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Organic field-effect transistors as high performance humidity sensors with rapid response, recovery time and remarkable ambient stability

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ABSTRACT

The stability of organic field-effect transistors (OFETs) under very high humidity condition has been the bottleneck in many applications. In this work, remarkable enhancement in ambient stability and performance of CuPc based OFETs are observed by exploiting the polarization of hydroxyl groups in Poly (vinyl alcohol) (PVA) dielectric layer, which is sandwiched between Al_2O_3 and Poly (methyl methacrylate) (PMMA) layer. The devices are used to fabricate OFETs based humidity sensors, which show exceptional ambient stability and rapid response to the water molecules in moisture. In a controlled experiment, the sensors demonstrate 0.73 s as response time and 0.52 s as recovery time. Such results are the fastest responses observed on humidity sensors fabricated based on OFETs. The enhanced responses of the sensors are due to the systematic polarization of the hydroxyl groups present in PVA layer by the additional dipole field arising from the adsorbed water molecules, which are also polarized under gate-field. The devices show no variation in threshold voltage as well as field-effect carrier mobility, measured throughout a year under ambient exposure. The specific design of the sensors with tri-layer dielectric system plays crucial role in enhancing the stability and moisture sensitivity, which can make the devices technologically very relevant.

1. Introduction

Studies on organic electronic devices have drawn significant interests among the researchers in recent years due to their potential applications in flexible displays, smart card badges and different sensors, which have high importance in our daily life [1–3]. Among the variety of chemical and biological sensors, humidity sensors are being extensively used for monitoring relative humidity (RH) in industry, hospital and daily life. Different humidity sensitive materials were used for the fabrication of such sensor devices. This includes inorganic materials as active layers in the form of nanoparticles, nanowires, nanotubes and thin films [4–9]. There are also examples of humidity sensors based on organic composite materials, supramolecules, graphene oxide, hybrid micro-cavity etc. [10–14]. Some of these devices showed efficient performances with ultra-fast responses. Most of these devices used various techniques of transduction by measuring the changes in capacitance, resistance, frequency or in mass as a result of adsorbed moisture. Among different sensing devices, field-effect transistor (FET) based sensors have attracted more attention due to their ability to amplify signal within the device and allow for compatibility with well-developed microelectronic fabrication techniques. Such devices can easily be integrated into sensors with the necessary electronics. OFET based chemical and biosensors have been fabricated by exploiting the highly sensitive nature of organic semiconducting materials to different volatile gases and biomolecules [15–19]. Yet, there are only few reports on the use of OFETs for humidity sensor applications [20–24]. Main advantage of OFETs are the multi-parameter sensing capabilities, since various

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device parameters such as saturation current, off current, threshold voltage, sub-threshold slope, carrier mobility are highly sensitive to the adsorbed volatile gases. In addition, the organic semiconductors used as active channel of the device, can be easily functionalized with different functional groups to enhance the sensitivity of the sensors and can be prepared by the simple solution and low temperature processing methods unlike the inorganic sensors that requires expensive preparation techniques [25].

In general, OFETs are very sensitive to ambient environmental conditions, like relative humidity, light, temperature etc. Under humidity conditions, the devices show very poor performance since the adsorbed gas molecules act like charge traps. In addition, adsorbed water molecules interact with the dipoles attached to the polar dielectric polymers and degrade the dielectric properties. As a result, devices fabricated with hydrophilic dielectric layers usually showed very poor ambient stability. Considering the immense significance of humidity sensors in different sectors, the development of low cost, highly sensitive and stable humidity sensor devices are necessary to be integrated easily with the required electronic circuits. The selection of materials together with the specific device configuration can reduce the possible degradation of the devices under austere environmental conditions [26]. In general, p-type organic semiconductors (e.g. CuPc, Pentacene, P3HT and etc.) have shown high air stability and efficient performances compared to n-type [27,28]. In most of the sensors, organic semiconducting channel is used as the sensing layer that monitors the changes in drain current (I_{DS}). The sensing response is due to the interaction of adsorbed molecules with the organic molecules, that results in the change in mobility and other device parameters [20]. The sensitivity of such sensors crucially depends on the thickness and morphology of the sensing layer. The lower thickness with higher roughness ensures the efficient absorption of water molecules. However, the carrier mobility decreases in such conditions. Therefore, a balance is required between the performance and the sensitivity of the sensors. In addition, chemical interaction of the adsorbed water molecules with the active material can decrease the performance by changing the chemical properties of the active channel. In order to achieve reproducible sensitivity and long-term usability of the sensors, the water molecules should be physisorbed and be easily removed from the active channel maintaining same chemical state of the organic molecule as earlier.

Recently, the tri-layer combination of dielectric system was demonstrated to significantly enhance the performance and stability of CuPc based OFETs. Such devices were also found to be highly sensitive to adsorbed polar gases. In addition, a model to understand the origin of such response to the polar gas molecules has also been proposed [29]. In this work, the fabrication and characterization of OFET based humidity sensors for the efficient performance with remarkable ambient stability is reported. The chemical vapor detection with OFET is based on the change in device parameters induced by the absorption of gas molecules on the surface/interface. We have used a tri-layer dielectric system consisting of a polar polymer layer sandwiched between a hydrophobic polymer layer and a high-k inorganic layer. We present the performance of the device to different competing target chemical vapors at room temperature. We found that the response of the devices is highly sensitive to the polar gas molecules. However, the device exhibited superior responses to the water molecules which is very unusual. Thus the effects of relative humidity on OFET device properties and performances were investigated using the model proposed in our earlier work [29]. We have demonstrated for the first time that the influence of polarization by a polar dielectric layer can be felt by varying the concentration of adsorbed water molecules. Humidity sensors fabricated by exploiting this unique principle showed significant enhancement in sensitivity of the devices with outstanding ambient stability.

2. Experimental section

2.1. Materials and device fabrication

OFETs with top-contact and bottom gate structure were fabricated on pre-cleaned glass substrates by using thermally deposited 150 nm thick aluminium layer as a gate electrode. To reduce the leakage current and to optimize the subsequent polymer layers, the top surface of the aluminium was anodized to get 10 nm Al_2O_3. The PVA dielectric was prepared by dissolving PVA (Sigma Aldrich, MW = 76,500–81,000 kg/mol) 30 mg/mL in de-ionized water and spin coated onto an anodized substrates at 3000 rpm for 60 s, followed by annealing at 100 °C for 1 h in vacuum oven. On to this, PMMA layer (Sigma Aldrich, MW = 5,50,000 kg/mol) 10 mg/mL dissolved in anisole (sigma Aldrich) of ~30 nm was deposited by spin coating at 3000 rpm for 60 s, followed by vacuum annealing at 120 °C for 2 h to remove residual solvent and to improve the film quality. The 60 nm thick CuPc (purchased from Sigma Aldrich) films were deposited on the polymer dielectrics in a high vacuum evaporator ($<3 \times 10^{-6}$ mbar) with a substrate temperature of 80 °C at a rate 0.2 Å/s. The surface morphology of the dielectric and semiconducting films were characterized in air by the atomic force microscopy (Agilent AFM/STM 5500) in tapping mode, and the dielectric thickness was measured by the Dektak profilometer. Finally, 50 nm thick copper was deposited onto the organic layer as source and drain electrodes through a shadow mask with a device channel length (L) and channel width (W) predefined as 25 μm and 750 μm, respectively with width/length (W/L) as 30. Electrical characterization of the OFETs was carried out in a probe station (Lake Shore, $<1 \times 10^{-4}$mbar) with different humidity percentages, examined by introducing into the probe station chamber via a leak valve. These RH levels were independently monitored by using a standard hygrometer. All the capacitance-electric field (C-E) measurements, current–voltage (I–V) characteristics and bias-stress measurements of OFETs were collected with a Keithley 4200-SCS semiconductor parameter analyzer with two source measure units (SMUs). The field effect mobility (μ_{sat}) was calculated by fitting the plot of the square root of I_{DS} versus V_{GS} using the following Equation (1) [30].

$$\mu_{sat} = \frac{2LI_{DS}}{WC_{diel}(V_{GS} - V_{Th})^2} \tag{1}$$

The key device parameters such as on/off current ratio (I_{on}/I_{off}), and threshold voltage (V_{Th}), were extracted from the transfer curves, where, C_{diel} is the capacitance of the dielectric layer per unit area, V_{GS} and V_{Th} are the gate voltage and threshold voltage, respectively. All the data listed in the paper are average values of at least 10 devices on each of the samples.

2.2. Sensor chamber design

The indigenous sensor chamber was fabricated and equipped with feed-throughs for the electrical source, drain and gate contacts. The fabricated device was then placed inside a humidity cell. For the sensing measurement, the prepared sensing devices were placed in a closed chamber that contained inlet and outlet connections for gas flow. The measurements were performed with the variation of humidity. Moisture-argon mixtures of varying RH were passed into the humidity cell through the inlet. The humidity control was achieved by injecting water vapors into the chamber with a flow rate of 10 mL/min. Electrical measurements were carried out using a Keithley 4200 SCS. A commercially available