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Interaction between DC Plasma and Substrates in Spatial PEALD

***Eric Dickey*[1], *William A Barrow*[1], *Bryan Danforth*[1], *Markus Bosund*[2]**
Lotus Applied Technology, Hillsboro, Oregon
[2]*Beneq, Oy, Espoo, Finland*

ABSTRACT

Plasma Enhanced Atomic Layer Deposition (PEALD) is a coating method that provides high quality thin films at relatively low substrate temperatures, allowing deposition on temperature sensitive substrates such as polymer films. DC plasma is not compatible with conventional pulse-based ALD, particularly for deposition of dielectric films, as the plasma electrode would be coated with the dielectric. But with spatial ALD, film deposition is limited to only the substrates, and this enables the use of direct or indirect DC plasma for PEALD. In this work we examine a Spatial PEALD process which operates in the pressure range of 1-2 Torr, where a stable DC diode discharge may be maintained with voltage in the range of 300-600 V, and the mean free path of radicals is in the range of tens of microns. By controlling the power, pressure, and electrode spacing, the electron and ion densities at the substrate may be modulated, along with the kinetic energy of the gas molecules. In this work, optimization of these parameters is used to demonstrate minimal substrate interaction for PEALD of metal oxide films on oxygen- sensitive surfaces such as rare earth metallic thin films, and temperature sensitive polymers including polypropylene film.

INTRODUCTION

Atomic Layer Deposition (ALD) is a unique thin film growth method capable of depositing high quality films with precise thickness and uniformity control. This is enabled by the self-limiting growth characteristics of the process, resulting in pinhole-free coatings, high film density with low intrinsic stress, and extreme conformality [1]. Historically, ALD processes have been performed using pulsing and purging of precursors from a common substrate chamber, a method known as *temporal* ALD. Using this method, all components in the reaction chamber are coated with the ALD film, limiting potential plasma processes to Radio Frequency (RF), Remote, or Inductively Coupled Plasma (ICP). For some of these methods, only small densities of radicals are generated at the substrate surface, while for others, substrate interaction can be too energetic to allow deposition directly onto sensitive surfaces.

More recently, ALD processes have been developed that accomplish the sequential precursor exposures by moving the substrate between precursor zones which are separated in space, a method commonly referred to as *spatial* ALD [2]. Using this method, only the substrate areas which are transported through both precursor zones are coated with the ALD film, while the rest of the chamber surfaces remain uncoated [3]. By using this technique, DC plasma may be employed, as the metal plasma electrode remains unaffected by the process, and may be used indefinitely without coating buildup. This type of plasma has been shown to be very effective as the oxygen source for spatial PEALD of metal oxides, providing conformal trench coatings at deposition rates of 5 Å/second or higher [4]. However, very little has been published about the general characteristics of a DC diode discharge in the pressure range of 1-2 Torr

For the work discussed in this paper, a simple DC diode glow discharge plasma was used for PEALD of metal oxides, with the processing gas consisting of a mixture of N_2 and CO_2. The electrical characteristics at the substrate surface were studied using a Langmuir probe, at varying electrode to probe distances and process gas pressures. The optical emission characteristics of the plasma were also studied, to provide a qualitative measurement of the generation of oxygen radical species. The qualitative level of bombardment of the substrate was then characterized empirically, by depositing PEALD SiO_2 directly onto thin gadolinium films, and comparing the level of oxidation of the gadolinium before and after deposition. Chemical reactivity at the substrate surface was examined by measuring the etch rate of optical photoresist. And finally, a barrier coating was deposited on Biaxially Oriented Polypropylene (BOPP) film, a thermally sensitive substrate material. These experiments will show that high levels of precursor oxidation can be generated at the substrate surface with minimal interaction with the substrate itself.

EXPERIMENTAL METHODS

Plasma Generation

For electrical and optical characterization of the plasma, an aluminum plate, approximately 100 mm x 100 mm in size, 3 mm thick was used. The plate was suspended from the top of the reactor by an electrically isolated Ultra-Torr compression feedthrough. This allowed vertical height adjustment relative to the Langmuir probe and the optical emission spectroscopy (OES) observation point. The electrode was electrically connected to a 1.5 KW DC sputtering power supply manufactured by Materials Science Inc., which was operated in current control mode. In this mode, the voltage was allowed to float, and generally fell within the range of 400-550 V for all conditions. The electrodes used for film deposition were also aluminum suspended from the top of the reactor, operating under similar conditions. The process gas consisted of a mixture of 4 parts N_2 to 1 part CO_2.

To understand how parametric changes in the plasma process might affect the substrate, the Langmuir probe tip was suspended near the center of the reactor chamber, in the same plane as the optical collection point for the OES system. Data was collected at pressures of 0.9 Torr, 1.1 Torr, 1.3 Torr, and 1.5 Torr, and electrode current densities of 0.15 mA/cm^2, 1.2 mA/cm^2, 2.5 mA/cm^2, and 5 mA/cm^2. The distance between the electrode and measurement point was varied between 8 mm, 15 mm, and 25 mm.

Characterization Using the Langmuir Probe

The probe hardware and software used for this work was the ESPION Langmuir Probe system, manufactured by Impedans, Ltd. To avoid oxidation, platinum probe tips were used, with a diameter of 45 µm and a length of 1 cm. The electrical data was extracted using a combination of the automated data analysis software where possible, combined with manual input where the noise in the data was excessive.

Characterization Using Optical Emission Spectrometry

An EMICON 1MC Plasma Control and Monitoring System, manufactured by PLASUS GMBH, was used to collect the data on relative intensity of emission from oxygen ions. The monitor was connected to the reactor via an optical fiber cable and collimator optics feedthrough assembly, also manufactured by PLASUS. To ensure that the emission spectrum was collected in a relative plane that represented a fixed distance from the plasma electrode, the upper and lower portions of the cylindrical collimator were masked off, leaving a horizontal aperture of approximately 2 mm tall by 10 mm wide. Relative oxygen radical concentration was determined by monitoring the wavelength region centered near 777 nm, an emission peak associated with atomic oxygen, which provided a strong signal without any significant overlap with emission from nitrogen and carbon.

Characterization of Substrate Interaction

To examine the interaction with oxygen radical species, three relatively sensitive substrate surfaces were studied. The first was a 20 nm evaporated gadolinium film, deposited on a glass substrate. This material is sensitive to oxidation, but has sufficient stability in ambient room conditions to remove it from the evaporator and transfer it into the ALD reactor without complete oxidation. Following processing, the relative oxidation of the Gd film was determined by measuring the optical transmittance at 500nm wavelength using a Perkin Elmer Lambda 900 spectrophotometer. For etch rate tests, AZ 5214-E-IR photoresist was spun onto silicon coupons, which were subsequently continuously exposed to multiple conditions. The etch rate of the photoresist was determined by comparing the photoresist thickness before and after exposure using an ellipsometer. For deposition of a barrier coating on BOPP, an off-the-shelf film manufactured by Navis Industries, 50 µm thick, was used as substrate. No cleaning or surface preparation was done prior to the PEALD coating. A film consisting of a mixture of SiO_2 and Al_2O_3, fabricated by using alternating cycles of SiO_2 and Al_2O_3, was used as the barrier coating. Film shrinkage was determined by comparison of pre- and post-coating dimensions, and moisture permeation was measured using a model 7001 water vapor permeation analyzer manufactured by Illinois Instruments.

RESULTS AND DISCUSSION

Plasma Electrical Characterization

The overall level of ion density over the conditions tested ranged from a minimum of 1.2 x 10^{16} m^{-3} to 3.2 x 10^{17} m^{-3} These values are relatively high compared with other common vacuum plasmas used for ALD, including ICP and ECR systems [5, 6], indicating that the DC diode method can be highly efficient at generating ions and radicals for high speed PEALD. The range of values also indicates that the process can be tuned to modulate the ion density by nearly a factor of 30, even though the electrode current density is changed by only a factor of 5. The ability to modulate the ion density in this way can potentially be useful for tuning thin film properties, such as density and stress. The influence of varying electrode current and gas pressure is illustrated in Figure 1a, while Figure 1b shows the average current density from all data at each electrode spacing.

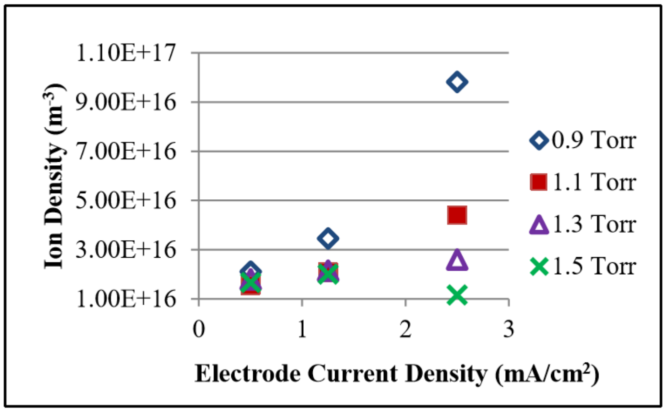

Figure 1a. Ion density as a function of plasma electrode current at various gas pressures, for an electrode to substrate distance of 25 millimeters.

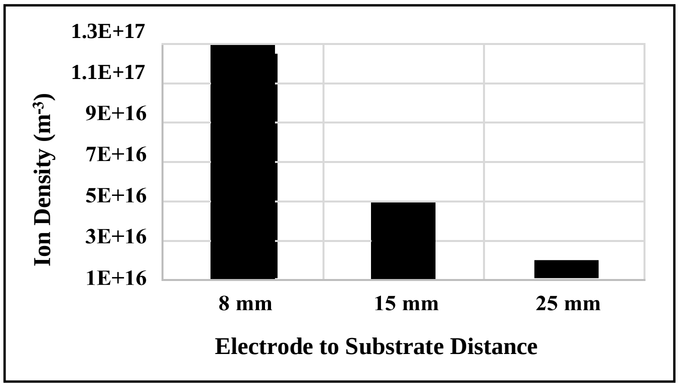

Figure 1b. Average ion density for all data taken at each electrode to substrate spacing.

Ion flux varied in a similar fashion, with values ranging from 4.7 x10^{19} m^{-2} s^{-1} to 1.2 x 10^{21} m^{-2} s^{-1}. The ion flux results are shown in Figures 2a and 2b.

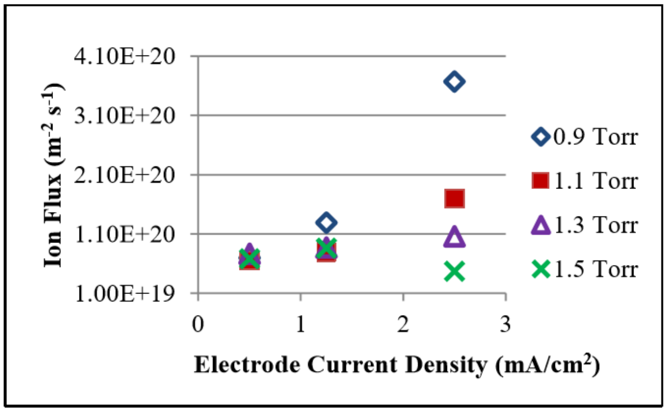

Figure 2a. Ion Flux as a function of plasma electrode current at various gas pressures, for an electrode to substrate distance of 25 millimeters.

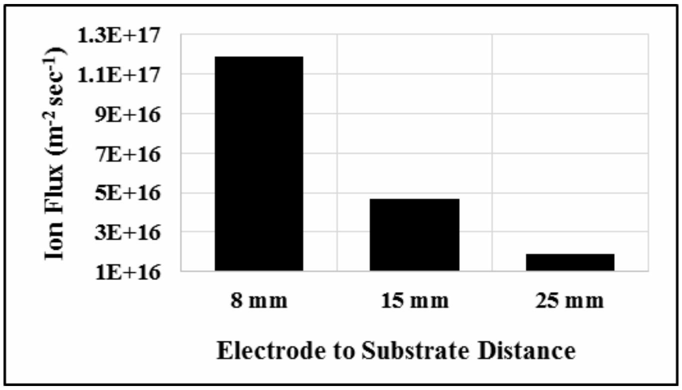

Figure 2b. Average ion flux for all data taken at each electrode to substrate spacing.

The floating potential and plasma potential were relatively consistent across the various electrode to substrate distances and electrode current values, with the floating potential averaging about -80 V, and the plasma potential averaging about -40 V. However, both the floating and plasma potentials varied significantly with gas pressure. This effect is illustrated by the data in Figure 3.

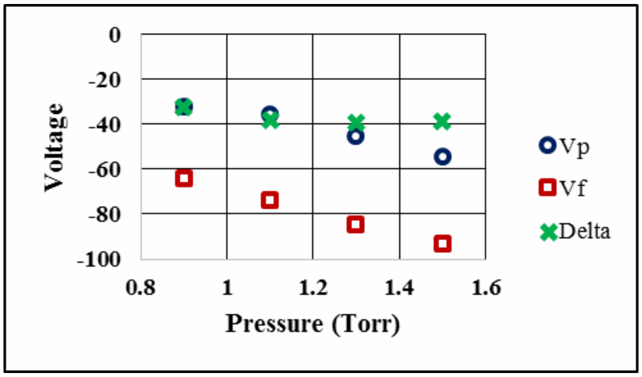

Figure 3. Effect of gas pressure on floating potential (Vf) and plasma potential (Vp). The data points each represent the average values measured for each pressure, with an electrode to substrate spacing of 25 mm.

Potentials this high could be cause for concern related to substrate damage or the incorporation of unwanted compressive stress. During deposition of dielectrics for example, the surface of the substrate will assume the floating potential, which has a net bias of approximately -40 V compared to the plasma potential. However, in the pressure range of 1-2 Torr, the mean free path for ions is in the range of a few tens of microns, limiting the kinetic energy that they can attain. For example, using the Langmuir probe data collected at 1.5 Torr of N_2/CO_2 (4:1) with 2.1 W/cm^2 input power, the Debye length was calculated to be 53 µm. This should correspond to an anode sheath width of a few hundred µm. At this pressure the mean free path of N_2 is 35 µm. Therefore, the effective acceleration distance of ions toward the anode is a small fraction of the width of the sheath. Bombardment of the substrate should be very limited under these conditions. By comparison, for a typical magnetron sputtering process operating at 10 mTorr of Ar with 1.5 W/cm^2 input power, the Debye length was calculated to be 11µm and the mean free path was calculated to be over 6,000 µm [7], which would result in much higher levels of bombardment.

Plasma Optical Characterization

The intensity of the 777 nm atomic oxygen peak was shown to vary over an extremely wide range for the process space examined. As the pressure was increased, the region of plasma optical emission contracted toward the electrode. As electrode current density increased, the region of optical emission expanded away from the electrode. Therefore, relative intensity at the substrate surface can be varied by gas pressure, electrode current density, or electrode to substrate distance, as illustrated in Figure 4.

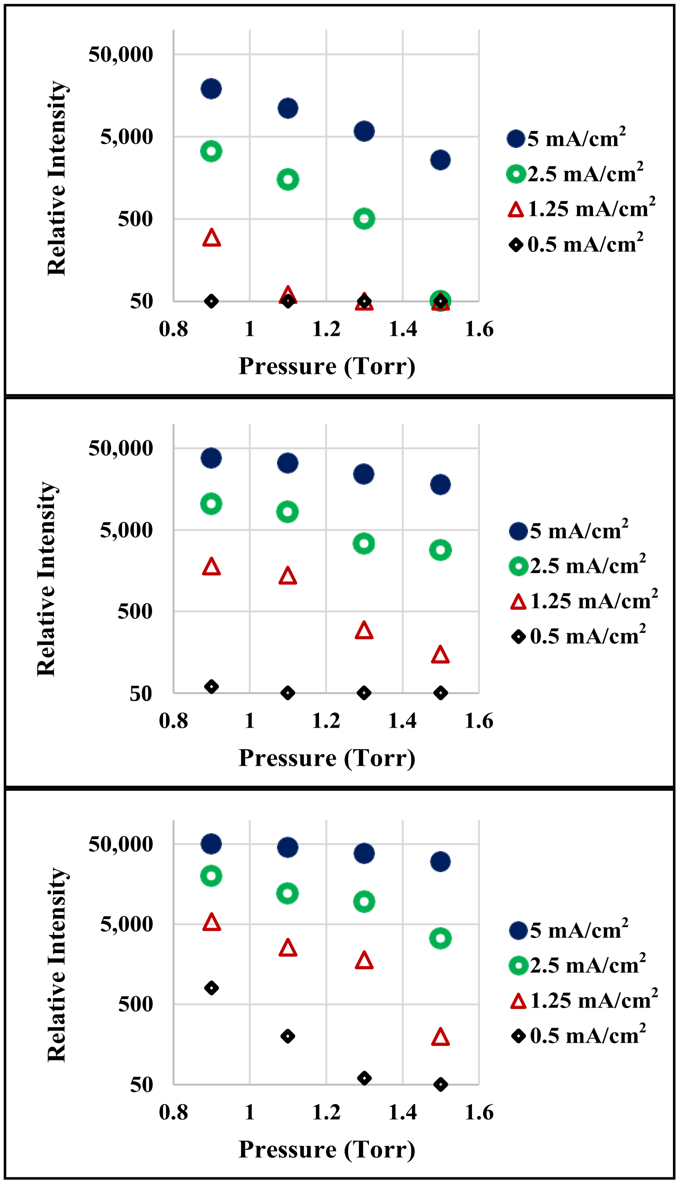

Figure 4. Relative intensity of the 777 nm atomic oxygen emission peak vs. pressure, for electrode to substrate distances of 25 mm (top), 15 mm (middle), and 8 mm (bottom). The approximate noise floor for the data was 50 counts, so signals below detection were plotted at this value.

The relative intensity values extend from 50,000 counts for the closest spacing and lowest pressure, to less than 50 counts, the limit of detection, for 11 of the conditions tested. This range of 3 orders of magnitude was demonstrated even for a single electrode to substrate spacing of 8 mm.

Substrate Interaction

Thin gadolinium metal films are relatively reactive with oxygen and do not self-passivate as many other metal films do, as illustrated in Figure 5.

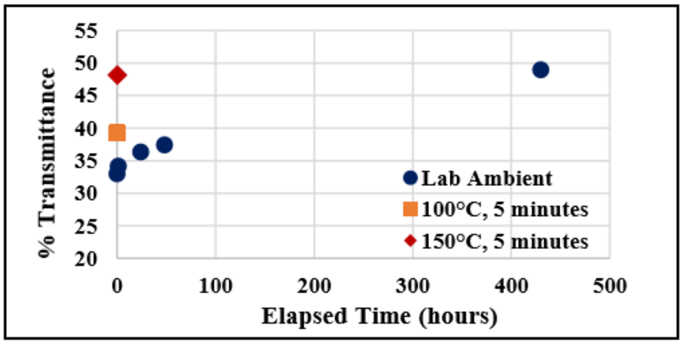

Figure 5. Transmittance of ~20 nm thick evaporated gadolinium metal film on glass over time. The oxidation can be strongly accelerated using moderate heating.

PEALD SiO_2 deposition was performed on the gadolinium films under one high intensity and one low intensity plasma condition. It should be noted that the exposure times to the plasma during this process are relatively short, as the path length of the substrate under the plasma is only about 8% of the path length of a full rotation. For example, at the rotation rate of 150 RPM, the exposure for each cycle is only about 32 milliseconds. Therefore, with a growth rate of approximately 0.1 nm per cycle, a film thickness of 1 nm will be formed with less than one full second of total exposure time. After roughly this thickness, it is likely that the accumulated film will largely block any additional interaction with the underlying surface other than thermal effects.

As a point of reference, one sample was exposed to RF reactively sputtered SiO_2 using a low power density of 0.8 W/cm^2. The process gas consisted of 10% oxygen in argon, at a pressure of 3 millitorr.

The results from these runs are shown in Table 1.From this data, it is qualitatively clear that the plasma intensity plays a role in the oxidation of the thin gadolinium film. At the lowest intensity, the oxidation level is nominally less than would occur after a day or two of aging in a laboratory environment, while the exposure to the high intensity plasma

Table 1. Transmittance of ~20 nm thick evaporated gadolinium metal film on glass, exposed to various oxidizing processes. It should be noted that the gadolinium films used for these tests were deposited in a different run than the samples used for the aging tests, and was slightly thicker. Therefore, the control sample has a nominally lower transmittance. Relative change from each control is considered more relevant than specific values.

Deposition Conditions	**OES Counts**	**Ion Current Density (m^{-3})**	**%T @ 500 nm**
Low Intensity PEALD 150 RPM	200	7.9 E^{16}	25.3
High Intensity PEALD 150 RPM	20,000	3.2 E^{17}	29.2
RF Reactive Sputtering			26.3
No Exposure (control)			24.5

produces oxidation comparable to several days of aging in a laboratory environment, but less than a sample heated to 100 °C for 5 minutes. In comparison, the oxidation level of the sample exposed to low power reactive sputtered SiO_2 falls in between the high and low intensity PEALD processes.

The etch rate of photoresist in a vacuum plasma is a useful proxy for the presence of highly reactive oxygen radicals, particularly the types of radicals that can serve to react chemisorbed metalorganic precursors during the ALD process. Here, photoresist films with a thickness of approximately 300 nm were exposed continuously to the DC diode plasma under various conditions matching the conditions used for data collection with the OES and Langmuir probe. The etch rates for the highest three current densities at the various gas pressures are shown in Figure 6.

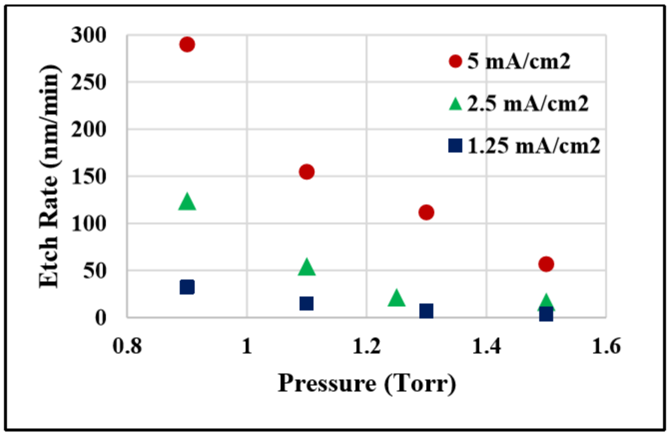

Figure 6. Etch rates for photoresist, continuously exposed to the N_2/CO_2 plasma, for various electrode current densities, with an electrode to substrate distance of 8 mm.

The etch rate can be varied over a very wide range, even for a single electrode to substrate distance. In this case, variation by a ratio over 70:1 was measured for a gap of 8 mm. At the lowest exposure conditions, an etch rate of just 4 nm per minute was observed. Overall, there is a reasonable correlation between the etch rate and optical intensity from the OES data, as illustrated in Figure 7.

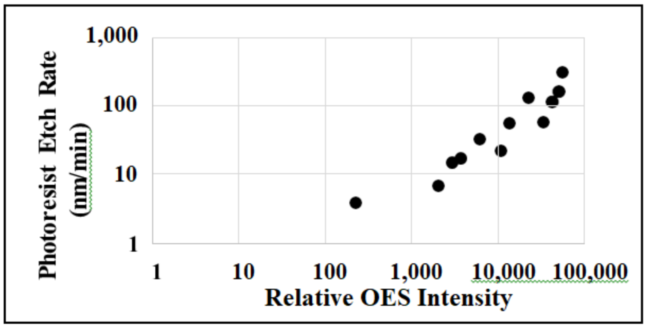

Figure 7. Correlation between the photoresist etch rate and optical emission intensity associated with atomic oxygen.

This correlation indicates that atomic oxygen is likely the dominant radical species responsible for the etching, as might be expected given its high chemical reactivity.

The BOPP substrate material chosen for the barrier coating was a deliberately challenging one. This material has thermal shrinkage specifications of <5% in the Machine Direction (MD) and <3% in the Transverse Direction (TD) when heated at 130 °C for 5 minutes, and thus is quite thermally sensitive compared with other commercial films such as PET. Further, due to its chemical makeup consisting only of carbon and hydrogen, it is a very challenging material on which to apply a high quality vapor barrier using conventional commercial methods [8]. Coating of a high quality barrier is further complicated by the highly defective surface of this commercial packaging material, which is not even a grade typically used for metallization in the packaging industry. It has a high number of inclusions, indentations, and de-laminations of the skin layer from the bulk, as illustrated in Figure 8.

The barrier coating was comprised of a mixture of Al_2O_3 and SiO_2, and was 34 nm thick. The total deposition time was 3 minutes. A nominal substrate temperature of 65°C was used, and relatively high intensity plasma conditions were chosen, with an electrode current density of approximately 3.5 mA/cm^2, and a pressure of 1.2 Torr. Following deposition, no measurable change in dimension of the substrate could be detected, with an estimated uncertainty of approximately ± 0.5%. The Water Vapor Transmission Rate (WVTR), measured at 38 °C and 90 % relative humidity was 0.006 g/m^2/day, a relatively good barrier given the quality of the substrate.

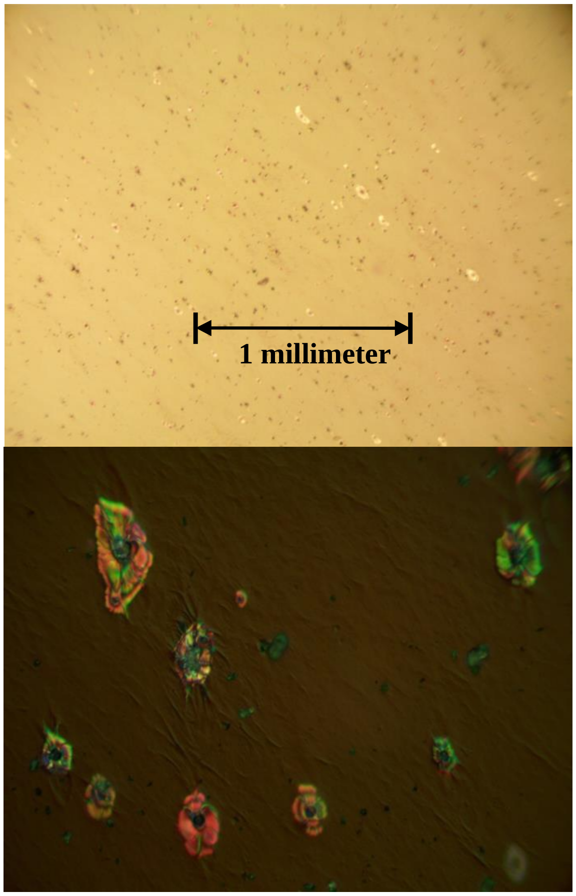

Figure 8. Micrographs of the surface of the biaxially oriented polypropylene (BOPP) substrate. The top image demonstrates surface defect density on the order of 100 per square millimeter. The higher magnification image on the bottom shows the wrinkly surface and points of delamination between the skin layer and bulk material at imbedded defects.

CONCLUSIONS

A novel DC diode plasma process operating in the pressure range of 0.9 to 1.5 Torr has been characterized electrically and optically. The resulting data shows that ion density, atomic oxygen levels, and chemical interaction with the substrate can be modulated by orders of magnitude by modifying pressure, electrode current density, and electrode to substrate distance. Furthermore, even at some of the highest plasma intensities tested, interaction with sensitive substrate surfaces is limited due to the low kinetic energy of the ions and the relatively very short exposure times, typically in the range of a few tens of milliseconds per ALD cycle. Therefore, this plasma method is well suited for high speed spatial PEALD, even on heat and oxygen-sensitive substrates.

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FOR FURTHER INFORMATION

E.R. Dickey,
Lotus Applied Technology, Inc.
Hillsboro, OR 97006,
eric.dickey@lotusat.com,
503-597-2571.