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Printed electronics: the challenges involved in printing devices, interconnects, and contacts based on inorganic materials

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Printed electronics represent an emerging area of research that promises large markets due to the ability to bypass traditional expensive and inflexible silicon-based electronics to fabricate a variety of devices on flexible substrates using high-throughput printing approaches. This article presents a summary of work to date in the field of printed electronics and the materials chemistry involved. In particular, the focus is upon the use of metal- and metal oxide-containing inks in the preparation of contacts and interconnects. The review discusses the challenges associated with processing these types of inks and ways to successfully obtain the desired features.

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Introduction

In the near future, a highly viable and innovative fusion of three technological areas—microelectronics, chemistry and printing—is foreseen that will create markets with annual revenues estimated at more than €200 billion.[1] The combination of conductive polymers and inorganic materials with printing technologies enables thin, lightweight and extremely cost-efficient electronic systems. Current market drivers are organic photovoltaics,[2,3] flexible batteries,[4,5] electro-optic devices,[6–8] displays, logic and memory components—including field effect transistors (FETs) and thin film transistors (TFTs),[9–13] sensor arrays[14–18] and radio frequency identification (RFID) tags.[19,20] All of these devices require contacts and conductive structures, with metals being the main system of choice due to conductivity.

As an additive technique, inkjet printing[21] is an attractive method for producing electronic devices, on account of its minimal waste generation and efficient handling of expensive materials. Inkjet printing of conductive precursor materials, usually metal nanoparticles[22] or metal–organic complexes,[23,24] has been used as a relatively fast technique that might enable roll-2-roll (R2R) production. However, the sintering step that is necessary to render the precursor compounds conductive typically requires >30 minutes and/or higher temperatures (>250 °C). In particular the long sintering time is not scalable to R2R production lines. As an illustrative example, a sintering time of 30 minutes and a web speed of 1 m s^{-1} mean that the production line is required to be at least 1.8 km in length.

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An additional consideration is the high sintering temperatures that are not compatible with common polymer foils, such as polyethylene terephthalate (PET) or polycarbonate (PC), which have relatively low glass transition temperatures (T_g). This restricts choice to more expensive polymers such as polyimide (PI). Both the temperature and the time required for sintering clearly need to be reduced and this has been the focus of research over the last few years.[22,23,25,26]

Conductivity values need to reach a certain application dependent value. Typically the obtained conductivity after the sintering step is only a fraction of the bulk metal conductivity since the conversion of the precursor ink into bulk material is affected as the processing temperatures are well below the melting temperature of bulk metal. Printing additional layers increases conductivity but this leads to increased materials usage and lengthened processing times. Therefore, a trade-off appears between the processing conditions and the feature's conductivity.

This article is divided into three sections: the first section describes the inkjet printing of conductive precursor ink, including inorganic nanoparticles and metal–organic decomposition (MOD) inks and the advantages of using these materials. The second section introduces various selective post-printing processes to convert the precursor inks into conductive material in such a way that the substrate is unharmed. Conventional sintering techniques, like standard convection ovens, will be compared with new, alternative and more selective methods. Moreover, the mechanisms involved in the sintering process will be discussed. The final section discusses the use of metal oxides, which are typically employed as transparent electrodes. Finally, a summary of the recent achievements in printed electronics and comments on the future of the field are provided.

Printing metallic inks

Contacts and interconnects

The 'solution processable' nature of conductive polymers has led to the reality of printed electronic devices. The mechanical flexibility of polymeric electronics has also opened up new areas such

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as flexible and stretchable electronics, applications that are currently beyond conventional silicon-based devices.[27] Contacts and interconnects, which are necessary for electronic circuits,[28] can be printed using either polymeric or metal-containing inks. Although such contacts have been formed using lithographic techniques, the contactless direct write ability of inkjet printing has considerable appeal on account that it significantly decreases the number of process steps.[21,29]

Contacts and interconnects are mostly printed using metal-containing inks because of the much higher values of conductivity that can be obtained compared to conductive polymers. There are two main types of ink that are used. The first type of ink is a suspension of nanoparticles, and is known as a nanoparticle (NP) ink.[30] The second type of ink is known as metal-organic decomposition (MOD) ink, an example of which involves a silver salt dissolved in a suitable solvent.[24,31,32] Each type of ink has its advantages and disadvantages. For example, MOD inks are solutions, which reduce nozzle clogging, and do not require colloidal stabilisers. NP inks usually have a higher particle loading, are more widely available commercially and have been reported as having lower contact resistances.[10] Although both types of ink can be converted at temperatures of 300 °C,[19,32,33] lower temperatures are often used; for example, excellent values of conductivity have been obtained for single layered lines composed of an MOD ink, which were converted at 150 °C for five minutes, as can be seen in Fig. 1.[31]

The overprinting of more layers onto the original layer can also increase conductivity. Teng and Vest found that the sheet resistances of their inkjet printed silver MOD lines were similar to those of thin-film evaporated silver after four to five layers had been inkjet printed.[32] A reduction in resistance with increased layer number has also been observed for NP inks.[30] In both cases, line width increases as more layers are added. Apart from improved conductance, another advantage of adding more layers is a decrease in variability, thereby improving reproducibility.

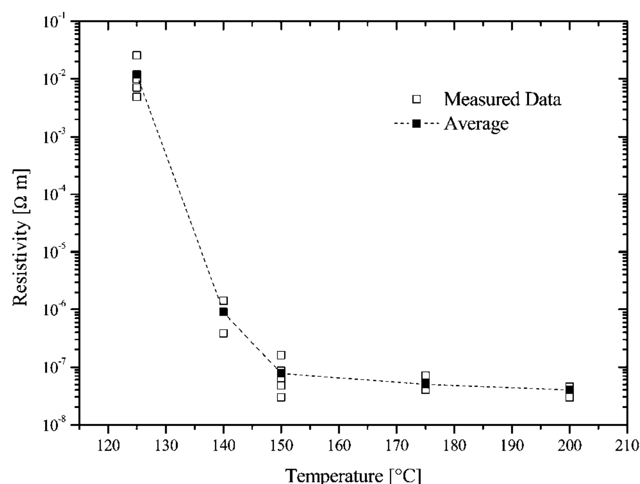

Fig. 1 Graph showing the change in resistivity as a function of curing temperature for an inkjet printed solution of silver neodecanoate in xylene. Each measurement was for a single layered track which was cured for five minutes. Reprinted with permission from ref. 31, copyright 2010, Wiley-VCH Verlag GmbH & Co. KGaA.

Choice of metals

The main issues with regard to which metal to choose for a solution-processable ink are related to bulk resistivity, price and ease of handling. The ideal metal-containing ink would be cheap, easy to prepare, store and jet, and would give high values of conductivity after deposition and post-processing. In terms of bulk resistivity, silver has the lowest, 1.59×10^{-8} Ω m, followed by copper, 1.72×10^{-8} Ω m, and then gold, 2.44×10^{-8} Ω m. In terms of price, an ounce of gold costs about \$1100, whereas an ounce of silver costs \$17 and one ounce of copper is about 20 cents.[34]

A significant factor in determining which metal to use is the ease of obtaining a suitable ink. Although cheap and possessed of a high conductivity, copper presents handling difficulties as its nanoparticles oxidise spontaneously in air.[35] Gold, on the other hand, is almost prohibitively expensive. Currently, silver is the metal that has been most reported, although metals such as aluminium (2.82×10^{-8} Ω m) and nickel (6.99×10^{-8} Ω m) are also used.[21] The price of an ounce of aluminium and nickel is approximately 6 and 53 cents, respectively.[34]

Recently, a significant amount of work has been devoted to inkjet printing copper. Moon *et al.* have reported on the inkjet printing of a copper MOD ink,[36] which needed to be converted in a 3% H_2 atmosphere. Magdassi *et al.* encapsulated copper nanoparticle cores in silver shells,[35] which allowed them to use the ink in air. The approach appears to be stable as no oxides were found to have formed on the inkjet printed copper patterns after several months. A similar approach which used graphene-coated copper nanoparticles was reported a year earlier by Stark and co-workers.[37]

Post-printing processes for metallic inks

Both NP and MOD inks require an additional processing step to form a conductive pattern. In MOD inks, this additional step typically uses heat to precipitate the metal and burn off the organic component or, in the case of NP inks, the heat decomposes the organic stabiliser. Both types of ink require that the particles then sinter together to form a conductive feature. The reduced sintering temperatures offered by NP inks are due to the size of the nanoparticles.[38] MOD inks, on the other hand, generate the nanoparticles *in situ*, which also require lower temperatures.

For NP inks, the curing temperature is defined as the temperature where particles lose their organic shell and start showing conductance by direct physical contact. Whereas sintering (which is often mistakenly used instead of curing temperature) takes place at a higher temperature when all the organic material has been burnt off and necks begin to form between particles.

Although evaporation of the solvent forces the particles close together, conductivity only arises when metallic contact between the particles is present and a continuous percolating network is formed throughout the printed feature. An organic layer between the silver particles as thin as a few nanometres is sufficient to prevent electrons moving from one particle to another.[39–41] The adsorbed dispersant stays on the surface of the particles and, typically, is removed by an increase in temperature.

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In the field of sintering two properties are very important: firstly, the lowest temperature at which features become conductive, which is mainly determined by the organic additives in the ink.[42] Secondly, obtaining the lowest possible resistance of the printed features at the lowest possible temperature. To achieve a low resistance, sintering of the particles is required to transform the initially very small contact areas to thicker necks and, eventually, to a dense layer. High conductivities, hence low resistance, can then be obtained through the formation of large necks, which decrease constriction resistance and eventually form a metallic crystal structure with a low number of grain boundaries.

In the low temperature regime, the driving forces for sintering are mainly surface energy reduction due to the particles' large surface-to-volume ratio, a process known as Ostwald ripening.[43,44] Ostwald ripening is one of the modes of particle growth wherein large particles grow at the expense of smaller ones. Such a redistribution arises because small particles have a small radius of curvature: smaller spheres are bent more sharply and thus have a higher curvature, which is equal to the reciprocal radius for a sphere. As a consequence, smaller particles have a higher chemical potential (μ) than larger particles.[45]

Ostwald ripening triggers surface and grain boundary diffusion rather than bulk diffusion within the coalesced particles, as schematically depicted in Fig. 2. Grain boundary diffusion allows for neck formation and neck radii increase, which is diminished by the energy required for grain boundary creation.[46,47] The process of Ostwald ripening stalls when a particle diameter of approximately one and a half times their original size is reached, leaving behind a porous structure, and lower conductivity values than the bulk material are obtained. The transport of material between particles during Ostwald ripening is non-convective and purely of a diffusive nature.[48,49]

Larger particles are formed due to particle migration and coalescence. During sintering, the relative density increases with increased temperature or pressure but decreases with increased particle size.[50] Full densification, *i.e.* closure of pores, can be obtained either with a fast diffusing gas or with a high pressure.

Conventional sintering techniques

Mostly, the conversion of non-conductive precursor inks into their conductive counterparts has been reported by simply applying heat: usually requiring temperatures above 200 °C.[51–53] However, only expensive high-performance polymers, like polytetrafluoroethylene, polyetheretherketone and polyimide can be used at high temperatures, which represent a drawback for implementation in large area production and are not favourable in terms of costs.

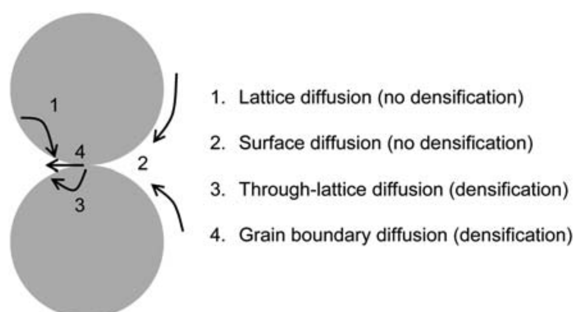

Fig. 2 A schematic representation of various atomic diffusion paths between two contacting particles. Paths 1 and 2 do not produce any shrinkage whilst paths 3 and 4 enable the sphere centres to approach one another, resulting in densification. Reprinted with permission from ref. 47, copyright 2010, Elsevier Science.

Lee *et al.* describe an aqueous silver colloid dispersion which is prepared mainly with environmentally friendly chemicals, like water and diethylene glycol.[54] Although short times of only 10 minutes are necessary, high temperatures (200–300 °C) are required to obtain good conducting lines. Similarly, Miettinen *et al.* have reported multilayer inkjet printed interconnects on epoxy-moulding materials as substrates for the integration of functional systems, *i.e.* system-in-package.[55] After inkjet printing successive layers with a silver nanoparticle ink from Harima Chemicals the sintering was performed at a temperature of 220 °C for one hour. To improve the sintering process a pre-heating step prior to printing and sintering was done and, therefore, the substrates were heated for 60 minutes at 250 °C. This resulted in a resistivity that was one order of magnitude lower than without pre-heating.

An attempt at lowering the curing temperature was made by Schubert *et al.* who formulated a silver ink using a very low amount of organic additives.[22] The silver ink was prepared using silver powder from Mitsui and weakly adsorbing binding materials, like poly(ethylene oxide) or poly(vinyl alcohol), instead of amines, amides or mercapto groups, which usually are strong binding groups towards silver particles. The low content of organic additives is reflected in the thermogravimetric analysis curve, as depicted in Fig. 3a. Therefore, this ink revealed conductivity already at a temperature of 80 °C. Fig. 3b and c show scanning electron microscopy (SEM) images of the printed particles before and after sintering, respectively. Similarly, very low sintering temperatures have previously been reported by Huang *et al.* for gold inks,[25] again formulated using very low molar mass organic additives.

A drawback of using a very low content of binding materials is that the resulting ink is hard to inkjet print. Organic binders promote the printability of the ink and are often added to the ink to assure mechanical integrity and adhesion to the substrate. Steric stabilisation of the particles in solvents substantially screens van der Waals attractions and introduces steep steric repulsion between the particles at contact, which avoids agglomeration.[56]

Alternative and selective sintering methods

More selective sintering techniques have been developed to leave thermo-sensitive substrates unharmed. The group of Poulikakos used an Argon ion LASER beam to sinter the printed nanoparticles, in which the LASER follows the printed line and converts the central region of the line into their conductive counterparts, without affecting the substrate. Using this approach lines with conductivities of up to 25% of bulk gold and line widths of 8 μm were reported.[57,58] A washing step was necessary after sintering to remove the unsintered material. The drawback of this approach is that it is relatively slow with translative velocities of 0.2 mm s^{-1}, with the highest conductivities obtained at the slowest write speeds.[59]

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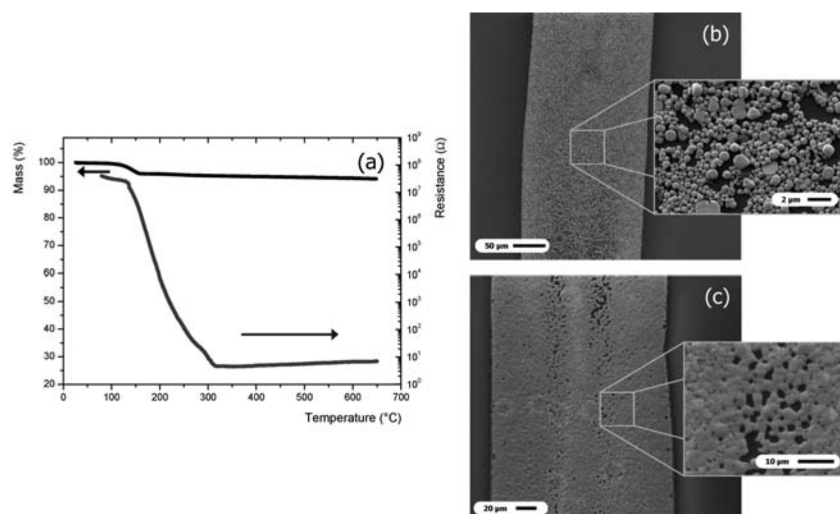

Fig. 3 Resistance over a single inkjet printed line with a length of 1 cm as function of temperature and thermogravimetric analysis (TGA) of Mitsui silver ink (a). Scanning electron microscopy (SEM) image of inkjet printed Mitsui silver particles at room temperature (b) and after heating to 650 °C (c). Reprinted with permission from ref. 22, copyright 2010, the Royal Society of Chemistry.

The use of microwave radiation presents a second example of selective sintering.[60] Typically, metals have a very small penetration depth: the distance into the material at which the incident power is reduced to 1/*e* (36.8%) of the surface value. For example, the penetration depth of 2.45 GHz microwaves for metal powders of silver and copper is 1.3 and 1.6 μm, respectively.[61] It is believed that the conductive particle interaction with microwave radiation, *i.e.* inductive coupling, is mainly based on Maxwell–Wagner polarisation, which results from the accumulation of charge at the materials interfaces, electric conduction, and eddy currents.[62,63] However, the main reasons for successful heating of metallic particles through microwave radiation are not yet fully understood. In contrast to the relatively strong microwave absorption by the conductive particles, the polarisation of dipoles in thermoplastic polymers below T_g is limited, which makes the polymer foil's skin depth almost infinite, hence transparent, to microwave radiation. As well as sintering, the exposure of metallic nanoparticles to microwaves decreases the sintering time by a factor of 20. The conductivity values are similar when using conventional radiation–conduction–convection heating.[51]

Further improvements to decrease the sintering time have been reported; sintering times of only a few seconds can be obtained by placing conductive antennae around the structures to be sintered as depicted in Fig. 4.[64] After sintering, the tracks revealed conductivity values of 10 to 34%, when compared to the bulk silver value. This process of improved sintering in the presence of conductive antenna structures can be implemented into roll-to-roll (R2R) production. The antennae do not need to make contact with the unsintered features, which makes recycling of the antennae possible. It was found that sintering took place even with a gap of up to 0.5 cm. However, increasing the distance reduces the final conductivity.

A third example of selective sintering is exposure to a low pressure argon plasma.[65] This process shows a clear evolution starting from a sintered top layer into *bulk* material (see Fig. 5) and yielded resistivity values of 2.5 to 3 times the bulk silver value. Through-sintering does not occur with greater thicknesses than the penetration depth of the plasma species. Plasma processing causes substantial cross-sectional area and height loss, indicating that densification and sintering take place.

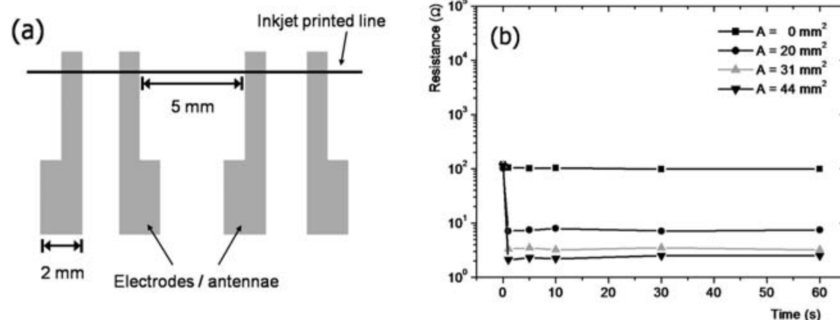

Fig. 4 Schematic representation of the printed template onto a PEN substrate (a), with four silver antennae in gray and a single silver line inkjet printed on top of the antennae in black. Influence of the total surface of the four electrodes on the template for an initial line resistance of 100 Ω (b) on microwave flash exposure for 1 to 60 seconds. Reprinted with permission from ref. 64, copyright 2010, Wiley-VCH Verlag GmbH & Co. KGaA.

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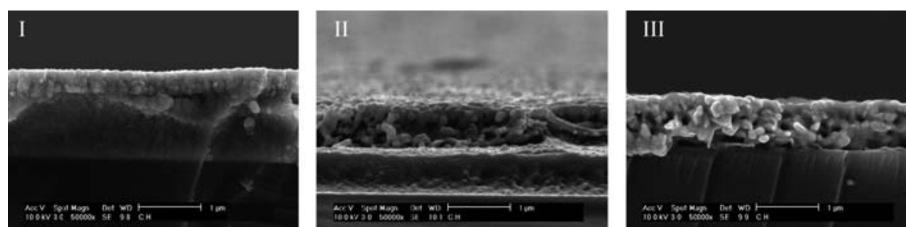

Fig. 5 Temporal evolution of the sintering process on glass, cross-sections of the deposited material after plasma sintering at 80 W for 7.5, 30 and 60 minutes, respectively I–III. Reprinted with permission from ref. 65, copyright 2010, the Royal Society of Chemistry.

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Other techniques that are reported in the open literature and have been used for nanoparticle sintering include exposure to UV radiation,[66,74] high temperature plasma sintering,[67] photonic curing[68] and pulse electric current sintering.[69,70] Allen *et al.* describe sintering by a DC current; although this technique requires the features to be slightly conductive prior to sintering, application of a current pre-sinters the features within 60 seconds, depending on the power density. To initiate the sintering process within a reasonable time a power density of at least 100 nW μm^{-3} was required. The conductivity of the printed nanoparticle layer increases by more than five orders of magnitude during the sintering process, with the final conductivity reaching almost 60% of bulk silver, within a very short time of 2 μs.

Room temperature sintering

There are a number of ways of obtaining conductive features at room temperature. One way simply allows the solvent to evaporate slowly, which causes the stabiliser to collapse onto the particle surfaces. The nanoparticles then coalesce.[71,72] However, this process is rather lengthy. A swifter route lies in the chemical neutralisation of the stabiliser, which causes the particles to sinter together. In a recent example, Magdassi *et al.* prepared conductive silver features from a silver NP ink by exposing the inkjet printed features to HCl vapours.[73]

In another method, Smith *et al.* used UV light to create 'latent images' in inkjet printed MOD ink, which is then chemically reduced.[74] The process is rapid and results in conductivities that are 10% of bulk silver.

The appeal of MOD inks is that they generate the nanoparticles *in situ*. However, they often require heat to remove the unwanted organic component of the salt. Instead of inkjet printing a ready-made nanoparticle or MOD ink and subsequently post-processing after pattering, it could be more preferable to create the conductive materials on demand and *in situ* on the substrate—a technique called reactive inkjet printing.[75]

Calvert *et al.* have recently reported the preparation of conductive copper lines by using reactive inkjet printing.[76] Conductive copper lines were directly written on paper through inkjet printing of a copper salt and sodium borohydride ($NaBH_4$) as a reducing agent sequentially from two separate compartments of a multi-colour HP cartridge. After successive printing the obtained conductivity was 1/30 that of bulk metal copper. Oxidation of the printed copper lines was followed using EDS elemental analysis. McGorman *et al.* formed silver nanoparticles *in situ* by jetting ascorbic acid followed by silver nitrate.[77] The silver nitrate was reduced to silver, and a final conductivity that was 0.3% of bulk silver was obtained. This method of reactive inkjet printing further reduces the amount of processing steps and may become revolutionary, although currently only being applicable at lab-scale.

Metal oxides

In recent years, there has been tremendous interest in metal oxide based systems as materials for printed electronics; primarily due to their transparency, which makes them attractive for numerous display applications. An additional advantage of metal oxide systems is that they typically offer excellent oxygen stability, allowing for processing in air without the need for inert processing or vacuums.

Transparent metal oxides are being pursued for two main applications in large area printed electronics. First, there is interest in the development of conductors for use as a replacement for indium tin oxide (ITO). This is due to the fact that costs of indium have been rising steadily due to increased demand, and also because ITO itself typically requires relatively high temperature processing to achieve optimal conductivity and transparency. Most interest has focused on doped zinc oxide systems for this application. The second area of interest is the use of transparent metal oxides as a semiconductor material. This application is being pursued for various reasons.[78] First, the transparency allows for the elimination of the traditional trade-off between aperture ratio and pixel transistor sizing in most active matrix displays. Second, the air stability of metal oxides allows for easier processing than many other semiconductors being considered for printed electronics. Third, these materials are typically *n*-type and offer relatively high performance.[79]

Various pathways to synthesise zinc oxide nanoparticles have already been reported.[80–82] Volkman *et al.* report on the formation of ZnO nanoparticles by precipitating zinc oxide from zinc acetate in an isopropanol bath by the addition of sodium hydroxide. The size of the precipitates increases with time. By adding an encapsulant such as an alkanethiol at an appropriate time, it is possible to control the size of the resulting nanoparticles. The resulting particles consist of zinc oxide encapsulated by an alkanethiol ligand. Such synthetic processes are not limited purely to the formation of zinc oxide; for example, doped zinc oxide nanoparticles have also been demonstrated.[83] Therefore, nanoparticulate processes such as these should also be applicable to doped zinc oxide nanoparticles for use in the formation of highly doped conductive films.

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Next, inks are formulated, printed, and dried. The resulting film consists of a densely packed thin film of individual ligand-encapsulated nanoparticles. The film is then cured. To date, only thermal curing has been demonstrated in the literature. The thermal curing is used to drive off the ligand. Unlike conductor films, which show appreciable conductivity even with substantial amounts of ligand remaining in the film, semiconductor films require much higher purity to demonstrate a good behaviour in devices. Upon ligand evolution, the nanoparticles come into contact with each other and fuse, resulting in grain growth and polycrystalline film formation. The film quality shows a strong dependence on the curing temperature. Curing at too low temperatures prevents efficient removal of the ligand, resulting in poor-quality films. Curing at too high temperatures results in rapid, "explosive" ligand removal, forming films with poor electrical and crystalline quality. This effect is exhibited in Fig. 6, which shows X-ray diffraction spectra obtained from films sintered at 150 °C and 170 °C, respectively.

The above films have been integrated into substrate-gated test devices to illustrate the potential for use of printed metal oxide nanoparticles in printed transistors.[78] Despite the fact that the Au source/drain electrodes used in this work were not work function-matched to ZnO, reasonable solution-processed ZnO thin film transistors are realised (mobility of ~0.2 $cm^2 V^{-1} s^{-1}$), with performance on-par with many solution-processed organic semiconductor devices. The ZnO films show good transparency, and, importantly, all processing and operation may be done in air. Fig. 7 shows the characteristics of transistors formed using the aforementioned nanoparticles.

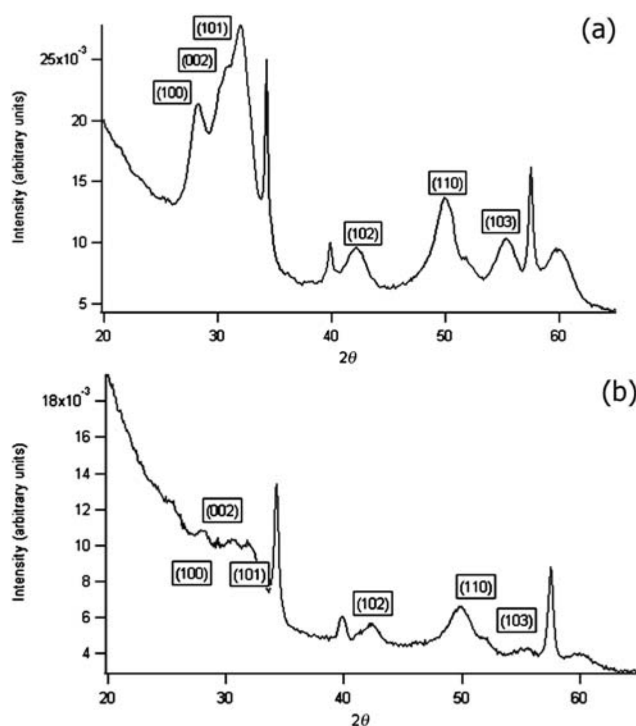

Fig. 6 X-Ray diffraction characteristics of ZnO nanoparticle films annealed at 150 °C (a) and 170 °C (b). Note the differences in crystallinity observed. Reprinted with permission from ref. 78, copyright 2010, IEEE.

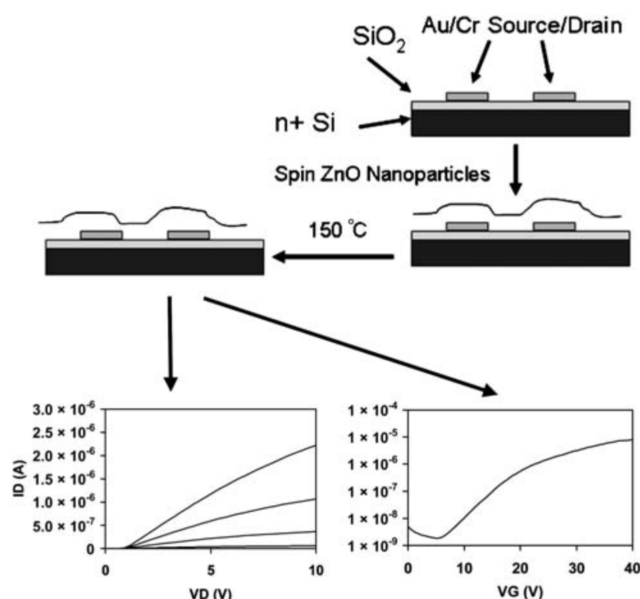

Fig. 7 ZnO TFTs (W/L = 100/5 μm) realised using spin-coated ZnO nanoparticles. Field-effect mobilities as high as 0.2 $cm^2 V^{-1} s^{-1}$ have been realised. The ZnO film was 50 nm thick. Reprinted with permission from ref. 78, copyright 2010, IEEE.

Conclusion

This article has focussed upon the use of metal containing inks and metal oxide containing inks, which have been used to prepare contacts and interconnects in printed electronic devices. The main processing issue relates to the conversion of the ink in its non-conductive state to a final conductive print. Typically, heat has been used to effect this conversion by either removing the organic surfactants that have been used to stabilise the nanoparticles (NPs) against agglomeration, or by burning off the organic component of the metal-organic salt used in metal–organic decomposition (MOD) inks. Over the last few years, research has focused upon reducing the conversion temperatures and the time taken for conversion to be complete. The goal has also been to ensure that low conversion temperatures and short conversion times result in acceptable levels of conductivity.

For NP inks, reductions in curing temperature can be readily achieved by lowering the amount of organic additives present in the ink. However, such reductions can adversely affect the printability of the ink, and have unwelcome implications for mechanical integrity and adhesion. For MOD inks, an apparent strategy for reducing temperature seems less obvious although in some cases curing temperatures are already lower than for most NP inks.[23,31]

Ultimately, it would be pleasant if one could obtain conductive features at room temperature, and recent work has demonstrated that such a goal is easily within reach. Magdassi *et al.* have obtained conductive silver features by exposing an NP ink to HCl vapours.[73] Smith *et al.* have also obtained silver at room temperature by exposing an MOD ink to UV and chemically reducing it.[74]

Chemical reduction lies at the heart of reactive inkjet printing, which allows materials to be produced *in situ*. It has been demonstrated recently that Cu and Ni lines can be produced by

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printing the reduction agent $NaBH_4$ in series with Cu and Ni salts. In a similar approach also silver could be obtained using $AgNO_3$ and ascorbic acid.

Currently, silver has been the metal that has been the most reported. This distinction has resulted as a consequence of it being cheaper than gold, and more air stable than copper. However, promising strides have been made with inkjet printable air-stable Cu, with encapsulation offering an answer. Silver and graphene have been used to form an outer shell, which protects the copper interior.

Metal oxides have attracted interest from the displays community due to their conductive, transparent natures and the fact that they can be processed in air. As with metals assiduity has been devoted to finding cheaper alternatives to indium tin oxide (ITO) that offer comparable performance, with ZnO evincing considerable potential.

The outlook for this overall area suggests that attention will increase as the room temperature options for producing conductive metal features from inkjet printed inks become more widely known. Reactive inkjet printing, which couples reducing agents with metal precursors offers fascinating possibilities. Whether such approaches can also be used with metal oxides is a question that has yet to addressed. However, in this particular area the main challenge lies with displacing ITO, due to its decreasing availability. Whereas silver's role as the metal most reported for contacts clearly looks as though it will be supplanted by copper, as a consequence of the increasingly large amount of effort being given to inkjet printing copper containing inks.

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