Some ten years ago Professor Jim Williams set about investigating why it was that silicon’s structural properties changed when you stamped it. He wasn’t trying to solve a problem for industry, it was simply an interesting question. Since then he’s taken over as the Director of the Research School of Physical Sciences and Engineering (RSPSE) and most of his time is spent coping with the growing complexity of running one of Australia’s foremost physics research centres. However, he still finds the odd moment to focus on his research on stamping silicon. Not only has the original investigation opened up rich new possibilities for the whole semiconductor industry, Professor Williams believes his ongoing contact with the research is the one thing that keeps him sane.

Press down on silicon and new possibilities open up

“Like much of the science done at the Research School of Physical Sciences and Engineering, the work on stamping silicon started as a fairly fundamental research activity,” says Professor Williams. “It was curiosity driven.

“It’s been known for some time that when you press down on silicon it deforms by changing its phase from one crystal structure to another. Then, when you release the pressure, it changes again to other phases. Why is this, and what can we learn by understanding this? These were the questions we started out attempting to answer. We weren’t seeking to answer a specific industrial problem.

“So, some eight to nine years ago we decided to get a good student to work on this question, and that student was Jodie Bradby. As it’s turned out we’ve been remarkably successful, and part of that success is that Jodie is an excellent experimentalist. She has brought to bare a range of analytical techniques that had not been applied to this system before. In so doing we have uncovered some exciting possibilities.”

Now, when you press down on this silicon at quite a high pressure, say over 10 gigapascals of pressure, then the material is compressed and its density increases by over 20%. Under this pressure it changes phase and turns into silicon II (Si-II), a metallic version of silicon with a tetragonal crystal structure very similar to the metal tin, a sister element in the periodic table.

“While 10 gigapascals of pressure sounds extreme, it’s easily achieved when stamping the silicon with a small point of a harder material like a diamond tip,” comments Professor Williams. “This is actually what we do with a device known as an indenter. It’s tiny diamond tip presses down on the silicon wafer. Indenting silicon holds the key to opening up new applications for the semiconductor industry.

Stamping silicon

So what’s all the fuss about? Let’s begin by describing what it is that the researchers have discovered. They started out by investigating what happens when you press down on the silicon found in silicon chips. This is crystalline silicon with a diamond cubic structure. It’s referred to as silicon I (Si-I) and it behaves as a semiconductor.

An atomic force microscope image of an indent on a silicon wafer. Indenting silicon holds the key to opening up new applications for the semiconductor industry.
A (Nano) stamp of approval
(continued from previous page)
substrate with a known force creating an indent.”

Si-II has the electronic and mechanical properties of a metal and not a semiconductor. However, this phase only persists for as long as the pressure is maintained. As the pressure is released or unloaded (as the diamond tip is raised), the silicon does not return to Si-I but turns into one of two other phases depending on how quickly the pressure is released.

If you release the pressure very quickly you end up with amorphous silicon with no crystalline structure – a material that behaves as an electrical insulator.

If you unload slowly it will transform into a mixture of two other crystal phases of silicon – silicon-II (a body-centred-cubic structure) and silicon-XII (a rhombohedral structure). One is a semiconductor and the other is a semi-metal though both have yet to be studied to determine their properties.

“We have also found that if you have certain dopant atoms in the silicon to begin with, these two phases can be very conducting,” says Professor Williams.

“And the other thing we’ve found is that if you start off with amorphous silicon and you press down on that you can produce a number of other phase changes. And, if you then heat it up, to say 150 degrees Celsius, you can come back to silicon-I.”

Which all adds up to an amazingly flexible and completely new way of working and modifying silicon – the world’s most common semiconductor.

A silicon revolution
“We can start off with a sheet of amorphous silicon and then press down on little bits of it, transform it, heat it up a little bit and indent it back to silicon-I, a semi conducting form,” explains Professor Williams.

“Or we can start with semiconductor silicon and transform it to an insulator. The beauty of this is that we can cycle between conducting and insulating phases as we like.

“Now if you think about it, this stamping approach offers us a fundamentally different way of working with silicon semiconductor wafers. In the past you’ve started with a silicon wafer that is all the same, and you’ve patterned it to locally change the properties by introducing something else onto or into that silicon. Here we’re not introducing anything else into the silicon. We’re using the fundamental pressure-induced properties of silicon itself to change its properties from a conducting to an insulating phase or phases (or vice a versa).

“This opens up a whole new world of possibilities in working with semiconductors. Where ever you want to selectively write lines or patterns of conducting or insulating material on a silicon wafer this technique has applications.

“We can change insulating silicon to conducting silicon for example, which leads to an ability to make little memory cells by changing these properties and then joining them up.

“But it’s also a patterning process because you can draw conducting lines by drawing a line of dots. Therefore, it’s a fundamentally new way of making circuits with a minimum of patterning as you’re making the patterning while you’re changing the properties.

“What’s more, you can actually measure the electrical properties as you’re carrying out the indenting so we know, even before you finish the indentation process, whether we’ve achieved what we intended to achieve. So, it’s a very attractive process because you’re doing the testing while you’re actually doing the modification.”

Why has it taken so long?
Given that silicon is such a widely used and researched material, why has it taken so long for materials scientists to twig to this effect.

“Prior to us beginning this research there were indications in the literature that silicon underwent phase changes when you pressed down on it,” says Dr Bradby. “However, there was no understanding of the sequence of those changes or of the properties of the resulting phases.

“And even now a lot of people working with silicon would not know about these aspects of silicon because these changes are produced using quite high pressures. In the regular handling and processing of this material you’d never see this type of behaviour because you’re actually avoiding these regimes.”

“Of course, any application requires the engineering to be developed to deliver it to an industrial process, however, the concept is sound,” says Professor Williams. “We’re very optimistic that there are a whole range of potential applications and that many of them can be implemented in a fairly straightforward way.”

Stamping a market niche
“There are two distinct areas where this approach has special benefit,” he explains. “The first is where the application needs to be cheap. In other words, applications where you can’t from a cost perspective undertake the expense of developing the traditional pattern forming processes. However, a simple stamp that in one step defines the region you want to change might be possible.
“Small businesses, for example, might want to have a way for writing information electronically into materials that they can read but it has to be very cheap because they haven’t got the infrastructure of Intel and similar sized companies.

“Consider smart cards as an example. If you want a cheap way of writing information into a smart card this might be the way you do it, and it’s much much less sophisticated than conventional memory technology. You might have a smart card or something similar that has all the circuitry in there to enable you to do something but what you need to do is to connect a few of those bits to customise the chip with information specific to individual users. Well, to make a specific chip for a person or a business is a pretty costly business. However, with a stamp it might be a simple, cheap and trivial process using your corporate stamp.”

Moving into new territory

“The other set of applications for this stamping method are where you simply can’t create what you’re after using more traditional techniques,” he says. “This is where a potential memory technology comes in that works at the nanoscale.

“By pressing down with a diamond tip of an atomic force microscope, for example, its possible to create a domain that has dimensions of less than 10 nanometres. In so doing you’re creating a memory cell that is less than that which can be made from conventional silicon chip technology. The footprint you need to make a transistor using conventional technology, no matter how small the widths between the various bits of the transistor are, fundamentally can’t be less than 10 nm because you reach the physical limits of the material.

“So, here is a case where conventional technology has a fundamental limit to how small it can get but there’s no limit to this new way of making conducting lines on silicon through indentation.

“However, those applications that are more sophisticated are going to take much longer to engineer simply because the level of sophistication you need to make billions of interconnected very small domains. Some of the simpler applications that are justified by the lower cost, however, maybe be much easier and faster to implement though even here there are still many engineering challenges to overcome.”

New technology

“One example of the challenges we need to meet is that there are no instruments yet available to create such a sophisticated stamp,” explains Professor Williams. “We’re working with diamond-tipped indenters. You could imagine that the commercial stamp would need to be coated with glassy carbon or diamond-like carbon in thin films in order to make stamps hard enough to transform silicon.

“I think it’s a matter of putting together different technologies to achieve it. In other words, you can make stamps with very fine dimensions. In principle you can coat these with diamond-like carbon or what have you.

“One issue that we need to resolve is the flatness of the stamp. That is, every protrusion of the stamp must meet the silicon at the same time and the same pressure. As you can see, there’s an engineering challenge here to get uniformly flat stamps. Whereas many stamps are used to stamp plastic, the plastic is giving and you don’t have to have an enormously flat surface. Silicon is not giving and it’s a different situation.

“So, there are engineering problems to solve when you make such a sophisticated stamp. Though it needs to be kept in mind that while the stamp itself might be expensive, you’re stamping many many potential products at the same time so the cost per unit produced is inexpensive.

“The engineers need to work this out. For example, would you have a stamp that is flat or would you use a roller where you only have to make a much smaller section that is flat and then roll it over the sample to imprint your information or your pattern.”

A research stamp of approval

Of course, Professor Williams is also the Director of the Research School of Physical Sciences and Engineering so finding time to maintain contact with the research is a challenge in itself. However, he believes it’s important to make the effort.

“The research revivals me, indeed it keeps me sane,” he says. “I need... continued on back page
Welcome to my material world

Mixing science with wearable art at reSkin

It was with a little trepidation that six presenters from the ANU Centre for Science and Engineering of Materials (CSEM) got up in front of a group of artists and crafts people from all over Australia to discuss various aspects of materials science and engineering. After all, artists are a different race from scientists and engineers. They think differently, use different language and approach things in a different way. Could materials science offer any thing of value or of interest to them?

The occasion was a workshop called ‘Welcome to my material world’ and it was run as part of reSkin, a Media Lab run by the Australian Network for Art and Technology (ANAT). The Lab is running at the ANU School of Art over the second half of January and involves around 30 artists designing and producing wearable technology.

CSEM was asked if it could arrange a workshop in which some of the University’s work on materials might be showcased. The hope was that the artists might find some inspiration in the research, a possible reference point for their own work. The six presenters were David Salt (Materials Monthly/CSEM), Tim Senden (Applied Maths), Erica Seccombe (artist in residence/ Applied Maths), Ray Prowse (Centre for Sustainable Energy Systems) and Milli Styles (Department of Engineering).

As it turned out, the CSEM presenters had nothing to worry about. The artists found the presentations informative, educational and exciting. Following the talks the reSkinners engaged the speakers in lengthy discussions over drinks.

Possibly the best summary of the presentations was provided by Sarah, one of the participating artists who posted her impression on the reSkin blog the next day:

This led into the ‘My Material World’ section, introduced by David Salt of ANU. His relationship with the work he presented was wonderfully visual – we saw ‘nano-lollipops’, ‘little cauliflowers’ and a ‘mess or a mass of nanotubes’. His enthusiasm was infectious, and despite it being the graveyard shift, all the presenters followed gave exemplary performances, building tension and introducing humour in a way that put us ‘arty’ folk to shame.

Tim Senden physically demonstrated ‘wetting’ and the power of the last nanometre to change the properties of materials – the ‘duck-o-meter’ of the 1950s caused some to lose momentary control (to measure the efficiency of detergent, first find your duck; place it in the bowl of soapy water – and watch it sink as the oil is stripped from its feathers).

Erica showed us a tiny plastic octopus undergoing an X-ray CT scan and six foot prints of a chocolate centipede, and Milli Styles showed us her work on ultra-light aluminium structures reminiscent of Aero bars.

Ray Prowse answered wearables developers’ dreams with his group’s research on sliver solar cells. These use a thirty-sixth of the pure silicon needed to make conventional solar cells, through clever slicing and flipping to maximise surface area, and achieve transparency with minimal loss of efficiency through a reflective back surface. We can expect these flexible power supplies to be on the market in about five years’ time, just right for globally warmed systems.

And I mustn’t forget Tim Wetherall, who described the fear as the bioreactor he had built with Stelarc leaked two hours before the big opening – lamb muscle cells dying on a composite scan of an ape and Stelarc’s face, - would they make it in time?????? Of course they did, with some distilled water from the garage and at least as much ingenuity as had gone into the original design – the lesson being don’t trust specs.

Exhausted and inspired, the company adjourned to the foyer to relax with a hard earned glass of vino and to admire the first exhibits in the nascent exhibition. Material scientists, MIT alumni, early career wearables developers and craft professionals mingled happily and what seeds were sown for the future there, only time and this blog will tell.

To find out more about reSkin, visit their website <http://www.anat.org.au/reskin/index.php> or read the article in the October 06 issue of Materials Monthly (see <http://www.anu.edu.au/CSEM/newsletter.php>)
Wood-cement composites a winner

Last year, research carried out at ANU on wood-cement composites was recognised with three international research prizes. The awards went to Professor Phil Evans and three of his former researchers for their work on improving the manufacture and properties of wood-cement composites used in a variety of applications in low cost building and construction.

Wood-cement composites are a cheap and efficient building products that are playing an increasingly important role in many developing countries. The research undertaken at ANU focussed primarily on wood-wool cement board which is made from debarked softwood or hardwood logs that have been stored for varying periods of time to reduce the starch and sugar content of the wood (which interferes with the setting of the cement). After storage, logs are shredded to produce wood-wool (which is typically made of strands which are around 3 mm wide and 0.5 mm thick with lengths up to 40–50 cm).

The wood-wool is air-dried and mixed with cement. The cement-coated wood strands are then deposited on a forming board and pressed in a hydraulic press at room temperature for 24 hours. The pressure is released and the boards are then cured for 2-3 weeks before being trimmed and finished. The product is cheap and durable; resistant to fire, termites and fungus; and is flexible in terms of strength and density depending on the wood used and the conditions under which it is pressed.

Professor Evan’s team has made many important contributions to the development of wood composite boards over the years and this was acknowledged last year with the Professor Evans receiving a Commonwealth Forestry Association Medal for Innovative and Successful International Forestry Initiatives.

Along with Dr Kate Semple and Professor Ross Cunningham, he also received the George Marra Award of Excellence in research and writing exhibited in the journal Wood and Fiber Science for the paper. Their paper was titled: Manufacture of wood-cement composites from Acacia mangium: Mechanistic study of compounds improving the compatibility of Acacia mangium heartwood with Portland cement. (Wood & Fiber Science 36:250-259).

And Professor Evans also received the Philippine Agriculture and Resources Research Foundation R&D Award (Research Category) with Dr Rico Cabangon for research on development of innovative wood composites. The award recognizes the work they did to develop wood-wool cement composites with improved properties (resulting from the alignment of wood strands prior to pressing). Work is currently underway in the Philippines to commercialise this research (though not with wood but with bamboo because it’s easier to orientate the bamboo strands than wood-wool).

Though the research that has been recognised in these awards was performed at ANU, the researchers have now all moved on to work at other institutions. Professor Evans, a former Director of CSEM, is now serving as the Director of the Centre for Advanced Wood Processing at the University of British Columbia in Vancouver. Though based on the other side of the world, he maintains close contact with ANU.

“I’m a regular follower of materials research at ANU through Materials Monthly,” he says. “I’m pleased that ANU research on wood is alive and well. It’s an area that has been overlooked by many in the past but it’s being taken more seriously now that people can see the environmental benefits that could be derived from substituting petroleum-based synthetic materials with wood composites, which sequester carbon and are derived from a renewable resource (trees!).

More info: Professor Phil Evans <phil.evans@ubc.ca>
to have an outlet from the constant grind of administration, and that outlet is research like this.

“I also think that when you’re director of a research school it’s important that you have research credibility. How can I talk to other researchers at the school about research performance if my performance isn’t out there for everyone to see and comment on.

While the work on indenting semiconductors lies within the Department of Electronic Materials Engineering at RSPSE, Professor Williams and Dr Bradby are quick to point out that many researchers from outside of the Department and the School have made important contributions to the work.

“One of the techniques we rely on to monitor our indents is atomic force microscopy and the experts on that are in Applied Maths,” says Dr Bradby. “They’ve given us much valuable advice. And then there are a range of electron microscopists who have provided us with important assistance. For example, we’ve had significant collaboration with John Fitzgerald and the transmission electron microscope he operates at RSES.

“And, very recently in this project, we’ve need to look at ways of treating surfaces, particularly with our amorphous materials and amorphous substrates. To this end we’ve begun interacting with Rod Boswell’s plasma processing group.”

Innovative nanotechnology

And is the Research School of Physical Sciences and Engineering a good place for innovative nanotechnology to take off?

“Yes it is,” says Professor Williams. “It has strength and diversity, and a surprising synergy between activities across the school. I think our success lies in the fact that our research programs are all focussed physics activities that go from fundamental research right through to the applied end.”

Of course, as Director, you’d probably expect him to say something like that. However results speak louder than words and the success his group is having stamping silicon suggests whatever approach the school is using, it appears to be paying off.


Materials Monthly comes out 10 times a year (February to November). We welcome your feedback and contributions. Please send them to David Salt, Editor, Materials Monthly, care of CSEM.

Please let us know if you wish to be added to our electronic or postal mailing lists.

Electronic copies of Materials Monthly, useful links and additional information about CSEM can be found at our website: www.anu.edu.au/CSEM