Novel “broken” barrier layer in SiOx-based flexible barrier coatings.

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Abstract: High performance barrier coatings for oxygen, CO_2 and water vapour for flexible electronic applications are usually obtained by the overlap of ceramic barriers and flexible spacing organic layers in a multi-stack design. Here we propose a novel multilayer design with improved flexibility by the substitution of the SiO_2 brittle ceramic barriers with thinner layers. The thinning of the SiO_2 layers below the threshold of 30 nm stops their growth at the pre-coalescence of islands, leading to non-continuous or “broken” layers. This design allows obtaining an increase in the flexibility of the coating since the “broken” design decreases the stiffness of the ceramic layers. Moreover this increased flexibility can be obtained without any performance loss relative to the standard design by the increase of the number of barrier layers, using the conductance-limited diffusion of spacing layers.

Keywords: PECVD, gas barrier, multilayer, flexible, transparent

1. Introduction

Transparent and flexible gas barrier coatings are developed for various applications from food packaging or medical devices to OLEDs. The applications have different performance requirements in terms of permeability reduction, ranging from 1 up to 4 orders of magnitude, and in terms of gas selectivity. CO_2 barrier coatings with barrier improvement factors (BIF) of about 10 can be suitable for beverage bottles [1], oxygen barriers are needed for organic electronic device encapsulation with barrier factor of even 10000, water vapour barriers are for example requested in biopolymer packaging. In order to achieve high performance barrier properties a multilayer design is usually applied using the stacking of vacuum-deposited ceramic or metallic layers and polymer layers. The organic layers serve to maintain the substrate flexibility, enhance adhesion and mask surface defects. The inorganic layer acts as the gas barrier. In multilayers, multiple barrier are introduced and therefore gas permeation is delayed and reduced. The barrier is usually composed by a dense film with low defect concentration of silicon oxide, silicon nitride, silicon oxynitride, aluminum oxide or mixed oxides [2]. An example of such high performance coating is the ‘Flexible Glass’ developed by Vitex System, consisting of Al_2O_3 layers alternated to poly-acrylate layers on a PEN-based substrate [3].

The ceramic barrier layer introduces a limit in the flexibility of the devices since its mechanical properties do not allow high strain elastic deformations. This limit is due to the number of barrier layers needed to achieve the permeability required and to their smallest thickness that can be used. In fact below a certain thickness threshold the ceramic layers may not grow in a continuous way. For example Erlat et al. [3] showed the presence of a thickness threshold of 30 nm for SiO_2 layers deposited by PECVD in order to obtain continuous layers.

With the aim of overcoming this limit, in this work a novel multilayer design with ceramic “broken” layers thinner than 20 nm is presented. The silica-based coatings were deposited in a simple single-step RF-PECVD [4]. HMDSO has been used as precursor in an oxygen atmosphere and the ceramic or organic layer behaviour is obtained just pulsing the precursor flow in order to change the precursor/oxygen ratio and keeping all the other parameters constants. In particular the “broken”/continuous layer growth threshold was investigated, showing by nanoindentation measurements how the “broken” design can influence the mechanical properties. Moreover, the increase of flexibility is demonstrated, with no performance losses relative to standard design by the increase of the number of barrier layers.

2. Experimental

The coatings have been deposited by RF-PECVD in a capacitive coupled plasma apparatus produced by Plasma Electronics [4]. In order to obtain the multilayer structure of the silica-based coating, the oxygen flux was maintained constant at 300 sccm, while the HMDSO flux was varied between two values 50 sccm to obtain more inorganic layers and 800 sccm for more organic layers, hereafter named respectively “ceramic” and “polymeric” due to their mechanical behaviour [5]. RF power and pressure were maintained constant in the process and respectively at 0.1 W/cm^2 and 8×10^{-2} mbar. The sample holder was placed at the cathode position.

The substrates used were silicon (100) for the compositional and mechanical characterisations and polystyrene (PS) biaxially oriented foils 130 µm thick (Goodfellow ST311125) for the CO_2 permeability measurements. Silicon substrates were cleaned using a CO_2 snow-jet, while the PS foils just wetting the surface were cleaned with isopropyl alcohol. The samples for the deposition were just leaned on the sample holder.

The mechanical properties have been investigated by means of nanoindentation (MicroMaterials platform) on 2 µm thick coatings using a Berkovich diamond tip with maximum load of 3 mN and maximum depth lower than 200 nm. The islands/continuous film growth transition have been evaluated by means of spectroscopic ellipsometry in the wavelength range from 250 to 800 nm using a GES-5 (Sopra) model in reflection conditions at an angle of 70° from the sample normal. The experimental curves were fitted by using a Cauchy model for the real part of the refractive index: $n = A + B/\lambda$, while the transparency of the films allowed to neglect absorption. The CO_2 permeability measurements have been performed using a Multiperm System provided by Extrasolution srl. All measurements were performed with 2 hour of conditioning time, 60% of relative humidity and a temperature of 33°C.

3. Results

In order to study the “broken” design, at first the threshold for the continuous “ceramic” SiO_2 layer has been investigated in our deposition process. As already pointed out by Erlat et al [3], even in no interface conditions but with a direct growth of ceramic films on a substrate, at first small SiO_x clusters nucleate on the substrate surface and grow through coalescence with adjacent clusters to produce a continuous film. Therefore, below a certain thickness the ceramic layer lacks of uniform surface coverage leading to reduced barrier performances. This threshold thickness is usually called critical thickness. In order to estimate the critical thickness in our experimental conditions, some monolayer ceramic films with different thicknesses have been deposited on silicon substrates and their refractive index has been measured by ellipsometry. Figure 1 shows the variation of refractive index as a function of the coating thickness. Since their composition does not change and can be considered chemically homogeneous, their density, and therefore their porosity or defect density, is accountable for variation in refractive index [6]. The density of the ceramic layers has been calculated relative to the thickest film (750 nm) using the Lorenz-Lorenz equation [3,6], the results are shown in figure 1.

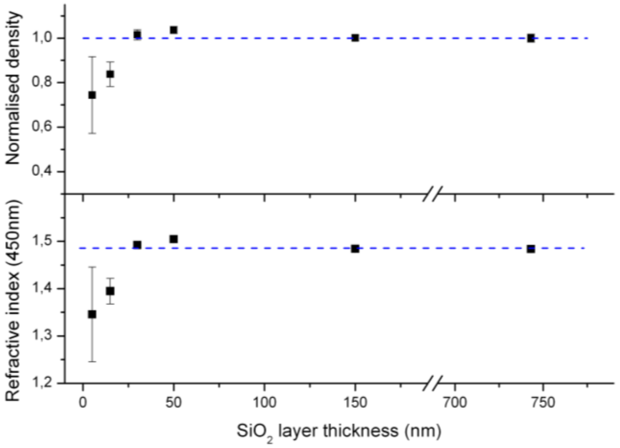

Figure 1. Refractive index of “ceramic” SiO_2 layers as a function of their thickness and density variations relative to the thickest coating (750 nm).

Since from the measurements the deviation from the bulk density arises for thicknesses below the 30 nm, the critical thickness should be identified between 15 and 30 nm.

In order to show that the “broken” design can improve the mechanical properties of the multilayer barrier, two series of samples have been deposited on silicon substrates changing the thickness of the “polymeric” and “ceramic” layers but keeping the overall coating thickness constant (2 µm). Table 1 summarizes the design parameters of the two series: in the former the number of periods in the multilayer is constant and the “ceramic” layer thickness is changed, whereas in the latter the number of periods is increased maintaining the “ceramic” layer thickness lower than the critical threshold (“broken” design).

series	ceramic (C) and polymeric (P) layer thickness (nm)	periods
As a function of ceramic layer thickness	5C 95P	20
	15C 85P	
	30C 70P	
	50C 50P	
As a function of the number of periods (“broken” design)	15C 385P	5
	15C 185P	10
	15C 50P	30
	15C 25P	50

Table 1 Samples deposited for the nanoindentation test on silicon (100) substrates. All the multilayers are 2 µm thick.

The samples have been characterized by nanoindentation. Figure 2 shows the results of hardness (H) and elastic modulus (E). Since the stiffness of the coating depends on “ceramic” layers and on their thicknesses, the data are presented as a function of the overall “ceramic” SiO_2 content in each coating. In the figure the values of H and E for the “polymeric” and “ceramic” thick films are shown as reference. As it can be observed increasing the SiO_2 content in the multilayers the hardness and the elastic modulus increase in both series, but the trends for the two series are different. The “broken” design series, even if the overall “ceramic” content is increased, shows lower H and E values, keeping its mechanical behaviour closer to the “polymeric” layer values. These data suggest that in fact the “broken” design is more flexible and therefore able to follow the elastic substrate deformation without cracking during bending.

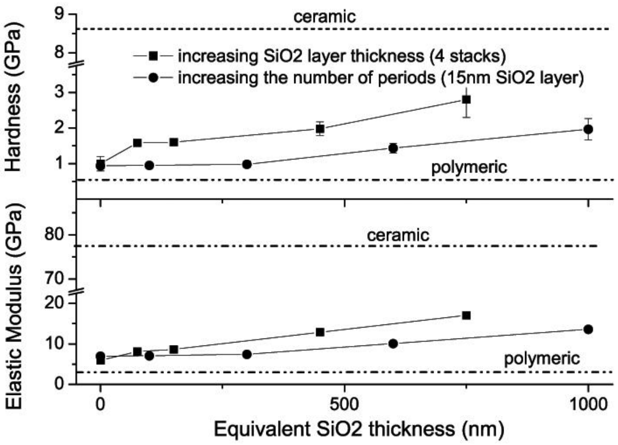

Figure 2. Nanoindentation hardness and elastic modulus measurements of the series as a function of ceramic layer thickness and as a function of the number of layers in “broken” design as a function of the overall SiO_2 “ceramic” thickness in each coating.

In order to evaluate the macroscopic behaviour, 400 nm thick multilayers have been deposited on polystyrene and bent with a radius of curvature of 5 mm. The surface was then wetted with acetone in order to visually highlight the cracks passing through the whole thickness of the coating (polystyrene is easily dissolved by acetone, causing a marked visual transition from transparent to opaque). Figure 3a,b depicts the micrographs of two samples of 4 periods multilayers with 30 nm and 15 nm thick “ceramic” layers, respectively. As it is clear from figure 3a, in the 30 nm multilayers the acetone has passed through the cracks of the coating reaching the polystyrene substrate. Few cracks can be observed in figure 3b, however in this case the acetone does not appear to have reached the substrate. Therefore in the “broken” design the cracks don’t propagate straight through the whole thickness of the coating, highlighting an effective increase of the flexibility of such design.

This ability of preventing straight propagation of the cracks can be observed also by SEM cross section imaging of the thicker samples deposited on silicon substrates. Figure 4 shows a cross section of sample 15C 50P (2 µm thickness with 30 periods). In this image, a cross section obtained by silicon fracture, the crack does not propagate for all the layers in the same position. That tortuous crack propagation in the multilayer can be an explanation also of the ability of preventing the acetone to reach the polystyrene substrate after the bending test, even if optically some cracks can be observed in the micrographs.

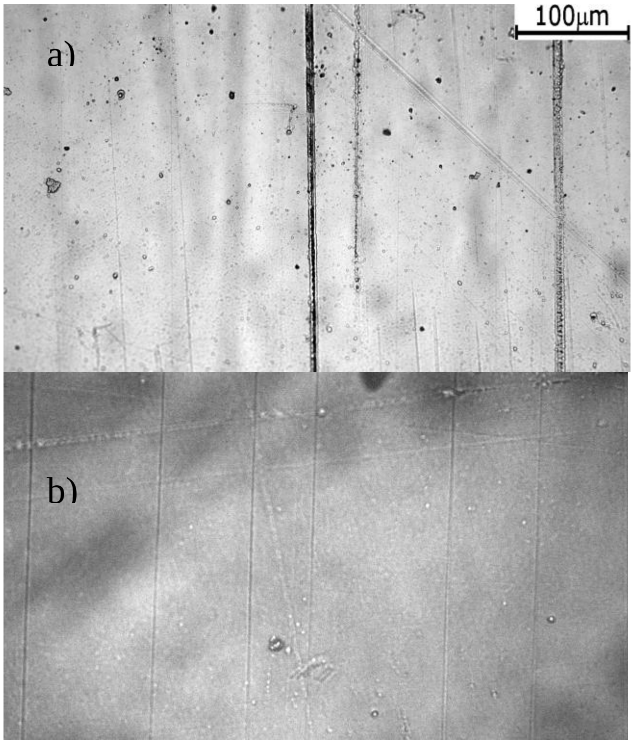

Figure 3. Micrograph of 400 nm multilayers on polystyrene after bending with a 5 mm radius of curvature and surface wetting with acetone. a) multilayer with 4 periods and 30C 70P, b) multilayer with 4 periods and 15C 85P.

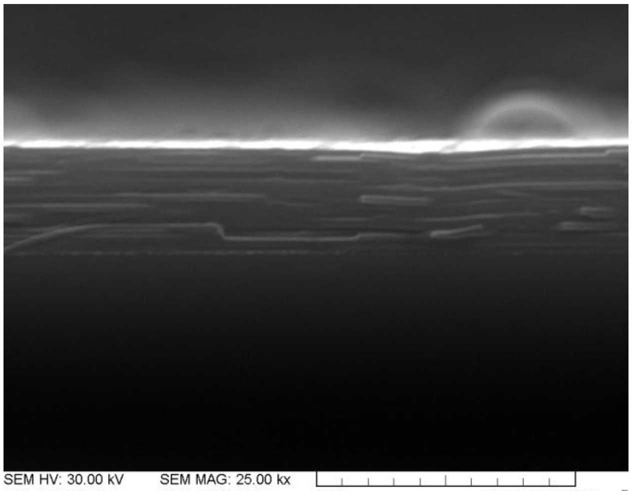

Figure 4 SEM cross section of the sample 2 µm thick 15C 50P with 30 periods obtain by silicon substrate crack propagation.

The improvement of the mechanical properties by the reduction of the "ceramic" layer thickness also leads to a decrease in barrier properties, especially if the layer thickness is below the critical threshold. In order to verify how the "broken" design influences the permeability behaviour, CO_2 transmission rate measurements have been performed on 400 nm-thickmultilayers deposited on polystyrene The results are shown in table 2 and highlight that the "broken" design has lower barrier properties for the same number of periods. However, if the number of periods is increased, performances similar to the coatings with "ceramic" layers above the critical threshold can be achieved. This result is probably due to the conductance-limited diffusion of the spacing "polymeric" layers [7].

Multilayer	Number of periods	PS CO2 TR ($cc/m^2 24h$ bar)
Polystyrene substrate		4700 ± 138
30C 70P	4	105.9 ± 5.3
15C 85P	4	434.9 ± 21.7
15C 25P	10	122.6 ± 6.2

Table 2 CO_2 trasmission rate values for multilayers coatings**.**

Conclusions

The proposed multilayer "broken" design has been characterized, showing the effective increase of flexibility by the elastic modulus reduction compared with standard design. This increase in flexibility has been macroscopically verified by bending tests. Moreover, the increase in the number of periods preserved its barrier performances. Therefore, the "broken" design can be considered a promising improvement for gas barrier coatings in food packaging.

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