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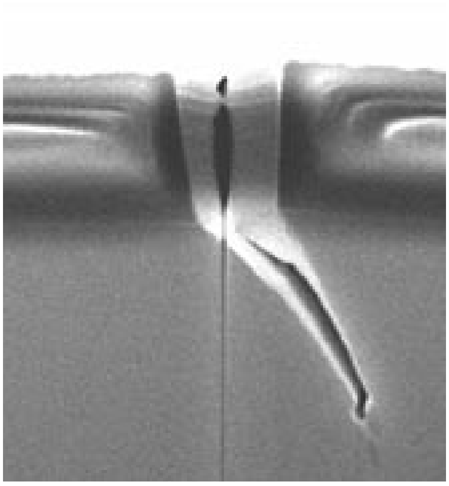

Cracking in thin deposited films is not an uncommon problem. Research in the Department of Electronic Materials Engineering is throwing new light on what's actually happening.

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Cracking under stress

As scientists build increasingly complex structures from deposited thin films they're discovering a host of new problems relating to the physical nature of these layered systems. Stresses building up inside the layers can lead to cracking, distortion and delamination of films and to catastrophic failure of devices. Researchers in Electronic Materials Engineering, RSPSE, have been studying these process and have observed a spectacular new form of cracking behaviour. They believe the process is similar to what happens when mud on the bottom of a puddle dries out.

Designer films

Depositing thin films on silicon wafers is becoming increasingly sophisticated. We can lay down multiple layers and control the thickness of each layer down to submicron accuracy. We can also doctor each layer during the deposition and subsequent processing to ensure a specific chemical make up and structure. By exercising such control it's possible to build structures with made-to-order properties, and these films are increasingly critical to the operation of many modern devices used in areas such as microelectronics, optoelectronics, photonics, and micro-electro-mechanical systems.

But these films often fail because of cracking arising from a build up of stress in the film. While cracking is not an unusual event, materials scientists (Professor Rob Elliman, Dr Tessica Dall, Mr Marc Spooner and Mr Taehyun Kim) in the Department of Electronic Materials Engineering (EME) have recently witnessed a particularly amazing form of cracking behaviour in amorphous silicon-rich oxide films deposited on silicon wafers.

"We have observed two novel modes of crack propagation, one that produces straight cracks aligned with specific crystallographic directions in the silicon substrate, and a second that produces near-perfect sinusoidal, or wave-like, cracks aligned along different directions," says Professor Rob Elliman, Head of EME. "The sinusoidal cracks have a wavelength of around a hundred micrometres and can propagate over centimetre distances with near constant form. This long-range periodicity suggests a simple interplay between two competing processes and we are trying to understand these in detail."

The silicon-rich oxide layers are being deposited on silicon substrates by plasma-enhanced chemical vapour deposition (PECVD). Individual layers are between 100-1500 nm thick and are deposited onto a heated silicon wafer from a plasma containing a mix of silane (SiH_4) and nitrous oxide (N_2O). The researchers are interested in silicon-rich oxide films because these are precursors

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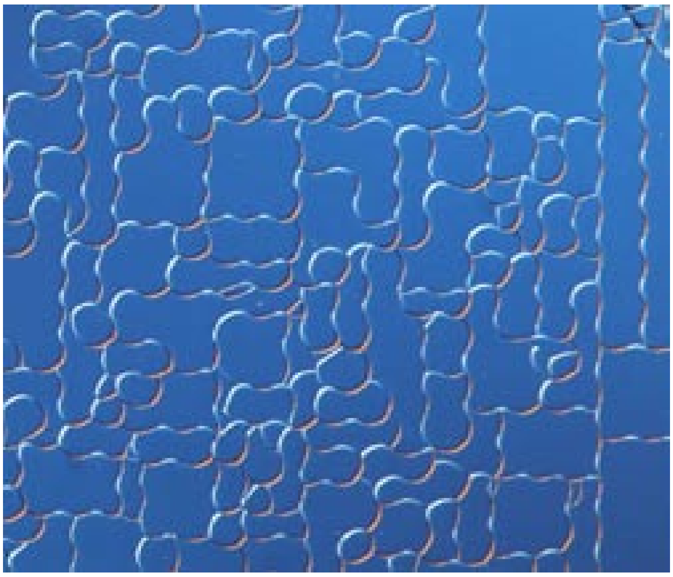

The researchers have observed many bizarre variants of the cracking behaviour. Pictured here is a form they have dubbed 'chain -mail' created from a network of interlinked wave cracks.

Cracking under stress

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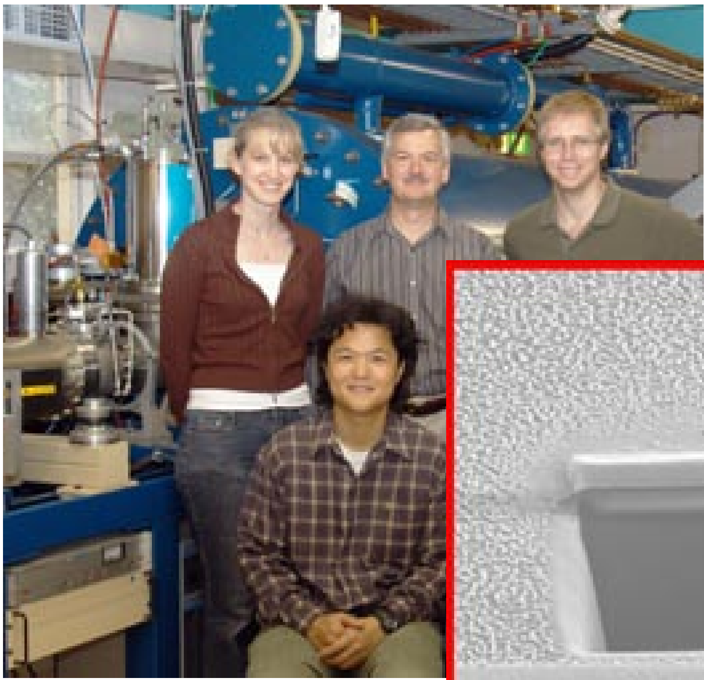
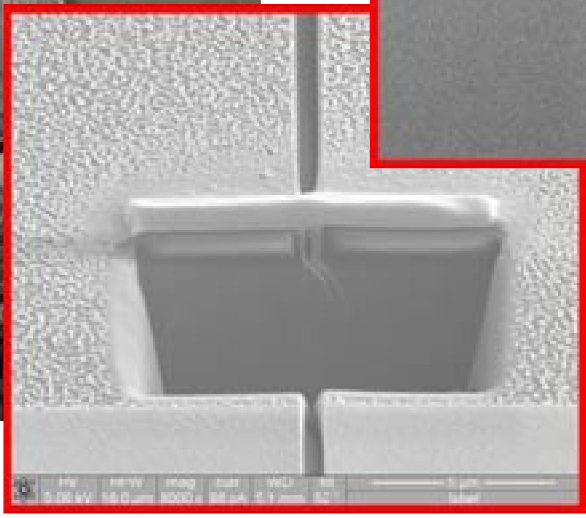
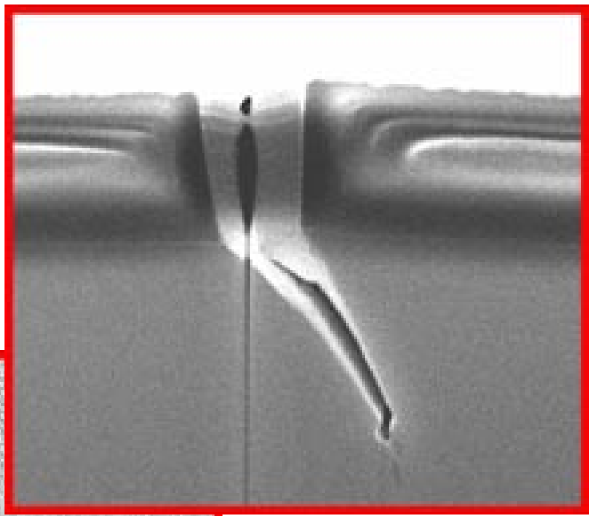


The crack team at EME. (From the right) Tessica Dall, Rob Elliman, Marc Spooner and Taehyun Kim (seated in front). (Photo by Tim Wetherell)





To study the cracks the researchers used a focussed ion beam to excavate a pit across the fracture (centre pic) and then a scanning electron microscope to image a transverse section of the crack (above). You can see how the crack goes all the way through the surface layer (about 1.2 micrometres deep) and then angles into the underlying silicon subtrate.

for the formation of light emitting silicon nanocrystals (see the September 2001 issue of Materials Monthly for a discussion on silicon nanocrystals).

After the film has been deposited it is then heated to precipitate the silicon nanocrystals during which it experiences temperatures of up to 1100°C. It's during this heating that the cracking occurs.

Straight cracks and wavy cracks

"It appears that straight cracks begin to form first followed by the wavy or oscillating cracks," says Professor Elliman. "Both sets of cracks, straight and wavy, lie parallel to particular crystallographic directions in the underlying silicon substrate. Interestingly, the wavy cracks do not appear to have been observed before in such thin films. However, similar cracks have been observed in thin glass plates that are heated at one end and cooled at the other and in rubber sheets stretched more in one direction than the other."

To understand what's happening Professor Elliman's team has been studying several aspects of the process, specifically the effect of heating on the film stress and the amount of hydrogen it contains.

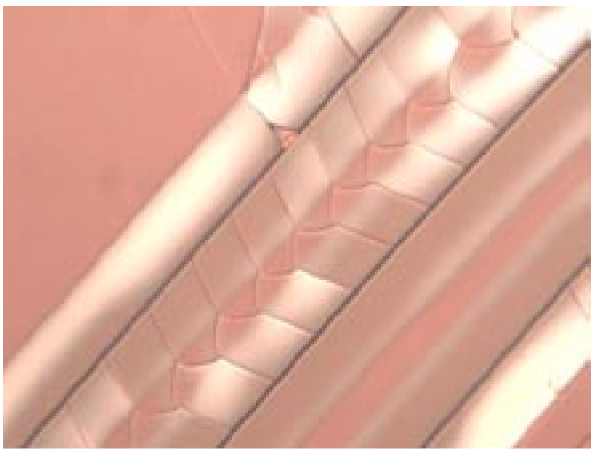
"The film stress can be determined from the curvature it induces in the silicon subtrate," explains Professor Elliman. "These measurements show that the as-deposited film is is in compression, much like a sponge squeezed into a small box. As the film is heated during annealing this stress changes from compressive to tensile as the film appears to 'shrink' or densify. This stress rises quickly as the sample is heated from 400°C to 650°C, eventually leading to crack formation."

"Interestingly, the temperature range over which the tensile stress develops corresponds to the range over which hydrogen is lost from the film, leading us to suspect that it's the progressive loss of hydrogen and the associated compaction of the film that causes the stress in this case.

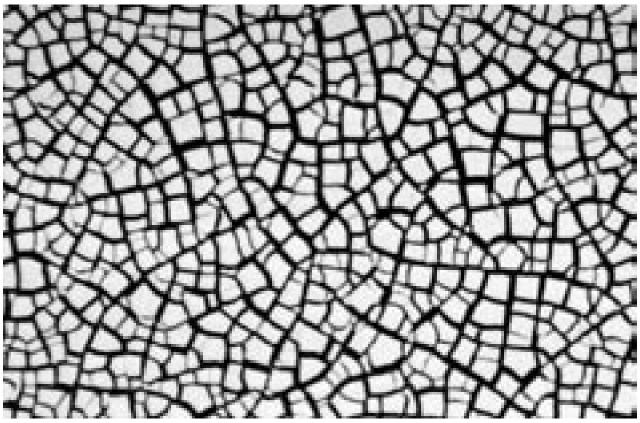
"The as-deposited films contain a lot of hydrogen, as much as 25 atomic percent, due to the high concentration of hydrogen in the plasma used for deposition" he says. "That's a direct consequence of using silane in the deposition process. However, when the samples are annealed this hydrogen is progressively released as the temperature increases and we've shown that most of this release occurs between 400°C to 650°C.

Something like mud

"It's a similar process to mud drying on the bottom of a puddle or dam. As the water evaporates from the mud it shrinks creating a tensile stress that eventually results in a crazy cracking pattern. Similar 'mud-crack' patterns are observed in many thin films, including pottery glazes. Such random patterns result when the stress is isotropic, meaning that it pulls equally in all directions across the surface.



The researchers called the cracking pattern above 'snake skin' for obvious reasons. It's formed by two parallel straight cracks with repeated curved cracks in between. This form of cracking occured relatively slowly, over several seconds. It could be observed happening by eye. The wavy cracks, in contrast, grow very quickly, too fast to observe.



Crazy mud cracking patterns such as shown above (dried mud) and on the right (thin film of aluminium oxide) occur when materials experience isotropic stress. Clearly something different is happening with the thin silicon films.

"However, while we think it's the same basic process that generates the stress that creates the cracks, the actual cracks that we're seeing are quite different to the random 'mud-crack' patterns. You only have to look at the cracking in these silicon-rich oxide films to see that the cracks have well defined orientations. They're not random at all. As it turns out, the cracks have specific alignment corresponding to specific crystallographic planes in the underlying silicon crystal that makes up the substrate. This suggests that the anisotropic mechanical properties of the silicon substrate influence crack propagation.

"To investigate this we have used focussed-ion- beam (FIB) sectioning to excavate trenches across the cracks to expose transverse sections of the material. These show that the cracks often extend through the thin film and into the silicon substrate along particular planes. Cracks could therefore be guided along particular directions by their interaction with the silicon crystal, which is known to have different mechanical properties along different directions.

Getting to the bottom of the waves

"The processes responsible for producing the regular wave-like cracks is a bit harder to explain," says Professor Elliman. "Sections through these cracks show a complex relationship between the thin-film crack and that in the substrate, with both oscillating between well defined directions as the crack advances. However, it remains unclear as to whether the oscillating crack first forms in the film with the substrate crack propagating subsequently, or whether the cracks propagate together as a compound crack in the film and substrate." .

And are there any applications for these attractive sinusoidal cracks?

"Absolutely none that we can think of at this stage," says Professor Elliman. "However, understanding how stress develops in thin films and why and how cracks form is fundamental to the successful application of thin film technologies. For example, our results clearly show that hydrogen release can be used to tailor the stress in thin films to produce stress-free films or films with a particular stress. This is particularly important to the builders of micro-electro-mechanical systems or MEMs where film distortion or failures caused by internal stresses can quickly destroy a device."

"Having said that, one never knows! Being able to produce a regular sinusoidal crack that can extend over several length scales might prove extremely valuable in the future. As is often the case in science, the serendipity of discovering previously unknown phenomena can lead to new and novel applications."

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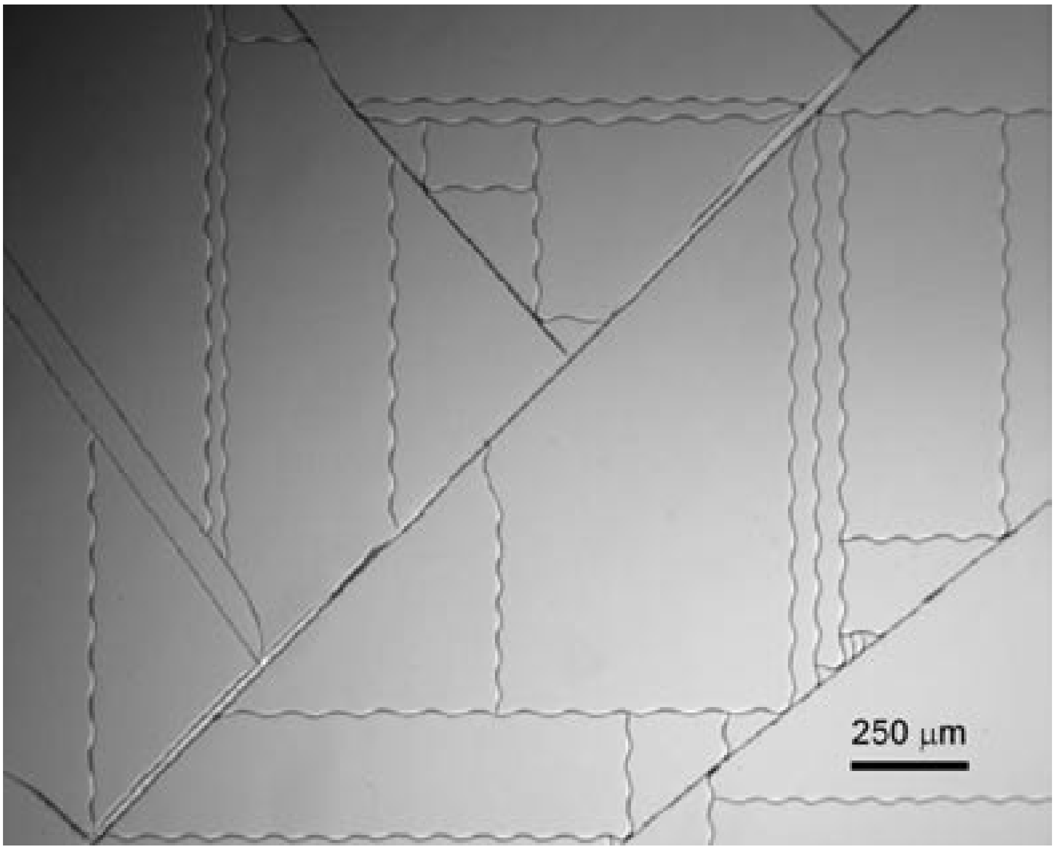


The cracks in the thin silicon films are clearly following an alignment corresponding to specific crystallographic planes in the underlying silicon crystal that makes up the substrate. The wavy cracks have never been observed before and the exact mechanism by which they are created is still being investigated.

Making sense of complex materials

It's one thing to have the technology to visualise a complex three dimensional structure, and quite another to have the capacity to then make sense of that structure. According to Dr Adrian Sheppard, the Department of Applied Maths is blessed with both attributes.

"Our X-ray computer tomography facility is one of the best in the world," says Dr Sheppard, a Research Fellow in the Department. "When it comes to mapping the fine structure of complex materials over length scales of microns to millimetres there are few other facilities anywhere that can match our capacity. There maybe a handful of third-generation synchrotrons out there that could capture finer detail but those are billion dollar facilities. Our CT facility, by contrast, is smaller, cheaper and far more flexible to use."

The Applied Maths' Computer Tomography (CT) facility uses X-rays to image slices of a sample and then a computer to put these slices together to build a 3D model of its structure. The data sets for each constructed model can be enormous, sometimes containing tens of gigabytes of information and need hundreds of gigabytes of computer system memory to analyse, which demands the power of the Australian Partnership for Advanced Computing's National Facility (APAC-NF), run by the ANU Supercomputer Facility. (For more information on the CT facility see the April 2002 issue of *Materials Monthly*).

"Having detailed 3D images of a structure is great, but it's really only the first step towards understanding that structure, especially when it's a highly irregular structure like many rock types," says Dr Sheppard. "The approach that I have been using in attempting to make sense of these structures is to transform them into networks based on the voids and connective passages embedded through their structure."

Dr Sheppard is part of the porous media group in the Department and his particular interest is in understanding a variety of different rock structures.

Adrian Sheppard with one of the rock samples he's analysing. "Understanding complex materials is much more than imaging their structure."

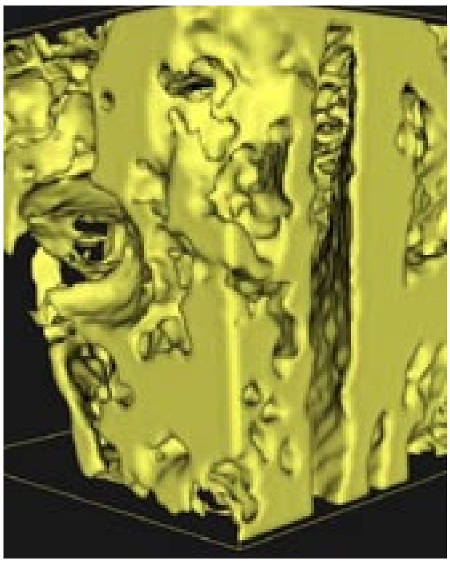
"In terms of understanding porous media, analysing rocks is a great way to go," says Dr Sheppard. "They offer enormous variety and there is also a strong commercial interest in understanding their complex structures. The oil industry in particular is starting to pay close attention to our work on understanding how oil and water behave in porous rock. That's only to be expected when you consider that an oil well only extracts about one third of the oil contained in an oil deposit. The remaining two thirds is much more difficult to extract and in the past is left underground.

"Of course, with oil prices going through the roof this position is being reconsidered and now there's strong interest in understanding how more of the oil might be brought up. Techniques involving the pumping of various gases down into the oil-bearing rock to force the oil up are being considered but to really understand what's possible you need to understand the porous network in the rock and how it interacts with oil, water and gas.

"Understanding these complex structures can be fiendishly difficult

1. A close up of a fragment of Mt Gambier limestone showing fossilised remnants of the marine organisms from which it's composed. How do you make sense of such a complicated structure?

2. A computer tomograph of a small block of Mt Gambier limestone allows the three dimensional structure of the rock to be visualised.



3. A tiny section of the tomograph shown in 2. The structure has been rendered to show the solid rock and the void spaces.

because you can't reduce them down to a simple formula. However, our approach here at Applied Maths in visualising the three dimensional structures and then modelling them as complex networks is proving very fruitful.

"We describe and 'type' the rock using an approach that's both reductionist and holistic. By partitioning the structure into small components, we can analyse each piece in reductionist isolation, but also step back and study how all these pieces connect together to form a huge complex network."

A good example of the approach being used by Dr Sheppard is an analysis he undertook of Mt Gambier limestone. This fossiliferous carbonate rock is made up of billions of skeletons of tiny marine animals that lived in the seas covering the south east of South Australia some 30 million years ago. Today the rock is a popular stone material used in South Australian homes. Understanding its highly irregular structure has proved extremely difficult.

"With structures like these you can't break them down to some basic unit and then build a model of how it works. What we do instead is visualise it's structure and then model the network of the voids and connections through the rock. We describe and 'type' the rock by analysing its topology - that is the connectivity of its internal space.

"We've done this for a variety of rock types and it's thrown up some very interesting results. For example, two samples of sandstone we recently imaged seemed very similar in terms of grain size and structure, and probably would have been classified as being closely related. However, when we analysed their topologies we found they were quite different and consequently would have behaved very differently. This is critical information if you're making big investments on drilling into different rock types.

"However, this understanding isn't just about rocks. It can be applied to all forms of porous media such as inks in paper and urine in nappies."

Working with complex networks isn't for the faint hearted cautions Dr Sheppard.

"The size of data sets involved are enormous, and processing and manipulating these models requires tremendous computer grunt and parallel processing capacity," he explains. "One of the areas where Applied Maths is leading the way has been in the development of algorithms that can cope with the parallel processing required to work with these data sets."

According the Dr Sheppard, it's Applied Maths' strength over a range of fields that gives it the edge.

"It's not just about having good imaging technology," he says. "It's just as much about having a suite of skills in image processing, program writing, network modelling and synthesis. Applied Maths possesses a diverse team of researchers skilled in a wide variety of fields. You need a transdisciplinary approach if you're going to tackle complexity. All of the skills you need to extract a better understanding of complex structures are readily on tap in the Department. It's a great place to be if you want to push your understanding of complex materials to the next level."

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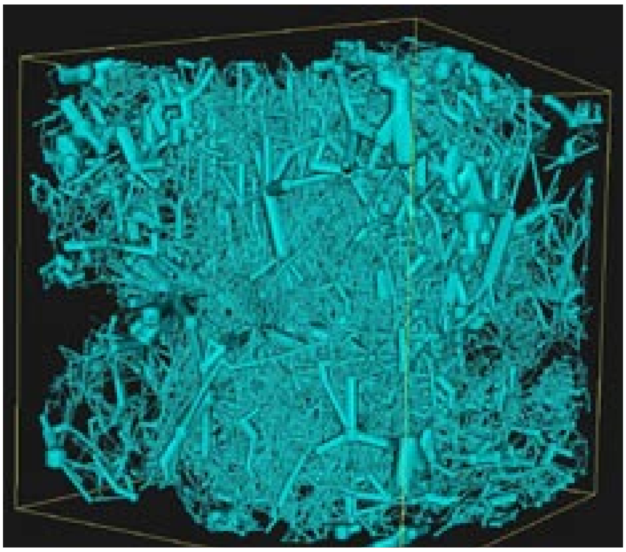
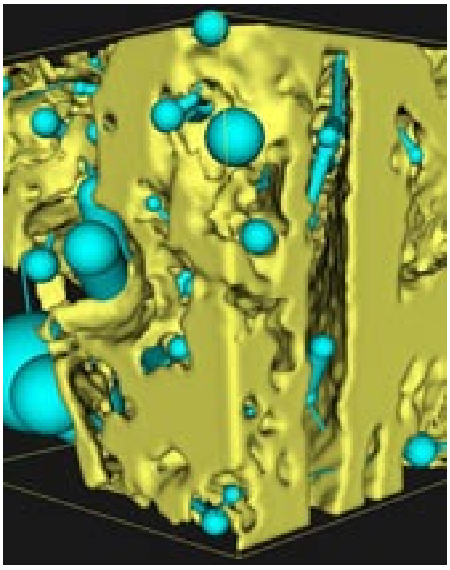
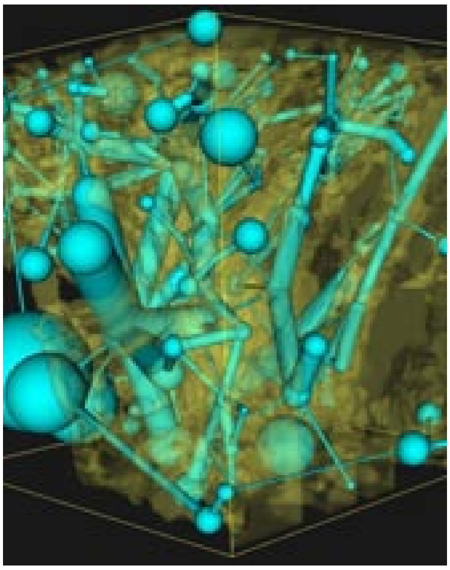


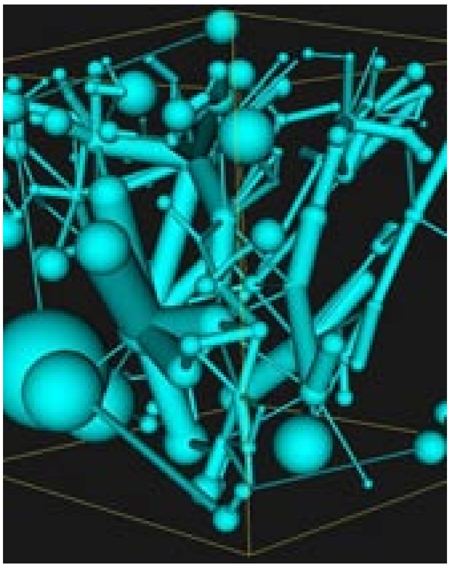
The topology of the pore space of a tiny sample (2mm cubed) of Mt Gambier limestone visualised at a larger scale to pictures below. Producing and manipulating data sets such as this requires enormous computational power and the use of sophisticated parallel algorithms.



4. The pores and connecting passages are now modelled as balls and rods with the size of the balls reflecting the size of the voids and the size of the rods reflecting the size of the interconnections between the void spaces.



5. The solid rock matrix is then removed...



6. ...leaving a representation of the network topology of the limestone.

Building near-perfect rubber

Last month it was announced in *Nature* that Australian scientists had replicated one of the insect-world's wonder materials to produce a near-perfect rubber called resilin. The research was led by CSIRO's Dr Chris Elvin and his team at CSIRO Livestock Industries, and ANU played an important role in the early development of the project.

Resilin is an elastic protein found in most insects. It's the material in the spring which gives fleas their remarkable jumping ability and helps insects fly. It has an amazing capacity to recover or 'bounce back' after stress is applied (hence its name – based on the word 'resilient': the ability to bounce back). Resilin also possesses extraordinary durability with the capacity to function throughout an insect's life without needing replacement. It enables bees to flap their wings in almost frictionless motion 500 million times in their lifetime.

The outstanding mechanical properties of resilin were discovered four decades ago during studies of the flight systems of desert locusts and dragonflies. Dr Elvin became aware of this research several years ago and wondered how it might be possible to create a synthetic resilin. No-one at that point had been able to reproduce a material that had the same rubber-like elasticity and durability of resilin.

In attempt to replicate the amazing material, Dr Elvin's team inserted a gene from the fruit fly, *Drosophila*, that was believed to code for resilin into the bacterium *E coli*, and then let this microbe express the protein in usable quantities. Professor Nick Dixon at the ANU Research School of Chemistry collaborated in this phase of the research.

Nick Dixon in his Protein Structure and Function lab at the Research School of Chemistry.

"Our Protein Structure and Function research group at RSC has substantial experience with protein expression in bacteria," says Professor Dixon. "Though the actual work was carried out in Chris's CSIRO lab, I played a consultative role and assisted with the protein purification."

And the experiment worked. For the first time, researchers had produced a purified resilin protein – but in a soluble form.

"In a way, 'pulling out the gene' was the easy bit," says Dr Elvin, who prior to working at CSIRO spent several years at ANU. "We needed it in a solid form to be able to do anything with it."

After trialing several different methods to produce a solid material from the soluble resilin the researchers found success by using a rapid photochemical method to crosslink the soluble recombinant protein so that it formed an insoluble gel.

Structural testing of this material showed that it displayed near perfect resilience (97%), far exceeding that of synthetic polybutadiene 'superball' high resilience rubber (80%) and outperforming elastin (90%). Elastin is an elastic protein in humans which accounts for the elasticity of structures such as the skin, blood vessels, heart, lungs, intestines, tendons, and ligaments.

The hope is it may one day serve in a variety of applications in industry and medicine. Its special properties would make it ideal in spinal disc implants, heart and blood valve substitutes, and as a high-efficiency rubber in industry. Who knows, perhaps it will even add some extra spring to the heels of running shoes.

Dr Chris Elvin holds up a piece of solid resilin (Photo by Frank Filippi)

Besides the collaboration with ANU, the research also involved inputs from the University of Queensland, the University of South Australia and several other CSIRO Divisions.

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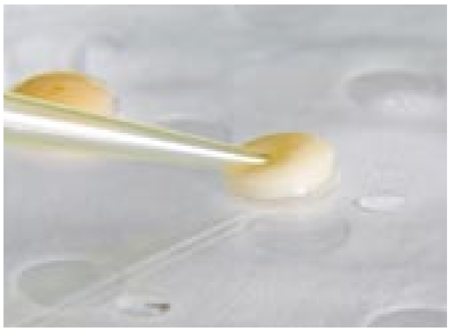

Solid resilin (Photo by Frank Filippi)

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