TSRP: Polymer and Molecular Electronics and Devices (2006-2009)

Project 052-117-0030: Inkjet-Printed Films and Devices

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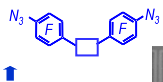
Institute of Materials Research & Engineering: Eric Ou, Lin Ke, Soo-Jin Chua

Project summary

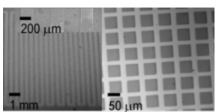
In this project, we have successfully set up an inkjet-printer base at NUS for materials and device inkjet-printing (IJP) research together with a number of characterisation techniques suitable for such films. The IJP base comprises a Litrex 120 industrial printer and a Dimatix 2831 formulation printer. Using this platform we have developed efficient in-house (ONDL) protocols for the IJP of plastic electronic materials for field-effect transistor and solar-cell applications. We have also developed the following state-of-the-art characterisation protocols for inkjet and spin-cast polymer semiconductor thin films: (i) a new methodology in variable-angle spectroscopic ellipsometry (VASE) to measure optical properties and the variation between the two interfaces of these films, (ii) a near-edge X-ray absorption fine structure spectroscopy (NEXAFS) methodology to measure chain orientation and interchain interaction in the frontier layers of these films, (iii) charge-modulation spectroscopy (CMS) in the UV-Vis-NIR-MIR range to measure the fundamental character of the charge carriers, and (iv) electrical noise (EN) characterisation to measure carrier trapping, in addition to our standard field-effect and power conversion efficiency characterisation of the devices. In addition, we have also innovated two key advances on the materials/ device architecture aspects that open new opportunities in IJP plastic electronics: (a) photocrosslinking additives that can achieve general and efficient deep-UV crosslinking of a variety of polymer semiconductor and dielectric materials for multilayer plastic electronics, and (b) printable nanometal inks dispersed in polar solvents and with the lowest coalescence temperatures on record. These two developments will make possible advanced device technology for plastic electronics with lesser materials constraints than previously possible. The IJP base together with these IJP and film characterisation protocols are now available to support industry partners.

General-purpose photocrosslinkers

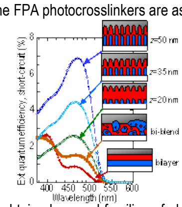
We have developed new families of bis(fluorinated phenyl azide) (FPA) photocrosslinkers that can be readily formulated as additives into polymer solutions suitable for IJP and other forms of solution deposition. We have achieved general and efficient crosslinking of the deposited polymer semiconducting films for the first time under the action of deep UV light (254nm). The structure of the FPA photocrosslinkers are as follows:



General structure of bis(fluorinated phenyl azide)



Photopatterned plastic electronic thin film



Enhanced polymer photovoltaic cells enabled by nano-structuring and photo-crosslinking the donor layer.

By changing the bridging group and the fluorinated rings, we obtained several families of photocrosslinkers for water- and alcohol-soluble polyelectrolytes; and aromatic-solvent-soluble polymer semiconductors and polymer dielectrics. We demonstrated crucially that this methodology does not degrade the semiconductor properties. This thus opens the possibility to fabricate refined heterostructures for high-performance and energy-efficient plastic electronic devices, including polymer LEDs, polymer solar cells, and thin-film transistors. High-efficiency separate-confinement-heterostructure polymer LEDs with advanced charge injection and confinement layers have been demonstrated. High-performance polymer solar cells with two new donor-acceptor heterostructures, contiguous and back-infiltrated heterostructures, have also been demonstrated. The power conversion efficiency of rrP3HT:PCBM devices with the back-infiltrated heterostructure reaches 4.5%, higher than the 3-4% (typical) made from blends. Crosslinking may further help stabilise the device against certain types of degradations. For more information, please see below.

Patent applications: WO2007/004995, US61/266,561.

Publications: (i) Khong et al, *Advanced Functional Materials* 17 (2007) 2490; (ii) Png et al, *Applied Physics Letters* 91 (2007) 013511; (iii) Png et al, *Nature Materials* 9 (2010) 152.

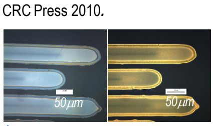
in collaboration with Prof Richard Friend (Cambridge) and Jeremy Burroughes (CDT)

Printable nanometal inks

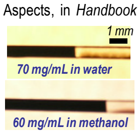
We have developed new water- and alcohol-soluble nanometal "inks" (both Au and Ag) that are suitable for IJP and that can sintered to the near-bulk conductive state (> 10^5 S/cm) at temperatures as low as 150ºC. These characteristics are superior to what were commercially available up till 2009. We achieved this through two new concepts of mixed and sparse ligand protection. Their polar solvent and low coalescence temperature characteristics make them compatible with plastic electronics with organic underlayers on commodity/ engineering plastic films. Thus they are suitable for applications as current-carrying bus lines for organic LEDs, solar cells and TFTs. We have also developed a key approach to improve adhesion of these nanometal films with the substrate and cohesion within the metal film, which overcomes the previous microcracking problems. For more information, please see below.

Patent applications: WO2007/004033, US61/267,498

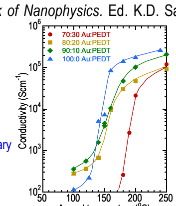
Publications: (i) Sivaramakrishnan et al, *Nature Materials* 6 (2007) 149; (ii) Sivaramakrishnan et al, *Applied Physics Letters* 94 (2009) 091909; (iii) Anto et al, *Advanced Functional Materials* 20 (2010) 296. For the design rule of nanometal inks, please see our **Book Chapter:** *Bibin et al,* Printable Metal Nanoparticle Inks for Thin-Film Metallization: Physicochemical Aspects, in *Handbook of Nanophysics*. Ed. K.D. Sattler, Francis&Taylor, CRC Press 2010**.**



Thin IJP nano-gold tracks before and after thermal annealing



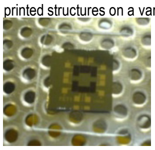
Nanometal inks in capillary tubes, showing high dispersability in water



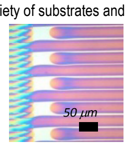
Conductivity-temperature plots of polar nano-Au, measured at a rate of 2ºC/min.

The ONDL printing protocols

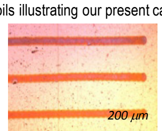
We are developing printing protocols that can give suitable inkjet printed semiconductor, insulator, and conductor layers for use in TFTs and solar cells. This is a long on-going project. We have in-house knowledge of (i) ink formulation considerations, (ii) substrate surface treatments and (iii) print waveform and print pattern management. Contact person: Loke-Yuen Wong (phywly@nus.edu.sg). Below are some examples of inkjet printed structures on a variety of substrates and foils illustrating our present capabilities:



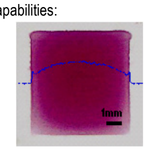
IJP organic transistor on litho Au source-drain array



IJP plastic conductor lines with 7-μm channel



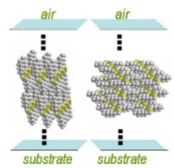
IJP plastic conductor lines on polyimide foil



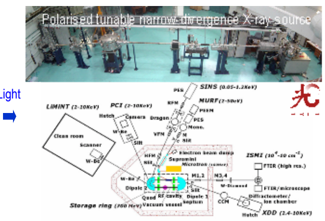
IJP organic solar cell active layer with near ideal profile

Characterisation of IJP film morphology

Near-edge X-ray absorption fine structure spectroscopy (NEXAFS)



Face-on and edge-on stacking



Singapore Synchrotron Light Source

in collaboration with Prof Andrew Wee and the Singapore Synchrotron Light Source Team

We have developed an experimental protocol to measure the C_{1s} NEXAFS spectra of polymer semiconductor films and to model the results using quantum chemical calculations. These spectra yield important information of the chain orientation and packing at the top 3.5 nm of the film, which is relevant to charge injection in LEDs and solar cells, and transport in TFTs. We have also determined the damage threshold and information depth in a model polymer semiconductor rrP3HT. We have also applied this technique to show that spin-cast, drop-cast and IJP films differ greatly in the vary greatly in their average chain orientation and interchain packing in the frontier layers, although details are still being understood. For more information, please see:

Publications: (i) Chua et al, Langmuir 22 (2006) 8587; (ii) Ho et al, Advanced Materials 19 (2007) 215; (iii) Wong et al, Langmuir 26 (2010) 15494.

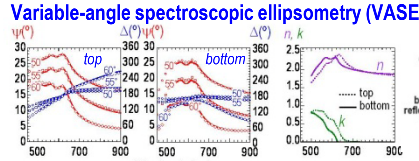
Charge-modulation spectroscopy (CMS)

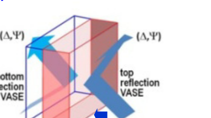
We have developed an experimental protocol to measure the spectrum of the charge carriers across the UV-Vis-NIR-MIR spectral range in organic semiconductor films. These spectra yield important information of state of delocalisation of the charge carriers, which is relevant to their mobility in LEDs, solar cells and TFTs. For the MIR range, we developed a new technique of interferogram modulation which is superior to the conventional ON-OFF method. Using these techniques, we have established (i) injection-dedoping as an electrochemical degradation mechanism in plastic electronics, (ii) the characteristics of Ohmic contacts, (iii) the Madelung potential effect in organic work function, and (iv) surprising hole delocalisation at the Fermi level in PEDT. For more information, please see:

Publications: (i) Chia et al, Advanced Materials 19 (2007) 4202; (ii) Zhuo et al, Physical Review Letters 100 (2008) 186601; (iii) Chia et al, Physical Review Letters 102 (2009) 096602; (iv) Zhou et al, Physical Review Letters 103 (2009) 036601.

CMS experiments were set up in collaboration with Dr Wee-Sun Sim

Variable-angle spectroscopic ellipsometry (VASE)





New VASE methodology

We have developed a new VASE experimental and modeling protocol to determine the (*n*,*k*) spectrum of polymer semiconductor thin films to reveal differences between the top and bottom interfaces, and as a function of solvent and film deposition methods (e.g., IJP vs spin-casting). We found that top interface of spin-cast films shows a red-shifted absorption that is characteristic of better order than at the bottom, across a wide range of film thicknesses. This disparity diminishes in drop-cast and multipass IJP films, and disappears in amorphous films. For more information, please see: Wong et al, *Langmuir* 26 (2010) 15494

Electrical noise measurements

We have set up an electrical noise measurement system to characterise the noise in plastic electronic devices. This work is done by Dr Lin Ke and Prof Soo-Jin Chua at IMRE. The results reveal a significant aspect of the dielectric surface modification is to locally affect the polymer semiconductor organisation which affects carrier trapping and electrical noise, for both spin-cast and inkjet-printed polymer semiconductor films. For more information, please see: (i) Ke et al, *Journal of Applied Physics* 104 (2010) 124502; (ii) Ke at al, Applied Physics Letters 93 (2008) 153507.

Statistical data:

No. of PhD graduates trained: 7	No. of post-docs trained: 4	No. of publications: 19
No. of patent applications: 4	No. of research assistants trained: 2	No. of conference presentations: 9

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For commercial licensing: Director, Industry Liaison Office, NUS

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