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A novel gate insulator for flexible electronics

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Abstract

Field effect transistors using a poly(triaryl amine) p-channel organic semiconductor in conjunction with anodised aluminium oxide as the gate insulator (Al_2O_3 on Al) are demonstrated. Anodised films are pinhole-free, homogenous oxide layers of precisely controlled thickness. The anodisation process requires no vacuum steps; anodised Al_2O_3 is insoluble in organic solvents, and Al films are cheaply available as laminates on flexible substrates. Anodised Al_2O_3 is confirmed to have high gate capacitance (≈60 nF/cm^2) and electric breakdown strength (>3 MV/cm in the working device). This property profile answers to the demands on gate insulators for flexible electronics applications.

1. Introduction

The concept of using organic semiconductors in transistor applications has been researched at least since the 1980s [1]. Circuits made from organic field effect transistors (OFETs) are now projected to enable extremely cheap, low-performance logic circuits with applications such as electronic price-tags, postage stamps, or 'smart' cards. Applications with higher added value such as active matrix addressing of displays are another area of current research [2]. Early on, it was realized that for the manufacture of high quality OFETs, the organic semiconductor is not the only critical component. It is also very important to find a suitable gate insulator. The demands on the gate insulators' property profile are rather strict. Firstly, the same requirements apply as for gate insulators in inorganic transistors. The crucial figures-of-merit are the maximum possible electric displacement $D_{\max}$ a gate insulator can sustain, $D_{\max} = \varepsilon_0\varepsilon_r E_B$, with ε_r the dielectric constant and E_B the dielectric breakdown field, and the capacitance per area $C_i = \varepsilon_0\varepsilon_r/d$, with d the insulator thickness. C_i is controlled not only by ε_r but also by the minimum thickness d at which a pinhole-free film can be achieved, and thus may reflect deposition procedure as much as a materials property. Secondly, OFET gate insulators have to fulfil demands specific to organic electronics, which are related to the requirement to manufacture organic circuits at low cost. OFET gate insulators should be consistent with flexible substrates and ideally, will be processable from solution, but should be insoluble in the solvent used for organic semiconductor deposition.

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In current inorganic integrated circuit technology, SiO_2 grown in situ on doped Si gates is the most widely used gate insulator, although it has not got a particularly high dielectric constant ($\varepsilon_r = 3.9$) and will soon reach its limitations [3]. OFETs using SiO_2 gate insulators have been demonstrated [4]. Other inorganic oxides have been used to good effect for OFETs, for example electron-beam evaporated Ta_2O_5 ($\varepsilon_r = 21$) [5]. These insulators, however, do require processing steps under vacuum.

Alternatively, OFETs with polymeric gate insulators have been demonstrated. Sirringhaus et al. have prepared poly(vinyl phenol) (PVP) from isopropanol onto a water-soluble synthetic metal (PEDOT/PSS) gate without dissolving it [6]. Onto PVP, all-plastic electronic circuits processed entirely from solution have been prepared. However, like most polymers, PVP displays low dielectric constant and needs to be rather thick to be reliably free of pinholes ($d \approx 400$–500 nm [6]). Consequently, C_i will be small, which leads to higher gate switching voltages.

Recently, an interesting approach to high quality gate insulators for OFET applications has emerged in the form of anodised metal films. In anodisation, a positive bias is applied to a metal (or doped Si) immersed into an acid bath that is equipped with a counterelectrode to complete the electric circuit. For some metals (e.g. Ta or Al), the resulting current drives an electrochemical oxidation on the anode metal surface, thus depositing a thin insulating layer such as Ta_2O_5, Al_2O_3 or SiO_2. Anodisation is a well-established industrial process for the corrosion protection of Al, and the manufacture of 'electrolytic' capacitors [7]. For a number of reasons, anodisation is particularly appealing for electronic applications: Thickness d of the resulting films can be controlled very precisely via the anodisation voltage V_A, with $d = cV_A$. c is known as the 'anodisation ratio' and is related to the electric breakdown field E_B via $E_B \approx c^{-1}$. During the anodisation process, pinholes close themselves; resulting oxides often have high ε_r; and the process takes place in aqueous medium and requires no vacuum.

Tate et al. [8] have recently demonstrated p- and n-channel OFETs based on anodised Ta and anodised doped Si. In this contribution, we provide proof-of-principle for OFETs based on anodised Al. The use of anodised Al for inorganic amorphous silicon TFTs has been demonstrated previously [9]. However, Al films are a particularly attractive substrate for flexible electronics, as thin (order 10 μm) aluminium films can be laminated reel-to-reel onto conventional (PP or PE) plastic film. Such laminates are cheap and are widely used e.g. as disposable food wrappers for snack foods.

2. Manufacture and characterisation of anodised Al gate insulators

For Al anodisation, we have closely followed the procedure discussed in a classic review [7]. As electrolyte, we used 0.01 M citric acid in deionised water as a weak acid. For proof-of-principle, we have used ≈500 nm thick Al films evaporated onto clean glass slides, as these have a smoother surface than commercial Al foils (e.g., kitchen foil or commercial Al alloys). This is no restriction of the general use of cheap Al foils for OFETs, as these can be treated by electropolishing [10] to yield smooth surfaces. The anodisation bath was degassed with Ar before use, and was stirred throughout. A constant current of $j \approx 0.6$ mA/cm^2 was driven through the electrolyte, using a Pt counterelectrode. Constant current across the growing insulating Al_2O_3 layer was maintained by ramping up the voltage up to a limiting anodisation voltage V_A, which was then maintained constant for several minutes until the current had completely decayed. V_A was varied in the range (20–100 V). With the anodisation ratio $c_{Al} \approx 1.3$ nm/V [7], this corresponds to Al_2O_3 layers of 26–130 nm thickness. After anodisation was complete, anodised films were washed in deionised water. While the original Al film had the appearance of a good quality mirror, the anodised surface displayed a uniform interference colour with no visible defects. The colour depends on V_A, i.e. film thickness.

To characterise electrical breakdown, electrodes were deposited onto the anodised layers by applying conductive epoxy glue from circuit works with a wire that was connected to a Keithley 2400 source/measure unit. Voltage was ramped up with the bottom (Al) electrode biased either positively (as it was during anodisation), or negatively (as it would be in a p-channel transistor). Dielectric breakdown voltage V_B was assigned when a sudden, irreversible surge in the I/V characteristic was observed. Fig. 1 shows the results. We see that the expectation $V_B = V_A$ is confirmed to good approximation regardless of bias direction. Below breakdown, leakage currents less than 10^{-9} A/cm^2 at 1.54 MV/cm (±5 V) were observed for a $V_A = 100$ V film [8]. That is one order of magnitude less than for an anodic Ta_2O_5 film made with $V_A = 35$ V.

The capacitance per area, C_i, of an anodised film is given theoretically as $C_i = \varepsilon_0\varepsilon_r/cV_A$. From literature data [7], we calculate $C_i = 75$ nF/cm^2 for an Al_2O_3 film anodised at 100 V. We have evaporated 20 nm thick gold electrodes onto a $V_A = 100$ V Al_2O_3 film and connected the resulting capacitor to an Iso-tech 9023 capacitance meter via Karl Süss MicroTec PH100 miniature probe heads. We found $C_i = 60.7$ nF/cm^2, in reasonable agreement with the calculated value.

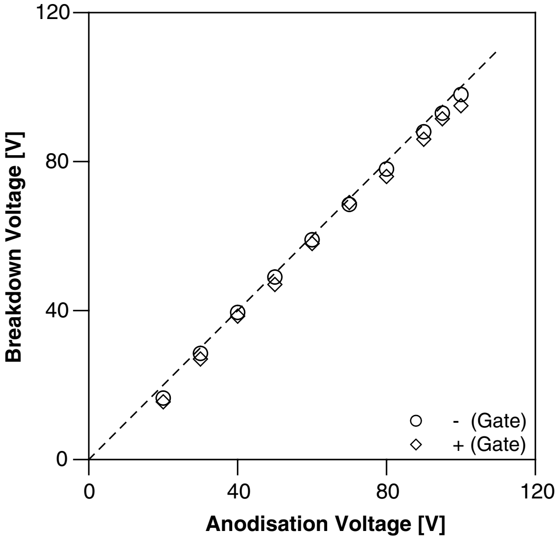

Fig. 1. Breakdown voltage V_B of anodised films versus anodisation voltage V_A: (◇) bottom electrode positive; (○) bottom electrode negative; (- - -) $V_B = V_A$.

3. Manufacture and characterisation of transistors with anodic Al_2O_3 gate insulators

To confirm the suitability of anodised Al for organic electronics applications, we have manufactured transistors on the basis of an Al gate/anodised Al_2O_3 substrate with $V_A = 100$ V. As organic semiconductor, we used a proprietary material supplied by Avecia of Manchester, UK. This material is an air stable p-type poly-(triaryl amine) (PTAA) with a hole mobility of $(1\ldots5)\times10^{-3}$ cm^2/V s under optimized conditions [11]. A 10 g/l PTAA solution in toluene was spun onto the anodised substrate at 1000 rpm. A 20 nm thick layer of gold was then evaporated through a shadow mask to form source and drain electrodes. Channel length L was 40 μm and width W was 1 mm. Devices were contacted via Karl Süss MicroTec PH100 miniature probe heads with tungsten probe tips. The output characteristics of the resulting OFETs were characterised with an Agilent 4155C semiconductor parameter analyser for a variety of gate voltages V_G. Results for $|V_G|$ up to 40 V are shown in Fig. 2(a). During the scan with $V_G = -50$ V, the dielectric broke down. This corresponds to $V_B \approx \frac{1}{2}V_A$, instead of $V_B \approx V_A$ when the insulator was tested in the absence of an applied semiconductor (see Fig. 1). However, this still represents a dielectric breakdown strength in excess of 3 MV/cm. If the reduction of breakdown field due to the application of an organic semiconductor is a general feature of anodised gate insulators, or specific to Al_2O_3, is not clear at this stage. Previously published results on anodised Ta_2O_5 and SiO_2-based OFETs [8] only report characteristics for $V_G \ll V_A$, well below a possible breakdown.

The output characteristics of Fig. 2(a) are of the familiar form for hole-transporting FETs. At a given negative V_G, I_D initially rises linearly with negative V_D for $|V_D| < |V_G|$, and saturates for $|V_D| \geqslant |V_G|$ due to pinch-off of the accumulation layer. A slight anomaly at very low V_D ($|V_D| < 2$ V) is an artefact of gate leakage. From theory [12], we expect

$$I_{D,sat} = \frac{W}{2L}\mu C_i(V_G - V_0)^2. \tag{1}$$

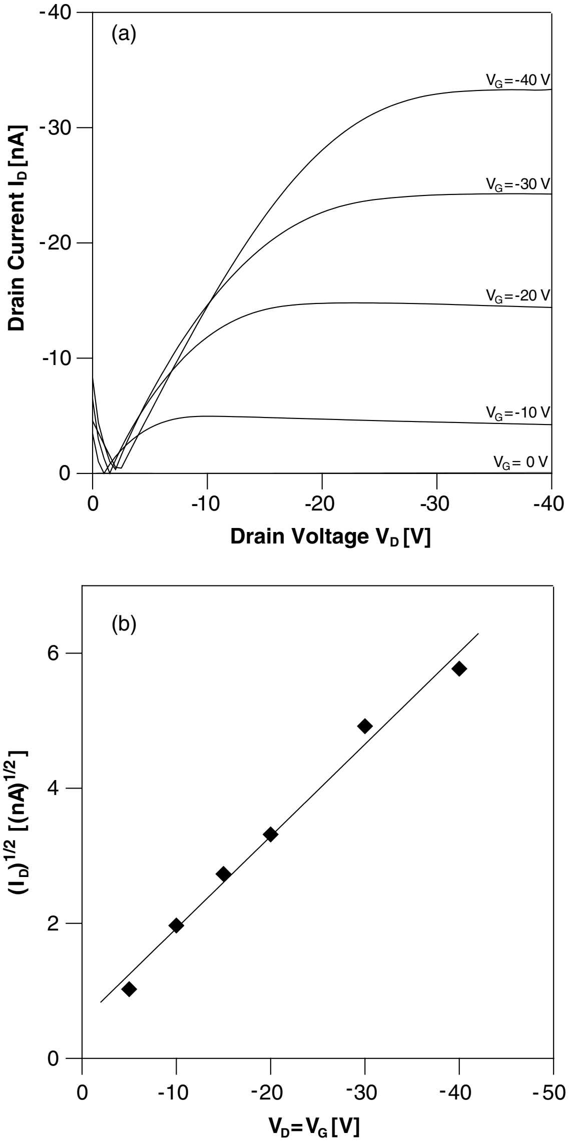

Fig. 2. (a) Output characteristics for OFETs with anodised Al_2O_3 gate insulators; $V_A = 100$ V. (b) $\sqrt{I_{D,sat}}$, evaluated at $V_D = V_G$, versus $V_D = V_G$, includes data from additional scans not shown in (a).

The approximately straight line relationship in a plot $\sqrt{I_{D,sat}}$ versus $V_D = V_G$, Fig. 2(b), confirms that our OFETs follow Eq. (1). From the slope of that line, we calculate the FET mobility of PTAA on anodised Al_2O_3 as $\mu_{FET} = 2.7 \times 10^{-5}$ $cm^2/V\,s$. This is two orders of magnitude lower than the PTAA mobility observed before on a different substrate [11]. However, we have recently found that OFET mobility may depend strongly on the semiconductor–insulator interface, and in particular, on the polarity of the insulator surface [15]. High polarity surfaces introduce energetic disorder into the semiconductor HOMO, in a manner similar to that of a bulk effect described by Bässler's model [13]. Previously, the highest mobilities for PTAA were obtained using either apolar surface treatments [11], or with low permittivity polymeric gate insulators [15]. Similarly, Salleo et al. have shown that OFET mobilities of a hole-conducting fluorene copolymer on SiO_2 can be increased more than 20-fold when the insulator surface is treated with an apolar self-assembling monolayer (SAM) of octadecyltrichlorosilane (OTS) [14]. As we have not taken any measures here to control interface polarity, the low mobility on Al_2O_3 is not surprising.

For one example ($V_G = 20$ V), Fig. 3(a) compares output characteristics during ramping up/ramping down $|V_D|$, revealing moderate hysteresis ($\Delta I_D/I_D < 10\%$). Hysteresis may be due to both trap filling at the polar insulator surface and/or electret properties of the insulator bulk. A small number of ions, or highly polar $Al(OH)_3$, has to be expected in anodised Al films. Similar phenomena are observed in non-anodic SiO_2-based transistors, as well [14], and are often referred to as 'gate bias stress'.

Fig. 3(a) also shows the gate leakage current density during the same scan. The leakage is considerably larger at $V_D \approx 0$ V than at $V_D \approx V_G$. In all cases, at $V_D = V_G$, gate leakage current I_G was considerably smaller than saturation drain current $I_{D,sat}$. Consequently, the measurement of saturation current is not compromised by gate leakage, and our evaluation of mobility remains valid. Taking into account the overlap area between drain and gate, leakage current density j_G at $V_D = 0$ V (i.e., at maximum leakage) was calculated. Fig. 3(b) shows j_G scaling linearly with V_G, with a slope corresponding to a gate insulator resistivity $\rho \approx 3.3 \times 10^9$ $\Omega\,m$. This resistivity is several orders of magnitude lower than that of non-anodic inorganic oxides, which we rationalise as a consequence of the electrolytic growth

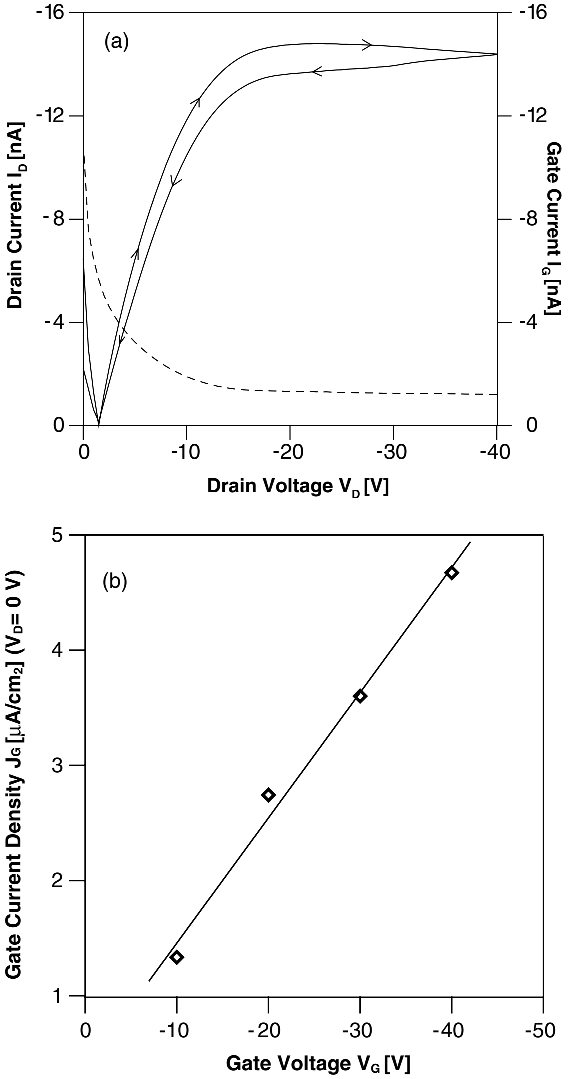

Fig. 3. (a) (—) Output hysteresis at $V_G = -20$ V, (- - -) gate leakage current I_G against V_D, at $V_G = -20$ V. (b) Maximum (i.e., $V_D = 0$) j_G versus V_G.

environment. Gate leakage currents in working devices are rarely reported in the OFET literature, and our figures are therefore hard to compare to those in OFETs with other gate insulator materials. However, gate leakage is at a level low enough not to compromise our characterisation. Also, the ratio between drain current and gate leakage current scales with mobility. Consequently, gate leakage will become less of a problem when semiconductors and/or surface treatments are employed that lead to higher mobilities, without any adjustments to the bulk insulator.

4. Conclusions and future work

This investigation provides proof-of-principle for the use of anodised Al as gate electrode/gate insulator combination for OFETs. Future work will address the following points. Firstly, we will use Al foil instead of evaporated Al. Al foils require pre-anodisation treatments such as electropolishing to give a surface quality comparable to evaporated films, but this procedure is well established in the aluminium industry [10]. Secondly, we will control surface polarity with a view towards improved interface mobilities. Trichlorosilane SAM chemistry can be applied to Al_2O_3 in the same way as to SiO_2. Thirdly, we will attempt to control possible insulator electret behaviour and gate leakage by anodising with ammonia salts instead of citric acid, as it was advised by Brock and Wood [16].

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