

## Physics and Fabrication of Nanostructured Materials and Devices

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Nanometre scale electronic and opto-electronic devices are of ever increasing scientific and economic importance. Around the world there is an enormous ongoing investment in nanotechnology research because of the potential to improve existing devices by making them smaller, and because of many possibilities for creation of completely new kinds of devices and products.

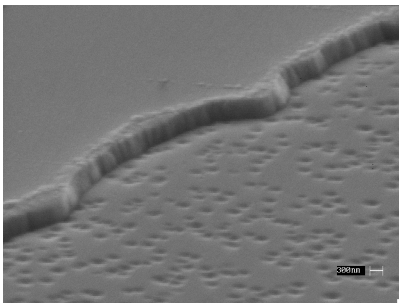
One of the interesting aspects of nanotechnology is the extent to which it is a multidisciplinary field: for example, engineers and scientists have different views of what aspects are interesting, but engineering and scientific developments are strongly related.<sup>1</sup> For an engineer, the advantages of nanoscale devices include increased speed and packing density, and novel functionality. Engineers are interested in how to make, for example, faster and better computers, and in how to make new kinds of electronic and opto-electronic devices (like the laser for your CD player – we take them for granted now, but they have only been around for 10-15 years). For scientists, nanoscale devices reveal many exciting and unexpected new fundamental phenomena, and allow tests of basic ideas in quantum mechanics that would not be possible in any other way.<sup>2,3</sup>

The interaction between developments in engineering and advances in fundamental physics of nanoscale devices is exemplified by the discovery of the quantum Hall effect<sup>4</sup>. This new state of matter, which is a property of electrons that ‘live’ in a two dimensional world, was first observed when a MOSFET (the kind of transistor that was developed to power modern computers) was cooled to very low temperatures. Both the MOSFET and the quantum Hall effect rely on a layer of electrons that is a few nanometres thick, formed at the interface between a piece of silicon and the silicon oxide on its surface.

The interdisciplinary nature of nanotechnology underlies the structure of our research programme<sup>5</sup>. The programme comprises a number of linked fundamental science and applied engineering research projects, and takes advantage of the complimentary skills and resources of teams around the country. The broad objectives of our work are:

1. to develop a fundamental understanding of basic nanofabrication processes and of building elements of nanoscale systems.
2. to develop techniques for fabricating new materials and devices with nanoscale dimensions.
3. to feed the results of 1) and 2) into engineering projects with clearly defined technological goals.

The long term applications of this work are in areas such as optical communications, high density information storage, and electronics. We present here an overview of the extended group’s recent research<sup>6</sup>, and highlight a few of the recent successes.



*Nanoscale step in a GaN surface, showing the desired vertical edge profile.*

### Gallium Nitride

Gallium Nitride (GaN) devices have already made a huge impact in the blue-green laser diode and high-brightness LED market and are poised to find applications in high-power/high temperature electronics.<sup>7</sup> Blue lasers can be focussed to a spot ~4 times smaller in area than the infra-red laser used in a DVD player, and therefore allow ~4 times more information to be stored. GaN LEDs are already being used in green traffic lights because their lifetimes are virtually unlimited compared to ordinary bulbs, and they consume ~1/10<sup>th</sup> the power. Blue LEDs are also needed for full colour displays (previously only efficient red and yellow light emitters were available). The foci of our work on GaN are

to develop the technology needed to make nanoscale GaN devices, and to develop a new form of GaN, amorphous GaN, which could be far cheaper and easier to make than the usual crystalline form of the material (see next section).

Although they are already commercially available, blue lasers are currently extremely expensive<sup>8</sup>. One of the potential techniques that could be used to dramatically improve existing GaN lasers would be to create a 'photonic band gap'<sup>9</sup> in the light emitting material: what is needed is essentially an array of nanoscale holes or pillars. To do this special etching techniques are needed because GaN is difficult to etch with wet chemistry, and because the features need to be deep with very straight sidewalls. Dry etching (i.e. bombardment of the material with reactive ions) is critical to GaN device fabrication, however, bombardment with energetic ions can also lead to material damage that affects the optical and electronic properties of the material. Systematic studies of the optical and electrical behaviour of etch-induced damage are essential for the development of future GaN devices. We have lead the way in understanding the optical properties of etched GaN<sup>10</sup>, and in the process discovered some new memory effects<sup>11</sup> and also made progress towards understanding some long standing problems associated with defects in this material.<sup>12</sup> This work is ongoing. A further part of our effort is focussed on developing fabrication techniques for solar-blind and UV-blind photo-detectors.

### Amorphous Superlattices

This work is based on nearly 20 years of research concerning the vapour deposition and physics of films containing many nanometre thick amorphous layers. The VUW/IRL group were among the first to discover that even amorphous constituents can form thin layers with smoothness and compositional integrity at the sub-nanometer scale. Starting from a focus on interface photochemistry in a specific semiconductor-semiconductor system (Ge/Se), the electronic and vibrational physics of many superlattices, grown using a range of material types (semiconductors, insulators, metals and superconductors), have been investigated.

One recent study that is near completion is of the dynamics of the "gas" of vortices in multilayered superconductors, which are similar to the cuprate (high  $T_c$ ) superconductors. A melting transition from a glass to a vortex state has been observed, driven both by temperature and by a dimensionality (3D-2D) transition.<sup>13,14</sup>

In the past year we have begun investigating the preparation of amorphous GaN, AlN and InN by ion-assisted deposition, with the intention to establish the properties and exploitation opportunities of their superlattices. In this case even the constituent materials have not previously been prepared reproducibly, but now we are confident that our films are of sufficient quality to begin exploring superlattices and quantum wells.<sup>15,16</sup>

### Evanescence Near Field Optical Lithography (ENFOL)

Optical lithography is the standard process used in the integrated circuit industry. It involves printing a predefined pattern (from a mask) through a system of lenses onto a substrate (usually a silicon wafer). However, the resolution of features that is achievable through this process is usually limited by diffraction to approximately the illumination wavelength  $\lambda$ . In other words it is impossible to focus a beam of light to a spot with diameter smaller than  $\lambda$ . This limit can be overcome by working in the so-called near field region:  $\lambda/40$  resolution has been demonstrated for microscopy<sup>17</sup> and sub-wavelength resolution has also been achieved for optical lithography. The University of Canterbury team's

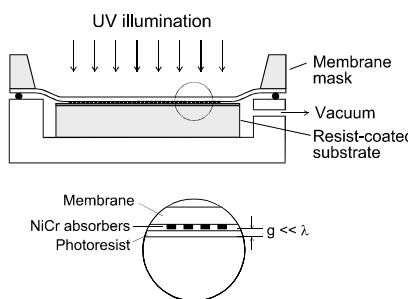
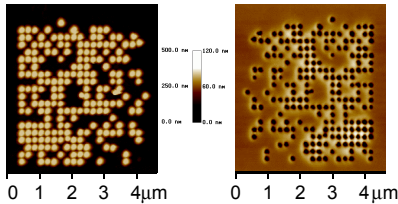


Illustration of the ENFOL process

evanescent near field optical lithography (ENFOL) technique has given better than  $\lambda/5$  resolution<sup>18</sup>, with features as small as 70 nm being formed (this is less than half the size of the smallest features on the current generation of silicon chips). ENFOL is a relatively simple process in which a master mask is held in intimate contact with a very thin layer of photosensitive material (a photoresist), and the mask is then illuminated from above – a shadow pattern of the mask is transferred into the photoresist. Provided that the mask and photoresist are in intimate contact diffraction cannot occur, and the resolution of the pattern is theoretically unlimited. The challenge now is to make this a repeatable and reliable process for the manufacture of future nano-scale circuits and systems.

## Nanoimprint Lithography

Nano-imprint lithography (NIL) is a physical molding process in which a mold with nanostructures on its surface is pressed against a substrate coated with a polymeric resist material. By heating the system the pattern on the mold can be replicated faithfully. This technique is not limited by wave diffraction, substrate reflections or interference, which are major limiting factors in current optical projection lithography, and there are no electron scattering problems as in electron beam lithograph. In addition NIL is a high throughput low cost nanofabrication technique with seemingly no resolution limits: features down to 10 nm have already been demonstrated.



*Mold (left) and result of imprint into a polymer (right)*

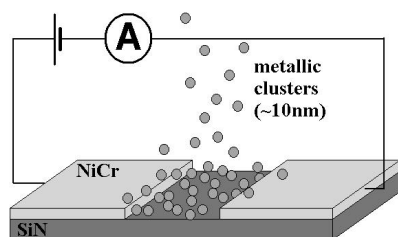
The NEST group is investigating some fundamental issues that are related to the ultimate resolution limits of this technique and whether imprint can be used in the fabrication of complex devices such as multilevel, 3D structures. We have demonstrated that imprint at low temperatures is possible for simple structures using silicon nitride as a mold<sup>19</sup>. Imprint at low temperature is important for patterning materials that are intolerant of high temperatures or when the mold and substrate have different thermal expansion coefficients. Applications of nanoimprint range from high-speed transistors with T-shaped gates to sculptured nanostructures for sorting cells or molecules.

## Advanced Surface Texturing for Solar Cells

Surface texturing reduces optical reflection from solar cells by increasing the probability of light being captured and absorbed inside the material - untreated silicon solar cells reflect more than 35% of the incident light which limits their efficiency. Texturing with upright and inverted pyramids has been used widely for light trapping to improve solar cell efficiency, however these structures are non-optimal. The light trapping ability depends on the type of surface texturing and the range of incident light angles. To maximise efficiency, the shape and spacing of the surface texturing must be varied. In addition, anisotropic chemical texturing processes used at present for crystalline material are not effective with low cost poly-crystalline or thin film substrates. In this project nanolithography and Reactive Ion Etching (RIE) techniques are employed to develop efficient surface texturing technologies for multi-crystalline silicon. RIE has the capability to etch controlled profiles on crystalline and poly-crystalline substrates. RIE offers advantages over laser technologies in that it is a parallel process and introduces less damage. This results in lower surface recombination rates and consequently improved overall solar cell efficiency. Texturing low cost poly-crystalline silicon will reduce reflection and improve light trapping as well as increasing the surface-area and effective thickness of the cell. The present trend and demand for low cost buildings with integrated photovoltaic systems imposes a new requirement for texturing various materials on a large scale which we believe can be met using RIE techniques.

## Atomic clusters

As discussed above, a great challenge for nano-engineering is to fabricate structures that are smaller than those possible with current lithographic techniques. One new idea is that structures on the scale of a few nanometres could be formed using atomic clusters<sup>20</sup>, which are nanoscale particles that can be formed by simple evaporation techniques. It has been shown that the clusters can diffuse across a substrate and line up at certain surface features, thus generating structures resembling nanoscale wires<sup>21</sup>. This approach is promising because the width of the wire is controlled by the size of the clusters, but the problem of positioning the clusters to form real devices on useful substrates has yet to be solved.



*Schematic of deposition of atomic clusters onto predefined contacts*

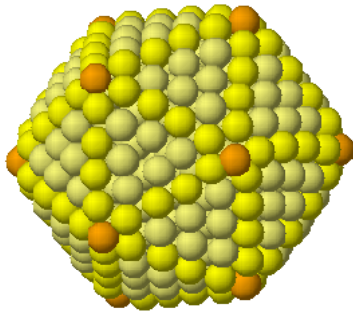
We are attempting to create nanoscale surface features on a substrate that force clusters to assemble into nanoscale wires, with the aim of developing new electronic devices, including quantum effect transistors. We have already been successful in producing simpler nano-electronic devices containing films of atomic clusters, and are currently attempting to patent these devices. This project has enormous potential if successful: cluster based devices could be revolutionary since their extremely small size would allow operation of quantum effect electronics at room temperature.

The characteristics of any device containing clusters would be strongly influenced by the structure of the particles, since structure

underpins all physical and chemical properties<sup>22</sup> (similarly, the properties of a bulk material depend on the underlying crystal structure – for example, graphite is very different to diamond). Clusters can, *and do*, adopt atomic arrangements forbidden in bulk crystals (such as five-fold symmetric structures), because an energetically favourable arrangement of surface atoms can compensate for a less than ideal arrangement in the interior. We have a unique electron diffraction apparatus<sup>23,24</sup> that allows us to determine cluster structures and hence to attempt to resolve many fundamental issues. One such issue is how do clusters transform from one structure to another (as successive atoms are added) during growth? For example, how can a small icosahedral particle grow into a large face-centred cubic particle?

### Molecular Dynamics

Computer simulation of objects and materials at the atomic scale is becoming an increasingly important tool for physicists. On the nanometer scale, the quantum mechanical behaviour of electrons is one of the most important factors in determining the behaviour of atoms. In many situations, however, we can simply picture each atom as a billiard ball interacting with other atoms via *chemical forces* (much as planets interact in the solar system with gravitational forces). This allows us to ignore the complicated behaviour of the electrons in each atom.

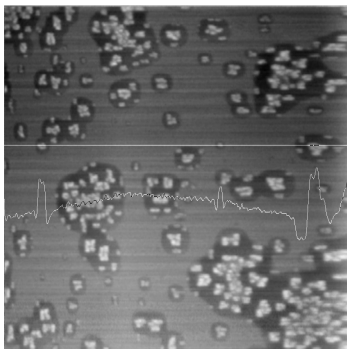


*MD simulated 5-fold symmetric icosahedral cluster.*

With a good understanding of these chemical forces (developed either from experiment or by modelling the electrons directly) we can simulate the behaviour of millions of atoms on desktop computers. This type of simulation is known as molecular dynamics. Such simulations allow us to perform "computational experiments" that are extremely difficult (or even impossible) to perform in the laboratory. Our simulations of atomic clusters<sup>25</sup> provide us with a detailed picture of the cluster's structure which is difficult to infer from experimental data alone, and which allows a much better interpretation of structure experiments.

### Molecular Beam Epitaxy

The basic concept behind the MBE technique is the thermal evaporation of solid sources into an ultra-high vacuum (UHV) environment. The evaporated material is deposited onto a heated substrate used for both mechanical support and as a template for the alignment of atoms into a crystalline structure. Typical growth rates are relatively slow, so that a final layer thickness of approximately 1 micron (compared to ~100 microns for the diameter of a human hair) is not uncommon. The incorporation of a computer-controlled shutter above each evaporation source allows atomic-layer precision during deposition, and hence MBE is commonly used to fabricate complex multi-layered structures, where each layer is typically a few nanometers thick i.e. where the layer thickness is comparable to the size of an electron wave. Such structures form the basis for laser diodes, far infrared detectors, and completely new types of electronic devices.



*Si nanowhiskers (white dots, typical height 25 nm, width 5 nm) embedded in ultrathin layer of understoichiometric SiN*

At present, one growth chamber is used to create layers of metallic nitrides based on column III elements such as boron, gallium, aluminium and indium (see GaN section above). A second growth chamber, connected to the first via a UHV transfer tube and load-lock system for substrate insertion and removal, will be used to investigate magnetic semiconductor structures. These structures are of interest for "spin filter" devices, sometimes referred to as "spintronics." The basic concept behind spintronics is to exploit the fact that electrons have two possible quantum-mechanical spin states- up and down. Devices that can select a particular spin state are of interest as high-speed transistors as well as for computer memory.

### Silicon nano-whiskers

Silicon nano-whiskers<sup>26,27</sup> are tiny filaments of silicon which have potential applications in sensing and microelectronics. Specific growth conditions allow the production of whiskers with varying heights from 10 to 100 nm. However, up to now, their distribution on a surface and

fluctuations in dimensions are not easily controlled – such control is essential for fabrication of devices. Understanding the formation process of silicon whiskers is fundamental to better control of the production process and, thereby, the successful manufacture of nano-sensors tailored to specific, new functions. Possible applications of such pillar-like Si nano-whiskers are light emission, field emitters in flat-panel displays and sensor devices for ultra high-resolution scanning probe systems, for example. This research aims to resolve the mystery of the formation process of the whiskers. What is the role of the choice of silicon substrate and annealing by electrons? How does the low-energy nitrogen implantation fundamentally change the materials properties at the interface? The answers to these questions will open the door for new possible application of the whiskers in the sensor industries.

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