As originally published in the Pan Pacific Symposium Proceedings.

NANOTECHNOLOGY IS NOW STARTING TO FIND APPLICATIONS IN ELECTRONICS

Alan Rae
TPF Enterprises LLC
Wilson, NY, USA
alan@tpfenterprises.us

ABSTRACT
Four years ago we outlined some of the areas where nanotechnology might be applied to electronics. We are now seeing real examples of use, particularly in new areas such as photovoltaics, but there are applications in more conventional applications such as solder and surface finishes.

INTRODUCTION
The first presentation on nanotechnology at Pan-Pac predicted that nanomaterials would be entering the electronics supply chain and being assembled into products. Today, there are indeed products in use – not as many as anticipated and not necessarily the same products as predicted. We will explore some of these products and the areas in which they are being used.

We have seen controversy about nanomaterials in the workspace, we have seen completely new materials families such as graphenes emerge and we have seen new electronics markets such as solar photovoltaics where nanomaterials play a key role in their success. Other areas have taken longer to develop than expected.

THE iNEMI 2009 ROADMAP
The iNEMI roadmap (www.inemi.org) is a comprehensive document that reviews the key issues affecting the electronics supply chain. Gaps in the technology or infrastructure that can adversely affect NEMI members are identified, and the NEMI Research Committee was formed to prioritize and disposition the tasks and identify companies, universities and government laboratories that can address them for the mutual good. The results are published in the Research Priorities {1}, downloadable from the iNEMI web site.

Almost every roadmap chapter in the 2009 roadmap identifies aspects of nanotechnology that can enhance existing products or replace their structure or function.

Nanotechnology in semiconductors beyond the normal feature size shrinkage is raising interest in electronics circles. The novel 3-D structures known as FinFETs are predicted to be used in the next generation of semiconductor devices arriving in 2011-2012 and nano-wire based structures will be starting to appear in the same time frame. These are highly complex structures made by sophisticated processes. Most nano applications that are reaching the market today are actually much more basic and many are concentrated in the area of improved materials.

Small size features – around the wavelength of light – can produce very interesting properties. Below the wavelength of light, nano structures can become invisible to the naked eye; band gaps in semiconductor materials can be modified to alter electrical and optical properties; metals can sinter and coalesce well below their melting temperatures and nanotubes and nano-wires can behave as individual transistors. Structured surfaces can be scratch-resistant, ultrahydrophobic or self-cleaning.

Nanotechnology has been described as a toolkit for the electronics industry in that it gives us tools that allow us to make nanomaterials with special properties modified by ultra-fine particle size, crystallinity, structure or surfaces. These will become commercially successful when they give a cost and performance advantage over existing products or allow us to create new products.

SEMICONDUCTORS AND PACKAGING
In 2009 we saw 45 nm node semiconductors deployed and real progress being made towards the next nodes. We haven't yet come to the "brick wall" predicting the end of Moore's Law... but it is still on the horizon.

Packaging continues to be a concern and we are starting to see a real emphasis on 3D packing to address integrated functionality, speed, form factor, and cost (yes, better-faster-smaller-cheaper still rules, especially for smart phones and netbooks). Nanomaterials use has generally been limited to evolution of filler systems used in packaging materials and underfills.

Replacement concepts for silicon semiconductor technology have focused for several years on carbon nanotubes. This technology has been slowed by the difficulties of separating metallic and semiconducting nanotubes produced together in the synthesis process which differ only in the stacking sequence of carbon atoms in the tubes. Better process control and new separation processes have allowed separation to take place but there are still cost and other issues involved.

Shepherding individual nanotubes into useful devices has also proved tricky. One approach is to create a random

As originally published in the Pan Pacific Symposium Proceedings.

mesh (rather like a non-woven fabric) that is then cut to shape; the other approach, pioneered by the NSF Center for High-Rate NanoManufacturing, {2} is to assemble them into lithographically formed features. We are still some way from widely deployed applications of nanotubes in electronics although structural applications and those based on bulk conductivity are growing.

INTERCONNECTION

We predicted a widespread use in interconnection, which has proved rather more difficult to achieve in practice. In composites and coatings the law of mixtures is always difficult (conductivity is dominated by the less conductive material especially if conductivity is directional, as with carbon nanotubes) and so concentrations required to reach acceptable conductivity may be higher than is economic.

The iNEMI nano solder project showed that nano-sized SAC alloy could sinter at 180^{O}C and below but that flux formulation was problematic. Nano-sized metals can catalyze some flux ingredient decomposition as low as 120^{O}C and flux residues could really hinder solidification. Work is continuing on solder and solder replacement.

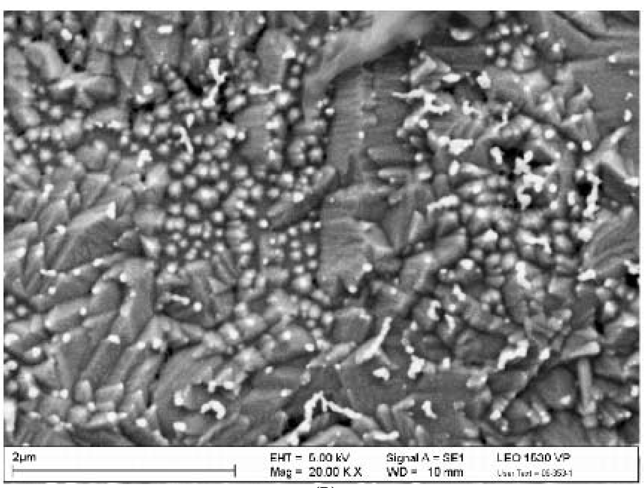

Figure 1 Enthone Nanofinish$^{(R)}$ (with permission)

Nano Surface finishes have been faster to market. Nano surface finishes have been commercialized by Enthone (Cookson Electronics Inc.) Their novel surface finish, originally developed by Ormecon in Germany, combines a conductive polymer with a nano silver to combine the best features of OSP and silver. This product is potentially a substitute for ENIG as well as other surface finishes due to its superior, aging, oxidation and solderability properties coupled to multiple reflow capability {3}

Printed electronics as a discrete industry has not developed as fast as the marketing reports suggested – except in the solar area (see below). Nano inks, particularly those based on silver, are compatible with polymer substrates but are in general waiting for the markets to develop.

CLEAN ENERGY

Clean tech represents a huge growth opportunity for electronics. For the first time ever, alternative energy sources outstripped nuclear electricity in the USA in the first half of 2009 - 0.7 quadrillion BTU January-May 2009, according to the Department of Energy's Monthly Energy Review {4}. Alternative energy depends heavily on nanomaterials used in electronics structures – in nano silver inks for current collectors for silicon cells, in printable thin film copper indium gallium selenide (CIGS) cell materials themselves as well as the conductors in the newer types of rigid and flexible cells that can lower cell costs below $1 per peak watt. They are an area of increasing focus for EMS companies, with Jabil, Flextronic and Celestica among others very active in the field.

Nanomaterials have many potential applications in fuel cells and alternative fuel catalysis but their first widespread application has been in solar photovoltaics.

In the “Front End” or cell formation process, reactive exothermic nano foils formerly produced by RNT Inc. are now supplied by Indium Corporation.{5}.This novel process uses a local exotherm to provide controlled heating and reliable mounting of sputter targets to backplates.

Printable CIGS (Copper Indium Gallium Sulpho-Selenide) cells are being produced using nano inks by NanoSolar Inc. {6}. The nano ink is coated onto a metal backplate to allow the formation of these flexible and potentially low-cost cells.

At the “Back End” of the process, metallization inks based on silver are used on the front surfaces of silicon solar cells. These metallizations together with back side aluminum and silver are co-fired at 800^{O}C causing cracking and distortion of the cells. Nano silvers processing at 200-300^{O}C are available but have yet to be widely accepted.

DISPLAYS

The use of carbon nanotubes as “self-sharpening” cold cathodes in plasma televisions has been limited by improvements in the competing LCD televisions and concerns over the energy consumption of large plasma TV sets, California has enacted ground-breaking legislation limiting the energy consumption of TV sets {7} and other states are likely to follow. Plasma TVs are typically less energy-efficient than LCD TVs which are becoming more efficient as LCDs replace fluorescent backlights.

Indium Tin Oxide (ITO) is used not only in TV sets but also monitors, phone displays and solar cells and is supply limited. Nano alternatives being given serious consideration include carbon nanotube and graphene containing films.

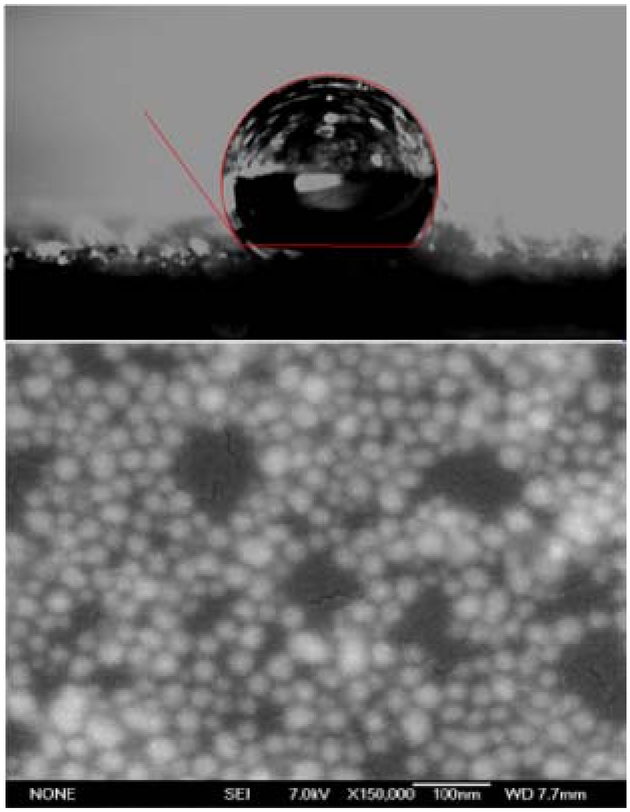

Figure 2 Hydrophobic and antibacterial coating of 80nm Ag in polyurethane (NanoDynamics)

Anti-smear nano coatings are being sold by suppliers including Aculon Inc {8}. Hydrophobic and oleophobic coatings of this kind will be increasingly used for screens and other surfaces.

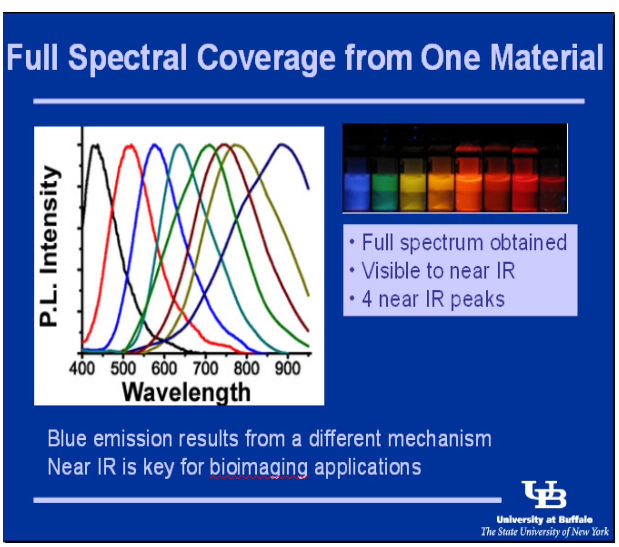

Figure 3. Spectral Coverage of Si quantum dots (University of Buffalo)

LEDs are replacing fluorescent tubes in TV and monitor screens to reduce power usage and mercury usage. Eventually they will start to replace fluorescent lighting more generally as costs start to fall. Efficiency and spectral performance can be modified using quantum dots, nano-sized particles of silicon that absorb unwanted frequencies and re-emit at desired frequencies. Silicon quantum dots will replace the first generation Cd materials.

NEMS

NEMS – Nano-Electro-Mechanical Systems are the nano equivalent of the micro systems in MEMS. Two examples below are the NEMS nose and nanotube-based memory.

Figure 4. Schematic of a NEMS single molecule detector. Plan view is in the left, side view is on the right

The "NEMS Nose" is being developed by groups such as the Roukes Group at CalTech {9}. Here a nano-sized resonator can be used to detect molecular mass by alterations in the resonant frequency of a vibrating cantilever. Arrays with different surface treatments can be used for selective detection of chemical species and here we have created a NEMS analog of a mass spectrometer. This reduces the detector size from a device the size of a refrigerator to a NEMS device that can fit in a handheld detector. This has obvious applications for emergency services and medical use – and in addition, if the coating on the cantilever contained palladium, an extremely sensitive detector for hydrogen would be created – a sensor that will become vital if the hydrogen fueled vehicle becomes a reality. Hydrogen has an extremely wide explosive range – from 4% to 75% in air, much wider than gasoline which has a range from 1% to 7%. Hydrogen leaks in enclosed spaces are bad news!

Polymer based NEMS sensors such as those produced by NEMS AB {10} promise to be very inexpensive to produce and can be made selective to specific molecules.

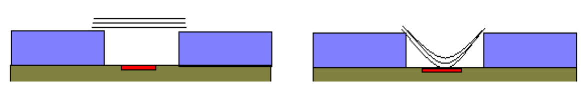

Figure 5. Schematic of the two possible states of a carbon nanotube based memory cell (NRAM).

Nantero's NRAM {11}uses bundles of carbon nanotubes in arrays that can be switched to form a n array of 0's and 1s depending on whether they have moved position under an applied field. This non-volatile memory promises to be faster and more durable than flash memory and to use a lot less power then SRAM, fast and low power but can not hold a lot of data, or DRAM, slow and high power consumption but high capacity. Interestingly, as 2GB RAM memory is getting to be about the minimum memory requirement for a PC, cooling of memory is now an issue.

Totally new devices for new applications are quite rare and difficult to predict! These are totally new concepts giving us new tools to address opportunities that we don't know how to address just now. An example from the past was the AFM (Atomic Force Microscope) which allowed us to explore surfaces in previously unknown detail using a totally new principle. “Killer apps” like this may have shortcomings – there are a limited number of AFMs needed in the world and relatively few companies producing the detector heads.

NEMS can also enhance existing MEMS applications. These enhanced MEMS devices could detect smaller changes in acceleration, pressure, flow etc. Here the cost-benefit analysis is fairly straightforward if there is a clear market need for this type of measurement. This type of product will often be developed by established MEMS manufacturers

NEW MATERIALS REACHING COMMERCIALIZATION

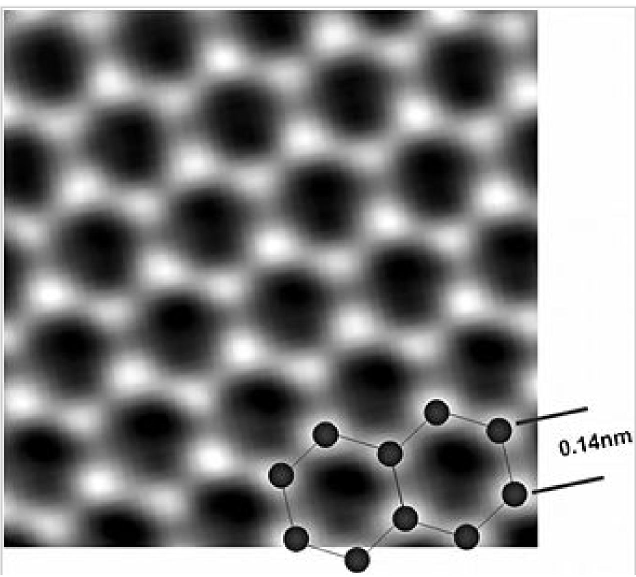

Figure 6. TEM of Graphene (Wikipedia)

One key new materials system has surfaced in the past 4 years. Graphene – composed of sheets of carbon atoms one atom thick – which seem to have many of the desirable properties of carbon nanotubes without the high cost and potential health and safety concerns. Potential applications include ITO replacement

Many nano materials have been developed because of their interesting properties and companies have been founded on products for which there is limited market demand (technology push). This tends to produce leading edge products with very limited immediate commercial potential. Work by iNEMI and others suggests the time for deployment in the electronics industry is typically 7 years for a new product that fits with the existing infrastructure and 15 years for a disruptive product. Doubters only need to look at the intensive phase of lead-free solder qualification and implementation (1999 to 2009…and still not complete for complex boards) or the implementation of MEMS devices in accelerometer applications – 30 years! The electronics industry is fast moving in term of ultimate product development but very conservative when it comes to accepting new materials, devices and systems.

MANAGING HSE ISSUES

There continues to be a lively discussion internationally about whether nanomaterials should be regulated separately from traditional materials There are many opinions and the challenge is the diversity of types and diversity of applications – how do you equate nanosized silver, carbon nanotubes and liposomes, or nanomaterials in cosmetics, wind turbine blades, injected for medical image enhancement and automotive clear coat? Some nanomaterials behave differently at below 100nm – for example silver which can be sintered as low as 120^0C, well below its 961^0C melting point – and others such as sodium chloride (which you inhale every time you go to the beach) do not appear to behave differently.

At the moment products are registered under EPA's TSCA and, if appropriate, FIFRA programs. Only two materials have been singled out for special attention, carbon nanotubes because of their unique structure and properties, and silver because of the large number of antibacterial products being launched – not all of them properly registered – including computer keyboards and mice.

ISO TC 229 “Nanotechnologies” is at the forefront of the harmonization task. As with any new technology there is a “land grab” by national and international standards and other organizations; ISO is looking to harmonize nomenclature, metrology, health and safety guidelines and communication (data sheets, MSDS, labeling etc) to bring some order to the process.

It is highly likely that all nanomaterials presented to the electronics board fab and assembly industries will be in some way encapsulated as inks, as pastes, in resins or as coatings compatible with existing processes and probably will not be subject to specific regulations.

CONCLUSIONS

Nanomaterials are starting to be more widely used in electronics but it takes a significant time for these applications to take hold and for significant business to result. Most applications will be evolutionary rather than revolutionary but will still yield significant performance and economic benefits.

ACKNOWLEDGEMENTS

Past colleagues at NanoDynamics Inc; current colleagues and associates at Graphene Devices Ltd, University of Buffalo, Purdue University, Global Solar Technology, Cookson Electronics, iNEMI, ISO and the Inventures Group.

REFERENCES

[1] “Research Priorities”, iNEMI Inc., http://thor.inemi.org /webdownload/RI/2009_Research_Priorities.pdf
[2] Center for High-Rate NanoManufacturing http://www.northeastern.edu/chn/
[3] Enthone Ormestar Ultra (tm) http://www.enthone.com/ pwb/index.aspx
[4] US Department of Energy Monthly Report http://www.eia.doe.gov/mer/
[5] “Indium Corporation Acquires Assets of Reactive Technologies” http://www.indium.com/news/ nanotechnologies/
[6] NanoSolar Inc. http://www.nanosolar.com/technology
[7} CA TV restrictions http://www.wired.com/gadgetlab/ 2009/03/california-tv/
[8}Aculon Inc. display coatings http://www.aculon.com/ displays.html
[9] Roukes Group CalTech http://nano.caltech.edu/
[10] NEMS AB http://www.nems.se/
[11] Nantero NRAM http://www.nantero.com/mission.html