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The impact of the nano-pore filling on the performance of organosilicon-based moisture barriers

Alberto Perrotta^{a,b,*}, Gianfranco Aresta^a, Erik R.J. van Beekum^a, Jurgen Palmans^a, Peter van de Weijer^d, M.C.M. Richard van de Sanden^c, W.M.M. Erwin Kessels^{a,e}, Mariadriana Creatore^{a,e}

^a Department of Applied Physics, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

^b Dutch Polymer Institute (DPI), P.O. Box 902, 5600 AX Eindhoven, The Netherlands

^c Dutch Institute for Fundamental Energy Research (DIFFER), P.O. Box 1207, 3430 BE Nieuwegein, The Netherlands

^d Philips Research, High Tech Campus 4, 5656 AE Eindhoven, The Netherlands

^e Solar Research SOLLIANCE, High Tech Campus 5, 5656 AE Eindhoven, The Netherlands

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ABSTRACT

Promising results in terms of moisture and oxygen permeation barrier properties have been reported for organic/inorganic multilayers, but the impact of the organic interlayer on the overall barrier performance is still under discussion. It is generally accepted that the organic interlayer acts as a smoothening layer, allowing for the decoupling between defects/pinholes present in the polymer substrate and the inorganic layer. It is, however, also hypothesized that the organic interlayer infiltrates into the nano-pores present in the inorganic barrier layer, therefore affecting the barrier properties at microstructural level. In the present work, the moisture permeation barrier performance of SiO₂/organosilicon multilayers deposited by means of initiated- and plasma enhanced-chemical vapor deposition is investigated. Calcium test measurements were used to discriminate between the overall water permeation (*effective* water vapor transmission rate, WVTR) through the layer and the permeation through the matrix porosity (*intrinsic* WVTR). The improvement in terms of *intrinsic* barrier performance was found to correlate with the residual nano-porosity content, due to the filling/infiltration of the organosilicon monomer in the SiO₂ nano-pores. However, such improvement upon the deposition of the organosilicon interlayer is limited to a factor four. These results, in combination with the analysis of the local defects present in the multilayer structure, lead to the conclusion that the main contribution of the organosilicon interlayer to the overall barrier performance is the decoupling of the above-mentioned local defects/pinholes.

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1. Introduction

The state-of-the art in the field of ultra-high moisture diffusion barriers is represented by a multi-layer solution in which an inorganic (e.g., Al₂O₃, Si₃N₄ or SiO₂) thin film (<100 nm) barrier is coupled with an organic (generally an acrylate- or organosilicon-based polymer) interlayer, with thickness ranging from hundreds of nanometers to micrometers¹. It is worth addressing that, next to the multilayer solution, inorganic nano-laminates are growing in importance in the moisture barrier field. This solution consists of alternated ultra-thin inorganic layers (e.g., ZrO₂, TiO₂, Al₂O₃) [55]. [1]. This approach has led to water

vapor transmission rate (WVTR) values in the 10⁻⁶ g m⁻² day⁻¹ regime [2–4], therefore suitable for the encapsulation of high-end devices, such as thin film solar cells and flexible organic light emitting diodes [5].

In multilayer barrier systems, the inorganic/organic dyads are generally deposited by a hybrid approach: sputtering or plasma enhanced-chemical vapor deposition (PE-CVD) of the inorganic barrier layer, in combination with flash evaporation/condensation of the organic monomer, and followed by curing/polymerization [2,6–9]. Additionally, different deposition approaches such as atomic layer deposition (ALD) in combination with molecular layer deposition [10–14], and all PE-CVD developed multilayers have been reported in literature [15–18]. Coclite et al. [19] reported on the deposition of multilayers based on organosilicon chemistry, in which the inorganic barrier layer is deposited by means of PE-CVD and the organic interlayer is deposited by means of initiated-CVD (i-CVD) [20–22]. Recently, Spee et al. reported on the deposition of SiN_x/poly-glycidylmethacrylate/SiN_x, where the inorganic layer was deposited by hot wire chemical vapor deposition (HWCVD) and the organic layer by i-CVD [4]. The appeal of the i-CVD technique is its compatibility with vacuum systems and the full retention of the monomer chemistry, similarly to liquid phase polymerization processes

* Corresponding author at: Department of Applied Physics, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands. Tel.: +31 402474095; fax: +31 402456442.

E-mail addresses: a.perrotta@tue.nl, m.creatore@tue.nl (A. Perrotta).

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[23,24]. Furthermore, compared to the classical flash evaporation/polymerization method, i-CVD is well acknowledged for its high conformality. This is guaranteed by the polymerization mechanism, which occurs only at the substrate surface.

The need for a multilayer barrier technology derives from the limits associated with single inorganic layers, their permeation barrier level being ultimately controlled by the presence of defects. These defects range in diameter from the nanometer-scale (*i.e.*, well above the water kinetic diameter of 0.27 nm), up to substrate/process-induced macro-defects (*e.g.*, pinholes and particles with a diameter in the range of micrometers) [25]. The successful application of a multilayer is generally attributed to the smoothening effect associated with the organic polymer layer, which allows for a more controlled growth of the subsequent inorganic barrier [2,26,27]. Additionally, Graff et al. [28] carried out numerical simulation studies and reported on the development of a “tortuous” path for the permeant molecule upon the application of a multilayer. Hence, the organic interlayer was found to lower the overall barrier permeability by decoupling the pinholes/defects present on the inorganic layers.²

Although defects/pinholes represent an unhindered path for the permeant molecule [29,30], the kinetic diameter of the water molecule allows it to permeate through (sub-)nm sized pores, *i.e.*, the nano-porosity or free volume of the inorganic matrix. Affinito and Hilliard [26] highlighted that the estimated area density of the nano-pores can be approximately up to 15–20 times larger than the one of the defects/pinholes, leading to a higher permeation flux than through macro-defects. Therefore, an additional role of the organic interlayer was proposed, *i.e.*, the infiltration of the organic monomer in its liquid phase into the nano-porosity of the inorganic barrier layer underneath. Eventually, this infiltration is expected to influence the local water permeation through the filled pores. Recently [31], we reported on the experimental evidence for the infiltration of an i-CVD monomer into the nano-pores (from 1 to 2 nm in pore size) of single PE-CVD SiO₂ barrier layers during the initial stages of the polymerization process. These studies confirmed that the hypothesis of Affinito et al. [26] also applies for a CVD-based process.

The present work focuses on PE-CVD/i-CVD multilayers and addresses the contribution of the afore-mentioned infiltration in the nano-porosity to the *intrinsic* moisture permeation barrier performance. In order to discern between the effect of the filling/infiltration (affecting the porosity of the matrix of the barrier layer) and the decoupling effect (associated with the defects/pinholes in the layer), both *effective* and *intrinsic* WVTR were determined by means of the calcium (Ca) test [32]. The *effective* WVTR refers to the overall oxidation of the Ca-layer, whereas the *intrinsic* WVTR excludes the defects/pinholes as far as they are visible in the Ca test as white spots. More details on the test can be found in the experimental section.

The relative content of porosity accessible to the organic monomer was monitored by ellipsometric porosimetry (EP) [33–37]. EP is based on the adsorption of a probing molecule on the layer, which leads to a change in the layer optical properties, and these are followed by means of spectroscopic ellipsometry (SE). The variation of the optical properties as function of the ratio between the partial pressure (P_M) and the vapor pressure (P_{sat}) of the monomer at constant temperature results in the classical adsorption/desorption isotherm [35,38,39], which provides information on the microstructure of the layer and an estimation of the (average) pore size.

The paper is organized as follows: in the experimental section a description of the deposition chamber is provided, together with the diagnostic techniques, *i.e.*, IR spectroscopy, *in situ* spectroscopic ellipsometry, EP measurements, and Ca test. The section Results and Discussion

addresses the comparison in terms of chemistry and barrier properties of the i-CVD/PE-CVD and all PE-CVD developed multi-layers. Differences in the barrier properties of the two systems are investigated and correlated to the extent of monomer infiltration, measured by means of *in situ* ellipsometry studies. Then, a series of PE-CVD SiO₂ films showing a wide range of porosity is studied in terms of their nano-porosity content and *intrinsic* barrier properties. First, the nano-porosity accessible to the organosilicon monomers is characterized by *in situ* spectroscopic ellipsometry for the two extremes of the series. Next, the effect of the infiltration of the organosilicon monomer in the porosity of the (barrier) layer is investigated for the whole series and justified on the base of the nano-pore content.

2. Experimental details

All the layers were deposited without breaking the vacuum in a custom-built setup which allows for thin film deposition by means of both PE-CVD and i-CVD approaches [31,37]. The wire system for i-CVD is mounted on a magnetic movable arm, and during the i-CVD process it is inserted into the deposition chamber at a distance of 2 cm from the substrate holder. 1,3,5-trivinyl-1,3,5-trimethylcyclotrisiloxane (V₃D₃, purity > 95%, Gelest, $d_{V_3D_3} = 1$ nm) was adopted for the i-CVD process after 3 freeze–thaw cycles. The initiator (di-tert-butyl peroxide: TBPO, purity > 98%, Aldrich) is mixed together with the monomer in a buffer and injected into the deposition chamber through a ring placed above the grid. The grid is connected to a custom-built DC power supply system, equipped with a feed–loop system. During the PE-CVD process, the grid is transferred from the deposition chamber to a load-lock chamber. The SiO₂ and SiO_xC_yH_z layers are deposited by means of a parallel plate RF-plasma, and V₃D₃ is adopted as precursor. Before each deposition, the chamber is evacuated to a pressure of 10^{−5} mbar, and the setup is arranged for either the i-CVD or PE-CVD process. Table 1 reports the experimental conditions for all the processes. In the case of the poly(V₃D₃) layer, the conditions were chosen according to previous studies aimed at the deposition of stable, smooth layers with a high conversion (*i.e.*, >85%) of vinyl groups [40]. The setup is equipped with spectroscopic ellipsometry (SE)-compatible windows to study the film growth during each process.

In order to further investigate the infiltration of the organic polymer into the matrix of the inorganic layer, another organosilicon monomer was chosen with a dimension smaller than V₃D₃, 1,1,3,5,5-pentamethyl-1,3,5-trivinyltrisiloxane (TVTISO, purity > 95%, Gelest, $d_{TVTISO} = 0.85$ nm). First, the i-CVD process was optimized in order to find a process window for stable, dense polymers. The polymerization and polymer characteristics were investigated by following the same procedure adopted for V₃D₃ and explained in Ref. [40]. For the TVTISO monomer, a process window was identified at P_M/P_{sat} values below 0.2.

2.1. Film growth study and single layer characterization

The film growth process was followed by means of *in situ* SE, at an angle of incidence of 71.5°, wavelength range of 245–1000 nm, 1.6 nm resolution, by using a J.A. Woollam Co. M-2000F ellipsometer. The data analysis was performed by using the J.A. Woollam Complete EASE™ software, and the mean squared error between the experimental data and the model is minimized by adjusting the fit parameters using the Levenberg-Marquardt algorithm. The optical model for the film growth study consists of a Si substrate, native SiO₂ (~1.5–2 nm), Cauchy and Cauchy coupled with the Urbach absorption tail functions for the SiO₂ and the organosilicon interlayer (SiO_xC_yH_z, poly(V₃D₃) and poly(TVTISO)), respectively, according to Eqs. (1)–(2):

$$n(\lambda) = A + B/\lambda^2; k(\lambda) = 0 \quad (1)$$

$$n(\lambda) = A + B/\lambda^2 + C/\lambda^4; k(\lambda) = \alpha \cdot e^{\beta[12400(1/\lambda - 1/\gamma)]} \quad (2)$$

² It is worth mentioning that in this simulation it is assumed that the moisture permeation occurs only through the defects/pinholes present in the barrier layer which is considered elsewhere as impermeable.

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