need to remind you what a semiconductor is. When atoms are brought together to form a solid, the outermost electrons are shared between neighbouring atoms. The individual electron states that can be occupied by electrons broaden into bands of states. In a semiconductor, the uppermost band of states (at absolute zero) that is completely occupied by electrons, is called the valence band. This band is separated from the next available empty band of states, by what we call a band gap. Energy is required for an electron to be excited from the valence band to the conduction band. This energy can be supplied at ordinary temperatures (i.e. room T or thereabout) by heat.



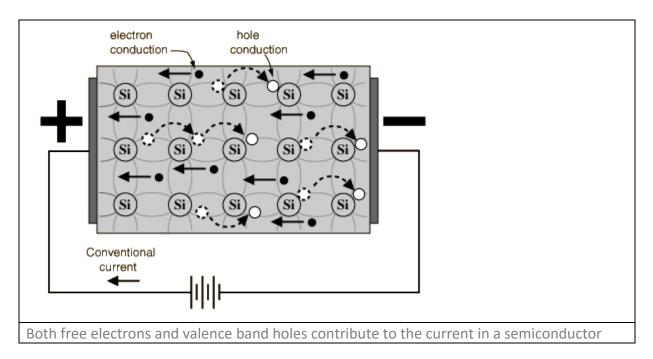
When a valence electron is excited out of the bonds between neighbouring atoms, it becomes free to move under the influence of an electric field. We say it becomes a conduction electron, and it occupies a state in the conduction band. Interestingly, the empty state in the valence band, which we call a hole, can also move. It behaves like a particle, with mass different from that of the conduction electron and with a positive charge.



The ability of a hole to move in the valence band is often explained using the parking garage analogy. When a car moves from the lower level to the upper level, the empty space on the lower level allows the cars to move around on this level also. When car number 2, say, moves one space to the right, and bearing in mind that our cars are in fact electrons and cannot be distinguished from each other, the effective change on the lower level is the motion of one empty space to the left.

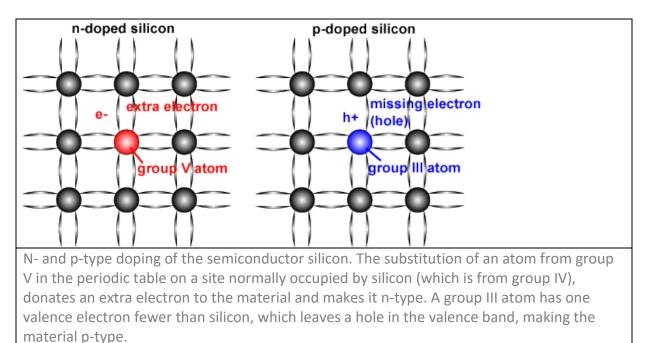


Because both free electrons/conduction band electrons and holes/empty states in the valence band are mobile in an electric field, both types of particles contribute to the current in a semiconductor.



One of the unique properties of a semiconductor is our ability to change its conductivity, either by changing the number of conduction electrons or by changing the number of holes in the valence band. The conductivity can be changed over many orders of magnitude, and

this is achieved by doping. When an impurity is introduced (either during the production of the material, or afterwards by diffusion or implantation) which has one valance electron more than a constituent atoms of the material, this electron will be donated to the material and behave like a conduction electron. Example: P in Si. When an impurity with one fewer valence electron than the host atom is introduced, it will accept an electron from the material, leaving a valence hole. Example: B in Si. When conduction is due to the fact that we have introduced more electrons by doping, than in a material without impurities, we call it an n-type semiconductor. When doping results in the majority free charge carriers being holes, we speak of a p-type semiconductor.

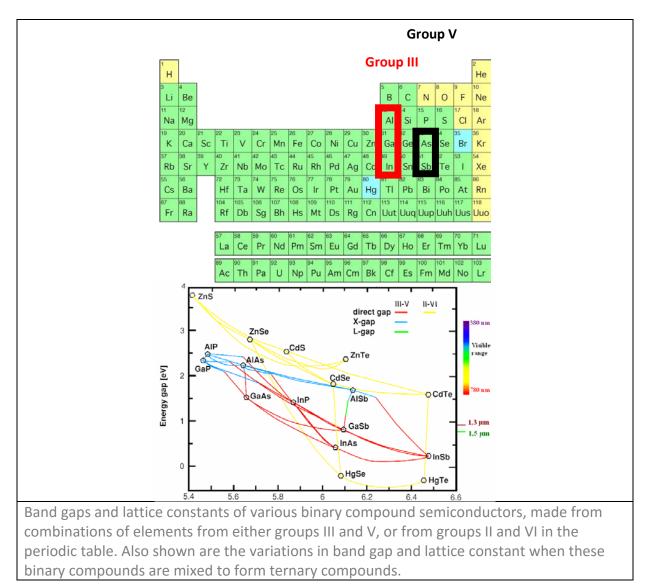


The ability to dope a semiconductor is probably the only way in which we can make these materials useful. Moreover, the ability to form p- and n-type regions next to each other, allows us to create an internal electric field which is crucial to the functioning of devices like transistors, photovoltaic cells, photodetectors and light emitting diodes. The placement of the junction and the difference in impurity concentrations across the junction provide a means of tailoring and optimising the performance of these types of devices.

One of the fundamental properties of a semiconductor is its band gap. Linked to this is its lattice constant (related to the interatomic spacing and the symmetry of the arrangement of the atoms in the solid). Our interest in semiconductors during the past 25 plus years has mainly centred on a family of compounds called III-V semiconductors. These are semiconductors formed from stoichiometric mixtures of two elements, one from group III and one from group V in the periodic table. Because their building blocks contain only TWO different elements, they are referred to as binary compounds. Examples of these are AlAs, GaAs, InAs, GaSb, etc. Because the atoms have different radii and different affinities for electrons, the strength of the bond as well as the interatomic distance between different elements from group III and the same element from group V, will differ. For example, the band gap decreases when combining arsenic from group V with the group III elements Al, Ga

or In as we move down group III to to form AlAs, GaAs or InAs. At the same time the lattice parameter increases. Similarly, when Ga (a group III element) binds with As or Sb (both group V elements), the band gap decreases (and the lattice parameter increases) as we move down group V to form GaAs and GaSb.

The importance of the band gap of a semiconductor is that it defines the cut-off wavelength for which photons (light) will be absorbed. Photons with wavelength longer than (or energy smaller than) this magic gap, will not be able to excite an electron from the valance band to the conduction band, but simply pass through the material.

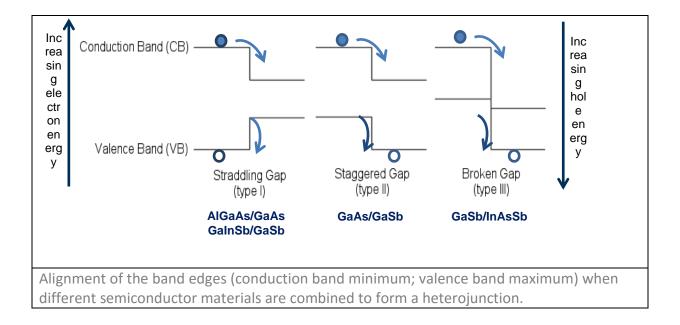


• Back to heterostructures

While the different binary III-V semiconductors have well defined band gaps, allowing them to operate as light emitting/light sensitive devices in unique wavelength ranges, this does not allow a lot of freedom in terms of tailoring the wavelength sensitivity for a specific application. Fortunately, many binary semiconductors are perfectly miscible, which means that they can be mixed during growth to form a solid solution with a pre-determined ratio of each of two chosen binaries. As an example, when GaSb and InSb are mixed to form GaInSb, the band gap will change depending on the ratio of Ga and In atoms in the resulting ternary compound (I remind you that a ternary system has three different elements as building blocks). Naturally, the lattice parameter will also change due to different bond strengths and different atomic radii. When GaInSb and GaSb are combined in the same structure, it is referred to as a heterostructure, because it contains different materials.

The beauty of this is that one can change the wavelength sensitivity of the structure, because of the dependence of the band gap on the composition of the ternary. This is called band gap engineering, a term which dates back to the 1960's, when techniques for the controlled deposition of thin semiconductor films (such as metalorganic vapour phase epitaxy and molecular beam epitaxy) were developed. While simple heterostructures, having one junction between two dissimilar materials (i.e. one heterojunction) offer certain advantages, the ability to combine multiple thin layers of two or more semiconductors in one structure, has provided device engineers with previously undreamt of possibilities for device engineering. Most of these advances stem from the demonstration of artificial structures like quantum wells and superlattices in the 1970's. I will return to these types of structures shortly.

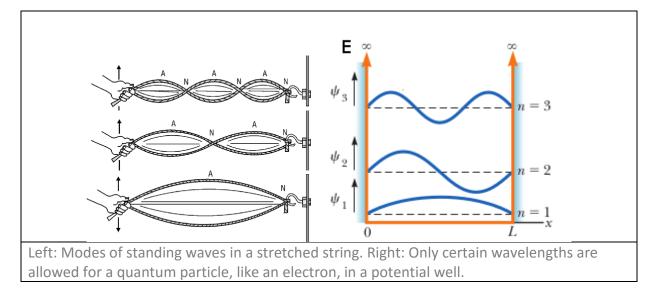
Many of the advantages of heterostructures derive from the interfaces between different materials. These interfaces define regions where the electron and hole energies change abruptly. The result is the creation of potential energy steps, which can be used to either localise electrons and holes in the same part of the structure, or in neighbouring parts of the structure. It also allows the separation between dopant impurities and the electrons or holes that they donate to the material. The band edges (i.e. the minimum energy of an electron in the CB and the minimum energy of a hole in the valence band) will align in different ways at a heterojunction, as shown in this diagram.



I need to remind you that electrons and holes have opposite charge. This means that in these diagrams, the electron and hole energies increase in opposite directions. Electrons tend to sink to the lowest energy states in the conduction band (like stones in a pond), while holes will "float" to the highest available energy states in the valence band (like pieces of cork released under water). This leads to the localisation of conduction band electrons and valence band holes either in the same material, or on opposite sides of the heterojunction.

Apart from the ability to localise electrons and holes in certain parts of the structure, different materials have different refractive indices. This allows one to also engineer the confinement of light in these structures, which has distinct advantages in the design of solid state lasers.

One might wonder if it is possible to join any material combination in a heterostructure. Unfortunately, nature is not that kind. The problem is that different materials have different lattice parameters, as already mentioned. Differences of more than a few per cent are difficult to accommodate in these structures, but provided that individual layers are kept thinner than a certain critical thickness, the material can be elastically distorted or strained and perfect interfaces can be achieved. Very interesting phenomena occur on these scales (typically a few tens of nanometers and smaller). Quantum size effects begin to play a role. These effects are related to the wave-nature of electrons and holes. When a layer becomes comparable to or less than the wavelength of the electron or hole, the motion of the charge carrier perpendicular to the plane of the layer can no longer be described by a travelling wave, but rather by a standing wave. Only certain wavelengths are allowed as shown here.



We say the wavelength is quantized. The allowed wavelengths are similar to the situation for the standing waves on a stretched string fixed at both ends: the length of the string will be multiples of half-wavelengths in order to sustain standing waves. Since the wavelength of the electron is related to its momentum (and therefore its kinetic energy), quantum confinement leads to the discretization of the energies of the confined particle. This provides yet another tool for band gap engineering.

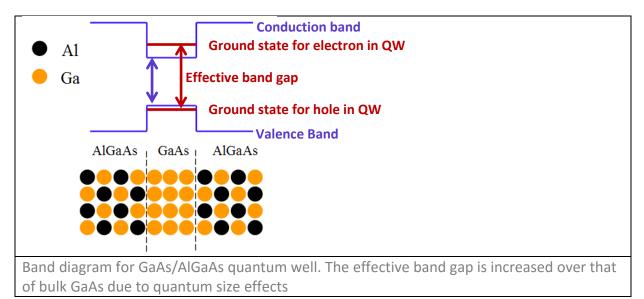
Low dimensional structures

I will conclude the scientific part of this presentation with examples from our own research. For years we have focused on the development of III-V and II-VI compound semiconductor structures that can be used as photodetectors in the infrared part of the spectrum, as well as for light emitting devices in the visible/UV spectral range.

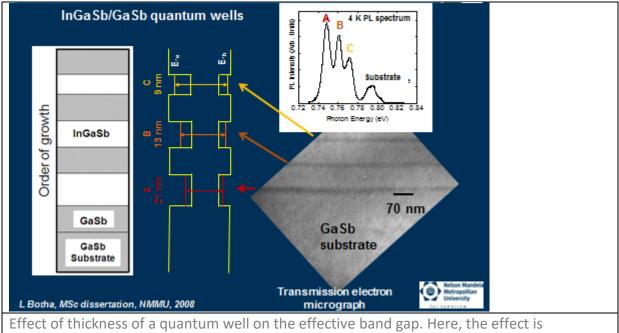
• Quantum wells and superlattices: 2-Dimensional Structures

In a semiconductor quantum well, a thin layer of (for example) a narrow band gap material is sandwiched between two layers of a larger band gap material. Depending on the alignment of the CB and VB edges, a situation may arise where the lowest electron and hole states are in the middle layer. If this layer is thin enough for quantum size effects to dominate, we call it a quantum well. This is an example of confinement in 1 dimension, and the actual structure is called a 2D structure since electrons and holes still have two degrees of freedom.

This is shown for the well-known system of GaAs sandwiched between two AlGaAs layers. The effective band gap of the quantum well is now different from that of bulk GaAs, and is in fact increased by the quantum confinement energies of the electron and the hole. The very first GaAs/AlGaAs quantum well structures in our Physics Department were grown by Andrew Leitch in 1987, using what was at the time a state-of-the-art metalorganic vapour phase epitaxial system. This machine is still in operation today.

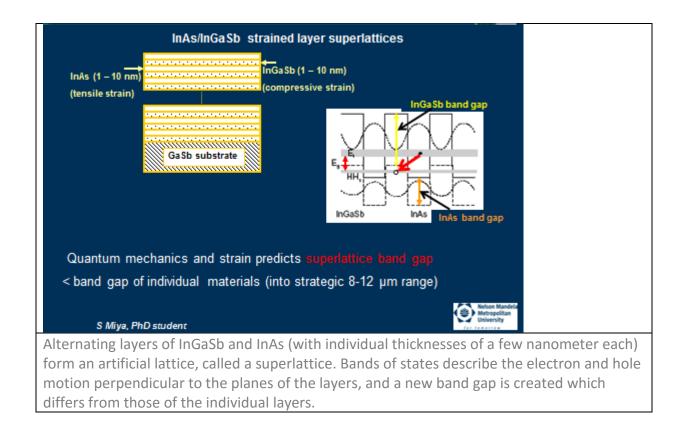


Quantum mechanics predict that the confinement energies for the charge carriers depend on the thickness of the QW as well as the depth of the potential well. The thinner the QW, the shorter the wavelengths allowed by quantisation and therefore the higher the kinetic energy of the particle (the energy is inversely proportional to the wavelength). This is illustrated for InGaSb QWs within GaSb barriers below. The structure contains three thin InGaSb layers, each having a unique thickness, with GaSb spacers in between. This material combination yields confining potentials for electrons and holes in the InGaSb layers. In a photoluminescence experiment, this structure can be excited with light from a laser, which produces extra electrons and holes. These will carriers will recombine, emitting light. The photon energies are indicative of the effective band gap of the QW in which recombination takes place. Three distinct peaks labelled A to C are seen in the photoluminescence spectrum, resulting from recombination in each of the three InGaSb quantum wells.

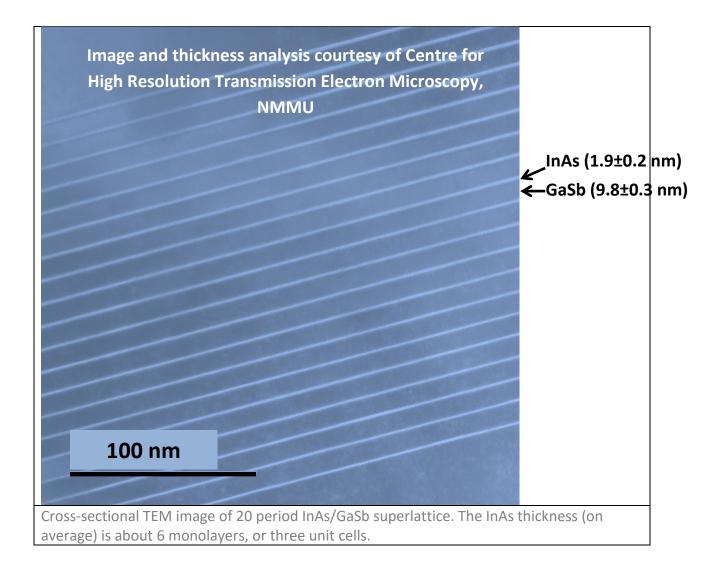


illustrated for three thin InGaSb layers sandwiched between much thicker GaSb layers. Electrons and holes excited by a laser in a photoluminescence (PL) experiment are trapped in the thin InGaSb layers before recombining. The energy of the light emitted upon recombination depends on which layer the electron and hole was when they recombined. Each InGaSb quantum well in this structure has a different thickness, which means a different effective band gap.

The InGaSb/GaSb quantum well can be used as a test structure for superlattices containing ultra-thin InGaSb constituent layers. In a superlattice, the individual layers are so thin that electrons and holes can tunnel through the thin potential barriers separating them, creating new bands of energy states analogous to what happens when atoms are brought together in a solid. In this case, however, the bands are not influenced by the periodicity of the atomic arrangement, but rather by the periodicity of alternating layers of two different compounds. This is illustrated for an InAs/InGaSb superlattice here.

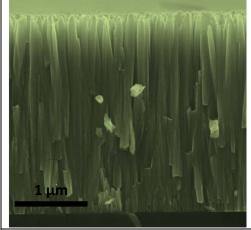


Depending on the ratio of the individual thicknesses and the periodicity, the effective band gap can be tuned to wavelengths in the far infrared, making this type of structure an ideal competitor for the current industry standard in the production of mid to far infrared detectors, namely mercury cadmium telluride. These structures impose severe demands on the crystal growth system, and we were pleasantly surprised to see that our old reactor can still produce the extremely thin layers required in such a structure.



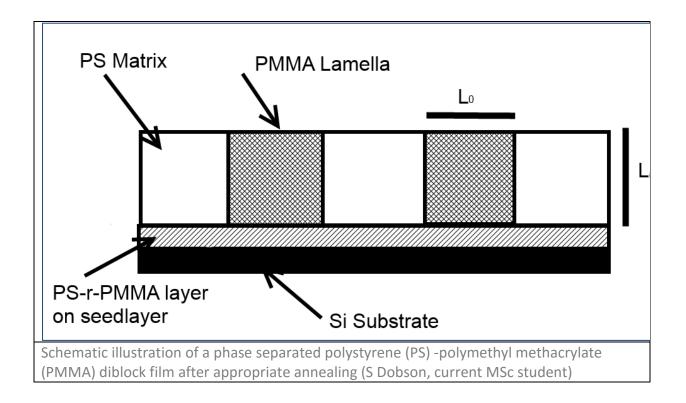
• ZnO Nanorods: 1-Dimensional Structures

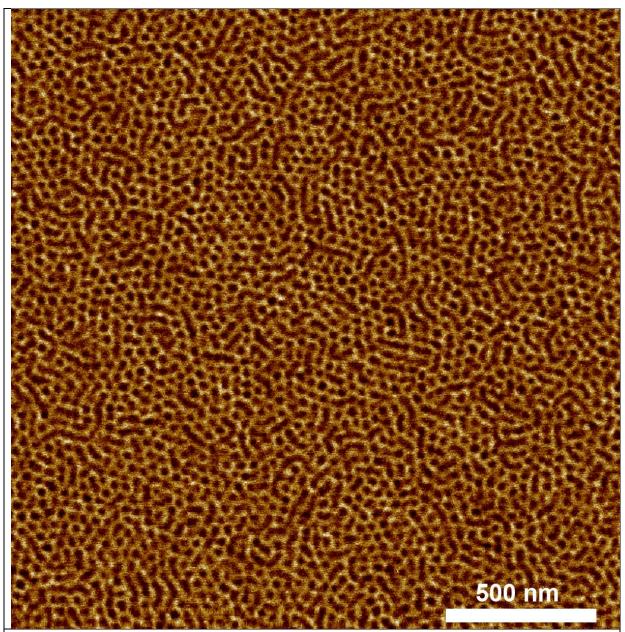
ZnO is a compound with a band gap in the near ultraviolet. When grown on silicon (which is cheap) and produced with the right architechture (i.e. in the form of nanorods, all perpendicular to the substrate), this material can be used as a very efficient light emitting diode for solid state lighting applications. In a nanorod, the motion of charge carriers is restricted in 2 dimensions, leaving one degree of freedom parallel to the axis of the rods. Hence, they are examples of 1D structures. They are also efficient wave guides, meaning that depending on their geometry, certain wavelengths will be guided down the axis of the rods, which will also enhance their performance of light emitting devices. We have spent considerable time understanding the deposition of these structures from solution, using a technique called Chemical Bath Deposition. It is cheap, simple and scalable, and produces rods of high quality with relative ease.



ZnO nanorods on silicon substrate for UV light emitters. Chemical Bath Deposition was used to produce needle like rods on a seed layer of ZnO nanoparticles. The rods have diameters ranging from just below 100 nm to 200 nm, and are oriented to a large extent perpendicular to the substrate. (PhD thesis ZN Urgessa, (NMMU, 2013)

One of the key problems we have encountered using the current procedures, is the accurate control of the diameter of the rods. Also, the direct deposition of the ZnO on a seed layer produces extremely dense arrays of rods, with a degree of randomness in their orientation relative to the substrate. One possible way of improving these aspects is to use a template made from a di-block copolymer containing polystyrene (PS) and polymethyl methacrylate (PMMA) chains. This can be dissolved in toluene, spin-coated onto the seeded silicon substrate and annealed above the glass transition temperature of the polymer components to yield a thin film with phase separated domains of PS and PMMA. Under the correct conditions (film thickness, annealing temperature, annealing ambient) nanosized lamellae of PMMA in a PS matrix will form perpendicular to the substrate. Subsequent exposure to UV light will break down the PMMA, which can then be removed by an appropriate solvent. This will open up nanosized pores in the film, which can be used as a template for further growth.

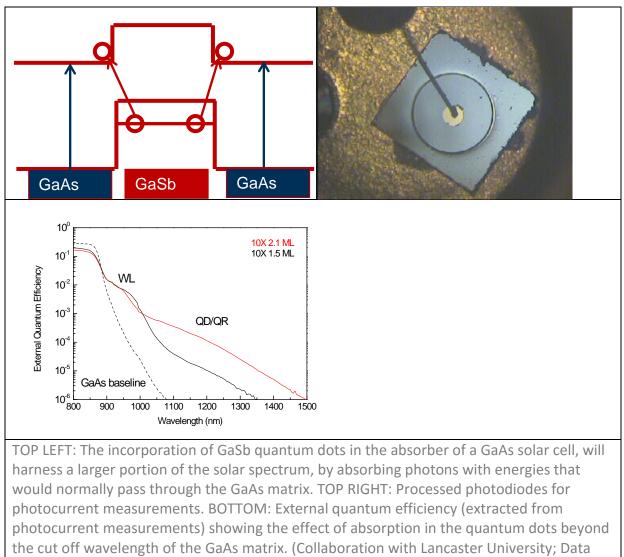




PMMA-Polystyrene templates can allow the synthesis of controlled arrays of nanostructures from both inorganic and organic compounds. The dark regions in this AFM image are PMMA domains, while the lighter regions are PS (S Dobson, current MSc student)

• Quantum dots: 0-Dimensional Structures

I have already referred to the tunability of the wavelength of the light emitted by CdSe quantum dots. In a quantum dot, the motion of charge carriers is restricted in all three dimensions, leaving them zero degrees of freedom. Therefore they are also referred to as OD structures. A few years ago we started collaborating with a group at Lancaster University on the characterisation of GaSb dots in a GaAs matrix. These structures are grown by Molecular Beam Epitaxy in Lancaster, and are formed by a process of self-assembly. It is a bottom-up process therefore. The idea here is to employ the absorption of light in the GaSb dots (which have a smaller effective band gap than that of GaAs) in order to harness more of the solar spectrum in high efficiency GaAs-based solar cells. The GaSb/GaAs system has a type II band alignment, with the holes strongly localized in the GaSb and the electrons weakly localized in the surrounding GaAs, which will enhance the electron contribution to the current produced by the absorption of light.



supplied by MC Wagener)

The enhancement in the photocurrent at longer wavelengths (due to light absorption in the dots) has been demonstrated, but no improvement of the efficiency of the solar cells has been obtained to date. This provides an interesting challenge for future research collaboration.

Summary

On this note, I have to stop. I trust that I have been able to share with you some of the exciting developments in nanotechnology. A lot has been promised by scientists and engineers active in this field, and some of these promises have already materialized. However, much more is required in terms of true cross-disciplinary research before this technology will deliver on its true promise, namely to revolutionize the world we live in. And this is at best, my humble opinion.

I thank you for your time.