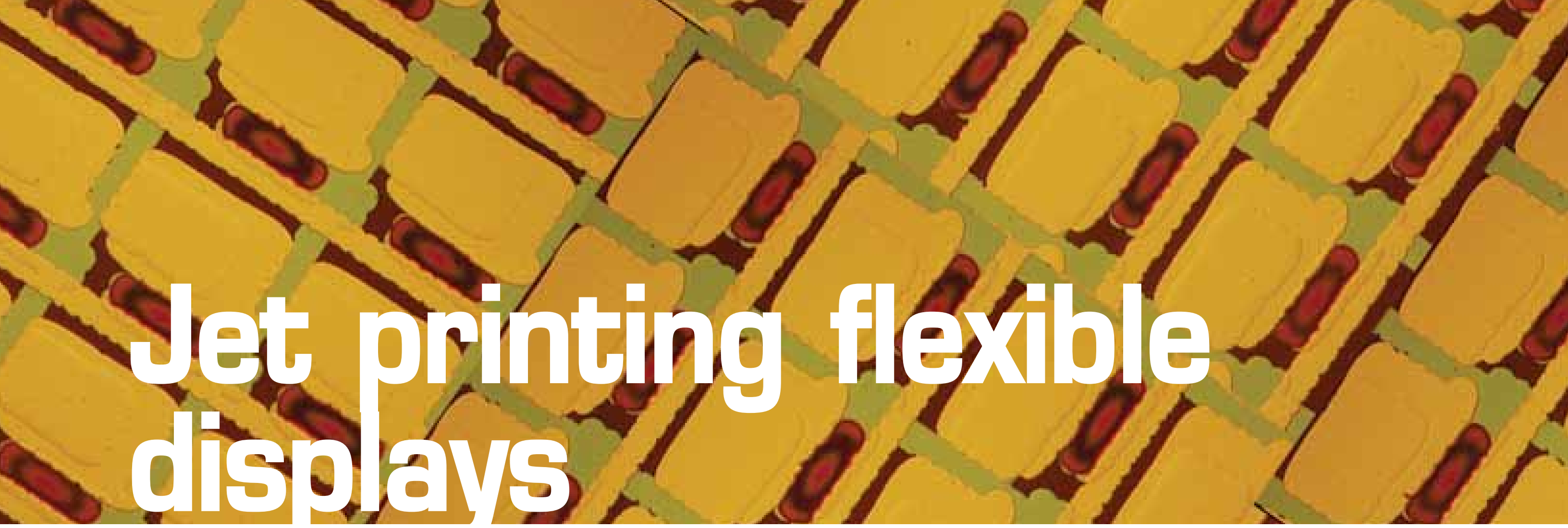

Jet printing flexible displays

Jet printing is an interesting patterning technique for electronic devices because it requires no physical mask, has digital control of ejection, and provides good layer-to-layer registration. It also has the potential to reduce display manufacturing costs and enable roll-to-roll processing. The technique is illustrated with examples of prototype printed displays using amorphous silicon and polymer semiconductors.

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Flat panel displays for computer monitors and televisions are a $60 billion industry, and one that is growing rapidly. The most advanced facilities make panels on ~2 m x 2 m glass, and the substrate size has doubled every two to three years since 1990. Display manufacturing uses photolithography techniques developed for Si integrated circuits (ICs). However, instead of reducing transistor size – as in Si ICs, where the reduction has gone from 10 μm to 50 nm in 30 years – the size of transistors in displays has remained roughly constant while the substrate size has increased. Building deposition and lithography equipment for huge substrates is challenging and expensive, and raises the question of whether there is an alternative manufacturing method. This is the basis of the interest in jet printing[1-5].

The document printing industry is also huge, and its technology also patterns material (ink) on large substrates, usually paper. Why not use printing technology to make electronic devices? The idea was conceived a decade ago[6-9], and is now reaching fruition in display applications[10]. The problem is that the requirements of patterning electronic circuits are more challenging than printing a document. A document pixel element is a drop of ink, while a display pixel is a circuit comprising different materials precisely formed and aligned.

Both contact printing and droplet-ejection (ink-jet) printing have been applied to pattern electronic devices[11-13]. Contact printing creates the pattern with a preformed master, and examples are screen-printing, gravure, offset, and microcontact printing. Jet printing, on the other hand, is a noncontact process, requires no master, and has digital control of ejection, which provides drop-on-demand printing. Although contact printing can be faster, much of the printed electronics technology has focused on ink jet, primarily because there is greater control over feature position and layer registration.

The initial impetuses to create jet-printing technology for displays were the deposition of polymer light-emitting diodes (PLEDs), for which conventional photolithography is difficult because of material sensitivity[6,14], and the reduction of the fabrication cost of color filters for liquid crystal displays (LCDs). Presently, jet-printed color filters are the leading application of the technology in production[15].

Multiejector jet-printing systems

Most jet printers for electronics use piezoelectric rather than thermal actuation. The piezo actuator is outside the print-head cavity and does not interact directly with the printing ink, while in thermal jet printers the ink is heated to vaporization and this must not harm the ink. Piezo

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actuation also provides greater control over droplet ejection because the waveform that drives the actuator can be tuned for different materials and to control the ejection velocity.

Print speed requires multiejector print heads to achieve speeds compatible with display manufacture. The time t_P to coat an area A is:

$$t_P = A / [d^2 f N_J N_H] \quad (1)$$

where d is the drop spacing for the chosen printing grid size, f is the ejector firing frequency, N_J is the number of ejectors in a print head, and N_H is the number of heads. Printing a 2 m x 2 m substrate in 100 s, with 40 µm grid size and a frequency of 25 kHz, requires 1000 ejectors. Most of the print heads developed for electronics have 100-1000 ejectors[16], and systems with multiple print heads have been developed by several companies[17]. The requirements will depend on the application – a finer grid requires more ejectors, but sparse printing may be considerably faster.

Fig. 1 shows a photograph of a research printer built at the Palo Alto Research Center (PARC)[18]. The key parts of the system are the print head, translation stages, heated substrate holder, and alignment camera. The requirements of the printer involve printing precision and pattern definition. Since a mechanical system connects the print head to the substrate, in principle the print head location can be made as accurate as required, although for a large system this can be a challenging engineering problem. Apart from mechanical errors in the placement of the head, the deviations δx, δy in printed drop location can be described in terms of the parameters of the printhead by:

$$\delta x = \frac{u.s}{v}\left[\frac{\delta v}{v} + \frac{\delta s}{s} + \frac{\delta t}{t}\right] + s\delta\theta; \quad \delta y = s\delta\theta + \beta\delta T \quad (2)$$

where u, v, s, t, θ, and T, are the head velocity, drop velocity, head-substrate gap, drop ejection time, drop angle variation, and temperature, respectively. The placement error δx applies to the print direction and contains terms that are proportional to $u.s/v$. This component of the error increases with head velocity, but is reduced by increasing the drop velocity and reducing the head-substrate gap. There are lower limits to the gap, since the ejected drop has a tail that usually does not separate from the print head until the drop has travelled about 0.5 mm – with some liquids it can be a much larger distance. Fig. 2 shows typical ejected drops before and after the tail has merged with the main drop. The drop velocity variation δv is the most important contribution to the printing accuracy, and some print heads allow for velocity calibration to reduce the error. The drop angle variation error $s\delta\theta$ applies to both the print and perpendicular direction, and can be reduced by minimizing the head-substrate gap.

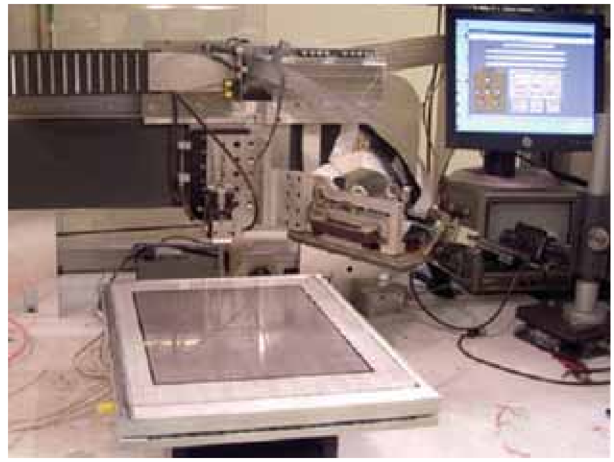

Fig. 1 Photograph of a research printer developed at PARC, showing the print head, substrate holder, alignment camera, and translation stages. In this system, the print head moves in one axis and the substrate in the orthogonal direction. (Reprinted with permission from[4]. © 2005 Korean Information Display Society.)

The error perpendicular to the print direct δy is generally smaller because it does not depend on the velocity of the head. The perpendicular accuracy is affected by thermal expansion of the head so that the temperature must be controlled to within 1-5°C, depending on the size and material of the print head. The straightness of a line printed in the process direction is determined by the perpendicular accuracy, and vice versa. Hence, the edges of features printed in the process direction are more accurate than those printed in the perpendicular direction. Fig. 3 shows that it is possible to position drops to within ~5 µm, and higher precision can be expected in the future as parameters are optimized. The drop position distribution contains both fixed pattern errors and variable drop-to-drop errors.

Jet printing of a pattern is constrained by the relative positions of the ejectors. For some applications, it may be sufficient to require that the pattern be commensurate with the pitch of the ejectors, but there is a need to print an arbitrary pattern. Particularly for flat panel displays, the pixel dimension sets the repeat scale for the printed pattern. There are two general solutions to the constraint problem. One option[19] is to tilt the print head to an angle ψ so that the effective pitch P_H of the head becomes $P_H \cos\psi$. This approach provides commensurate printing at any desired pitch at the expense of

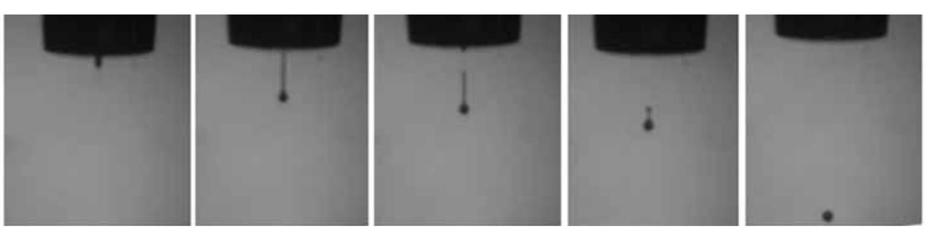

Fig. 2 Time sequence photographs for the ejection of a 60 µm diameter drop from a nozzle, showing the tail that eventually releases and merges with the main drop.

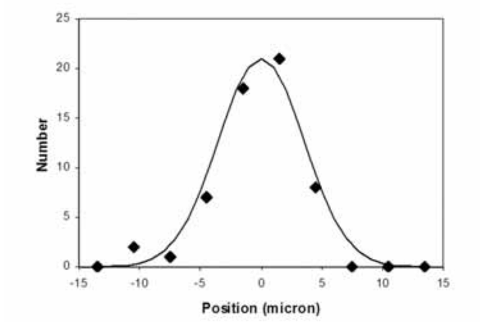

Fig. 3 Histogram of jet-printed drop position deviation in the print direction δx for ~50 drops from individual ejectors in a multiejector print head compared with a Gaussian distribution having a standard deviation of 3.5 μm. The print head has velocity normalization.

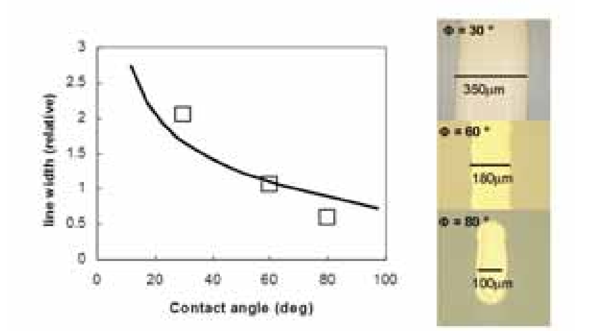

Fig. 4 Calculated line width as a function of wetting contact angle, assuming a small cylindrical liquid pattern. Data points and photographs show line width measurements for a Ag nanoparticle ink printed on surfaces of different contact angles.

greater complexity in the timing of the ejector firing, since the ejectors are offset in the print direction by $P_H \sin \psi$. The second approach is to design the printer for high addressability using either many ejectors or planning for multiple printing passes. Drops are located on a grid finer than the ejector pitch size but still cannot be positioned arbitrarily. The best solution typically depends on the application and, for display color filter printing, an angled print head seems to be the preferred choice.

Printing processes

The fundamental parameters controlling jet-printed liquids are the viscosity and surface energy[20]. The pattern formed when an ejected drop hits the surface depends, in large part, on the ink-surface interaction. The wetting contact angle determines the spread of a liquid drop on the surface and depends on the relative surface energy of the solid-liquid, solid-vapor, and liquid-vapor interfaces. High energy surfaces result in a small wetting angle and an extended drop, while a low surface energy results in a smaller footprint. The surface energy and wetting angle also relate to the adhesion of the liquid to the surface. Strong adhesion is associated with wetting and low adhesion with large contact angles. Unfortunately, most situations need a high contact angle to limit the spread of the drop and good adhesion to the surface. In general, inorganic solids have high surface energy while organic solids and liquids have low surface energy, so solvents will usually wet inorganic surfaces. Chemical modification, such as with a self-assembled monolayer, can decrease the surface energy and reduce wetting.

Jet printing fine features onto a flat surface, e.g. an electrical interconnect, is a problem because of the difficulty in controlling the spread of the liquid on the substrate. Fig. 4 shows how the printed line width decreases as the contact angle increases for a simple model of a small volume of liquid with a cylindrical surface. Measurements of printed nanoparticle metals on different surfaces follow the expected trend[21]. Furthermore, in the common situation that the liquid comprises a solvent and the active material, the drying pattern depends on the contact angle (Fig. 5). A high surface energy results in the well-known coffee stain effect. Enhanced evaporation at the perimeter of the drop causes material to flow to the perimeter where it is deposited[22].

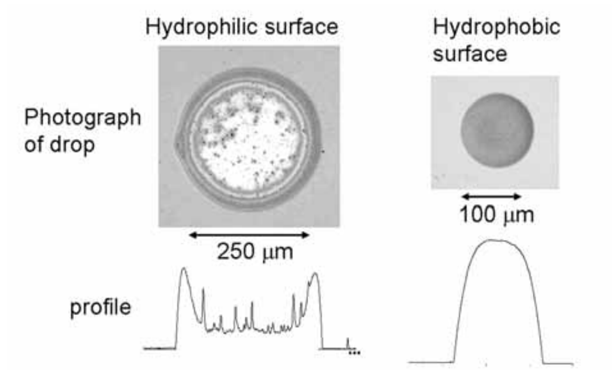

Fig. 5 Photograph and vertical profile of printed drops after the solvent has evaporated for hydrophobic and hydrophilic surfaces. The hydrophobic surface gives a smaller drop without the coffee stain effect. The measurements were made at PARC.

Jet printing into a defined well made by a previously patterned feature is a technique that controls the liquid spread and the drying pattern (Fig. 6)[23]. The liquid flows over the surface until it reaches the well wall, which prevents further spread. Since the resulting pattern does not depend on exactly where the liquid is injected, the precision requirement for the printing system is reduced. Both PLEDs and color filters are made using this technique, and are expected to be the first applications of jet printing to reach display manufacture.

One of the long-term goals of printed electronics is the fabrication of electronic devices by roll-to-roll (R2R) processing. Most high-volume document printing is R2R, and can be done at meters per second speed with minimal cost. Achieving similar results for electronics is extremely challenging because of the layer-to-layer registration requirements, the sensitivity of device performance to material properties, and the need for very few defects. The flexible substrate needed for R2R also introduces its own issues, particularly the problem of dimensional stability. Conventional displays are made on glass, which is a high-modulus, rigid material. Plastics are soft and have low modulus, which means that stresses on the substrate cause significant dimensional changes. In addition, most plastics absorb moisture, which also induces dimensional change. Maintaining layer-to-layer registration over large

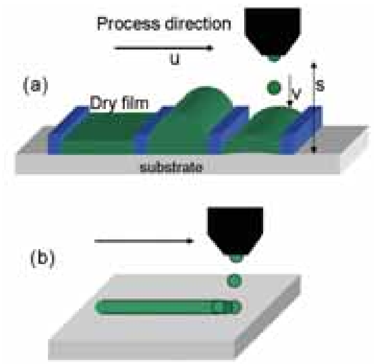

Fig. 6 Schematic showing (a) printing into a previously fabricated well, as used for PLEDs and color filters, and (b) printing unconstrained lines on a free surface. The head velocity u, the drop velocity v, and the head-substrate gap s are indicated.

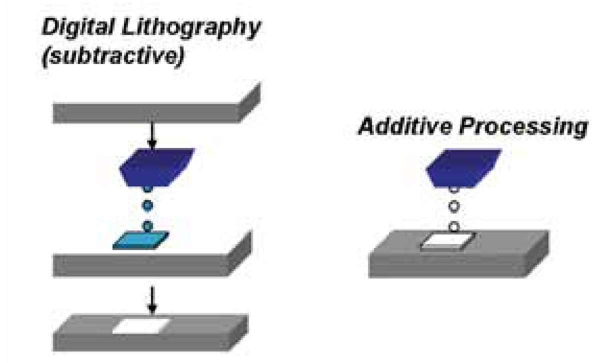

Fig. 7 Illustrations of additive and subtractive (digital lithography) jet-printing processes. (Reprinted with permission from[4]. © 2005 Korean Information Display Society.)

sizes is a key challenge. A design with 1000 pixels and run-out limited to 5% of the pixel size requires 50 ppm dimensional stability. Humidity alone can easily give >200 ppm dimensional changes[24].

Digital lithography

Digital lithography is the process of jet printing an etch mask. It simplifies the conventional photolithography process by reducing the number of steps (Fig. 7) and can be used to pattern many materials. First, a thin film is deposited by any convenient means. The mask pattern is then jet printed directly onto the substrate. The film is etched to reproduce the pattern and then the etch mask is removed. Fig. 8 shows a pattern after the etch mask is deposited and the film is etched.

In digital lithography, there is no confining structure to the printed pattern. The problem of the flow of the printed liquid on the surface is solved by printing a wax[25-27]. The wax is liquid at the elevated temperature of the print head (~120°C) and freezes on contact with the surface. Hence, the pattern on the surface is almost independent of the surface energy and is mostly controlled by adjusting the temperature of the substrate[28], typically in the range 30-50°C. Wax is a good resist as it is insensitive to many etchants for metals and other inorganic materials, and can be removed by common solvents.

The fabrication of a thin-film transistor (TFT) display backplane provides a good example of the use of digital lithography. The electronic circuit is quite simple but requires multiple layers of patterning to complete. The transistors are conventionally made from amorphous Si with sputtered metal address lines and deposited oxide or nitride dielectrics. Fig. 8 shows a small part of a TFT array made at PARC by digital lithography. The backplane is an ordered array of pixels and so the pattern is repetitive. It is therefore convenient if the pixel dimension is commensurate with the ejector pitch of the print head, and the backplane in the figure is designed to satisfy this constraint. Hence, the pattern is printed simultaneously in multiple pixels. Even though the pattern is formed by multiple drops, the patterned features have smooth, straight edges. This is important for precise control of device size, since uniform transistor performance depends on having precisely controlled device dimensions. In the print direction, drops are ejected at high frequency so that the previous drop is still partially liquid when the next arrives. Surface tension causes the line edge to straighten before the wax freezes. When a line is printed perpendicular to the print direction, it is printed with several passes and the wax has frozen before the next drop is printed. In this case, the line edges have a scalloped appearance from the individual drops.

Fig. 8 Photograph of an array of amorphous Si TFTs patterned using digital lithography. The pixel size is 340 μm.

Accurate pattern formation with wet etches requires that the resist adheres well to the surface so that the etchant does not infiltrate along the surface and cause undercutting. A size comparison of the printed mask and the final pattern confirms that there is no significant undercutting[29]. The feature size presently possible with digital lithography is much larger than conventional photolithography because the drop size is large. Many print heads used for printing electronics are based on document printing for which 40 μm is a typical drop size. However, the technology of piezo jet printing is certainly capable of smaller drop sizes, and drop sizes below 5 μm have been reported[30].

Gap sizes much less than the feature size can be made through a combination of accurate drop placement and good line edge definition, and a gap of <20 μm is shown in Fig. 8. This capability is useful for TFT arrays because the smallest feature in a typical array is the gap between the source and drain contacts of the TFT that forms the channel.

Additive printing

Additive printing of active materials (Fig. 7) is the ideal cost-effective process to fabricate devices, since each material is deposited where it is needed in a single process step and the only wasted material is the solvent. Achieving an additive process requires solution-based materials and printing processes with the necessary properties and printing precision. Two early examples in display technology are PLED displays and LCD color filters[31]. The attraction of jet printing for these applications is that the light emission and color filter materials readily come in solution, both are moderately expensive materials so that low waste is important, and both need three material variants (red, green, and blue) to fabricate a display. The technique of printing into a well is used; the back matrix forms the well for color filters and a fabricated well is made for PLEDs. The loading of active material in the printed solution is small (10-20% by volume) so that a relatively large volume of printed liquid must be confined within the well. The general strategy is to arrange that the liquid wets the surface to be coated but not the well walls. The combination of hydrophobic wall material and hydrophilic surface also results in the film drying to a uniform thickness. Both PLED and color filter arrays have been successfully printed, and jet-printed color filters have recently started in production.

Jet printing of polymer semiconductors to form TFTs is also attractive for displays, radio-frequency identification tags, and other applications[32]. Fig. 9 illustrates the printing of a semiconductor to form a bottom-gate TFT with source and drain contacts already in place. Such devices have been printed with polyfluorene[33,34], polythiophene (PQT12)[35,36], and pentacene from a soluble precursor[37]. Since the TFT current flows very close to the semiconductor-dielectric interface, nonuniformity in thickness and roughness in the top surface of the semiconductor as a result of the printing process are not important. Furthermore, it does not matter if the semiconductor extends over the source and drain contacts, so long as the channel region is coated completely. In a TFT array, the semiconductor must be patterned to avoid leakage paths between neighboring TFTs, so jet printing nicely fulfills all the device requirements.

Fig. 10 illustrates the performance of a printed TFT made at PARC from a polythiophene solution. It gives a *p*-channel accumulation mode TFT with a high on-to-off ratio, a reasonable threshold voltage, and a mobility of about 0.1 cm^2/Vs, which is in the range needed to drive a display. Control of surface energy is, again, critical to both the printing and the TFT characteristics. The semiconductor gives much better performance when deposited on a hydrophobic surface, as this leads to improved ordering of the material as it dries[38].

Fig. 11 shows an example of an array of printed polythiophene TFTs, and Fig. 12 shows a complete array on a plastic substrate. The jet-printed devices have comparable TFT performance to spin-coated films,

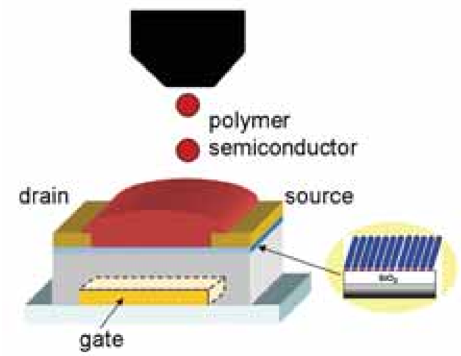

Fig. 9 Illustration showing the structure of a printed polymer, bottom-gate coplanar TFT in which the polymer is jet printed onto a hydrophobic surface after the source and drain contacts have been formed.

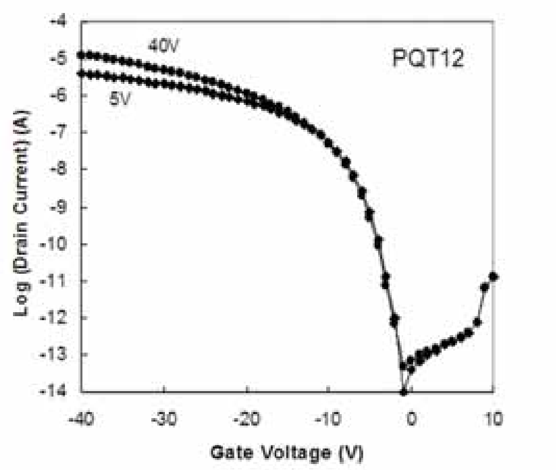

Fig. 10 Example of PQT12 polymer TFT transfer characteristics at drain voltages of 5 V and 40 V, showing good mobility, high on-off ratio, and turn-on near V = 0.

so there is no performance degradation introduced by the printing process. In general, TFTs must be passivated, and this is also a process that can be done by jet printing. Indeed, we have shown that deposition of the semiconductor and passivation can be performed in a single-step process by printing a polymer blend. A blend of polythiophene and poly(methyl methacrylate), or PMMA, will phase separate on the surface so that the polythiophene deposits on the dielectric interface and the PMMA separates out on the free surface. This is one example of the possible simplifications to processes that can be expected from jet-printing technology.

The ultimate goal is to fabricate all the layers of the device by additive processing. It is therefore essential to have an additive process for the metal address lines and transistor contacts. Conducting polymers such as poly(ethylenedioxythiophene) have been jet printed to form contacts for polymer TFTs[39]. However, the conductivity is too low for the address lines of typical displays. The past few years have seen active development of solution-based nanoparticle metals that can be jet printed[40,41]. One great advantage of these materials is that particles of very small dimensions have a reduced melting temperature because of

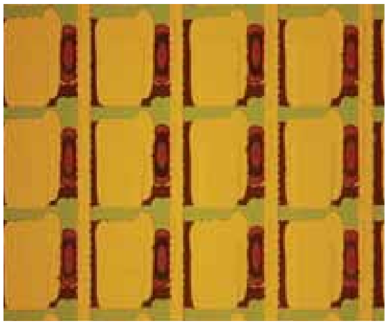

Fig. 11 Photograph of a TFT array fabricated at PARC with jet-printed PQT12 polymer. The other layers are patterned using digital lithography. The backplane is designed for a reflective display.

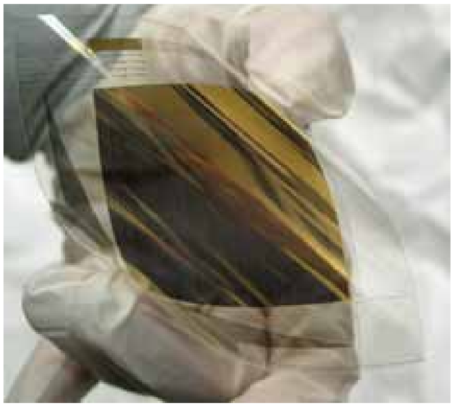

Fig. 12 Photograph of a jet-printed polymer TFT array on a flexible plastic substrate.

thermodynamic effects related to the surface energy[42]. Nanoparticle inks sinter at temperatures below 200°C and are suitable for the low-temperature processes required of flexible plastic substrates. At present, the best performance nanoparticle metals are Ag and Au, which are not ideal for low-cost electronics. Other metals are under development, but metals that readily oxidize are an obvious problem. As with other solution-based liquids that can be jetted, the unconfined printing of metals are subject to line width and uniformity issues that depend on the surface energy (Fig. 4). A printed line of liquid can distort by either dewetting into individual droplets or spreading nonuniformly, both of which affect the performance of the printed device.

Summary

Jet printing with multiejector print heads is a fast and versatile method of patterning electronic devices. The combination of printed etch masks (digital lithography) and additively printed active materials allows the deposition and patterning of almost any combination of thin-film materials. Challenges for the technology are the control of liquid-surface interactions as printed feature sizes are reduced. The availability of nanoparticle metal solutions, polymer semiconductors, and dielectrics provides a basis for developing complete additive printing processes for TFTs. mt

Acknowledgments

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