Abstract

Nanotechnology is a key enabling technology for printed electronics. Low temperature reactivity, reaction speeds, flexibility and fine pitch considerations dictate that nanomaterials should be given serious consideration in many of the process steps in printed electronics.

Introduction

The National Nanotechnology Initiative – www.nano.gov – has supported a significant scientific and technical effort in the USA that is now being translated into manufacturing. According to Government statistics, over $18B has been invested in novel materials and systems. These production and processing technologies are applicable to both nano-sized and near-nano materials. Some are new techniques; some are modifications or new applications of older techniques, often applied in different ways or at a different scale than traditional methods.

There is a great deal of printing already in use in electronics, ranging from photolithography to screen printing. The target of roll-to-roll printing has been hampered by materials issues and competition from other forms of circuit formation that are mature, low cost and have been incrementally improved. Companies with great technology in roll to roll processing such as Polaroid and Kodak have created the technology base for companies to develop printed electronics for a range of applications.

If we look at the traditional route to circuit board manufacture, glass cloth impregnated by resin is sandwiched between layers of thin copper foil, itself formed by continuously plating copper on a cylindrical electrode. The copper is patterned using photolithography and etched to produce conductive paths and then the laminates are joined together with intermediate glass-epoxy layers, aligned and densified in laminating presses.

Layer to layer interconnections are drilled using mechanical drills or lasers and plated to form inter-layer connections. The filling may be completed using further plating or screened conductive paste and subsequent layers may be built up by sequential deposition of epoxy and copper patterns using photolithography.

Protective surface finishes such as OSP (Organic Solderability Preservative) solder or silver are applied by liquid coating, hot metal dipping, electroless plating or plasma techniques and the board is ready to receive its solder mask (patterned by photolithography) and solder paste (patterned by stencil printing).

Integral resistors or inductors may be printed or plated and embedded capacitors are normally developed by etch revealing dielectric layers sandwiched between copper foil.

Roll To Roll Printing And Nanotechnology Implementation Challenges

In contrast to conventional planar printing used widely in electronics processes, roll to roll printing of electronics will allow us to use

- High speed and low-cost processes;
- Low-cost low-temperature flexible substrates
- Additive processes which reduce the environmental burden (and therefore cost) of conventional additive / subtractive processes.
Challenges to the use of nanomaterials in printing processes include

- The efficiency and installed base of traditional deposition techniques – vapor deposition and plating are highly cost-effective on a range of substrates.
- Thermal resistance of cost-effective substrates – in order to be economic, low cost substrate materials mass-produced for other applications, such as polyesters, must be used. The materials available to form circuits on these low temperature substrates (organic semiconductors or conductive adhesives) just have not had enough electron mobility or conductivity.
- Many application markets are flat – such as current displays – and roll to roll processing is not an obvious candidate for production. In flat markets in particular, sputtering and other vapor deposition techniques are cost-effective and have been used widely in the production of RFID antennae, displays and solar cells.

A major challenge to nanotechnology implementation has been environmental concern. Particularly in Europe, nano hype has been followed by nano pushback from potential customers, environmental groups and other NGOs.

- The potential use of nanomaterials inks in clean room environments makes production engineers anxious to avoid cross-contamination. Great care must be taken to prevent the dispersion of aerosols during processing or of dried materials post processing but with proper controls there is no issue.
- As with any new material, there is no epidemiological information and toxicological information is sparse. Much of the early work on toxicology of nanomaterials was allegedly carried out on impure materials such as carbon nanotubes containing up to 30% Ni or other catalyst residue as well as amorphous carbon, or buckyballs that had been dispersed in a toxic organic solvent. It is almost impossible to separate the effects of the impurities and the actual material and there appear to be a great number of contradictory and confusing publications in the literature.
- Silver, a critical conductor material, has been also given enhanced attention due to its widespread use in antimicrobials (it is the leading antimicrobial agent in burn dressings) despite nano silver’s widespread use for centuries as colloidal silver and also in photographic films. Silver appears to be relatively toxic to aquatic life when present as an ionic species.
- At present there is no “smoking gun” that shows that nanomaterials per se are more toxic than conventionally sized materials or salts but they have shown a capability to cross biological barriers in the same way as ionic materials do and caution is appropriate if there is a potential for exposure. Recent studies contradicting earlier findings have shown that nanomaterials find it difficult to penetrate skin unless they are engineered to do so. (1)
- NIOSH and others have carried out studies and it appears that normal plant engineering controls such as respirators are effective in the production environment; in normal use electronic products are designed not to “shed” nanoparticles in coatings and composites; and at disposal most materials would be destroyed by incineration or be encapsulated and relatively inert in landfill. Recovery of valuable metals would take place by dissolution or incineration. Careful monitoring and dust collection will be required during shredding or grinding of circuits where dusts might be generated and these are being studied at a number of centers.
- At present there are no specific requirements for manufacturers to disclose that their products contain nanomaterials except in France. In the USA the EPA is keeping a special watch on nano silver (for antimicrobial use only) and on carbon nanotubes (for all applications which nanotube manufacturers need to specify in advance). Other restrictions have been discussed but not implemented but a few local governments (such as in Cambridge MA) have taken things into their own hands and require disclosure that companies process nanomaterials.
- A major step forward for the industry was the clarification issued by the European Community in their statement in October 2012

“In the light of current knowledge and opinions of the EU Scientific and Advisory Committees and independent risk assessors, nanomaterials are similar to normal chemicals/substances in that some may be toxic and some may not. Possible risks are related to specific nanomaterials and specific uses. Therefore, nanomaterials require a risk assessment, which should be performed on a case-by-case basis, using pertinent information. Current risk assessment methods are applicable, even if work on particular aspects of risk assessment is still required.
Important challenges relate primarily to establishing validated methods and instrumentation for detection, characterization, analysis, completing information on hazards of nanomaterials and developing methods to assess exposure to nanomaterials.

The recent definition of nanomaterials will be integrated in EU legislation, where appropriate. The Commission is currently working on detection, measurement and monitoring methods for nanomaterials and their validation to ensure the proper implementation of the definition…

…Overall the Commission remains convinced that REACH sets the best possible framework for the risk management of nanomaterials when they occur as substances or mixtures but more specific requirements for nanomaterials within the framework have proven necessary. The Commission envisages modifications in some of the REACH Annexes and encourages ECHA to further develop guidance for registrations after 2013.” (2)

**Nanomaterials Relevant To Printed Electronics**

A wide range of materials are potentially useful, including

- Phosphors – quantum dots, rare earth phosphors based on yttrium aluminum garnet for lighting and taggant applications.
- Solar cells – CIGS, CdTe, carbon nanotubes, graphene, silver, copper, silicon, quantum dots, silicon.
- Semiconductors – an arsenal of semiconductors, dielectrics and conductors produced by a range of vapor deposition and plating techniques. Packaging – silica, carbon black, taggants (similar to phosphors), nano clay.
- Passive components – dielectrics based on barium titanate, strontium titanate, neodymium titanate or similar materials, plus copper, silver, nickel used for internal and external interconnects.
- Interconnects – copper, solder, silver.
- Functional Coatings – hydrophobic, oleophobic, scratch resistant, solderable – alumina, silica organo-fluorine, nitrides, silica, silver, diamond-like composites by plating, chemical vapor deposition, physical vapor deposition, atomic layer deposition and many other techniques.

**The iNEMI Large Area / Flexible Electronics Roadmap**

This section of the 2011 iNEMI roadmap (www.inemi.org) was written by over 50 participants in the global supply chain (participant companies and universities worldwide include Printovate, A*STAR, Binghamton University, Western Michigan University, Rotadyn, Henkel, DuPont, Kodak, Polyera, Corning, H.C. Starck, Speedline, Cornell University, Endicott Interconnect, NIST, Kyocera and the Ukrainian Academy of Sciences) and runs to 151 pages with over 250 references. It analyzes the technology and supply chain for printed electronics worldwide. Display and other applications are increasing in volume and government funded work under the EU 7th Framework, Singapore, Japan, Korea, China and the USA is increasing as higher performance materials become available. The availability of functional inks and processes as well as characterization techniques are seen as key enablers for this market and there is much work to be done in this emerging business sector!

Table 1 shows the classes of electrically functional Inks and their critical attributes. Inks are required for both passive and active devices.
Table 1. Classes of Functional Inks and Critical Attributes (iNEMI Roadmap, 2011)

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<th>Functional Inks</th>
<th>Attributes</th>
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| Conductor       | • Metal, organic based  
                  • Sub-micron particulates  
                  • Bulk conductivity >10^4 S/m  
                  • Low processing temperature (<200 °C) |
| Dielectric      | • Polymeric or Nano particulate based  
                  • Electrical resistivity >10^{14} Ω-cm  
                  • Film thickness <5 μm  
                  • Permittivity (2-20), low loss  
                  • Semiconductor compatible band gap  
                  • Low processing temperature (<200 °C) |
| Semiconductor   | • Organic, inorganic, hybrid  
                  • Electron mobility 10^{-2}-10^{-2} cm^2/V s  
                  • Low processing temperature (<200 °C) |
| Resistive       | • Organic, metal, or inorganic  
                  • Resistance (10-100K Ω/□)  
                  • ±10% Nominal resistance tolerance |
| Light emitting  | • |
| Photovoltaic    | • |

Each practical printing technology – gravure, flexography, offset lithography, screen, drop on demand inkjet and aerosol jet has specific viscosity and other process demands. Low viscosity inks have real difficulty suspending dense materials like silver (specific gravity 10.5). Conducting and semiconducting polymers usually have a limited range of effective solvents available with restricted drying characteristics. A key sentence in the roadmap says that the “rate of commercialization of materials …is occurring too slowly to meet the cost/performance/utility demands to enable near-term product launches. Ink jet inks usually have a low solids content so drying times may be protracted. Many ink process aids can interfere with electrical properties also.

Conductive and capacitive inks based on nanomaterials already show significantly higher performance than organic conductors such as PAN (polyacrylonitrile) or PEDOT (polyethylenedioxythiophene). Resistive inks are often based on nano or near nano carbon. Active inks are improving rapidly with the best electron mobilities based on pentacene systems with inorganic nanomaterials based inks catching up rapidly.

Efficient Processing Of Nanomaterials In Printed Electronics
Three examples of this are the processing of copper nanomaterials by Novacentrix (www.novacentrix.com to directly form additive circuits, the high speed-speed printing of silver inks at Clemson University’s Sonoco Institute of Packaging Design and Graphics presented at FlexTech 2012, and electrophoretic / transfer printing of nanomaterials at the NSF Center for High-Rate NanoManufacturing.

Novacentrix Conductive Copper Processing
Photo-initiated sintering of copper particles produces impressive densification in 5 milliseconds resulting in high quality conductors on substrates including PET and paper.
Sintering: Fusing the Ink Particles

Metalon® JS-B25P Inkjet on Coated PET

As-Printed / Air Dry

After PulseForge Tool Processing

Air Cured: 2 hours

PulseForge tool: ~5 milliseconds

Sheet Resistance

150 milliOhms/sq

60 milliOhms/sq

Figure 1. Sintered copper conductors on PET (courtesy Stan Farnsworth, Novacentrix)

This process does at last allow us to reach the long awaited goal of sub-5 cent RFID tags.

Flexographic Printing At Clemson University
An extensive designed experiment carried out by Dr. Bruce Kahn and the team at Clemson on the Omet Varyflex printing equipment, presented in detail ate FlexTech 2012 (www.flextech.org) has revealed some surprising and favorable results. The printer is modular with 7 stations (flexure, gravure, rotary screen), can accommodate water, solvent and UV inks and can handle substrates 12-600 microns thick, up to 50cm wide and speeds up to 200m/min. This is important as several inks will be needed to accommodate different inks incorporating different nanomaterials – ceramic, metal, polymer, carbons etc. and different print stations will be needed to accommodate these.

Figure 2. Omet Varyflex 530 Press (Courtesy Bruce Kahn, Clemson University)
Results of the extensive designed experiment are impressive:

- High speed (200 m/min) and throughput (100 m²/min)
- Inline complete curing (5 second residence time) at low temperature (120°C)
- High conductivity (resistivity ~ 3X bulk Ag metal)
- Small feature sizes (<50 μm wide, ≥ 80 nm thick)
- Increased performance (higher conductivity, larger aspect ratio, decreased sensitivity to anilox cell volume) with speed
- Practical application (transparent conductive grids)

Electrophoretic Templating of Nanotube and Other Materials at the Center for High-Rate Nanomanufacturing.

Novel ways to develop circuits for sensor and other applications have been developed at the NSF Center for High-Rate Nanomanufacturing in Boston. Transfer printing and other techniques have been modified to produce circuit elements in a practical and reproducible way.

Figure 3. Template development and results of printing carbon nanotubes (Courtesy Ahmed Busnaina, Center for High Rate NanoManufacturing).
Techniques For Manufacturing Printable Nanomaterials
While this is not an exhaustive list of resources or techniques it gives an idea of the types of equipment and processes used to produce nanomaterials outside semiconductor wafer fabs. These processes are all operated at the Nanomaterials Innovation Center in Alfred NY.

Precipitation
Ultrasonic processing systems are designed for dispersing, homogenizing, de-agglomeration, particle size reduction, sonochemistry, emulsification, or emulsification of liquids in flow or batch operation. It has been used to successfully produce both nano-sized pure metals and alloys such as SAC.
**Vapor Phase Synthesis**

Plasma synthesis is one of the leading ways to produce powders from solution or other types of liquid feed – for example it is has been used to produce millions of tons of titanium dioxide pigment by reacting titanium tetrachloride in an oxygen flame. This microwave plasma torch can operate using a variety of gases or mixture of gases and is capable of pyrolyzing chemically prepared stoichiometric solutions to temperatures as high as 5000°K. Controlled atmospheres and temperatures in the processing chamber yield dispersed nanoparticles ranging from 2 nm to 80 nm. This system is currently capable of producing up to 4 Kg of material per hour. The unit can handle basic or acidic solutions; sodium hydroxide, ammonium hydroxide or nitric acid. Materials as diverse as metal powders, ceramics and graphene can be produced by plasma.

The carbon nanotube system is a laboratory sized catalyzed Chemical Vapor Deposition (CVD) system capable of enabling synthesis of single-walled and multi-walled carbon nanotubes. Carbon feedstock is provided from the decomposition of gases such as Methane or Ethylene while processing temperatures of 800°C - 1000°C for SWNT and 550°C - 750°C for MWNT encourage the growth of nanotubes on catalyst sites on the selected substrate. Although CNT’s have slipped from being the...
hot item in the scientific community, many companies are developing applications in electronics areas such as non-volatile memories. Nantero (www.nantero.com) is a pioneer in this field.

![Image of carbon nanotube synthesis](NMIC)

**Figure 7. Carbon nanotube synthesis. (NMIC)**

_Drying_

Where drying is unavoidable (normally it is preferable to supply wet material and to disperse nanomaterials from a solution or slurry form into the polymer, ink or other vehicle desired by the client) processes include conventional tray drying ovens plus an atmosphere-controlled spray drier and a freeze dryer.

The spray dryer shown is an explosion proof (solvent-capable) system. Used primarily as a process tool for investigating new mixtures of binders, plasticizers, and chemistries, it is used with nanomaterials to create large (mm sized) flowable particles containing readily removable binders. The spray dried powder flows easily and can be formed into shape by normal ceramic or powder metallurgy tooling.

![Image of spray dryer](NMIC)

**Figure 8. Spray dryer. (NMIC)**

Freeze dried materials are formed by evaporating ice from slurries or frozen blocks under vacuum. This is especially useful for reactive mixtures or to shape materials into a mold with a polymer binder that will be removed in subsequent heat treatment.
Thermal treatment
Conventional and microwave processing can be used to process powders, shapes and have even been used for thermal; treatment of electronic assemblies. Microwave processing in air, vacuum or inert gases can provide rapid heating and cooling of materials, avoiding long thermal soaks which can cause crystal growth and property degradation. Selective heating can be obtained, as can very high temperatures >1600°C.

Figure 9. Freeze dryer. (NMIC)

Figure 10. Active and passive microwave ovens. (NMIC)
The continuous microwave pusher kiln shown below yields 12 KW of continuous output power in a 1-meter long hot zone. It is capable of operation in air, nitrogen, inert gas, or mixed gases to a maximum temperature of 1425°C. The kiln has already demonstrated its abilities to process electronic materials in a fraction of the time required for conventional processes.

Summary
Several nanomaterial types are critical to the implementation of scalable printed electronics. Practical materials and solutions are starting to evolve and these will be the key enablers for printed electronics commercialization. Once designers know the capabilities and cost benefits, then applications and the markets for printed devices can develop rapidly.

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References