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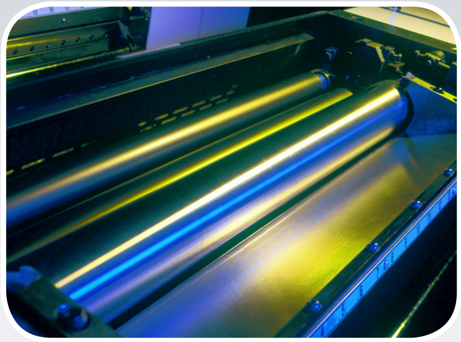
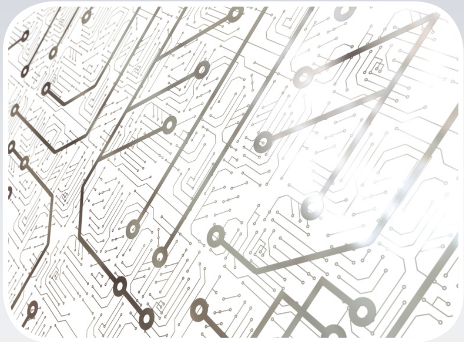
Conductive Inks



As the worlds of print and electronics merge and overlap, suppliers are exploring a wealth of possibilities with the development of high-value conductive inks. This e-book sets out the latest technology breakthroughs and innovations, and forecasts trends to 2015.

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Introduction

For decades, membrane switches and circuit boards have been printed with conductive inks using screen printing. The thick film was required to ensure sufficient conductivity. With a constant push for devices that are smaller, lighter, faster and cheaper, the industry is looking for innovative materials and processes.

Nanoparticle Silver Inks

The conductive inks industry responded to the new requirements with the development of nanoparticle silver inks, which offer several advantages over the older formulations. The small size of the particles increases the exposed surface area of the silver. This accomplished several things: less silver materials needed to be used to achieve the same conductivity, thus a thinner film could be printed and the inks could be sintered at a lower temperature, which enabled the use of flexible substrates. Many of the companies who had supplied conductive inks to the industry expanded their portfolio with nanoparticle formulations.

Table E.1 Suppliers of metallic conductive inks

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Nanoparticle Copper Inks

Although nanoparticle silver inks enabled the new printed electronics, the escalating price of silver has caused some concern. The logical choice for an alternative was copper, which has 90% of the conductivity of silver, but is approximately 10% of the cost. Formulating copper inks has been a challenge because of the tendency of the metal to form oxides on the surface and the necessity of a special environment to manufacture copper inks. However, nanoparticles solved the latter problem and companies found innovative technology to solve the former. In the past few years, five companies—Applied NanoTechology, Cima NanoTechnology, Hitachi Chemical, Intrinsiq Materials, and NovaCentrix—have introduced copper inks to the marketplace. There are likely to be more.

Conductive Polymers

An alternative based on organic materials, i.e., conductive polymers has also emerged in the industry. While there are still issues with the conductivity of such inks, there are areas where the high resistivity of conductive polymers serves them well, for example in lighting and OLED displays. They are also being used to improve efficiency in printed organic photovoltaics.

Table E.2 Suppliers of conductive polymers

CLICK TO VIEW TABLE

Carbon-based Inks

As the printed electronics industry moves forward, there is a complementary need for semi-conducting inks. One of the most significant breakthroughs in the conductive/semi-conductive ink is the introduction of carbon-nanotube-based inks. These inks offer better conductivity than conductive polymers, as well as unique thermal and electrical properties. Coupled with their small size, these properties will enable them to become serious contenders in many printed electronics applications including biological sensors, transistors, field emitters and integrated circuits with demand for mass production, high speed and efficiency. The immediate application for these inks is in a printed conductive film as a

With a constant push for devices that are smaller, lighter, faster and cheaper, the industry is looking for innovative materials and processes.

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replacement for ITO, which is expensive, brittle and tends to crack. CNT-based films offer an improved alternative, particularly as the electronics industry moves towards flexible substrates for many devices. This area is likely to grow significantly.

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Table E.3 Carbon-based ink suppliers

Silicon Inks

Another category of innovative inks that have come to the forefront recently are those based on silicon. These inks combine the proven performance advantages of silicon with the lower-cost additive manufacturing processes, such as printing or aerosol deposition. Furthermore, use of such inks would enable printing on flexible substrates, something precluded today with the harsh environments needed for electronics manufacturing using silicon. Several companies have introduced silicon inks in the past several years, and it is an area where there is likely to growth.

CLICK TO VIEW TABLE

Table E.4 Suppliers of silicon-based ink products

Printing Processes

There is still much discussion in the industry as to what printing process is best suited for printed electronics. While inkjet has been widely used for research and development and prototypes, to achieve high speeds, flexo and gravure would be better choices. Conductive inks and the new semi-conductive inks are offered for all of the printing processes. One of the most important considerations in deciding which process to use is the process capability to print the particular product/device, including ink thickness, lateral resolution, registration and surface uniformity. As with graphic arts, it seems that the end-use application will most often dictate the process which is most suitable.

Table E.5 Comparison of printing processes for printed electronics

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Applications and Outlook

As indicated in the tables listing the manufacturers of conductive and semi-conductive inks, these inks can be used in many diverse printed electronics applications. In addition to the traditional membrane switches and printed circuit boards, radio frequency antennas are frequently printed today. The new printed electronics market is estimated at $1.6 billion today and is expected to grow to approximately $50 billion by 2015. Printed batteries, sensors, displays and lighting and novelty items are all experiencing expanded use of printed electronics. Photovoltaics is an exploding area fueled by the demand for affordable renewable energy sources. This is an area that is being targeted by silicon-based ink and conductive polymer manufacturers alike. Touch screens —and further down the road, flat panel displays—are another enormous potential target area; in this case the material would be conductive films printed with CNT-based inks or metallic inks used as a replacement for ITO. OLEDs and lighting are areas where conductive polymer inks offer advantages. Sensors, particularly in medical applications also offer tremendous potential.

There is almost no limit to the potential for printed electronics for the future, especially now that there are innovative conductive

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and semi-conductive inks available. The emerging technologies will need time to improve and move to scale production, but there is enormous work being done to achieve that goal.

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Introduction and Methodology

Report Scope

This report is intended to examine trends in conductive inks. By definition, a conductive ink is an ink that conducts electricity. Such conductive inks—usually consisting of metallic particles in a medium which allows them to be printed—have been used to print membrane switches and circuits for decades. They were applied in a thick film by means of screen printing. However, times and technology have changed. A new area of electronics, printed electronics, is emerging, which has necessitated conductive inks to be printed in thin films for improved product properties. This is one area that the report will cover—conductive inks that are able to be printed in thin films for the emerging printed electronics applications.

However, as market demands and applications change, so too do material requirements. Traditional conductive inks, including the improved nano-metallics, are often neither sufficiently transparent for some applications, nor conductive enough for others and are inherently not semiconducting. To address these areas has required the development of new materials and methods. This report will also examine these ink developments, which are innovations, not improvements on conventional conductive inks.

The composition of electronic devices requires three components: conductive materials, semi-conductive materials and non-conductive or insulating materials also know as dielectrics. It is important to note that as requirements for conductive and semi-conductive materials advance, so too will those for dielectric materials. However, that is a topic for another day. This report will only focus on conductive and semi-conductive inks. A further note, there is a class of inks, i.e., electronic inks that are used in printed electronics, specifically for e-paper applications. However, these are not conductive inks and will not be discussed in depth in this report.

The report will examine the competitive landscape of the current conductive inks area, with a look at the major suppliers to the market. It will detail recent technological improvements and innovations in the area and forecast how conductive inks will evolve over the next five years. The report will also examine the manufacturing processes and materials used for formulating conductive inks, as well as the emerging innovative inks for semiconductor use. In addition, it will discuss the printing processes used to apply the inks, as well as other processes—which are additive methods, but not traditional printing—which have been recently introduced. The report will also explore the main applications for these inks, both for today and for the near future. Finally, the report will look at how the marketplace for conductive inks might evolve in the next five years.

Report Objective

As the emerging printed electronics technology begins to move forward, there are serious market drivers that require new materials and processes to meet demands for high volume, low cost methods of printing electrodes, as well as the ability to print on a variety of low cost, flexible and often proprietary substrates; there is also a complementary need for highly conductive and transparent coatings. While conductive inks remained fairly stable for decades, in recent years, there have been improvements, as well as innovative new inks to meet the challenges offered by printed electronics. As printed electronics gains momentum, these

A new area of electronics, printed electronics, is emerging, which has necessitated conductive inks to be printed in thin films for improved product properties.

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new materials will take on increased importance. They will be the enablers to push commercialization and widespread adoption of the new technology.

Methodology

The information contained in the report has been gathered from multiple sources, both primary and secondary. The secondary data has come from technical papers, conference proceedings, internet searches and material provided by companies interviewed. In additional, scores of interviews were conducted with various industry experts across the supply chain in the market.

List of Definitions

Allotrope Some chemical elements can exist in two or more forms, which are known as allotropes of that element. Graphite, carbon nanotubes and diamonds are allotropes of carbon. In each allotrope, the element's atoms are bonded together differently.

Aspect ratio The aspect ration of a shape is the ratio of its longer dimension to its shorter dimension, for example the length and diameter of a rod.

Carbon nanotubes Carbon nanotubes (CNT) are allotropes of carbon with a cylindrical nanostructure. These carbon molecules have properties that make them potentially useful in applications such as nanotechnology, electronics and materials science.

Chirality Basically, chirality is "handedness." Unlike a pair of hands, some geometric figures are identical to its image in the mirror. The underlying issue is the identity of an object and its reflection. Any object that is different from its reflection is said to be chiral. Otherwise, it is called achiral.

CIGS Copper Indium Gallium (di)Selenide (CIGS) is a compound semiconductor material composed of a solid solution of copper indium selenide and copper gallium selenide. It is used as a light absorber material for thin-film solar cells.

Conductive inks Conductive inks are inks that conduct electricity. They are typically made of metallic particles such as silver or copper flakes in a retaining matrix, or carbon flakes/particles in a retaining matrix. Today, that matrix is usually polymer, (known as Polymer Thick Film, PTF). Since the retaining matrix is not conductive, or weakly conductive, it needs to be reduced by curing so that the conductive particles in the inks can touch. This curing can be done with heat, UV light, or most recently photonic light.

Doping In semiconductor production, doping is the process of intentionally introducing impurities into an extremely pure (also referred to as intrinsic) semiconductor to change its electrical properties

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DSSC Dye-sensitized solar cell (DSSC) is a relatively new class of low-cost solar cell based on a semiconductor formed between semiconductor formed between a photo-sensitized anode and an electrolyte, a photoelectrochemical system.

EL displays Electroluminescent displays are a flat panel display technology that uses electroluminescent materials—materials that emit light, but not heat, when exposed to an electric field—sandwiched between conductive electrodes. Most EL displays are monochrome, typically yellow orange.

Flexographic printing Flexo is a direct printing process using relief plates inked with anilox rolls. It is primarily use din packaging.

Graphene Graphene is a one-atom-thick planar sheet of -bonded carbon atoms that are densely packed in a honeycomb crystal lattice. It resembles an atomic-scale chicken wire made of carbon atoms and their bonds. Graphite consists of many graphene sheets stacked together. Graphene is the basic structural element of some carbon allotropes including graphite, carbon nanotubes and fullerenes.

Gravure Gravure is a high-quality direct process using engraved cylinders to apply inks.

Inkjet printing Inkjet is a type of non-impact digital printing process that utilizes tiny droplets of highly fluid ink that are jetted onto the substrate.

Nanometer A unit of measurement that is one-billionth of a meter

PEDT/PEDOT Abbreviation for the conductive polymer Polythiophene derivative, poly(3,4-ethylenedioxythiophene).

PICs Printed Integrated Circuits.

Printed electronics Printed electronics (PE) refers to the use of traditional graphic art printing technology as a manufacturing tool to manufacture circuits on media such as polymer films, paper, textiles and other materials.

PVs Photovoltaics (PVs) are arrays of cells containing a solar photovoltaic material that converts solar radiation into direct current electricity. Materials presently used for photovoltaics include monocrystalline silicon, polycrystalline silicon, microcrystalline silicon, cadmium telluride, and copper indium selenide. Due to the growing demand for renewable energy sources, the manufacture of solar cells and photovoltaic arrays has advanced dramatically in recent years.

Screen printing Screen is a process, which consists of an ink or paste being pushed through a stencil attached or embedded in a mesh that is stretched over a printing frame.

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Sintering Sintering is a method for welding objects together from powder by heating the material below its melting point until its particles adhere to each other. Generally, after a nano-ink has been printed onto a substrate, it is thermally cured or exposed to UV or photonic light, and, upon solvent evaporation, forms a continuous conductive thin film comprising the printed feature.

Solder mask A solder mask or solder resist is a lacquer-like layer of polymer that provides a permanent protective coating for the copper traces of a printed circuit board (PCB) and prevents solder from bridging between conductors, thereby preventing short circuits.

Xenon pulse lamps Lamps that use a pulse of xenon rather than a mercury arc as a light source to cure the inks and coatings.

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Conductive Inks: the competitive landscape

Introduction

When printed electronics first began to make a splash in the news, one of the biggest issues challenging its development was the lack of materials, particularly conductive inks that could meet the necessary electronic requirements in a thin-film. Conductive silver inks for circuit boards and membrane switches printed in a thick layer via the screen process had been available for many years; but the new printed electronics would require similar conductivity in a much thinner film to meet the requirements of the potential applications cost effectively.

Since silver metallic inks were used for those formulations, it was a logical development that silver metallic inks with improved formulations would be the next step. Several smaller niche companies began offering new silver inks to address the emerging market, while larger specialty companies began research and development in the field. As the printed electronics began to expand, the landscape began to change. Additional suppliers entered the market with alternative products and some larger companies began to absorb the smaller niche start-ups.

Today, many suppliers who have served the traditional electronics market are now expanding their product portfolio to include improved thin-film silver inks; some companies have developed other metallic inks, such as copper, as a cost-effective alternative to rising silver prices; others have gone in a totally different direction exploring organic and composite inks for greater functionality, lower cost and a more environmentally-friendly solution. Only two manufacturers of graphic arts inks also supply materials to the printed electronics market. These are Sun Chemical Corporation and Toyo Ink. Both have been suppliers of thick film screen inks to the electronics industry for decades.

As the market develops, the landscape will continue to evolve and expand to meet the changing requirements of additional applications in printed electronics. Following is a look at the companies currently supplying the marketplace, their products and strategy for the future.

As the market develops, the landscape will continue to evolve and expand to meet the changing requirements of additional applications in printed electronics.

Suppliers of Metallic Ink Products

The largest supplier group is those involved with metallic inks, mainly silver and more recently copper inks. Many of these companies have traditionally supplied silver conductive screen inks for electronics and are now expanding their portfolio to include nanoparticle inks to meet the demands of the new thin-film printed electronics. They are also developing inks for other printing processes, such as flexo and gravure and inkjet.

Table 2.1 Metallic ink manufacturers

CLICK TO VIEW TABLE

Advanced Nano Products Co Advanced Nano Products (ANP) is a Korean materials company offering a variety of products of which silver inks are a small but growing part of the business. Its nano silver inks can be applied with several different printing technologies including silk screen, gravure, flexography, and micro-contact printing methods. It also offers a silver ink for inkjet printing.

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Applied Nanotech Holdings, Inc Headquartered in Austin, Texas, Applied Nanotech Holdings, Inc., has been recognized for its work in developing Cu-iJ70, a nanoparticle copper ink, which can be processed at temperatures lower than 100°C. It was the first of its kind in the industry. Suitable for solar applications, ANI's Ni-iJ70 nickel nanoparticle ink is formulated to print narrow conductive electrodes and to form low resistance electrical contacts for solar cells. The nickel ink can be printed by inkjet printing and aerosol jet printing techniques and cured to form conductive patterns on substrates such as silicon, ceramics, and Kapton. The company's portfolio also includes Ag-iJ10 nanoparticle silver inks with low processing temperatures (70-200°C) and aluminum inks. Suitable for flexible polymer substrates, the solids content on the silver inks can be adjusted from 10-70% to suit customer applications. The company can also supply the inks in paste form for screen printing applications.

Cabot Founded in 1882, Cabot Corporation is a global performance materials company, headquartered in Boston, Massachusetts. Cabot has developed several types of ultra-fine coated silver particles, which can be incorporated into inks and pastes for standard printing processes, as well as inkjet and aerosol jet printing. For the emerging PV industry, Cabot provides ultra-fine particles comprised of silver and etching glass, which can be used for screen printing or non-contact methods such as inkjet and aerosol printing for front grid electronics.

Cima NanoTech Cima NanoTech was founded as a spin-off from Aveka to pursue nanotechnology research. Headquartered in St. Paul, MN, it offers silver and copper inks for ink-jet printing. The ink products are based on silver nanoparticles, which are coated with organic materials to prevent agglomeration and dispersed in conventional graphics industry vehicles. Cima NanoTech has also developed a patented technology– Self-Aligning Nano Technology for Electronics (SANTE™) which allows silver nanoparticles to self assemble into microscopic networks providing simultaneous transparent and conductive networks. The flexible SANTE™ Film is claimed to have better electronic resistance than conventional indium tin oxide (ITO) coatings. Cima has partnered with Toray Industries of Japan to mass produce SANTE films for flat panel displays. The company also offer silver nanoparticles for customers who wish to formulate their own inks. In 2006, Xaar, Cima and Imaging Technology International (iTi) develop inkjet material deposition system for conductive inks.

Creative Materials Founded in 1986, Creative Materials is based in Massachusetts. The company has developed an entire line of conductive inks which can be applied through pad-printing, which is especially useful in applying material to contoured or uneven surfaces. Other products are designed for screen printing or flexo. Recently, Creative Materials introduced an economical silver conductive ink, 125-10, with typical sheet resistivity of 15 milliohm/square/mil, as a cost alternative to standard conductive inks. The inks can be applied with screen printing, syringe dispensing, as well as flexo and gravure and spraying processes. Applications include RFID antennas, polymer thick film circuitry

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and membrane switches.

Creative Materials has also introduced a Medical Grade Electrically Conductive Ink, which can be used in a range of medical electrode applications, including ECG and TENS electrode applications, transdermal drug delivery, defibrillation, and monitoring systems. These products can be used for a wide variety of surfaces, including polyester, polyimide, and glass.

DuPont Microcircuit Materials Having supplied materials for electronics markets for over 40 years, DuPont Microcircuit Materials (MCM), part of DuPont Electronic Technologies, has expanded its portfolio of products with a silver conductive ink formulated for use in applications such as touch screens and OLEDS. The new screen printable inks include: DuPont 7723, a low temperature firing silver ink suitable for printing on glass, and DuPont 9169, a low temperature curing silver ink designed for flexible substrates. The company also offers DuPont™ Solamet® photovoltaic metallization inks for solar cells. MCM ink technologies can be applied using screen printing, flexo, gravure, photo-imaging, pad printing, and other processing techniques. Ink jet materials are in development. MCM also offers multiple substrate materials for printed electronics. However, with all its products, DuPont's activities in this field are fairly narrow in scope; its inks are primarily thick film compositions for application onto ceramic substrates using screen printing.

Ferro Founded in 1919, Ferro Corporation is located in Cleveland, OH. Although it does not produce inks, it is believed to be the largest single supplier of silver powders for silver conductive inks in the world. Ferro's Electronic Material Systems group introduced a nanosilver powder, Nano Silver 7000-95, intended for fine-line flexible circuit, targeted to applications such as RFIDs and backplanes..

Five Star Technologies Headquartered in Cleveland, OH, Five Star Technologies is an advanced materials company focused on inks and pastes for the electronics industry. The company has products targeted to displays and touch screens, photovoltaics and printable electronics. The company says that the use of its patented cavitation technology enables improved dispersion and particle size control in ink formulations. For the photovoltaic market, ElectroSperse S-series conductor pastes include screen-printable silver inks for front surface contact to both conventional and high-resistance emitters. A new generation of front contact inks with improved flow properties is under development for dispensing via non-contact printing methods.

Harima Chemical Headquartered in Osaka, Japan, Harima's electronics products group offers an electroconductive paste, which is formed by dispersing small conductive particles inside thermosetting resins, which can then be printed on a substrate. Its NanoPaste, silver conductive inks use thermo-curing at low temperature and can be printed using inkjet technology.

Hitachi Chemical Headquartered in Japan, Hitachi Chemical, a supplier of electronic materials, recently developed an inkjet printable low temperature sintering copper ink. Because surfactants are not used to stabilize the dispersion, it does not need high

Conductive Inks: the competitive landscape

temperature to sinter. The company says the resistivity of the copper inks is near to bulk copper. Hitachi has also developed organic insulating inks, an inkjettable resistor ink and a printable organic gate dielectric for transistors.

InkTec Headquartered in Korea, InkTec Corporation has supplied inkjet inks since 1992. Its expanded product line includes a Transparent Electronic Conductive (TEC) silver ink using nanotechnology for applications such as RFID tags, PCBs, reflective film and displays. One of the significant features of TEC inks is that it is transparent in the liquid form before firing. Furthermore, it is not formulated by particle structure, so it is stable at normal temperatures. It is available in several forms, depending on the sinter temperature as well as a silver paste. Additional products include conductive silver inks for flexo and gravure printing. Its silver paste ink is due to be commercialized into touch screen panels for cell phones by a Chinese manufacturer.

Intrinsiq Materials Headquartered in Hampshire, UK, Intrinsiq Materials is an advanced materials company spun out of QinetiQ in 2007. Its DC plasma process also manufactures a wide range of advanced metals and additional patented developments have enabled organic or metal coated particles to be dispersed in a variety of media, including solvents for ink jet inks. Intrinsiq CI, an ink jettable copper ink is now available; nanoparticle silicon, nickel and aluminum formulations are due to be released later in 2010. Intrinsiq CI is a stable, 12wt% copper ink formulation designed for photonic curing at room temperature in air and can be printed on substrates such as paper, polyimide and FR4 (grade of fiberglass widely used as an insulator for printed circuit boards). The resultant conductivities are comparable to commercial silver inks with significantly higher metal loadings. Production quantities will be soon be available as production scaling is implemented.

NanoMas Technologies Headquartered in Endicott, NY, NanoMas Technologies, Inc. was founded in 2006 by three inventors, recognized as experts in the field of nanotechnology, ink development and material science. The company's ink portfolio includes silver and gold nanoparticle inks, conjugated polymer inks, and polymer dielectric inks. It is developing conductor and semiconductor nano-crystal inks for printable electronics, including: displays; RFID antenna and integrated circuits; printed circuit boards; and printable solar cells.

NovaCentrix Headquartered in Austin, TX, NovaCentrix was founded in 1999 as Nanotechnologies Inc., to focus on technology for nanopowders and dispersions. It changed its name in 2006, as it shifted its focus to solar power and printed electronics. Using nanoparticles and flakes, the company's Metalon inks are offered in silver and copper. ICI-003: Inkjet copper is an inkjettable, aqueous, copper-based ink formulated for coated PET substrates. This ink is formulated for very high conductivity. Suitable for piezo-style inkjet heads, JS-015 is an aqueous, nano-silver ink formulated for a broad variety of porous and non-porous substrates, such as plastic films, papers, glass, quartz, and even silicon. Formulated for thermal inkjet heads, JS-011 is an aqueous, nano-silver ink specially formulated for porous paper substrates. HPS are screen printable, aqueous silver inks. Also available are additional silver and copper

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inks that can be applied using flexographic and gravure printing. FS-066 / FS-067: Spray deposition in solvent is a stretchable, nano-silver, solvent based ink that retains conductivity with up to 100% elongation. This ink was formulated for polyethylene film, and is also compatible with other plastic substrates. FS-066 is formulated for spray deposition, and FS-067 is for gravure deposition.

Complementary to its conductive inks, NovaCentrix offers The PulseForge family of tools to sinter or anneal thin-film materials in only milliseconds, on a wide variety of substrates, including low temperature, flexible materials. According to the company, these tools are intended for product innovators and manufacturers in printed electronics who need options to traditional use of materials and processing techniques and to enable new types of products in applications like solar, RFID, displays, smart packaging, and even flexible circuits.

PChem Associates Headquartered in Bensalem, Pa, PChem Associates was founded in 2004 to provide printable conductor materials that could be used on conventional printing equipment at normal operating speeds with minimal process modification.

The company had delivered several metallic nanoparticles, aqueous dispersions and inks for use in printed electronics, mainly for flexographic and gravure printing. To avoid the need for expensive curing systems, these inks have been formulated to cure at a low temperature with conventional thermal dryers. The company's PFI-700 Series can be applied with both flexographic or gravure printing methods. Other products include PF1-200, a flexo printing ink formulated with rheology modifiers and humectants to allow for improved processability in flexographic printing applications. However, the ink will not adhere to most untreated and uncoated substrates. Such inks are suitable for scratch off lottery tickets and electronic scratch tickets. PF1-201 is a similar ink which includes binders to provide adhesion to most untreated substrates. Both formulations have a typical silver concentration from 38-45 weight % silver and are suitable for RFID antennas. PGI-100 and PG1-101 are gravure/Intaglio printing inks that are counterparts to the flexo versions for treated and treated substrates, respectively. The distinguishing factor with this company is its emphasis on flexo and gravure inks. Since printing electronic circuits at 200 feet per minute poses significant challenges for existing printing presses, these inks are formulated to overcome some of the challenges.

Sun Chemical Corporation Sun Chemical Corporation is the larges global printing ink manufacturer, as well as one of the world's largest pigment producers. A subsidiary of Tokyo-based DIC (Dainippon Ink & Chemicals) Sun Chemical has been a leading supplier of various materials including conductive inks to the electronics industry for decades. Recently, Sun Chemical has significantly increased its investment in the printed electronics field. It has opened a state-of-the-art 3,000-square-foot clean room in research facility in Carlstadt, NJ, to research and test photovoltaic solutions for customers. The current focus is on improved metallic materials for the front side and back side for crystalline silicon solar cells, but future targets include polymer based silver, dielectric and graphite formulations for thin-film and organic PVs, as well as

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display technology. The company's printed electronics portfolio is destined to include both contact and non-contact products. To help accomplish the task, Sun Chemical has invested in emerging technologies, such as the Optomec aerosol deposition system.

While working on products for emerging applications, Sun Chemical's strategy is to also deliver value to the customer for his process today. For example, there is a trend in the industry to use thinner silicon wafers in manufacturing crystalline solar cells. As a result, bowing the cells could lead to micro-cracking or breakage. Furthermore, thinner cells mean a shorter optical path, i.e., less thickness to absorb sunlight. In response, Sun is developing an aluminum paste with significantly lower bowing and improved reflectivity. With its extensive experience in manufacturing inks, the company is developing metallization systems to meet future challenges.

Sun Ray Scientific Headquartered in Mt Laurel, NJ, SunRay Scientific had its origins in the former Bell Labs and AT&T. The company has been providing thick silver inks and dielectrics for flex circuits for nearly 20 years and has recently launched the NANGLOW™ product line. Designed for flexographic/gravure printing, the new inks will be complementary to SunRay's existing MAXIGLOW™ portfolio of silver/carbon inks, dielectrics, and epoxies which are designed for screen printing of membrane switches, and other printed electronics applications.

Taiyo-Ink America Located in Carson City, NV, Taiyo-Ink America is a manufacturing subsidiary of Taiyo Ink Mfg. Co in Japan. Established in 1990, the company is the largest supplier of high quality solder mask for rigid and flexible printed circuit boards and packaging substrates in North America. At customer request, the company expanded its product line to include dielectric and conductive ink products for producing solar cells and inks that are applied with inkjet technology for traditional legend and printed electronics applications. The ECM™ 100 includes a series of screen printable silver-bearing pastes for use in solar cells as well as membrane, touch panel and other printed electronic applications. ECM®-100 inks are capable of excellent high resolution, fine line printing, down to 30 to 50 µm line width. In addition, Taiyo America has added its TCM™100 line of conductive inks for a wide range of end product applications which can be customized and manufactured to meet customer specific requirements. .

Toyo Ink Group Based in Tokyo, Toyo Ink is the third-largest global printing ink manufacturer. It has developed its REXALPHA™ series of conductive silver paste products for the printed electronics and RFID markets. Providing low resistance with thin film, these conductive silver pastes can be used for a variety of applications, including rotary screen, flat screen, flexo and gravure printing. It is UV curable with screen and flexo. It also supplies LIOMETAL, Silver nanoparticles that enable formation of conductive films quickly at low temperatures.

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Xerox Headquartered in CT, Xerox has introduced a silver ink that can be applied to plastics as well as fabrics for conductive circuitry. Xerox now supplies materials for all three components of a circuit: semi-conductor, conductor and dielectric. The initial target for the material is smart packaging. Formulated so its molecules align for optimal conductivity, the ink can be applied using conventional inkjet printing, creating lines between 50μ and 40μ.

Carbon-based ink Suppliers

Carbon nanotubes (CNTs) have long held promise because of their unique electrical and thermal properties, but there have been issues with large scale production of high quality product and formulation into inks. These challenges have been overcome and several companies are offering conductive and semi-conductive inks based on CNTs. Not only do the inks offer potential for printed electronics, but the conductive films made with the inks offer an attractive alternative to ITO in touch screens and flat panel display screens.

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Table 2.2 Carbon-based ink suppliers

CNano Technology Headquartered in Santa Clara, CA, CNano was founded in 2007 to manufacture carbon nanotubes from technology developed at Tsinghua University. The company has a proprietary catalytic process for continuous production of carbon nanotubes with tonnage capacity. It has commissioned a CNT production line with the world's largest production capacity of 500 tons per year to be located in Beijing, China. With the new process, the agglomerates can be distributed into a variety of matrix including liquid, polymer, metal, ceramics and more. The patented technology eliminates the low yield and batch production limitations of many traditional processes to make carbon nanotubes. CNano has signed Marubeni Information Systems as exclusive distributor of CNano's carbon nanotube related products in Japan.

Eikos Founded in 1996, Eikos manufactures water-based inks based on carbon nanotube technology. Variables such as solids content, surface tension, and viscosity can be tailored for a specific substrate, as well as a target conductivity and transparency. The products can be applied by means of spray deposition, gravure, dip, and inkjet processes. Eikos can also formulate specialty inks for hydroscopic or reactive substrates or high temperature coating processes. Using the inks, the company also manufactures Invisicon® a highly transparent conductive coating with durability, index matching and anti-reflective properties. The film is developed by means of a variety of deposition and patterning methods in air onto a range of substrates. Eikos selected by National Institute of Standards and Technology (NIST) to demonstrate commercially viable large scale, low cost length separation of carbon nanotubes. The company claims the selection affirms its leadership role in development and manufacture of CNT based inks and conductive coatings.

Nantero Located in Woburn, MA, Nantero is a nanotechnology company using carbon nanotubes for the development of next-generation semiconductor devices, including memory and logic. Founded in 2001 by Harvard chemistry PhDs, Thomas Rueckes and Brent Segal, and entrepreneur, Greg

Conductive Inks: the competitive landscape

Schmergel, Nantero does not make products, but rather licenses its intellectual property to manufacturing companies. Microelectronic-grade carbon nanotubes are now commercially available in a transparent coating (ink) through Nantero's licensee Brewer Science. The coating is easily applied by spin, spray, micro-dispensing or ink-jet printing. The company is also working with HP to explore the use of Nantero's carbon nanotube (CNT) formulation to create flexible electronics products and develop low cost printable memory applications such as RFID tags.

SouthWest NanoTechnologies Located in Norman, OK, SouthWest NanoTechnologies Inc. (SWeNT) was founded in 2001 to commercialize nanotube technology developed at the University of Oklahoma. The company manufactures carbon nanotubes and CNT-based inks using a V2V Ink Technology developed at Chasm Technologies. The company's CoMoCAT® catalytic method produces single-wall nanotubes of high quality at 90% selectivity and with a remarkably narrow distribution of tube diameters, resolving one of the major issues with CNT manufacture in volume scale. SWeNT is working with Brewer Science under National Institute of Standards and Technology) (NIST) funding of $6.5 M on developing methodologies to improve methods for commercialization of CNT metallic and semi-conducting inks. The company has also been awarded two grants from the Oklahoma Center for the Advancement of Science and Technology (OCAST) to develop LED lighting with CNT printed electrodes. The goal is the next generation of single-walled carbon nanotubes with higher electrical conductivity and transparency than is currently available commercially. Such materials would also find application in photovoltaics, super-capacitors, batteries and displays.

Unidym Headquartered in Sunnyvale, CA, Unidym is a majority-owned subsidiary of Arrowhead Research Corporation. The company is a leader in the manufacture and application of carbon nanotube (CNT)-based ink and conductive film products. Based on the work of the late Dr. Richard Smalley and Professor George Gruner at UCLA, the company has created an expansive intellectual property patent portfolio (more than 200 applications with 90 issued patents). Unidym is focused on the electronics industry where its initial product is a transparent electrode for touch screens, flat panel displays, solar cells, and solid state lighting. Under development are thin film transistors for printable electronics and the emerging flexible display market.

There have been several recent developments from the company. A touch sensitive MP-4 player, which incorporates Unidym's printable CNT films, was displayed at the China Electronics fair by G Star Laser. Joint venture partnership with Wisepower (Unidym Korea) will co-develop and market Unidym's CNT-based inks and films in Korean touch panel and display industries. Joint venture with major LCD manufacturer will target integration of CNT transparent conductive films onto liquid displays; agreement with LG Display calls for similar work.

Vorbeck Materials Vorbeck Materials was founded in 2006 to develop commercial applications for graphene technology. The company's proprietary grapheme material, Vor-x™ was developed at Princeton University. Vor-Ink™ is one of the first products on

Conductive Inks: the competitive landscape

the market to incorporate grapheme. The ink can be applied with screen printing for RFID antennas, keypads, and display backplanes directly onto paper or cardboard stock. Vor-ink gravure and flexo inks provide good coverage at low film thicknesses and high printing speeds. Unlike metallic conductive inks, the graphene ink does not have to be heated after printing. Vorbeck Materials is also working on inkjet conductive inks.

According to the company Vor-ink creates robust films with excellent flexibility and crease resistance, which retains its rated conductivity even in thin coatings. Thus Vor-ink's fills the performance gap between less conductive carbon-filled inks and expensive silver-based inks. Furthermore, since it is not metallic, Vor-ink can be dried and cured under the same conditions as graphic ink. At its facility in Jessup, Maryland, Vorbeck has the capability to manufacture grapheme in ton quantities. It has also received approval from the EPA to manufacture the graphene as an additive for ink.

Suppliers of Conductive Polymer Products

CLICK TO VIEW TABLE

Table 2.3 Suppliers of conductive polymer products

H. C. Starck H.C. Starck is an international group of companies, which produces refractory metals and liquid conductive polymers. Its product Clevios™, which is a trade name for a family of products focusing on the chemistry of 3,4 Ethylenedioxythiophene, can be used to fabricate a key component for the next generation of flexible displays. Most recently, H.C. Starck Clevios entered into a patent cross-licensing agreement with Agfa-Gevaert N.V. to settle intellectual property disputes between the parties. H.C. Starck Clevios is also participating in NEMO (New Materials for OLEDs) project, supported by German Federal Ministry of Education and Research German Federal Ministry of Education and Research. H.C. Starck Clevios GmbH is working on highly conductive polymer anode materials that could serve as an alternative to ITO.

Panipol Oy Founded in 1978 as a spin-off from the Finnish company Neste Oy. Panipol Oy is working on developing conductive polymers. The company's product line includes coating systems and conductive inks and conductive polyaniline salt in a powder form. An Italian company, Kiian, s.r.l. has introduced electrically conductive inks based on Panipol's polyaniline technology.

Plextronics Headquartered in Pittsburgh, Pa, Plextronics was founded in 2002 as a spinout from Carnegie Mellon University. Based on the conductive polymer technology developed by Dr. Richard McCullough, the company features three categories of products: Plexcore OC organic conductive inks, Plexcore OS organic semiconductive polymers and Plexcore PV organic photovoltaic ink systems.

Plexcore® OC ink is a multi-functional conductive material, which is compatible with a several printing methods including spin-coating, ink jet printing, and contact printing. The inks can be used in multiple applications including OLED mobile phone displays, OLED point-of-purchase signage, flexible OLED displays, printed solar cells, organic smart labels, and organic field effect transistors. Plexcore® PV is a ready-to-use ink system designed for printed solar power. The ink system consists of a p/n photoactive ink and a custom-designed hole-transport ink that are solution-processable. The combination of the Plexcore® PV inks in a printed solar cell enables consistently improved device efficiency, which results in the ability to convert more sunlight into power. Based on polythiophene chemistry, Plexcore® OS is a p-type organic semiconductor designed to deliver charge transfer control for high-volume production of printed circuitry and power applications. It can be formulated into printable inks with properties customized for a wide range of electronic applications.

In 2009, Plextronics, Westinghouse, Allegheny Energy, EQT, CONSOL Energy and BPL Global founded the United States Center for Energy Leadership, whose mission is to establish a stable energy environment for the United States that includes energy independence, stable energy pricing and a portfolio approach to meeting increasing energy needs. Plextronics has also partnered with NTERA to demonstrate solar-powered NanoChromics™ displays. The e=paper display is directly powered by a Plextronics Organic Photovoltaic solar cell printed with the company's ink technology. In 2009, the company completed a $14 million financing round.

Silicon Ink Suppliers

Table 2.4 Suppliers of silicon-based ink products

CLICK TO VIEW TABLE

Innovalight Innovalight based in Sunnyvale, CA is a venture capital start-up founded by Conrad Burke, which originated in the University of Texas and The University of Minnesota In 2009, working with Roth & Rau AG, leading suppliers of plasma process systems for the photovoltaics industry, Innovalight completed the installation of the world's first silicon-ink based solar cell production line in Sunnyvale, CA. The production line has the capability of producing 10 Megawatts of solar power and can be easily scaled to many hundreds of megawatts of electricity production.

Recently, Innovalight was awarded a U.S. patent which covers a novel process for the commercial manufacture of high efficiency selective emitter solar cells with silicon ink. In addition, the company has raised $18 million in additional capital, which will be used to expand the company's proprietary silicon ink production for customers. On a more practical front, JA Solar Holdings Co. is working to commercialize a new generation of high-performance solar products using silicon ink technology from Innovalight, Inc. JA Solar is currently developing silicon ink-based high efficiency solar cells at its R&D pilot line in Yangzhou, China with plans for initial commercialization in 2010.

Kovio Founded in the MIT Media Laboratory under the leadership of Dr. Joseph Jacobson (a cofounder of E Ink), Kovio Is a privately owned Silicon Valley company developing a new category of semiconductor products using printed silicon electronics and thin film technology. In 2008, the company developed the world's first RFID tag based on silicon inks and the company's printed silicon RFID platform for item-level intelligence, which would enable the development of affordable item-level RFID intelligence solutions for various markets, including retail, pharmaceuticals, transit, logistics and asset management. Kovio's technology platform combines high-performance silicon inks and graphics printing technology, to enable fabricating silicon devices over large areas, on flexible substrates. The first products based on this patented platform technology are printed silicon HF integrated circuits (PICs) with 128 bits of printed read-only memory. Soon after, the company moved to a 95,000 square-foot facility in Milpitas, CA, to facilitate commercialization of the technology.

Earlier this year, Kovio, Inc. entered a joint collaboration with Nissan Chemical Industries, Ltd., (NCI). NCI will commercially produce Kovio's proprietary silicon ink technology and supply Kovio with silicon ink products for its RF products and other strategic applications. Moreover, as exclusive supplier of Kovio's silicon inks in the Asian display area, NCI announced plans to commercialize silicon ink products in that area. Such future silicon printed electronics products would include thin-film transistor (TFT) backplanes in LCD, OLED and eBook displays.

NanoGram Located in Milpitas, CA, NanoGram has been a manufacturer of advanced materials for photovoltaic, optical and electronic applications since the late 1990s. Its silicon inks for printed electronics are based on its proprietary laser pyrolysis process. Similar to Kovio, NanoGram intends to make complete devices, both solar cells and transistor circuits in its sights.

Previously the challenge to silicon ink manufacture was achieving the appropriate particle sizes and size distributions, which enable low temperature processing when the ink is used to create devices. NanoGram has developed techniques for doping the silicon particles during the reaction in highly controllable doping levels. The company claims it has passed the mobility of amorphous silicon, and believes that mobility in the range of >100cm 2/Vs is achievable. While the sintering temperature of the deposited transistors is confidential, one of NanoGram's partners is a plastic substrate supplier.

Summary

As the printed electronics market continues to expand, material suppliers are actively engaged in research and development to create new materials to meet the changing requirements of thin-film printed electronics. The traditional suppliers of metallic silver conductive inks have expanded their product portfolios to include nanoparticle silver inks for printing thin-films with the required conductivity that can be sintered at low temperatures for flexible substrates. Several of these companies have also introduced nanoparticle copper inks as a lower-cost alternative to silver conductive inks. More of these products are likely to reach the market in the next several years.

At the same time, there have been significant breakthroughs in carbon-nanotube based materials for both conductive inks and semi-conductive inks, as well as for films printed with such inks as a

Conductive Inks: the competitive landscape

substitute for ITO coatings. There has also been continued research and development in the conductive polymer area. In addition, a new category of semi-conductive inks–silicon-based inks–has begun to emerge. These offer the advantages of silicon, yet are solution processible to enable the use of printing technology. All this makes for an exciting time in the conductive and semi-conductive area as the competitive landscape shifts along with the evolution of printed electronics from screen printable thick ink films towards thinner films on flexible substrates.

3

Technology Forecasts

Introduction

Conductive silver inks have become the leading metallic ink printed in a large number of current printed electronics products such as UHF antennas for RFIDs, membrane keyboards, and battery testers for many years. These inks were screen printed thick pastes. As the electronics industry changed and began demanding thinner films, companies developed nano-silver inks to achieve the necessary conductivity without a thick paste film. Thinner films required sintering after printing to achieve the required conductivity, but the nanoparticles could be sintered at lower temperatures, so the inks could now be processed on substrates such as paper, and PET.

In addition, silver is the best conductive material. Consequently, silver inks are the dominant player in the printed electronics industry, with the use of nanoparticle silver inks expanding. That is not likely to change overnight, but there are definite challenges to silver's role in the market. Unfortunately, the cost of silver has escalated recently, in part due to diminishing silver supplies and the increased demand from China, India, Russia and Eastern Europe. Furthermore, it is not only the rising cost, but the wide fluctuations in prices that are causing problems. Those costs are not likely to drop, thus the emerging printed electronics industry is increasingly looking for alternatives for metallic printing inks. Moreover, there are some concerns that silver is a biocide; if the metal leaks into water, its antimicrobial properties can be detrimental to treatment systems.

Figure 3.1 Technology map showing available conductive/semi-conductive inks

CLICK TO VIEW

Copper Inks

Traditionally, copper had been the conducting metal of choice for the printed circuit board industry. Ironically, silver had replaced the more abundant copper in many of these applications because the copper, while having excellent electrical conductivity (about 90% of silver), had to be slowly electrodeposited and wastefully etched afterwards. There were also additional challenges to printing copper. Some of these include which copper precursor ink to use, poisoning of circuits, high temperature needed to anneal copper precursor inks, their toxicity and resulting conductivity being much less than bulk. Furthermore, oxidation was a problem with copper inks. Copper all too readily creates insulating oxides on its surface making printing of copper conductor patterns a challenge because interconnection may be necessary because of its insulating oxide on the surface. Silver coated copper, which has the same conductivity as silver, eliminates the oxidation issue and is somewhat less expensive than silver inks. The other issue with printing copper was that the high annealing temperature needed to ensure conductivity could preclude the use of low cost substrates in reel-to-reel printing processes such as those employing PET and PEN films.

However, there are now innovative copper inks available from several companies which have changed all that. It is an important step that is likely to continue as conductive inks suppliers look to copper inks as a potential solution for replacing silver in applications where metallic inks are currently used. One of the main drivers in the electronics industry is to reduce the cost of making devices, so a low-cost alternative to silver is very attractive. Most of the companies supplying nanoparticle copper inks, also manufacture silver nanoparticle inks.

One of the main drivers in the electronics industry is to reduce the cost of making devices, so a low-cost alternative to silver is very attractive.

Copper Oxide Ink One of the challenges in developing a copper inks is coping with the formation of copper oxide, which is an insulator. Copper readily oxidizes in air, and as a result the synthesis and processing of copper inks for conductors has been expensive. A possible solution, introduced by NovaCentrix, is a copper oxide ink, which consists of copper oxide (CuO) and a reducer. When processed in the company's PulseForge system, the film undergoes a chemical reduction to render a highly conductive copper film. Since both the ink synthesis and the processing are scalable, a good, inexpensive, printed conductive pattern is now a reality.

Why copper oxide rather than pure copper? The answer is that a reducible metal oxide ink approach has several advantages over a pure metal ink. Foremost perhaps is that copper oxide is inherently cheap. Nanoparticles of copper oxide are an order of magnitude cheaper than current nano-copper sources and even more than an order of magnitude cheaper than nano-silver. Furthermore, copper oxide particles are easier to disperse because they have more surface charge than copper particles. In addition, the dispersions are more stable. The density of copper oxide is only 6.31 g/cc. That is 30% less dense than copper and 40% less dense than silver, meaning that it also doesn't settle as readily in the dispersion over time. Moreover, sintering in solution or plating of various printing components is minimized as the surface energy of copper oxide is much less than copper. Finally, working with an oxide means that one doesn't need to worry about the particles oxidizing. The inks are developed for inkjet printing. Similar to nano-silver inks, the copper oxide inks need to be sintered after printing.

Table 3.1 Copper nanoparticle inks currently available

CLICK TO VIEW TABLE

Semi-conductive Inks As some companies search for an inexpensive alternative to silver because of cost concerns, others are looking to address different issues. While today's conductive inks serve well in specific areas of several applications, they are not widely used in much of what we term printed electronics today. There are two main reasons for this: either the inks are not transparent enough for some applications, or they are not conductive enough for others. Most importantly, conductive inks are not inherently semiconducting. To address these areas has required the development of new materials and methods.

Carbon-based Inks

Carbon nanotubes (CNTs) have become a hot topic offering potential as a breakthrough material for the 21^{st} century. The traditional electronics manufacturing process is poised for a paradigm shift away from expensive photolithography toward inkjet technology, and carbon nanotubes are enabling this paradigm shift. CNTs high conductivity and nanoscale size enables the production of new inks that create the needed conductive paths at much smaller feature sizes than is currently possible. Depending on their chemical structure, CNTs can be used as an alternative to organic or inorganic semiconductors as well as conductors, but the cost is currently the greatest restraint.

CNTs consist either of only one graphite layer—single-walled carbon nanotubes, (SWNTs), or multiple ones—multi-walled carbon nanotubes, (MWNTs). Dimensions are usually ~1 nanometer in

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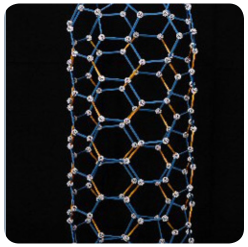

Figure 3.2 Graphic representation of the structure of carbon nanotubes
Source: Nantero

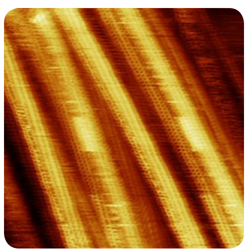

Figure 3.3 Close up photo of carbon nanotubes
Source: Lieber Group, Harvard University

diameter and several micrometers in length. They can be viewed as rolled sheets of graphene with a hollow core and round end caps. The unique structure of these CNTs results in unique optical and electrical properties, remarkable strength and flexibility; and high thermal and chemical stability. In addition, when dispersed into a vehicle to formulate an ink, these CNTs can be printed via inkjet. CNTs have been said to resemble

Following are some of the benefits of carbon nanotubes:

- Flexible and durable printing
- Easy scalability
- Simplified manufacturing eliminates masking steps
- Allows for high speed manufacturing processes
- Nanoscale size can deliver next generation circuit features

As we mentioned above, CNTs can either be metallic or semiconducting. The conducting state of SWNTs depends on the chiral angle and diameter of the tube. In the case of MWNTs, whether the properties are metallic or semiconducting depends solely on the outermost shell. In the conductive state, the electrical current density can be more than 1,000 times greater than in metals like silver, at least in theory, and the conductivity exceeds those of conducting polymers. In reality, the reactivity of carbon nanotubes highly depends on several parameters such as structure, size distribution, agglomeration state and purity.

Until recently, the coexistence of semiconducting and metallic CNTs after synthesis and the difficulty in separating them have presented significant limitations for the usage of carbon nanotubes in electronic applications. Several separation methods have been discovered over the last years and these companies are now offering CNT-based inks, and transparent conductive films using those inks.

Table 3.2 Carbon-nanotube inks currently available

CLICK TO VIEW TABLE

Graphene Inks

Although only isolated a few years ago, graphene—a single layer of carbon atoms tightly packed in a honeycomb structure—is generating interest in the material science community because of its combination of outstanding mechanical, structural, electronic, and other properties, Moreover, it offers bright opportunities to fashion circuit components from graphene for use in computing, digital displays, and other types of electronic technologies.

However, while the potential was appealing, the reality was elusive. The challenge with graphene was separating the individual layers of the graphite, which has been described as a three-dimensional crystal built from graphene layers. A research team in Manchester, UK actually stuck flecks of graphite onto adhesive tape, folded the sticky sides against the tiny crystals, and pulled the tape apart, cleaving the flakes in two. Obviously, this was not a process that was going to create commercial product. One significant fact that the research did provide was that the material was very stable, even at room temperature.

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However, Vorbeck Materials is preparing to make graphene in ton quantities. It has licensed a chemical exfoliation process which was developed by researchers at Princeton University, headed by Ilhan A. Aksay, and Robert K. Prud'homme. The result is Vor-ink™, the company's graphene-based conductive ink. The graphene is readily dispersible in a variety of solvents. As a result, the company has introduced formulations for gravure, flexo and screen printing. Furthermore, Vor-ink requires no sintering; standard drying/curing/fusing equipment can be used. It cures at lower than 80°C, so it can print on temperature-sensitive, substrates such as paper, paperboard, and label stock

Table 3.3 Comparison of surface resistivity (ohm/sq)

CLICK TO VIEW TABLE

Conductive Polymers

There is another category of conductive inks under development, conductive polymers. For printed electronics to be able to take advantage of the benefits of high volume printing methods, all of the components of the device would need to be fabricated. Organic or conductive polymers are the materials that are being developed to do that. . The use of electro-conductive polymers is growing rapidly in many fields of application from antistatic coatings to through-hole plating in printed circuit boards and new displays. If these materials can be improved to offer enough conductivity, it might take minutes or seconds to make a chip, rather than the days needed now for silicon technology.

Polymers are traditionally employed as insulators in electronics. However, there is a special class of polymers –the intrinsically conductive polymers –that have conductivity levels between those of semiconductors and metals (up to 10^2 - 10^3 S/cm). The combination of metallic and polymeric properties offers significant potential in numerous applications, particularly in the electronics industry, which were previously not possible**.** It is important to note that the first generation of conductive polymers like oxyacetylene or polypyrrole were not suitable for practical applications due to low long term stability of the conductivity and/or low processability.

Table 3.4 Conductive polymer inks currently available

CLICK TO VIEW TABLE

Table 3.5 Comparison of conductivity of conductive polymers with other materials

CLICK TO VIEW TABLE

Silicon Inks

One of the areas which are receiving increasing attention is printing silicon. Such a process would combine the proven performance advantages of silicon with the lower cost additive manufacturing processes, such as printing or aerosol deposition. In addition, many of the printing techniques that would be applicable for silicon inks could be extended to other traditional semiconductor materials.

Silicon is the most widely used material in the electronics industry. It is also the material of choice for thin-film transistors and thin-film photovoltaic cells. However, the current manufacturing method is not only expensive, but involves harsh environments. One of these environments is high temperature would preclude the use of flexible substrates, particularly polymers, which is where the electronics industry is moving. In addition, silicon manufacturing

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is now done in a vacuum in batches, which is lower throughput than roll-to-roll processes. Using a silicon ink in an additive printing process offers a solution to many of these issues. Furthermore, since so much of the electronics industry—in terms of equipment and facilities—are built around silicon, replacing the silicon with silicon inks, rather than a new untested material, would reduce the need for new capital expenditure—at least for the short term. Several companies have introduced silicon inks in the past several years, and it is an area where there is likely to growth.

CLICK TO VIEW TABLE

Table 3.6 Silicon inks currently available

There are several other companies such as Epson who are also working on silicon-ink technology in Japan. It is likely that the engine of the new printed electronics will be printed transistors on flexible substrates that can be one tenth to one hundredth of the cost of those in simple silicon chips.

Photonic Curing Systems

Many printed electronics applications are moving from research and development and pilot scale to commercial production. However, one of the key technological hurdles challenging the printed electronics arena was the availability of commercial equipment to advance production in applications such as printed logic and energy,

One of the disadvantages of nano-particle metallic inks is that because the ink vehicle is non-conductive, it has to be removed before the metallic particles can achieve the required conductivity. Thus, the inks must be processed after printing. Originally the printed ink was cured or sintered using thermal drying. However, one of the key technological hurdles facing the printed electronics industry had been the development and availability of the commercial equipment necessary to advance production in applications such as printed logic and energy, including solar, batteries, and ultra-capacitors, where non-metallic inks are utilized.

The PulseForge™

NovaCentrix first introduced The PulseForge™ 1100 tool for research and development purposes, as an alternative to traditional processing methods to sinter or anneal thin-film materials in only milliseconds. Next, came The PulseForge 3100 tool designed specifically for production-scale processing (150 feet per minute) at power levels optimal for metal-based inks and films. The technology can be used with most conventional printing processes including inkjet, flexo, gravure, aerosol, and screen print. It has also been demonstrated to work effectively with the new copper inks.

The most recent innovation is The PulseForge 3300 tool, which is designed to process materials demanding higher energy levels, such as silicon, zinc oxide and ceramics, used for printed logic, display, and photovoltaic applications on low-temperature substrates. The 3300 product is designed for roll-to-roll and conveyor-based materials processing. The processing system generates the very high processing temperatures required for recrystallization and annealing, but without damaging low-temperature underlying materials like polymeric substrates or adjacent organic materials. The key to the process is the use of proprietary high-intensity lamps

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at very short pulse durations.

Because high surface heating is needed for semiconductor materials, the PulseForge 3300 processing tool is capable of delivering a maximum peak power in excess of 100 kW/cm^2, with a sustained peak operating delivery of 5 megawatts (5 MW) to the target materials. Furthermore, the systems can deliver exposure as short as 30 microseconds. The pulse spectrum can also be controlled, from UV to near IR (200 nm to 1000 nm) so materials can be processed which require UV energy, as well as those which could be damaged by UV energy.

Xenon Pulse Lamps Headquartered in Wilmington, MA, Xenon Corporation has been a leader in pulsed light technology since 1964. It offers the RC-847 system for curing/sintering metallic inks. The RC-847 system features a high intensity pulsed xenon lamp that provides a broadband spectrum, from 200 nm to 1000 nm with 505 Joules/pulse energy. The high peak energy enables sintering in less than 1 millisecond with 1 pulse and has an adjustable exposure intensity. The pulsed light technology allows conductive nanoparticles to be heated and fused at room temperature without significantly heating the substrate or adjacent thermally sensitive components.

The photonic curing system upon which the Pulse Forge tool is built makes use of Xenon Pulse lamps. Such systems with a high peak pulse, delivered in milliseconds, heat the inks and not the substrate. The high energy removes the solvent and leaves just the metal flakes which are sintered or annealed. The substrate is not affected by the pulsed light. One advantage of the speed by which the sintering occurs is that copper ink can be cured so quickly it does not develop an oxide layer that can typically form on the surface, thus improving conductivity. The flexibility of Xenon's RC-800 series offers the ability to customize a system to match the curing needs of a range of nanoparticle inks.

Figure 3.4 Xenon pulse lamp

Source: Heraeus Noblelight

Pulsed Laser Annealing of Power Devices

As silicon wafers are reduced in size, they become more difficult to handle. A possible solution is to bond the thinned wafers to a support carrier, but these are not compatible with the temperatures of annealing and activation. Using pulsed laser annealing allows the achievement of the needed process temperature on the exposed surface, but avoids excess temperature on the bonded surface. Innovalight is one manufacturer of such systems. For other vertical power semiconductor products which have metal contacts on the front side, pulsed laser annealing reduces the number of process steps. The front side can be fully processed, including metal contacts, and the back side is annealed with pulsed laser radiation afterwards. The short pulses keep the temperature on the front side low and the metal contacts intact.

Aerosol Jet Deposition System

Another area of technology where there has been innovation is in the process used to apply the conductive inks. While inkjet printing is used today, other improved methods have been developed, such as the Optomec Maskless Mesoscale Materials Deposition (M3D) Aerosol Jet System.

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The Aerosol Jet technology, commercialized by Optomec, was originally developed under a DARPA contract. The system was designed to fill a neglected middle ground in microelectronic fabrication. Then-known manufacturing techniques could create very small electronic features, for example by vapor deposition, with screen printing used for large ones. However, there was no technology capable of satisfactorily creating crucial micron-sized (10-100 µm) production of interconnects, components, and devices. In addition, as electronic devices continue to shrink, the physical limits of screen printing were being approached.

While not a traditional printing method, aerosol jet spray deposition is an additive manufacturing process, so it brings benefits that cannot be realized by means of the subtractive methods currently used. Traditional subtractive manufacturing methods use masking and etching processes to remove material to get to the final form. During additive manufacturing, material is deposited layer by layer to build up structures or features. Some of the advantages of additive manufacturing processes include direct CAD-driven, design-to-device processing, which eliminates expensive hard-tooling, masks, and vertical/horizontal integration. Thus there are fewer overall manufacturing steps. These advantages contribute to greater design and manufacturing flexibility; time compression and better manufacturing agility; lower cost; and a greener technology.

In addition, the aerosol spray offers advantages over traditional and emerging printing processes, such as inkjet.

Table 3.7 Comparison of aerosol jet deposition versus thick-film screen printing and inkjet printing

CLICK TO VIEW TABLE

Aerosol Jet Technology Basics In the first step in the process, the inks are atomized. This includes low-viscosity liquid nanoparticle inks and high viscosity pastes. A high density aerosol of 1-5 µm diameter, with high load droplets, is created. This aerosol is focused within the deposition head by an annular sheath gas. This high-viscosity material is jetted from the nozzle and remains collimated 3-4 mm above the substrate. The systems enables features as small as 10µm to be printed on planar and non planar surfaces. This latter feature enables printing 3D conformal objects. By increasing the size of the nozzle head and thus the numbers of nozzles, the system is scalable for both larger areas and multiple fluids.

Figure 3.5 Aerosol spray jet technology versus inkjet

CLICK TO VIEW

Figure 3.6 Diagram of Optomec aerosol spray deposition system

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While inkjet printing has become fairly widespread for research and development purposes, as well as pilot projects in thin-film printed electronics, it does have limitations, particularly in light of some of the newer inks being developed. The Optomec aerosol spray deposition system reduces many of these limitations. Inkjet printing works well with low-density inks, while the aerosol spray system allows a wide range of vehicles, dispersants, additives and metal loadings. These include both organic solvent-based and water-based conductive metallic inks. There have been definite challenges with clogging of inkjet nozzles; there are no closing issues with the spray system. In addition, inkjet delivers single drops of ink in a random fashion, while the aerosol spray deposition system delivers a continuous feed of inks in a tightly focused direction. Some additional features of the system include the delivery of between 1 and 5 micron size aerosol droplets at a dispersing rate of 0.25 micro liters per second, in print line widths of between 10 and 150 microns. The system has also been used with copper inks on polyamide substrates with sintered copper lines that measured 60 microns wide and 8 microns thick.

The Aerosol Jet 300 system is aimed at low volume manufacturing and rapid prototype product development. Equipped with a single nozzle deposition head, it can write at speeds up to 200 m/s with a high level (±6 µm) of dynamic accuracy. As higher volume applications are developed, there is a need to scale up the speed of the Aerosol Jet manufacturing. For these higher volume applications, the Aerosol Jet system can be equipped with multi-nozzle deposition heads and high performance atomizers to meet production requirements. The company claims the system would provide solutions for RFID antennas, fuel cells, strain gauges, printed structures, printed transistors, embedded structures, molded interconnected devices and already has partnerships with companies in several areas. Optomec provides the print platform and sometimes the automation component, while working with material partners and domain experts.

Testing Instruments

As the use of printed electronics grows, an emerging concern for the manufacturers of printed circuitry will be to insure adhesion to a chosen substrate and the inks ability to withstand cracking. If this happens, the ink can fail to transmit electrical current. One such instrument available today is the Nanovea Mechanical Tester, which in its nano scratch testing mode can measure the load required to cause failure to a silver nano-ink on a polymer substrate. A 2 µm diamond tipped stylus is used at a progressive load ranging from 0.015 mN to 20.00 mN to scratch the coating. The point where the coating fails by cracking is taken as the point of failure. This scratch testing method is a very reproducible quantitative technique which can be used to compare the behavior of various coatings. Just as various methods such as spectrophotometry and densitometry have become standard in the graphics arts industry to measure the ink film for various properties, so too as the industry matures, so too will the need for testing methods for conductive inks.

There is a lot of activity in the conductive and semi-conductive ink area which will significantly impact future growth. As printed electronics expands, so too will the materials needed to ensure that expansion. Many innovative and breakthrough products have emerged recently and it is likely that there will be more to come.

Technology Forecasts

Introduction

In simple terms, graphic arts inks are a mixture of pigments (which provides color) suspended in a vehicle/varnish (resin, which provides specific characteristics) along with additives to enable it to transfer to a substrate. This third component, additives provide special properties that cannot be achieved by the pigment and varnish alone. Materials such as waxes, surfactants and driers are all additives. A more significant additive is oils and solvents, which provide the flow properties and serve as the vehicle which carries the ink through the printing process. Soy and linseed oils are examples of oils; these are used for paste inks which are used in lithography. Solvents are petroleum-based products, but in many cases these are being replaced today by aqueous solutions. Solvents and aqueous solutions are used in flexography, gravure, screen and inkjet printing. After printing, the ink is dried to form an ink film. The vehicle and additives are gone, only the color remains. UV inks are a different breed, containing photoinitiators and oligomers, which enable the components in the ink to cross link when exposed to UV light and actually cure to a solid, almost plastic, film.

A conductive ink is very similar. However, rather than a pigment to provide color, it has conductive powders or flakes, made from silver or carbon like materials. Metallic flakes were an improvement over powders because particles with elongated geometries like metallic flakes increased conductivity. This is because longer metallic paths through the flakes and fewer passes across the resistive junctions between the percolated particles produce less total resistance to the current flowing through the material. These printable conductors or conductive inks have been used for decades in the manufacture of wafer-based PV solar cells, windshield defrosters, medical test strips, and membrane touch switches
The silk screen printable inks used for these applications can be classified as fired high solids systems or polymer thick film (PTF) systems.

Table 4.1 Graphic arts inks compared to conductive inks

CLICK TO VIEW TABLE

Printed electronics is the term that defines the use of traditional graphic printing methods to manufacture circuits on media such as polymer films, paper, textiles, and other materials. The promise of low-cost, high-volume, high-throughput production of electronic components or devices that are lightweight, small, thin, flexible, inexpensive and disposable has spurred the recent growth in development of PE technology. However, fired high solids systems would not work on flexible substrates because of the high temperatures used for sintering and thick films were a definite shortcoming for the new printed electronic devices, which required thin films.

Nanoparticle Metallics

To address the shortcomings, new conductive silver and copper inks based on metallic nanoparticles, mainly silver an copper were developed. However, these inks were a challenge to disperse because the smaller sized particles are inherently thermodynamically unstable and tend to agglomerate to reduce their specific surface area. Ironically, this same instability enables the particles to sinter into cohesive metallic films at much lower temperatures than the older PTFs.

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Manufacturing Conductive Inks

Many of the actual manufacturing processes and formulation in these new nanoparticle inks and other innovative conductive and semiconductive inks that this report examines are proprietary and patent protected. In addition, there are almost as many different approaches to the manufacture of these new materials as there are companies developing them. We will discuss some of those where information is available.

Nanoparticle Inks for Flexo and Gravure The target for PChem Associates was to develop nanoparticle inks for high-volume, roll-to-roll printing technology such as flexo and gravure. Consequently, the thermal sintering temperature needed to be 150°C or below with very short residence times. The company developed a simple, scalable, aqueous-based chemical precipitation process with in situ surfactant stabilization of the particles, which was similar to the process used for the synthesis of the primary particles used in silver flake manufacture. The difference was the elimination of the need for subsequent mechanical attrition steps to mill the spherical particles into flake shapes. Furthermore, the nanoparticle inks can be dried with infrared ovens and do not need more expensive processing methods such as xenon pulse lamps or pulsed laser annealing.

Varying Resin Chemistries DuPont MCM formulates its range of functional low-temperature curing inks similar to graphic arts inks by using various advanced resin chemistries to provide the ink with specific properties, thus enabling a variety of adhesion, flex and thermal properties and compatibility with a broad range of substrates, including paper, polyethylene napthalate (PEN), polyethylene terephthalate (PET), polycarbonate (PC), FR4 and transparent conductive oxides. The company designs the active phase of its ink with each specific end-use application in mind, to ensure the correct conductive, resistive or dielectric properties. DuPont MCM's wide range of ink vehicle systems is suitable for screen print, flexo, gravure, photo-imaging, pad printing and other processing techniques. New ink-jet formulations are also under development.

Nanoparticle Copper
While nanoparticle copper inks are formulated similar to nanoparticle silver inks, copper offers additional challenges. The companies supplying copper nanoparticle inks differ in their approach to manufacturing the materials and formulating them into inks. One of the keys to the Metalon series of inks from NovaCentrix is the use of the Pulse Forge Tools to sinter the inks. Because this is done in milliseconds, it controls the tendency of the copper to oxidize.

Solid Phase Manufacturing Cima NanoTech's nanosilver and nanocopper are based upon a proprietary solid phase manufacturing process which coats the particles with organic materials to prevent agglomeration when the particles are dispersed in a liquid vehicle. The company uses solvents familiar to and proven in the graphics industry to create the dispersions. Additional solvents, binders, surfactants, and additives modify the properties of the ink to suit the printing system and customer application.

...there are almost as many different approaches to the manufacture of these new materials as there are companies developing them.

Manufacturing Conductive Inks

Plasma Production System Intrinsiq Materials uses a proprietary plasma production system, which involves vaporizing feedstock materials such as silicon or copper in a very high temperature plasma stream and then controlling a rapid cooling process to yield a fine nanoparticle powder. The key to the process is control of the processing variables to allow the manufacture of materials with particular specifications including high purity and well-controlled mean particle size. According to the company, some of the features of the process include:

- Ability to freeze in meta-stable and non-stoichiometric states
- Multiple feedstock injection for mixed and exotic compounds
- Optional in-flight coating techniques to prevent agglomeration and ease dispersion
- Variable gas compositions and a controllable atmosphere
- Extremely low impurities pick-up and even impurities reduction

The process is especially well suited to metals such as, copper and nickel, but can also make nanoscale silicon, oxides, carbides and nitrides. These materials offer potential for a range of applications including conductive inks for printed electronics (e.g. copper, nickel and silver) and thin films of nano-particles for solar cells (silicon). Intrinsiq has already developed a copper ink for inkjet printing and plans to develop other conducting and semi conducting inks suitable for inkjet systems in printed electronics.

Conductive Polymers
Plexcore™ technology begins with the design and chemical synthesis of high-performance conductive and semi-conductive polymers. The type of polymer that is created depends on certain key characteristics such as molecular weight, polydispersity, HOMO/LUMO energy levels, energy absorption band-gap and end-group functionality. After the polymer is created, the ink is formulated based on two significant variables: process parameters and device application requirements. The process parameters include: printing/coating technique, viscosity, surface energy, film thickness and surface morphology. The requirements for the end-use application of the device include performance metrics, such as efficiency and lifetime; device architecture; operating environment and use case. Since conductive polymers are by nature soluble, a variety of ink formulations are possible using different proprietary methods and materials.

Silicon Inks
As we mentioned previously, as a conductive material silicon offers significantly higher performance, lower power consumption and environmental stability, over alternatives such as organic electronics. Moreover, the use of silicon would leverage a 50 year knowledge base and ecosystem, including design, fabrication, packaging, testing and infrastructure. However, while silicon has the greatest potential as a conductive ink, the idea of the formulation of silicon inks was almost an unreachable "Holy Grail" for decades. One of the reasons is that silicon is a very tough material to keep under control.

Manufacturing Conductive Inks

Therefore, the key to silicon ink manufacture is to achieve the appropriate particle sizes and size distributions, which enable low temperature processing when the ink is used to create devices. The particle sizes in a given range need to be within a controlled distribution, and the particles need to be non-agglomerated. Until now, this tendency to agglomerate was a serious challenge. Furthermore, particle oxidation has to be avoided to be able to achieve high performance in printed electronic devices. In addition, the ink formulations from the particles must be stable so as to be compatible with standard printing techniques such as ink jet printing and wide area coating.

Several companies have succeeded in overcoming these obstacles and formulating silicon inks. These include NanoGram, Kovio and Innovalight. In each case, the manufacturing information is proprietary, but some information is available.

CLICK TO VIEW TABLE

Table 4.2 Comparison of silicon ink manufacture

Nano Particle Manufacturing NanoGram has developed a proprietary process technology called Nano Particle Manufacturing (NPM™), which is based on laser pyrolysis. In conjunction with equipment developed by the company, it is able to create nanoscale materials. In the system, silicon compounds in a gaseous phase (such as silane gas) are injected into an optically modified laser beam field, which causes the tremendous energy absorbed by the precursor to break the compounds into its constituent materials, such as silicon metal and hydrogen. These re-form in the reaction zone to form pure silicon nano particles and hydrogen gas. As the silicon nano particles exit the reaction zone, they are rapidly cooled so the particle size and crystallinity are maintained. They are then collected in a filter.

Differing from conventional processes, such as milling, sol-gel and metal vaporization, the conditions of particle formation are uniform for each particle and reaction byproducts are easily separated. This enables the resulting particles to have a controlled surface chemistry. Coupled with the company's surface modification method, a high level of agglomeration-free nanoparticle dispersions with uniformity in both hydrophobic and hydrophilic continuous phase can be manufactured. The techniques can be applied to many different nanoparticle compositions and high particle loading can be achieved. By using different precursors, a range of materials can be created, including dielectrics. These particles can then be formulated into inks for further processing via inkjet printing for example.

The company has also developed a new technology– Laser Reactive Deposition (LRD™)–for applying its nanoparticle materials onto substrates. The deposition is made possible by a combination of inertial, thermophoretic, and/or electrophoretic forces. Heat generated from the exothermic combustion and particle formation processes are transferred to the particles. Because the laser zone is uniform, the resulting particle stream is uniform; thus the deposition is also uniform. Using this method, the company is able to manufacture a high quality optical doped silicon glass film in terms of defect count, purity, composition uniformity, thickness uniformity, and low stress. Because of precursor flexibility, the

Manufacturing Conductive Inks

LRD process is capable of creating a wide range of complex film compositions. Furthermore, sequential multi-layer depositions are possible because of the module character of the laser zone. Single-pass depositions of up to 30 μm thickness can be achieved, as well as dense film deposition.

Layering Silicon with Nanoparticle Powder Kovio has addressed the problem in part by layering silicon ink with a solvent made of nanoparticle powder. The ink was integral to the company's first product, a radio-frequency identification tag with a digitally printed chip in it. The process employs temperatures too high for plastic substrates, which is why Kovio uses a stainless steel foil substrate. The fab, which the company has built, can accommodate the high temperatures, but it does not require either the expensive processing equipmentt or the clean-room environment of single-crystal silicon fabs. The silicon ink devices can be fabricated on roll-to-roll printing equipment. Furthermore, the silicon ink demonstrates 80 centimeters squared per volt second (sq cm/Vs) electron mobilities. While it is less than crystal silicon transistors at 600 sq cm/Vs, it is fast enough for transistors for RFID and most other electronic interface protocols. The company states that the speed of its RFID tags exceeds the specifications for both HF (high-frequency, or 13.56 MHz) and UHF (ultra-high frequency, or 900 MHz) bands.

Radiofrequency Plasma Although most details remain tightly guarded secrets, a patent filed in 2005 suggests that Innovalight might be using 'radiofrequency plasma' to make its nanoparticles. By blasting silicon rich molecules with an electromagnetic field (at a radio frequency) it is possible to generate a gas in which some of the molecules have lost an electrical charge. While charged, the molecules are extremely reactive and, with a bit of careful chemistry, can be coerced into forming nanoparticles. These nanoparticles can be suspended in a solvent to formulate a silicon ink.

Similar to metallic inks, the printed nanoparticles are not interconnected and so the film has a high electrical resistance. To lower the resistance, the nanoparticles have to be joined by heating them until their edges are melted, at which point neighboring particles can fuse. This sintering process can be done in several ways using heat, photonic energy or UV energy. Since the melting point of bulk silicon is over 1400° C, the cost of heating is a substantial cost in the production of crystalline silicon solar cells. However, using smaller particles can lower the melting temperature. Innovalight is vague as to how the silicon inks are sintered, saying it uses temperatures between 300 and 900° C, (possibly at high pressure and for times that could be anywhere between 5 minutes and 10 hours).

Whatever the efficiency, and despite the difficulties that are inevitable in developing a new technology, an advantage of Innovalight's manufacturing process is that there is a number of variables that can be adjusted to optimize the cells. For example, nanoparticles can be grown in a variety of shapes and sizes or different nanoparticles can be mixed to determine the exact properties of the printed cell. Perhaps, germanium and tin nanoparticles could be added to the ink so that the light absorption properties can be tuned. Another possibility is printing successive layers with different absorption properties, so that tandem solar cells could be built that would allow higher efficiencies to be reached.

Carbon-Based Inks

Although carbon nanotubes were first discovered in the 1990s, it is only recently that they have become the focus of global research and development. These materials not only offer small size, but excellent thermal and electrical properties. However, there were challenges to their development into inks. These have been overcome and several companies now offer CNT-based inks.

CoMoCAT® Process One of the challenges in the synthesis of single-wall nanotubes (SWNT) is to maintain tight control of the process; otherwise the resulting product will not exhibit the necessary properties. SouthWest NanoTechnologies uses a patented catalytic method called CoMoCAT® Process. The resulting nanotubes have a very selective, narrow distribution of tube diameters. Using this method, SWNT are grown by CO disproportionation (decomposition into C and CO_2) at 700-950°C in flow of pure CO at a total pressure that typically ranges from 1 to 10 atm. Moreover, the process is scalable; the company says it can grow significant amounts of SWNT in less than an hour with a 90% selectivity rate.

Using V2V Ink Technology developed by Chasm Technologies, SouthWest Nano Technologies mixes the CRT paste with a vehicle to formulate a CNT ink, which can be applied by screen, gravure and flexographic printing. The paste can contain any grade of CNT material, either conductive or semi-conductive depending on customer specifications, and the ink viscosity can also be tailored. The inks dry at low temperatures (<100°C) and most importantly, the V2V™ vehicle evaporates completely, so there is no post processing required.

Catalytic Process CNano Technology has developed a patented catalytic process that allows the production of carbon nanotubes in a continuous mode with tonnage capacity. The Company has already scaled up their manufacturing technology to reach a production capacity of 500 tons per year for multiple wall carbon nanotubes. Previously, manufacturing processes were restricted to batch production with low yield. CNanoTechnologies produces CNTs, not the formulated inks. General methods for dispersing nanotubes include both physical and chemical methods. Since CNTs often exist as entangled agglomerates, the company offers guidelines for dispersion

Table 4.3 Guidelines for CNT dispersion

CLICK TO VIEW TABLE

Graphene Inks

Because synthesizing pristine graphene is a costly painstaking process, which still cannot be done on a large scale, Vorbeck Materials is making what is called 'defective' graphene in large quantities. While the electrical properties of this graphene are not good enough to support transistors, it is still strong and conductive. The method starts with oxidizing graphite with acids, then separating it into atom-thin sheets. This expanded graphite is then rapidly heated, creating carbon dioxide gas that builds

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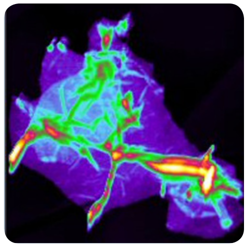

Figure 4.1 Crumpled graphene: This atomic-force microscope image is colorized to show the topography of a piece of graphene of the type used in Vor-ink.

Source: Ilhan Aksay and Hannes Schniepp - Princeton University.

up pressure, forcing the graphene sheets apart. To this point, the process is fairly well-known. However, the company has developed monitoring methods to improve the yield and ensure that the graphene sheets completely separate. At this point, heat is applied to the sheets to remove the oxygen groups. As a result of this process, the sheets are crumpled so they don't stack together again. However, the conductivity is close to that of pristine graphene. The resulting powder can be added to a solvent to make inks or added to polymers to make composites such as tough tire rubber.

Currently, silver inks are more conductive than the graphene inks, but also more expensive and need some sort of treatment process to complete the conductivity of the inks after printing. Graphene ink requires no heat treatment and is more conductive than other carbon-based alternatives to silver inks.

Table 4.4 Comparison of resistivity of various conductive materials

CLICK TO VIEW TABLE

Printing Processes

Before examining each of the printing processes individually, there are general considerations that impact the choice of printing process used. The first consideration is economics, both capital expenditures and operating expenses. Capital expenditures would mean equipment costs and integration costs; operating expenses are usually a function of throughput.

The next consideration would be the capability to print the product/device. This includes issues such as ink laydown (thickness), lateral resolution, registration and surface uniformity.

The final consideration would be the suitability for printing on the substrate of choice. There are significant differences between the printing technologies and no one process seems to be a clear favorite for printing electronics. Rather, similar to graphic arts printing , the end-use application, or in the case of printed electronics the device or component of the device significantly impacts which process would be best suited in that particular circumstance. In many cases, a combination of several different printing processes would provide the solution.

Table 4.5 Comparison of printing processes for printed electronics

CLICK TO VIEW TABLE

Offset Lithography Offset lithography has traditionally been the dominant printing process in the graphics arts industry. It derives its name because it is not a direct printing process, but rather the image is offset onto a blanket commonly made of rubber. It is still widely used in publication printing. However, on the packaging side, gravure and flexography have steadily gained market share, with flexo becoming the dominant player in package printing. One of the advantages of the offset litho process—being able to lay a thin coat of ink or coating on a substrate for fine printing—is one of the factors that make it a poor choice for printing electronics. The process only prints layers that are approximately a micron thick. While high-quality graphics are successfully achieved with precise dots in a thin film, functional inks/coatings require a thicker layer to ensure the needed conductivity for the applications. Offset litho is a high throughput and high resolution process, but at present it is not widely used for printing electronics. One of the major factors is the ink formulations, which are almost like a paste.

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The reason for this is that the high speed of the presses causes extensive shearing (thinning) of the inks by the rollers. Therefore, the inks need to be formulated with large amounts of resins, often high-molecular weight resins, to enable them to change from thick pastes initially to thin inks as the high shear forces of the press react on them. These resins, which are electrically inactive, remain on the substrate after drying, and this can cause problems with conductivity. As mentioned before, the thin ink layer also impedes conductivity, so often multiple passes through the press are necessary to achieve the needed functionality for printed electronics. Litho inks also contain various other additives to enable them to print properly and these additives also can create issues in printed electronics.

Inkjet Printing Inkjet is a type of non-impact printing process that utilizes tiny droplets of highly fluid ink that are given an electric charge. Inkjet delivers consistent drop volume and accurate drop placement, which is important in printing electronics, because of the size of the circuitry. Inkjet can also provide the layer-to-layer registration needed for PE. However, compared to flexography and gravure, which in traditional graphics printing can reach 1,000 to 3,000 feet per minute, and even in printed electronics can reach 400-500 feet per minute, inkjet is a relatively low throughput process. On the other hand, because inkjet is a digital process it images the design directly onto the substrate. This eliminates flexo plate and gravure cylinder costs and reduces makeready times. Moreover, inkjet is capable of printing resolutions on the order of a few microns and it has the added benefit of excellent registration, which can be critical when printing layers, particularly in large-area applications such as displays, lighting panels and sensor arrays. Because of the newer nanoparticle inks, ink-film thickness is no longer an issue. These inks enable higher conductivity in thin films at lower processing temperatures. Another advantage of inkjet is its ability to handle different fluids or inks.

Conversely, one of the challenges of inkjet has been the ability to deposit overlapping drops so that the device printed has continuous features. A missed dot in graphic arts printing is usually invisible to the naked eye; but a missed drop in an electronic application can cause the device to fail. Several companies using inkjet to print electronics have resolved this issue by printing arrays which overlap. The throughput for inkjet is continually improving. A

Inkjet has been used in printing portions of flexible electronics, but the challenge for other applications is more difficult. Drop size requirements need to be about one picoliter (1.25 diameter of a human hair). The control of the volume to achieve uniform thickness, straightness and accuracy from one jet to another has only recently been achieved. Some of the inkjet manufacturers involved in the area of printed electronics include: Conductive Inkjet Technology, FUJIFILM Dimatix, HP, Imaging Technology International, Litrex, Xaar and Xennia.

Screen Printing Although originally called silk screen printing, today, stainless steel or polyester is used to make the screen rather than silk. It has been used for decades for printed and etched circuit boards in electronic equipment, EMI shielding and membrane switches. Basically, the process consists of an ink or

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paste being pushed through a stencil attached or embedded in a mesh that is stretched over a printing frame. There is no intermediate transfer vehicle, so the ink's consistency or viscosity is not limited. Screen printing is a relatively low throughput process. Until recently, this was a moot point because there was no other choice to achieve the thick ink layer required for the necessary conductivity in electronics applications. However, the introduction of nanoparticle inks have enabled increased functionality in thinner films opening the doors to use of other analog and digital processes that have higher throughputs. Despite its limitations, screen is suitable for printing RFID antennas, especially 13.56 MHz applications, which require high conductivity. Since RFID antennas are currently being produced commercially, screen's role is important, but it will diminish over time.

Flexo Printing Flexography is a direct printing process, which uses relief plates made of rubber or photopolymer and anilox rolls for inking metered by a cambered doctor blade system. Although today it is a high-quality printing process, it began as a "rubber stamp" process for corrugated boxes. Its main advantage has always been its ability to print on a variety of substrates. While its quality is close to gravure, because it uses plates, the set-up costs are much lower than the engraved gravure cylinder.

Initially, it did not seem that flexography would be able to lay down a thick enough ink film to meet conductivity requirements for functional materials. However, with the improvements in conductive inks, which now make use of nanoparticles, which are easier to sinter at low temperatures to increase conductivity, flexo is quite capable of printing electronic devices with the necessary conductivity. The resolution in high quality flexography today is approximately 20 µm. Since it is widely used in packaging, it is a natural fit for RFID antennas or complete tags and other smart packaging applications. It is used to print on uneven substrates, since its inception was printing corrugated boxes. Flexography is a high-volume printing process capable of printing anywhere from 750 to 1200 feet per minute.

Flexography is currently used to print RFID antennas on labels. Many printers are using the equipment that was already in their shops for label printing, but have modified the system to accommodate additional drying if necessary and to insert the label inlays. Not only can flexo print silver inks, but conductive organic polymers also. Flexo will continue to be used for printing RFID antennas and there is interest in using it for EMI shielding. Although much of the work is being done under non-disclosure agreements, flexo is being used to print batteries, organic circuits, photovoltaics and low-cost lighting. Flexo may move into more complex applications such as display backplanes. Certain press manufacturers and flexographic printers are already working with an electronics firm on prototypes for flexo printed backplanes.

Mark Andy, the world's leader in narrow-web printing equipment, has been involved with printed electronics for over 10 years. It became engaged because its customers were historically comfortable with approaching Mark Andy for custom solutions. Nilpeter, located in Copenhagen, Denmark has also supplied flexo equipment for printing electronics, e.g., the Nilpeter Rota label FA3300/5.

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Gravure Printing Gravure printing is also a direct printing process, which uses engraved cylinders for inking. While this enables the image quality to remain consistent through long runs, the engraved cylinders are very expensive, which means high set-up costs. There have been some recent innovations such as sleeve technology, to offset this expense. Because of this high set-up cost, gravure does not lend itself to a research and development environment, which, until very recently was what most PE operations were. Gravure is, however, very high speed (1,200-3,000 ft/minute) and the highest quality and the most precise of the traditional printing processes. In addition, gravure has traditionally been able to print on a wide variety of substrates, so it is a flexible process. Gravure is used for many packaging applications, so it would be a natural extension of the gravure printing process to then add the tag, if printed.

Gravure is also capable of printing the largest range of ink/coating formulations, so it would lend itself to new materials such as functional inks. It is also capable of deposing different amounts of ink in different areas, something none of the other printing process can do. In addition, the repeat length is infinitely variable, minimizing waste and producing, continuous, random and nested images from a gapless image carrier. However, because of the nature of the engraved cells on the image cylinder, the edges of the printed features may not be smooth and straight.

Gravure is also being used today to print RFID antennas, but the printers wish to remain anonymous. They are printing 21/2-3 microns at 400-500 feet per minute.
Perhaps because the traditional markets for gravure are disappearing, and portions of the markets that still exist are moving to different printing processes, gravure printers are aggressively seeking alternative growth areas. Engraving manufacturers, particular Max Daetwyler, are active in the printed electronics area, but the small printing resolutions needed for printing electronic devices has been a difficult challenge for gravure printing.

While much of the research and development and prototype work has been done using inkjet printing because it is easier to test new fluids in small batches, its throughput is still slow compared to the more traditional contact processes. It is continually improving and is likely to remain the printing process of choice for the near term. However, if high speed, high-volume manufacturing is required, printed electronics needs to move to the other printing processes. Although the cylinder manufacturers in gravure are aggressively working on solutions, for now flexography is a better choice in terms of high volume.

5

Applications

The printed electronics market is estimated at $1.6 billion with dramatic growth forecast to almost $50 billion in 2015. Although the market growth to this point is not what had been originally forecast by many industry analysts, it is beginning to gain ground and significant breakthroughs have been achieved. Even if estimates are overly optimistic, it is clear that the printed electronics market is poised for expansion.

Areas such as photovoltaics, RFID, printed batteries and sensors, displays and lighting and novelty items are all experiencing expanded use of printed electronics. In particular, it is commonplace in the RFID area. Printed electronics in flexible displays, OLEDs and organic photovoltaics are the future. The area is being driven by advances in both materials and equipment. Breakthrough research and development is ongoing at companies both large and small, as well as at the university level. Much of the technology that was previously developed by educational institutions is now become commercialized in the marketplace.

At the material level—in the conductive ink area and particularly in the semi-conductive ink area—there has been significant improvement and the introduction of several breakthrough products. However, while the materials and manufacturing aspect may be similar across diverse applications, there are often separate market forces at work. These must be considered when a company is deciding which applications to focus on.

Photovoltaics

Due to the growing demand for renewable energy sources, as well as improvements in technology, the manufacture of solar cells and photovoltaic arrays has advanced dramatically in recent years. One of the features that make solar energy appealing is that it offers a broad approach to produce electrical energy where the feedstock (sunlight) is basically free, even though upfront costs are high. Printing photovoltaics would reduce that initial investment, but there are additional considerations to the proposition. One of the most important is that PV offers predictable pricing because the cost of the fuel does not fluctuate. In this current market of escalating and unstable oil prices, this gains increasing significance. Moreover, PV is today able to offer price points that are competitive not only because of technology improvements, but also because other fuel sources have risen so dramatically in price.

In addition, there are significant subsidies to be gained from local and national organizations looking to reduce the cost of PVs so as to spur their growth. Japan and Germany have favorable policies towards solar energy and there are also tax incentives in the US for using solar energy. Furthermore, solar energy is considered not only environmentally friendly, but renewable, which is increasingly important is the push towards global sustainability. The photovoltaic industry also seems to be an area that venture capitalists and strategic investors are willing to support with their funding.

Despite these drivers, however, industry sources report that solar cells still represent less than 0.1% of electricity generated. There are several reasons for that. One is that the cost of manufacturing the

The printed electronics market is estimated at $1.6 billion with dramatic growth forecast to almost $50 billion in 2015.

Applications

solar cells using crystalline bulk silicon are so high, and the inability of the bulk silicon to capture all the soar wavelengths. This makes current solar cells rather inefficient. If these challenges can be overcome, the solar market offers tremendous potential.

Photovoltaics 101 In simple terms, photovoltaic technology transforms radiation or solar energy into electrical energy, which takes place in the solar cells. The concept was developed by Edmund Becquerel in the 1800s, when he discovered that as cells are hit by solar radiation, a current is generated. Consequently, he found he could produce electricity directly from sunlight.

Traditionally, interconnected wafers made from silicon are the key element in solar cells. Three things can happen when sunlight strikes a PV material—photons will either pass through, be reflected or be absorbed. If the photon is absorbed, its energy is transferred to an electron in an atom of the PV material. Energy is produced when the single cells are connected into modules, then into arrays. Since its development more than 50 years ago in Bell Laboratories, crystalline silicon photovoltaic technology –known as first-generation solar technology– has been used. While it has achieved some market penetration, first-generation, wafer-based silicon solar technology is limited by polysilicon feedstock and the high cost of manufacturing.

Second-generation thin-film inorganic technologies are typically made by depositing a thin layer of photoactive material (by means of sputtering or printing) onto glass or a flexible substrate, such as metal foils or polymers. Second generation thin-film inorganic solar technology is still not cost competitive, and the popular materials used, like cadmium and indium, are toxic, expensive, and not scalable to meet global demand. Third-generation photovoltaic technologies are currently under development; these include organic photovoltaics (OPVs) and dye-sensitized solar cells (DSSC).

Organic Photovoltaics Printed organic photovoltaics are constructed a bit differently than traditional solar cells based on silicon wafers. In printed solar cells, as seen in Figure 5.1, the photoactive layer collects sunlight, which creates charge carriers. Applying voltage to the device causes these carriers to be separated into positive and negative charges and then directed to the conductive electrodes (cathode and transparent anode) to create power. Companies such as Plextronics are working on methods to improve extraction efficiencies. The hole transport layer improves extraction of positive charges from the photoactive ink by matching of energy levels to photoactive ink. The combination of the Plexcore® PV inks in a printed solar cell enables consistently improved device efficiency, which results in the ability to convert more sunlight into power.

Figure 5.1 Plexcore PV for printed solar power

The most attractive potential of OPVs is the capability for high-speed manufacturing in roll-to-roll coating and/or printing production. Furthermore, OPVs are light-weight, thin, and flexible, which can significantly reduce systems cost and enable solar cells to be placed anywhere. The downside to OPV cells are relatively low efficiency and low lifetimes compared to other thin film

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technologies. However, that is already changing. The company claims a 5.4% improvement in efficiency with its Plexcore PV™ ink system. In 2009, Plextronics became the first company to deploy organic solar modules at National Renewable Energy Laboratory (NREL) outdoor testing facility as a complement to similar testing at the company's facility in Pittsburgh. The deployment will help build a database of "real-world" performance of the company's solar technology and move OPV technology closer to commercialization. The company also states that within the next five years, OPV technology will find expanded usage as a power source in non-grid applications, i.e., portable devices. However, while future generation organic photovoltaic (OPV) technology has the promise to be the low-cost renewable energy solution, there is a more immediate solution available, printable silicon inks.

Silicon-Based Inks Another company working in the solar energy field, Innovalight has developed The Cougar™ platform, which is a set of patented technologies to enable crystalline silicon cell manufacturers to increase solar cell efficiencies up to 19% with a lower cost per watt. At the core of the platform is the company's screen printed silicon ink. The proprietary material is comprised of silicon nano-particles dispersed in an environmentally friendly blend of chemicals

In the wings is the company's Puma™ Platform, a multi-crystalline based Selective Emitter. According to the company, the Puma Platform cell conversion efficiency gain is expected to be slightly less than the efficiency gain of the Cougar Platform because of the relatively poor quality of multi-crystalline substrates as compared to the pure mono-crystalline wafers which are addressed in the Cougar Platform. In the next several years, the company plans to develop platforms to cost effectively increase the conversion efficiency past twenty percent for mono-crystalline wafers and eighteen percent for multi-crystalline wafers. In addition, the proprietary ink has been formulated for inkjet printing, which will be required as the thickness of wafers continues to be reduced.

Silicon Deposition Another approach in the solar field is from NanoGram, who has developed SilFoil™, a 35 µm multi-crystalline silicon technology to produce solar cells. In this technology, the silicon is deposited on a substrate after the high-rate cooling to create large grain multi-crystalline silicon cells. The company has IP on both cell and module manufacturing. A 5 MW line is scheduled to be completed this year, with full production of 50 MW to follow next year. To spearhead the activity in this area, NanoGram has structured a focused product company, NanoGram Solar.

Improved Metallic Inks Some metallic suppliers, such as Sun Chemical Corporation and DuPont Micro Materials have developed products, which are designed to increase the efficiency of current solar cells. However, while this offers a partial solution to the efficiency issue, it does not address the high cost of manufacturing the solar cells using crystalline bulk silicon.

Conductive Films The front of conventional solar cells requires a high transparency, high conductivity, durable electrode. Cima Nanotech claims its Self-Aligning Nano Technology for Electronics (SANTE™) Films, which are based on silver nanoparticles, are

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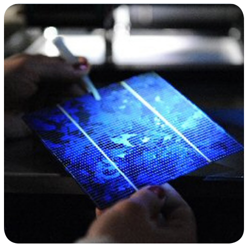

Figure 5.2 DuPont™ Solamet® metallization paste is designed to increase solar cell efficiency and electrical output.
Source: DuPont Micro Materials

candidates for use in the photovoltaic space, from single or poly crystalline silicon (cSi) substrate based solar cells, all the way to organic photovoltaic cells. For instance, in crystalline silicon solar cells, the small line width and small pore size of the SANTE™ Mesh allow for the production of what would be a "narrow" finger and bus bar design. Further, the tall/narrow nature of the silver network improves the conductor aspect ratio over conventional screen printing, allowing for more efficient use of the top surface illuminated area, and thus higher overall cell power conversion efficiency. Finally, the wet, additive, non-contact deposition technique for SANTE™ Films allows for manufacturers to reduce wafer breakage owing to screen printing forces and continue to thin substrates as necessary for overall system cost. The ability to manufacturer using a roll-to-roll process offers additional advantages. Furthermore, compared to ITO equivalents, the SANTE ™ film network is said to reduce lost electrical power in the front electrode itself. Additional advantages are the ability to employ a roll-to-roll process. There are multiple companies involved in developing conductive films as an alternative for ITO and most of them are using CNT-based inks for printing those films. These include: CNano Technology, Eikos, Southwest NanoTechnologies and Unidym whose transparent conductive films are CNT-based. Plextronics has just started development with Cambrios for such films based on conductive polymers. Most of the companies are targeting the display industry, rather than solar cells right now.

Displays

A second explosive area in the printed electronics sector today is in the display market. As electronics manufacturers are looking for increased functionality in smaller and smaller devices at lower cost, they need innovative solutions and the conductive ink manufacturers are supplying them. There is also a move towards flexible displays, which will require inks that can bend with the substrate without cracking or losing adhesion.

Bistable Displays One of the application areas for printed electronics that has been widely commercialized is bistable displays. This market is definitely a success story for printed electronics and its full potential is not yet realized. These are displays, which use electronic ink for the frontplane module, which contains the text and or artwork. This is then attached to a backplane module, which contains the electronics. Some backplane manufacturers include HP, NEC, Plastic Logic, Polymer Vision, Prime View International, Ricoh, Samsung, Seiko Epson.

An electronic ink by definition is an ink that carries a charge enabling it to be updated through electronics. For example, in electrophoretic technology, the electronic ink is composed of tiny microcapsules, about the diameter of a human hair. Each microcapsule contains positively charged white particles and negatively charged black particles suspended in a clear fluid. When a negative electric field is applied, the white particles move to the top of the microcapsule where they become visible to the user, and the screen appears white at that spot. Simultaneously, the black particles are pulled by an opposite electric field to the bottom of

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the microcapsules where they are hidden. By reversing this process, the black particles appear at the top of the capsule, which now makes the surface appear dark at that spot. There are several different technologies used to create electronic inks, including electrophoretic, electrowetting, electrochromic, reverse emulsion electrophoretic displays (REED), electrofluidic, cholesteric, and photonic crystals, with a significant number of companies involved in the development and commercialization of the technology.

CLICK TO VIEW TABLE

Table 5.1 Companies involved in electronic ink technology

These e-paper technologies are already in widespread use in e-readers , e-newspapers, Point of Purchase (POP) displays and for smart shelves in retail stores. Other applications include smart cards, smart packaging, e-magazines , informational signage. The companies who have developed the technology usually manufacture the frontplane, while the electronics companies incorporate it into the actual display. While the inks are printed, they are not conductive inks.

Display Touch Screens In particular, the touch screen component of many displays is under examination to find alternative materials. One of the areas receiving a lot of attention is replacement of sputtered indium tin oxide (ITO) and copper mesh transparent conductive films. ITO is widely used as the material for transparent electrodes in a diverse range of electronic devices including LCD panels, plasma display panels (PDP), touch panels, e-paper, solar cells and organic electroluminescent (EL) panels. In some of these applications, however, new transparent electrode materials are beginning to replace ITO.

Indium is not only expensive, but supply is limited. In addition, ITO layers are fragile and lack flexibility—this is becoming more significant as the display industry moves towards flexible—and even bendable screens. Furthermore, the vacuum deposition process required for the layers is expensive. Both inherently conductive polymers and carbon nanotube-based films are currently being developed as alternatives for ITO. Typically the conductivity is lower for conducting polymers than inorganic materials, but they are also more flexible, inexpensive and environmentally friendly in processing and manufacture.

Some of the advantages of the CNT-based films for touch screens include:

- improved durability and wear resistance
- lower product cost
- improved readability in ambient light, which is especially important for outdoor application.
- reduced reflection
- higher production capacity with speeds up to 50-100 times faster than ITO deposition
- shorter lead times
- ability to be used on emerging rigid plastic screens
- more environmentally friendly process, because it eliminates acid-based wet etching
- enables reducing processing steps and simplifying device architecture
- offers flexibility, so cracking is avoided

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Projects Already Underway The concept of using alternatives for ITO in touch screens is receiving increasing attention as it moves towards commercialization and sources indicate growth rates as high as 300% for such products over the next five years. Following are some examples.

Bridgestone Corp of Japan, has prototyped an e-paper display using a conductive polymer for transparent electrodes instead of ITO, because they wanted to use printing technology for a light, flexible e-paper display. In addition, to the difficulties of using ITO with printing technology, it also breaks when bent. The conductive polymer has not reached the needed performance levels, but the company expects that to come shortly.

Major touch panel manufacturer **Nissha Printing Co Ltd** of Japan plans to use conductive transparent ink with minute Ag wires mixed in (Ag wire ink) as the transparent electrode material for projected capacitive type touch panels. The company is working with Cambrios Technologies and Plextronics to develop the ink. One of the reasons for the switch is that the new material is almost colorless; current ITO film used on touch panels is slightly yellow. A transparent touch panel would provide better color fidelity for the displayed image. And again, the new materials could be coated, reducing manufacturing costs. The Ag wire ink also bends easily, which would enable three-dimensional touch panels, which could be mounted on curved surfaces.

Eikos has develop the Invisicon® technology, which is a 2-step process to form a highly transparent conductive coating exhibiting exceptional characteristics such as durability, index matching, and anti-reflective properties. All this is accomplished using a wide variety of deposition and patterning methods performed in air with water based inks onto virtually any substrate. The advantage of this approach is that it allows independent engineering of the chemical, electrical, mechanical, and optical properties of the layer, while utilizing industry standard processing and materials technologies.

Unidym's CNT-based inks, which are applied to films, have been demonstrated in touch screens for MP-4 players. The company also has a joint venture partnership with Wisepower, to market and co-develop Unidym's proprietary film and electronic ink products into the Korean touch panel and display industries. The newly formed entity will be called Unidym Korea.

Cima Nanotech has developed a highly transparent coating based on inorganic nano materials that are applied via a simple, low-temperature deposition process which creates a flexible alternative to these materials. One of the main improvements is the simplification of the multi-step, photolithographic manufacturing process which produces the copper mesh to a simple coating process on a roll-to-roll manufacturing line which produces the self-assembled transparent conductive coating and eliminates the moiré optical effect.

Figure 5.3 Transparent conductive foil by PolyIC: suitable for applications such as touch sensors, displays, electric heating elements or for ESD / EMC protection
Source: PolyIC

Plextronics has also targeted the display area with it conductive polymer inks, but in a different vein. In conjunction with NTERA, a demonstration of a NanoChromics™ e-paper display using a solar cell printed with Plextronics conductive ink as a power source. This is not only a novel use of the technology, but also a demonstration of the enormous potential for printed electronics components when coupled in innovative ways. Moreover, while showing the value that integrated printed electronics solutions can deliver to the market., it serves as a key milestone in the evolution of printed electronics. The printed color changing display technology used in the e-paper device has additional application in smart packaging, Point of Purchase advertising and smart cards.

PolyIC in Germany produces printed electronic devices. It is manufacturing its own materials based on organic polymers. It recently introduced a transparent conductive film at LOPE-C (Large Area Organic Printed Electronics Conference (June 2010).

Flat-Panel Displays Thus, the use of alternative materials for ITO in touch screens is already expanding its use. For flat panel displays, which would be the next step for the technology, there are also considerable advantages. These include:

- Higher yield and productivity
- Low-temperature CNT deposition/printing limits out-gassing
- Fewer defects which can come from ITO sputtering and patterning
- Ability to process at ambient temperatures
- No vacuum deposition
- More environmentally friendly process- eliminates waste disposal of strong acid needed to etch for ITO
- Reduction in process steps
- flatter transmission curve
- better image quality
- conformal coatings on non-planar surface

Unidym has entered into a joint development agreement with a major liquid crystal display manufacturer to integrate CNT transparent conductive films into glass-based liquid crystal displays. Moreover, it is working with Samsung Electronics to integrate its conductive films into flexible displays.

Novel Display Technologies Although there is increasing activity to find alternative materials and processes in the display area, there is still opportunity for nanoparticle silver inks. LCD displays with silicon TFT backplanes don't use much silver, but the current market is not likely to change for several years. Furthermore, in the past year or so, new display technologies that use, or are highly likely to use, printed silver have begun to appear as real products in the marketplace. While the introduction of OLED TVs was stalled by the recession, these displays still hold great potential for the future. OLED TVs may have an important use for silver. The experience with large OLED panels is that long passes of current through transparent conductors result in voltage drops that appear visibly

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as dimmed portions of the OLED. Distances of more than 10 cm or so between electrical connections can be problematic. Using silver (probably nanosilver inks) for printing bus bars at appropriate intervals enables larger OLEDs without the dimming problem. Silver may also have a growing role as an electrode material. For OLEDs, both big ones and small ones this time, silver would have an advantage over the conventional cathode materials such as calcium, which are extremely sensitive to environmental conditions. Industry sources note that printed silver is being used for this application, but how extensive that use might become is still a question.

The larger potential in OLEDs is for conductive polymers. While there are some issues with the conductivity of such materials, in this application that becomes a benefit. In OLEDs, highly conductive materials tend to light up multiple pixels simultaneously. However, the display manufacturer wants to control the pixel light up. So here, conductive polymers, with a high resistivity, have an advantage.

Perhaps a bigger opportunity lies in backplane electrodes. Silver has been the favored electrode material for organic TFTs (OTFTs) in the lab and as these products approach commercialization, this lab scale use for silver may become a volume application.

Lighting Electroluminescent lamps represent an application for printed conductive polymers that is on the verge of implementation. While EL lamps are competing against other technologies, their thin form factor, ruggedness and energy efficiency are definite advantages. In this area, conductive polymers are making headway.

Plextronics and Novaled have agreed to jointly develop doped and solution processed organic materials for OLED applications. With its flexible design and energy efficiency advantages, OLEDs are expected to become a major component in flat displays, as well as drive a new era in lighting innovation. The specific focus of the collaboration will be to develop a solution processible Hole Injection Layer (HIL) for OLEDs. Lighting is another area where conductive polymers bring and advantage. In these applications, there is a large area of light on a sheet, and the ideal is to have the light to be homogeneous with the same look and temperature over the entire area. High conductivity is not suitable for such homogeneity.

Novaled doped HIL is a part of the company's PIN OLED® technology, which had shown both high power efficiency and long lifetime. By leveraging the two technologies, the companies aim to offer a solution processed HIL with the same performance as a Novaled doped small molecule HIL deposited in a vacuum process. In addition, Plextronics and Novaled will co-market Plexcore® OC inks that incorporate Novaled dopant materials.

Silver Opportunities Solid-state lighting is the wave of the future. Both U.S. and European energy efficiency legislation effectively bans the use of conventional incandescent light bulbs after 2012 or so. While fluorescent lighting technology will be the immediate

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successor to these bulbs, fluorescent lighting has issues. One is the use of mercury—which is a problematic heavy-metal—and there are quality issues with fluorescent lighting. So it would seem that the future belongs to solid-state lighting or more specifically inorganic LED and OLED lighting. OLED lighting panels, which are likely to become much larger than the OLED display market, will likely also require silver bus bars to create an even lighting effect.

Memory

Logic, i.e. memory and transistors, are slated to represent a large portion (about a third) of the emerging future printed electronics market. An essential part of most electronics, memory is required for identification, tracking status and history, and is used whenever information is stored.

There have already been breakthroughs in this area. Founded in 1997, Thinfilm Electronics ASA is a wholly owned subsidiary of Opticon. Working with Xaar, the company developed the first fully printed memory cell in 2006, and the first roll-to-roll printed memory tags in 2009. Most recently, Thinfilm Electronics and PolyIC GmbH & Co. have jointly manufactured fully functional re-writable polymer products in a high volume roll-to-roll printing process. The current printed memory consists of five printed layers: bottom electrode, memory film, top electrode, protective layer (passivation) and carbon contact pads. While the voltage generated is relatively low, the memory product is capable of meeting the low voltage requirements for consumer products such as toys and games. This is the area where Thinfilm sees its near-term commercial opportunities. The joint venture is also geared to address printed RFID applications.

Because its business strategy is licensing technology, Thinfilm has other production partners—Sologie in the United States and InkTec in Korea. In Korea, the bottom electrode is printed using gravure printing; the memory film is printed using micro gravure coating and the remaining layers are printed using rotary screen printing. Because InkTec's ink uses a proprietary silver complex compound, which is non-particle based, it has enabled roughness control and integrity of the printed memory film. Another important aspect of the silver complex compound is that most suitable solvents for the production of inks are entirely compatible with the printed memory film thereby avoiding shorts and the use of protection layers.

Thinfilm's non-volatile ferroelectric polymer memory technology is well suited for use with other printed electronics devices as power consumption during read and write is negligible, and during stand-by, no connection to external power is required. Data is retained without power consumption and the current required to write information is so small that operation using a standard battery would last years and likely be limited by the battery's own lifetime.

The technology is based on using a ferroelectric polymer as the functional memory material sandwiched between two sets of electrodes in a passive matrix – each crossing of metal lines defines a memory cell. The memory function is related to the orientation of the polymer chains. There are two different ways in which the polymer chains can be oriented, and each state is stable without

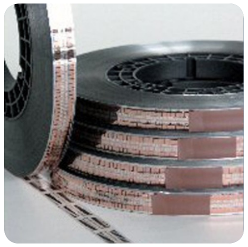

Figure 5.4 Roll-to-Roll printed re-writable memories on flexible substrate

Source: PolyIC

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the application of an external field. The technology is referred to as a non-volatile memory, and the intrinsic character of the polymer enables the technology to be scalable. Passive matrix allows for packing of high density memories as well as the possibility to stack memory layers on top of each other. The passive array memory architecture allows the memory portion to be separate from the read/write electronics enabling stand alone application without integration with printed logic.

Printed Batteries

Thin-film and printed batteries is an application area that offers great potential for printed electronics, particularly in smaller applications where size, form factor and higher cost of use limit traditional batteries. Companies engaged in the printed battery market are using proprietary technologies and materials they manufacture themselves to produce the batteries which they supply to customers who want a small thin power source embedded in the device. For example, using battery assisted passive (BAP) technology in RFID can deliver increased read range, as well as consistently higher read rates. BAP labels have an integrated power source so there is no need for energy from the reader to initiate the signal. Most of the development work in printed batteries originated at Oak Ridge National Laboratories and is the technology used by many companies offering printed batteries.

In many cases, the companies are not only printing the batteries, but the actual printed electronics product. For example, Power Paper has firmly established itself in the cosmetic patch market with a series of partnerships.

Table 5. 2 Leading printed battery manufacturers

CLICK TO VIEW TABLE

Radio Frequency Identification

From automatic toll collection booths to retail stores, managing supply chains, and much more, RFID promises to be a technology that can add great convenience to our lives, while reducing losses and automating processes. An RFID tag consists of an antenna, and a receiver (or transceiver). Although ultimately seen as a replacement for the ubiquitous bar code, RFID tags go well beyond barcodes in terms of functionality—in addition to containing a unique identification for the product, they can also contain information related to the supply chain processes that the product has gone through, instructions on the usage of product, price, and much more—limited only by the imagination of the innovator and of course, the capacity of the tag.

The vast majority of tags are passive tags—that is, they don't require a battery. Instead they get power from the electromagnetic field created by the RFID reader's signal. Generally, passive tags are what are being currently specified in retailer/end user specs. The alternative is active tags that contain their own batteries. Wal-Mart is perhaps the best known RFID user at the present time and is important partly because of its huge size and influence in the retail market, but also because the firm is pushing the RFID market towards larger volumes and more advanced technologies. Other large retailers such as Metro Group and the U.S. Department of Defense are also mandating RFID from their suppliers. While this area was thought to have great potential for printed electronics in general and conductive inks in particular, the prohibitive cost of

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RFID technology has kept it at the case and pallet level. Several companies such as GSI Technologies and Toppan Printing are printing RFID antenna, using silver conductive inks in high volumes.

PolyIC is the most visible producer of completed printed RFID tags, using roll-to-roll printing with organic (conductive polymer) inks. Cypak, in Sweden, has shown that conductive inks can be deposited onto paper boxes, and used to detect tampering. Organic ID, which is now a Weyerheuser company, recently announced fabrication of a simplified CMOS 13.56 MHz RFID device that includes much of the critical circuitry needed for an electronic product code (EPC)-compatible device.

There are applications for the concept of RFID other than the well-known label on pallets and packaging. A recent example involved collaboration between PolyIC and a leading mail-order group. The customer's catalog was tagged with a printed electronic ticket, which was activated when it came close to the customer terminal at a conference and began playing a movie of the catalog. The company has also demonstrated a coffee machine with contactless operation, thanks to printed radio chips, and an interactive marketing application. The next generation for such concepts is interactive games, where the printed playing card interacts with the player via an activator. A similar application involves tickets with interactive displays.

Next-generation PCBs/Switches

One of the key markets for silver inks in the past has been in printed circuit boards and membrane switches and the new nanoparticle silver inks will definitely find a role. Similar to many electronic areas, a key trend in the PCB industry is miniaturization. The miniaturization of electronic products continues to drive printed circuit board manufacturing toward smaller and more densely packed boards with increased electronic capabilities. In turn, PCB makers want to print very fine features via inkjet or other direct-write approaches. Another motivation for using printed silver in the PCB application is as a way to replace expensive/wasteful processes such as photolithography/etching, which are widely used in PCB manufacture. Finally, although silver inks will clearly have to compete with copper inks in this application, silver's higher effective conductivity would be regarded as an advantage where only fine lines were possible.

A similar area is printed membrane switches, where thick silver screen inks have been in used for many years. As these applications move towards thinner films, it will continue to provide a market for conductive inks.

Sensors

Printed sensors represent a unique opportunity for conductive inks. The sensor market as a whole is being driven by such trends as an aging population in industrial countries, the war against terrorism, and growing environmental concerns, resulting in significant fast growing markets. Printed sensors can potentially bring entirely new price points to markets such as smart packaging and point-of-care medical diagnostics; markets where there is a pent-up demand for cheaper sensor products, with printing promising significantly improved economics. Moreover, printing sensor arrays onto flexible

Figure 5.5 DuPont Microcircuit Materials introduces new conductive inks for printed circuit boards

Source: DuPont Microcircuit Materials

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Figure 5.6 Printing medical electrodes is a large potential market for conductive inks.
Source: Creative Materials

substrates brings with it the capability to create novel sensor array products for various applications such as smart textiles. Flexible sensors are a unique product that only printed electronics can create. It is an area where many of the products are unique. Currently it is the sensing layer that is printed, but potential all the components of a sensor could be printed.

Some Projects Already Underway There are almost endless examples of sensor projects underway and potential applications. Following are just a few cases.

Tekscan has developed a pressure measurement device to provide accurate, reliable data for a wide range of medical diagnostics applications. These sensor arrays are screen printed with metallic and plastic inks onto a flexible substrate.

VTT is involved in several projects to develop novel materials and processes for printing organic electronics. Under the BioOulu project, it is studying and developing methods, including printing, to manufacture inexpensive, disposable biosensors.

Fraunhofer Institute is involved in researching sensors consisting of pyroelectric and piezoelectric- polymers which can now be processed in high volumes by screen printing. The sensor is combined with a printed organic transistor, which strengthens the sensor signal.

GE is developing sensors that combine RFID tracking with an acute gas sensing capability, which can detect the presence of potentially harmful chemical agents in the air. Because these sensors can be made at a size smaller than a penny, they can be part of a typical identification badge and serve as a pre-emptive or early warning sign for people regarding the presence of chemical agents in the air. The sensors could also serve as an early warning sign for diseases by identifying volatile biomarkers associated with different types of diseases such as diabetes, lung diseases and metabolic disorders.

Start-up **Aneeve Nanotechnologies** is providing sensors which can help detect chemical imbalances for medical diagnosis, which may be able to help by providing consumer based easy to use sensors that detect estrogen and progesterone hormone levels in menopausal women.

Milone Technologies has developed a device which electronically measures the depth of liquid in a container. It is like an electronic tape-measure that, once submerged in a fluid or powder, emits a signal that is picked up by an electronic device or computer. The eTape™ incorporates a printed silver circuit and a small gold-plated solder tab connector (made using conventional printed circuit methods) encapsulated in a paper-thin PET envelop. The company is currently working on applications for consumer products, the medical industry where low cost, single-use products are required, and in industrial

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applications where non-fouling, reliable fluid level measurement

EMI Shielding

Electromagnetic interference (EMI) from unwanted electromagnetic fields can interrupt, obstruct, or degrade the effective performance of electronic devices. Vacuum deposition metals were traditionally used to provide EMI shielding, but these are susceptible to corrosion and delamination. In addition, metal screen EMI shielding is heavy, rigid, and does not exhibit uniform shielding over a range of frequencies. Alternatives for EMI shielding, which are more robust, lightweight and exhibit strong shielding across all wavelengths, are CNT-based inks applied to films, as well as transparent SANTE™ films from Cima Nanotech. EMI shields are used in plasma displays.

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Table 5.3 Current versus future materials for PE applications

Overall the market for conductive and semi-conductive inks looks bright for the future. There are many traditional applications which will continue for some time and there are potential uses that are emerging all the time. As improvements continue to be implemented for existing inks and breakthroughs emerge, many of the stumbling blocks to the expansion of printed electronics will be overcome. The materials, in particular the conductive and semi-conductive inks, that are needed for printed electronics are a significant factor in driving the industry forward.

6 Outlook to 2015

Introduction

Smaller, faster, lighter, cheaper—these are the device characteristics that are the goal for the electronics industry for the future. And while the industry is striving to achieve these goals with traditional materials and methods, increasingly it is evident that there is a need for both innovative materials and different manufacturing processes to provide solutions. As the electronics industry seeks a means of manufacturing that is lower cost and higher throughput, the advantages of printed electronics become increasingly attractive.

- Solution-based materials are less expensive than silicon
- Printing offers high-speed production at lower cost
- Flexible substrates enable roll-to-roll production and ease of use.

Materials in general and conductive inks and semiconductive inks in particular will play an increasingly important role in those advantages. As companies in the industry continue to think 'out-of-the-box' and seek to develop innovative solutions, rather than just improving existing materials, printed electronics will encroach into more and more electronics applications. While it may not happen as quickly as originally anticipated, there is a ground swell in the electronics industry pushing the expansion of printed electronics. Printed electronics will become a major part of our daily lives for the future. One of the continuing challenges to the use of conductive inks is the electronic manufacturer who does not really understand the capabilities and the limitations of printing methods. Real opportunities will arise as customers realize that there are new materials available that will enable new devices incorporating the capabilities of these inks.

However, as we look to discuss the outlook for the future, it is important to understand the realities of today. As the only printed material that has become mainstreamed, silver inks and pastes will continue to occupy a unique position in the printable electronics industry for some time. Applications such as membrane switches, automotive window and mirror heaters, capacitors, conductive tracks in PCBs, and conventional photovoltaics (not thin-film PVs) routinely use printed silver inks, as do certain classes of EMI shielding. In many of these instances, that silver is still screen printed with thick films. Given the large scale manufacturing base of both silver particles and inks and their widespread use, that is not likely to change for some time. Nanoparticle silver inks will find usage in more demanding applications and slowly replace these thick-film screen inks.

Smaller, faster, lighter, cheaper—these are the device characteristics that are the goal for the electronics industry for the future.

Silver's Advantages

Silver—whether paste or nanoparticle ink—still represents the largest supplier base in the conductive inks area. While there have been issues regarding silver prices, it is still the best conductor, and even the oxides that form on its surface are conductive. Moreover, given its history of use in the electronics industry, manufacturers have a deep understanding of the material and also how to handle Ag on the disposal end of those products mentioned above. The new silver nanoparticle inks offer considerable improvement over conventional silver inks and pastes, including the ability to print the fine lines needed for the new thin-film electronics. The small

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particles also enable the inks to be sintered at low temperatures, so they can print on flexible substrates. Furthermore, nanoparticle silver inks are likely to undergo improvements also, enabling them to continue to meet the changing needs of the printed electronics industry.

So, it seems apparent that silver pastes and inks, particularly the new nanoparticle inks that can cure at low temperatures have a future market potential. Many of the companies that have supplied traditional silver pastes and inks to the electronics industry are expanding their portfolio to include products that address the new printed electronics. Other companies, such as Xerox, are entering the space with the introduction of nanoparticle conductive inks.

Finally, there are additional start-up firms entering the field and finding sufficient funding. One of the indicators that the potential for printed electronics is strong is the continued availability of venture capital investment. Although investment activity in the economy in general has been tight since the global recession started, investors have continued to support the printed electronics sector—to the tune of more than $2 billion last year according to industry estimates.

When all is said and done, silver is still the best conductor there is, and despite competition from alternatives, it will find a place in printed electronics for some time to come. So the future outlook for silver is promising, at least for the next several years.

New Metallic Nanoparticle Inks
On the other hand, it is obvious that changes are underway. The dramatic increase in the price of silver is a growing issue, but perhaps more significant is the wide fluctuation of those prices. The electronics industry is definitely looking for alternatives in both conductive and semi-conductive inks and suppliers are developing and introducing innovative products. The introduction of copper inks will have a definite affect on silver, particularly in low-cost applications. Copper is around 10% of the cost of silver, yet it has approximately 90% of the conductivity. Its use as an ink was hindered by challenges, such as the tendency of copper to oxidize, but these have been overcome and multiple companies have introduced a nanoparticle copper ink that sinters at low temperatures so it can be used on flexible substrates. It is likely that more companies will also develop similar products.

As volumes of RFID antennas increase, these may move to nanoparticle copper inks from the current nanoparticle silver because of price considerations. The exception to that is the high end of the RFID market; where tags are used for animal tracking or inventory management of expensive items, These areas are less price-sensitive than item-level tagging of supermarket products, but also much lower value markets. A similar case is medical patches and medical imaging electrodes.

Semi-conductive Ink Breakthroughs Of equal, if not greater significance than the introduction of nanoparticle copper conductive inks, however, are the breakthroughs in carbon-nanotube semi-conducting inks. First discovered in the early 1990s,

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CNTs have also overcome the challenges that prevented their use in printed electronics. Their small size, as well as unique thermal and electrical properties will enable them to become serious contenders in many printed electronics applications including biological sensors, transistors, field emitters and integrated circuits with demand for mass production, high speed and efficiency. They are more conductive than conductive polymers and the use of CNTs is likely to expand in the near future. The immediate application for these inks is in a printed conductive film as a replacement for ITO in touch screens for today, and plasma displays for the future. Touch screens are an explosive market. In 2009, 606 million units were shipped, a 29% percent increase over the previous year. Manufacturing methods will continue to improve enabling consistent high quality product and the use of these inks will grow substantially for the future.

The potential for these materials cannot be over emphasized. Unseen and unnoticed, transparent conductive oxides play a major role in our daily lives. In computer monitors as well as other displays including touch screens, electric current needs to be transported invisibly to other places in the device. While ITO and related materials such as aluminum-doped zinc oxide and fluorine-doped-tin oxide have served well for many years, the trend toward flexible substrates is enormous. All of the above materials are brittle and tend to crack when bent. While ITO has been sputtered onto foils, these have a limited life. So alternatives must be found. Coupled with the ability to use printing methods in a roll-to-roll process, the advantages of these new materials increases to makes them extremely attractive products for future use in printed electronics.

Other Ink Improvements

The movement towards flexibility will also impact conductive inks. These too must be able to work with new substrates as they become more flexible, bendable and/or conformal. Different polymer binders will be needed to resist cracking, flaking and adhesion loss. There will also be more movement away from screen printing. For printed electronics to be truly economic, high-speed manufacturing methods must be implemented. For the short term, it will be inkjet, but for the long term, this means more flexo and gravure printing. It might also mean new additive processing methods. The problem with flexo and gravure compared to inkjet is the ability to print fine lines accurately, often in layers. There are new equipment options today, such as aerosol jet spray deposition, which offers high speed, yet fine resolution and control of the ink onto the substrate. It is interesting that UT Dots was formed in 2005 to commercialize 'Chemical Aerosol-Flow Synthesis' technology from the University of Illinois at Urbana-Champaign. While its nanoparticle silver inks can be used with inkjet, the company says they are best suited to aerosol jet spray printing produced by Optomec.

And finally, the nanoparticle inks are already enabling expanded use of printed electronics in thin-film applications. These new inks offer performance at a lower cost. Because it is the surface of the material that is responsible for the conductivity, the larger surface area with these nanoparticle inks enables the same conductivity using less material. The smaller particles also enable sintering at lower temperatures, which is an additional benefit, especially with the move towards flexible substrates.

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Conductive Polymers

Organic materials were originally thought to be best solution for inks for printed electronics. However, there are still issues with their conductivity. While improvements are in development, there are areas where the high resistivity of conductive polymers serves them well, for example in lighting and OLED displays.

While electroluminescent lamps are competing against several other technologies such incandescent bulbs, fluorescent tubes and inorganic light emitting diodes, they offer advantages that cannot be dismissed. Principal among these is their thin form factor (less than 1 mm). Coupled with their energy efficiency and ruggedness, they are already being used in cell-phone keyboards and instrument panel backlighting in automobiles. This is an application where conductive polymers are beginning to make breakthroughs. Conductive polymer inks meeting the requirements of EL lighting are already available. It is an area where the use of conductive polymers shows great promise.

Because display manufacturers want control over the individual pixels which create color, higher conductive metals, which can often cause multiple pixels to light up simultaneously, are not always a good fit. This is where the high resistivity of conductive polymers is a better choice.

Conductive polymers are also making some inroads in solar applications. Plextronics offers its Plexcore PV ink system, which can increase the efficiency of solar cells through its implementation. Other applications are under development. It is apparent that significant cost and time savings could be realized if transistors or indeed entire electrical circuits could be printed. These goals might be possible if the necessary materials can be made solution processable, which would enable them to be printed. Conductivity in these materials is improving all the time, and thus conductive and semi-conductive polymers could play important role in future printed electronics. PolyIC, a manufacturer of printed electronics, manufactures its own materials as well as producing its own devices. Conductive polymers are the material used in the company's commercial products.

Figure 6.1 Mile long printed logic circuits for RFID tags

Source: PolyIC

Environmental Considerations

Aside from all the drivers for faster, smaller, lighter, and cheaper in the electronics market there are additional issues as the industry moves towards the future. Concern for the environment and the increasing movement towards sustainability are important considerations for any industry today. Because printing is an additive process, compared to traditional subtractive etching processes that are currently used for manufacturing electronics, there is considerable savings of waste involved. Coupled with the cost savings of less waste, this could be a significant factor moving forward as environmental legislation continues to become more restrictive. In addition, many of the new materials are chemically synthesized, so there are no issues with the use of natural resources. This is particularly important in the area of photovoltaics, which uses energy from the sun, so it is a renewable and sustainable process. Consequently, printing electronics for the future may become more of a requirement than a 'nice to have' method of manufacture. This push will also expand the use of inks of all types that will be needed for that printing.

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Industry Standards

One of the changes that are likely to occur in the industry within the next several years is the beginning of industry standards or specifications. Currently, many of the products are custom formulated based on a range of variables such as end-use application, printing process to be used, substrate materials etc. This acceptable for now, because the industry is still young and very diverse and still in a research mode to determine which method is best to accomplish a result. However, as the industry expands, a list of best practices and industry specifications for various end markets will begin to evolve. As the business begins to grow, there will not be sufficient lead time to develop new products for each project, so electronics manufacturers will have to rely on existing products and processes to get their product to market quickly. However, this evolution is further down the road as the printed electronics industry increases product commercialization.

Industry Partnerships

An important consideration when discussing printing materials on large areas is the issue of reliability. Consequently, cooperation between material manufacturers, substrate suppliers, device and tool manufacturers and OEMs has become an essential part of the process. Printed electronics is a diverse market and many suppliers have found that the key to success lies in partnerships. The companies involved in developing conductive and semi-conductive inks are increasingly working with potential customers to develop the materials needed for specific applications and test them in real world conditions. The partnerships are also indicative of another trend—that of integration of systems, for example polymer solar cells combined with printed batteries; e-paper devices powered by printed solar cells; or devices combined with printed sensors.

It would be impossible to mention all of the partnerships, but industry news is filled with such announcements.

- ANI is working with Arima Eco Energy Technologies to improve solar modules.
- CimaNanotech partners with Toray Industries of Japan to mass produce SANTE film; Xaar, Cima and Imaging Technology International (iTi) develop inkjet material deposition system for conductive inks.
- Unidym's enters JV with Wisepower in Korean display market; JV with major LDC mfg to incorporate CNT-based films into displays; JV with LG Display.
- H.C. Starck enters cross-license agreement with Agfa-Gevaert
- Plextronics is a founding member of United States Center for Energy Leadership (USCEL) to establish stable energy environment for US; collaboration with Novaled on development of organic lightning technology; Plextronics and NTERA demonstrate Solar-Powered NanoChromics™ Displays

Ongoing Research

While companies in the conductive and semi-conductive area are involved in research and development, there is also intense work going on in universities and research centers around the world. Clearly, there is a push to improve existing materials and processes and develop new ones to expand the use of printed electronics.

Many of the innovative products that have been introduced into the marketplace were first discovered in research institutes and universities. Countless start-up companies such as Nantero, South West NanoTechnologies, and Vorbeck Materials were spun out from academic research.

Some of the work that is ongoing includes:

- Holst Centre, Netherlands, gathers suppliers from the industry to work in its pilot-production roll-to-roll line for printed electronics. This type of collaboration allows defining open standards and smart interconnect technologies that will allow manufacturers to easily combine foils into end-products.
- University of Cape Town, South Africa, is researching printed silicon using screen-printed, water-based acrylic inks to create printed silicon systems.
- Rice University is working on refining and sorting nanotubes so ink can be produced, without the costly and difficult sorting step, enabling unsorted nanotube circuits to be ink-jet printable without presorting. The method inkjets unsorted nanotubes in layers. Controlling the layers enables control of the conductivity.
- H.C. Starck Clevios has launched a project called 'New materials for OLEDs from solutions' (NEMO) together with Merck KGaA and other renowned partners from industry and science.
- Stanford University researchers have shown that the way boundaries between individual crystals in a film are aligned can make a 70-fold difference in how easily current, or electrical charges, can move through transistors.
- Sunchon National University, South Korea is exploring single walled carbon nanotube-based thin film transistor using gravure printing.
- Welsh Centre for Printing and Coating, UK is examining how to improve resolution of flexo printing for R2R for electronics.

Summary

There is no doubt that the economic recession slowed the progress of printed electronics, and in turn the business of conductive and semi-conductive inks suppliers. While the sector did not suffer as some industries, it was a challenging time. However, better times seem to be approaching and industry sources are optimistic for the future outlook.

There is a tremendous amount of research and pilot projects, although volume manufacturing is still rather a niche area. There is also evidence of major consumer goods companies, security companies, games and toy manufacturers becoming more interested in getting started in PE. Suppliers are looking to work with such customers to develop realistic prototypes that will be compelling for consumers. The consumer is the key in much of the outlook for the future. One industry source noted that the smart cell phone market is exploding in part because of consumer demand. Until that happens in other areas such as smart packaging, it will not become a reality. The technology exists, but the impetus to

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commercialize the technology has not yet come.

While organizations continue to see printed electronics technologies as a source of enabling technology for applications ranging from energy generation and storage to consumer-level sensors and displays, the development cycle to take technologies all the way to marketed products is rather long. There are several reasons for this—economic considerations, but also because in many cases the printed electronics technologies being incorporated are still new.

'New technologies being used in new products is a recipe for an extended commercialization program,' noted a conductive ink supplier. Some applications will commercialize before others, but industry sources feel the challenges will eventually be overcome. Regardless, there has been forward movement for some time and new products enabled by printed electronics will begin to commercialize in the next several years. If industry forecasters are on the mark, printed electronics is poised for major expansion.

CLICK TO VIEW TABLE

Table 6.1 Summary of the outlook for conductive and semi-conductive inks, 2010-2015

Table E.1 Suppliers of metallic conductive inks

Company	Technology	Applications
Advanced Nano Products	Silver inks	Electrodes displays, RFID.
Applied Nanotech Holdings	Nanoparticle silver, copper aluminum and nickel-based inks	RFID, smart labels, electronic paper disposable electronics on paper, solar electrodes
Cabot	Silver particles and inkjet ink	Front grid electronics, displays
Cima NanoTech	Organic coated nanoparticle silver and copper inks Self-aligning nanotechnology for electronics (SANTE™) film	RFID tags and front electrodes for solar cells SANTE™ film used in flat panel displays, touch screens, OLEDS, organic EL
Creative Materials	Silver inks for screen, pad printing and flexo Medical grade and translucent conductive inks	RFID antennas, membrane switches Medical electrode Printed EL panels
DuPont Micro Materials	Range of silver and silver nanoparticle inks	Touch screens, RFID, Medical electrodes
Ferro	Silver powders, not inks	RFID, backplanes
Five Star Technologies	Silver inks and pastes	Displays and touch screens, solar cells
Harima Chemical	Silver paste	PCB
Hitachi Chemical	Copper nanoparticle inks	RFID
Ink Tec	Transparent silver inks; silver nanoparticle inks for inkjet, flexo and gravure	RFID, Touch screens, EMI Shields
Intrinsiq Materials	Nanoparticle silver and Copper inks	RFID
Nano Mas	NanoSilver™ and NanoGold™, dielectric inks	RFID, displays, PCBs, EM shielding, EL lighting
NovaCentrix	Metalon silver nanoparticle inks and copper oxide inks PulseForge™ tools to sinter inks	RFID, Displays, PVs, Medical, smart cards
PChem Associates	Nanoparticle silver for flexo and gravure Working on transparent conductive films	Electronic game cards, RFID antennae, sensors, smart packaging. Displays and solar applications, EMI shielding.
Sun Chemical	Silver, aluminum nanoparticle inks for screen and inkjet	Photovoltaics, Displays
SunRay Scientific	Silver inks, and dielectrics, NANOGLOW™ nanoparticle inks for flexo and gravure	RFID, Displays, Sensors, PVS, smart textiles
Taiyo-Ink America	Solder masks; dielectric and silver screen and nanoparticle inkjet inks.	Membrane switches, solar cells, touch panels
Toyo Ink Group	REXALPHA™ silver pastes for screen, flexo and gravure printing. LIOMETAL™ nanoparticle silver inks.	RFID, Displays
Xerox	Silver Inks	Smart packaging, display screens

Source: Pira International Ltd.

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Table E.2 Suppliers of conductive polymers

Company	Technology	Applications
HC Starck	Liquid conductive polymers, under product name Clevios™.	Key component for the flexible and flat-panel displays..
Panipol	Coating systems/conductive inks	Smart packaging, RFID, OLED displays.
Plextronics	Plexcore® PV ink system Plexcore® OC organic conductive ink Plexcore® OS organic semiconductive polymers	Solar Cells Phone displays, smart labels, POP signage, OLED displays, printed memory, sensors, smart textiles.

Source: Pira International Ltd.

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Table E.3 Carbon-based ink suppliers

Company	Technology	Applications
CNanoTechnology	CNT, which can be formulated into inks	Most PE applications
Eikos	CNT-based inks, Invisicon™ conductive films	Touch screens, EM Shielding
Nantero	IP company licenses CNT technology	Printed memory
SouthWest NanoTechnologies	CNTs and CNT-based inks	Lighting, photovoltaics, touch screens
Unidym	CNT inks and films	Transparent electrodes for touch screens, flat panel displays, solar cells and solid-state lighting
Vorbeck Materials	Graphene, Vor-x™ ink for screen, gravure and flexo printing	RFID antennas, smart cards and smart packaging

Source: Pira International Ltd.

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Table E.4 Suppliers of silicon-based ink products

Company	Technology	Applications
Innovalight	Cougar™ platform using inkjet printed silicon-based inks.	Increase efficiency of solar cells.
Kovio	Inkjet printed silicon ink.	HF integrated circuits with memory for RFID.
Nano Gram	Silicon inks and SilFoil™solar cells.	Photovoltaics. Future transistors for display backplanes

Source: Pira International Ltd.

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Table E.5 Comparison of printing processes for printed electronics

Process	Advantages	Disadvantages
Lithography	High resolution High throughput	Low ink film thickness Ink almost pastelike
Inkjet	High resolution Accurate and precise Good ink film thickness (~0.1 µm) Many suppliers working on materials and processes Ability to create in small volumes	Low throughput
Screen	Thick ink film (100 µm)	Low throughput
Flexography	Good ink film thickness (3-8µm) Fair resolution, High speed	Resolution could use improvement.
Gravure	Very high speed, Good ink film thickness (2-5µm)	High cylinder costs

Source: Pira International

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Table 2.1 Metallic ink manufacturers

Company	Technology	Applications	Activity notes
Advanced Nano Products	Nano Silver inks	Electrodes	Can be applied via screen, gravure, flexo and micro-contact printing.
Applied Nanotech Inc. *	Nanoparticle silver, nanoparticle copper, nanoparticle aluminum and nanoparticle nickel inks	RFID, smart labels, electronic paper and disposable electronics on paper. Narrow electrodes for Solar cells	Revenues up 22% for 1Q 2010 over 1Q 2009. Working with Arima Eco Energy Technologies to improve solar modules. Developed copper ink for aerosol deposition and inkjet printing for flexible substrates.
Cabot	Silver particles for ink formulation. CCCI-300 Silver inkjet ink.	Front grid electronics, displays	In 2003, Cabot materials were used for the first fully functional, inkjet printed, plastic electronics, active-matrix display. There has been little news since on the PE front.
Cima NanoTech *	Organic coated nanoparticle silver and copper inks. Metallic nanoparticles for ink formulation. SANTE Film	RFID tags and front electrodes for solar cells. SANTE film used in flat panel displays, touch screens, OLEDS, organic EL.	Partnership with Toray Industries of Japan to mass produce SANTE film. Xaar, Cima and Imaging Technology International (iTi) develop inkjet material deposition system for conductive inks. Partnered with Motorola to develop RFID components.
Creative Materials	Conductive inks for screen, pad printing and flexo. Medical grade conductive ink. Translucent conductive ink.	RFID antennas, membrane switches. Medical electrode applications such as transdermal drug delivery. Printed EL panels	A long time supplier of conductive inks to the electronics industry, the company recently introduced products for fine line printing and medical electrodes.
DuPont Micro Materials	Range of silver and silver nanoparticle inks	Touch screens, RFID, Medical electrodes	Major supplier of all types of silver inks for all applications.
Ferro	Silver and nanosilver powders, not inks Dielectrics	Conductive inks	Largest supplier of silver powders for conductive inks.
Five Star Technologies	Silver inks and pastes ElectroSperse S-series for thin-films.	Displays and touch screens, sensors. Front surface contact in photovoltaics.	Developing new generation of front contact inks for non-contact printing methods.
Harima Chemical	Silver paste and nanopaste for inkjet.	PCB	In main, solder manufacturer. Now supplies silver and nanopaste inks.
Hitachi Chemical *	Copper nanoparticle inks.	RFID.	Copper ink can be printed using inkjet. No dispersants needed and low-temp curing
InkTec	Transparent non-particle silver inks for microgravure. Silver nanoparticle inks for inkjet, flexo and gravure. Also provides print services.	RFID, Touch screens, EMI shields	Delivered silver (Ag) paste ink to China for 20 million mobile phones. JV with SD Flex to develop EMI shields. Printing memory in collaboration with Thin Film Technologies.
Intrinsiq Materials *	DC plasma process enables advanced materials including copper inks. Nanoparticle silicon, aluminum and nickel to come		Secured rights to low temperature route to making nanoparticles, which is complementary to company's high temperature DC plasma processing platform. Production quantities will be soon be available as production scaling is implemented.
Nano Mas	NanoSilver™ and NanoGold™, dielectric inks.	RFID, displays, PCBs, EM shielding, EL lighting	Little news since early 2009.
NovaCentrix *	Metalon silver nanoparticle inks and copper oxide inks. Pulse Forge Equipment	RFID, displays, PVs, medical.	Pulse Forge 3300 model Equipment enables mass production of nanoparticle inks.
PChem Associates	Nanoparticle silver for flexo and gravure	Electronic game cards, RFID antennae, sensors, smart packaging. Future-transparent conductive films for display and solar applications, EMI spray shielding.	Dowa Electronics Materials acquires exclusive sales rights in Japan and the Asian region for silver conductive ink developed by PChem
Sun Chemical	Silver, aluminum nanoparticle inks for screen and inkjet.	Photovoltaics, displays	Major supplier of graphic arts and conductive inks, opens clean room in its Carlstadt, NJ, research center for PE R&D. Strategy is to deliver value for customer's current process, as well as target future innovations.
SunRay Scientific	Silver inks, dielectrics, NANOGLOW™ nanoparticle inks for flexo and gravure. ZTACH ™ anisotropic conductive adhesives	RFID, Displays, sensors, PVS, smart textiles.	Longtime supplier to electronics industry, expanding into nanoparticle silver inks.
Taiyo-Ink America	Solder masks; dielectric and silver screen and nanoparticle inkjet inks.	Membrane switches, solar cells, touch panels	Long time supplier of conductive inks, recently expanded product line.
Toyo Ink Group	REXALPHA™ series of conductive silver paste products for screen, flexo and gravure printing. LIOMETAL nanoparticle silver inks.	RFID, Displays.	Major ink manufacturer for electronics and graphic arts.
Xerox	Silver Inks	Smart packaging, display screens	The ink was introduced in late 2009.

Source: Pira International Ltd.
*Note: * Next to the company name indicates that it also supplies copper inks.*

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Table 2.2 Carbon-based ink suppliers

Company	Technology	Applications	Activity notes
CNanoTechnology	CNT, which can be formulated into inks.	Most PE applications	Commissioned the world's largest carbon nanotube production line in China. Partnered with Marubeni Information Systems for distribution in Japan.
Eikos	CNT-based inks, Invisicon™ conductive films	Touch screens, EM Shielding	Part of NIST program to demonstrate commercially viable large scale, low cost length separation of carbon nanotubes
Nantero	IP company who licenses CNT technology.	Printed memory.	Partner Brewer Science is manufacturing inks for conductive film. Also working with HP to develop CNT inks.
SouthWest NanoTechnologies	CNTs and CNT-based inks for screen, gravure and flexo. Working on CNT conductive films	Lighting, photovoltaics, touch screens	CNT-inks based on V2V™ ink technology developed at Chasm Technologies. Working with Brewer Science on conductive coatings. Capable of mass production at low cost.
Unidym	CNT inks and films	Transparent electrodes for touch screens, flat panel displays, solar cells and solid-state lighting. Future TFT for backplanes.	CNT-based touch screen displayed in MP-4 player at China exhibition. JV with Wisepower in Korean display market. JV with major LDC mfg to incorporate CNT-based films into displays. JV with LG Display.
Vorbeck Materials	Graphene, Vor-x™ ink formulated for screen, gravure and flexo printing.	RFID antennas, smart cards and smart packaging, illuminated displays, sensors	Receives EFP approval to manufacture graphene as additive in inks. JV with BASF. Has capability for mass manufacture.

Source: Pira International Ltd.

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Table 2.3 Suppliers of conductive polymer products

Company	Technology	Applications	Activity notes
H.C. Starck	Liquid conductive polymers, under product name Clevios™.	Key component for the flexible and flat-panel displays.	Cross-license agreement with Agfa-Gevaert which covers PEDOT-PSS materials. Participates in NEMO (new materials for OLEDS) project
Panipol	Coating systems and conductive inks Polyaniline – non-conductive emeraldine base form as well as conductive polyaniline salt (both dry powders)	Smart packaging, electronic stamps, RFID, OLED displays, intelligent paper.	Inks have been used with flexo and gravure printing. Screen printable inks for EL applications.
Plextronics	Plexcore® PV organic photovoltaic ink system Plexcore® OC organic conductive ink Plexcore® OS organic semiconductive polymers	Solar Cells, mobile phones, smart labels, POP signage, field effect transistors, Flexible OLED displays, printed memory, sensors, smart textiles. s	Founding member of United States Center for Energy Leadership to establish stable energy environment. Collaborated with Novaled on development of organic lightning Plextronics and NTERA demonstrate solar-powered NanoChromics™ displays. Plexcore OC improves performance of P-OLEDs

Source: Pira International Ltd.

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Table 2.4 Suppliers of silicon-based ink products

Company	Technology	Applications	Activity notes
Innovalight	Cougar™ platform adds screen printing of silicon ink to solar cells; inkjet inks in development.	Increase efficiency of solar cells.	Achieved record 19% conversion efficiency with cells processed with silicon ink. Chevron testing seven solar cell technologies, including Innovalight for its facilities. JA Solar developing silicon ink-based solar cells in China; commercialization planned for late 2010.
Kovio	Inkjet printed silicon ink.	HF integrated circuits with 128 bits of printed read-only memory for RFID. Future- TFT for backplanes in LCD, OLED and eBook displays.	Raised $20 to begin volume shipments. JV with Nissan Chemical Industries, who will supply silicon ink for its Kovio's RF products. NCI to commercialize silicon ink-based products in Asian display industry.
Nano Gram	SilFoil™solar cells. Silicon inks based on its proprietary laser pyrolysis process.	Photovoltaics Future- Transistors for display backplanes	Structuring NanoGram Solar. A 5MW line is due in 2010 for pre production devices, with a 50MW line to follow next year. JV with Tijin to develop silicon ink printed transistors. JV with Tokyo Electron to develop deposition tools for photovoltaics.

Source: Pira International Ltd.

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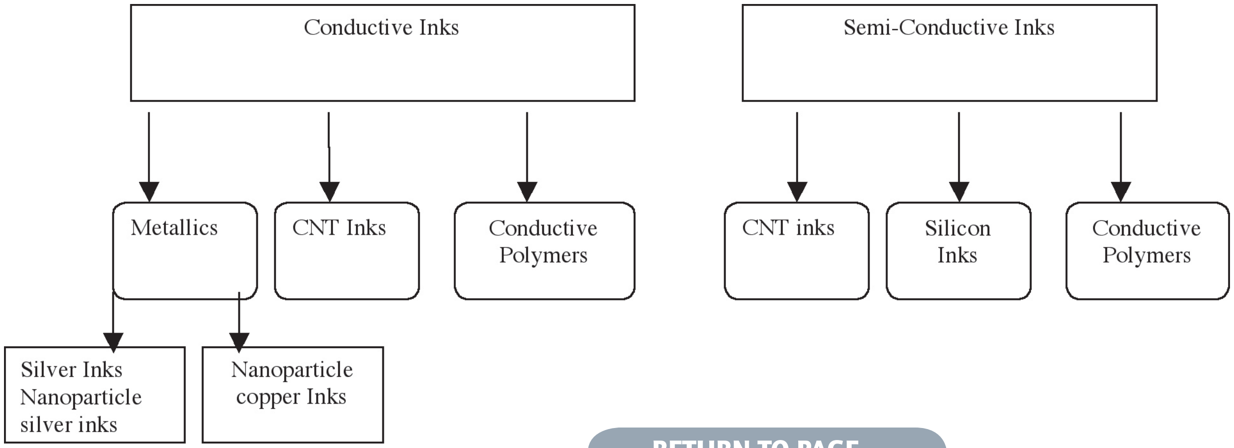
Figure 3.1 Technology map showing available conductive/semi-conductive inks



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Source: Pira International

Table 3.1 Copper nanoparticle inks currently available

Company	Product notes
Applied Nano Technology	Proprietary technology enables sufficient numbers of copper with pre-designed properties. Careful choice of vehicles and dispersants. Can be sintered at low temperatures by electromagnetic irradiation, for example using a laser. Able to be manufactured with good stability in air without the need of exotic inert gases. Inks have a drying temperature less than 100 °C. Broad range of viscosities, dispersants, additives and copper loadings.
Hitachi Chemical	Ink jettable copper ink. Does not need special environment. Electrostatic repulsion of nanoparticles is said to be 10-100m, so the ink is dispersant free. No surfactants are present in the ink, so it can be sintered at low temperatures (below 180°C), yet it is said to have the same level of reliability as copper foil.
Intrinsiq	Most recent introduction. Intrinsiq CI is a stable 12wt% copper ink formulation designed for photonic curing at room temperature in air. The nanoparticle copper inks can be printed on various substrates such as paper, polyimide and FR4 (grade of fiberglass widely used as an insulator for printed circuit boards). The resultant conductivities are comparable to commercial silver inks with significantly higher metal loadings. Production quantities will be soon be available as production scaling is implemented.
Cima Nanotechnologies	Copper nanoparticles are organic coated to prevent agglomeration. Can be printed with inkjet Solvent and aqueous dispersions, with up to 60% solids. Dispersions similar to graphic arts formulas; surfactants, binders, additives can be added to desired properties.
NovaCentrix	Copper oxide ink consists of copper oxide (CuO) and a reducer. Company also manufactures Pulse Forge System to process/sinter metallic inks. Both inks and system are scalable for volume manufacturing.

Source: Pira International Ltd.

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Table 3.2 Carbon-nanotube inks currently available

Company	Product Notes
CNano Technology	Proprietary technology overcomes issues with CNT surface chemistry and their tendency to agglomerate and enables CNT to be distributed into variety of mediums, including liquid, polymer, metal and ceramics. Produces CNTs, not inks, but offers dispersion guidelines for customers. Has a catalytic technique for continuous production of carbon nanotubes with tonnage capacity.
Eikos	Water-based CNT inks. Solids content, surface tension and viscosity can be tailored for specific substrate, target conductivity and transparency. Gravure, inkjet, spray deposition can be used to apply inks. Invisicon™ conductive transparent films. Formulates specialty inks for hydroscopic or reactive substrates or high temperature coating processes.
Nantero	IP company who licenses CNT technology.
SouthWest Nano Technologies	CoMoCAT® catalytic method produces single-wall nanotubes of high quality at very high selectivity, with a narrow distribution of tube diameters. Selectivity rate is 90%. Process is readily scalable. Carbon Nanotube inks based on V2V™ technology developed at Chasm Technologies. Inks can be printed with screen, gravure, and flexography.
Unidym	Uses fully-scalable, and proprietary chemical vapor deposition (CVD), a plasma enhanced chemical vapor deposition (PECVD)production process and HIPCO® - (High Pressure Carbon Monoxide) process, CNTs are manufactured. Solution processing methods such as coating and high volume printing processes used to print CNT inks printed into conductive film for touch screens and flat panel displays. Developing thin film transistors for PE and the emerging flexible display market.

Source: Pira International Ltd.

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Table 3.3 Comparison of surface resistivity (ohm/sq)

10^{16}	Plastics
10^{14}	
10^{12}	Antistatic
10^{10}	
10^{8}	static dissipative
10^{6}	
10^{4}	Conductive composites
10^{2}	Carbon based inks
10^{0}	Vor-ink™
10^{-2}	
10^{-4}	metals
10^{-6}	

Source: Vorbeck Materials

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Table 3.4 Conductive polymer inks currently available

Company	Product Notes
H.C. Starck	CLEVIOS™ electro-conductive polymers based on thiophenes to be used as conductors and semi-conductor inks. The product is a waterborne dispersion of the polymer complex poly(3,4-ethylenedioxythiophene)/ polystyrene sulfonate (PEDT/PSS). The dispersion consists of submicrometer sized gel particles which upon drying form a continuous film which is conductive and transparent. The coatings may be applied by conventional coating methods such as brushing, spin-coating, printing processes, spraying, dipping, and roller-coating techniques. Other binding agents may be added. Conductivity (or surface resistance) of the coating depends on the concentration of the conductive polymer in the formulation, amount of conductivity enhancers, the binder content and the conductivity of the specific polymer type used. When coating the same layer thickness, the surface resistance of the coating will depend
Panipol	Polyaniline powders which are partly soluble in toluene and xylene. Inks based on the powders. There are several systems available. The solvent systems include: Panipol T, polyaniline in toluene; Panipol X, polyaniline in xylene; Panipol M, polyaniline in NMP (n-methylpyrroldinone); and Panipol L, polyaniline in DMSO (dimethylsulfoxide). These materials contain just the solvent and doped polyaniline. Typical polyaniline concentrations are between 1-10 %. Normally there are no binders included into these coating systems. Those binders are typically selected case by case depending on the application. Panipol W is a dispersion of conductive polyaniline in water, with various dopant options. Pani W may be diluted down to desired concentration simply by adding water-many so called water based systems do not allow this. Plasticizers such as DOP, DIDP and DINP have been made conductive with polyaniline. Transparent coatings, with various shades of greenish color, can be made by varying layer thicknesses and solution concentration.
Plextronics	Plexcore® PV organic photovoltaic ink system, a ready-to-use ink system that consists of a p/n photoactive ink and a custom-designed hole transport ink that are solution-processable. Plexcore® OC organic conductive ink, a multi-functional conductive material compatible with a number of printing techniques including spin-coating, ink jet printing, and contact printing. The inks are customizable to possess a wide variety of film properties, dependent upon its desired function and performance requirement. Plexcore® OS organic semiconductive polymers, a p-type organic semiconductor designed to deliver superior charge transfer control for high-volume production of printed circuitry and power applications. Based on polythiophene chemistry, Plexcore® OS is readily formulated into printable inks with tailored material properties for a wide range of electronic applications. Plextronics has capabilities to provide the materials in volume quantities.

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Source: Pira International Ltd.

Table 3.5 Comparison of conductivity of conductive polymers with other materials

10^{6} 10^{4} 10^{2} 10^{0}	Metals- Silver Copper Iron Mercury	*Shows typical conductivity range of coating materials based on conductive polymer technology.*
10^{-2} 10^{-4} 10^{-6} 10^{-8} 10^{-10} 10^{-12}	Semi-conductors Germanium Silicon	
10^{14} 10^{-16} 10^{-18}	Insulators- DNA Sulfur Quartz	

Source: Panipol

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Table 3.6 Silicon inks currently available

Company	Product Notes
Kovio	Introduced the world's first all-printed high-performance silicon thin-film transistor (TFT), a key building block for electronic devices. With mobility of 80cm^2/Vs, the TFT significantly exceeded the performance of previously all-printed TFTs using either organic or inorganic semiconductors. Developed the world's first silicon ink-based RFID tag and the company's printed silicon RFID platform for item-level intelligence. Products based on this patented platform technology were printed silicon HF integrated circuits (PICs) with 128 bits of printed read-only memory. Included in the PICs features are a synchronous tags-talk-first mode of operation, a 106kbps data rate, an integrated capacitor, and printed read-only memory. The integrated circuits were digitally printed on an ultra-thin foil substrate. JV with Nissan Chemical for commercial manufacture of silicon ink technology. Plans to make complete devices, not just sell inks.
Innovalight	Developed silicon inks for inkjet printing. Have over 60 patents at various stages of patent process. Focused on solar energy, so as to accelerate the commercialization of its technology. Working closely with leading research institutions, including the United States National Renewable Energy Laboratory (NREL). Demonstrated record 18 percent conversion efficiency with its silicon-ink processed solar cells. The industry standard size solar cell results were independently certified by two of the world's recognized solar cell testing centers, the U.S. Department of Energy's National Renewable Energy Laboratory (NREL) and The Fraunhofer Institute for Solar Energy Systems (ISE) in Germany. The company expects to boost efficiency to 20%. JA Solar Holdings Co., Ltd.), working to commercialize a new generation of high-performance solar products using silicon ink technology from Innovalight, Inc.
Nano Gram	NanoGram silicon inks for printed electronics are based on its proprietary laser pyrolysis process. NanoGram has developed processes to make large area, thin layers of silicon through printing nano-Si based inks. Technology passed mobility of amorphous silicon; believes that mobility in the range of >100cm2/Vs. Sintering temperature of the printed transistors is proprietary, however, NanoGram is working with Teijin, a plastic substrate supplier as a partner Target devices are solar cells and transistors, for application in display backplanes.

Source: Pira International Ltd.

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Table 3.7 Comparison of aerosol jet deposition versus thick-film screen printing and inkjet printing

Versus Thick Film Screen	Versus Inkjet Printing
Up to 10X finer features and pitch	>5X finer features
Higher volumetric tolerances, i.e., embedded resistors w/o laser-trim.	20-30X higher yield per nozzle; higher volumetric rates & metal loading.
Higher yields, i.e., pressure of screen-print can break fragile solar wafers.	Supports more materials, including high viscosity commercial pastes.
Better uptimes, i.e., aerosol jet multi-nozzle uninterrupted runtimes >24 hours.	Better Edge Definition
	Better uptimes, i.e., no clogging.

Source: Optomec

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Figure 3.5 Aerosol spray jet technology versus inkjet

Source: Optomec

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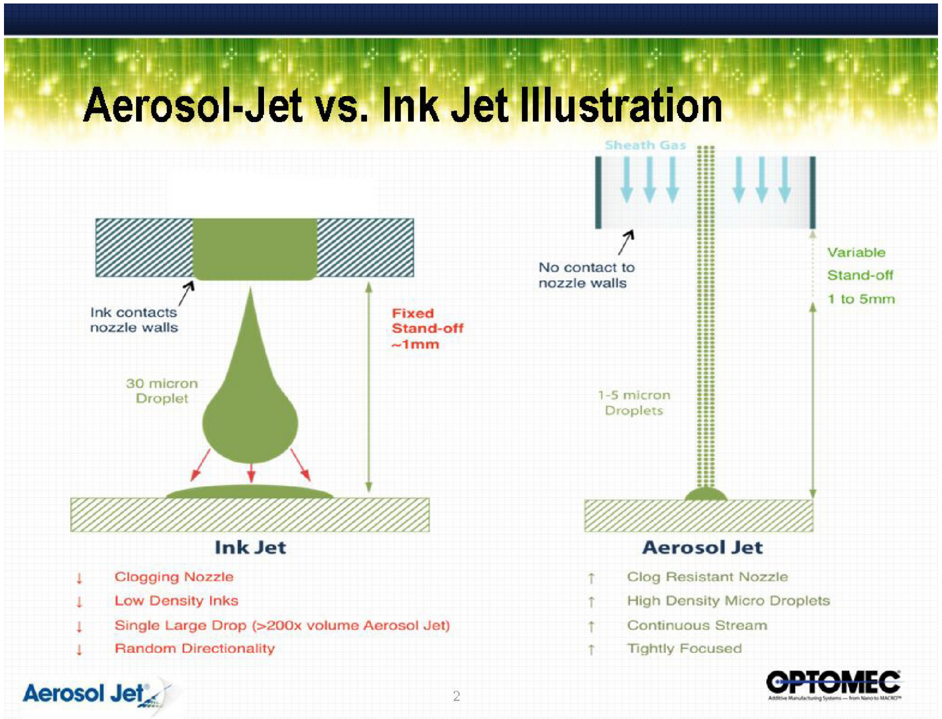
Figure 3.6 Diagram of Optomec aerosol spray deposition system



Source: Optomec

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Table 4.1 Graphic arts inks compared to conductive inks

Graphic Arts Ink	Conductive Ink
Pigment for Color	Conductive material
Resin/varnish in which pigment is suspended	Retaining matrix
Additives	Additives
Dried by thermal or infrared driers	Require sintering after printing

Source: Pira International

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Table 4.2 Comparison of silicon ink manufacture

Company	Technology
Innovalight	Radiofrequency plasma technology
Kovio	Layering silicon with nanoparticle powder
NanoGram	Nano Particle Manufacturing and laser deposition

Source: Pira International

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Table 4.3 Guidelines for CNT dispersion

High Viscosity	Medium Viscosity (e.g., polyols or epoxide prepolymers)	Low Viscosity, e.g., water or organic solvents
Melt impregnation	Three roll mill	Jet Disperser
Solvent impregnation.	Torus mill.	Ultrasonic treatment
In-situ polymerization	Ultrasonic treatment can be suitable if viscosity is lower three roll mill or a torus	Surfactants such as sodium dedocyl sulphate (SDS), dodecylbenzene sulfonate. (NaDDBS) are needed.

Source: CNano Technology

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Table 4.4 Comparison of resistivity of various conductive materials

Surface resistivity ohm/sq	Material
10^{16}	Plastics
10^{14}	
10^{12}	Antistatic
10^{10}	
10^{8}	Static Dissipative
10^{6}	
10^{4}	Conductive composites Carbon-based inks
10^{2}	
10^{0}	graphene
10^{-2}	
10^{-4}	metals
10^{-6}	

Source: Vorbeck Materials
Note: Electrical resistivity is a measure of how strongly a material opposes the flow of electric current. A low resistivity indicates a material that readily allows the movement of electrical charge. The international unit of electrical resistivity is the ohm.

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Table 4.5 Comparison of printing processes for printed electronics

Process	Advantages	Disadvantages
Lithography	High resolution High throughput	Low ink film thickness Ink almost pastelike
Inkjet	High resolution Accurate and precise Good ink film thickness (~0.1 μm) Many suppliers working on materials and processes Ability to create in small volumes	Low throughput
Screen	Thick ink film (100 μm)	Low throughput
Flexography	Good ink film thickness (3-8μm) Good resolution, High speed	Resolution could use improvement.
Gravure	Very high speed, Good ink film thickness (2-5μm)	High cylinder costs

Source: Pira International

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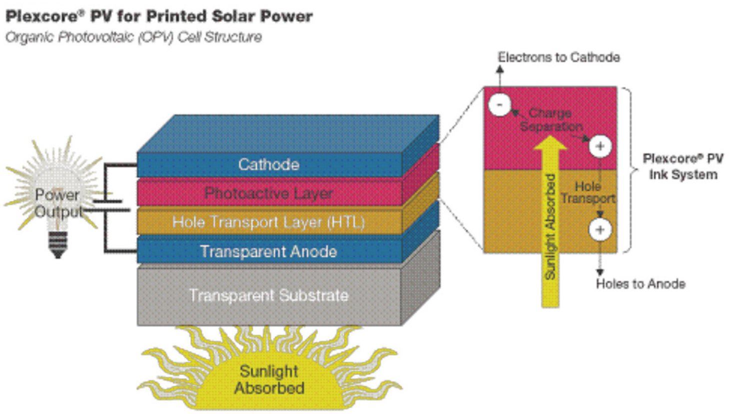
Figure 5.1 Plexcore PV for printed solar power



Source: Plextronics

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Table 5.1 Companies involved in electronic ink technology

Technology	**Companies**
Electrophoretic	E Ink Prime View International(acquired SiPix) Bridgestone
Cholesteric LCD	Fuijitsu Hitachi Kent Kodak Nemoptic ZBD
Electrowetting	LiquiVista
Electrofluidic	Gamma Dynamics
Electrochromic	Aveso Ntera Siemens
Photonic Crystal	Opalux
REED	Zikon

Source: Pira International

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Table 5. 2 Leading printed battery manufacturers

Company	Technology
Blue Spark Technologies	Carbon zinc
Cymbet Corpora8on	Lithium ion
Enable IPC	Nanowire based
Enfucell Ltd.	Manganese dioxide
Excellatron Solid State	Lithium ion
Front Edge Technology	Lithium ion
Infinite Power Solutions	Lithium Cobalt Oxide
NanoEner (Ener1)	Lithium manganese dioxide, lithium ion
Oak Ridge Micro Energy	Lithium, lithium ion
Planar Energy Devices	Lithium ion
Power Paper Ltd. Israel	Manganese dioxide
Qynergy	Radioisotope
Solicore USA	Lithium polymer
Thin Battery Technologies	Carbon zinc
Ultralife Batteries	Lithium ion
VARTA Microbattery	Lithium

Source: Pira International

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Table 5.3 Current versus future materials for PE applications

Application	Current Material	Future Trend
Photovoltaics	Silver bus bars	Silicon-ink based platforms Conductive films
Bistable displays	Electronic ink	Electronic ink
Displays Touch screens Flat Panel Displays LCD backplanes and OLEDs and electrodes	ITO ITO Silver	CNT-based films Transparent ink films SANTE films. Flat panel displays are the next step after touch screens for the above technologies, a bit further down the road. Silver
Lighting	Emerging	Silver
Memory	Emerging with conductive polymers	Conductive polymers
RFID	Silver antennas, some work with silicon inks and conductive polymers	Movement towards complete printed tags with organic materials and silicon inks; perhaps copper antennas
PCBs/Switches	Silver	Nanoparticle silver
Sensors	Emerging with silver and organics	Organics and silver
EMI Shielding	Metal screens	CNT-based films, SANTE films.

Source: Pira International

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Table 6.1 Summary of the outlook for conductive and semi-conductive inks, 2010-2015

	2010 landscape	2015 landscape
Conductive inks	Silver dominant, copper emerging as alternative. Introduction of CNT-based inks	Mainly silver, but more nanoparticle silver inks. Increasing use of copper. CNT-based inks have growing foothold.
Semi-conductive inks	CNT inks just emerging. Several products using CNT-based ink films Very limited use of silicon inks.	Widespread use of CNT-based inks and ink films. Increased use of silicon inks and more silicon-based inks products introduced.
Conductive polymers	Limited use	Expanded use, particularly in EL lighting but still rather small in comparison to alternatives.
Environmental	Strict environmental regulation, considerable waste involved in traditional electronics manufacture. Movement toward sustainability and use of renewable resources.	Even tighter regulation. Additive processes reduce waste and are more environmentally friendly. Strong push towards sustainability and use of renewable resources
Standards	None	Standards just beginning to evolve.
Partnerships	Strong partnership activity	Partnerships are essential to the industry.

Source: Pira International Ltd

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