

## Thin Films Division

### Room 104B - Session TF+AS+EL+EM+NS+PS+SS-ThA

#### IoT Session: Thin Films for Flexible Electronics and IoT

**Moderators:** Jesse Jur, North Carolina State University, Siamak Nejati, University of Nebraska-Lincoln

2:20pm **TF+AS+EL+EM+NS+PS+SS-ThA1 Ultraflexible Organic Electronics for Bio-medical Applications**, *Tomoyuki Yokota, T. Someya*, The University of Tokyo, Japan

**INVITED**

Recently, flexible electronics has much attracted to realize bio medical application for their flexibility and conformability [1-3]. To improve these characteristics, reducing the thickness of the device is very effective [4]. We have developed ultra-flexible and lightweight organic electronics and photonics devices with few micron substrates. We fabricated the 2-V operational organic transistor and circuits which has very thin gate dielectric layers. The gate dielectrics were composed of thin aluminium oxide layer and self-assembled monolayers (SAMs). Due to the very thin substrate and neutral position, our device shows the highly flexibility and conformability. The device doesn't be broken after crumpling.

And also we fabricated highly efficient, ultra-flexible, air-stable, three-color, polymer light-emitting diodes (PLEDs) have been manufactured on one-micrometer-thick parylene substrates. The total thickness of the devices, including the substrate and encapsulation layer, is only three micrometers, which is one order of magnitude thinner than the epidermal layer of the human skin. The PLEDs are directly laminated on the surface of skin and are used as indicators/displays owing to their amazing conformability as their superthin characteristics. Three-color PLEDs exhibit a high external quantum efficiency (EQE) (12, 14, and 6% for red, green and blue, respectively) and large luminescence (over 10,000 candelas per square meter at 10 V). The PLEDs are integrated with organic photodetectors and are used as pulse oximeter.

#### References

- [1] D. Khodagholy et al., *Nature Commun.* **4** 1575 (2013).
- [2] G. Schwartz et al., *Nature Commun.* **4**, 1859 (2013).
- [3] L. Xu et al., *Nature Commun.* **5** 3329 (2014).
- [4] D. H. Kim et al., *Nat. Mater.*, **9**, 511 (2011).

3:00pm **TF+AS+EL+EM+NS+PS+SS-ThA3 Molecular Surface Chemistry for Improved Interfaces in Organic Electronics**, *Jacob W. Ciszek*, Loyola University Chicago

Organic optoelectronic devices (OLED, OFETs, etc.) contain at least one, if not multiple instances of overlayers deposited onto organic semiconductors. The generated interface is inherently flawed with issues such as non-ohmic contact, overlayer delamination, or deposition induced damage arising. Traditionally, this is addressed by physical vapor deposition of yet another layer or by reengineering the materials in the device stack. In contrast, a reaction based approach allows for a wider range of function to be installed via molecular components in an organized and oriented manner, all while take advantage the inherent reactivity of the organic molecules which comprise the semiconducting layer. We have developed this approach via a "click-like" Diels-Alder chemistry whereby prototypical acene films (tetracene or pentacene) can be appended with a variety of small molecules to form an interfacial layer only ~5 Å thick. This chemistry is then applied towards improving the metal on semiconductor contact. As a demonstration of principle, Diels-Alder chemistry is utilized to form covalent bonds linking the organic semiconductor with a deposited metal contact thereby eliminating the poor adhesion present in this system. Application of the chemistry towards contact potential shifts is presented, while work towards sensing applications concludes the talk.

3:20pm **TF+AS+EL+EM+NS+PS+SS-ThA4 Investigation of Low Temperature ALD-deposited SnO<sub>2</sub> Films Stability in a Microfabrication Environment**, *Tony Maindron, S.M. Sandrez, N.V. Vaxelaire*, CEA/LETI-University Grenoble Alpes, France

For applications such as displays (LCD, OLED) or solar cells, it is mandatory to use Transparent Conductive Oxides (TCOs) so as to allow light to extract out of the circuit or for light harvesting, respectively. In display technology, TCOs are also studied so as to replace the silicon technology developed to make the semiconducting channel in thin-film transistors. The mainstream TCO today is indium tin oxide (ITO), (90% indium oxide and 10% tin oxide). It has the advantage of having a high conductivity and a low surface

resistivity, of the order of 10 ohm/square, while having a transmittance greater than 85% over the entire visible spectrum. However, it has several drawbacks, including the scarcity of indium and the high cost associated to its extraction process, which has prompted the scientific community to look for alternative TCOs. Among all TCOs, ZnO has been widely studied as a low cost single-metal oxide alternative material to ITO, as well as its multi-metal oxide derivatives using a dedicated metal dopant to control its electrical conductivity, as for instance with Al (ZnO:Al or AZO). One issue however with ZnO films lays in their relative chemical stability to water. It has been shown that films of ZnO or AZO change their physical properties when exposed to moisture: electrical conductivity decreases, roughness can increase, and optical characteristics are modified. By extension, when ZnO-based TCOs have to be finely patterned by photolithography, their high sensitivity to water-based solutions can be a severe issue. In our laboratory, we have noticed that ZnO and AZO films made by ALD at 150 °C typically are not stable in a microfabrication process: a large decrease (~ 20 %) of AZO thickness after the development step of photoresists used to pattern the TCO film has been noticed. One way to stabilize ZnO-based compounds is to anneal the films at high temperatures. However for some dedicated applications that use fragile substrates (plastic films for flexible organic electronics for instance), such post annealing processes at high temperature (typ. > 150 °C) cannot be applied. An alternative is to explore alternative materials to AZO: we found out that SnO<sub>2</sub> ALD (150 °C) shows very promising features regarding the stability under a microfabrication environment, while having good electrical and optical characteristics.

4:00pm **TF+AS+EL+EM+NS+PS+SS-ThA6 Dopant Distribution in Atomic Layer Deposited ZnO:Al and In<sub>2</sub>O<sub>3</sub>:H Films Studied by Atom Probe Tomography and Transmission Electron Microscopy**, *Y. Wu, B. Macco, Eindhoven University of Technology, The Netherlands; A.D. Giddings, T.J. Prosa, D.J. Larson, CAMECA Instruments Inc.; S. Kölling, P.M. Koenraad, F. Roozeboom, Erwin Kessels, M.A. Verheijen*, Eindhoven University of Technology, The Netherlands

Transparent conductive oxides (TCOs) are ubiquitous in many of today's electronic devices, including solar cells. Atomic layer deposition (ALD) is a promising method to prepare high quality TCO films due to its well-known virtues – i.e., precise growth control, excellent conformality and uniformity – combined with its damage-free character. Here we report on two types of TCO films that we have studied by a combination of atom probe tomography (APT) and high-resolution transmission electron microscopy (TEM). The aim was to get more insight into how the dopants are distributed in the films.

The first study was carried out on ZnO:Al prepared by alternating cycles of Zn(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub> and H<sub>2</sub>O with cycles of Al(CH<sub>3</sub>)<sub>3</sub> and H<sub>2</sub>O in a supercycle fashion at 250 °C. For this material it is known that the maximum conductivity achievable is limited by the low doping efficiency of Al. To better understand the limiting factors for the doping efficiency, the 3-dimensional distribution of Al atoms in the ZnO host material matrix has been examined at the atomic scale by the aforementioned techniques [1]. Although the Al distribution in ZnO films prepared by so-called "ALD supercycles" is often presented as atomically flat δ-doped layers, in reality a broadening of the Al-dopant layers was observed with a full-width-half-maximum of ~2 nm. In addition, an enrichment of the Al at grain boundaries was seen.

The second study involved In<sub>2</sub>O<sub>3</sub>:H prepared by InCp and a mixture of O<sub>2</sub> and H<sub>2</sub>O at 100 °C. This material provides a record optoelectronic quality after post-deposition crystallization of the films at 200 °C. Since both the H dopant incorporation and the film microstructure play a key role in determining the optoelectronic properties, both the crystal growth and the incorporation of H during this ALD process were studied [2]. TEM studies show that an amorphous-to-crystalline phase transition occurs in the low temperature regime (100-150 °C), which is accompanied by a strong decrease in carrier density and an increase in carrier mobility. Isotope studies using APT on films grown with D<sub>2</sub>O show that the incorporated hydrogen mainly originates from the co-reactant and not from the InCp precursor. In addition, it was established that the incorporation of hydrogen decreased from ~4 at. % for amorphous films to ~2 at. % after the transition to crystalline films.

- [1] Y. Wu, A. Giddings, M.A. Verheijen, B. Macco, T.J. Prosa, D.J. Larson, F. Roozeboom, and W.M.M. Kessels, *Chem. Mater.* **30**, 1209 (2018).
- [2] Y. Wu, B. Macco, D. Vanhemel, S. Kölling, M.A. Verheijen, P.M. Koenraad, W.M.M. Kessels, and F. Roozeboom, *ACS Appl. Mater. Interfaces*, **9**, 592 (2017).

# Thursday Afternoon, October 25, 2018

4:20pm **TF+AS+EL+EM+NS+PS+SS-ThA7 Roll-to-Roll Processable OTFT Sensors and Amplifier**, *Kai Zhang*, University of Oxford, Department of Materials, UK; *C.-M. Chen, B. Choubey, H.E. Assender*, University of Oxford, UK

The high flexibility and relatively low cost of organic electronics are gradually providing more possibility for their application. Compared with conventional silicon based electronics, organic electronics have relatively short lifecycles and processor speed, but they are more promising in the market of wearable and flexible devices, for example, wearable health care devices, simple memory devices and flexible displays. In recent years, some flexible and wearable sensors have been developed, e.g. skin-touching sensors embedded in a sports suit can detect the change of heart rate, blood pressure, ion concentration of perspiration, or infrared radiation from the human body.

In most sensors based on organic thin film transistors (OTFT) made to date, the semiconductors are employed directly to detect analytes. However, (1) the lifecycles of this design is short due to the low stability of organic semiconductors; and (2) any modification for selectivity needs to be compatible with the semiconductor.

In this paper, we present sensors based upon an extended floating gate in order to separate the sensory area from the semiconductor. Transistors are manufactured, using our roll-to-roll vacuum webcoating facility, using a high-throughput all evaporation process (Ding et al., 2016, Taylor et al., 2015). We have demonstrated the principle of operation of a floating gate sensor integrated with the vacuum-deposited OTFT, by means of a simple strain sensor, using ferroelectric PVDF on the extended floating gate to directly act as a sensory material. To amplify the sensor signal further, a series of current mirrors and differential amplifiers have been designed based on the properties of single OTFTs. The combination of organic amplifier and OTFT sensor will be helpful to transduce sensing signal to a suitable level for wireless signal reading from flexible devices.

## Reference:

DING, Z., ABBAS, G. A. W., ASSENDER, H. E., MORRISON, J. J., YEATES, S. G., PATCHETT, E. R. & TAYLOR, D. M. 2016. Vacuum production of OTFTs by vapour jet deposition of dinaphtho[2,3-b:2',3'-f]thieno[3,2-b]thiophene (DNFT) on a lauryl acrylate functionalised dielectric surface. *Organic Electronics*, 31, 90-97.

TAYLOR, D. M., PATCHETT, E. R., WILLIAMS, A., DING, Z., ASSENDER, H. E., MORRISON, J. J. & YEATES, S. G. 2015. Fabrication and simulation of organic transistors and functional circuits. *Chemical Physics*, 456, 85-92.

4:40pm **TF+AS+EL+EM+NS+PS+SS-ThA8 Functionalization of Indium Gallium Zinc Oxide Surfaces for Transparent Biosensors**, *X. Du, S. John, J. Bergevin, Gregory Herman*, Oregon State University

Amorphous indium gallium zinc oxide (IGZO) field effect transistors (FETs) are a promising technology for a wide range of electronic applications including implantable and wearable biosensors. We have recently evaluated the functionalization of IGZO back channel surfaces with a range of self-assembled monolayers (SAM) to precisely control surface chemistry and improve stability of the IGZO-FETs. The SAMs evaluated include, n-hexylphosphonic acid (n-HPA), (3,3,4,4,5,5,6,6,6-nonafluorohexyl) phosphonic acid (FPA), and (3-aminopropyl) trimethoxysilane (APTMS). A comparison of the surface chemistry is made for bare and SAM functionalized IGZO back channel surfaces using X-ray photoelectron spectroscopy and electronic device measurements in air and phosphate buffer solution (PBS). We find significantly improved device stability with the SAMs attached to the IGZO back channel surface, both in air and PBS. We related this to the reduction of traps at the back channel surface due to SAM passivation. To further evaluate the IGZO-FETs as biosensors we have immobilized glucose oxidase (GOx) to the APTMS functionalized IGZO back channel surface using glutaraldehyde. We find that both the FPA functionalized and the GOx immobilized surfaces are effective for the detection of glucose in PBS. Furthermore, the GOx immobilized IGZO-FET based glucose sensors have excellent selectivity to glucose, and can effectively minimize interference from acetaminophen/ascorbic acid. Finally, we will discuss fully transparent IGZO-FET based glucose sensors that have been fabricated directly on transparent catheters. These results suggest that IGZO-FETs may provide a means to integrate fully transparent, highly-sensitive sensors into contact lenses.

5:00pm **TF+AS+EL+EM+NS+PS+SS-ThA9 Large Area Atmospheric Pressure Spatial ALD of IZO and IGZO Thin-film Transistors**, *C. Frijters, I. Katsouras, A. Illiberi, G. Gellinck, Holst Centre / TNO, Netherlands; Paul Poort, Holst Centre / TNO and SALDtech B.V., Netherlands*

Atmospheric pressure Spatial ALD is able to deliver high deposition rates while maintaining the advantages of conventional ALD, such as low defect density, high conformality and thickness uniformity. An emerging application for Spatial ALD is flat panel (OLED) display manufacturing. Examples include oxide semiconductors and dielectric layers for use in thin-film transistors (TFT's), and thin-film encapsulation for flexible OLED displays. As today's displays are fabricated on glass plate sizes in the order of several square meters, a remaining challenge is the development of large-area Spatial ALD deposition technology that is able to combine high throughput with uniform performance across very large areas.

We are developing large area Spatial ALD technology, and as a first step between the lab and the display fab, we have installed a large area Spatial ALD sheet-to-sheet tool which can handle up to 400x325 mm<sup>2</sup> sized substrates. With this tool we are able to deposit uniform films across a deposition width of 400 mm and thickness non-uniformities of ~ 1%. The whole tool is operated under an atmospheric pressure but inert N<sub>2</sub> environment. The tool can be used to deposit a variety of materials using both thermal and plasma-enhanced Spatial ALD.

We will present about the fabrication and performance of 30 cm x 30 cm TFT backplanes with InZnO<sub>x</sub> (IZO) and InGaZnO<sub>x</sub> (IGZO) oxide semiconductors deposited by spatial ALD. The IZO and IGZO films were deposited by plasma enhanced Spatial ALD using co-injected In-, Ga- and Zn-precursors and an atmospheric pressure N<sub>2</sub>/O<sub>2</sub> plasma. The deposition process has been optimized in terms of film composition and electrical properties on a lab-scale reactor before being translated to the large area spatial ALD reactor. We will report on the yield and performance of the 30 cm x 30 cm TFT backplanes, including electrical properties such as the field effect mobility, V<sub>on</sub> and bias stress stability and compare it with state-of-the-art sputtered IGZO TFT's. Finally, the challenges in up-scaling Spatial ALD to plate sizes of 1.5 m and beyond will be discussed.

5:20pm **TF+AS+EL+EM+NS+PS+SS-ThA10 Thin Film Ink-Jet Printing on Textiles for Flexible Electronics**, *Jesse Jur, I. Kim, H. Shahariar*, North Carolina State University

Inkjet printing of thin film flexible electronics on textiles is an emerging field of research with advances in wearable technology. In this study we describe for the first-time a reliable and conformal inkjet printing process of printing particle free reactive silver ink on textile surfaces. Reactive silver ink is printed on fibers with eclectic polymers ranging from polyester and polyamide, and different structures of textiles such as knitted, woven, and nonwoven fabrics. The conductivity and the resolution of the inkjet-printed tracks are directly related to the fiber structures in the fabrics. Multiple passes of printing layers are needed to confirm the percolation of the metal network on porous, uneven surfaces. The conformality and the electrical conductivity of the inkjet-printed conductive coating on PET textiles are improved by in-situ heat curing the substrate during printing and surface modification, for example, by atmospheric oxygen plasma treatments. The in-situ heat curing potentially minimizes wicking of the ink into the textile structures. We have achieved the minimum sheet resistance of 0.2 Ohm/sq on polyester knit fabric, which is comparable to the conductive thick-paste used in the screen-printed process, as well as other traditional physical and chemical deposition processes on textile fabrics/yarns. Additionally, we have constructed textile knit structures which changes electric percolation depending on structural deformations of the knit loops, providing positive and negative gauge factors upon stretching. The printed patterns are post-treated with diluted silicone/UV curable aliphatic water-soluble polyurethane coating to improve the durability during washing. These findings open up the possibility of integrating inkjet printing in the scalable and automated manufacturing process for textile electronic applications.

5:40pm **TF+AS+EL+EM+NS+PS+SS-ThA11 Flexography Oil Patterning for In-line Metallization of Aluminium Electrodes onto Polymer Webs: Commercial Roll to Roll Manufacturing of Flexible and Wearable Electronics**, *Bryan Stuart, T. Cosnahan, A.A.R. Watt, H.E. Assender*, University of Oxford, Department of Materials, UK

Vacuum metallisation of aluminium through shadow masks has been commercially used for decades for depositing electrodes on rigid semiconductor devices, however recent developments have enabled large area, continuous deposition of patterned metallization in the aesthetic printing industry and has the potential for electrode interconnects for

# Thursday Afternoon, October 25, 2018

devices on flexible substrates such as Polyethylene Terephthalate (PET) and Polyethylene Naphthalene (PEN). Flexible polymer webs of PET were coated (*See Supplementary Figure*) with 50 nm thick, 165  $\mu\text{m}$  wide aluminium electrodes by commercially compatible manufacturing at roll-to-roll web speed of  $2.4 \text{ m min}^{-1}$  showing tremendous potential for large scale manufacturing of wearable electronic devices in transistors, low level energy generation (Thermoelectric generators), energy storage (thin film batteries) or display technologies (LED displays) [1].

The in-line patterning process relies on adaptation of flexography ink printing which typically transfers ink to a rubber patterned plate for printing images onto polymer webs. The flexibility of the printing plate accommodates for irregularities in the surface of the substrate making this process desirable for large area manufacturing. Metallization has been used to deposit aluminium onto a flexography applied pattern by replacing ink with a low vapor pressure oil (e.g. Perfluoropolyether, Krytox®). The radiative heating of aluminium metallization causes simultaneous evaporation of the oil pattern, thereby rapidly forming the desired metal pattern onto the un-patterned regions. Currently we are scaling-up the oil flexography/metallization process into an industrial-scale roll-to-roll coater with potential web widths of 350 mm and roll speeds of  $100 \text{ m min}^{-1}$ , in order to increase web speeds, and to expand the range of materials deposited and the functional devices to which they are applied.

This paper reports on in-line pattern deposition of aluminium and other materials as applied to functional devices, for example organic thin film transistors and thermoelectric devices. In particular we are able to demonstrate how the process can be compatible with other functional layers. We will report our studies of electrode precision (shapes/sizes) by patterned metallization and our first studies of sputtering with flexography patterning. The long term view is integration of this technology along the R2R production path for single pass/high speed production of low cost and flexible integrated circuits.

## References

1. Cosnahan, T., A.A. Watt, and H.E. Assender, *Modelling of a vacuum metallization patterning method for organic electronics*. Surface and Coatings Technology, 2017.

## Author Index

### Bold page numbers indicate presenter

— A —

Assender, H.E.: TF+AS+EL+EM+NS+PS+SS-  
ThA11, 2; TF+AS+EL+EM+NS+PS+SS-ThA7, 2

— B —

Bergevin, J.: TF+AS+EL+EM+NS+PS+SS-ThA8,  
2

— C —

Chen, C.-M.: TF+AS+EL+EM+NS+PS+SS-ThA7,  
2

Choubey, B.: TF+AS+EL+EM+NS+PS+SS-ThA7,  
2

Ciszek, J.W.: TF+AS+EL+EM+NS+PS+SS-ThA3,  
1

Cosnahan, T.: TF+AS+EL+EM+NS+PS+SS-  
ThA11, 2

— D —

Du, X.: TF+AS+EL+EM+NS+PS+SS-ThA8, 2

— F —

Frijters, C.: TF+AS+EL+EM+NS+PS+SS-ThA9, 2

— G —

Gelinck, G.: TF+AS+EL+EM+NS+PS+SS-ThA9,  
2

Giddings, A.D.: TF+AS+EL+EM+NS+PS+SS-  
ThA6, 1

— H —

Herman, G.S.: TF+AS+EL+EM+NS+PS+SS-  
ThA8, 2

— I —

Illiberi, A.: TF+AS+EL+EM+NS+PS+SS-ThA9, 2

— J —

John, S.: TF+AS+EL+EM+NS+PS+SS-ThA8, 2

Jur, J.S.: TF+AS+EL+EM+NS+PS+SS-ThA10, 2

— K —

Katsouras, I.: TF+AS+EL+EM+NS+PS+SS-  
ThA9, 2

Kessels, W.M.M.: TF+AS+EL+EM+NS+PS+SS-  
ThA6, 1

Kim, I.: TF+AS+EL+EM+NS+PS+SS-ThA10, 2

Koenraad, P.M.: TF+AS+EL+EM+NS+PS+SS-  
ThA6, 1

Kölling, S.: TF+AS+EL+EM+NS+PS+SS-ThA6, 1

— L —

Larson, D.J.: TF+AS+EL+EM+NS+PS+SS-ThA6,  
1

— M —

Macco, B.: TF+AS+EL+EM+NS+PS+SS-ThA6, 1

Maindron, T.: TF+AS+EL+EM+NS+PS+SS-  
ThA4, 1

— P —

Poodt, P.: TF+AS+EL+EM+NS+PS+SS-ThA9, 2

Prosa, T.J.: TF+AS+EL+EM+NS+PS+SS-ThA6, 1

— R —

Roozeboom, F.: TF+AS+EL+EM+NS+PS+SS-  
ThA6, 1

— S —

Sandrez, S.M.: TF+AS+EL+EM+NS+PS+SS-  
ThA4, 1

Shahariar, H.: TF+AS+EL+EM+NS+PS+SS-  
ThA10, 2

Someya, T.: TF+AS+EL+EM+NS+PS+SS-ThA1,  
1

Stuart, B.W.: TF+AS+EL+EM+NS+PS+SS-  
ThA11, 2

— V —

Vaxelaire, N.V.: TF+AS+EL+EM+NS+PS+SS-  
ThA4, 1

Verheijen, M.A.: TF+AS+EL+EM+NS+PS+SS-  
ThA6, 1

— W —

Watt, A.A.R.: TF+AS+EL+EM+NS+PS+SS-  
ThA11, 2

Wu, Y.: TF+AS+EL+EM+NS+PS+SS-ThA6, 1

— Y —

Yokota, T.: TF+AS+EL+EM+NS+PS+SS-ThA1, 1

— Z —

Zhang, K.: TF+AS+EL+EM+NS+PS+SS-ThA7, 2