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Electret mechanism, hysteresis, and ambient performance of sol-gel silica gate dielectrics in pentacene field-effect transistors

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The electret induced hysteresis was studied in sol-gel silica films that result in higher drain currents and improved device performance in pentacene field-effect transistors. Vacuum and ambient condition studies of the hysteresis behavior and capacitance-voltage characteristics on single layer and varying thicknesses of bilayer dielectrics confirmed that blocking layers of thermal oxide could effectively eliminate the electret induced hysteresis, and that thin (25 nm) sol-gel silica dielectrics enabled elimination of nanopores thus realizing stable device characteristics under ambient conditions. © 2007 American Institute of Physics. [DOI: 10.1063/1.2821377]

Printed electronic circuits comprising organic field-effect transistors (OFETs) are of great interest in applications ranging from identification tags to switching devices for active-matrix displays.^{1–4} Improvement of organic semiconductors, typically benchmarked by transport mobilities, has continued to be the major focus of research efforts. Although it has been recognized that the semiconductor-dielectric interfacial interactions critically influence mobility,⁵ hysteresis,⁶ and threshold voltage (V_{th});⁷ the bulk effects of dielectric films, unlike those in silicon microelectronics, have not been adequately studied.

The performance of dielectrics in ambient conditions and the influence of moisture on dielectrics are important considerations in their study as suitable dielectrics. The influence of moisture has been documented in dielectrics such as poly(4-vinylphenol) (PVP) and poly(vinyl alcohol) (PVA). The hydroxyl (–OH) groups within PVP/PVA films or moisture has been linked to its large hysteresis^{8,9} and increase in drain currents related to polarization in the dielectric.¹⁰ The influence of –OH groups and the effect of moisture have also been reported in inorganic¹¹/organic-inorganic hybrid⁶ gate dielectrics with high polarizability (or high dielectric constant, k), that results in hysteresis and negative V_{th} shift.⁵ Low temperature (60–100 °C), solution processed sol-gel deposited high k silica dielectrics with improved V_{th} , mobilities, high drain currents at low voltages have been recently reported.¹² In the polymer, inorganic, as well as the hybrid dielectric film based OFETs, hysteresis is believed to be re-

lated to electron injection from the gate to –OH groups; however, the extrinsic origin of charge trapping for an enlarged hysteresis, V_{th} instabilities, and higher off current in ambient air is far from understood.^{11,13,14}

In this work, the effect of –OH groups and moisture on the electrical performances of pentacene OFETs with sol-gel (SG) silica film in single and bilayer dielectric systems are studied in vacuum/ambient conditions so as to investigate their charge trapping mechanism and ambient moisture effects.

SG silica solution was prepared by a two-step acid-base catalyst procedure by mixing tetraethylorthosilicate (TEOS), ethanol, water, and HCl in the following molar ratios: 1:10:3.5:0.003. After stirring at room temperature for 90 min, three drops of the base catalyst (0.1M NH_4OH) was then added into the solution. The 3 day aged solution, under constant stirring at room temperature, was then spin coated (2000 rpm) to form ~330 nm thick film on blank n -type Si wafer as the single layer dielectric and on thermally grown SiO_2 (TOX) as the bilayer dielectric [Fig. 1(a)]. Sol-gel silica solution, diluted by 90% by w/w ethanol, was also used to deposit ~25 nm SG silica film in the bilayer dielectric structure. The SG silica films were dried at ambient conditions at 60 °C and were further heated at 100 °C, 10^{-7} mbar prior to pentacene deposition. A 50 nm film of pentacene was evaporated at 0.5 Å/s under a vacuum of 10^{-7} mbar at a substrate temperature of 100 °C. Gold source and drain layers were patterned using a shadow mask. All electrical measurements were done with a Keithley 4200 semiconductor parameter analyzer in a Desert Cryogenics probe station at a base pressure of 5×10^{-5} mbar and were also characterized in ambient air (~23 °C and 70%–80% relative humidity).

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FIG. 3. (Color online) (a) Transfer characteristics of bilayer dielectric pentacene OFET in ambient and vacuum. This phenomenon is reversible upon repeated measurements between ambient and vacuum for thick SG silica film (330 nm) on 80 nm TOX. The ambient stability is improved with thinner SG silica film (25 nm). (b) Capacitance-voltage (C - V) characteristics of MIS on n -type Si wafer for bilayer structure with thick SG silica (330 nm) and thin SG silica (25 nm), measured at $f=100$ kHz. (Note: F=forward, R=reverse.)

also been reported in the PVP film,^{8,10} could be illustrated from its significantly higher capacitances of the 330 nm bilayer dielectric, in ambient conditions [Fig. 3(b)]. The increase in k of the SG silica film from $k \sim 10$ in vacuum to $k \sim 21.5$ in ambient likewise signifies that dipolar polarization of the water molecules in SG silica is very fast and responds readily to the measuring frequency. Moreover, the hysteresis of C_i - V characteristics is negligible, suggesting that there are negligible interfacial traps or the traps are shallow in nature, responding very fast to the measuring frequency.

Standard transfer characteristics, including a high on/off ratio in ambient conditions, was brought about in the bilayer FETs by resorting to a SG silica thickness of 25 nm. Thinner SG silica results in a negligible nanoporous SG silica bulk layer while retaining the same denser silica skin layer on its surface, yielding a lower k value of ~ 4.5 . However, it could also be observed that there is a slight increase in I_{on} and I_{off} ; and positive V_{th} shift, compared to the 330 nm SG silica bilayer FET measured in vacuum. This could be ascribed to the higher C_i ($\propto 1/d$) and the reduced charge electrets in the thin nanoporous SG silica layer. The ability of these devices to operate in ambient also confirms a strong reversible hydrolysis and electrostatic charging effect rather than an electrochemical doping mechanism recently reported in polymer electrolytes.²¹

In summary, we have investigated the electret effect in SG silica dielectric films in pentacene FETs. Studies with cross-sectional TEM and with a blocking layer consisting of thermally grown oxide confirmed that the electret mechanism is related to electron injection into the hydroxyl groups

contained within the nanopores of the SG silica film. The SG silica bilayer film undergoes a reversible hydrolysis reaction in ambient and, as a result, there is an always on characteristics for these devices. Thin SG silica films (25 nm) eliminate the nanoporous hygroscopic regions of the films while facilitating the use of these dielectrics in printed electronic applications as interface layers or surface modifying layers to enable high mobilities coupled with low voltage applications in ambient environments.

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