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High Quality, High Rate Coatings by Plasma Enhanced Chemical Vapor Deposition on Large Area Substrates

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Abstract
A new thin film deposition technique, linear plasma enhanced chemical vapor deposition (Linear PECVD™), is entering the commercial rollout phase. In this paper, the latest results and the commercial status of the technology are presented. The Linear PECVD™ process deposits oxide and nitride films on plastic web at high speeds, e.g. 200nm-m/min for SiO₂, 180nm-m/min for TiO₂, 150nm-m/min for Al₂O₃, and 120 nm-m/min for Si₃N₄. The process uses a novel linear plasma source that has an internal, protected electrode to prevent electrode coating during full roll production runs. The high deposition rate and low deposition temperature enable coating on temperature sensitive polymer substrates. The process also produces coatings with virtually no compressive or tensile stress. This enables multilayer coatings with no web curling, no rippling, and high durability. One application reported here is a high performance 4 layer Anti-reflection (AR) coating stack on PET. Stacks of greater than 20 layers have also been demonstrated

Keywords: Linear Plasma Source, PECVD, Anti-Reflection, AR Films, SiO₂, TiO₂, Al₂O₃, Si₃N₄, Oxide, Nitride

Introduction
Most recently the Linear PECVD™ technology has been scaled to 1.25 meter wide substrates¹. Our goal is a more efficient, cost effective solution for metal oxide and nitride film deposition than reactive sputtering. Because of the low deposition rate, high heat of reactive sputtering, and high stress, multilayer AR films on polymer substrates such as PET are difficult to make. This paper presents our results using Linear PECVD™ to deposit AR films on both glass and plastic. As shown in this paper, GPI’s PECVD process can produce high quality, high performance AR films on PET at deposition rates not possible with reactive sputtering.

GPI Linear PECVD™ Technology
Figure 1 shows a Linear PECVD™ reactor module (a pair of plasma sources on a lid). Each source generates a magnetically confined plasma and delivers a dense, linear
plasma beam across a substrate. Similar to in-line sputtering, the substrate is moved relative to the source to achieve uniformity.

Figure 1: Linear PECVD™ reactor module for 1 meter substrates

GPI's reactor module operates with an AC mid-frequency power supply. Process gases are delivered both inside and outside the sources. The non-condensing gas, like oxygen, is delivered into the source. The precursor gas or vapor is distributed outside the source. Operating between 1 and 25 millitorr, the source is compatible with sputtering processes. This low operating pressure avoids the gas phase nucleation (powder formation) common to typical PECVD processes operating at 100 millitorr or greater. The plasma source physics has been reviewed in an earlier publication.

The key to a long running, continuous PECVD process is a protected electrode. In a PECVD process, the chemical precursor is delivered to the plasma and the plasma supplies the energy to disassociate the precursor to make condensable components. For instance, to deposit an SiO$_2$ film, a precursor such as TMDSO is used. TMDSO (Tetra-methyl-di-siloxane) is a low cost, relatively safe (like acetone) liquid with an SiO$_2$ molecule surrounded by 4 methyl (CH$_3$) groups and 2 hydrogen atoms. TMDSO can be readily vaporized and delivered as a gas. When this molecule encounters plasma, the energetic components of the plasma are sufficient to break the weak bonds holding the methyl groups and hydrogen atoms to the SiO$_2$ molecule. The SiO$_2$ molecule, now on its own, is no longer a volatile species and it will condense on the first surface it encounters. The methyl groups and hydrogen atoms remain in the gas phase and are pumped away. The challenge for PECVD has been to keep the SiO$_2$ molecule from condensing on the plasma generating electrode. With other PECVD sources and reactors, the electrode is in close proximity to the PECVD process. Particularly since the densest plasma is adjacent to the electrode, the exposed electrode quickly builds up
a dielectric SiO$_2$ coating. Within hours this causes arcing and process drift and the deposition process must be stopped.

In the semiconductor and flat panel display industries, PECVD is a commonly used process. In these applications, the electrode is a large plate with gas distribution holes positioned directly over the substrate. (For Gen 11 flat panel display applications, the substrate is 2.1m x 2.5m. This requires a large plate!). As would be expected, this ‘showerhead’ electrode does indeed become coated during the process. In this case however, the process is a batch operation and, after a set number of substrates are coated, the coating process is stopped and an etch back is performed. After the cleaning step, the system returns to depositing PECVD films.

While appropriate for high value added products such as semiconductors and flat panel displays, a batch type PECVD process requiring frequent etch back steps is not economical for products such as Low-E architectural glass, thin film solar cells or polymer web products. For instance, in a web coating application, it is not practical to stop after 100 meters of web has been coated to etch back. This would damage the web already coated and result in unacceptably low production rates.

In GPI’s plasma source, the electrode and plasma generation zone is remote from the plasma deposition zone. This insures that the surfaces encountered by the precursor molecules do not include the electrode. Figure 2 shows a diagram of this configuration. As shown, the key is to inject the precursor vapor closer to the substrate and farther away from the plasma generating electrode. This patent pending concept is crucial to a long running PECVD process.

Figure 2: Schematic showing remote precursor delivery and protected electrode
Experimental

SiO₂, TiO₂, Al₂O₃ and Si₃N₄ coatings and AR films are deposited on glass, silicon and polymer substrates by Linear PECVD™. The AR films are composed of four layers of silicon dioxide (SiO₂) and titanium dioxide (TiO₂). All four layers are deposited with one GPI Linear PECVD™ module. The plasma source is run continuously, while precursor gas and other process parameters are changed for each layer. The substrate passes through the plasma 4 times to make the 4 layers. (In a production system, 4 sources would allow a single pass, in-line process.) The precursors are delivered by direct vapor injection through a distribution manifold. As described above, the key feature of General Plasma’s Linear PECVD™ technology is the precursor is delivered nearer the substrate, outside the source cavity, eliminating deposition of coating on the internal electrode surfaces.

AR performance is characterized by reflection and transmission. AR reflection and transmission is measured by a Filmetrics F20-UV spectrometer. The thickness and refractive index of each layer is measured by a Metricon 2010M Prism Coupler. Deposition rate is calculated from the thickness given by the Prism Coupler at a given speed. First surface reflectance is calculated by subtracting the first surface of the substrate reflectance from the AR coated substrate reflectance.

Environmental stability is a key feature for AR film applications. The thin films are evaluated for adhesion, cracking and blistering after exposure to water or water vapor. Immersion tests in boiling D.I. water and exposure to 85%RH/85 °C for days are our standard tests. Adhesion is evaluated by a standard Mil-Spec cross hatched grid test before and after exposure to the environmental condition.

Results and Discussion

The four coatings are deposited using GPI’s Linear PECVD™ technology as shown in figure 2. Refractive index of the four thin films is shown in table 1.

<table>
<thead>
<tr>
<th></th>
<th>SiO₂</th>
<th>TiO₂</th>
<th>Al₂O₃</th>
<th>Si₃N₄</th>
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<tbody>
<tr>
<td></td>
<td>1.47</td>
<td>2.30-2.40</td>
<td>1.63</td>
<td>1.98</td>
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</tbody>
</table>

Figure 3: Refractive index of various PECVD coatings

All films pass adhesion and environmental tests on PET and glass, for both single and multilayers. Films were tested for environmental stability by submersion in boiling water for 20 minutes and 20 days in a humidity chamber at 85% humidity and 85 °C. No change is observed in optical or adhesion properties (films were measured before and after the environmental tests). Adhesion is tested by the standard Mil-Spec cross hatched grid test.
AR Films on Glass

AR coatings are deposited at room temperature on 215mm x 215mm x 4mm float glass. The deposition rate is 200 nm·m/min for SiO$_2$ and 180 nm·m/min for TiO$_2$. Optical performance is characterized by uniformity, transmission, and reflection. Good uniformity is particularly important for AR films because a change in thickness of any 1 layer will vary the reflection of the AR coating resulting in visible discoloration. The deposition uniformity is measured for each individual layer to be ± 1% from the average thickness. This excellent uniformity means the coated glass appears colorless and highly transmissive over the entire substrate. First surface AR reflection is calculated to be 0.48% average from 400nm-650nm visible wavelength. Percent increase in transmittance is 3.9% over the visible range. The Linear PECVD™ reactor in our R&D in-line tool is designed for a 250mm wide uniformity zone. The substrates are conveyed past the source in a carrier.

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**Figure 4:** Spectral reflectance of GPI AR coating on glass
These results demonstrate that GPI’s SiO$_2$ and TiO$_2$ Linear PECVD$^\text{TM}$ films are well suited for optical film applications such as anti-reflective coatings. This same type of coating would be well suited for anti-reflecting PET substrates. The processes for these films are stable and repeatable. This is independent of the process temperature (heated or ambient) and, due to our R&D in-line system only having one PECVD source, our need to switch back and forth between SiO2 and TiO2 processes. The process stability and repeatability are maintained for many days of process operation.

**AR Films on Polymer (PET)**

A two layer AR coating is deposited on 100m long x 0.25m wide x 127µm PET. The deposition rate is 200 nm-m/min for SiO$_2$ and 150 nm-m/min for TiO$_2$. Our R&D web coater has one PECVD source so the AR is made by running the web through twice to make the two layers. The coated web length in this case is 100m. During deposition the web is supported on a drum chilled to 18° C. The AR coating is a 2 layer V coat: 20nm of TiO$_2$ and 80nm of SiO$_2$. Optical performance is characterized by thickness uniformity, transmission, and reflection. Uniformity across the web is measured for each individual layer as $\pm$ 2% from the average thickness. Uniformity along the length of the web is $\pm$ 1%. First Surface reflection is minimized to .24% (above the back-side PET reflection) at 480nm wavelength. Percent increase in transmittance is 3.0% at 480nm wavelength.
Film Stress on PET

Excellent appearance and durability has been demonstrated for single and multilayer coatings on PET. This is due to the wide versatility and tunability of GPI’s Linear PECVD™ process. Figure 8 shows two Silicon Nitride films deposited by Linear PECVD™ with the same thickness and optical characteristics, but different stress.
Figure 8: High and low stress $Si_3N_4$ coating, 350nm on bottom side

The ability to control film stress enables deposition of single layers up to several microns thick or multi-layer coatings with more than 20 layers. This creates possibilities for web coatings that have not been possible before.

**Conclusion**

GPI’s Linear PECVD™ process has now been proven on a substrate width of 1.25 meters and sources for 1.75 meter width are shipping this quarter. Customers are using this new process to make high performance film on PET web including multi-layer AR’s and single layer oxides and nitrides. Other current Linear PECVD applications are solar passivation layers ($SiN:H$ and $Al_2O_3$ films), Anti-smudge coatings (Fluorinated carbon films) and TCO’s ($SnO_2:F$). In the next year we will have several systems running in the field involving these and other applications.

**Acknowledgements**

We would like to thank our technologists in the laboratory responsible for the process development activities: Gary Edmundson and Michael Whitney.

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\[^2\] J Madocks, W Seaman, M George, Q Shangguan, Society of Vacuum Coaters 53th Annual Technical Conference Proceedings (2010), ‘Plasma Enhanced Chemical Vapor Deposition (PECVD) of $SiO_2$ and $TiO_2$ for Large Area Applications’