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Plasma-assisted atomic layer deposition of Al_2O_3 moisture permeation barriers on polymers

E. Langereis,[a] M. Creatore, S. B. S. Heil, M. C. M. van de Sanden, and W. M. M. Kessels[b]
Department of Applied Physics, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

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Thin Al_2O_3 films of different thicknesses (10–40 nm) were deposited by plasma-assisted atomic layer deposition on substrates of poly(2,6-ethylenenaphthalate) (PEN), and the water vapor transmission rate (WVTR) values were measured by means of the calcium test. The permeation barrier properties improved with decreasing substrate temperature and a good WVTR of 5×10^{-3} g m^{-2} day^{-1} ($WVTR_{PEN}$=0.5 g m^{-2} day^{-1}) was measured for a 20 nm thick Al_2O_3 film deposited at room temperature using short purging times. Such ultrathin, low-temperature deposited, high-quality moisture permeation barriers are an essential requirement for the implementation of polymeric substrates in flexible electronic and display applications. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2338776]

Successful application of flexible organic light emitting diodes (F-OLEDs) requires excellent moisture permeation barriers to minimize the degradation of the OLED device.[1,2] Transparent moisture permeation barriers with an estimated water vapor transmission rate (WVTR) as low as 10^{-6} g m^{-2} day^{-1} need to be deposited.[1,3] Low deposition temperatures are required below the glass transition temperature of polymers and there is a strong preference for room temperature (RT) deposition because of process simplicity and compatibility with the OLED manufacturing process.[4,5] Because the moisture permeation properties of a single layer barrier are eventually limited by the defect density of the layer,[6] the deposition of multilayer structures is expected to be the path towards the WVTR requirements mentioned above.[7–9] The multilayer structures will become most effective when the individual layers themselves have excellent permeation properties.

The atomic layer deposition (ALD) technique is known to produce densely packed, virtually defect-free, highly uniform, and conformal films and can therefore be used to deposit high-quality single layer permeation barriers.[4,10,11] Groner *et al.* reported good permeation barrier properties (WVTR=1×10^{-3} g m^{-2} day^{-1}) of very thin (10–25 nm) Al_2O_3 films deposited from sequential trimethylaluminum (TMA) and water vapor exposures. However, they limited their deposition to a temperature of 120 °C to have a short ALD cycle time (60 s at 120 °C).[11] They also showed ALD of Al_2O_3 films at 33 °C, but this required 180 s of purging time to remove the residual water vapor, resulting in a total cycle time of 203 s.[12]

The plasma-assisted ALD (PA-ALD) technique has the same growth characteristics as thermal ALD, but the use of O_2 plasma radicals in the process enables deposition at room temperature without requiring long purging times. Furthermore, when admixing N_2 gas to the O_2 plasma, also N-doped Al_2O_3 can easily be deposited by PA-ALD, which has been investigated previously for its permeation barrier properties.[13]

In this letter, we show the ability of PA-ALD in obtaining good Al_2O_3 moisture permeation barriers films at low substrate temperature (from RT to 100 °C) on poly(2,6-ethylenenaphthalate) (PEN) substrates using short cycle times. A good WVTR of 5.0×10^{-3} g m^{-2} day^{-1} is obtained for a 20 nm thick film deposited at room temperature with a cycle time of 17 s.

Thin Al_2O_3 films were deposited in a homebuilt deposition reactor by PA-ALD from sequentially exposing the substrate to TMA vapor and a remote O_2 plasma. The deposition chamber was continuously purged by O_2 resulting in a pressure of 7.5 mTorr. The PA-ALD cycle, used at all deposition temperatures, consisted of multiple TMA dosing (1 s each) injected from a trapped volume, 5 s purge, 2 s O_2 plasma, and 5 s purge. The plasma was created in a remote inductively coupled plasma source operated on the O_2 background gas. The depositions were carried from RT up to 200 °C on *c*-Si substrates and up to 100 °C on PEN (DuPont Teijin Films, glass transition temperature T_g=121 °C). Prior to deposition, the PEN substrates were ultrasonically cleaned in ethanol and were heated overnight at 70 °C in the reaction chamber at a base pressure of 10^{-6} mTorr to remove residual water in the polymer. The moisture permeation barrier properties of the films were determined by means of the calcium test,[14] in which the change in transparency of a 100 nm thick Ca film was monitored in a controlled environment (T =21 °C and 60% relative humidity) to determine the WVTR of the film.

The PA-ALD Al_2O_3 films were characterized on *c*-Si wafers and the results are reported in Table I. Two different TMA doses were used, i.e., undersaturated dosing (one TMA dose) and saturated dosing (five TMA doses), providing information about the influence of the chemical composition of the Al_2O_3 film on the barrier properties. During deposition, the Al_2O_3 thickness was determined by *in situ* spectroscopic ellipsometry (SE). As expected, the growth rate of the saturated PA-ALD growth is higher compared to undersaturated TMA dosing conditions. The growth rate increased for decreasing substrate temperatures, as reported previously for ALD of Al_2O_3.[15,16] Rutherford backscattering spectroscopy (RBS) showed that the mass density of the Al_2O_3 films was

[a]Electronic mail: e.langereis@tue.nl
[b]Electronic mail: w.m.m.kessels@tue.nl

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TABLE I. Properties of ~30 nm thick Al_2O_3 films deposited at different temperatures on native oxide covered *c*-Si substrates using two different TMA dosing conditions in the PA-ALD cycle. The growth rate is determined from *in situ* SE; the mass density and film composition are determined from RBS. The first row gives the typical absolute errors on the results.

TMA dosing	Deposition temperature (°C)	Growth rate (nm/cycle)	Mass density (g cm^{-3})	Composition Al_2O_x
Undersaturated	25	0.12±0.005	3.0±0.1	3.60±0.05
	50	0.11	2.9	3.40
	100	0.11	2.8	3.40
	200	0.097	2.9	3.34
Saturated	70	0.17	2.9	3.20
	200	0.13	3.0	3.14

virtually independent of deposition temperature, yielding an average value of 2.9±0.2 g cm^{-3}. All the deposited Al_2O_3 films were oxygen rich and the amount of oxygen in the film increased for decreasing deposition temperature; however, the saturated growth condition resulted in a limited excess of oxygen in the film. Elastic recoil detection analysis showed that the films deposited by undersaturated and saturated TMA dosing contained 4 and 2 at. % H for the deposition at 200 °C, respectively. The hydrogen content increased at lower temperature up to 12 at. % for undersaturated deposition at RT and indicates the presence of additional hydroxyl groups in the films.

RBS and x-ray photoelectron spectroscopy on a relatively thick Al_2O_3 film (500 cycles) deposited by undersaturated TMA dosing at 100 °C showed the same chemical composition on *c*-Si and PEN substrates, i.e., the [O]/[Al] ratio was 1.7. These results indicate that the bulk material properties of the film deposited by PA-ALD are not affected by the substrate material used.

Figure 1 shows the WVTR of 20 nm thin Al_2O_3 films as a function of deposition temperature in the range from RT to 100 °C. The WVTR is found to improve for films deposited at lower temperatures and the saturated growth condition yields slightly better results. The trend with temperature is different than that reported for thermal ALD Al_2O_3 films prepared by TMA and H_2O by Park *et al.* who observed that the barrier properties deteriorated for lower deposition temperatures (80 °C).[4] The reason for the improvement of the WVTR for PA-ALD barriers is yet unknown but it can possibly be related to the observed increase in hydroxyl content in the Al_2O_3 films deposited at low temperatures (cf. Table I). It has been reported that the high polarizability of the (Al–)OH bonds of the film could obstruct water vapor permeation through the layer by means of H bonding with water vapor,[17] although H_2O dissociation at reactive hydrophilic sites is also suggested to occur.[13] The mismatch of the coefficient of thermal expansion of Al_2O_3 and PEN might be another explanation as it can lead to stress generation at the interface when the sample is brought to RT after deposition at elevated temperature and, therefore, induce deterioration of the barrier properties. This effect, for which no morphological evidence is available yet, could be related to the difference in initial growth on the polymer surface between plasma-assisted and thermal ALD. Thermal ALD films are hypothesized to nucleate inside the polymer matrix, whereas a more discrete interface could be present for plasma-assisted ALD as the O_2 plasma can create additional functional groups (e.g., OH) on the polymer surface during the early stages of growth.

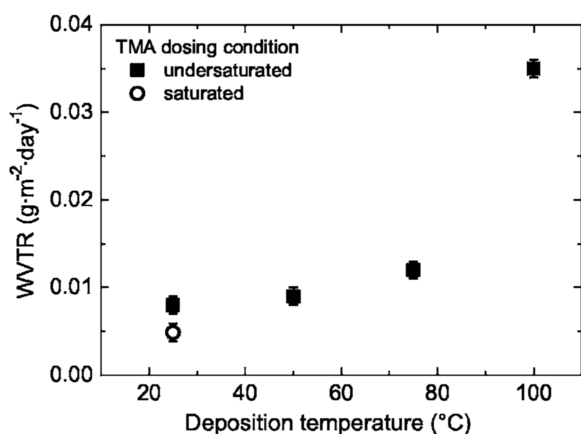

FIG. 1. Water vapor transmission rate (WVTR) of 20 nm thick PA-ALD Al_2O_3 films on PEN as a function of deposition temperature with undersaturated and saturated TMA dosing conditions.

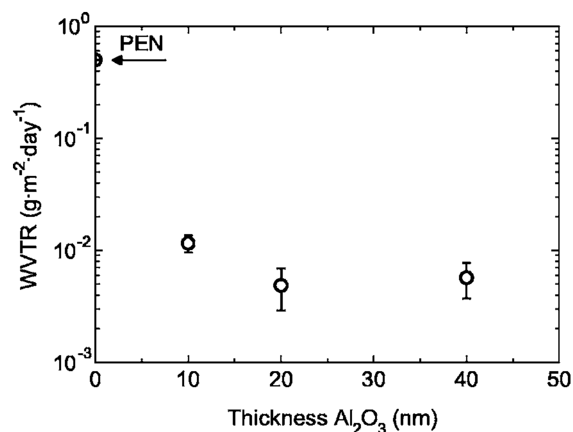

FIG. 2. Water vapor transmission rate (WVTR) of PA-ALD Al_2O_3 films on PEN as a function of film thickness. The films are deposited at room temperature with saturated TMA dosing conditions.

By adding N_2 gas into the O_2 plasma ($[N_2]/[O_2]=3:2$), N-doped (~1at. % N) stoichiometric Al_2O_3 was deposited and the nitrogen content in the film could be controlled by changing the plasma composition. The moisture permeation properties were briefly investigated for a deposition carried out at room temperature, resulting in a WVTR of 0.009 g m^{-2} day^{-1} for a 20 nm thick film and did not show improved permeation barrier properties compared to the Al_2O_3 films.[13] Preliminary investigation on AlN films deposited by PA-ALD at room temperature using a N_2/H_2 (3:2) plasma in the cycle showed negligible barrier properties.

The WVTR of the Al_2O_3 films as a function of thickness for deposition at RT is shown in Fig. 2. It is observed that a 10 nm thick Al_2O_3 film already shows very good barrier properties. The WVTR saturates for films thicker than 20 nm to the value of 5×10^{-3} g m^{-2} day^{-1}, which is good for a single layer barrier, especially in comparison to the 0.40 g m^{-2} day^{-1} for a magnetron sputtered 34 nm thick AlO_x film[18] and to the 0.045 g m^{-2} day^{-1} reported for plasma-enhanced chemical vapor deposited (PE-CVD) SiN_x films with a thickness of 130 nm.[19] Similarly, for the thermal ALD process using TMA and H_2O, Park *et al.* reported a

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WVTR of 0.062 g m^{-2} day^{-1} for a polyethersulfone film coated on both sides with 30 nm Al_2O_3 film deposited 90 °C.[4] On the other hand, the obtained WVTR values for deposition at RT were in the same order as the results reported by Groner *et al.* by ALD at 120 °C.[11] The improvement of barrier properties with respect to films deposited by PE-CVD can be related to the uniform and conformal ALD growth of the barrier layer on the polymer surface, which is porous, defective, and not particle-free. A saturation of the barrier properties with film thickness is, however, still observed. Plausible explanations are that the Al_2O_3 films are not completely pinhole-free or that "defects" on the polymer surface are not conformally "sealed" by the ALD film.

In summary, we have shown the feasibility of PA-ALD Al_2O_3 films at room temperature using short purging times in the order of seconds. The barrier properties of the Al_2O_3 films improved for lower deposition temperatures, which is promising from a manufacturing perspective of polymer substrates and for encapsulation of F-OLEDs at room temperature preventing device degradation.[20] Saturation in barrier properties was observed for increasing film thickness, which suggests that the mechanism of water vapor permeation through the barrier/polymer is still defect controlled. The room temperature PA-ALD of 20 nm thick Al_2O_3 on PEN resulted in a good moisture permeation barrier resulting in a WVTR of 5×10^{-3} g m^{-2} day^{-1}. In future experiments, the water and oxygen permeation mechanism will be further investigated focusing on the role of defects, nanoscale morphology, and the influence of the polymer substrate.

Note added in proof: After submission of this paper, Carcia *et al.* reported an excellent WVTR$<10^{-5}$ g m^{-2} day^{-1} for 25 nm thick Al_2O_3 film deposited by thermal ALD on PEN.[21] This experiment shows the potential of single layer barriers that can be obtained by ALD. Appropriate substrate cleaning and handling minimizing the amount of particles on the polymer surface is believed to be one of the key aspects in obtaining these superior barrier properties. For the experiments reported in the present work, no special care of substrate cleaning and handling was taken other than described in the text.

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