Manufacturing flexible light-emitting polymer displays with conductive lithographic film technology

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Abstract

We report on a new low-cost manufacturing process for flexible displays that has the potential to rapidly expand the market into areas that have traditionally been outside the scope of such technology. In this paper we consider the feasibility of using offset-lithography to deposit contacts for polymer light-emitting displays. We compare and contrast manufacturing criteria and present a case study detailing our initial results. It is expected that these developments will stimulate further progress in multilayer device fabrication.

Cheap, flexible conductive interconnects have the potential to find applications in a wide variety of device structures. For the more challenging exploitation areas in multilayer devices, such as displays, it was found that the properties of conductive lithographic films were not optimal in their current form. Three parameters (conductivity, surface roughness and surface work function) were identified as critical to device fabrication. Calendering and electroless plating were investigated as methods to improve these properties. Both methods aimed to modify the surface roughness and conductivity, with the plating study also modifying the work function.

1. Introduction

This paper investigates the suitability of using conductive lithographic films (CLFs) as part of a process for manufacturing polymer light-emitting displays. Printing a light-emitting display offers a route to manufacture a flexible display using a reel-to-reel process. The choice of printing technology is largely dependent on the volumes that are required. With the current demand for displays (forecast at US$30 billion in 2002) set to expand rapidly following the recent announcement of the launch of video mobile phones within the next 3 years, the industry requirement is for a fast, reliable, high-resolution process. Current research has demonstrated that offset-lithography is an alternative manufacturing process for the production of electrical interconnects.

CLFs are an emerging additive fabrication technique for a wide range of electronic circuits and systems [1, 2]. The process employs standard lithographic printing technology to fabricate conductive film patterns on a range of flexible substrates using a purpose-developed conductive ink. CLFs can be printed rapidly, using fewer processes and materials, and are, consequently, cheaper and cleaner to produce. The films are also robust, withstanding a range of standard environmental test regimes. The lithographic printing process offers excellent dimensional control and registration of substrate patterns coupled with high-speed production.

1.1. Conventional circuit boards

It was recognized that certain printing processes possess desirable characteristics that could be adapted to form the basis of a novel circuit fabrication technology, whilst permitting greater flexibility in the choice of substrate material. The characteristics of the lithographic process were considered particularly suited to circuit fabrication. CLFs can be printed rapidly via a one-stage printing process on a range of flexible substrates and are consequently cheap to produce.

The lithographic printing process relies on the action of two wetting functions on the surface of a smooth and unembossed printing plate. The plate chemistry repels water where the printed image is dark, allowing an oil-based ink to adhere. A water film repels the ink in light regions of the image. Contact with an ink and a moistening roller allows the printing plate to attract both water and ink as required, and to form the image to be printed. The image is not printed directly onto the substrate material (e.g. paper), but is instead transferred to an intermediate or 'blanket cylinder' that has a yielding surface. The blanket cylinder then presses the ink film onto the surface of the substrate, which is now supported on a separate impression cylinder. The printed substrates rely on evaporation and/or oxidation of the ink film to fix the image.

The standard lithographic printing machine used in this study has the following characteristics.

- High speed (typically 3000–10 000 impressions h−1).

- Good dimensional control and excellent registration of images:

    * 40 μm in side-lay alignment,

    * 20 μm in front-lay alignment,

    * 80–100 μm track resolution with a 60 μm gap.

- Low cost per sheet (low ink volume/substrate).

- Widespread availability of necessary production facilities.

1.2. Conducting polymer devices

There is great interest in the use of conjugated polymers to make light-emitting displays following the discovery of polymer electroluminescence [4]. Polymer light-emitting diodes (LEDs) offer the prospect of colour light-emitting displays that are flat and operate at low power, compared to backlit liquid crystal displays [5, 6]. These devices typically consist of one or more polymer layers of total thickness of approximately 100 nm in between two contacts. When a voltage is applied, the polymer emits light. To date the contacts have generally been deposited by thermal evaporation or sputtering.

Offset-lithographic printing is much faster than the use of thermal evaporation or sputtering to produce the electrodes. Both evaporation and sputtering methods require vacuum conditions to be met, which preclude a high-throughput process. CLFs could lead to much improved manufacturability of polymer displays by negating the requirement for a vacuum stage. There is currently interest in designing doped polymer systems specifically for processing for ink-jet printing [9, 10]. Researchers have demonstrated the feasibility of this technique to deposit organic materials that have greater processability than traditional electroluminescent polymers. Also, printing technology is much more able to accommodate flexible substrates and is a step towards the ultimate aim of a reelto-reel manufacturing process [11, 12]. There has been interest in combining the CLF technology with conducting polymers to produce very low-cost active devices and these are finding application in the area of sensors and other multilayer devices [3].

2. Manufacturing polymer light-emitting displays

2.1. Current methodology

There are five principal steps in the manufacture of a polymer display:

- deposition of conductive electrode material (anode) and patterning of the anode;

- organic light-emitting polymer deposition;

- deposition/patterning of cathode material;

- encapsulation;

- integration into a circuit.

Current methods rely on the processing of these devices as discrete units requiring specialist conditions to achieve the optimum performance and lifetimes. A basic 'rigid' light-emitting display is constructed by first patterning the bottom electrode from an indium tin oxide (ITO)-coated glass substrate to define an appropriate pixel structure. The active polymer layer is then spin coated from solution onto the anode. The cathode layer(s) are vapour deposited under vacuum. Encapsulation involves the addition of a second glass substrate to seal the device. The display unit is then incorporated as a component rather than as an integral part of the circuit.

2.2. Manufacturing goals

The ultimate aim of any new manufacturing process is to produce the same or better product at the lowest possible cost, without compromising quality, and resolving design issues in the process. Considering the five manufacturing steps in turn.

- Anode patterning. Anodes are typically formed from patterning ITO substrates to provide the pixel structure. Photolithography can be employed as a subtractive patterning method to achieve an image resolution in the nanometre scale. This method generates a waste product that requires disposal and also increases the time required to complete this step. A second method requires the additive patterning of an insulating layer onto an ITOcoated substrate and requires the pattern to be defined. An ideal process characteristicwould be the rapid additive patterning of a high resolution image.

- Polymer deposition. The active polymer layers are currently spin coated to achieve a uniform thickness of typically 100 nm. A non-uniform thickness will lead to a failed pixel. Spin coating is necessary because it allows the polymer solution to be processed under controlled conditions, which usually exclude oxygen and water, so as to inhibit polymer degradation. This is a major constraint to the large-scale manufacture of such devices. Also, spin coating itself is a tremendously wasteful process. Typically greater than 75% of the solution is wasted, which, considering the extremely high value of the polymer, leads to a high intrinsic cost step. There is currently a major research initiative to modify chemically the polymers to achieve greater processability under less stringent conditions to allow an alternative, less wasteful, deposition step.

- Cathode deposition. This usually takes place by vapour deposition. This technique allows very precise control over the thickness and composition of the cathode layers. This control is very important when matching the electrode requirements to the polymer employed. This technology is currently used in reel-to-reel processes for the metallization of films, but is viewed as a limited throughput method because of the time required to meet the vacuum conditions.

- Encapsulation. Very few substrates offer appropriate barrier properties to protect the conducting polymer against oxygen and moisture to achieve acceptable device lifetimes. Glass is the cheapest and most available substrate suited to this purpose, but is limited by its rigidity. The market demand for the next generation of displays requires a high degree of flexibility for advanced applications.

- Integration. The ideal process characteristic would be the manufacture of the display as an integral part of the circuit interconnect. Current manufacturing processes do not allow for integration at this level to take place.

Examination of the current manufacturing steps reveals that there are several obvious and desirable aspects that could be improved by the application of the offset-lithographic printing process. These are as follows.

- Electrode deposition. The areas where CLFs will have the greatest effect will be in the area of electrode patterning. There is the potential to pattern both the anode (as an ITO paste to mimic current methodology), and the cathode with the current Brunel conductive ink formulation.

- Encapsulation and circuit integration. These can be more easily accommodated in a reel-to-reel process. Integration can take the form of a printed CLF interconnect as an extension of the printed light-emitting display electrode structure. Encapsulation can be a part of an extended post process, such as lamination or the application of a protective conformal coating. Offset-lithography is limited in this regard by the requirement for a flexible substrate, which restricts the use of glass. Vitex systems (http://www.mcgweb.com /vitex/) have recently launched a flexible substrate 'Flexible Glass' and a conformal coating 'Barix' which it is claimed will dramatically reduce the ingress of moisture and air and greatly facilitate the transfer of this technology into high-volume applications.

- Polymer deposition. Because of the processing constraints affecting polymer deposition it is unlikely that offset-lithographic printing can accommodate the current generation of light-emitting polymers without detriment to their operating efficiencies. However, with exponential advances in polymer chemistry and processability the potential for combining these aspects may soon be resolved. Recently Cambridge Display Technology and Seiko–Epson have ink-jet printed the active polymer layer, which clearly indicates that the active polymers are becoming more robust.

There are a number of parameters that require optimization to integrate CLF and light-emitting display technologies and these are discussed below.
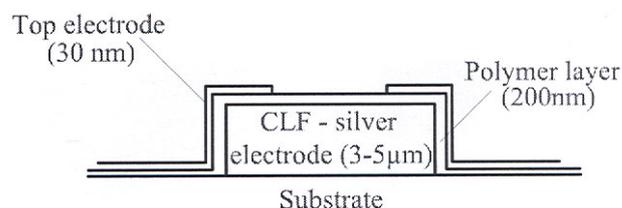

Figure 1. Schematic diagram of a typical CLF/LED 3D multilayer device.

3. Design criteria of CLFs for light-emitting display fabrication

There are three main parameters that need to be controlled for optimal device fabrication. They are conductivity, surface roughness and the surface work function. The issue of conductivity has already been resolved in an earlier study [13], the remaining issues are examined below.

3.1. Surface roughness

The surface roughness of the CLFs (on average 3–5 μm) currently falls within acceptable parameters for electrical interconnects. However, multilayer sandwich devices require much smoother surfaces (submicrometre for active devices).   The use of surfaces with submicrometre roughness lowers the need for a thick (micrometre) polymer sandwich layer of a potentially high-value material. Figure 1 shows a multilayer device and gives the layer thicknesses of a typical CLF/LED. If, in a multilayer device, the sandwich layer is much thinner than the electrode layer (nanometres as opposed to micrometres), minute changes in the CLF surface roughness can grossly affect the active layer and allow direct contact between electrodes, creating a short circuit in the structure.

3.2. Work function

The work function is defined as the energy required to move an electron from the Fermi level to the vacuum level and is different for each element (see table 1). Work functions are important when applying CLFs as electrodes in multilayer devices, such as LEDs and field effect transistors that require the injection of charge from electrodes. In LEDs there is generally a barrier to charge injection at each electrode. The choice of contact is not primarily an issue of conductivity, but rather a question of selecting contact materials with appropriate work functions to achieve the balanced injection of positive and negative charge. ITO is commonly used as an anode, and metals with relatively lowwork functions such as aluminium or calcium are generally used as the cathode. Current variations in CLFs all depend on the use of a silver particulate to give conduction and hence onework function is obtained. To obtain others, new inks have to be formulated or silver inks have to be coated. As it is not economically feasible to formulate inks containing precious metals, such as gold and palladium, which have desirable work functions, alternatives have to be considered.

Table 1. Work functions of metals employed as device electrodes. Note that the work functions are given in their polycrystalline form.

Metal	Work function (eV)
ITO	4.8
Calcium	2.87
Silver	4.26
Aluminium	4.28
Tin	4.42
Copper	4.65
Gold	5.1
Palladium	5.12

4. Case study: printed anodes

This study highlights the issues raised from the combination of the two technologies and how the problems were addressed.

4.1. Substrate choice

The need for a substrate with properties to protect the organic layer from the ingress of water and oxygen is paramount for a significant device lifetime to be observed. The current industry standard is glass which presents a limit to the flexibility of devices. The ultimate goal for light-emitting display manufacture is a flexible display which requires the investigation of new substrate materials to assess their suitability.

Patterns were printed using a standard offset-lithographic process that has been described elsewhere [1, 2]. The printed films were all air cured except in the case of Melinex[TM] films, which were cured under an array of infra-red heaters. Substrates tested are summarized in table 2.

GlossArt[TM] and PolyArt[TM] substrates were employed in the surface roughness investigation while Melinex[TM], Teslin[TM] and PolyArt[TM] were utilized in the work function study. Surface profiles were taken on a Dektak 8000 surface profilometer situated in a clean room. A 1 mm track was measured with a 2 μm diamond stylus. The instrument had a vertical range of 650 kÅ and a resolution of 10 Å. Measurements were taken from a control group and compared against the metal-plated and calendered samples.

4.2. Changing the surface roughness

It became apparent, due to the high rate and mode of failure, during the examination of devices fabricated with CLF anodes, that surface roughness was a barrier to the usefulness of these devices. Analysis of the surface roughness of the printed electrodes showed a significantly larger surface roughness than could be attributed to the substrate alone [14]. Surface profiling showed micrometre-sized' spikes which punctured through the organic layer to directly contact the cathode, shorting the circuit. Research was then directed towards attaining a smoother printed electrode surface.

Calendering is a smoothing process that finds wide use in the paper making and finishing industry. A typical instrument consists of two contra-rotating cylinders providing variable compression. Two types of calender were utilized:

- a chrome/rubber calender for pressures up to 45 bar (652.7 psi), and
- a steel/cotton 'super' calender for pressures up to 68.9 bar (1000 psi).

In each instance the PolyArt[TM] and GlossArt[TM] printed films were passed once through the calender at a pre-set pressure.

After calendering, the electrical resistivity of the films was remeasured and the surface roughness was ascertained. It was observed that the substrate choice has a profound influence on the size and distribution of the sheet resistivity. The GlossArt[TM] samples have a much wider distribution and magnitude than the PolyArt[TM] samples, indicating that the smoother gloss paper is a less consistent substrate. After calendering, the distribution of the GlossArt[TM] samples is narrower, indicating that calendaring reduced any imperfections in the film. It is thought that this is wholly due to the low calendering pressures available. Chrome/rubber calender gave better results than the steel/cotton (supercalendered) samples even at the lower pressures employed. This was thought to be due to a combination of the elastic nature of the substrate under compression and that of the cotton calender.

It is considered that sheet resistivity will be greatly reduced if a high enough pressure can be employed, ideally on a chrome/rubber calender. While analysis of the calendered samples showed a decrease in the surface roughness of the printed films there seems to be little overall change between the samples calendered at different pressures. This was thought to be due to a combination of the significant surface roughness contribution from the substrate and the elastic nature of the substrate during compression.

Figure 2 shows the surface topography by scanning electron microscopy (SEM) of the printed ink surface before and after calendering. The images are very demonstrative of the effect of calendering with the uncalendered film having a very rough surface with gaps in the conductor clearly visible. The calendered film, by contrast, has a much smoother surface with the silver particulate obviously flattened but retaining the grain boundaries. The surface roughness was shown in the best case to halve, giving a surface roughness average of 0.5 μm [14].

4.3. Changing the surface work function

Because of the current limitation of only a single (silver) work function electrode it became of increasing importance to expand the available options. Plating technology has a wide range of application areas from jewellery to state-of-the-art electronics [7]. This technology was seen as a cost-effective way of modifying the existing surface to achieve different work functions. Copper plating was employed using the Shipley Cuposit CP78-2 process [8]. Typical methodology involves the activation of the area to be plated, known as the seeding layer, with a palladium activator before copper plating. As the printed seeding layer employed a novel silver/copper ink, this rendered the activation step redundant and reduced the plating time by half (a significant cost reduction and a step towards the viability of plating as a manufacturing post process). This formulation was used throughout for plating the seeding layer. Printed films were immersed in the copper plating solution for 5 or 10 min, giving a rate of 4μmh-1. Some copper-plated samples were overplated with tin, a technique commonly employed in the electronics industry to prevent degradation of the copper surface.

Table 2. Substrates employed in device evaluation.

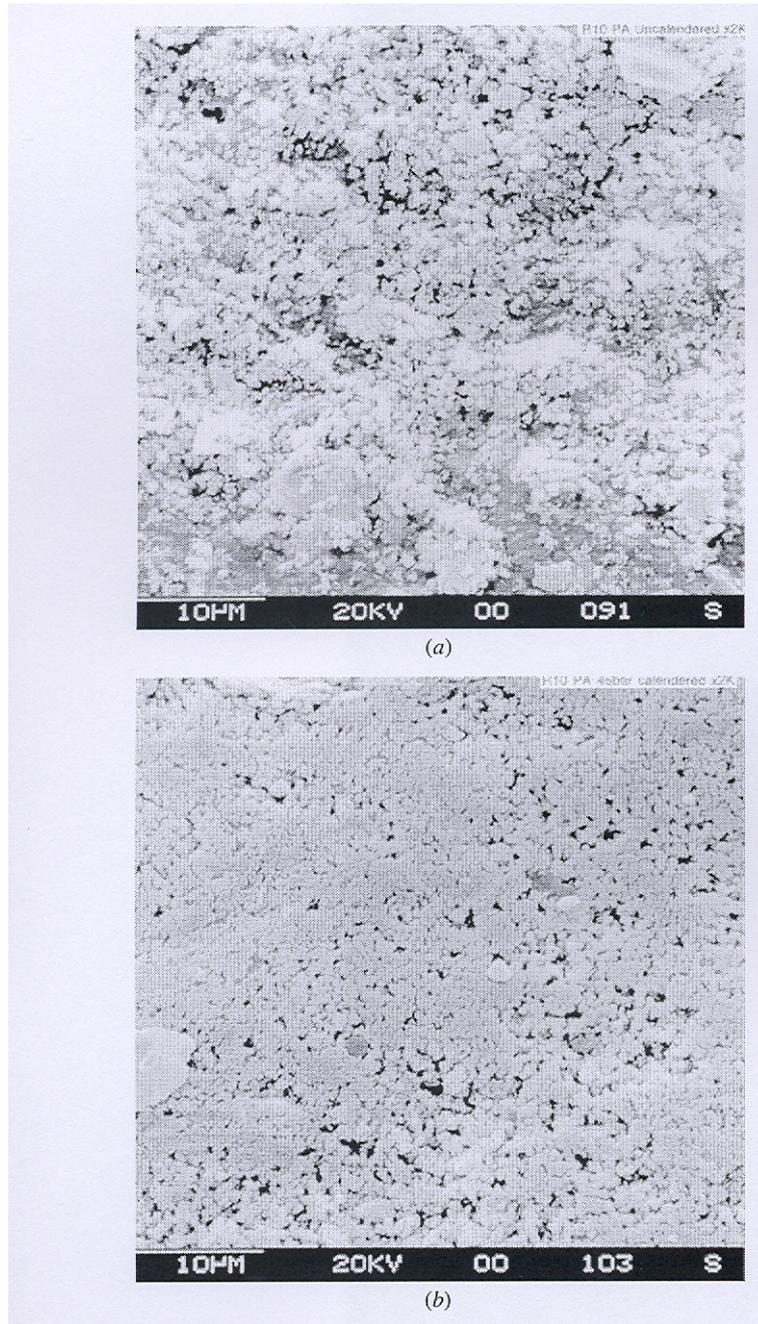| Subsrate	Composition	Average roughness (peak to valley) (μm)
GlossArt^{TM}	Kaolin coated cellulose paper	0.25 (1.20)
PolyArt^{TM}	Polythene with a proprietary coating	0.51 (2.95)
Teslin^{TM}	Silica- and air-filled polythene	1.25 (6.20)
Melinex^{TM}	Polyester with a proprietary coating	0.01 (0.07)

Figure 2. SEM micrographs of uncalendered (*a*) and calendered (*b*) conductive lithographic films on PolyArt[TM].
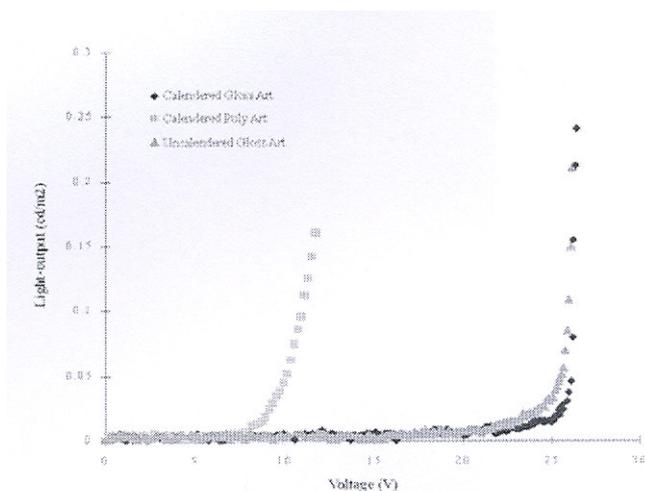
Figure 3. Voltage–light output characteristics for devices made from calendered GlossArt[TM] and PolyArt[TM] and uncalendered GlossArt[TM].

Palladium plating was achieved by immersing the printed films in a Shipley Activator 472 bath for 5–20 min. No data were available to indicate the rate of deposition although after deposition a reduction in resistivity was observed. Gold plating was achieved using the Shipley Aureus 7950 process. The printed films were immersed in the bath for 5–20 min giving a deposit of 0.05–0.10 μm.

4.4. Device fabrication

CLF LEDs were fabricated by spin coating a solution of MEH-PPV (more fully known as poly(2-methoxy-5- (2′-ethyl-hexoxy)-1,4-phenylene-vinylene) from a chlorobenzene solution onto a CLF printed track. The concentration of the solution, spin speed and duration determined the polymer layer thickness. The top electrode, a 30 nm aluminium layer, was thermally evaporated at a pressure of 10^{-6} mbar. The thin top contact layer thickness was necessary to allow light to pass through.

5. Results

5.1. Electrodes modified for work function

Having successfully plated the CLF electrodes with a new range of work function electrodes, the samples were then analysed for surface roughness. The average roughness was found to be significantly greater (almost double) that of the unplated samples with very large peak to valley measurements. Unfortunately this meant that the materials were unsuitable for incorporation as electrode structures for devices, as LED structures constructed from them short circuited when a voltage was applied.

Table 3. Efficiency and brightness of the LEDs.

Sample	Maximum brightness (cd m−2)	Maximum efficiency (%)
Uncalendered PolyArt^{TM}	—	—
Calendered PolyArt^{TM}	0.16	8.2×10^{-4}
Uncalendered GlossArt^{TM}	0.21	1.8×10^{-4}
Calendered GlossArt^{TM}	0.24	2.0×10^{-4}

It was hoped that the plating process might have planarized the CLF thereby lowering the surface roughness, but instead the initial surface roughness was amplified. Attempts to calendar these samples resulted in the delamination of the electrolessly plated layer. Consequently no data could be obtained from these structures.

5.2. Electrodes modified for surface roughness

Testing of the devices was performed under vacuum. Of the uncalendered CLFs tested the only successful device was fabricated from a GlossArt^{TM} sample. It was thought that this was because it had the smoothest surface of the uncalendered CLFs under investigation. When calendered samples were tested, both GlossArt^{TM} and PolyArt^{TM} devices gave light.

The voltage–light output characteristics, figure 3, are nonlinear and typical of characteristics for polymer LEDs, apart from a relatively high turn-on field due to the large device thickness of typically 260 nm for the polymer layer, and large barrier to charge injection due to the work functions of the contacts used.

Devices made from calendered and uncalendered GlossArt^{TM} give similar characteristics. This may be because after calendering there is little reduction in surface roughness of the GlossArt^{TM} samples.

The PolyArt^{TM} samples are initially rougher and show a greater decline in surface roughness and sheet resistivity. This reduction after calendering brings the PolyArt^{TM} samples on a par with GlossArt^{TM}, which might explain why only the calendered PolyArt^{TM} samples can be successfully fabricated as LED devices. It is apparent that there is a boundary roughness level after which LED fabrication becomes problematic.

The brightness and efficiency data are given in table 3. In all cases the devices emitted an orange light, typical for the polymer layer used, across the whole pixel. The low brightness and efficiency of the devices can be attributed to two factors. The first is that thework functions of the electrodes give a large barrier to charge injection. The second is that only part of the light generated in the device can pass through the aluminium electrode, whereas in conventional LEDs the ITO electrode used is transparent.

In figure 4 it can be seen that the light output is proportional to the current flowing through the device, as seen in conventional polymer LEDs. This is a convenient feature for the drive electronics of displays.

6. Conclusions

We have examined the current process requirements for the manufacture of organic light-emitting displays and compared these against the requirements of a reel-to-reel manufacturing process. We have considered these processes in light of the potential benefits of employing a printing technology to achieve this goal, in particular offset-lithography and conductive lithographic films. Research has shown that there are a number of inter-related parameters requiring optimization. CLFs incorporated into multilayer devices require optimal surface roughness. Changing the work function of the printed electrode, by electroless plating, was shown to influence surface roughness directly. The conductivities required for use in polymer LEDs were readily exceeded and needed no further optimization.
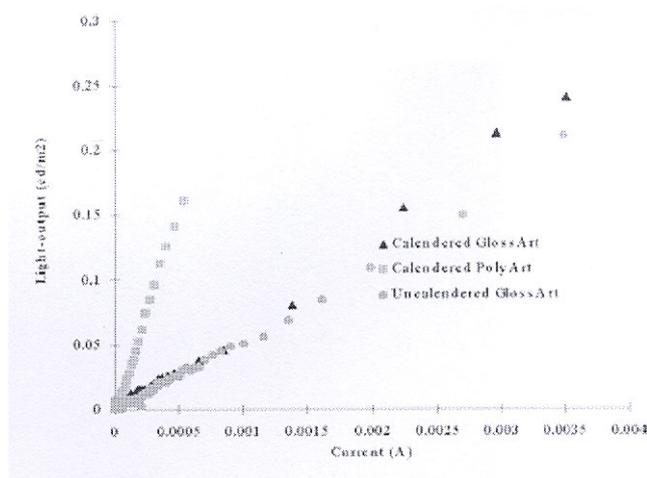
Figure 4. Current–light output characteristics for devices made from calendered GlossArt[TM] and PolyArt[TM] and uncalendered GlossArt[TM].

We have successfully demonstrated that polymer LEDs can be fabricated from silver-based conductive lithographic film printed contacts. The properties of these devices are further enhanced when the printed films are calendered. These results represent a significant step in the low-cost manufacture of flexible light-emitting displays.

Obstacles still remain, namely the processability of the organic polymer and the encapsulation of the device to attain meaningful device lifetimes and efficiencies. But the authors are optimistic that these are surmountable in the short term and it would be easy to imagine a flexible display as 'how soon' rather than 'when or how'.

References

[1] Ramsey B J, Evans P S A and Harrison D J 1997 A novel fabrication technique using offset-lithography *J. Electron. Manufact.* **7** 63–7

[2] Evans P S A, Ramsey B J, Harrey P M and Harrison D J 1999 Printed analogue filter systems *IEE Electron. Lett.* **35** 306–8

[3] Harrey P M, Evans P S A, Ramsey B J and Harrison D J 1999 A novel manufacturing process for capacitors using offset-lithography *Proc. 1st Int. Symp. for Inverse Manufacturing (Waseeda University, Tokyo, Japan, February 1999)*

[4] Burroughes J H, Bradley D D C, Brown A R, Marks R N, Mackay K, Friend R H, Burns P L and Holmes A B 1990 Light-emitting-diodes based on conjugated polymers *Nature* **347** 539–41

[5] Friend R H *et al* 1999 Electroluminescence in conjugated polymers *Nature* **397** 121–8

[6] Samuel I 2000 Polymer electronics *Phil. Trans. R. Soc.* **358** 193–210

[7] Deckert C A 1995 Electroless copper plating—a review: part 1 *Plating Surface Finishing* February 48–55 and references therein

[8] Lochun D, Evans P S A, Green S, Goosey M and Harrison D J 1999 Electro and electroless plating technology as a post-process for conductive lithographic films *Confidential Internal Report*

[9] Hebner T R, Wu C C, Marcy D, Lu M H and Sturm J C 1998 Ink-jet printing of doped polymers for organic light emitting devices *Appl. Phys. Lett.* **72** 519–21

[10] Bharathan J and Yang Y 1998 Polymer electroluminescent devices processed by ink-jet printing: 1. Polymer light-emitting logo *Appl. Phys. Lett.* **72** 2660–2

[11] Rogers J A, Bao Z, Makhija A and Braun P 1999 Printing process suitable for reel-to-reel production of high-performance organic transistors and circuits *Adv. Mater.* **11** 741–5

[12] Bao Z 2000 Materials and fabrication needs for low-cost organic transistor circuits *Adv. Mater.* **12** 227–30

[13] Ramsey B J 1999 Electronic circuit manufacture by offset lithography *PhD Thesis* Department of Design, Brunel University

[14] Lochun D, Kilitziraki M, Jarrett E, Green S, Ramsey B J, Samuel I D W and Harrison D J 1999 Post-processing of conductive lithographic films for multilayer device fabrication *Proc. 24th IEEE Conf. (Austin, TX, 18–20 October, 1999)*