Nanomaterials and MEMS:
THE CHANGING FACE OF GAS SENSING

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Hardly a day goes by without the media telling us of the thrill or the dangers of nanotechnology. Likewise, Micro-Electro-Mechanical Systems (MEMS) are showing up in our daily lives with devices such as tyre pressure gauges and car airbag sensors. As these technologies develop, opportunities for improved gas sensors are being explored by companies and academics alike. So should we expect to see improved gas sensors over the next years, and if so, what can we realistically expect?

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Nanomaterials: shrinking our world

Nanotechnology has been around for many years, and our analytical tools and processing technologies have improved, so whereas before we were capable of arranging crystals, we are now capable of arranging atoms.

Nanotechnology is the study of things very small, with the generally accepted definition that items smaller than 100nm are nanomaterials, which can be inorganic, organic or biological. Our bodies are full of nanotechnology: DNA is an excellent example of a nanoprogramme for creating proteins (nanomaterials) to very specific design rules. With over $1 billion/annum research effort by the USA alone, nanotechnology (more correctly titled Nanoscale Science and Engineering (NSE)) is THE buzz word in research.

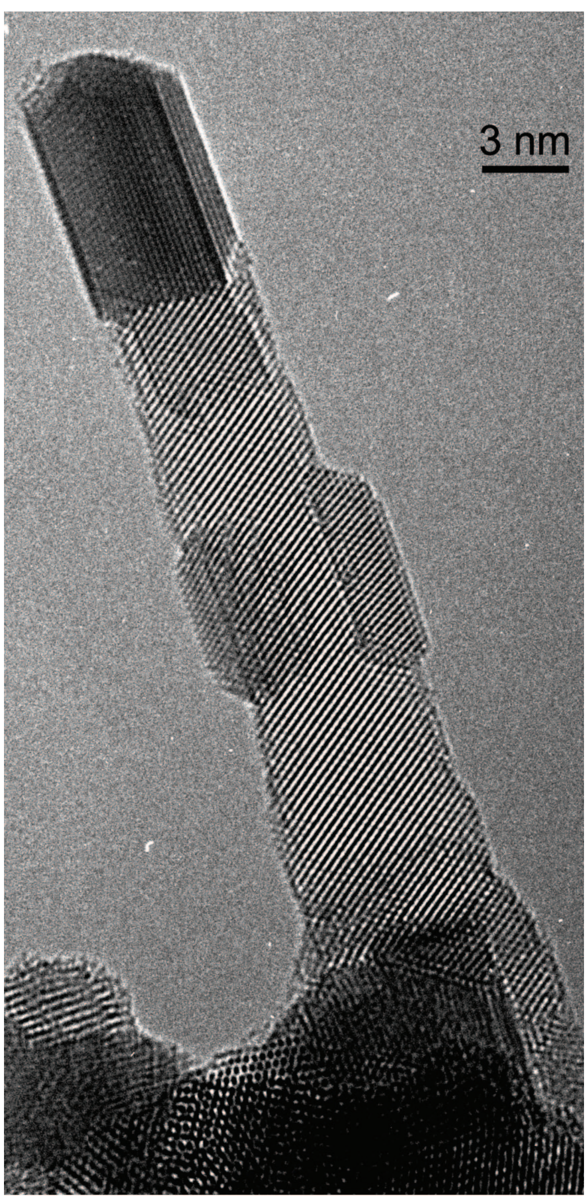

Figure 1. Precious metal catalyst forms into nanorods, only 4nm in diameter. Courtesy Alphasense Ltd.

The important feature of nanomaterials is that as particle size decreases, the percentage of bulk material decreases and the surface area increases, with the extreme being materials such as single walled carbon nanotubes (SWCNTs) which, being only one atom thick, are only a surface. As a material becomes mostly surface area, then quantum mechanics dominates, with electronic and thermal conduction, and optical and mechanical properties no longer simply predicted from the elements' position in the periodic table.

Nanotechnology can be approached from the 'top down' attitude where we just keep shrinking processes: integrated circuit track widths are now below 100nm and new, quantum mechanical problems appear at these small sizes. The alternative "bottom up" approach uses atoms deposited or synthesised into a nanomaterial; an example is carbon nanotubes (CNTs), small tubes of pure carbon, six or more atoms in diameter and thousands of atoms long. Inorganic nanodots are spheres of atoms, with diameters from ten to hundreds of atoms, normally synthesised using toxic and exotic organometallic precursors.

Nanomaterials in Gas Sensors

How can nanomaterials be used to improve gas sensors? Gas sensor nanotechnology is not new: the platinum catalyst used in carbon monoxide electrochemical sensors has a primary particle size of three to 20 nm, classifying it as an extremely small nanomaterial. Figure 1 shows a nanorod of precious metal catalyst, with each atom easily identified. A major difficulty with nanomaterials is not the manufacture of very small particles, but trying to avoid the particles coalescing into a larger particle. Figure 2 shows how nanoparticles with an average size of 5nm cluster into a larger, albeit still very small particle.

Research with other nanomaterials over the last seven years has produced results in gas detection that have yet to be commercialised. Attempts at Pennsylvania State to make nanoparticulate titanium have resulted in laboratory hydrogen sensors operating at 300C. Further work to control particle size and anodisation is needed.

Carbon Nanotubes

Carbon nanotubes (CNTs) are a focus of the popular press, but the underlying knowledge has been around for decades. Buckeyballs and fullerenes are spherical nanocarbon materials, which were identified decades ago, but rod-like carbon nanotubes are only ten years old.

CNTs can be built using plasma, physical and chemical vapour deposition. At £600/gram, these materials are only a research material at this time, but new production methods will dramatically reduce these prices to a price where they can be used as affordable sensing layers in gas sensors. The University of Cambridge and Thomas Swan have teamed to manufacture a low cost source of CNT, and market costs should eventually approach the cost of platinum of £25 per gram. Elicarb™ can be found at the Thomas Swan website.

Carbon nanotubes are generally classed as two types.

- Single walled carbon nanotubes (SWCNTs) with single layered atoms of carbon, wrapped into a tube, thousands of atoms long.
- Multiwalled carbon nanotubes (MWCNTs) where several atomic layers of carbon are wrapped into tubes, with the tubes stacked together in various formations. The three dimensional structure of MWCNTs is a research topic in itself. Figure 3 is a micrograph of a MWCNT

Carbon nanotubes are being studied as alternatives to metal oxides, where the response to gases such as nitrogen oxides, hydrogen, ammonia and oxygen is measured as a change of the electrical conductivity. The chemical sensitivity of CNT is much greater than its macro cousin, graphite, and is potentially more selective than metal oxides to specific gases.

The conduction and electrochemistry of CNTs can be modified by adding organic molecules or inorganic atoms to either inside or onto the surface of a CNT. Opportunities to improve selectivity and sensitivity by this "doping" of CNTs are being explored in laboratories worldwide. For example, Vanderbilt University has been doping CNTs with palladium to make a material that acts like a Schottky diode whose barrier height changes in response to hydrogen gas.

A curious problem of CNTs is that two rods next to each other are not the same: one will be electrically conducting and the other will be semiconducting. If we can learn how to make 100% semiconducting CNTs, then many more gas sensing opportunities will become available.

CNTs offer great opportunities for customised, repeatable gas sensors with better selectivity and repeatability, but the research has only begun, and, without a stepwise breakthrough, we may have to wait years before an improved sensor with CNT technology is commercially available.

Metal Oxides

Metal oxide (MO) sensors can be very sensitive, but their lack of selectivity has always let them down. Metal Oxide sensors (also called mixed metal oxides: MMOs) are the most popular gas sensor. The ubiquitous tin oxide sensor is manufactured in millions per year, but lacks selectivity and stability. It was previously believed that shrinking metal oxide particles to the nano scale would give greater selectivity, but apparently it only yields improved sensitivity, which allows ppb resolution for applications such as environmental monitoring and indoor air quality. Researchers in Singapore have tested ZnO, ITO, InZnO and CuO, using a combinatorial chemistry approach to see which nano MOs work best.

As we combine smaller particle size with the chemistry of other metal oxides, then the combination of our elemental knowledge of materials such as gallium, vanadium and praseodymium cerium oxides, along with reduced particle size gives new possibilities for improved gas sensor selectivity. By producing new nano-metal oxides, we should have more selective and stable gas sensors in three to five years with the advantages of greater sensitivity; much work is required to optimise this improved selectivity and repeatability.

Organic Molecules and Polymers

We can also learn a few tricks from biotechnology. Biotechnologists frequently create self-assembling structures using binding reactions such as thiols to gold layers. From this they get a 'field of wheat' type structure of organic chains that are highly ordered and hence give repeatable and well-characterised sensitivity and selectivity. By careful control of the active site,

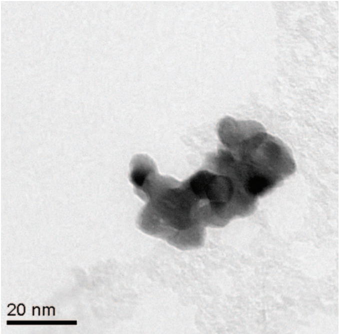

Figure 2. Nanoparticles can cluster, resulting in a larger particle than one would expect from the primary particle size. Courtesy P Midgley, University of Cambridge

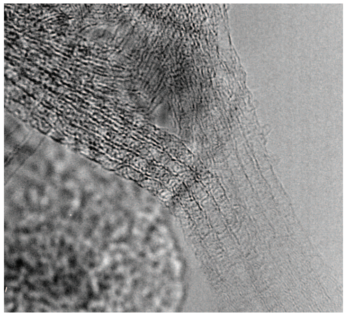

Figure 3. Electron micrograph of a multiwall carbon nanotube courtesy C. Ducati, University of Cambridge

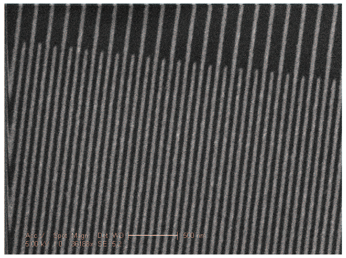

Figure 5. e-beam written electrodes used as sensing electrodes on a MEMS platform for gas sensor. Courtesy E. Hill, UMIST

classes of materials such as pyrroles and porphyrins can selectively target gases such as NOx and ammonia. But how do we measure property changes which happen when gases interact with our highly ordered nano organic structures? We can measure the change of index of refraction with surface plasmon resonance, or the change in mass using surface acoustic waves and quartz crystal microbalances. A satisfying combination of MEMS technology and nano technology. These methods can measure property changes as small as 10^{-6}, 10^{-7} .

Quantum Dots

Quantum dots (QDs) have now arrived. Being developed mainly as fluorescent markers to assist in biological and cancer identification, quantum dots are frequently made of toxic materials such as cadmium sulphide and cadmium selenide. To reduce toxicity, quantum dots are often enclosed in a larger, non-toxic particle. These materials are now being offered by companies such as Nanoco for use in gas detection. The synthetic routes are now known, the quantum dots are there, and other quantum dot materials including gallium arsenide and indium antimonide are also becoming available. These materials could be close to market for gas sensors, but it all depends on the QD performance, price and stability.

Using quantum dots as fluorescent markers has not yet been exploited for gas detection, but may offer a gas sensor with unique selectivity. Figure 4 shows how different particle sizes in Nanoco quantum dots emit light at different wavelengths.

MEMS: learning from silicon technology

MEMS devices are more prosaic, but equally important, taking advantage of our knowledge of silicon processing gained over the last decades. Instead of producing simple electronic circuits, silicon foundries are now using silicon as a starting material for producing three dimensional structures such as suspended platforms, microhotplates, resonant cantilevers and micromirrors. Besides accelerometers in airbags and pressure sensors in the latest car tyre technology, new MEMS products include infrared cameras, micromirrors for desktop projectors and self-correcting telescope optics. When we turn to gas sensors, MEMS offers new opportunities including microhotplates for metal oxide sensors, pellistors and microscopic resonant cantilevers to monitor mass changes of organic sensing layers as they absorb and adsorb various gases. Motorola developed a CO sensor based on polysilicon heated microhotplates, which are now being further developed by MicroChemical Systems in Switzerland.

With electron beams ("e-beams") we can now write directly onto silicon. Figure 5 shows electrodes only 40nm width for use as a gas sensor in the DTI funded NOAH programme.

Combining the Two

Why not combine the two technologies and use nanomaterials as a sensing layer and MEMS as the transduction method?

A Californian company, Nanomix has done just this. They use a platform where they create a field effect transistor (FET) and then grow carbon nanotubes directly onto the gate. The charge of the carbon nanotubes controls the gate voltage and the charge of the carbon nanotubes varies in response to different oxidising and reducing gases. A sensitive and potentially low cost method of making chemical sensors, this technology needs to develop the selectivity and sensitivity that the industry requires.

So the combination of silicon technology and advances in materials science is finally offering the gas sensor industry opportunities to improve sensor performance, which has been, until now, a very slow process.

Figure 4. As CdSe/ZnS quantum dot size changes, so the luminescent wavelength also changes.

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