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Engineering organic/inorganic alumina-based films as dielectrics for red organic light emitting transistors

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ABSTRACT

In this work, the fabrication, the electrical and optical characterization of red organic light emitting transistors using thin film made of alumina grown by atomic layer deposition (ALD) coupled with PMMA (poly(methylmethacrylate)) as gate dielectric material are reported. Use of ALD-grown Al_2O_3 is shown to greatly reduce the operation range and the threshold voltage in this class of devices as compared to polymer-based dielectric counterpart, while at the same time comparable optical performances are maintained. Further, reducing the oxide layer thickness demonstrates the possibility of fine tuning the device working conditions, while maintaining optoelectronic performances, robustness and very low leakage current.

1. Introduction

Organic semiconductor-based devices such as organic light emitting diodes (OLEDs), solar cells, memories and organic field-effect transistors (OFETs) are expected to reduce fabrication costs and enable novel functionalities with respect to devices and systems based on conventional materials [1–4]. In the last few years, organic light emitting transistors (OLETs) have been increasingly gaining interest within both the scientific and technological community due to their twofold functionality of behaving as a thin-film transistor and at the same time being capable of generating light under appropriate bias conditions [5–9]. Although this technology platform is only at its early stage of development and it is yet to be fully established and exploited, it has been shown that it can potentially outperform OLED equivalent in terms of device efficiency when using the same set of materials [10]. In addition, OLETs present a number of potentially interesting advantages as compared to equivalent OLED devices, including: (i) a simplified structure due to less number of layers required, (ii) spatial control of the light emission region through the gate voltage, (iii) no shorts between electrodes due to the presence of the gate dielectric and (iv) flexibility in device architecture since organic materials and electrodes can be placed in different planes within the device.

Further on, the architectural and optoelectronic characteristics of OLETs are particularly suitable to develop flat panel displays with simplified structure both at the backplane level (which allows the use of lower quality Thin Film Transistor (TFT) technology like a-*Si*-TFT and OTFT) as well as in term of organic stack, where a considerably lower number of organic layers are in need as compared to the state-of-the-art OLED, with relative reduction in fabrication time, manufacturing costs and increased yield.

To achieve high-performance organic light emitting transistors, the integration of high-mobility organic semiconductors with high insulating films that act as the gate dielectric is very crucial. The interest in alternative dielectric materials is mainly two-fold: (i) *technological*, related to the need for reduction of the operation voltage essential for applications in electronics and (ii) *market-driven*, where reliable and cheap fabrication processes are highly desirable. A key role in the quest for low-bias applications is played by the high permittivity (k) dielectrics that allow overcoming currently faced limitations in commonly used oxides, such as SiO_2 [11]. High-k dielectrics have been widely investigated as gate dielectrics in field effect devices, with most of the work devoted to inorganic materials [12,13] and in more recent years to organic FET [14–16]; however the use of high-k dielectrics in organic light emitting transistors is yet unexplored. Although improvement in the electrical characteristics of this class of devices is likely to be confirmed, none is in advance known about any possible effect on the device light output.

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Preferably, dielectric materials should have a large dielectric constant and should be processable into thin high-quality, *defect-free* films to form OFETs with reduced operating voltage, fast switching speed and large ON/OFF ratio. Low deposition temperatures are also desirable to allow for fabrication on plastic substrates, thus enabling applications in flexible electronics. Atomic layer deposition (ALD) is a fabrication technique that allows for the deposition of highly conformal, defect-free thin films at relatively low temperature [17–19]. Dielectric films grown by ALD have a high resistivity and good barrier properties [20], and therefore are excellent candidates for gate insulators [21–22]. The ALD deposition process ensures thickness uniformity over large areas, control of film thickness and composition at the atomic level, compatibility with various substrates and with irregular shapes [23,24].

As an alternative to commonly used oxide and nitride systems, a great amount of work has been carried out on high-k metal oxides, the thickness of which can be engineered to achieve reduced leakage whilst preserving high gate capacitance. In this scenario, aluminum oxide (Al_2O_3) is a very stable and robust material and it has been thoroughly investigated to address different applications, with a large focus on optics and micro-electronics. The large exploitation of Al_2O_3 is the results of the combination of many properties like large band gap, band offset to silicon, amorphous nature, kinetic stability, thermodynamic stability on Si up to high temperatures, good interface with silicon and low bulk defect density [25–27]. Aluminum oxide, integrated as gate dielectric in pentacene-based OFET [28–30] by various methods, including RF sputtering [31], anodization [32], and ALD [15] has been shown to lead to satisfying performances in terms of leakage current and surface roughness when deposited at room temperature [33].

In this work, we investigate the potentials of Al_2O_3 films grown by atomic layer deposition as gate dielectric in this class of devices represented by organic light emitting transistors. We show that by using ALD-grown Al_2O_3 is possible to considerably reduce OLET operation bias range and threshold voltage as compared to polymer (PMMA)-based dielectric and more importantly, at the same time to retain the emission of light. Further, we study how the oxide thickness can be tuned in order to optimize both optical and electronic properties, while keeping device robustness and low leakage currents.

2. Experimental

Alumina films were deposited by thermal ALD on pre-patterned indium-tin-oxide (ITO) film on glass substrate at a temperature of 300 °C, temperature at which the conducting properties of the ITO electrode are preserved. As a result of the growth process, Al_2O_3 films grow conformably to the surface, with the Al_2O_3 film reproducing accurately the underlying ITO surface and retaining the same roughness of ITO itself (1–2 nm). To favor interfacial compatibility between the organic semiconductor and the aluminum oxide layers [34], we have selected a *double-layer* dielectric approach, which includes the deposition by spin-coating of a thin layer of poly(methyl-metacrylate) (PMMA) on top of Al_2O_3. The thin polymer layer is then cured in vacuum at 90 °C for 18 h to remove any residual water molecule which might affect the performances of the devices [35]. Although this approach has the overall effect of reducing the effective permittivity of the entire dielectric stack, as a result of the capacitor series formed by the Al_2O_3 film and the PMMA layer, preliminary tests showed that the compatibility between the dielectric (organic polymer) and the organic stack plays a crucial role in the correct device operation and performances. Large and not negligible values of gate leakage currents are found for organic transistors fabricated directly on Al_2O_3-only dielectric (not shown).

As previously demonstrated [10], a tri-layer organic stack can be exploited to generate light, which can itself be modulated by applying a gate voltage. In this work, a Bottom-Gate-Top-Contact device configuration, as shown in the schematics in Fig. 1, is used. The device active region consists of three different organic layers: the first, in direct contact with the dielectric, and the third layers are field-effect hole-transporting (α,ω-disubstituted-quaterthiophene with hexyl, *DH-4T*, 15 nm) and electron-transporting (5,5‴-bis(3,5-difluorobenzoyl)-[2,2′:5′,2″:5″,2‴-quaterthiophene) (*SLV131*, 30 nm provided by Polyera Inc.) semiconductors, respectively, whereas the intermediate layer, where the electron-hole recombination and emission processes take place, is a host-guest matrix system. In particular, we used an 8% blend of tris(8-hydroxyquinolinate) aluminum (*Alq_3*) and platinum-octaethyl-porphyrin (*PtOEP*) [Alq_3:PtOEP, 30 nm], combination which is widely used in organic light emitting devices targeting red emission at and around 650 nm in the visible spectrum [36]. Gold drain and source electrodes (70 nm) are finally deposited on top of the uppermost organic layer. For the choice of the *n*- and *p*-type semiconductor layers, we refer the Reader to [37,38] for considerations on energetics of the tri-layer heterostructures (see also Fig. 1.b).

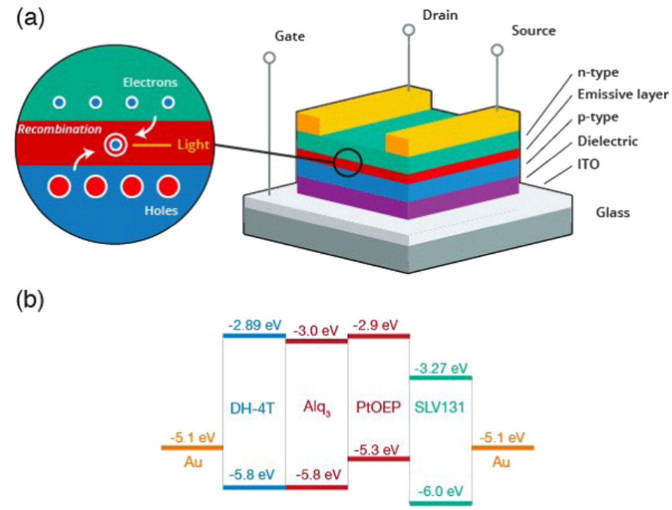

Fig. 1. Red organic light emitting transistors (OLETs) device structure. (a) Schematic representation of the tri-layer OLET device along with the (b) energy-level diagram of the entire hetero-structure used in the present work. The dielectric layer is either PMMA (polymer standard) or Al_2O_3/PMMA (double-layer approach). The active region is constituted by blend of Alq_3 and PtOEP (8%) sandwiched between a (bottom) *p*- and (top) *n*-type organic semiconductor layers. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

2.1. Dielectric properties of ALD-grown Al_2O_3 film

As a preliminary study to evaluate potentials of Al_2O_3 as a dielectric material, basic film properties have been investigated. Capacitor-like structures (*i.e.* ITO/Al_2O_3 (43 nm)/metal) have been fabricated on standard glass substrates in order to measure capacitance per unit area and evaluate breakdown voltages of the film itself. Each test capacitor is formed from ITO (bottom contact) and a metal (Au) electrode on top of Al_2O_3 (top contact). We found values of the capacitance per unit area $= 2.3\ nF/cm^2$, which lead to an estimated value of the dielectric constant of about 8.1. In terms of electric breakdown, we found breakdown voltage values in the range of 30–40 V for all analyzed test capacitors, as shown in Table 1 and consistently with literature [39]. This intrinsic characterization of the electrical properties of the Al_2O_3 film will determine a safe bias operating regime.

Table 1
Breakdown voltage study of Al_2O_3 films.
Breakdown voltage (V_B) measured for different test-capacitors for a 43 nm-thick Al_2O_3 film.

Test-capacitors (Al_2O_3, 43 nm)	A	B	C	D	E	F	G
V_B (V)	38.4	33.4	41.1	39.3	30.5	39	41.1