A STUDY OF DEFECT NUMBERS AND DISTRIBUTIONS IN PECVD SiO_2 AND SiN TRANSPARENT BARRIER COATINGS ON PET: THEIR RELATIONSHIP WITH GAS PERMEATION

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ABSTRACT

Transparent ceramic barrier films on plastics can reduce the permeation rate of oxygen (OTR) and/or water vapor (WVTR) by several orders of magnitude. We prepare silicon dioxide (SiO_2) or nitride ("SiN") barrier layers on polyester (PET) film by plasma-enhanced chemical vapor deposition (PECVD). We have shown that OTR (and WVTR) decrease with increasing coating thickness, d, to a certain asymptotic minimum value, when $d \geq 50$ nm; the residual permeation is attributed to the presence of microscopic defects in the coating. Since the coatings are transparent and very thin, the detection of defects and the analysis of their origin are very difficult.

We have recently developed techniques based on reactive ion etching (RIE) in oxygen plasma to render visible micrometer- or sub-micrometer-sized defects in transparent barrier coatings on transparent polymers, e.g. PET. These techniques can be used to better understand the origins of defects in these coatings on a microscopic scale, as well as for mapping and counting defect density on a macroscopic scale (tens of cm^2 or more).

In this article we present a correlation between measured O_2 transmission rate (OTR) values and the number density and size distribution of defects in SiO_2 and SiN barrier coatings. The coatings, with thicknesses, d, in the range $8 \leq d \leq 200$ nm, were deposited by dual-frequency (MW/RF) plasma. Excellent agreement between measured and calculated OTR values allows us to confirm that residual OTR is, indeed, controlled by pinhole defects; furthermore, there is excellent qualitative overlap of the OTR and defect density plots over the entire range of d values, for both SiO_2 and SiN. Our results also compare well with published data for aluminized PET.

1. INTRODUCTION

Transparent barriers against oxygen and/or water vapor permeation, deposited by plasma-enhanced chemical vapor deposition (PECVD), are the object of increasing interest in the packaging, pharmaceutical, optical, and electronics industries. Such barriers can decrease permeation through flexible films of commercial or optical grade polymer substrates, or through rigid walls of plastic containers by several orders of magnitude. The advantages of

dielectric barrier films over their metallic (e.g. Al, see below) counterparts is that they are "microweavable", and can be recycled.

Typically, coatings obtained by PECVD, such as silicon dioxide (SiO_2) or nitride (Si_3N_4, hereafter SiN), provide an excellent barrier even when they are extremely thin. We have shown [1] that O_2 and H_2O permeation decreases as much as thousand-fold with increasing coating thickness, d, to a certain asymptotic minimum value, when the thickness exceeds $d \approx 15$ nm for SiO_2 and $d \approx 8$ nm for SiN. The residual permeation is attributed to the presence of microscopic defects in the coating [1,2], which may result from dust particles on the substrate surface, from geometric shadowing and stress during film growth at sites of high surface roughness, or from other causes. So-called antiblock particles, which are incorporated into commercial polymer films to prevent adhesion between adjacent layers on a roll, constitute an important example of localized microroughness.

The detection of micrometer- or sub-micrometer defects in an opaque coating, for example in the case of aluminized polyester (PET), can quite readily be done by optical microscopy using transmitted light [3]. However, the detection of defects in an ultra-thin transparent layer on a transparent substrate evidently presents a sizable challenge. In this article, we first briefly describe techniques we have developed to render visible such defects in transparent films, and to characterize them; important aspects of this include reactive ion etching in oxygen plasma, followed by optical and/or electron microscopies. We then correlate the observed defect statistics (size, number density) with OTR data, both experimental and theoretical. We also compare our results for transparent SiO_2 and SiN barriers with those for aluminized PET.

2. EXPERIMENTAL METHODOLOGY

PECVD coating is carried out in a pilot-scale reactor for plasma processing continuously-moving, flexible web materials up to 30 cm in width; a schematic top view is shown in Fig. 1. This reactor, which has been described in detail elsewhere [1], can function in three distinct modes of operation, namely microwave-excited plasma (MW, 2.45 GHz), capacitively-coupled radiofrequency plasma (RF, 13.56 MHz), and dual-frequency excitation (MW/RF), comprising simultaneous use of MW and RF power; in the work reported here, only the latter (MW/RF) mode was used. The substrate is a 13 μm bi-axially oriented commercial PET film (ICI 800).

To visualize micro-defects in coated PET films with the help of optical microscopy, we have developed a technique based on reactive ion etching (RIE) in low-pressure oxygen plasma, which has been described in detail elsewhere [4,5], and will therefore not be repeated here. Suffice it to say that the so-called undercutting effect, due to etching by atomic oxygen (AO) in the O_2 plasma, greatly magnifies the apparent radius of a defect site. By measuring its radial evolution with exposure time to AO, t, and extrapolating back to $t = 0$, the original defect radius, R_0, can be determined. Also, appropriate image-analysis software allows us to determine the defect density, n (number of defects per mm^2 of coated polymer film).

3. RESULTS AND DISCUSSION

Figure 2 shows a plot of oxygen permeation rate (OTR) [1] and of the defect density, n, versus the coating thickness, d, for the case of SiO_2 films deposited by dual-frequency MW/RF plasma. For comparison, the OTR value for the uncoated PET is also indicated on the ordinate axis. Oxygen permeation is seen to change little with increasing coating

thickness, until it reaches a certain "critical" value, d_c, where the OTR value drops by about two orders of magnitude. For $d > d_c$, OTR continues to decrease, but at a lesser rate. In a manner similar to the OTR behavior, the defect density n is also seen to change little when $d < d_c$, but for $d > d_c$, n first decreases sharply with increasing coating thickness, but then it reaches a certain minimum value (approximately 80 defects/mm^2) for $d \geq 50$ nm. It is noteworthy that OTR also appears to have reached its lower asymptotic limit for $d \geq 50$ nm.

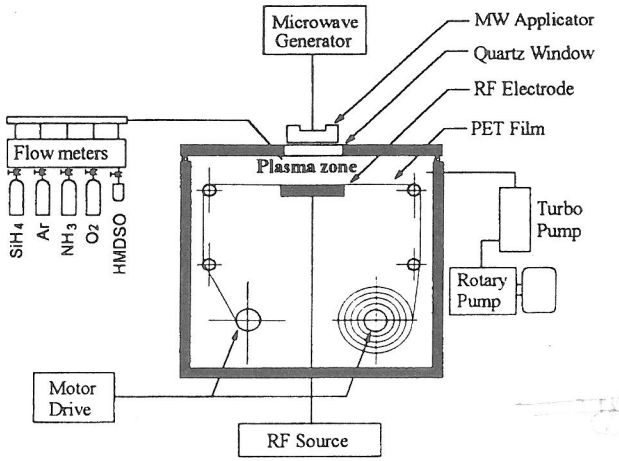

Figure 1. Schematic view of the single-and dual-frequency pilot-scale reactor used to deposit SiO_2 and SiN films.

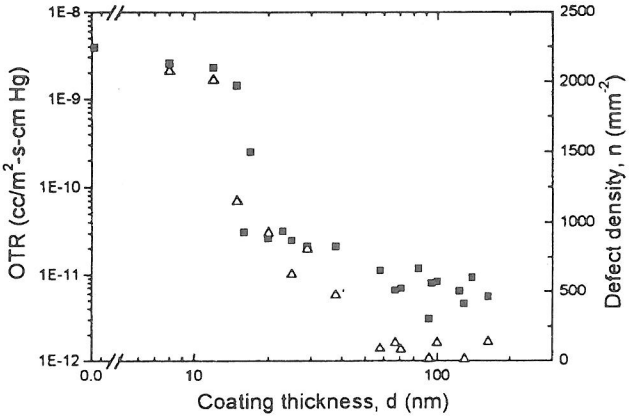

Figure 2. Defect density, n (Δ), and oxygen permeation rate (OTR) (■) versus plasma-deposited SiO_2 coating thickness, d, on 13 μm PET.

Figure 3 shows a similar plot of OTR and n versus d, but this time for the case of SiN films. As for SiO_2, OTR decreases with increasing SiN coating thickness, but the d_c value is significantly lower (8 nm for SiN, compared with 15 nm for SiO_2). The minimum OTR values for thicker films ($d \geq 100$ nm) are very similar for both SiO_2 and SiN films. As for the case of SiO_2, the defect density, n, decreases sharply near $d \approx d_c$, continues decreasing at a lesser rate for $d > d_c$, until it finally reaches a minimum value of about 70 defects/mm^2 for $d \geq 50$ nm. We also note that the density of defects for coatings with thicknesses varying between d_c and $d \approx 50$ nm is lower for SiN than for its SiO_2 counterpart, in accord with the excellent barrier properties observed for SiN coatings with thicknesses beyond about 8 nm.

It should be noted here that the lower limit for reliable OTR measurements of our (MOCON) instrument is about 3×10^{-12} cc/m^2-s-cmHg (or 0.2 cc/m^2-day, in units more familiar to most readers). Collaboration with another laboratory which possesses a more sensitive instrument, and using the smoothest ("optical") grade PET substrate material, has shown our "best" SiO_2 and SiN barrier coatings (with $d \geq 100$ nm) to display OTR values as low as 0.005 cc/m^2-day, SiN being particularly favorable. In other words, the true asymptotic lower limit of OTR for $d > 100$ nm in Figs. 2 and 3 is, in fact, at least an order of magnitude below the lowest values shown on these figures.

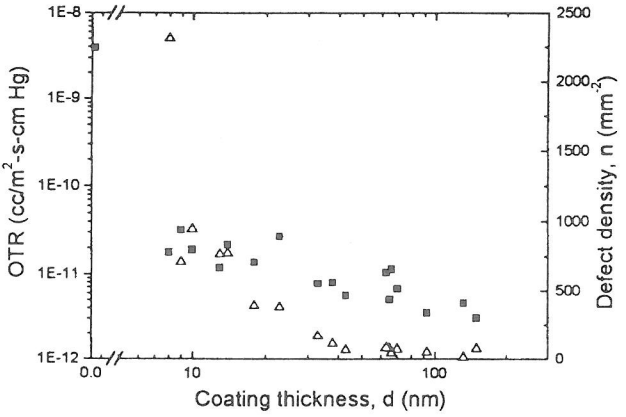

Figure 3. Defect density, n (Δ), and oxygen permeation rate (OTR) (■) versus plasma-deposited SiN coating thickness, d, on 13 μm PET.

To further confirm the apparent correlation between OTR and defect density, n, we show these two quantities for SiO_2 and SiN plotted against one another in Fig. 4. For comparison, we also show the data of Jamieson and Windle [3] for the case of 15 to 45 nm thin evaporated Al layers on 12 μm PET. For coatings having $d > d_c$, SiO_2 and SiN data display very similar behavior, namely a power law relationship which differs from that of the evaporated Al films, although there is a significant, not unexpected scatter among the data. These results confirm that, first and foremost, OTR is dictated by the size and number density of defects in the barrier coating, roughly independent of the SiO_2 or SiN coating material, but quite distinct from evaporated Al. We should note here that the very lowest OTR values,

especially for SiN films with the lowest n values, are data provided by a collaborating laboratory with a more sensitive instrument than our's (see above).

As already pointed out, the power law relationships between OTR and n are quite different, comparing the data for Al and SiO_2/SiN barrier materials in Fig. 4, but the two data sets appear to merge for high n values. These differences in behavior are likely due to the nanocrystalline nature of the Al films, in contrast with the amorphous, essentially featureless SiO_2 and SiN deposits: for the case of Al, the presence of grain boundaries facilitates mass transport, which explains their higher OTR values for any given n, as seen in Fig. 4. On the other hand, one can estimate the OTR value of "perfect" SiO_2 barriers, on the basis of the well-known model of Deal and Grove [6] for thermal oxidation of crystalline Si, which assumes diffusive transport of oxygen through an existing thin layer of thermal oxide: Taking d = 100 nm, and evaluating the thermally-activated (E_a = 27 kcal/mole) diffusion coefficient at 300 K, we calculate an OTR value of about 10^{-26} cc/m^2-day; in other words, oxygen transport through a flawless SiO_2 layer at ambient temperature is completely negligible. Therefore, the measurable OTR value (~0.06 cc/m^2-day, see Fig. 4) for the "best" films with d $\gtrsim$ 100 nm must be due to defects.

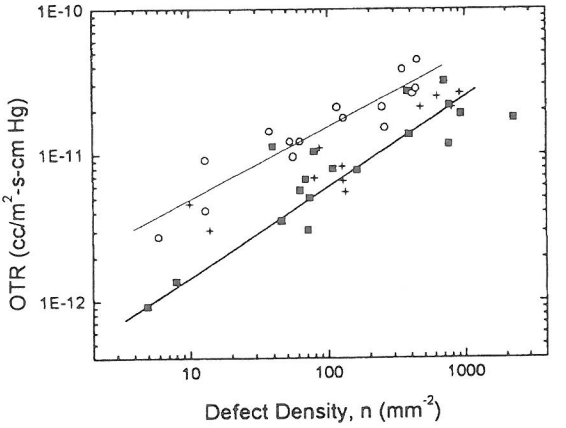

Figure 4. Oxygen permeation rate (OTR) versus defect density for deposits with with $d > d_c$ (see text): (■) SiN/PET, (+) SiO_2/PET, present work; (O) Al/PET, from ref. [3].

This latter statement can be tested quantitatively, as follows: the mean radius $\langle R_0 \rangle$ of defects in a 70 nm thick SiO_2 film is 0.6 μm, and their number density is about 80 mm^{-2} [4,5]. Rossi and Nulman [7] published a theoretical model, in which the permeation through a circular hole in an otherwise "perfect" barrier coating is calculated by numerically solving Laplace's equation in cylindrical coordinates, using the appropriate boundary conditions. Assuming that the present 80 defects/mm^2 are spaced apart and non-interacting, we calculate OTR = 0.6 cc/m^2-day [1], which compares well with the measured value for this 70 nm barrier (0.4 cc/m^2-day, see Fig. 2). Repeating this calculation for the lowest defect counts (n ≈ 5 mm^{-2}) yields an OTR value of 0.04 cc/m^2-day, in fair agreement with the data shown in Fig. 4. All the results presented above strongly support the view that "residual" permeation

through SiO_2 and SiN films can be attributed to the cumulative effect of isolated pinhole defects in the barrier coatings. As mentioned earlier, the main sources of defects in PECVD coatings (dust, surface roughness, etc), and their microscopic and "macroscopic" (tens of cm^2 sample area) observation by optical and electron microscopies, are reported in references [4,5,8]. The lowest possible permeation values can be achieved by working in a clean (dust-free) environment, and by using high-quality (smooth) substrates.

CONCLUSIONS

Ultra-thin transparent coatings on polymers are increasingly being used as permeation barriers [1,2,9], and for various other functional uses such as protective coatings on spacecraft materials [10]. We have reported methods by which point defects ("pinholes") and extended defects (cracks or scratches) of μm or sub-μm dimensions can be rendered observable and characterized. A comparison of measured and calculated OTR values, the latter based on observed defect sizes and concentrations, show that the developed methodology is reliable, and that "residual" permeation can be attributed to these defects.

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