Inkjetted Organic Transistors using a Novel Pentacene Precursor

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ABSTRACT

Pentacene is one of the most promising organic materials for organic transistor fabrication, since it offers higher mobility, better on-off ratio, improved environmental stability, and better reliability than most other organic semiconductors. However, its severe insolubility renders it useless for the solution-based fabrication of electronic devices. Solution-based processing is the key to enabling ultra-low-cost circuit fabrication, since it eliminates the need for lithography, subtractive processing, and vacuum-based film deposition. Using a recently developed soluble pentacene precursor, we demonstrate the first inkjet-printed pentacene transistor fabricated to date. This is achieved using a substrate-gated transistor structure in conjunction with an inkjet-printed pentacene precursor active layer. After deposition, the precursor is converted to pentacene via heating, through the decomposition of the Diels-Alder product. As the anneal temperature increases above 120°C, performance increases dramatically. The process is therefore compatible with numerous low-temperature plastics. As the anneal time is increased to several minutes, performance likewise increases through increased precursor decomposition. However, exposure to excess temperatures or times tends to degrade performance. This is caused by morphological and chemical changes in the pentacene film. Optimization of the anneal process alone has resulted in the demonstration of transistors with an on-off ratio of $>10^5$ and field-effect mobility of $>0.01\text{cm}^2$/V-s, attesting to the great promise of this material.

INTRODUCTION

Recently, there has been great interest in the development of printed organic electronics technologies, which are expected to see use in low-cost, flexible displays and disposable electronics applications. Given the tremendous postulated price-per-area cost advantage of printed technologies over the competing amorphous and polycrystalline silicon based technologies, all-printed displays are expected to have tremendous cost-performance advantages over their incumbent silicon-based counterparts [1]. Similarly, low-cost RFID tags, with cost points in the sub-one cent range, are also compelling application for printed electronics, since they may be used to replace UPC barcodes on consumer products, ushering in an era of enhanced consumer convenience and warehousing efficiency, through a realization of real-time price and product controls, automated inventory processes, and automated checkout.

All-printed circuit technologies are attractive for several reasons, with their main advantage being cost-related. They eliminate the need for most of the major cost points in semiconductor manufacturing, including the most expensive cost point – lithography. Printed electronics also eliminate the need for high-vacuum processing, including PVD, CVD, plasma etching, etc., all of which have major impacts on system cost. Additionally, printed electronic systems use an additive fabrication process, which reduces the waste abatement costs. Thus, they should result in a substantially reduced cost making them suitable for use in disposable consumer products.

Over the last ten years, there has been tremendous emphasis on the development of soluble organic semiconductors, suitable for printing. Much progress has been made in this regard, with

mobilities higher than 10^{-2} cm^2/V-s being reported for polythiophene and F8T2. Unfortunately, all results reported with these and similar soluble materials have not achieved the performance levels reported in insoluble organic semiconductors such as pentacene. In these materials, mobilities well above 0.1cm^2/V-s are routinely achievable (in fact, mobilities as high as 3cm^2/V-s have been reported using pentacene [2]). Furthermore, pentacene is generally much more stable (particularly in terms of oxygen and moisture stability) than most soluble organic semiconductors, and is therefore much closer to realization in a manufacturable technology.

Over the last few years, several attempts have been made to synthesize soluble pentacene precursors [3], which potentially combine the cost advantages of soluble materials with the performance advantages of pentacene. These materials are printable, and may be subsequently converted to pentacene by thermal cycling. Unfortunately, the processes reported to date are challenging from a synthetic perspective, and have therefore not seen widescale adoption. Recently, researchers at IBM [4] demonstrated a novel, relatively simple, synthetic pathway for achieving a soluble pentacene precursor. Using a spin-coating process, the researchers demonstrated mobilities higher than 0.5cm^2/V-s. Here, we apply the same synthetic pathway to develop an inkjetted pentacene precursor technology. We study the effect of variations in the time/temperature of the annealing process used to convert the precursor to pentacene on device performance, and using the optimization strategies developed therewith, demonstrate organic TFTs with inkjetted pentacene active layers for the first time. We report on the characteristics of these devices, and develop optimization strategies for further enhancing the performance.

EXPERIMENTAL DETAILS

The experimental process consists of three stages – the synthesis of the pentacene derivative, the optimization of the anneal process, and the fabrication of TFTs with inkjetted active layers.

Precursor Synthesis

The precursor synthesis follows that previously reported by IBM [4]. Pentacene (0.5g), obtained from commercial sources without further purification, was added to N-sulfinylacetamide (0.57g) and methyltrioxorhenium (0.0045) in chloroform(30mL). The mixture was allowed to reflux for 2 days, after which the product was purified by flash chromotography. N-sulfinylacetamide was made using previously disclosed methods [5]. The resulting material is easily converted to pentacene using the reverse reaction, as shown in figure 1.
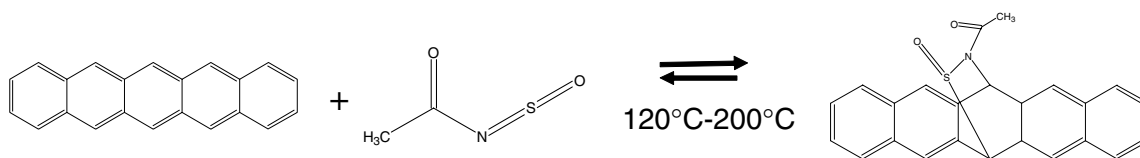
Figure 1: Reversible Diels-Alder reaction used to produce the soluble pentacene precursor.

Anneal Process Optimization

As discussed above, a thermal anneal process is used to convert the pentacene precursor back to pentacene by a reverse Diels-Alder reaction. Obviously, the time/temperature of this thermal cycling is expected to have a strong impact on the performance of the final device. To optimize the conversion process, we used substrate-gated TFTs with 100nm thermal SiO$_2$ gate

dielectrics and evaporated gold source/drain pads as test vehicles. The pentacene precursor synthesized above was dissolved in chloroform at a concentration of 1 wt%, and was spin-coated on these substrates in an inert ambient at 6000rpm. In the same ambient, experiments were performed to determine the effect of the anneal conditions on final device performance. Anneal temperature was varied from 120°C to 205°C, and anneal time was varied from 1min to 1hr.

Inkjetted Pentacene Device Fabrication

Using the optimal conditions developed above, devices were fabricated with inkjetted pentacene active layers. All inkjet experiments were performed using a custom inkjet system, shown in figure 1. The overall testbed consists of translation stages, inkjet dispensers, a hot chuck for heating and cooling the substrate, and software to control the various systems. For all experiments, we used piezoelectric heads manufactured by Microfab, Inc., with nozzle diameters varying from 30μm to 60μm. Custom software was used to provide overlay, translation, and head control.
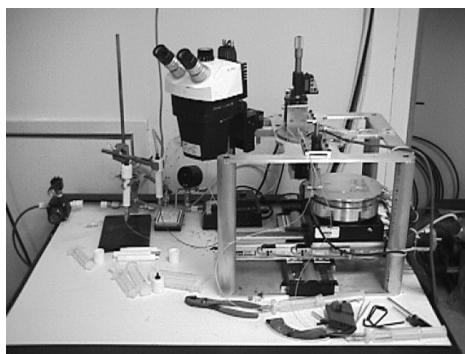

Figure 2: The custom inkjet system for printed electronics fabrication.

The pentacene precursor was dissolved in anisol. This solvent was chosen over chloroform due to its slower evaporation rate, making it more suitable for inkjet printing (solvents with high evaporation rates such as chloroform are highly susceptible to clogging). Inkjet voltage waveform parameters were optimized to produce stable droplets with good repeatability and absence of satellite drops. Pentacene was inkjetted onto oxidized silicon wafers with evaporated gold source/drain pads to form substrate gated TFTs with 100nm thermal SiO_2 gate dielectrics. The resulting TFTs were characterized and electrical parameters were extracted.

RESULTS

The characteristics of TFTs fabricated using this pentacene precursor were found to be strongly dependent on the temperature at which conversion to pentacene was performed. The effect of anneal temperature on device performance is shown below, in figure 3. Clearly, there are two regimes associated with the anneal process. At low temperatures, mobility increases with increasing temperature, while at high temperatures, mobility is degraded with increasing temperature. These effects are easily explained by considering the conversion process and the stability of the resulting pentacene.
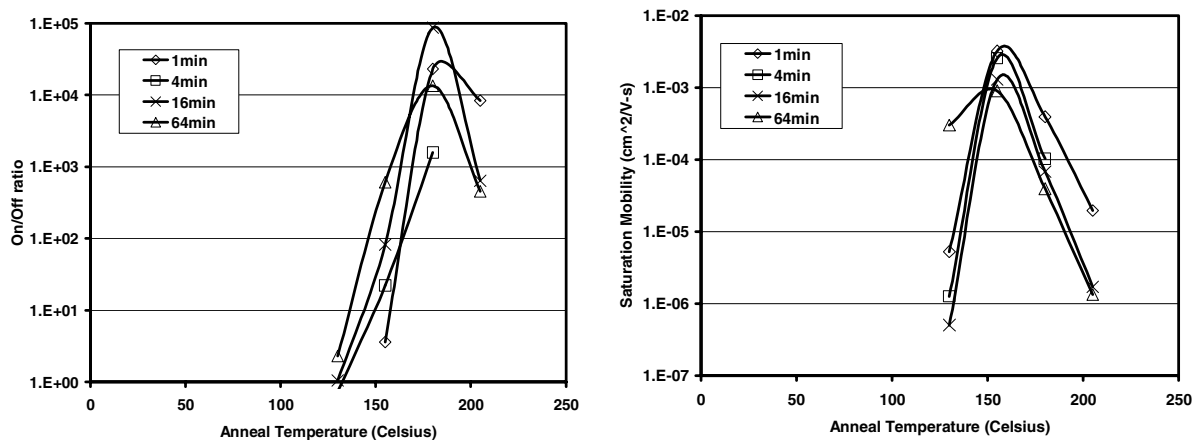
Figure 3: Effect of anneal temperature on (left) on-off ratio and (right) saturation mobility.

The conversion from the pentacene precursor to pentacene occurs through a reverse Diels-Alder process, in which the Diels-Alder side-chain (with the N-S=O linkage) is cleaved from the central ring of the pentacene. The aromaticity of the pentacene is therefore restored, converting it back into semiconducting pentacene. The N-S=O product is evolved into the gas-phase, and diffuses out of the pentacene. At low-temperatures, the conversion of the precursor to pentacene is poor; indeed, at 120°C, no semiconducting behavior is measurable, indicative of negligible conversion. As the anneal temperature is increased, the efficiency of conversion is greatly increased, and substantially larger fractions of precursor are converted back to pentacene. This effect, as expected, results in a time-temperature dependence; at lower temperatures, longer times are needed to facilitate conversion, while at higher temperatures, short times appear to be sufficient, as is evident from figure 4, which plots the effect of anneal duration on drive current. Similar effects are also seen for mobility and on-off ratio.
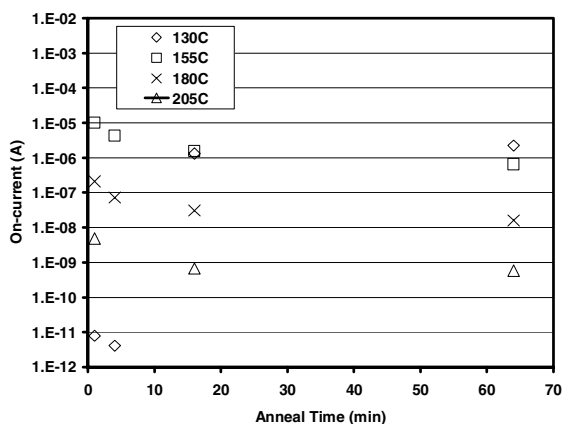
Figure 4: Effect of anneal duration on drive current for different anneal temperatures.

As is also apparent from figure 3, at elevated temperatures, the mobility is degraded. This is most likely caused by the thermal degradation of the pentacene itself. As the temperature is increased, more of the pentacene is degraded, resulting in a substantially degraded mobility. Again, this also shows a time dependence, evident in figure 4.

The analyses above indicate that optimal conditions for pentacene precursor formation exist between 155°C/4min and 180°C/1min. These anneal conditions were used on inkjetted pentacene TFTs. Best-case device characteristics are shown in figure 5. Clearly, there are substantial contact resistance problems with these devices, and further optimization is needed. However, despite the lack of optimization, mobilities as high as 0.02 with on-off ratios as high as 10^5 have been achieved. This attests to the potential viability of the technology. With further optimization, higher performance devices should be achievable.
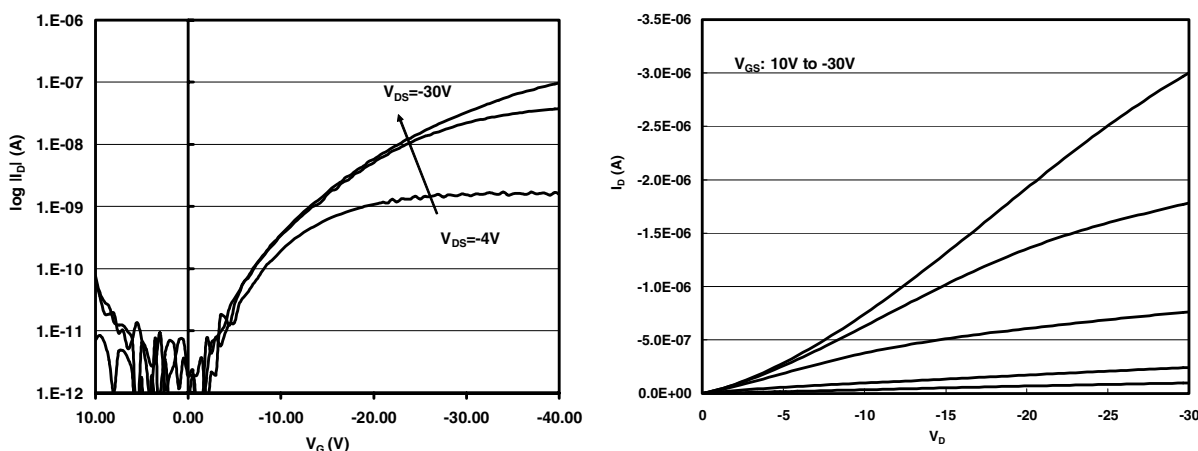
Figure 5: Best-case electrical characteristics obtained using pentacene precursor. Anneal was performed in nitrogen at 155°C for 4 minutes.

DISCUSSION

The analysis above indicates that the pentacene precursor process is a promising technology for fabrication of printed TFTs. With further optimization, it should be possible to substantially enhance the performance of printed TFTs to achieve results similar to those achieved using spin-coating. Given, the significant volume change that occurs during precursor-to-pentacene conversion, it is unlikely that the ordering in these printed films with ever achieve the ordering (and therefore performance) levels reported using evaporated pentacene; however, these results, and those previously reported by spin-coating, are very promising when compared with other printable organic semiconductor-based TFTs, particularly when the comparatively improved air-stability of pentacene over most soluble organic semiconductors is taken into account. Furthermore, the conversion of the precursor into comparatively solvent-resistant pentacene is an added advantage, since it simplifies integration of multilayer printed structures; solvents in overlying layers are expected to have less impact on underlying pentacene layers than on layers of soluble organic semiconductors. This makes this precursor route vary attractive for all-printed circuits, which will involve multiple layers of printed semiconductors, dielectrics, and conductors.

CONCLUSIONS

We have demonstrated the use of a soluble pentacene precursor to fabricate TFTs with inkjetted active layers. Optimization strategies for conversion of the precursor to pentacene have been explored and inkjetted TFTs have been fabricated. Mobilities as high as $0.02cm^2$/V-s and on-off ratios as high as 10^5 have been achieved. Further optimization of the materials synthesis should result in substantially enhanced performance. These results therefore represent an important step towards the demonstration of a robust printed TFT technology for all-printed low-cost electronic circuits.

ACKNOWLEDGEMENTS

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