Effects of Process Parameters on PECVD Silicon Oxide and Aluminum Oxide Barrier Films

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Keywords: PECVD Permeation barrier films Oxide films

ABSTRACT

Silicon oxide based barrier films from organosilicon precursors have been deposited on PET film in a lab-scale coater using plasma-enhanced chemical vapor deposition (PECVD). Exploratory work on aluminum oxide films from a trimethylaluminum (TMA) precursor, as well as mixed silica alumina films is also reported. Deposition experiments were performed in a cylindrical coater containing a central axial RF electrode with gas flow in the axial direction. Coatings were deposited on 2 mil PET films in contact with the central electrode. The primary objective was to map out, using designed experiments, the behavior of SiO$_x$ - based film properties over a range of process parameter settings. Factors studied were RF power, precursor concentration, gas velocity and gas pressure. Oxygen permeation rates of coated PET films were measured in a Mocon analyzer. Film deposition rate and index, compositional characteristics as measured by FTIR analysis, and thickness uniformity along the electrode axis, will also be described. Film permeability and deposition rate varied by more than an order of magnitude over the range of process variables tested. The TMA precursor was found to be more reactive than an organosilicon precursor such as HMDSO, and had a greater tendency for non uniform film deposition.

INTRODUCTION

Transparent oxide barrier films for reducing gas and water vapor permeation through plastic packaging materials are of commercial interest for various food and beverage applications. Numerous papers have described physical vapor deposition (PVD) and plasma-enhanced chemical vapor deposition (PECVD) processes for low temperature deposition of oxide barrier films, primarily on plastic web [1-4]. However, few systematic studies of low temperature PECVD process behavior have been published. This paper presents an experimental study of plasma-enhanced deposition of SiO$_x$ thin films from hexamethyldisiloxane (HMDSO) precursor. The framework for this study is a four-factor statistically designed experiment of the central composite type. Some exploratory work on AlO$_x$ deposition from trimethylaluminum (TMA) precursors is also reported. The experiments were performed in a lab scale reactor having a simple cylindrical tube geometry to allow control of gas flow and plasma distribution. The main purpose of this work was to determine how local process conditions affect film growth characteristics and oxygen barrier effectiveness. A related paper in this conference [5] describes some mechanical properties of SiO$_x$ films produced by the same process.

EXPERIMENTAL

Coater and Process Description The cylindrical PECVD tube coater is shown schematically in Fig. 1. It consists of a 6.25 in (16 cm) ID by 18 in (46 cm) long, thick-walled glass tube surrounding a central RF electrode assembly. The glass tube serves as the vacuum chamber. It is capped by a stainless steel flange containing the O$_2$ and precursor vapor injectors. The electrode is a 2.5 in (6.4 cm) OD by 5.5 in (14 cm) polished aluminum cylinder capped by Delrin insulator disks to constrain the...
discharge to the cylindrical surface. The plastic film to be coated is wrapped snugly around the electrode. A polycarbonate spacer tube positioned above the electrode provides an annulus of nearly constant cross section (~167 cm²) along the length of the chamber. Reactant gases injected at the top mix as they flow through the chamber and are pumped through an annular port surrounding the electrode base.

RF power from an ENI Plasmaloc 2HF power supply, at a frequency of 250 KHz, is applied to the electrode via an Astech Model ATK-100 RF matching network. RF power is monitored using a Bird Model 4411 RF wattmeter. Reactant gas flow rates and chamber pressure are controlled by an MKS feedback control system. HMDSO vapor flow is controlled by an MKS Model 1150C vapor mass flow controller. TMA vapor flow rate is controlled by a needle valve. Flow rate was estimated to ± 20% from pressure rate-of-rise measurements, compared with known HMDSO flow rate vs. rate-of-rise curves.

For all work reported here, the substrate film was 2 mil (51 µm) thick Dupont Mylar PET type A (untreated, biaxially oriented). Barrier film deposition was at approximately room temperature, as the solid aluminum electrode acted as a heat sink for the PET film. Small silicon witness samples (~1.5 cm x 1 cm), cut from double side polished <100> Si wafers, were attached to the PET substrate at various positions on the electrode. These were used for SiOₓ film property measurements.

**Design of Experiment**

Response surface methodology [6] employing a four-factor central composite experimental design was used to characterize the SiOₓ deposition process. This design consists of 31 runs: a full factorial (runs 1-16) with star points (runs 17-24) and repeated centerpoint (runs 25-31) as listed in Table I. Process factors (variables) tested were precursor concentration (1E-10 moles/cc), average gas velocity or "plug" velocity (cm/sec), pressure (mTorr), and RF power density (W/cm²). Average gas velocity is the volumetric gas flow rate divided by cross sectional area.
Precursor concentration was calculated from the ideal gas law. The area of exposed electrode was ~ 205 cm², so a power density of 0.5 W/cm² required ~ 103 W of load power. All of the factor settings, as well as actual O₂ and HMDSO gas flow rates for each run, are listed in Table I. These settings span most of the practical operating range of the reactor system. For each response measured, the data were analyzed and fit to a second degree polynomial using the statistical visualization software package JMP [7].

Thin Film Characterization Film thickness and index of refraction were measured using an automated Gaertner Model L116A ellipsometer, while chemical characteristics were obtained by FTIR (Fourier transform infrared) transmission spectroscopy using a Bomem Model MB155 spectrometer. Because of experimental difficulties in measuring characteristics of thin films on PET substrates, the ellipsometry and FTIR measurements were performed on films deposited on the Si witness samples mentioned earlier.

O₂ Permeation Measurements Oxygen permeation transmission rates (O₂TR) of barrier coated 2 mil PET film samples were measured using MOCON (Modern Controls, Inc.) instruments. Most measurements were performed on a MOCON OXtran Basic (50 cm² test area) at 23°C, under wet O₂ conditions. PET films intended for O₂ permeation test had one witness sample attached (at 7 cm level, out of the test region) to confirm SiOₓ film thickness.

RESULTS AND DISCUSSION

SiOₓ Film Compositional Characteristics The Fourier transform infrared (FTIR) spectrum over the range 4000 cm⁻¹ to 400 cm⁻¹ was obtained and analyzed for SiOₓ films from each run of the central composite experiment (on Si witness samples from the 3 cm and 7 cm positions). All of the films shared basic spectral characteristics, the most prominent being the large Si-O-Si stretch peak that lies at 1075 cm⁻¹ for thermal SiO₂. The Si-O-Si stretch peak for these films ranged from 1062 to 1040 cm⁻¹, as listed in Table I. Also evident were: a broad OH peak at 3650 ~ 3350 cm⁻¹; a small, broad C=O peak at 1730 ~ 1690 cm⁻¹; and in some cases, a small Si-CH₃ at 1275 ~ 1260 cm⁻¹ from residual precursor. FTIR characteristics of similar SiOₓ films have been previously described in detail by Theil, et al [8]. The normalized areas (peak area/film thickness) for each of the above four peaks were treated as responses and were fit to second degree polynomial models using the JMP [7] software. Both the Si-O-Si and Si-CH₃ normalized areas could be fit well. The Si-O-Si wavenumber also fit well, i.e., it responded in an orderly manner to changes in the process settings. The JMP model fit showed that HMDSO concentration and process pressure strongly affected the peak wavenumber, although in opposing directions. Gas velocity and pressure density effects were relatively weak. Correlation of FTIR features with O₂ permeation rates will be discussed in future paper.

Refractive Index The average index of refraction (averaged from the 3, 7, and 11 cm witness sample positions) for each run is also listed in Table I. Index ranged from 1.436 (Run 1) to 1.498 (Run 21), compared with 1.467 for thermal SiO₂. Statistical analysis showed a moderate positive effect of HMDSO concentration on index, and a moderate negative effect of pressure.

SiOₓ Film Deposition Rate and Uniformity The average SiOₓ deposition rate (Rav) for each run condition is listed in Table I. Rav was obtained from film thickness measurements at the 3, 7, and 11 cm positions on the electrode. A uniformity factor defined as Rav/Rmax, where Rmax is the maximum deposition rate is listed in the next column. Rav varies by an order of magnitude, from 328 Å/min for the low-HMDSO starpoint of Run #17, to 3,938 Å/min for Run #16. Rav for the seven centerpoint runs is 2,537 Å/min ± 83.4 Å/min.

Axial SiOₓ film deposition-rate profiles for the centerpoint deposition condition (A) and for a lower gas-velocity condition (B) are plotted in Fig. 2. The top (upstream) end of the electrode lies at the 0 cm position. For both cases, deposition rate rises rapidly as the reactant gases encounter the plasma zone. For (A), the profile is quite symmetric, with a peak rate of nearly 3,000 Å/min. The decline in deposition rate beyond midplane is attributed to both a decrease in the plasma density and to
HMDSO depletion in the reactant gas mixture as the gases flow downstream. For the lower gas-velocity case (B), $R_{\text{max}}$ is much lower than for (A), and it occurs farther upstream.

The contour plot presented in Figs. 3a shows how the average SiO$_x$ deposition-rate responds to changes in HMDSO concentration and power density, at a pressure of 250 mTorr and gas velocity of 150 cm/sec. This plot was calculated from the second degree polynomial fit generated by the JMP [7] software. This behavior is typical of other pressure and velocity settings also. Generally, at a fixed power density, $R_{\text{av}}$ increases almost linearly with HMDSO concentration. At fixed HMDSO concentration, $R_{\text{av}}$ first increases then reaches a maximum and falls off with increasing power. The model predicts that $R_{\text{av}}$ continues to rise with both increasing power density and HMDSO concentration. Fig. 3b shows an example of the effect of pressure and average gas velocity on $R_{\text{av}}$, in this case at 0.5 W/cm$^2$ and 3.0 E-10 moles/cc HMDSO. $R_{\text{av}}$ reaches a maximum at ~ 350 mTorr and 240 cm/sec gas velocity. Again, this behavior is typical of that seen over most of the factor settings examined here.

Examples of the effects of deposition parameters on SiO$_x$

![Contour plots](image)

Fig. 3. Contour plots of the average SiO$_x$ deposition rate (Å/min), as a function of A: HMDSO concentration and RF power density at 250 mTorr and gas velocity of 150 cm/sec. B: gas velocity and pressure, at power density of 0.5 W/cm$^2$ and HMDSO concentration of 3.0E-10 moles/cc. Both plots are typical of the deposition rate behavior over most of the experimental range studied. They were generated from a second degree polynomial fit to the data. $R^2 = 0.967$ for this fit.

![Contour plots](image)

Fig. 4. Contour plots of the SiO$_x$ film thickness uniformity factor as a function of HMDSO concentration and RF power density, at two conditions of pressure and gas velocity: A) 150 mTorr, 200 cm/sec; B) 350 mTorr, 100 cm/sec; C) 0.5 W/cm$^2$, 1.2E-10 moles/cc. $R^2 = 0.915$ for this model fit.
film axial uniformity are given in three contour plots in Fig. 4. The response plotted here is the uniformity factor, \( R_{av}/R_{max} \). Axial uniformity is nearly 1.0 over a broad range of power density and HMDSO concentration in the low pressure (150 mTorr) high gas-velocity (200 cm/sec) region of Fig. 4a. High power at low HMDSO concentration causes non uniformity because of HMDSO depletion along the flow path. At higher pressure (350 mTorr) and lower velocity (100 cm/sec), Fig. 4b shows the onset of non uniformity at moderate power densities. Finally, Fig. 4c shows effects of pressure and gas velocity on uniformity, at 0.5 W/cm² and 1.2E-10 moles/cc HMDSO. Generally, uniformity improves with increasing gas velocity and with decreasing pressure. Both of these conditions tend to reduce HMDSO depletion along the electrode surface.

**O₂ Permeation Rates - SiOₓ Barrier Coatings**

Measured O₂TR rates that have been normalized to a 1,000 Å SiOₓ film thickness on 2 mil PET are listed in the final column of Table I. The barrier film thickness on the O₂ permeation test samples differed from sample to sample, but was typically in the range of 600 Å to 1,200 Å. Adjustment was made by calculating the O₂ permeability of each SiOₓ film based on actual film thickness, then using this permeability to calculate O₂TR for a 1,000 Å thick film. This calculation was based on the two-layer permeation equation:

\[
\frac{L_d}{P_s} + \frac{L_q}{P_f} = \frac{L_e}{P_e} = \frac{1}{R_e} \quad (1)
\]

where \( L \) and \( P \) are the thickness and permeability, respectively, of the PET substrate (s), the SiOₓ film (l), and the effective double layer (e). The effective permeability, \( P_e \) (cc mil/m² day atm), is derived by multiplying the measured O₂ permeation rate, \( R_e \) (cc/m² day atm) by thickness \( L_e \).

Examination of the O₂TR data in Table I shows a wide variation in O₂TR from run to run, from 1 cc/m² day to 30 cc/m² day. The O₂ permeation rate of the uncoated 2 mil PET substrate was about 30 cc/m² day. One obvious trend in the Table I data is that most of the low-HMDSO-concentration runs (Runs 1-8) of the factorial portion of the experiment produced relatively good barriers, the exception being Run 4, where film thickness distribution was very non uniform. In contrast, many of the high concentration runs of the factorial (Runs 9-16) produced relatively poor barriers. There was rather large variability in the O₂TR measurements, as is evident in the spread in the centerpoint O₂TR values (Runs 25-30). Good repeatability of O₂TR measurements on individual samples indicated that most of the observed variability resulted from sample preparation effects. Overall, the O₂TR data is intended to indicate general trends only.

*Typical contour plots for the polynomial fit to the normalized O₂TR data are given Fig. 5. At the centerpoint conditions of 250 mTorr and 150 cm/sec gas velocity (Fig. 5a), a broad minimum exists, centered at ~0.5 W/cm² and 1.8 E-10 moles/cc HMDSO. Comparison with Fig. 3a shows that process conditions producing the highest and lowest deposition rates produce poor barrier films. Poor barrier films can result from one or more of three factors: 1) high O₂ permeability of the SiOₓ film; 2) poor thickness uniformity, resulting in uncoated areas; and 3) low average thickness / deposition rate.*

**Fig. 5. Behavior of the measured oxygen permeation rate (O₂TR), adjusted for SiOₓ film thickness of 1000 Å, as a function of A: HMDSO concentration and power density, with pressure at 250 mTorr and gas velocity set at 150 cm/sec. B: gas velocity and pressure, with HMDSO concentration set at 2.1 E-10 moles/cc, and power density at 0.5 W/cm². Both plots are typical of the O₂TR behavior over most of the experimental range studied. \( R_{aq} = 0.699 \).**

An example of effects of pressure and gas velocity on the normalized O₂ permeation rate is plotted in Fig. 5b, where power density and HMDSO concentration are at the...
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<th>Power</th>
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Notes: (a) Foil masked. Tested over 5 cm^2 area. (b) Film thickness distribution too nonuniform for meaningful O2TR test over full area.

There is some evidence that HMDSO-rich process conditions, which yielded high deposition rates, produced SiOx films that did not show the decrease in O2TR with thickness expected from Eq. 1. An example is Run 16, where samples coated with films - 0.800 A and 2.000 A thick exhibited approximately the same effective permeation rates. Films deposited under relatively rich HMDSO concentrations also showed some evidence of deterioration of barrier effectiveness with aging.

Characteristics of AlOx and AlOx-SiOy Films
Experimental work on AlOx films made using the TMA precursor was exploratory and informal compared with the work described above. Fourteen runs using the same reactor setup as described above were performed. Run conditions and available data are listed in Table II. To compare TMA deposition behavior with the behavior of HMDSO in the central composite experiment, many of the TMA run conditions fell within the range used in the HMDSO central composite experiment.

In Runs A and B, seven Si witness samples were distributed along the electrode to measure the deposition-rate profile. These profiles are plotted in Fig. 6. The FTIR spectra from such films were similar to those reported by Bourreau, et al. [9] for PECVD AlOx films. The spectra contained features attributed to aluminum oxide, hydroxide, and oxy-hydroxide. AlOx films in Run A were deposited using factor levels near the centerpoint condition of the central composite experiment (250 mTorr, 150 cm/sec), except power density was somewhat higher, and precursor (TMA) concentration was three times higher.

Curve A of Fig. 6 shows that AlOx deposition rate was very high - above 16,000 Å/min - on the top half of the electrode, then drops off rapidly to near zero. At lower pressure and power density (150 mTorr, 0.30 W/cm^2), curve B shows better uniformity, but deposition rate still drops off rapidly on the bottom half of the electrode. The O2TR value for this condition (sample C), measured over a 50 cm^2 area, was 9.8 cm^2/day (3x barrier), so this AlOx was a relatively poor barrier. The non uniform AlOx film thickness distribution, even under high-deposition-rate conditions, indicates that the TMA reacts much more rapidly on the
electrode than HMDSO does. This correlates with the pyrophoric nature of TMA, whereas HMDSO is stable in air.

Several AlOx films deposited at low pressure (80 mTorr) to improve uniformity (Runs D, E, and F) contained microscopic blisters and cracks. These exhibited high O2TR values despite their 1 μm thickness. The added HMDSO in Run F did not improve the O2TR. Runs G through O used parameter settings similar to those in some of the HMDSO central-composite runs. These films were all quite non uniform, therefore full area O2TR measurements were not performed (except on G and H). For a TMA concentration of 1.2 E-10 mole/cc in Runs G and H, AlOx deposition rate at mid-plane was less than 300 A/min. Nevertheless, the O2TR for G was relatively low, indicating low film O2 permeability for this case. The uniformity factor calculated for Runs I - K (Table II) was much lower than for SiOx deposition (from HMDSO) under comparable conditions. Addition of 1.2 E-10 mole/cc HMDSO to the TMA in Runs M-O increased deposition rate, but uniformity remained poor.

CONCLUSIONS

A four-factor designed experiment has shown that the deposition rate and O2 permeability of SiOx films deposited from HMDSO precursor vary widely with process parameter settings. The best overall O2 barrier films were obtained under conditions of low pressure, low HMDSO concentration, and high gas velocity. An exploratory experiment using the precursor TMA has shown that AlOx films can be deposited at much higher rates than SiOx from HMDSO. Thickness uniformity was comparatively poor because of the higher reactivity of TMA.

REFERENCES

5. R.B. Heil, "Mechanical Properties of PECVD Silicon Oxide Based Barrier Films", to be published in proceedings of this conference.

7. JMP Statistical Visualization Software, Vs. 3.0.2, SAS Institute, Inc., Cary, NC

ACKNOWLEDGEMENTS

The authors are grateful to Dr. D. Showers for his encouragement of this work, and to Mr. A. Kovacich for sharing his expertise in oxygen permeation measurement techniques.