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13. SUPPLEMENTARY NOTES

14. ABSTRACT

This report results from a contract tasking Queen Mary University of London as follows: This project aims to exploit macrocyclic compounds as electronic materials that are adaptable to production printing processes for thin film organic transistors with the ability to harness both electronic functionality and chemical and biosensing capabilities using surface modification. Phthalocyanine will be processed by solution printing methods, studying closely the morphology of the films under varying deposition parameters (choice of solvent, viscosity, annealing) for device optimisation. Novel electronic aspects of electropolymerisable and printable conjugated polymeric systems in varying mono through to multilayer thicknesses. will be investigated studying (i) the effects of electric fields on charge transfer, charge separation, and recombination processes, (ii) the role of interfacial states on charge transport, (iii) the dependence of charge transport on supramolecular organisation, molecular aggregation and temperature annealing. The knowledge of in-plane and through plane conductivity will be useful for determining anisotropy in the transport mechanism. Low frequency current and voltage noise measurements will be carried out, providing quality assessment of the structures devised. Using advanced state of the art analytical facilities, nano-scale structural analysis of organised organic films includes the characterization of symmetry, size and orientation of grains/domains with a view to correlating the physical properties of the films with micro-structural behaviour. A series of experiments will be performed to examine active life for electrical performance, chemical and environmental stability. Study of the phase diagram is necessary since the temperature effect and the electric field bias effect on the conductivity of the material may be correlated with phase transitions. Once the printing dependent structure-property relationships are established, the second objective is to produce device components. Novel structures will be designed, fabricated and tested to act as representative technology demonstrators, providing the definition of gate electrodes and source/drain contacts, isolation of transistors, and formation of bias and interconnects with a view to achieving device integration. Existing studies have demonstrated that incorporation of bioreceptors, e.g. mono and poly-clonal antibodies, complementary nucleic acid and avidin influences electronic conducting properties. Importantly, affinity binding to the target molecule leads to modified AC impedance properties. The third objective is to characterise the thin film transistor for sensing. The modified structures bearing conjugated organic systems coupled with bioreceptors will be tested in array structures to evolve desired selectivity sensitivity and reversibility properties. The conducting systems will be operated at appropriate redox potentials and used in an analogous way to gated field effect transistors.

Milestones.

M1 Suitable self-assembled film formulations developed in lab and complete characterisation of biofilms. (1-12 months)

M2: First generation of TFT produced for test in QMUL and Initial test data received from discreet sensing TFTs.(13-24 months)

M3: Laboratory demonstration of sensing arrays and assessment of sensing devices to end users requirements. (25-36 months)

15. SUBJECT TERMS

EOARD, Nanoelectronics, Thin Film Transistors

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YEARLY REPORT

Design of novel organic thin film transistors for wearable electronics

FA8655-08-1-3034

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Date: 25 September 2009

Introduction

In this project, active components are successfully fabricated for wearable electronics using macrocyclic compounds such as phthalocyanines.

Phthalocyanines offer 16 substitution sites on the benzenoid rings + axial ligation sites at the central metal or metalloid. Substituents confer solubility eg $-\text{SO}_3\text{H}$ on ring for water solubility and aliphatic chains for organic solvent solubility and introduce new properties or 'tune' usual properties of the ring system. Solubility in organic solvents allows film deposition by (i) Spin coating, (ii) Langmuir Blodgett method and (iii) Self assembly to form SAMs.

Project Achievement

An n-doped silicon (100) wafer of resistivity $0.005 \Omega\text{cm}$ covered with 250 nm thick thermally grown oxide film was used as a substrate. The capacitance C_i of silicon dioxide (SiO_2) which acts as the gate dielectric was estimated to be 10 nF cm^{-2} . Two finger shaped gold (50 nm thick)/Ti (10 nm thick) layers were prepared as source and drain electrodes using photolithographic and sputtering techniques. The native oxide layer was removed from the reverse side of the Si wafer and a layer of Ga-In eutectic was then applied in order to form an Ohmic gate terminal. The fabrication of the bottom gated field effect transistors used for measurements was completed by depositing a 150 nm thick layer of 2,9(10),16(17),23(24)-(13,17-dioxanonacosane-15-hydroxy)phthalocyaninato zinc(II) (ZnPcR_4) [Figure 1]. The deposition took place at room temperature by spinning a small volume of the spreading solution of ZnPcR_4 in chloroform of 5 mg ml^{-1} concentration at 2000 rpm for 30s. The transistors were fabricated with different channel lengths ranging from $L=1 \mu\text{m}$ to $L=15 \mu\text{m}$ and the channel width W of all structures was 1 mm . All procedure of the device fabrications and electrical

measurements of device characteristics were performed in air using a Keithley 93 I-V system.

A set of reproducible, hysteresis-free output characteristics are shown in Figure 2 for both as-prepared and annealed $R_{16}LuPc_2$ field-effect transistors in terms of the drain-to-source current I_{DS} as a function of the drain-to-source voltage V_{DS} for different values of the gate voltage V_{GS} ($0V \leq V_{GS} \leq -50V$). The output characteristics were typical of behaviour of a p-type OFETs operating in an accumulation mode.. The conductance of the annealed devices was found to be greater than that of as deposited devices.

The graphs in Figure 3 was fitted to the well known quadratic equation describing the transistor behaviour in the saturation regime:

$$I_{DS(sat)} = \mu_h \frac{W}{2L} C_i (V_G - V_T)^2 \quad (1)$$

Values of the field effect mobility $\mu_{(sat)}$ in the saturated regime and threshold voltages V_T were estimated from the slope and the intercept at $I_{DS}=0$ of the linear graphs, respectively. Values of the on/off current modulation ratio were estimated from the transfer characteristics in terms of the dependence of drain current on the gate voltage at the fixed drain-source voltage.

The maximum density-of-states (trap density) present at the active semiconductor ((ZnPcR₄) and gate dielectrics (SiO₂) interface have been calculated using the equation;

$$N_t = \left[\frac{S \log(e)}{\left(\frac{kT}{q} \right)} - 1 \right] \frac{C_i}{q} \quad (2)$$

where S is the sub-threshold voltage swing, k the Boltzmann constant, T the operating temperature, q the electronic charge and C_i the capacitance per unit area of gate dielectrics. Calculations were performed for the transistors using as-prepared and annealed (ZnPcR₄) active layers and the results of the calculations were summarised in Table 1.

In summary, phthalocyanine molecules can be solution processed on silicon substrates or flexible substrates, providing economic benefits for *roll-to-roll* plastic substrate-based devices.

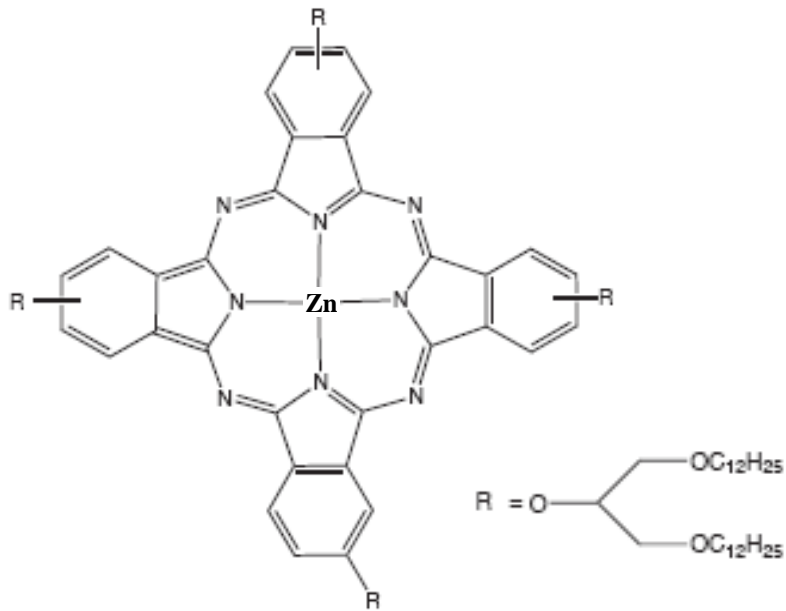


Figure 1. Structure of Zn(II) phthalocyanine derivative.

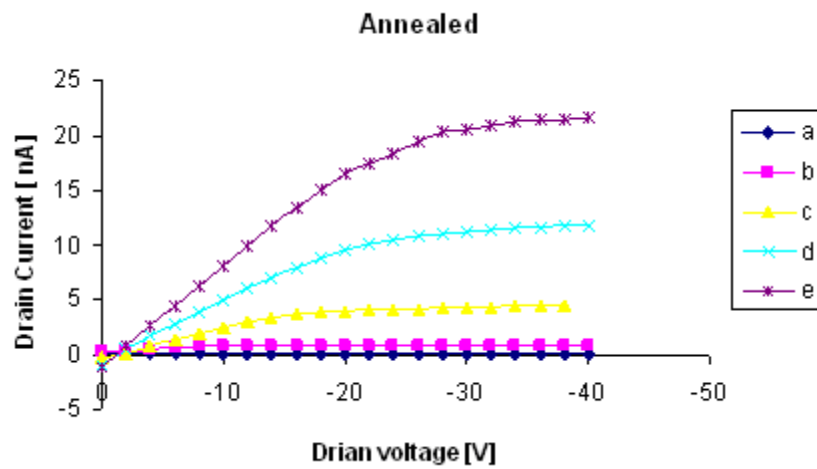
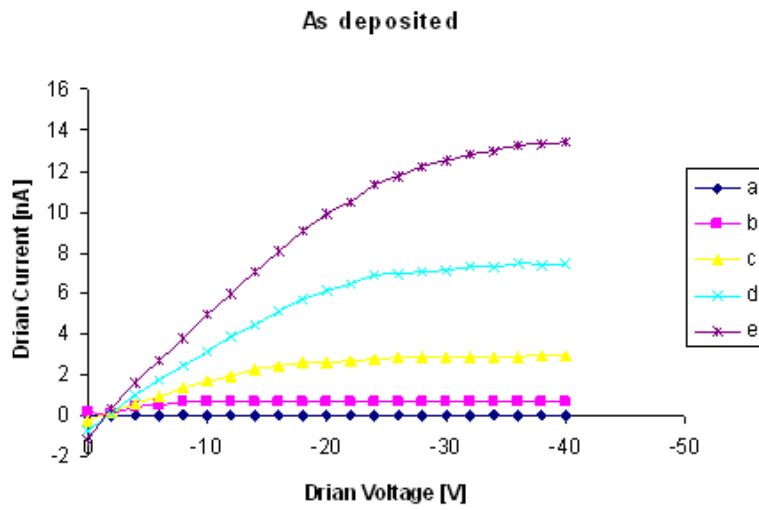
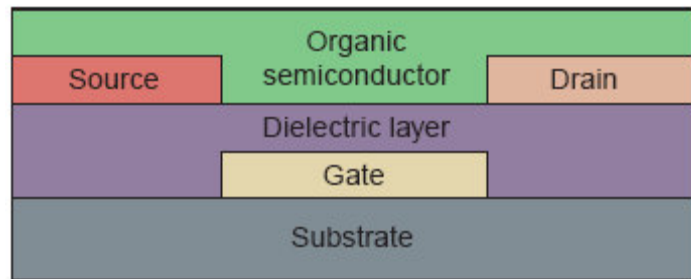


Figure 2 Transistor characteristics for at different gate voltages

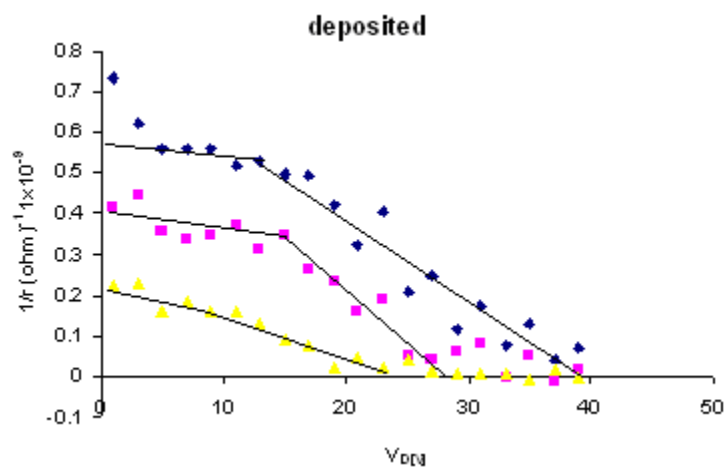
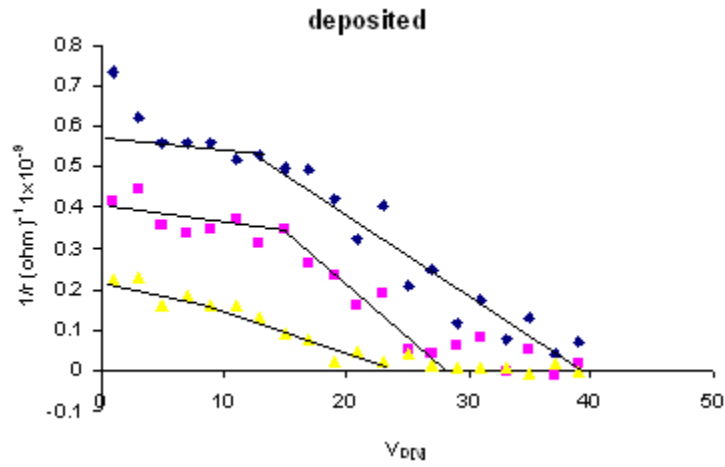


Figure 3: Plot of transistor conductance against the drain volage for different gate voltages

Table 1. Summary of transistor parameters measured for as-prepared and annealed devices.

(ZnPcR ₄) transistors	Mobility (μ) cm^2/Vs	On/off current ratio	Threshold Voltage, (V_T) V	Sub-threshold Voltage, (V/decade)	Interface trap Density, (cm^{-2})	Grain-boundary trap density, (cm^{-2})
As-prepared	18×10^{-6}	$\sim 10^3$	-26	3.81	1.06×10^{15}	1.24×10^{12}
Annealed	34.0×10^{-6}	$\sim 10^5$	-12	1.64	1.01×10^{15}	7.62×10^{11}

Publications in 2009

1. B. Pradhan, A. K. Sharma and A.K. Ray, **Nanoscale films of organic dyes for broadband environmental sensing** *Journal of Materials Science: Materials in Electronics* 20(3),267-271, 2009 (DOI .1007/s10854-008-9718-x)
2. B. Pradhan, A.K. Ray and A. K. Sharma , **A simple hybrid inorganic-polymer photodiode** *Journal of Physics D: Applied Physics Phys* **42**, 165308 (DOI: 10.1088/0022-3727/42/16/165308).
3. S. Sahu,, A. K. Sharma., M. J. Cook and A.K. Ray **Negative differential resistance effects in spun films of substituted phthalocyanine derivatives. films** *J. Materials Sci. Materials in Electronics*. DOI: 10.1007/s10854-009-9958-4