PECVD of SiOx Barrier Films

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ABSTRACT

Plasma-enhanced chemical vapor deposition (PECVD) processes have been utilized for the production of SiO_x -based ceramic barrier flexible materials. The aim of this study was to further investigate the deposition parameters and their effect on the coated material barrier properties. Results obtained from industrial scale and small laboratory scale roll-to-roll coaters will be discussed.

INTRODUCTION

The requirement for environmentally friendly clear barrier flexible materials for packaging applications continues. In addition interest in high barrier coatings for technical applications, such as flexible displays grows. For all applications the ever-increasing demand for higher and improved retention of barrier performance on a variety of substrates remains.

Many papers have been presented in recent years evaluating the limiting factors for ceramic thin film barrier coatings; many of these have been presented in the last few years at the SVC technical conference [1,2,3,4]. Various vacuum techniques for the deposition of the barrier coatings have been utilized. These include sputtering, evaporation and plasma-enhanced chemical vapor deposition and combinations of these techniques together with all types of plasma activation to improve performance. Many thin film coating materials have been considered. Some of these are $SiO_{x,}$ $SiO_{2,}$ Al_2O_3, ITO and TiO_2, together with their nitrides and oxynitrides. These have been applied to many substrates, with PET as the most widely studied substrate material [5,6,7].

Many workers have considered the mechanisms for the vapor permeation through the barrier coatings. Permeation through defects both gross- and nano-defect types and diffusion through the coatings are potential mechanisms. Possibilities of differing mechanisms for different gaseous species are likely, particularly for polar and non-polar molecules. The surface attachment of polar-molecules, like water molecules, possibly enhances the diffusion permeation route for these gas species [8,9].

PECVD SiOx coatings show a wide range of barrier performance. In this paper some of the process parameters and their effects on the barrier properties will be presented. Particularly the similarities and contrasts of oxygen and water permeation variation with process parameter changes will be discussed. These differences are discussed as a possible indication of the different permeation mechanisms for these molecules.

PECVD PROCESS

The PECVD process used in all the coatings discussed here has been presented previously [10,11,12,13]. A brief description of this process will be given, highlighting some of the more recent developments and some general properties of the coated materials produced.

The PECVD process here used HexaMethyl-DiSilOxane (HMDSO) as the precursor and reacted with oxygen and helium process gases to form the SiOx coating. The plasma was generated by capacitively coupling medium frequency, MF (e.g. 40 kHz) power between a drum electrode and a counter electrode. The polymer web (e.g. PET) ran on the drum, while it was coated by the adjacent magnetically enhanced plasma. A schematic of the process arrangement is shown in Figure1.

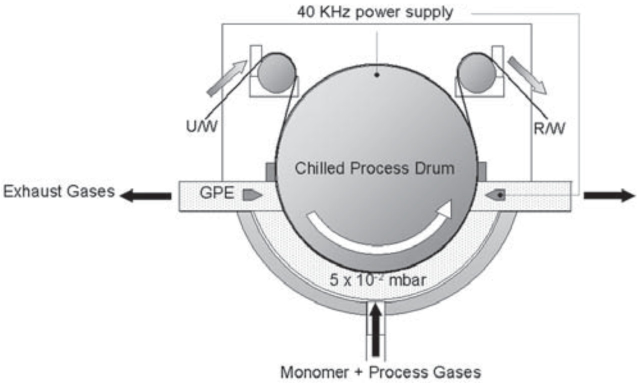

Figure 1: PECVD process arrangement.

The coatings were produced on industrial scale coaters of 1.5 m and 2.1 m widths and also on a small laboratory roll-to roll coater with a web coating width of 150 mm. The laboratory coater is shown in Figure 2 and consists of three connected chambers: unwind and pre-treatment chamber, process chamber and post-treatment and rewind chamber.

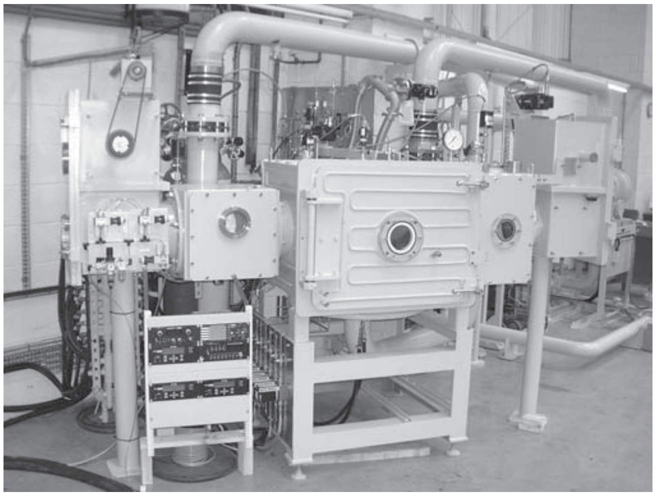

Figure 2.: Laboratory PECVD roll-to-roll coater.

The laboratory process chamber is shown in Figure 3. The photograph shows the coating drum and associated process gas injection, magnetic enhancement assembly and counter electrode system.

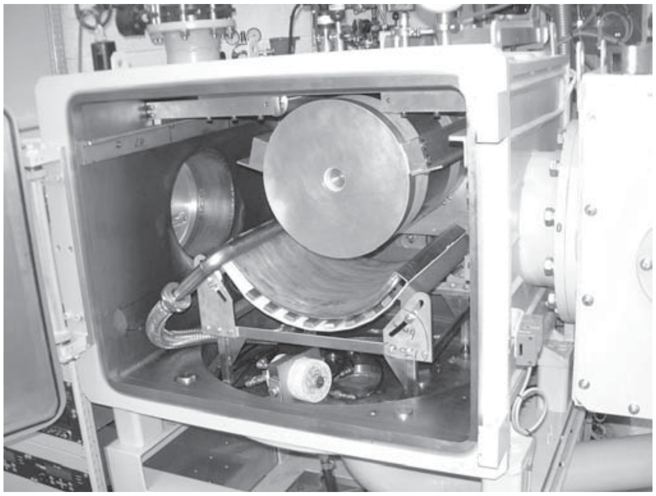

Figure 3: Laboratory PECVD roll-to-roll process chamber.

The original arrangement for this type of PECVD process utilized the gas confining magnet array as the grounded counter electrode. However, this gradually coated up with SiO_x, eventually causing instabilities of the plasma and arcing. This limited the length of roll which could be coated and the consistency of the barrier produced. To overcome these problems a non-contaminating active plasma counter electrode system (gas purged electrode, GPE) was developed. For the small laboratory coater one GPE was used, while for the industrial scale coaters four GPEs were used. A schematic arrangement for the electrode system used in the industrial coaters is shown in Figure 4.

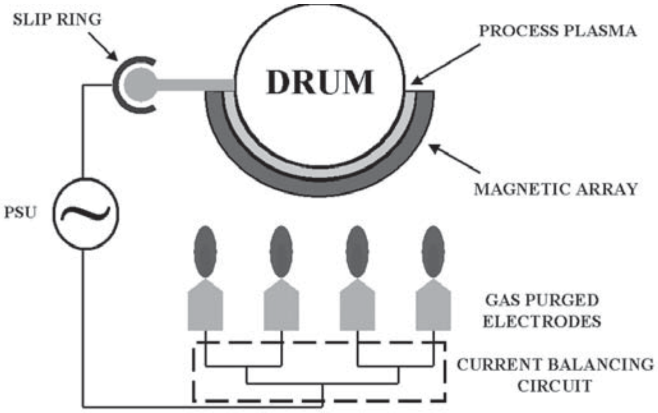

Figure 4: Schematic of the industrial scale counter electrode system.

The counter electrode system prevents coating and increasing impedance to the process. In addition the system activates the process by injection of charged species into the process lowering the impedance, increasing current and reducing voltage under constant power operation. The effects of this counter electrode on a typical process for a 2 m wide process zone are shown in Table 1.

Table 1: Comparison of processes with conventional and plasma generated counter electrode.

Counter Electrode	Conventional	Plasma
Monomer HMDSO	1.1 slm	1.1 slm
Oxygen	4 slm	4 slm
Helium	2 slm	2 slm
Pressure	$6x10^{-2}$ mbar	$6x10^{-2}$ mbar
Power	14 kW	14 kW
Voltage	610 V	430 V
Current	24 A	34 A
Counter Electrode current density	15 A/cm^2	~10^6-10^7 A/cm^2
Impedance	25-26 ohms	12-13 ohms

The capacitively coupled plasma current is driven through the web; the web covering the drum electrode has low impedance at the operating medium frequency. This current together with other bombarding species from the plasma impart some benefits to the growing thin film coating. The web surface is highly plasma activated; the coating has enhanced bombardment by charged species leading to increased activated chemical reaction and densification of the growing film. The above are believed, in part, to explain the production of a good barrier with relatively thin coatings and for the robustness of the coating to stretch and deform (Figures 5 and 6).

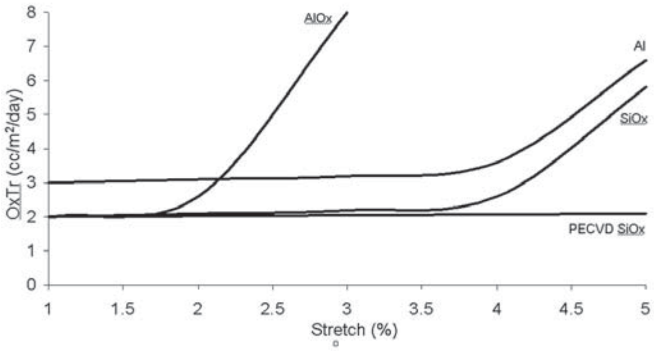

Figure 5: Effect of stretch on the oxygen permeation for coated 12 micron PET coated by different techniques. The Al, AlO_x and SiO_x coatings are by PVD techniques.

The thickness of the PECVD coatings was estimated from XRF measurements of the silicon content of the coatings. The effective thicknesses given are for coatings of equivalent silicon content and density to bulk SiO_2.

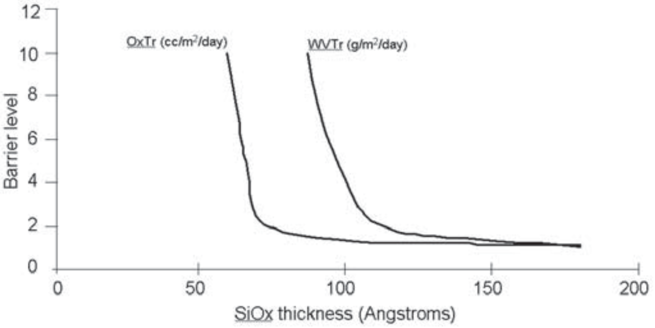

Figure 6: Barrier permeation as function of thickness for PECVD coatings. The samples were produced by a process for "good" oxygen and water barrier performance (see later).

RESULTS AND DISCUSSION

In the following discussion all results relate to permeation on 12 micron PET substrates. In general, a "good" barrier for oxygen permeation equates to <3 cc/m^2/day and a "good" barrier for water vapor relates to <3 g/m^2/day. Permeation measurements were conducted on Mocon permeation apparatus, oxygen permeation at 27C, 90% RH and water vapor permeation at 38C, 100% RH.

Large effects on the barrier properties of the coatings can be achieved by varying the process parameters. It is possible to achieve a "good" oxygen barrier (<3 cc/m^2/day) while achieving no water barrier enhancement (i.e. water permeation the same as the substrate). A good water barrier (<3 g/m^2/day) can be achieved but never without at least some reasonable (~5 cc/m^2/day) oxygen barrier performance. The effects of the process parameters on the barrier performance are summarized in Table 2.

Table 2: Process effects on barrier.

	Oxygen Barrier	Water Barrier
Process Power	Low-High	High
Process Pressure	Low-High	Low
Process O_2 Conc.	Medium-High	Low
Organic content	Low-high	High
Web creasing	Detrimental	Marginal
Critical thickness	7 nm	11-12 nm
Increased thickness	Little effect	Improved
Magnetic field	Marginal	High

Process power. For good oxygen barrier performance a wide range of process powers can be used; however, for good water vapor barrier performance higher powers must be used.

Process pressure. For good oxygen barrier performance a wide range of process pressures can be used; however, lower process pressures are necessary for good water vapor barrier performance.

Process oxygen concentration and organic (carbon) content. Good oxygen barrier performance can be achieved over a wide range of process oxygen concentrations apart from the lowest range where some loss is observed. No water barrier performance is observed at the higher process oxygen concentrations. Samples have been investigated for carbon content by XPS techniques. These show reducing carbon content with higher process oxygen concentrations.

Web creasing. This is detrimental to both barriers. However, there is a greater effect on the oxygen barrier performance.

Critical thickness. Oxygen barrier performance is achieved at thinner critical thicknesses (~7 nm) than for water vapor barrier performance (<11 nm).

Increased thickness. Increased thickness has little improvement on oxygen barrier performance above the critical thickness, thick films can reduce barrier performance due to onset of cracking. Water barrier performance improves with increasing thickness; thick coatings always give better barrier performance than thinner coatings for a given process.

Magnetic field. Reduced magnetic fields influence the oxygen barrier performance only marginally, while water vapor barrier performance is greatly affected.

From the above observations a reasonably consistent model for these types of PECVD coatings can be drawn. Oxygen barrier performance is less affected than water vapor performance by the process variables. Oxygen barrier loss is due to gross-defect generating operations (web creasing or particulate generation in the process). Only processes with low process oxygen concentrations reduce oxygen barrier performance.

Water vapor barrier performance is affected significantly by the process parameters. Low pressure, high power and high magnetic fields are required. This implies high plasma (particle bombardment) and higher chemical activity are required. This possibly indicates that the coating could be denser with higher chemical cross-linking. Higher inclusion of organics (carbon) for good water vapor barrier performance indicates a high chemical effect with water molecules. Improved barrier performance with thickness implies reduction in diffusion mechanisms through the bulk, along grain boundaries or nano-defects.

The grain structure of samples with a wide variation of barrier performances was carried out with an AFM. The samples showed little variation on the grain structure of the coatings. All samples showed similar grain sizes of around 50-70 nm. A typical AFM image is shown in Figure 7.

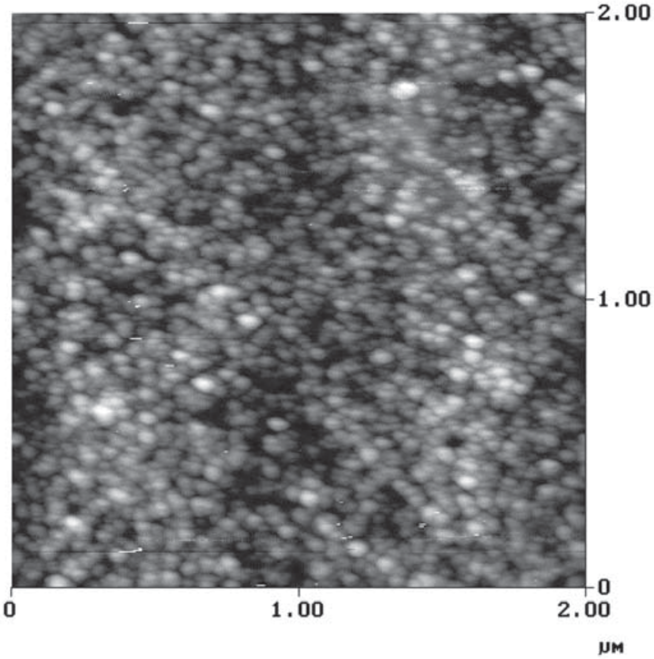

Figure 7: AFM image of PECVD coated PET with good oxygen (2 cc/m^2/day) and water (2 g/m^2/day) barrier performance.

CONCLUSION

The process parameter variations and their effects on the oxygen and water vapor permeation has given some insight into the mechanisms responsible for their permeation through these PECVD deposited SiO_x coatings. It is clearly shown in these samples that the mechanisms for oxygen and water vapor permeation are quite different.

Oxygen permeation appears consistent with a defect-dominated mechanism, while water permeation appears to be more related to diffusion through the bulk coating or via diffusion along grain boundaries and/or nano-defects. Indications for the chemical activity of the coating controlling the water permeation are also observed, with higher organic (carbon) content coatings giving improved water barriers.

REFERENCES

1. U. Moosheimer and H.-C. Langowski, "Permeation of Oxygen and Moisture Through Vacuum Web Coated Films," *42nd Annual Technical Conference Proceedings of the Society of Vacuum Coaters*, p. 408, 1999.

2. B.M. Henry et al., "Microstructural and Gas Barrier Properties of Transparent Aluminium Oxide and Indium Tin Oxide Films," *43rd Annual Technical Conference Proceedings of the Society of Vacuum Coaters*, p. 373, 2000.

3. G. Czeremuszkin et al., "Permeation Through Defects in Transparent barrier Coated Plastic Films," *43rd Annual Technical Conference Proceedings of the Society of Vacuum Coaters*, p. 408, 2000.

4. A.G. Erlat et al., "Growth and Characterisation of Transparent Metal Oxides and Oxynitride Gas Barrier Films on Polymer substrates," *44th Annual Technical Conference Proceedings of the Society of Vacuum Coaters*, p. 448, 2001.

5. D. Chahroudi, "Glassy Barriers from Electron Electron Beam Web Coaters," *32nd Annual Technical Conference Proceedings of the Society of Vacuum Coaters*, p. 29, 1989.

6. M. Isu et al., "High Performance Clear Coat Barrier Film," *36th Annual Technical Conference Proceedings of the Society of Vacuum Coaters*, p. 333, 1993.

7. R.S.A. Kelly, "Development of Aluminum Oxide Clear Barrier Films," *37th Annual Technical Conference Proceedings of the Society of Vacuum Coaters*, p. 144, 1994.

8. G. Garcia-Ayuso et al., “Relationship between the microstructure and the water permeability of transparent gas barrier coatings,” *Surface and Coatings Technology,* 100-101, 459, 1998.

9. B.M. Henry et al., “The Permeation of Water Vapor Through Gas Barrier Films,” *44th Annual Technical Conference Proceedings of the Society of Vacuum Coaters*, p. 469, 2001.

10. J. Felts, “Thickness Effects on Thin Film Gas Barriers: Silicon Based Coatings,” *34th Annual Technical Conference Proceedings of the Society of Vacuum Coaters*, p. 99, 1991.

11. J. Felts, “Transparent Barrier Coatings Update: Flexible Substrates,” *36th Annual Technical Conference Proceedings of the Society of Vacuum Coaters*, p. 324, 1993.

12. H. Chatham et al., “Process Capabilities of Wide-Web PECVD Coaters,” *39th Annual Technical Conference Proceedings of the Society of Vacuum Coaters*, p. 331, 1996.

13. F. Casey et al., “Clear Barrier Coatings,” *42nd Annual Technical Conference Proceedings of the Society of Vacuum Coaters*, p. 415, 1999.