Plasma Enhanced Chemical Vapor Deposition (PECVD) for Large Area Applications

J. Madocks, W. Seaman, M.A. George, and Q. Shangguan,
General Plasma, Incorporated, Tucson, AZ

ABSTRACT

A protected electrode linear plasma source technology is used for large area dielectric coating by PECVD. The obtained results for SiO_2 and TiO_2 films show high deposition rate, excellent optical transparency and good adhesion and environmental stability. In comparison to current reactive sputtering technology, PECVD significantly improves the cost of ownership in material and energy savings for a number of important applications. This technology is linearly scalable and applicable to in-line systems. The dynamic deposition rates achieved are 200 nm-m/min for SiO_2 and 135 nm-m/min for TiO_2. The films are deposited at pressures similar to those of reactive sputtering. In this paper the morphology, stress and optical properties of SiO_2 and TiO_2 films and present comparative cost data between reactive sputtering and this new PECVD process is reviewed.

INTRODUCTION

Plasma Enhanced Chemical Vapor Deposition offers the potential to fundamentally change the way dielectric materials are deposited for large area applications. PECVD can have high deposition rates compared to reactive sputtering and lower cost of materials. Conventional PECVD technologies have fallen short of this promise due to electrode coating, poor uniformity and powder formation. General Plasma, Inc. (GPI) has developed a new linear plasma source technology that addresses these problems and enables PECVD on large area substrates.

GPI's source technology operates with an AC mid-frequency power supply and features a protected electrode that stays free of dielectric build-up during operation. The source is capable of conversion efficiencies of chemical precursors in excess of 30% resulting in extremely low material costs. Operating between 1 and 25 millitorr, the source is compatible with sputtering processes. This low operating pressure also avoids harmful gas phase nucleation of particles that are problematic for sources that operate at pressures of 100 millitorr or greater. The high deposition rates, low material costs and energy efficiency of the source offer a compelling alternative to dielectric reactive sputtering processes.

Figure 1 shows the plasma sources in operation. The details of the plasma sources have been reviewed in earlier publications [1, 2]. The source implements a magnetically confined electrode to deliver dense plasma in a linear beam across a substrate. Similar to in-line sputtering, the substrate is moved relative to the source during deposition in order to achieve uniformity.

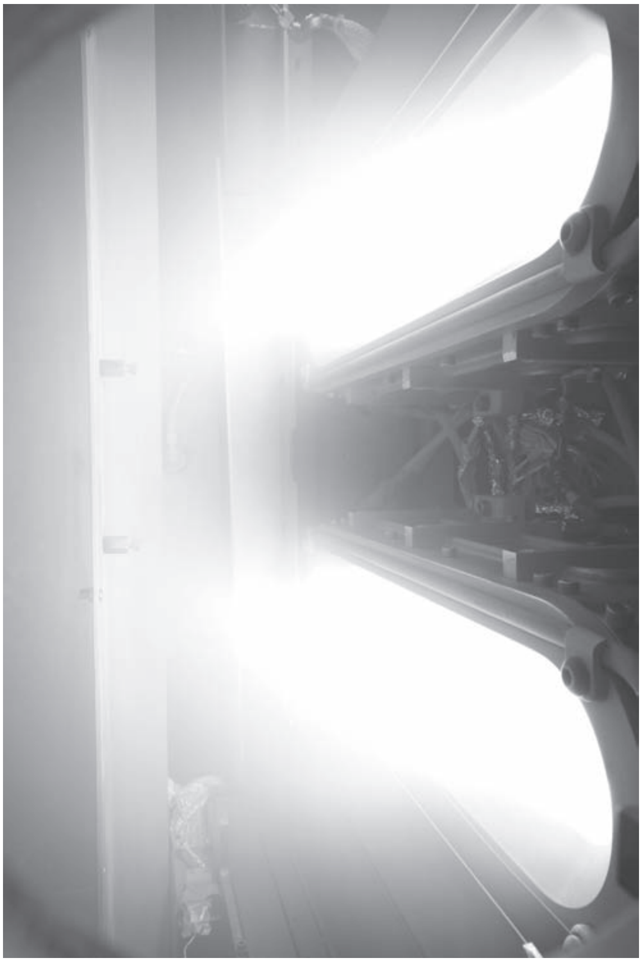

Figure 1: Linear PECVD source operating on 40 kHz AC power.

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EXPERIMENTAL

Silicon dioxide (SiO_2) and titanium dioxide (TiO_2) films are deposited on glass, silicon and polymer substrates. The films are deposited using a laboratory 300 mm wide chill drum web coater. The coater, shown in Figure 2, features a 400 mm wide linear PECVD source and chill drum. The high vacuum pumps are two 1200 L/s turbo pumps. Precursors are delivered by direct vapor to the source/substrate vicinity through a binary distribution manifold. A key feature of General Plasma's linear plasma PECVD technology is the precursor is delivered outside the source cavity practically eliminating deposition of coating on internal electrode surfaces.

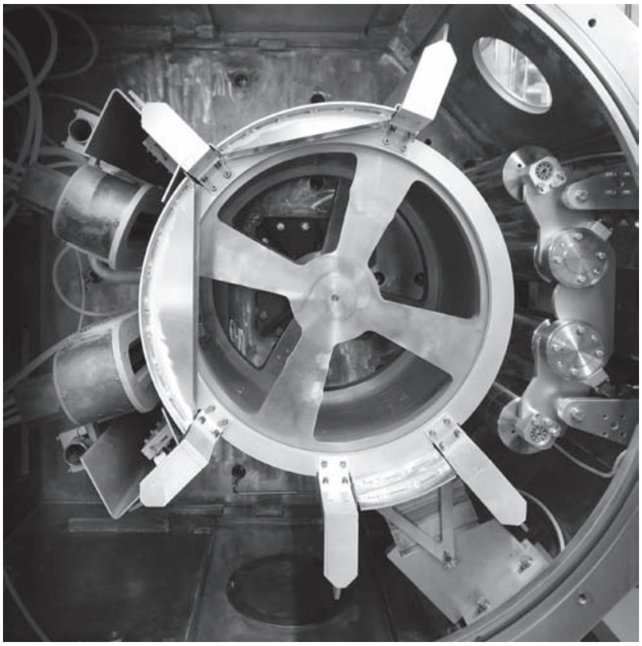

Figure 2: 300 nm web coating development tool.

A Filmetrics F20-UV spectrometer is used to measure both transmittance and reflectance of the deposited thin film and deduce the thin film thickness through optical modeling. Dynamic deposition rate is calculated from the known line speed. Index of refraction measurements are measured by both optical spectroscopy and a Metricon 2010M prism coupler at 632 nm.

Density of the thin films are evaluated by several methods. The wet etch rate of SiO_2 by a 6:1 (NH4F:49 wt% HF) buffered oxide etch (BOE) is a common method to evaluate the density and chemical stability of the thin film. A second method is by cross sectional SEM where the microstructure of the thin films is revealed.

Environmental stability is a key feature for many applications. Here the thin film is evaluated for adhesion, cracking and blistering after exposure to water or water vapor. Immersion tests in D.I. water for 30 minutes at room temperature and exposure to 85% RH/85°C for several days are common tests. Adhesion is evaluated by a standard Mil-Spec cross hatched grid test before and after exposure to the environmental challenge.

RESULTS AND DISCUSSION

PECVD SiO_2 Films

Silicon dioxide is perhaps one of the most ubiquitous materials used in thin film large area applications. Its low index of refraction, mechanical properties and environmental stability make it universally accepted for applications such as electrical dielectrics, optical layers for interference coatings and protective layers.

The deposition rate for the SiO_2 films reported here is 200 nm-m/min. This is 4-8 times faster than reactive sputtering. These films are deposited at room temperature on flexible PET. The index of refraction for the films is 1.48. The transmission spectrum is shown in Figure 3.

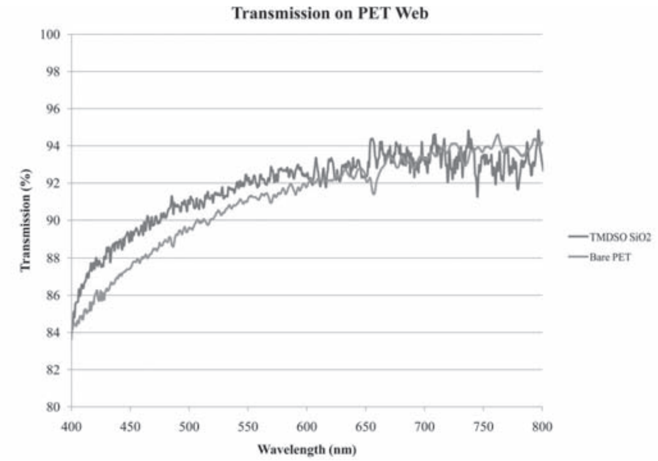

Figure 3: Transmission spectrum of TMDSO thin film on PET web.

The BOE wet etch rate of the film is 81 nm/min indicating a dense, high quality film. An SEM of the film is shown in Figure 4 confirms the void free, dense film quality.

Sodium Barrier Films

Sodium migration from soda lime glass is responsible for poor performing silver based low emissive solar control and transparent conductive oxide films. This can be controlled with the application of a barrier film and several options exist for doing so on float glass. One option is the application of a 100 nm to 200 nm thick sputtered SiO_2 layer. However, research has shown a superior sodium barrier can be applied by PECVD.

Table 1: Sodium concentration on the surface after annealing.

Sample	Elemental concentration ratio		
	Room Temperature	350°C for 1 hour	500°C for 1 hour
Uncoated soda lime	1.50%	27.91%	21.40%
Soda lime + 50 nm SiO_2	1.60%	16.66%	20.47%
Soda lime + 30 nm GPI barrier	3.60%	0.40%	0.96%

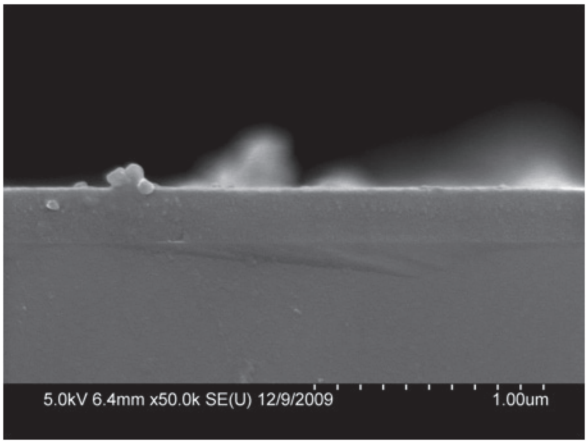

Figure 4: Cross-sectional SEM of TMDSO derived PECVD SiO_2 thin film at <80°C.

Table 1 shows XPS measurement of sodium concentration at the surface of samples after annealing at elevated temperature. In the study we compare bare soda lime glass as a control, 50 nm thick sputtered SiO_2 coating and 30 nm thick proprietary PECVD applied sodium blocker. The sodium content is reported as a Na/Si ratio. The Si concentration is constant throughout the annealing process.

The XPS result confirms sodium diffusion to the surface of the glass at elevated temperatures. The initial sodium on the surface at room temperature, prior to annealing is most likely from the environment. Sodium diffusion to the surface of uncoated soda lime substrate saturates after annealing at 350°C for 1 hour. Soda lime with SiO_2 shows an increase in sodium concentration from 16.7% to 20.5% after annealing at 350°C and 500°C for 1 hour each. The sodium concentration on the surface for the SiO_2 coated sample is similar to the control sample bare soda lime glass. This shows that SiO_2 is not effective in preventing sodium diffusion. The GPI proprietary PECVD barrier demonstrates very promising barrier properties as observed with XPS measurement. A thickness of a 30 nm of GPI PECVD barrier is enough to prevent sodium from the glass from diffusing to the surface (<1% after 350°C and 500°C annealing).

The Na barrier PECVD process is operated at 10 millitorr with a substrate temperature of <50 °C. The deposition rate of the process is >150 nm-m/min and can therefore be deposited at line speeds in excess of 5 m/min to achieve the 30 nm thick film.

Table 2 contains data for the TCO properties of a fluorinated tin oxide deposited with and without GPI's sodium blocker.

Table 2: Electrical properties comparison between FTO deposited on bare soda lime glass and soda lime glass with sodium barrier layer.

PCVD FTO	Soda lime glass	Soda lime glass+30 nm sodium blocker
Bulk resistivity (Ohm-cm)	9.4×10^{-4}	8.4×10^{-4}
Carrier concentration (# / cc)	-2.521×10^{20}	-2.741×10^{20}
Mobility ($cm^2/V.s$)	25.6	27.1

Both carrier concentration and mobility of TCO films deposited on bare soda lime glass are approximately 10% lower than those deposited on soda lime glass with a barrier film. This translates to higher resistivity of FTO film deposited on bare soda lime glass. The electrical properties results are consistent with sodium limiting grain growth and trapping electron carriers [3].

The uniformity of the PECVD source technology is excellent. Typical uniformity is better than +/-5% and can be tuned to better than 1.5% if required. Figure 5 shows one example of this uniformity for the barrier coating.

PECVD TiO_2 Thin Films

Titanium dioxide thin films are highly desired due to their high refractive index, environmental stability and potential for photocatalytic cleaning effect. The downside to common use of TiO_2 is the low deposition rate with magnetron sputtering. Even using enhanced reactive sputtering controls, the deposition rate for TiO_2 in large area production is limited to around 35 nm-m/min.

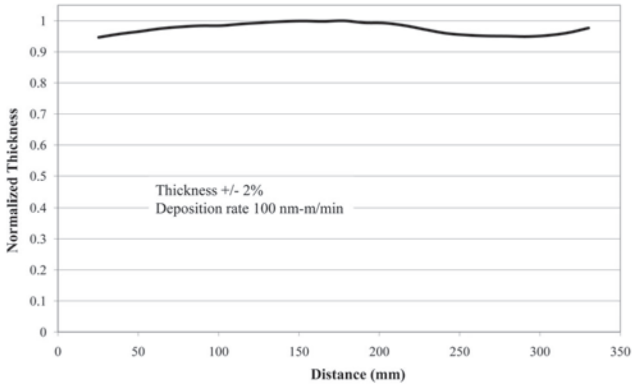

Figure 5: Uniformity of sodium barrier coating.

Using the GPI linear plasma source, a TiO_2 PECVD process capable of depositing TiO_2 films at rates of 135 nm-m/min has been developed. The films have an index of refraction of 2.36. A transmission spectrum of a 700 nm thick TiO_2 thin film on BSG is provided in Figure 6. The thin film shows little absorption above 400 nm making it suitable for high performance optical coatings. The films do exhibit absorption in the near infrared that is attributed to an ionized optical vacancy at 1100 nm described in previous work on TiO_2 [4].

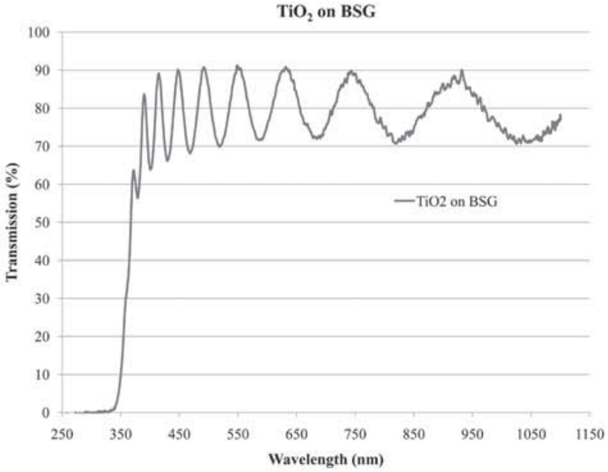

Figure 6: 700 nm thick TiO_2 thin film on BSG glass. Index of refraction 2.36 @ 630nm.

The films were deposited at room temperature. The high degree of ion flux to the growing thin film surface is responsible for the relatively high refractive index. This index of refraction normally is achieved at surface temperatures above 250°C for either DC magnetron sputtering or reactive evaporation [5, 6].

Economic Advantage of PECVD Compared to Reactive Sputtering

The economic value of the PECVD process is demonstrated by a comparison to rotary magnetron reactive sputtering of SiO_2 and TiO_2. The analysis considers the target and PECVD precursor material costs: Arc sprayed silicon and titanium target tubes for reactive sputtering and TMDSO and $TiCl_4$ for PECVD. A generous material efficiency for a rotary magnetron sputtering is 56% (75% target utilization and 75% flux utilization). The material efficiency of our PECVD process for SiO_2 is 50% and TiO_2 is 40%. Using these assumptions and data, the materials costs are compared for the same film thickness and deposition area. The results are shown in Figure 7.

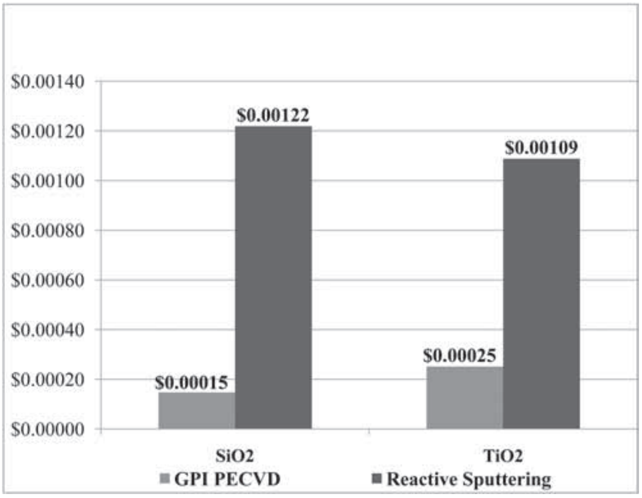

Figure 7: Material cost comparison between PECVD and reactive sputtering of SiO_2 and TiO_2 films. The metric used is dollars per square meter of substrate per nm of coating.

As can be seen, the PECVD materials costs are dramatically lower: 8x for SiO_2 and 4x for TiO_2. In addition to material savings there is a considerable energy savings (greater than 10x) due to the high deposition rate of PECVD vs. reactive sputtering (5x fewer sources are needed for the same film) and the lower energy required to dissociate the chemical precursor relative to the sputtering process. In Figure 8 material and energy costs for the two deposition methods are annualized for a theoretical double silver low-E layer stack in a production machine. This SiO_2 and TiO_2 stack would hypothetically replace current ZnO/SnO_2 and SiO_2/SiN sputtered film layers.

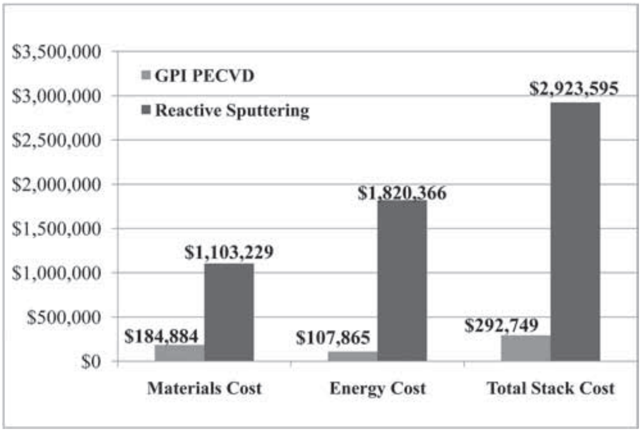

Figure 8: Annual materials and energy costs for SiO_2 *and* TiO_2 *films for a double silver low-E stack. Assumptions are: 3.6M square meters produced per year and $0.07/kWhr electricity cost. Calculated stack includes 144nm* SiO_2 *coating and 120nm* TiO_2 *coating.*

As shown in Figure 8, the cost savings for depositing the oxide layers by PECVD are significant. Given the large installed base of sputter machines, it is important to note that the low operating pressure of GPI's linear source technology allows these existing machines to be retrofitted with a PECVD process. In addition to materials and energy cost saving benefits, the dramatic reduction in the number of source bays and the length of the coater offer large savings in building size, machine and equipment costs and reduced maintenance.

CONCLUSION

High rate large area PECVD processes offer a disruptive technology to reactive sputtering of dielectric materials. This technology will dramatically lower production costs for important applications like low-e architectural glass, flat panel displays and broadband anti-reflection coatings.

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