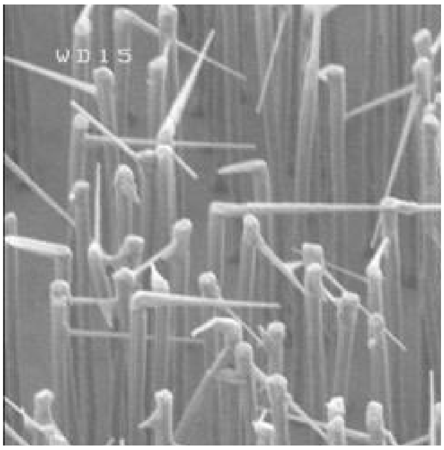
CSEM's

Materials Monthly

March 2006

Making materials matter

For all our mastery in depositing layers of atoms and carving out ever finer circuitry, our capacity to build optoelectronic devices is essentially a two dimensional pursuit. However, a revolutionary new approach to building circuits and devices is opening up as materials scientists work out a variety of ways of growing nanowires out from a semiconductor wafer.



The researchers are devising new ways of growing simple nanowires, compound nanowires and even branched nanowires as shown above. These structures are around 50 nm in width, and they may change the face of optoelectronics.

Inside this MM

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THE AUSTRALIAN NATIONAL UNIVERSITY

Growing nanowires

Opening up new frontiers in optoelectronics

Hitting the wall with 'top down'

Listen closely and you might hear the cold winds of change blowing through the halls of the electronics industry as they ponder the future of microelectronics and photonics. We're coming to the end of the age of miniaturisation as a top down process, and the hunt is on for new ways to build circuits and devices in the nanoworld.

By top down we mean beginning with a chunk of material – a wafer of silicon for example – and carving it down to create the circuits we need. What has been driving the tremendous expansion of the electronics industry has been its capacity over the years to find new ways to continually shrink those circuits and devices. These days industry can produce circuits with features only 90 nanometres apart. In the research lab they can go further drawing circuit lines that are separated by around 30 nanometres (see box). But, of course, it's not enough – the push is always there for smaller, faster more powerful circuits and devices.

However, the days of building smaller circuits by carving them out of a block of material are drawing to a close. Not only are we pushing these top-down techniques of using light to carve out circuits to their physical limits, we're also creating circuits that are becoming as small as they can get. When circuit lines get within a few nanometres of each other, electrons are no longer bound to stay in the circuit, they simply quantum tunnel across to another wire.

Going up

So, if we can't go smaller, where do we go to extract more

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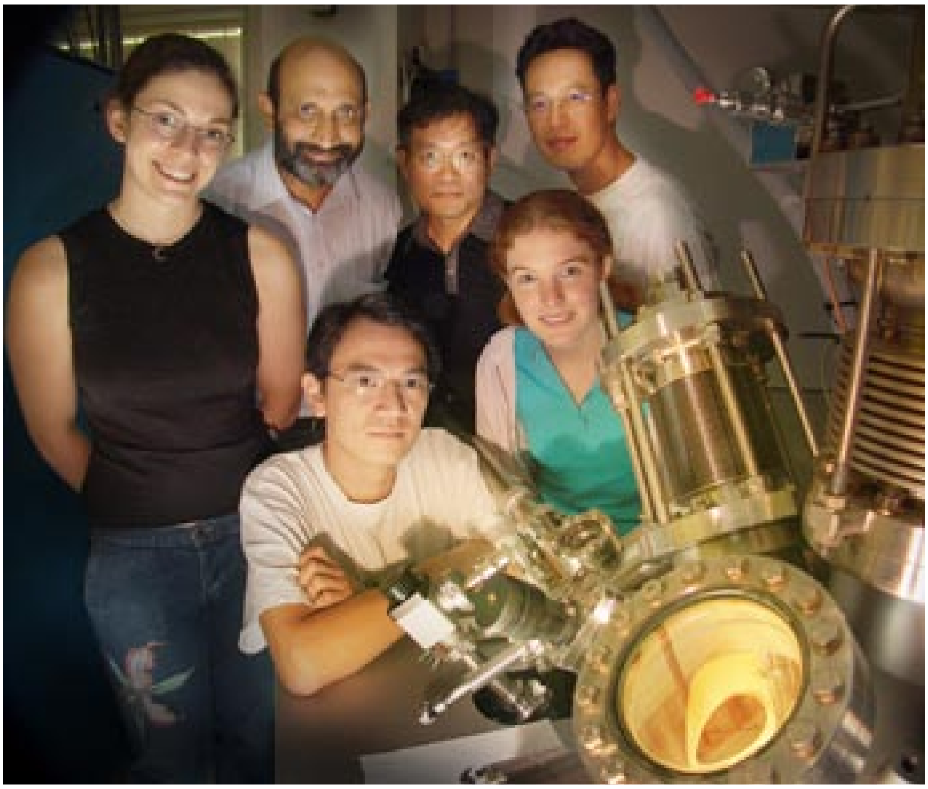


The nanowire team at EME: (from the left at the back) Ms Victoria Coleman, Professor Jagadish, Dr Yong Kim and Dr Qiang Gao. Up front are Dr Hoe Tan and Ms Hannah Joyce. "Our success in growing nanowires is testament to the passion shown for this research by everyone in the team," says Professor Jagadish. (Photo by Tim Wetherell)

Growing nanowires
(continued from previous page)

functionality from our electronics and optoelectronics? How about up? Our microchips are making wonderful use of two dimensions, why not build our circuits, structures and devices up into the third dimension?

The main reason we don't is because while it's possible to carve out circuits in two dimensions, it's a different proposition in three.

"When you etch out circuits on semiconductors, you create a lot of defects — there are missing atoms which can trap the electrons," explains Professor Chennupati Jagadish. "This isn't a problem when the circuits are big but it becomes a limiting factor when you're working at scale of tens of nanometres. Defects destroy these structures and the notion of carving out intricate three dimensional forms is simply out of the question.

"However, in recent years it has been demonstrated that while you can't carve out working 3D forms, it is possible to grow them from the bottom up. Our understanding of how to grow nanowires out of a semiconductor base is now proceeding in leaps and bounds and this could prove to be the gateway to a new age in optoelectronics.

"Of course, such statements abound in the nanotechnology game but there are good reasons to believe nanowires are going to make a huge impact. We're now able to grow a broad range of nanowires in different shapes and compositions. They're high quality and they can serve a number of important functions. We're not just making pretty shapes, we're actually building nanoscale devices."

Professor Jagadish is Head of the Semiconductor Optoelectronics and Nanotechnology Group in the Department of Electronic Materials Engineering, Research School of Physical Sciences and Engineering. For more than a decade his group has been building up expertise in working with compound semiconductors using a variety of techniques to create a range of devices including lasers, quantum dots and photodetectors.

Nanowires have become the focus of several labs around the world in recent years. The research builds on investigations in the 1970s on the growth of silicon 'whiskers' out of silicon wafers under droplets of gold. The nanowire research uses the same process in a scaled down version.

Growing nanowires

"To build nanowires we deposit nanoparticles of gold onto a semiconductor wafer of gallium arsenide," says Professor Jagadish. "This is done by placing a suspension of gold nanoparticles in water onto the wafer and allowing it to dry out. The gold suspension is purchased off the shelf from biotech companies where gold nanoparticles are used as biomarkers.

"The trick, we've discovered, is to make sure the gold nanoparticles don't clump together as the water dries out. We achieve this by priming the surface of the wafer with a solution of positively charged polyelectrolyte which serves to attract and immobilise the negatively charged gold nanoparticles.

"The next step is to place the sample into the metal organic chemical vapour deposition (MOCVD) chamber and then heat the sample up to around 600° C. This removes any surface contaminants and melts the gold so it forms an alloy with the gallium from the gallium arsenide wafer. This is a eutectic alloy in which the melting point of the alloy is lower than gold by itself. This is an important property in terms of what happens next.

"We then lower the temperature of the chamber to below the melting point of gold but above that of the gallium/gold alloy so it remains molten. At the same time we introduce into the chamber gases containing gallium and arsenic atoms.

"And then the most amazing phenomenon takes place – a tower of pure crystalline gallium arsenide begins to grow under the molten droplet of gold giving you a self-assembled nanowire."

From vapour to liquid to solid

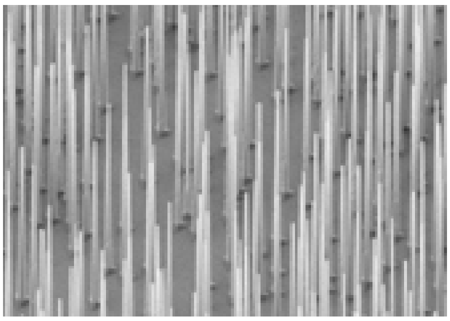
"While there is some controversy as to the exact process involved, most researchers believe that what we're witnessing is a vapour-liquid-solid growth pattern," explains Professor Jagadish. "Gallium arsenide in the vapour diffuses into the liquid gold/gallium droplet.

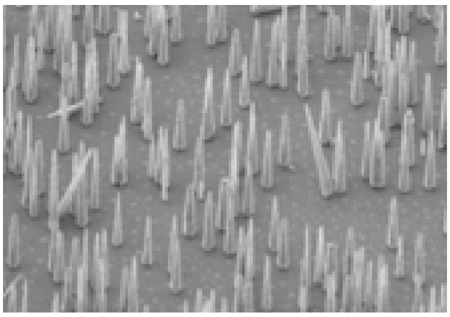
"The droplet quickly becomes supersaturated with gallium and arsenic atoms which crystallise into a gallium arsenide solid underneath the droplet.

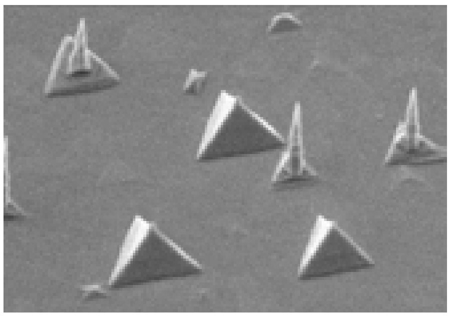
"More vapourised gallium and arsenic diffuses into the molten drop and more gallium arsenide then crystallises underneath causing the column to grow – and grow.

"From our trials we've learnt that the critical variables involved in growing nanowires under gold nanoparticles is the size of the particles, the density and distribution of the particles on the wafer, and the heat at which the nanowires form.

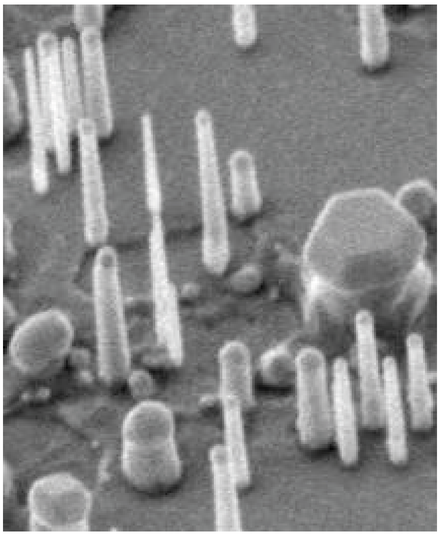
"Temperature, for example, has an enormous effect on the shape of the nanowires. If it's too hot the growth tapers too much making structures that look more like nano needles than nanowires. We've identified that for gallium arsenide nanowires 450 °C is ideal. However, if you raise it by just 30 degrees you start getting needles. Raise it another 30 degrees and you start building micro pyramids. These structures don't any value in optoelectronic devices at the

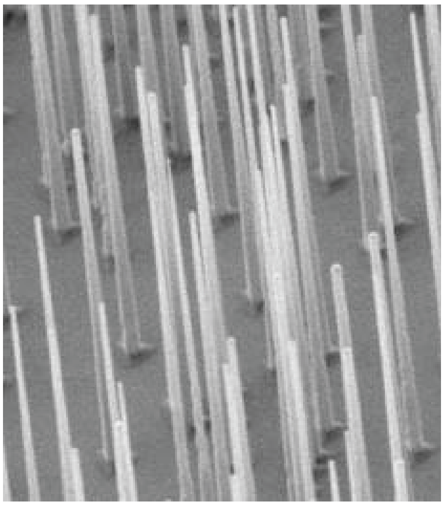






The critical variables involved in growing nanowires are the size of the gold particles under which they grow, the density and distribution of the particles on the wafer, and the heat at which they are formed. For gallium arsenide the researchers found the optimum temperature was 450ºC (left). These columns are around 50 nm thick.Thirty degrees warmer and instead of tall thin wires you get shorter, stubbier needles (centre) that are around 200 nm thick at the base. At 510ºC you get triangular pyramids (right) which are measured in microns across the base. While they look interesting, have no known useful optoelectronic properties.





One of the 'tricks' the researchers devised to more effectively grow the nanowires was to prime the surface of the wafer that the gold nanoparticles was added to with a polyelectrolyte. This prevented clumping of the gold nanoparticles The images above show the difference in nanowire growth between an unprimed surface (top image) and a primed surface (lower image).

The top down approach - what's state of the art?

The key to making better, faster, more powerful computer chips currently lies in our capacity to print ever smaller circuit lines onto wafers of semiconductor. Earlier this year, IBM researchers announced they had found a way to extend a key chip-manufacturing process to generate even smaller circuits on chips, potentially postponing the semiconductor industry's conversion to alternative ways. They claim to have created the smallest, high-quality line patterns ever made using deep-ultraviolet optical lithography - a technology currently used to 'print' circuits on chips.

The lines they printed had a uniform spacing of only 29.9 nanometres, less than one-third the size of the 90-nanometre features now in mass production (and below the 32 nanometres that industry believed was the limit for optical lithography techniques).

The semiconductor industry has long relied on continually shrinking circuits to drive increases in the performance of chips and the products that use them. But as chip features now approach the fundamental scale limits of individual atoms and molecules, the trend looked like hitting a brick wall. The new result indicates that a variant on deep-ultraviolet lithography known as 'high-index immersion' may provide industry a little more breathing space.

Micro chips are made by a process called photolithography, which transfers the various circuit design patterns onto a silicon wafer by projecting a uniform beam of UV light through a shadow mask and then focusing it onto a photosensitive 'photoresist' material that coats the silicon wafer. Subsequent development, etching, and materials deposition steps form the circuit features.

Over the years, the industry has created smaller circuit features - which typically lead to smaller, faster and cheaper electronics - by using ever-shorter wavelengths of light, stronger lenses and - most recently - inserting between the final lens and the silicon wafer a liquid, currently water, that enables even finer resolution.

Until now, it was not known if the industry could continue to adapt this optical immersion technique to produce sharp features smaller than 32 nanometers. New materials required to make such small features were thought to be incompatible with each other or capable of yielding only indistinct, blurred patterns.

As part of its research, IBM developed an interference immersion lithography test apparatus that uses two intersecting laser beams to create light-and-dark interference patterns with spacings closer than can be made with current chip-making apparatus. The new process will allow for the testing and optimizing of various high-index fluids and photoresists being considered for use in future deep-ultraviolet systems that would create such fine features.

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moment but you never know what the future holds.

"If you drop the temperature by just 15 degrees under 450 °C the nanowires start becoming too thin and a large number start breaking or folding mid length."

Nanowires with branches

While growing simple gallium arsenide nanowires is a significant achievement, because the chemical vapour deposition chamber the researchers use is so versatile in respect of the different elements it can introduce, they have developed a capacity to grow nanowires made of gallium or indium and arsenic, or nanowires made from gallium, indium and arsenic.

"By using different reactive species in the vapour such as indium, gallium and arsenic you can incorporate different compounds into the nanowire thereby giving it different electro optical properties", says Professor Jagadish. In this manner we've been able to grow indium arsenide and gallium arsenide hetero-nanowires.

"We've shown that when gallium arsenide starts growing on top of an indium arsenide base stem that the nanowire has a greater taper due to the fact that the gallium arsenide has a smaller lattice constant than indium arsenide."

Not only can they craft the shape and properties of individual stems, they can even grow branches on the nanowires.

"To grow a branch you need to supply another dose of gold particles to the nanowires you've already grown. Gold nanoparticles that adhere to the sides of the nanowires then become the starting points of new nanowire growth.

"As with the vertical nanowires, you can build in a range of elements depending on what you supply in the vapour. It's simply amazing the range of forms that we can produce."

Nanowires in patterns

And where will these nanowires be used?

"It's possible that the nanowires we are growing might be used as wires connecting circuits and devices. By breaking them from the wafer on which they've grown using ultrasonic treatment they can then placed into circuits," says Professor Jagadish. "However, we suspect their more significant value will come using them where they grow. They can serve as nanowire lasers, nanowire photo-detectors, photonic crystals and quantum dot lattices.

"Consequently, the next challenge will be to work out different ways of growing the nanowires in ordered arrays and we're currently experimenting with this by adding the gold nanoparticles onto a porous

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Growing nanowires

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alumina template so they sit at equal distances from each other. The subsequent nanowires will then also be equally spaced.

"In the near future we'll be setting up an electron lithography facility with ARC LIEF funding. This will allow us to create patterned surfaces on wafers on which the nanowires will grow and should further enhance our capacity to grow nanowires to order."

Which is where the traditional top down methods of carving out electronic circuits is joining forces with the new ways of bottom-up self-assembly.

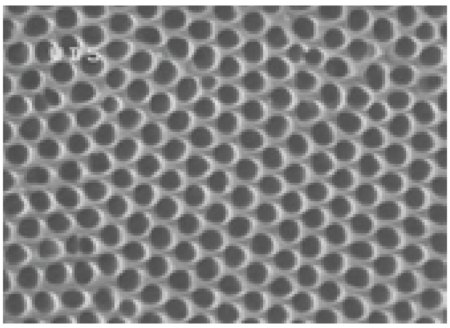
"No-one is suggesting that the traditional top down ways of building optoelectronics are going to be displaced by self-assembly techniques," says Professor Jagadish. "Indeed the growth of nanowire-based devices will likely rest on a combination of the two approaches.

Nanofutures

"It might take a few years but as our mastery of self-assembled nanostructures begins to match our traditional top-down mass-manufactured capacity it's likely a new world of possibilities will open. Instead of today's ubiquitous two dimensional micro chips it might be that the world of ICT is driven by three dimensional nanocubes performing tasks with unparalleled power and an efficiency.

"It's impossible to say exactly how it will progress. What's important is that Australia build a capacity to engage with these emerging technologies," stresses Professor Jagadish.

"It's taken considerable time and calculated investment for us to build our research capacity here at Electronic Materials Engineering. We're not as big as similarly focussed research groups overseas but we really are operating at the cutting edge.



A porous alumina template being trialled by the researchers in an effort to grow nanowires in ordered arrays. The holes are around 50 nm wide.

"Our work with nanowires has only been going for a bit over a year but we are already setting the benchmark in several areas of nanowire growth, including the first controlled growth of ternary indium/gallium arsenide nanowires. Such achievements are only possible because we have been working in this general area for some time. We have the understanding, the equipment, the flexibility and the passion to be a real player in this field."

In recognition of the importance of this emerging science, and of the track record of achievement of Professor Jagadish's research group, Professor Jagadish was recently awarded a Federation Fellowship to pursue the development of nanowires.

"Such awards are, of course, very gratifying but it needs to be stressed that this research is a group effort involving scientists from ANU and other institutions," says Professor Jagadish. Here in the Electronic Materials Engineering at the ANU the team includes includes Dr Yong Kim (a visiting Professor from DongA University, Pusan, Korea), Ms Hannah Joyce (a PhD. student), Dr Qiang Gao (an ARC Post-Doctoral Fellow), Dr Hoe Tan (an ARC QEII Fellow) and Ms Victoria Coleman (a Ph.D student).

"Researchers from other institutions working with us on nanowires include Dr Jin Zou and Mr. Mohan Paladugu from the University of Queensland, Associate Professor Matthew Phillips from the University of Technology, Sydney and Dr. Alexandra Suvorova from the University of Western Australia.

"The entire team is very passionate about this research and makes it an exciting project to work on."

More information: Professor Chennupati Jagadish < cxj109@rsphysse.anu.edu.au>

The MOCVD Lab

Professor Chennupati Jagadish with a MOCVD reactor used to grow gold tipped nanowires.

ANU operates one of the most sophisticated Metal-Organic Chemical Vapour Deposition (MOCVD) laboratories in the world, and thereby gives Australia the capacity to keep in touch with the latest developments relating to the industrial manufacture of optoelectronic devices.

The principle of MOCVD is quite simple. Atoms that you would like to be in your crystal are combined with complex organic gas molecules and passed over a hot semiconductor wafer. The heat breaks up the molecules and deposits the desired atoms on the surface, layer by layer. By varying the composition of the gas, you can change the properties of the crystal at an almost atomic scale. It can grow high quality semiconductor layers (as thin as a millionth of a millimetre) and the crystal structure of these layers is perfectly aligned with that of the substrate.

The MOCVD approach was chosen over other methods because of its flexibility in growing precision controlled layers for special applications as well as it's ability to be scaled up to industrial-scale production with relative ease.

Since it's establishment in 1991, the lab has recorded several world records for the highest concentration and most abrupt atomic layer doping, so-called delta doping, for carbon, silicon and zinc in GaAs and AlGaAs layers.

The group has also grown narrow multi layers, so called quantum well structures, with very interesting optical and phonon (vibrational) properties. More recently, the group has taken giant steps towards the fabrication of practical devices. For example, the group has fabricated laser sources, light reflectors and modulators.

Singapore story

CSEM's Director, Dr Zbigniew Stachurski, is currently giving a course to postgraduates students on Physics of Polymers for three months at the Nanyang Technological University (NTU) in Singapore. He's working in the School of Materials Science and Engineering which, with 1100 undergraduate students, 130 PhD students and 45 faculty staff, is one of the biggest MSE schools in the world.

Dean of the School is Professor Freddy Boey. Professor Boey studied as an undergraduate under Dr Stachurski back in the 80s at Monash University. He graduated top student in 1980. After a stint as a Failure Analyst in Singapore and a one year placement in an Aboriginal settlement at Doomagee Station (Gulf of Carpentaria), Professor Boey completed a PhD in 1987 from the National University of Singapore before joining NTU.

Professor Boey's research is on biodegradable drug-eluting stents for ureteric, cardiovascular and cranial therapy. The patented technology involves a multi-layered structure allowing the controlled release of multiple drugs.

He is now working on creating nano features on the surface of the stent to promote haemo-compatibility through endothelial cell growth. He has also patented a PZT blood pump, a frictionless PZT micro-pump for implanted drug release and a fully flexible polymer impedance pump.

Dr Stachursksi with Professor Boey at Nanyang Technological University

Professor Boey's early experiences at the Department of Materials Engineering at Monash University has encouraged him to run his school with an emphasis on the spirit of camaraderie and care for students. One of the school's mottoes is "we're family.....we care". He initiated part time jobs for needy students, one-to-one tuition and personal counselling for struggling students. He was inspired by help he obtained when he was a student at Monash. Another inspiration from his student days in Australia - teaching that generates "more inspiration, less perspiration'.

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ANU-BJUT Bilateral Materials Workshop

There has been increasing scientific and cultural interaction with China in recent years. Recently a new academic cooperation agreement was signed to promote student and teacher interchanges between Beijing University of Technology and the ANU. As a part of this agreement, a Bilateral Workshop on New Advances of Mechanics and Materials Science was held with CSEM at the ANU in February. Topics covered included topological optimization of continiuum structures, penny-shaped cracks in solid piezoelectric cyclinders, cracking of high pressure gas cylinders in corrosive environments, finite element analysis of blood vessels with residual strain, reversible elastic buckling of thin wall anistrophic domes and the dynamical analysis of gravity-driven thin film over wavy substrates.

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Pictured above are the participants in the workshop. To the left is the Dr Zbigniew Stachurski, Director of CSEM, receiving a ceremonial scroll from Professor Yun-Kang Sui. Dr Stachurski and Professor Yun-Kang chaired the workshop while Professor Qing-Hua Qin (standing behind them) from the ANU Department of Engineering was one of its main organisers.

The Chinese Chair & 2 Materials

Materials, craft and design were the focus of two exhibitions running at Craft ACT during February and March, and ANU played an important role in both.

The first, curated by Nigel Lendon and Rodney Hayward from the ANU School of Art, brought together an exquisite collection of six variations of Chinese chairs from private collections in Canberra, including a Ming Meditation Chair created by Canberra furniture maker and graduate of the Furniture/Wood Workshop, Peter Giles (see the October 2005 issue of *Materials Monthly*). The exhibition examined the individual history of each example and the Chinese cultural influence on modern chair design.

"The chair is a battlefield between the designer and the craftsman," says Dr Hayward, Head of the Furniture/Wood Workshop. "The designer is always looking to push the materials used in a chair to their limits whereas the craftsman is usually more conservative and remains within the bounds of what he or she is working with.

"The strategies open for the designer of a wooden chair derive from attempts to resolve the universal problem of conducting stresses through the union of vertical and horizontal components."

In the adjoining hall to The Chinese Chair is a second exhibition that focuses on the notion of duality through the use of two contrasting materials in each work. Entitled 2 Materials, the exhibition features work of Craft ACT Accredited Professional Members, several of whom are staff or former students at the ANU School of Art. These included Gilbert Riedelbauch (see the *March 2003* issue of Materials Monthly) who created a delicate light sculpture crafted from brass and ABS plastic, and Valerie Kirk (see the May 2005 issue of *Materials Monthly*) who produced four small tapestries from mixed yarns and gumnuts.

The exhibition highlights the art in using two materials, and the skills and concepts demonstrated by these professional contemporary craft artists.

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(Right) Peter Giles discusses his Ming Meditation Chair at the opening of The Chinese Chair. The chair stood in the centre of the exhibition which sought to explore design for the human form and historical and cross-cultural influences.

(Below) Gilbert Riedelbauch's light sculpture making use of brass and ABS plastic.

Contacting CSEM

Director
Dr Zbigniew Stachurski
Phone: (02) 6125 5681
Email: Zbigniew.Stachurski@anu.edu.au

Editor, *Materials Monthly*
David Salt
Phone: (02) 6125 3525
Email: David.Salt@anu.edu.au

CSEM Office
CSEM
Department of Engineering
Bld #32, ANU ACT 0200

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