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If iron was the element of the 18th and 19th centuries then it could be argued that silicon is the element of the 20th and 21st. Iron is the backbone of our buildings and transportation whereas silicon lies at the heart of our electronics and solar energy infrastructure. And yet these two mighty substances are fundamentally incompatible when it comes to solar cells. Researchers are showing that even the tiniest amount of iron contamination will degrade the performance of our most commonly used solar cells. Understanding what's happening has proved problematic because the concentration is so low that most characterisation techniques can't even detect the iron. Researchers in the Department of Engineering have now developed a technique that overcomes that problem – and it's as simple as switching on the light.

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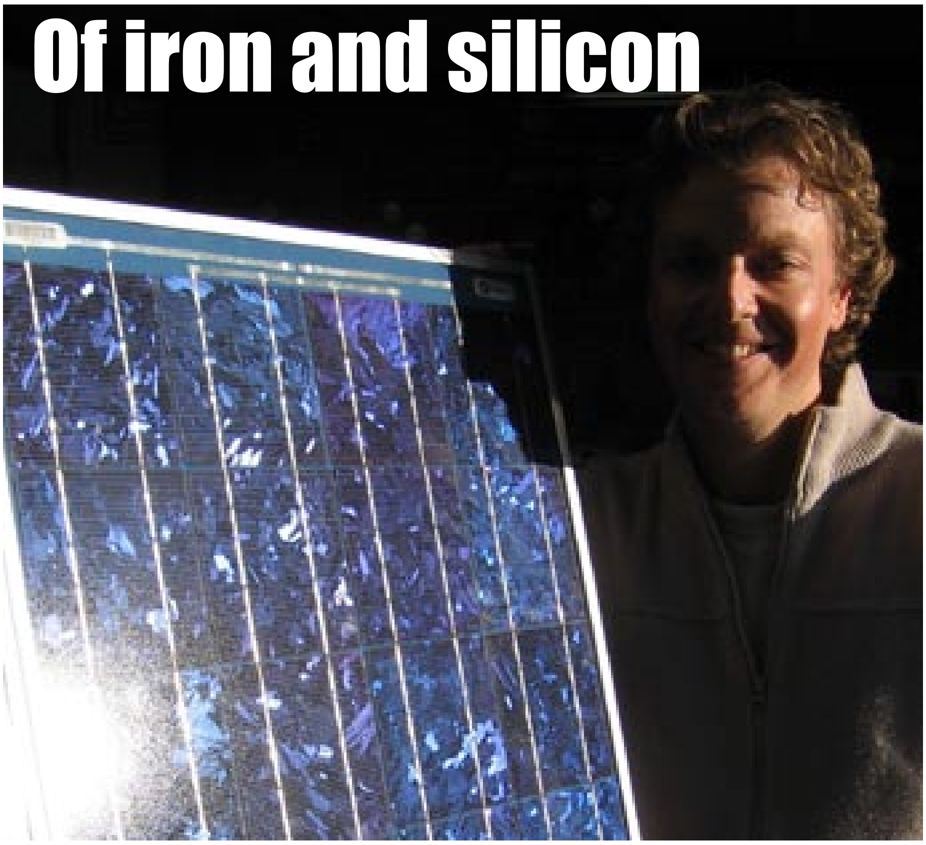
Of iron and silicon



Dr Daniel Macdonald with an array of multi-crystalline solar cells. A small number of iron atoms is all it takes to degrade the efficiency of the wafers. Measuring that iron, however, has proved extremely difficult.

How much iron does it take to degrade the efficiency of a multi-crystalline silicon solar cell? This is far from an academic question because iron, along with a range of other contaminants, inevitably creeps into the multi-crystalline silicon when it's being formed in large ingots. The iron is present in the crucibles in which the silicon is being melted. Once hardened the ingots are removed and sliced up into wafers for processing into solar cells. Multi-crystalline silicon dominates the world photovoltaic market, being the base material for about 60% of cells manufactured today, so any contaminant that degrades the operation of the final product is worthy of investigation.

So how much iron is enough to cause problems? According to the latest research, not much. Much less than 1% or 0.1% or even 0.0001%. Indeed, investigations by researchers in the Department of Engineering are suggesting that you only need one atom of iron in a mass of 100 billion (that's 10 to the power of 11) silicon atoms for the efficiency of the resulting solar cell to be significantly degraded. That's an astonishingly tiny concentration of iron – so small that most forms of materials characterisation have little chance of even detecting the iron. So, how do you investigate a contaminant if you can't even measure it?

Measuring iron

"Iron is the most important impurity in multi-crystalline silicon," says Dr Daniel Macdonald, a Postdoctoral Fellow in the Semiconductors and Solar Cells group in the Department of Engineering. "And, because of the importance of multi-crystalline silicon to the world photo voltaic market, we've done a lot of work on how to detect and measure iron contamination.

"Unfortunately, because the iron is usually present in very low concentrations it's not easy to detect using the standard techniques like Secondary Ion Mass Spectrometry or Rutherford Back Scattering. We even tried

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Inductively Coupled Plasma Mass Spectrometry using laser ablation but still had no success. These techniques, though powerful, are simply not sensitive enough. The problem is that all you see is silicon; you don't see the metal because it's too dilute.

"Indeed, there aren't many techniques that you can use. One that does work is Neutron Activation Analysis or NAA. Essentially this involves taking your sample, say a cubic centimetre of silicon, and placing it in a nuclear reactor where you blast it with a huge flux of slow neutrons. The neutrons hit the nuclei causing them to emit gamma rays. The energy of those gamma rays is different for different nuclei and the technique is very sensitive allowing you to pick what elements are present and in what amounts.

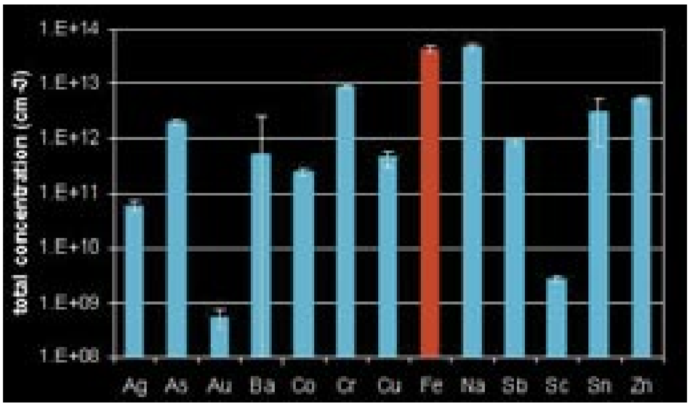
"It's a powerful technique but because it involves a specialised nuclear reactor there are only a few places in the world that can undertake this type of analysis. We rely on colleagues in Japan to undertake tests for us."

Using NAA, the Semiconductors and Solar Cells Group established that there are typically between 10^{13} to 10^{14} iron atoms per cubic centimetre of multi-crystalline silicon. That translates to around one iron atom for every 100 million silicon atoms. The analysis shows that iron isn't the only contaminant but that it was present in the greatest quantity.

Abundant and dangerous

"Iron is a dangerous impurity," says Dr Macdonald. "There are similar levels of sodium but it's basically inert, as is tin, whereas iron is abundant and dangerous. Obviously, you don't expect much gold because gold is such a rare element, and in some respects these concentrations reflect the natural abundance of these elements in the crust of the Earth. And they're present in the crucible and crucible lining in which the ingots of multi-crystalline silicon are created.

So, what makes iron so dangerous? According to Dr Macdonald the undesirable aspect of iron and other similar metal contaminants is that they introduce states in the middle of the band gap of silicon, and that reduces the capacity of the silicon to generate electricity from light.



NAA results showing levels of different impurities in multi-crystalline silicon wafers. It's common for there to be between 10^{13}-10^{14} iron atoms in every cubic centrimetre of silicon (shown in red).

In silicon the valence band is fully occupied with electrons and the conduction band is almost completely empty, and in between lies a band gap. When a photon gets absorbed in a wafer, it excites an electron, moving it up from the valence band into the conduction band where it can move around and be collected by the p-n junction, thereby contributing to the current of the solar cell.

"If you've got metals or other impurities they can introduce these localised states in the middle of the band gap," explains Dr Macdonald. "Then what happens is that before the electron gets collected it can fall back into this state and then back down into the valence band. It's kind of like a stepping stone that allows electrons to fall back to the valence band.

"Normally it's not so easy for electrons to fall back to the valence band from the conduction band. That's why silicon solar cells are quite efficient. However, if you have a lot of impurities then you introduce these stepping stones and whenever an electron goes near one it'll simply flop back down and you'll lose that electron."

And iron is an impurity that creates stepping stones right in the middle of the band gap making it much easier for electrons to cross back down into the valence band. Combine that with its relative high abundance and you have a problem, especially when there's so little of it (in absolute terms) that it's difficult to measure.

Measuring silicon

"One of the most important properties of silicon in making solar cells is the average lifetime," says Dr Macdonald." That refers to the length of time an electron spends moving around the wafer when excited by a ray of light. Impurities impact on the lifetime. Different impurities have a different effect."

Over the years, the Semiconductors and Solar Cells Group has developed considerable expertise in measuring the lifetime of electrons in silicon wafers. The group's leader, Professor Andreas Cuevas, was one of the co-developers of the QSSPC technique that is now a world standard for these measurements (see box: Measuring lifetimes).

Now, because this technique offers a very accurate way for making lifetime measurements, and considering that impurities can have a dramatic effect on the lifetime of electrons, then the question arises – can the measurement of lifetimes be used to measure the amount of impurity present, specifically iron? The answer turns out to be 'yes', but first you need to appreciate that iron exists in several forms in silicon.

Measuring lifetimes

In the world of photovoltaics, the term 'lifetime' refers to the length of time an electron spends moving around the wafer when excited by a ray of light. Accurately measuring it is important in determining the electrical properties of silicon wafers used for solar cells.

Over recent years a powerful new approach for measuring the 'lifetime' of electrons and holes has been developed. The approach is called the quasi-steady-state photo conductance (QSSPC) technique. QSSPC uses a metallic coil inductively-coupled to the silicon wafer to measure the total number of electrons moving around the wafer. At the same time, a solar cell is used to measure the intensity of the light the wafer is exposed to. This allows the rate at which electrons become excited to be determined. In a steady state the number of electrons becoming excited is equal to the number of electrons recombining with holes. Knowing the total number of excited electrons present and the rate at which electrons are becoming excited the average lifetime of electrons is able to be calculated.

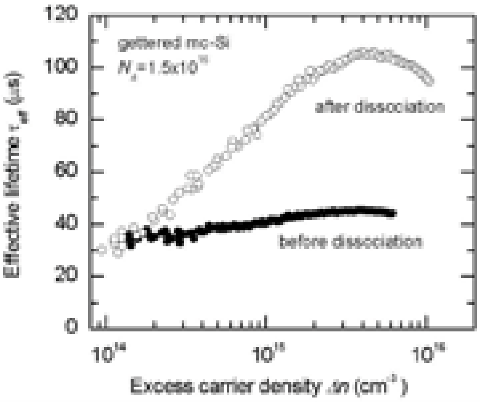
Many 'iron' s in this fire

"Iron can exist in a silicon wafer in several forms, and each form has it's own effect on the performance of the wafer as measured by average lifetime," says Dr Macdonald. "And it's these differences that enable us to use lifetime measurements to quantify how much iron is present.

"The most common form of iron is as a precipitate. This describes iron impurities in a bulk condition. It's produced when you've got so much iron in there that it literally precipitates out of molten silicon and comes together to make blobs of iron or iron silicide. You always have some iron precipitate in multi-crystalline silicon but it's not so dangerous to the carrier lifetime because the blobs tend to be very far apart. Each blob of precipitate is bad in itself but, because they are usually many microns apart, they only cause a localised effect and the overall impact on wafer performance is minimal.

"Single atoms of iron, referred to as interstitial iron in the silicon lattice, are a lot smaller in volume than blobs of iron precipitate but have a much bigger impact on carrier lifetime because it's usually spread throughout the silicon. These iron atoms sit in between the gaps in the lattice in the interstitial sites and can move around.

"Even at room temperature you'll find these iron atoms moving about. That's quite important because when the silicon has been doped with boron atoms to turn it into p-type silicon, and all multi-crystalline silicon used in commercial solar wafers are of this type, you'll find the iron atoms attracted to the boron atoms



Lifetime measurements of silicon show significant differences for iron-boron pairs (bottom curve) and intersitial iron (top curve). This difference allow the amount of intersitial iron present to be calculated.

Silicon in solar cells

Silicon was used to make some of the earliest photovoltaic devices, and it's still the most popular material for solar cells. However, to be useful as a semiconductor material in solar cells, silicon must be refined to a purity of 99.9999%. The majority of solar cells use either single-crystal or multi-crystalline silicon.

To create silicon in a single-crystal state, you first melt high-purity silicon. This melt is then allowed to solidify very slowly in contact with a single crystal 'seed'. The solidifying silicon adapts to the pattern of the single-crystal seed as it cools. This process grows a new rod of single-crystal silicon out of molten silicon.

Multi-crystalline silicon is mostly produced by casting molten silicon in a mold which is allowed to solidify into an ingot. The silicon slowly cools from the bottom to the top, and crystallises in this order. The crucible and crucible lining introduce impurities into the molten silicon including oxygen, carbon and metals such as iron, chromium and titanium.

Multi-crystalline silicon makes up about 60% of the photovoltaic market because it's cheaper, sometimes up to half the cost of the higher efficiency single crystal silicon wafers. Multi-crystalline wafers are up to 15% efficient, whereas the more expensive single crystal wafers are 16% efficient or more. Multi-crystalline silicon is less efficient because of its poorer quality. It contains many grain boundaries and crystal defects and a lot more impurities.

because they carry an opposite charge. They'll tend to combine and form iron-boron pairs.

"So iron is most commonly present in these three forms: as a precipitate, as free interstitial atoms, or paired up with boron. And each form has a different effect on the average carrier lifetime. The interstitial iron has a significant impact in reducing carrier lifetime because it's present in small quantities throughout the silicon and it introduces states or stepping stones near the middle of the band gap making it easier for electrons to drop back down.

"The iron-boron pairs introduces states that are close to the top of the band gap so they have a different effect again on the carrier lifetime.

"Iron precipitate doesn't have much effect at all because of the large distances between where it forms."

Shine a light

So how does all of this allow you to determine the level of iron in silicon? When you buy a standard multi-crystalline silicon wafer off the shelf (which will be made of boron-doped p-type silicon) it won't have any free interstitial iron in it because all the free iron atoms will have had long enough to find a boron atom and pair up, so all the iron is in iron-boron pairs.

"If we measure a standard multi-crystalline wafer that's been stored away for a while then we get a certain signature measurement of the average carrier lifetime," says Dr Macdonald.

"Now, if we then shine a bright light on the wafer the iron-boron pairs break-up, the iron moves away, and now there's a different effect on the average carrier lifetime of the silicon. Of course, there are more electrons flying around too because of the bright light. The amount of recombination through those states depends on how many excess electrons you've got and how much light is shining on the surface.

"In some regions the interstitial iron has a bigger impact on the lifetime but in other regimes it has the opposite effect. The essential point is that free interstitial iron and iron-boron pairs both have different affects on the lifetime. The really convenient thing is that we can toggle between these two states whether it's iron-boron pairs or interstitial iron by itself by simply shining light on the wafer."

"If we turn to the theory there are models for how these states in the band gaps affect lifetime, and it's easy to show that the difference in this lifetime is proportional to the iron concentration. In other words, it's possible to determine the concentration of iron by measuring the lifetime of the iron paired with the boron and then again when its disassociated because that change in lifetime is proportional to the iron concentration.

"It turns out that this approach, known as lifetime measurements, is amazingly sensitive for measuring iron, more so even than Nuclear Activation Analysis. What's more, our technique is far simpler and easier to carry out, and only requires relatively inexpensive

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The social impact of nanotechnology

In August, ANU hosted a symposium that examined the social impact of nanotechnology. In addition to bringing together a diverse range of perspectives, the symposium also showcased some innovative research techniques for exploring online environments.

Earlier this year a German cleansing product called Magic Nano was recalled after being connected with respiratory problems in users. The product, which claimed to use nanoparticles, was a spray that makes glass and ceramic surfaces dirt- and water-repellant. It's believed to be the first health-related recall associated with a nanotechnology product. But there's a twist in this tale because when authorities had a closer look at the product it was found not to contain any engineered nanoparticles.

So, on the one hand it appears the company marketing the product wanted to trade on the public's belief that 'nano' is associated with superior performance. On the other, 'nano' contributed to a wide spread anxiety when adverse health impacts were reported. Which all goes to show, while most people don't know much about 'nano' (beyond it describing something very small), it's still a potent tag that evokes a range of emotions.

The story of 'Magic Nano' was just one cautionary tale of many shared at a recent ANU symposium on 'The Social Impact of Nanotechnology' by keynote speaker Professor Bruce Bimber from the Center for Nanotechnology in Society, University of California, Santa Barbara. Professor Bimber used it as an example showing that the term 'nano' is already being manipulated, used and abused in a number of settings, and that the broader community is well advised to consider the possible impacts of nanotechnology if we are to avoid the mistakes made when genetically modified organisms were widely rejected within the European Union. Already there are several groups calling for a total prohibition of nano-products, even though at this time there are no well documented known risks associated with nanotechnology.

It's a topic the US government is taking very seriously. Accordingly, it has devoted 6% of the national nanotechnology research budget of $1.3 billion towards exploring possible impacts. The centre where Professor Bimber is based is a direct result of that funding.

Professor Bimber discussed how the nano-products and materials that are coming onto the market today are still centred on passive nanostructures such as coatings, particles and modified materials. In the coming decades we can expect new generations of nano-products that will be active and interact with the environment such as 3D transistors and diagnostic chips. Nanotechnology may even one day revolve around molecular, self replicating systems. He said that in the short term the main issues connected with nanotechnology will likely revolve around things like toxicity, regulation and public perception. However, the longer term impacts may involve bigger and more complex issues such as effects on the global economy, IP, environment and society.

The ANU symposium also included presentations from ethicists, environmental activists, lawyers, doctors, journalists and social scientists. There was even one nano scientist present in the form of Professor Chennupati Jagadish from the Research School of Physical Sciences and Engineering. Professor Jagadish gave a wide ranging talk on where nanotechnology was at and where it was going. He dazzled the audience with images and descriptions of a wide range of nano structures from nano particles through to nano wires, and discussed their properties and applications.

While the symposium was focussed on the social context in which nanotechnology was (and will be) operating, there were repeated calls from speakers for a greater engagement by nano scientists with the general community. Professor Julian Cribb from the University of Technology, Sydney, described a nightmare future scenario in which nanotechnology allowed every citizen to be monitored all the time by the government. This world, run with quantum computers and nanobots, he described as a 'nanocracy' and suggested it might be a world of total control and little personal freedom. He made a plea that nanotechnology researchers, the people who were forging these technologies, needed to take the broader public with them and accept more responsibility for the impacts that such technology might have. After all, he argued, scientists have probably the best insights on what this technology might make possible.

The ANU symposium on 'The Social Impact of Nanotechnology' was presented by VOSON – the Virtual Observatory for the Study of Online Networks. VOSON is based in the Centre for Social Research (Research School of Social Sciences) and its interest in the impacts of nanotechnology stem from its work on attempting to map and analyse online environmental activist groups.

There are a broad spectrum of environmental activist groups around the world and many of them are voicing an increasing anti-nano sentiment. For example, two groups, ETC and Friends of the Earth, are advocating a moratorium on all things nano. Many of these

The nanoethicist meets the nanoscientist. Professor John Weckert (left) from Charles Sturt University asked 'How does one tackle the ethics of nanotechnology', while Professor Chennupati Jagadish from ANU discussed what was happening in the nano lab.

groups have websites which are linked to each other and information flows through this online network along a number of paths. VOSON is conducting empirical social science research into online networks such as these and developing e-Research tools to facilitate this study.

One of the panel discussions held during the symposium where experts from various disciplines shared their perspectives on nanotechnology and its potential impacts. Pictured (from the left) are Professor Julian Cribb (science journalist, UTS), Ms Georgia Miller (environmental activist, Friends of the Earth), Dr Tom Faunce (doctor, Medical School, ANU) and Dr Mathieu O'Neil (social researcher, VOSON).

Dr Robert Ackland and Dr Mathieu O'Neil have been leading VOSON's research on environmental online networks and presented a summary of their approach at the symposium. They analysed how different environmental activist groups are engaging with and communicating views on nanotechnology. VOSON's approach for this analysis looked at both the hyperlinks and text posted on the websites of these various groups – some 162 groups in total. Using the example of nanotechnology they showed that online environmental organisations vary widely in the their adoption of new issues based upon that group's relative network prominence, length of presence in the field, and socio-cultural identity.

The United States believes that the impacts of nanotechnology on society are so important that it has devoted a significant portion of the nanotechnology research dollar towards its analysis. Australia leads the way in many fields of nanotechnology and is looking to this field of science to solve many of our current and future challenges. While it's impossible to know exactly what impact nanotechnology will have on society, maybe it's time we followed the example of the United States in investing more in research on the possible impacts of nanotechnology.

For more information on the symposium or VOSON please contact Robert Ackland <Robert.Ackland@anu.edu.au>

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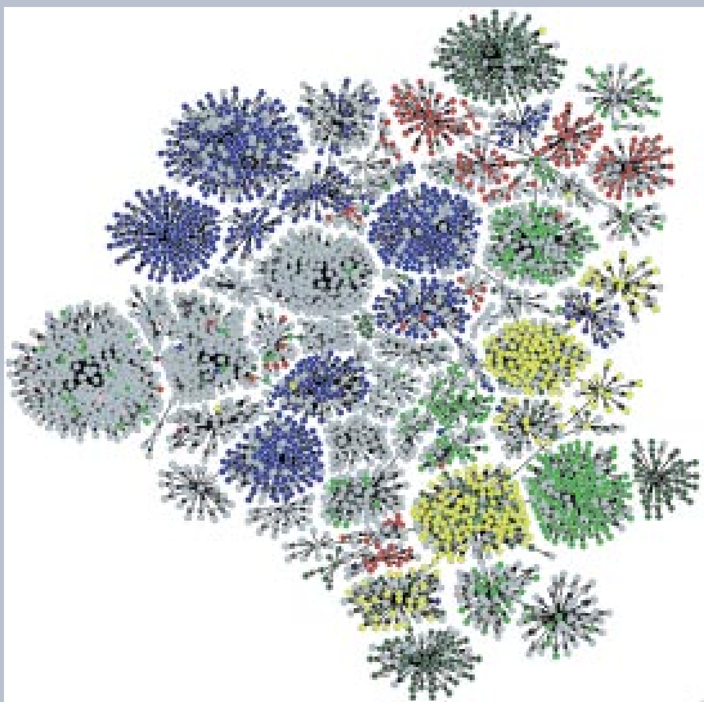
About VOSON

The World Wide Web has changed how humans interact. Some say it has ushered in the "Age of the Network". As online populations grow and the quantity and quality of interactions improve with new technology, social scientists are developing new approaches for understanding the impact of online networks on social interaction and economic and political participation. The vastness and dynamic nature of the web poses research challenges relating to data storage, management and computation.

The Virtual Observatory for the Study of Online Networks (VOSON) Project is conducting empirical social science research into online networks and developing e-Research tools to facilitate this research. VOSON uses web-based software incorporating web mining, data visualisation, and traditional empirical social science methods (eg social network analysis). VOSON research into online networks draws from the social sciences (primarily economics, political science and sociology) and other fields such as applied physics and the computer and information sciences.

More info: http://voson.anu.edu.au/index.html



The image shown here looks like a micrograph of a fungal colony but is actually a map showing the connections between the online network of an environmental activist group. It's been rendered by VOSON using a program called Large Graph Layout. The web sites that form the network are initially given random positions and modelled as electrostatic charges (repulsion forces that act to push nodes apart from one another). Hyperlinks between web sites are modelled as springs (attraction forces that act to pull together those sites that are connected to one another via hyperlinks). The algorithm shifts the position of nodes in an attempt to minimise the energy of the system leading to the identification of web clusters or communities - collections of sites that have more links to other members in the collection than to nodes outside the collection.

Research tools such as this are helping to generate insights on how information and views on nanotechnology spread through online networks. It's interesting to note that while this program is being used for mapping online networks connected with issues to do with nanotechnology, it was originally devised for mapping networks of proteins in biotechnology.

Of iron and silicon

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equipment. NAA, on the other hand, requires access to a specialised nuclear reactor.

"There is another technique available that is often used to detect interstitial iron," points out Dr Macdonald. "It's known as Deep-Level Transient Spectroscopy or DLTS. It's also very sensitive but it has the disadvantage of taking several hours to perform a single measurement, and it only measures iron very close to the surface of the wafer which can be affected by hydrogenation during sample preparation."

Iron insights

Lifetime analysis doesn't replace the NAA technique because each method measures something different. Indeed, the results they produce are quite complementary and reveal some interesting things about the nature of iron in multi-crystalline silicon.

"The average lifetime technique is only measuring the interstitial iron that is affecting carrier lifetimes," explains Dr Macdonald. "NAA is a nuclear technique that measures total iron concentration. It doesn't matter whether it's interstitial iron or a precipitate. By using both techniques it's possible, for the first time, to compare these two forms of iron.

"What we found was that over 99% of the iron in the silicon existed as a precipitate. That came as a bit of a shock. We always expected the precipitate form to dominate but not by so much. Indeed, when we first calculated this we thought our NAA results were wrong so had them done again, which confirmed our findings.

"What this shows is that interstitial iron is a much smaller part of the total iron than was previously thought and, therefore, it's also much more dangerous than precipitated iron than was previously believed.

"There are a lot other interesting things you can do with these measurements. For example, you can measure the concentration of interstitial iron from the bottom to the top of the ingot. Our measurements of wafers sliced from different parts of the ingot showed that interstitial iron is high at the bottom, low in the middle and then high again at the top.

"The reasoning on why this happens is that at the bottom the silicon is in contact with the crucible and there's the greatest opportunity for iron contamination to move into the silicon. The middle of the ingot is a long way from the crucible so it has low iron. You end up with a lot at the top because it's the part of the silicon ingot that's molten last. Iron is much more soluble in liquid silicon than in the solid form so iron gets injected into the liquid phase; it's segregated into the top layers.

Swings and roundabouts

When it comes to solar cells, iron is abundant and its dangerous, but it's not all bad news. The processing of the solar cells includes several steps that naturally tend to remove what iron is present. One step involves gettering, the other is the addition of an anti-reflective coating.

"Iron is easily gettered," comments Dr Macdonald. "It's a process that removes impurities such as iron, nickel, copper and palladium from the bulk of the wafer to a particular part of the wafer, in this case the surface. This usually involves diffusing the surface layer of the wafer with phosphorus giving a highly doped surface zone. This gives you your pn junction and is usually done at around 850 degrees. At this temperature the iron in the wafer moves around a lot. Because the iron is much more soluble in the highly doped region it tends to go there and stay there. Iron has much less impact when it's concentrated in the surface layer.

"Unfortunately, our research is revealing that the gettering can never remove all the iron. There's a lot of precipitated iron in this material and those precipitates will very slowly dissolve during the gettering process and release more iron into the wafer. That means you can never get it really clean because as soon as you're taking the interstitial iron out, the precipitate is dissolving more of it in, and it doesn't take much iron to cause problems.

Daniel Macdonald using an ion implanter at Electronic Materials Engineering (RSPSE).

"Then there's the anti-reflective silicon nitride coating used on most solar cells. It contains a lot of hydrogen, and when you print the metal fingers on top of that layer, and heat it up so the metal can dissolve through the nitride and make contact with the silicon wafer, this hydrogen diffuses into the silicon crystal. This process, known as hydrogenation, has the effect of changing the electronic properties of iron so that it is less effective as a stepping stone for recombination."

Up until recently investigations on iron and other impurities in multi-crystalline cells, and their involvement in treatments such as gettering and hydrogenation, has been hampered by our inability to accurately measure the small amount of interstitial iron present throughout the silicon. With this new technique pioneered at ANU these studies are now able to be carried out in most solar labs around the world. As far as solar cells are concerned, the iron age my soon be over.

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