Dopant mapping for the nanotechnology age

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The push for smaller microelectronics poses many challenges, such as locating dopant atoms in semiconductors with ever-increasing precision. The ideal technique must be able to detect single dopants with atomic resolution, and identify their electronic state. Neither is an easy task.

In 1965, Gordon Moore of Intel predicted that with each passing year there would be an exponential increase in transistor density on integrated circuits. "Moore's Law" has held true to this day, with the consequence that individual transistors have become smaller than a common virus — the size of critical features is now just a hundred or so atoms in length. The success or failure of a profitable manufacturing process is rapidly approaching the point at which a few atoms out of place can ruin a device. To appreciate the scale of the problem, imagine expanding the silicon wafer on which the circuits are made to the size of the United States: an individual transistor would be the size of a small car, and an individual atom the size of a pinhead. The challenge facing characterization experts today is akin to finding a misplaced pin in a car somewhere in the US before a customer experiences its inevitable and unfortunate consequences.

The key atoms that control electrical activity in semiconductors are called dopants. These are deliberately introduced impurity atoms that supply electrons or holes, which move freely through the crystal. Figure 1 shows a typical modern field-effect transistor. It works by using a gate electrode to control the flow of electrons in a channel between the source and drain (the entry and exit). The gate applies an electric field that can deplete or accumulate either electrons or holes in the channel, changing its conductivity. As the transistor shrinks, two problems concerning the placement of dopant atoms arise.

FEWER ACTIVE PLAYERS

The first problem is that not all dopant atoms are created equal. As the source and drain contacts shrink in size, the concentration of dopant atoms must increase to keep the contact resistance from rising too high. As their concentrations rise, more and more of the dopant atoms become electrically inactive, that is, they cease to contribute electrons or holes. The reason is that the dopant atoms become so closely packed together that, purely by chance, some of them get close enough to form electrically inactive pairs or clusters. To make matters worse, most commercial methods of introducing dopant atoms, for example ion-implantation, introduce unwanted defects such as vacancies and interstitials. These additional defects can also combine with the dopants to form electrically inactive clusters. Determining which clusters will form and why, goes a long way to determining whether there is a fundamental scientific limit to doping, or whether we can avoid today's limitations with sufficiently clever processing. The goal is to keep Moore's law, and the semiconductor industry[1], running smoothly.

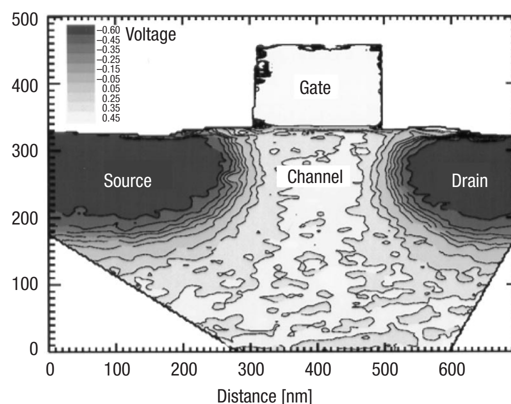

Figure 1 **The unrelenting miniaturization of microelectronics is throwing increasingly difficult challenges into the path of characterization experts. Of these, a particularly thorny issue is mapping electrically active and inert dopants in semiconductor transistors with atomic precision. Here, the electrostatic potential distribution in a 180 nm p-type MOSFET (metal oxide semiconductor field-effect transistor) is recorded by electron holography. Only electrically active impurities affect the image, which maps the 2D electrostatic potential inside the device with 5 – 10 nm spatial resolution and 0.1 eV sensitivity, although 0.5 nm and 0.05 eV sensitivity is needed to detect a single ionized impurity atom. (Image reproduced from ref. 8.)**

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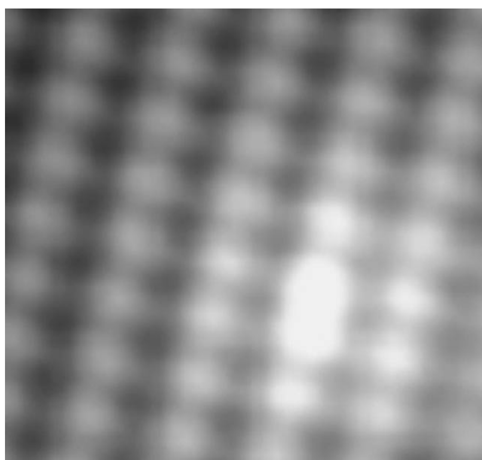

Figure 2 **Scanning tunnelling microscope (STM) image of a (110) cross section through a silicon-doped GaAs crystal. The regular atomic lattice (background pattern) is due to the empty electronic states of the Ga atoms. The protrusion in the centre is caused by a Si dopant sitting on a Ga site. (Figure adapted from ref. 18). Such 2D imaging by STM can identify electrically active dopants in the top few surface atomic layers of certain semiconductors (but unfortunately not silicon).**

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The second problem concerns reduced dopant concentrations in the channel. As the channel region shrinks, its resistance will come to depend on the presence (or absence) of only a few tens of dopant atoms. Statistical fluctuations in the number of dopants will then lead to unacceptable resistance fluctuations between different transistors. Moreover, if just a few dopant atoms from the heavily doped gate electrode diffuse through the thin, isolating layer (the gate dielectric) into the channel, it could seriously affect device performance. Finally, remote charge scattering from ionized impurities in the gate, or defects in the gate dielectric (usually SiO_2), can degrade the channel mobility. In fact, one of the biggest problems in finding a replacement for the ever-shrinking SiO_2 layer (another potential limit to Moore's law[2]) is limiting the number of charged defects in the gate dielectric material[3].

DOPANT DETECTION

Solving these problems comes close to requiring the ultimate in microanalysis: measuring the position, atomic species and electronic structure of all the atoms in the region of interest. We certainly need to know where all the dopant atoms are (position and chemical information) with atomic sensitivity and accuracy, and whether or not each atom is electrically active (electronic information). Measuring fundamental limits to dopant activation can be tackled by studying uniform layers over large areas, but the problem of statistical fluctuations requires that we characterize one device at a time. Add the fact that an atom or cluster at a free surface has a different local environment — that is, different electronic structure, number of neighbours, bonds, symmetries and the opportunity to relax or reconstruct — from an atom in the bulk, and the list of requirements becomes even more daunting. To date we cannot solve all these problems simultaneously.

So how are dopants measured at the moment? There's the direct approach, called secondary ion mass spectroscopy (SIMS), which involves sputtering the sample and mass analysing the atoms that come off. It has high sensitivity to dopant concentration, but cannot distinguish between active and inactive dopants, and the spatial resolution isn't sufficient for new technologies. Then there's the crude approach in which a needle is used to measure the local resistivity or capacitance of samples. This is a good method in that only the active component is measured, but the spatial resolution is very poor. However, that can be improved on by configuring the needle sensor as the probe in a scanning probe microscope. Another alternative is to use dopant sensitive chemical etches, and use microscopy to measure the extent of the etch pit. There are also well-established electron microscopy techniques, such as secondary electron imaging[4–6] and electron holography[7–9] (used to produce Fig. 1), both of which are sensitive to active dopants, but neither of which is sensitive enough to detect a single atom. For true atomic resolution dopant mapping the best technique until recently was the scanning tunnelling microscope (STM).

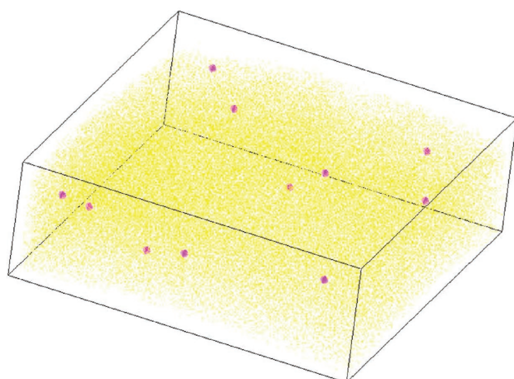

Figure 3 **Three-dimensional atom probe (3DAP) reconstruction of 11 boron dopants (large pink dots) in silicon (small yellow dots). The analysed volume is 20 nm × 20 nm × 5 nm. The 3DAP technique can detect the position and chemical species of dopant atoms within a small volume, but it cannot yet provide crucial information about their electrical activity.**

Image courtesy of Alfred Cerezo (University of Oxford) and David Larson (Seagate Technology).

THE ULTIMATE IN ANALYSIS

Almost all STM imaging of dopants in semiconductors has been done on cross-sectional (110) cleavage surfaces of zinc-blende III-V compounds[10]. This surface was chosen because it does not have any electronic states in the bandgap, so the Fermi level is not pinned by surface states. Dopant atoms have electronic states in the bandgap that pin the Fermi level, so they appear as depressions or protrusions in an STM image (Fig. 2). So what about the semiconductor industry's beloved silicon? All silicon surfaces have surface states in the bandgap, with the result that dopants can't be readily detected. That is why STM images of doped silicon surfaces never show any sign of their dopants. So although STM can provide unique information on the electronic structure of dopants, their distribution, and activity, it's no good for silicon (although some progress has been made on H-passivated surfaces), and is anyway limited to two-dimensional (2D) surface mapping. STM is a wonderful tool, and one of the drivers of nanotechnology, but some major development will be needed if it is to help solve the dopant-mapping problem in silicon.

Scanning transmission electron microscopy (STEM) is another way to detect single dopant atoms. The first atomic-resolution images of individual atoms (U and Pt on thin carbon membranes) were produced over 30 years ago[11]. An STEM works by shining an atomic-sized beam of electrons through the sample of interest. Because the electrons pass completely through the sample, STEM sees a 2D projection of the 3D sample structure. So STEM can, in principle, see dopants buried

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in a device, but it is only recently that bulk samples have been made thin enough, and with smooth enough surfaces, that individual dopant atoms became visible[12]. Previously, the signal from one dopant atom was easily swamped by surface roughness in mechanically thinned bulk samples. STEM works best with heavier atoms, but it is predicted that individual dopants, as light as boron, should be detectable at low temperatures[13].

Currently, STEM is well suited to solving the first problem mentioned above — to identify inactive clusters[12–14]. Recent advances in instrumentation may push things further. In principle, channelling of the electron beam means the signal is a function of depth, so adding some 3D information to the image[15] should be possible. Signal-to-noise ratios aren't yet good enough for this, but aberration-corrected STEM optics with huge increases in resolution, contrast and signal[16] may make this practical. Electron spectroscopy from a single column of dopant atoms is already possible[14]. In a microscope with a monochromator, core and optical spectroscopy from a single dopant atom — which would indicate its identity and its electrical activity — becomes a distinct possibility. The stumbling block remains sample preparation: the new preparation methods are reasonably quick, but they lack the positional accuracy to hit a given sub-100 nm device, making STEM less well suited to solving the second problem of locating every stray atom in a particular device.

IMAGING A SINGLE DEVICE

For solving this problem, the atom-probe technique is not as widely known as it should be. In the 3D atom probe (3DAP), successive layers of atoms are field-evaporated from the surface of a very fine needle. As the atoms evaporate they are mass analysed, and their original positions in the sample are determined from their trajectories[17]. This gives us the 3D position and the species of the atoms in a small volume, so are we getting close to the ultimate analysis? Figure 3 shows a 3D reconstruction of the location of 11 individual boron dopants in silicon. But now the issue of dopant activity reappears; the 3DAP can't distinguish which of the 11 dopants are active and which are not because it is not sensitive to the electronic state of the atoms. That would matter less if the 3DAP picked up 100% of the atoms coming off the sample (currently it detects 50 – 75%) and was more precise about their origin. It would then be possible to reconstruct all the inactive dopants involved in, for example, dopant clusters or dopant-interstitial complexes. So is a highly developed version of the 3DAP the solution to the semiconductor industry's dopant mapping needs? Possibly it is, but the pressing question remains as to whether the technique can be pushed to the required sensitivity and resolution.

Another approach to the ultimate microanalysis of dopants could exploit a property of active dopants not mentioned thus far: their ability to affect the local ionization potential (the energy difference between the top of the valence band and the vacuum level). Dopants that provide a hole (p-type) decrease the potential, and dopants that provide an electron (n-type) increase the potential. Inactive dopants have no effect at all on the ionization potential. This difference can be exploited, for example through secondary electron imaging in the scanning electron microscope[4–6] (Fig. 4), allowing dopant type and activity to be mapped rapidly in 2D. To push this technique to near-atomic resolution, the microscope would need to have a very fine electron probe of 0.1 nm cross-section, and to only build up the image using secondary electrons with a very short mean-free path. By stripping away successive layers of atoms, and re-imaging after each layer is stripped, one could build up a 3D map of the local electronic structure and hence of active dopants.

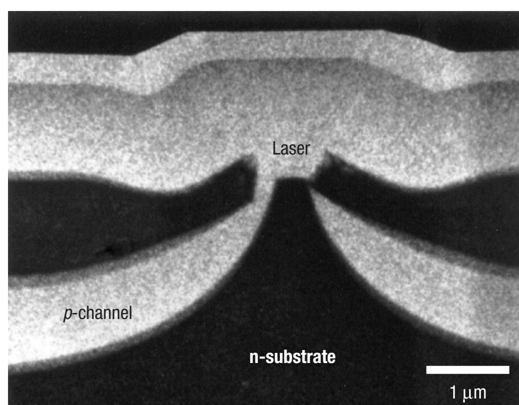

Figure 4 **Secondary electron image of a cross-section through an InGaAsP-based laser device taken by a scanning electron microscope (SEM). The secondary electron signal decreases with increasing ionization potential, so that n-type (electron donating) material appears dark, and p-type (hole donating) material light. This allows dopant type and activity to be mapped rapidly in 2D. This image shows regions of p-type dopants rising up from the n-type substrate to the laser region. (Image adapted from ref. 6.)**

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Nanotechnology seems poised to be the next industrial revolution. We can imagine whole new technologies that exploit the properties of materials at almost atomic dimensions. Some traditional industries, such as microelectronics, are also increasingly entering the nanoscience regime. Our future manufacturing efforts will be directed at creating devices fashioned at the atomic scale. At this scale, the chemical driving forces and surface energies mean that atoms rarely behave as they do in the bulk, or stay where we expect them to. Imaging these atoms is not only critical to proper device design, but it can also unravel complex and unexpected phenomena arising from the interplay of highly dissimilar materials. Developing a more complete technique for dopant mapping won't just help to keep Moore's law on track, it also opens new areas of materials exploration.

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