Structure and Characterization of Polystyrene Thin Films

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Electrical impedance spectroscopy (EIS) has been used to determine the presence of the density gradient from the surface to the bulk of a thin polystyrene (PS) film. It was shown by EIS that there is a density decrease from the bulk to the surface of the PS film. EIS has angstrom scale resolution in its spatial measurements and has proven to be a valuable characterization tool. It is hypothesized that the density profile near the surface of the polymer is continuous, but it was feasible to use a layered mathematical model to estimate the density gradient across the thickness of the film by separation of EIS data. The EIS was also used to measure the effect of CO_2 on the PS thin film. We were able to determine the swelling effect that CO_2 initially had on the density profile of PS and how the polymer relaxed as the CO_2 diffused out.

INTRODUCTION

Polymeric devices with nanoscale features are emerging as the forerunners of new technology in the medical community. Polymer thin films and surfaces have been a very active area of research for the past decade and it is now widely hypothesized that there is a reduction in the density of the polymer[1-3] or liquid-like layer[4, 5] near the surface. This layer of reduced density is on the order 10 nm;[6] similar in size to the desired nanoscale features. This can be used as an advantage to fabricate the nano-features; the surface can be plasticized at temperatures below the bulk T_g.[7, 8] Another technique that has great potential to plasticize only the surface layer is to contact the polymer with a dense gas, such as CO_2. This reduces the processing temperature even farther below the ambient T_g[9, 10] and the plasticization is easily tunable with CO_2 pressure. In this paper we will look closely at the density gradient near the free surface of the polymer both with and without the presence of CO_2.

The analytical tool used to detect subtle differences in the polymer density was EIS. This technique has been used recently for analysis of surface interaction in nano-scale for various systems,[11] while its fundamental principle was established in the 19th century, where it was used to prove that living cells were contained by a membrane.[12] The precision by which the phase angle and amplitude can be monitored has been significantly improved during the last decade and its frequency range has been expanded. New modeling techniques have been created to account for more than one homogenous layer. A sample can be modeled by breaking it down into layers of different resistances. This is advantageous for determining if a polymer thin film can be broken into layers of different density because as a non-conducting polymer increases in density, it also increases in resistance.

MATERIALS AND METHODS

Materials

Highly doped silicon wafers were supplied by Virginia Semiconductor, Inc in Fredericksburg, VA. Sulfuric acid (reagent grade 95-98%), hydrogen peroxide (35 wt.% solution in water), toluene (99.5+% A.C.S reagent) and sodium chloride (99%) were all supplied by Sigma-Aldrich. The polystyrene (M_n=214000 g mol^{-1}, M_w/M_n=1.03) was supplied by Polymer Source Inc. in Quebec, Canada.

Thin Film PS Preparation

Highly doped silicon wafers were cleaned in piranha solution (70% by volume sulfuric acid/ 30% by volume hydrogen peroxide) for 25 minutes at 90°C. The wafers were rinsed with Milli-Q Ultrapure water and air dried. This cleaned the surface of the wafer, but did not remove the SiO_2 layer. Polystyrene was dissolved in toluene at concentrations between 0.25-1.0 wt.%. These solutions were spin coated onto the silicon wafers using a Specialty Coating Systems G3P-8 Spincoater at 2500 rpm for 60 s, plus 10 s to accelerate. For all spin coated samples the toluene was allowed to dry off of the samples at ambient conditions for at least 24 hours. The PS was then annealed at 130°C and vacuum for at least 12 hours. The thickness of the PS on the silicon wafer was then measured using an ellipsometer (J.A. Woollam Co., Inc Spectroscopic Ellipsometer M-2000V).

Three different concentrations of PS in toluene were spin coated onto highly doped silicon wafers and measured using EIS. These were used to determine how the thickness of the film changed the EIS data. Next, four more wafers were spin coated and they all had a thickness between 43-46 nm. They were measured for thickness using an ellipsometer both before and after being exposed to CO_2 at 70ºC and 13.8 bar for 2 hours. The CO_2 depressurized was done over 8 minutes to avoid polymer foaming. All samples were measured immediately after depressurization, 24 after, and 48 hours after.

A third set of wafers were spin coated with approximately the same thickness (65-69 nm) of PS. These samples were also exposed to the same CO_2 conditions as the previous four. Each sample was run once before CO_2 exposure and one sample was run immediately after CO_2 depressurization, one was run 24 hours later, and the last was run 48 hours after depressurization.

EIS Measurements

The impedance of the PS thin films on silicon wafers in contact with 0.1M KCl solution was measured over a frequency range of 10^{-2}–10^{5} Hz using an INPHAZE Pty Ltd impedance spectrometer (Figure 1) with a resolution of 0.001° for the phase angle and 0.002% for the amplitude. The spectrometer applied an alternating current that was digitally generated as a sine wave, and the high input impedance amplifiers monitored the a.c. potential developed across the electrodes. This four terminal spectrometer had three separate electrodes; the reference electrode was Ag|AgCl, the counter electrode was platinum, and the working electrode was the silicon wafer with the PS thin film. Gallium-indium eutectic was applied to the bottom of the wafer to form a rear ohmic contact to the silicon wafer.

Wafers containing different thicknesses of PS were tested in the impedance spectrometer at all possible frequencies. In addition, PS samples were tested both before and after the exposure to CO_2. The impedance data was modeled using the INPHAZE Impedance Analyser© software.

RESULTS

EIS Measurement of PS Thin Film

The impedance data can be broken into capacitance and conductance, from which more information about the system can be derived. The capacitance vs. frequency of the experimental samples can be seen in Figure 2 (left). Each data point on the plot is the average of three measurements at a specified frequency (with error bars) and the line connecting these data points is the model that is fit to them. It is obvious that as the thickness of the PS film was increased from a clean silicon wafer (0 nm) to a thicker layer, the capacitance decreased

drastically at all frequencies except those above 10^3. The reason that all of the data converges to the same value at high frequencies is that this region is more affected by the KCl solution rather than the sample, and all samples were tested with the same KCl solution.
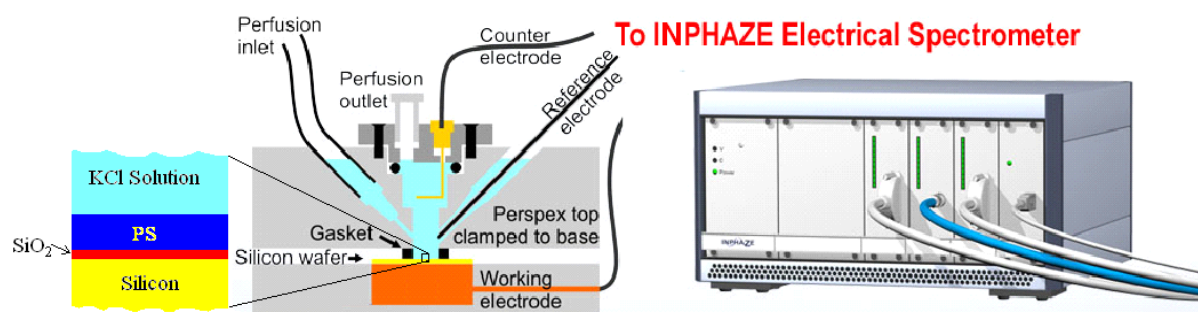

Figure 1: Schematic of the experimental setup for EIS measurements (Courtesy of INPHAZE Pty Ltd)
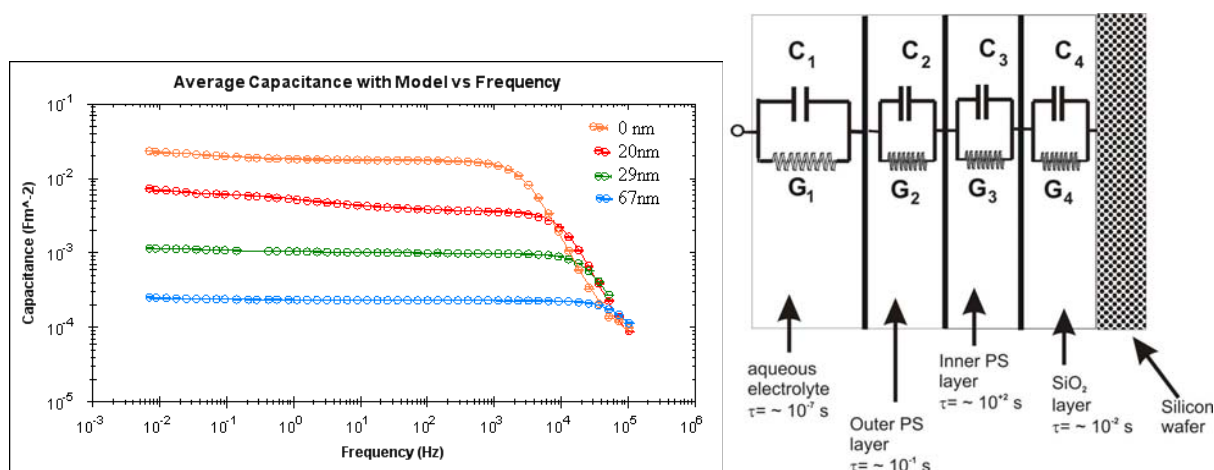

Figure 2: (left) Capacitance vs. frequency for different polystyrene film thicknesses, (right) Dielectric layered "sandwich" model fitted to the impedance spectroscopy data. This yields the values of the capacitances, C, and conductances, G, of each layer separately.

Each of the models fit to the data have a number of elements in series, where each element consists of the capacitance and conductance in parallel, more details are here.[12] Each data set was fit to a model consisting of 4 elements, see Figure 2 (right).

Identification of each layer is readily accomplished by calculating the electrical time constants, $\tau = C/G$, for each layer from the values of the capacitance, C, and conductance, G, of the sub-layers determined from the impedance spectroscopy measurements. Whilst C and G are dependent on the thickness as well as the intrinsic properties of the material composing the layer, the time constant is independent of the thickness and reflects only the properties of the material. Further, impedance spectroscopy measurements on a silicon wafer, with SiO_2 layer but without a PS film, further helped to identify the nature of the SiO_2 and electrolyte layers.

The model values for PS with the film thickness of 20 nm are shown in Table 1. Along with the conductance and capacitance, the resistance is also shown for each element and if the dielectric constant for that element is known it can be used to determine the dielectric

thickness of the corresponding element. Each element in this model corresponds to a physical layer of the system being measured.

The first row in this model corresponds to the KCl solution, that has a known dielectric constant of 78 [13]. The second row corresponds to the SiO_2 layer that is present on the surface of the Si wafer and has a dielectric constant of 4.4 which yields a thickness of 3.3 nm for the SiO_2 layer. The remaining 2 layers characterize the PS thin film. Of these two, the layer with the longest time constant can reasonably be assumed to be the inner layer in which water penetration is minimal. We therefore assigned the a value of 2.2 for its dielectric constant [14]. That immediately provides an estimate of its thickness from the capacitance determined for this layer with the value of 3.1 nm. As the ellipsometry measurements yielded a thickness of ~20 nm for this sample, the outer layer of the PS film is then estimated to be ~ 17 nm. From the capacitance value determined for this layer, we can then determine its dielectric constant, which yields a value of 60. This is considerably higher than that of a solid PS film, suggesting that KCl solution (dielectric constant 78) permeates this layer. In reality one might suspect that the PS film will have graded properties from the surface inwards. Here, however, we have arbitrarily divided it into 2 layers, in which case those layers would have the properties shown in the Table 1.

Table 1: Model values for the 20 nm thick polystyrene film

Conductance (S/m^2)	Resistance (Ohms m^2)	Capacitance (F/m^2)	Time constant (s)	Dielectric constant	Dielectric thickness	Identity (inferred)
2.7 E+2	3.7 E-3	5.1E-5	1.9E-7	78	>10 μm	Aqueous film
4.9E-2	3.8	1.2E-2	4.5E-2	4.4	3.3 nm	SiO_2
4.9E-2	2.0 E+1	3.9E-2	7.9E-1	60	17 nm	Outer polystyrene layer
4.9E-5	2.1E+1	6.3E-3	1.3E+2	2.2	3.1 nm	Inner polystyrene layer

EIS Measurement in Assessing the Effect of CO_2 on the PS Thin Film

Four PS films were prepared as described previously and measured for thickness with the ellipsometer before and after exposure to CO_2, see Figure 3. All four samples showed an initial increase in thickness due to CO_2 diffusion into the polymer film, see Figure 3. The sample measurements to determine whether PS films had relaxed back to their original thickness, after 24 and 48 hours, were inconclusive due to large errors. Measuring a difference of only 1 nm due to swelling was pushing the limits of the ellipsometer.

The plots of conducdance and capacitance vs. freqency can be seen for all three samples both before and after CO_2 exposure, see Figure 4. The first set of plots clearly show that CO_2 swelled the polymer film, due to the large decrease in the capacitance. This corroborates the evidence of swelling due to CO_2, first noticed by the ellipometry measurements after exposure to anolgous CO_2 conditions, shown in Figure 3.

The PS film that was exposed to CO_2 was analyzed 24 hours after depressurization. A large increase in capacitance at low frequencies was observed. This type of low freqency capacitance behavior has been linked to ionic diffusion polarization effects at the surface of the sample.[12] In one half cycle of the a.c. signal a charge builds up in the polymer due to either positive or negative ions diffusing into it, but at higher frequencies there is not enough time for this diffusion build-up to occur. The polymer film was still slightly swelled in this case, but most of the CO_2 had probably diffused out, and this could leave extra free volume

between the polymer chains for the ions to diffuse into, thus illuminating the behavior in the low frequency capacitance behavior. At the higher frequencies the capacitance was lower than the original sample corroborating that the polymer film was still slightly more swelled after 24 hours.

The EIS measurements indicated that the thickness of the PS film was thinner 48 hours after exposure to CO_2; this was determined by a higher capacitance at all frequencies. As mentioned earlier, the polymer films were annealed before running these experiments. Carbon dioxide can also assist as an annealing agent for polymers due to its plasticization effect; therefore, the polymer film may not have been completely annealed before the CO_2 exposure, but was annealed completely by the CO_2. Thus, allowing it to relax to a thinner film.
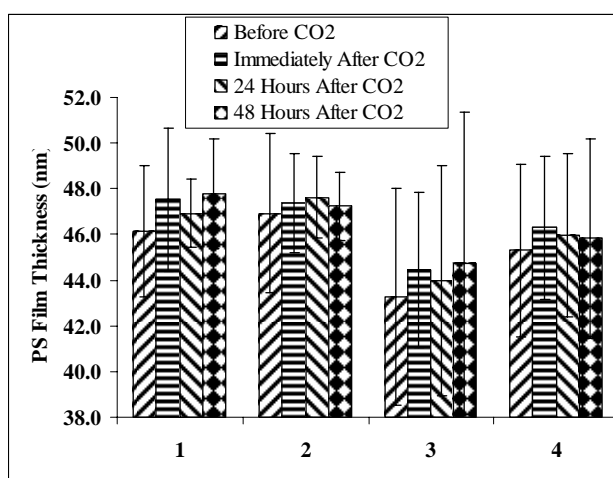

Figure 3: Film swelling due to CO_2 exposure in four different samples. Error bars are three standard deviations.

CONCLUSION
Electrical impedance spectroscopy has revealed that PS films formed on silicon substrates have graded properties; in the bulk of the outer part of the film (surface layer) water and ions penetrated, whilst the much thinner inner layer had a much lower conductance. It was also shown in this study that CO_2 swells the PS thin film, thus also decreasing the density further. The density decrease in this case was inferred from the data due to the apparent diffusion of ions deeper into the polymer free surface.

ACKNOWLEDGEMENTS

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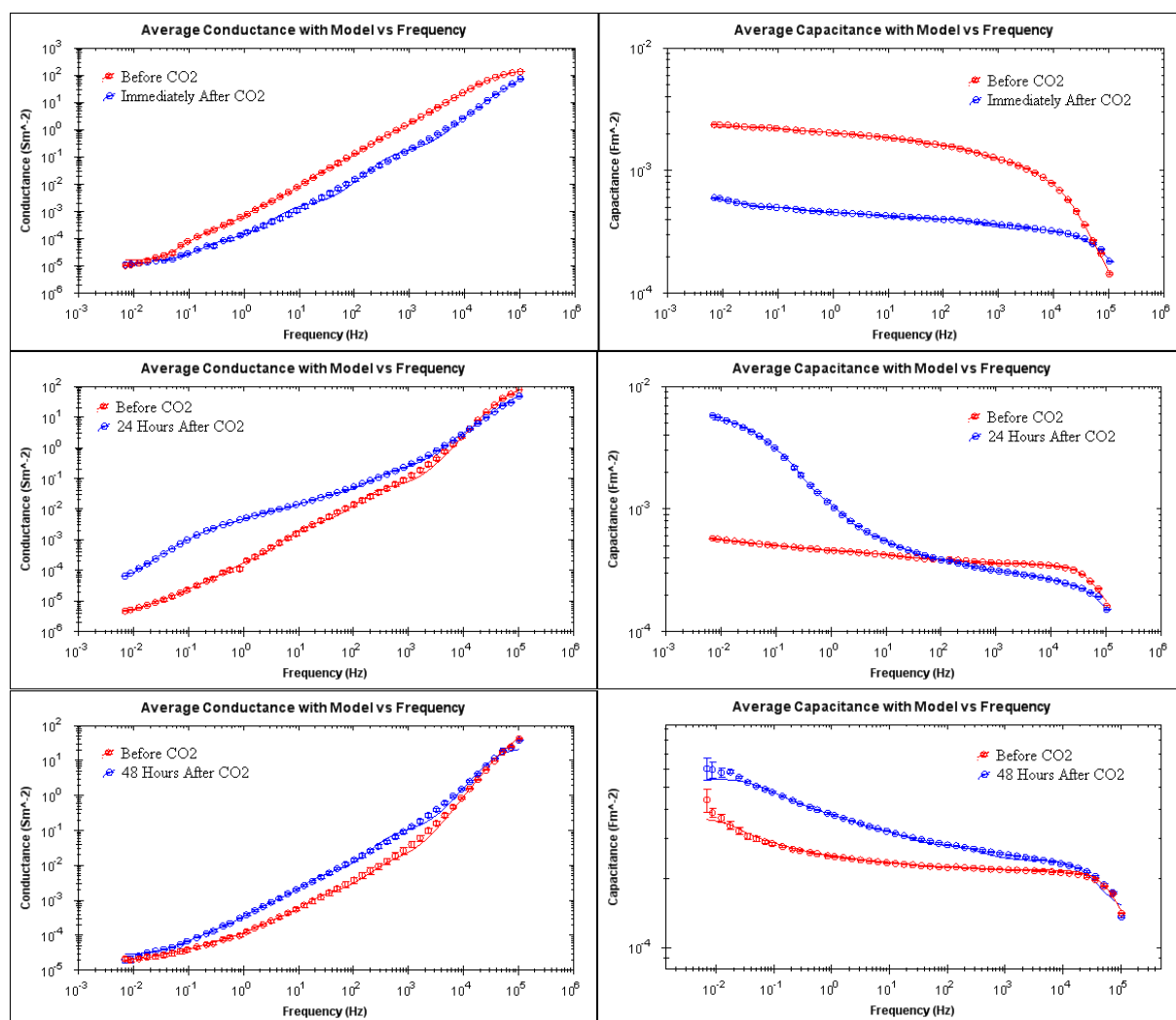
Figure 4: EIS data for before and after CO_2 exposure