Available online at www.sciencedirect.com
ScienceDirect
Organic Electronics 8 (2007) 407–414
Organic Electronics
www.elsevier.com/locate/orgel

Atomic layer deposited Al_2O_3 as a capping layer for polymer based transistors

S. Ferrari [a,*], F. Perissinotti [a], E. Peron [a], L. Fumagalli [b], D. Natali [b], M. Sampietro [b]

[a] *Laboratorio MDM-CNR-INFM, Via Olivetti 2, 20041 Agrate Brianza (Mi), Italy*
[b] *Politecnico di Milano, Dipartimento di Elettronica e Informazione, Via Golgi 40, 20133 Milano, Italy*

Received 13 December 2006; received in revised form 31 January 2007; accepted 1 February 2007
Available online 14 February 2007

Abstract

The strong sensitivity of organic/polymeric semiconductors to the exposure to O_2 and H_2O atmospheres makes the use of capping layers mandatory for the realization of stable devices based on such materials. In this paper we explore the realization of inorganic capping layers by atomic layer deposition (ALD) that provides smooth and pinhole-free films with a great potential as passivation layer for organic based devices. We show that the deposition of Al_2O_3 on transistors based on poly-3 hexyltiophene (P3HT) allows to obtain air stable devices. Whereas the growth of Al_2O_3 directly on the P3HT layer leads to a rough interface and significant intermixing between the oxide and the polymer, which results in a deterioration of transistor performances, an interlayer of a poly-alcohol such as poly-vinylphenol interposed between the Al_2O_3 and the P3HT gives a well defined Al_2O_3/polymer interface without degradation of the hole mobility. Transistors capped with Al_2O_3/PVP are very stable in air, with no appreciable differences in the electrical characteristics when measured in vacuum or in air. In addition no significant degradation of the transistors electrical properties was detected even after one month of air exposure.

PACS: 68.35.Ct; 68.35.Fx; 68.37.Lp; 73.50.−h; 73.61.Ph

Keywords: Organic thin film transistor; Capping; Atomic layer deposition; Aluminum oxide

1. Introduction

Due to the sensitivity of organic active materials to water and oxygen [1,2], organic based devices require the development of efficient encapsulating layers. Encapsulation by means of polymer layers such as cross-linked poly-vinyl alcohol [3–5] improves the lifetime of organic field effect transistors (OTFT) devices, yet the use of inorganic materials such as oxides [6] or nitrides [7] provides stronger resistance giving more effective permeation barriers against oxygen and moisture. Among different passivating layers, the Al_2O_3 shows excellent gas permeation properties [8–10]. For this reason in this paper we investigate its application as capping layer for OTFT.

* Corresponding author. Tel.: +39 039 6036383; fax: +39 039 6881175.
E-mail address: sandro.ferrari@mdm.infm.it (S. Ferrari).

1566-1199/$ - see front matter
doi:10.1016/j.orgel.2007.02.004

The deposition of Al_2O_3 on polymeric materials has been studied by different groups for various applications such as adhesion layer for organic based low-k dielectrics [11] and gas permeation barriers [12–14] most notably for OLED [15,8]. The preferred technique for the deposition of Al_2O_3 on polymers is atomic layer deposition, by using trimethyl aluminum (TMA) and H_2O as aluminum and oxygen precursors, respectively [16,17,12], or plasma enhanced ALD, by using oxygen or ozone instead of the H_2O as oxygen precursor [18,15,14]. Following the standard model of the ALD growth mechanism of Al_2O_3 on inorganic surfaces, the TMA is reacting at the surface hydroxyl groups in a self-limiting reaction. When the process is carried out on polymers lacking reactive groups, the TMA should be adsorbed physically into the polymer and the reaction with the H_2O should take place inside the polymer. This results in broad Al_2O_3/polymer interfaces [16,17]. Therefore the use of ALD deposited Al_2O_3 as an encapsulating layer directly on the polymeric semiconductor is problematic since it is expected that AlO_x is included into the semiconducting layer and degrades its electrical properties. In this paper we studied the mechanism of ALD Al_2O_3 growth on the polymeric semiconductor poly-3 hexyltiophene (P3HT), and the effect of the growth process on the electrical properties of transistors based on P3HT. We elaborate a strategy to prevent Al_2O_3 diffusion into the P3HT layer by proper engineering of the polymeric layer. We will provide a structural and chemical characterization of the Al_2O_3/polymers stacks by using transmission electron microscopy (TEM) and time of flight secondary ion mass spectrometry (ToF-SIMS) respectively, while electrical characterization on capped and uncapped transistors shows the effect of the capping layer on the electrical properties of the semiconductor.

2. Experimental details

The transistors schematized in Fig. 1 were prepared by a conventional optical lithography process. The gate dielectric is a thermally grown SiO_2 100 nm thick on a Si $p+$, that acts as a common gate. Source and drain were made by patterning Au lines by photo-lithography. Channel width varied from 3 μm to 18 μm. The SiO_2 surface in the transistor channel was functionalized with dimethyl-dichlorosilane prior to P3HT deposition to improve the mobility. Regioregular poly 3-hexyltiophene (RR-P3HT) (Aldrich) was fractionated and purified by a sequence of organic solvent extraction (molecular weight = 52000 g/mol, poly dispersity = 2.0). RR-P3HT films were spin-coated from a 0.5% wt/wt solution in chloroform in order to achieve a thickness of about 30 nm. Poly-vinyl alcohol (PVP) or poly(methylmethacrylate) (PMMA) were spin cast from ethyl-acetate on the RR-P3HT films at a concentration of 0.4% wt/wt. The resulting thickness of the PVP and of the PMMA are around 10 nm as verified by X-ray reflectivity (data not shown), so that the total thickness of the P3HT/PVP(PMMA) stack is about 40 nm.

The Al_2O_3 films were grown by Atomic Layer Deposition (ALD) in a flow type (F-120 ASM-Microchemistry) reactor. TMA and H_2O were used as aluminum and oxygen precursors, respectively. For each film, 600 pulse/purge cycles were programmed in order to achieve a thickness of about 50 nm. During the growth, the pressure in the reactor was between 4 mbar and 6 mbar and the substrate temperature was kept at 125 °C. For the chemical and structural characterization of interfaces, Al_2O_3/polymers stacks were deposited on flat SiO_2 substrates. ToF-SIMS depth profiling and imaging was performed using and ION-TOF IV instrument equipped with two ion guns. Sputtering was performed using Cs^+ at 0.5 keV, while Ga^+ at 25 keV were used for the generation of the analyzed negative ions. High resolution TEM images where collected by means of a Leo 922 Omega EFTEM operating at 200 KV. Electrical measurements were performed in vacuum at 10^{-5} mbar after about 24 h of permanence in vacuum, and in ambient air, using a Keithley 4200 Modular DC source/monitor.

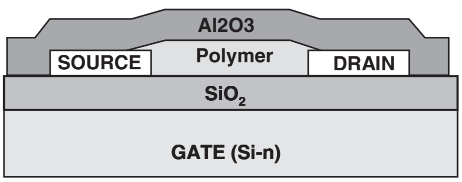

Fig. 1. Scheme of the encapsulated organic field effect transistor.

3. Results and discussion

3.1. Deposition on bare P3HT layer

The growth of Al_2O_3 by ALD on bare P3HT is expected to follow a mechanism analogous to other polymers such as poly-ethylene [16,17]. Due to the absence of highly reactive functional groups in the polymer, the nucleation process of Al_2O_3 during