Operationally Stable Flexible Organic Field-Effect Transistors on Unconventional Substrates

A Thesis submitted by

Vivek Raghuwanshi

in partial fulfillment of the requirements for the award of the degree of

Doctor of Philosophy

॥ त्वं ज्ञानमयो विज्ञानमयोऽसि ॥

Indian Institute of Technology Jodhpur
Electrical Engineering

April 2020

7
Conclusions and Future Scope

In spite of the fact that numerous aspects of OFETs operational stability and fabrication on the unconventional substrate were explored and various related objectives were accomplished in this dissertation, still a ton of innovative work and research needs to be done before utilizing these OFETs in future applications and fabricating devices which have minimal damage to the environment. In this chapter, the scope of expanding the research work and a brief summary of the main findings of the dissertation work is discussed.

7.1 SUMMARY

As the awareness of the effect of electronic waste on the environment is increasing and considering the demand for flexible electronic products, researches are working around the globe to develop devices on substrates that are biodegradable or easily recyclable. Along with limiting environmental pollution, device operational and electromechanical stability is another major concern for device engineers. Keeping the above aim in mind TIPS-pentacene was selected as a semiconductor material for the active layer in this dissertation work. The molecule was chosen because of its air-stable nature, high mobility, and easy solution processing. Improving device performance, reducing operational voltage and realization of improved device performance on the paper substrate were among the major goal of this thesis work. With these aim, various experimental analyses were carried out and the inferences made are as follow;

I. The critical role of the mixing ratio of the semiconductor and polymer solutions on the performance and electromechanical stability of the flexible blend OFETs were comprehensively investigated. Air stable organic semiconductor TIPS-pentacene and insulating polymer binder polystyrene (PS) were used as semiconductor polymer pairs. The vertical phase separation governed dielectric: semiconductor interface leads to high performing OFET devices. In addition, the performance of devices was found to be highly dependent on the content of semiconductor and polymer in the mixture solution.

II. Higher polymer content in the solution resulted in semiconducting crystals with a high degree of crystallinity and a better quality dielectric: semiconductor interface with lesser traps. The devices were found to have a high electrical performance with negligible hysteresis in the transfer characteristics. The maximum field-effect mobility of OFETs fabricated with blend films was found to improve by more than six-fold when compared to OFETs with neat TIPS-pentacene. The 1:3 semiconductor: polymer blend resulted in highly electromechanical stable devices. The devices have shown ~2% and ~11% decay in normalized drain current when stressed by external stress of V_{DS} = V_{GS} = -5 V for 1 h. for pristine and after 1.27 % (R_{bend} = 5 mm) tensile strain application respectively. Blend devices also exhibited superior reliability with a negligible shift in threshold voltage and ON current, when the transfer scans were measured continuously more than 100 times for both the pristine and strained devices.

III. In order to realize devices on flexible substrates like PET/PEN etc., which have low glass transition temperature, processes need to develop where processing could be done at low temperatures so that the substrate doesn't lose its integrity. The operating voltage of the device is another crucial parameter to minimize in order to use the devices in portable applications. Amorphous $Ba_{0.5}Sr_{0.5}TiO_3$ (BST) was proposed as a high-k dielectric to resolve the above-said issues. The behavior of the BST film with varying deposition temperature is first studied. It was found that the BST deposition parameters can enormously affect the film properties like dielectric constant, surface morphology and crystallinity. Room temperature deposited BST films were found to be amorphous in nature with low leakage current. With the increasing deposition temperature, surface roughness was found to increase. Variation of more than one order in the surface roughness was observed between the amorphous and the polycrystalline film. In addition, no significant variation in capacitance with frequency was observed for the amorphous BST films, however, the polycrystalline film exhibited a large variation in capacitance in the given frequency range. The optimized BST films compatible with flexible substrates were then used to fabricate OFETs.

IV. A comprehensive and detailed study of OFETs with optimized BST as gate stack was performed. In particular, the electromechanical stability of the fabricated devices was demonstrated. BST film was deposited at room temperature and high dielectric constant allowed the devices to be operated at a low voltage of -5V. The fabricated flexible OFETs with optimized BST films have shown excellent electrical performance with max. field-effect mobility (μ_{max}) of 1.01 $cm^2\ V^{-1}\ s^{-1}$ with a near-zero threshold voltage (V_{TH}) and I_{on}/I_{off} of ~10^5. Devices have shown negligible hysteresis in the transfer characteristics. Devices have shown high electromechanical stability and the variation in mobility ($\Delta\mu_{sat}$) and threshold voltage (ΔV_{TH}) was not severe and found to be 0.09 $cm^2\ V^{-1}\ s^{-1}$ and 0.06 V respectively even after bending the devices to a radius as small as 5 mm. These small variations were due to generation and propagation of microcracks/micro defects in the semiconducting crystals, however, electrical properties of BST films were found intact even after bending the device. The investigation has demonstrated that the proposed room temperature deposited BST is a suitable candidate for gate dielectric in low voltage operated, long term electromechanical stable flexible OFETs.

V. High-performance TIPS-pentacene: PS blend OFETs were further explored for operational stability on low-cost polyamide (Kapton tape) substrate. The limiting factor for device fabrication over these substrates was the surface roughness. PVA was used as a planarizing layer to smoothen the rough surface of the substrate. A bi-layer gate stack which was a combination of an organic and inorganic dielectric layer was used in the study. Two types of devices with HfO_2/PVP and HfO_2/PVA as gate dielectric stack were fabricated and examined for their electrical performance and stability. Bilayer stack was used to provide a smoother surface for semiconductor film and to reduce the operating voltage requirement. AFM analyses of both types of films revealed that surface morphologies were favorable to OFET fabrication and the root mean square (RMS) roughness (Rq) of 0.84(±0.08) nm for HfO_2/PVP device and 0.61(±0.05) for HfO_2/PVA device was obtained. The devices exhibited average and maximum field-effect mobility of 0.25(±0.10) and 0.37 $cm^2\ V^{-1}\ s^{-1}$ for PVP/HfO_2 devices and, 0.35(±0.18) and 0.69 $cm^2\ V^{-1}\ s^{-1}$ for PVA/HfO_2 devices respectively with low threshold voltage while operating at -10V.

VI. The two types of devices with HfO_2/PVP and HfO_2/PVA gate layers were tested for operational stability. HfO_2 layer which is deposited over PVP and PVA is helping in two ways. First, the high-k dielectric helps in reducing the operating voltage requirement, secondly, it is acting as an encapsulation layer to the beneath polymer layer consist of polar hydroxyl groups and doesn't allow the migration of water molecules to the beneath layer and restricts the direct contact of the semiconductor film to these hydroxyl group originated traps. Due to lesser traps both types of devices shown negligible hysteresis in the transfer characteristics. The devices exhibited long term ambient stability when tested for more than 5 months in ambient storage. Transfer characteristics were found completely overlapped with negligible variation in device parameters for more than 5 months. Bias stress characteristics were also observed for devices after storage in ambient. Maximum drain current decay of ~15.5 % and ~26% was observed even after 5 months of storage in the ambient environment. Bilayer dielectric stack has resulted in OFETs with high performance and long term operational stability on the polyimide substrate.

VII. OFETs with bilayer hybrid dielectric and TIPS:pentacene: PS blend as active layer were implemented on paper substrate. The rough paper surface was first planarized with the PVA layer which also acted as a barrier layer to protect the substrate from further chemical processing. The devices were fabricated on PowerCoat™ HD 230 paper from Arjowiggins creative papers which has avg. surface roughness (Rq) of 11.9(±4.0) nm, which is quite uneven for the OFET fabrication process. The polymeric PVA layer suppressed the surface roughness to a value of 3.3 (±1.1) nm. Using the bottom gate and bilayer dielectric further suppressed the surface roughness and the top layer over which the active layer was deposited, achieved the surface roughness of 0.81(±0.06) nm, which is suitable for viable active layer deposition.

VIII. Paper OFETs have shown excellent p-channel characteristics with maximum and average field-effect mobility of 0.44 and 0.22(±0.11) $cm^2 V^{-1} s^{-1}$ respectively, near-zero threshold voltage and current on-off ratio (I_{on}/I_{off}) approaching 10^5 with relatively lower operating voltage of -10 V. These paper OFETs exhibited very less decay in normalized drain current (~ 8.5 %) when stressed for 1 h. at $V_{DS} = V_{GS} = -10$ V. Devices experienced less charge trapping due to fine quality dielectric: semiconductor interface. When devices were subjected to 100 continuous transfer characteristic measurement cycles, there found negligible variation in device characteristics and complete overlap in electrical characteristics were obtained, which further indicate a minimal degree of charge trapping. Devices also sustained the extremely humid conditions and have not shown any significant variation in device parameters when stored in humidity for more than 1h. The performance of devices largely remains unaffected under the effect of ambient exposure when stored in ambient for more than six months. This is one of the longest shelf lifetime reported for OFETs on paper substrate. Such excellent air stability can be jointly attributed to the air-stable and water repellant nature of the TIPS-pentacene and PS film respectively. Furthermore, device characteristics when analyzed with annealing temperature varying from 40 to 100 °C. It was found that at initial annealing of 40 °C device ON current and threshold voltage was improved which is due to evaporation of residual solvent and release of any strain present in the active layer because of the redistribution of grains at low-temperature annealing. However, with increasing annealing temperature the device performance was drastically deteriorated. There found a decay of ~ 81% in mobility value when the devices were annealed to 100 °C, this is due to the physical degradation of the active layer crystals because of the thermally generated cracks and their propagation. The paper OFETs were also explored as low-cost, low-voltage photo-OFETs for UV ray detection. The photoresponse of devices was measured under illumination with UV light. Under illumination, the drain current increased and there found a positive shift of 1.04(±0.53) V in V_{TH} which is due to the combined photoconductive and photovoltaic effects (visualized as an increase in the drain current and positive shift in V_{TH} respectively). The devices were also explored with increasing UV illumination time, with initial illumination the drain current increases, whereas at higher values of illumination time, drain current is reduced due to UV induced permanent deterioration (bond rupture and defect generation) of the active layer.

7.2 CONCLUSIONS

After observing various results obtained in the thesis it can be concluded that high performing, air-stable and environmentally friendly OFETs can be fabricated with proper selection of substrate, dielectric stack, organic semiconductor, and necessary surface engineering. TIPS-pentacene is one of the promising organic semiconductors and has great potential in many organic electronics applications. This dissertation reported enormous improvement in OFETs performance when TIPS-pentacene is blended with insulating polymer PS. Dielectric: semiconductor interface obtained through vertically phase separation leads to minimal traps at the crucial interface and the results are discussed in chapter 3 where devices with varying TIPS-pentacene: PS ratio were demonstrated with HfO_2 dielectric on PET substrate. To lower down the operating voltage requirement and reducing the processing temperature, RF sputtered BST was proposed as a gate dielectric with a high dielectric constant. Devices were demonstrated with TIPS-pentacene: PS blend as the active layer and room temperature deposited BST as gate dielectric on PET substrate and the results are demonstrated in chapter 4, where the devices have shown high electromechanical stability with the proposed gate dielectric. Furthermore, the devices were fabricated on polyimide (Kapton tape) substrate, and bilayer hybrid (organic/inorganic) dielectric stack layers were explored. Results are shown in chapter 5 and the devices have shown long time air stability for more than 5 months with high performance. External load inverter circuits were also demonstrated with these OFETs. To lower the substrate cost and utilizing substrates that have minimal impact on the environment after use, OFETs were fabricated on a rough paper substrate with PVA as a planarizing layer. These Paper OFETs have shown maximum field-effect mobility of p-channel characteristics with maximum and avg. field-effect mobility of 0.44 $cm^2 V^{-1} s^{-1}$ with a high On-off current ratio of ~10^5. These Paper OFETs have shown long term air stability for more than 6 months with minimal variation in device parameters. In addition, the devices exhibited a fair photo response towards UV light illumination. Results of paper OFETs are discussed in chapter 6. All these outcomes suggest that there is immense potential for solution-processed organic TFTs to be used in low cost, high performing circuits and sensors with less impact on the environment.

7.3 FUTURE SCOPE

The main objective of the dissertation was to optimize various parameters to obtained high performing, operationally stable OFETs and to realize them on the unconventional substrate. Though the main objectives of the research work were largely met this accomplishment does not limit the future scope for extending this work. Some of the future scopes are listed as follows;

I. Effect on device performance with other air-stable semiconductor and their blend with different insulating polymers can be explored to achieve further high performance. This can be a vast exploration where the effect of various molecular weights of insulating polymers and different solvents can be explored.

II. Dielectric stacks with high dielectric constant and easy processing can be explored for low voltage operation. Solution-processed gate dielectric providing high capacitive density will further help in reducing fabrication costs. Another important factor is the optimization of dielectric layer thickness. Thinner dielectric layers of materials providing high capacitive density with low leakage current will help in the reduction of material used for dielectric fabrication.

III. Devices in the dissertation were fabricated without any surface treatment to dielectrics and contact pads. Dielectric surface treatment can further reduce traps at the interface. Contact (source/drain) treatment can improve the charge injection capability with a reduction in contact resistance. Various surface treatment methodology can be explored.

IV. Other biodegradable substrates and dielectric stacks can be explored. Gate, source/drain electrodes can be explored through solution processing with the use of some conductive inks so the devices can be fabricated with roll to roll processing.

V. Mechanical flexibility is one of the major concerns in flexible organic devices and various aspects of it need to be explored. In the dissertation, the paper substrate used was thicker and during the bending test, the devices suffer failure in operation due to the distribution of strain to the actual device. Thinner unconventional substrates can be explored to demonstrate the flexible aspect of these devices.

…