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Variable-angle, spectroscopic ellipsometry study on the repeated application of First Contact Polymer on silicon-based surfaces

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ABSTRACT

First Contact (FC) Polymer™, developed by Photonic Cleaning Technologies, is used to clean and protect surfaces from contamination. The polymer creates a peelable coating that renders the surface clean while not leaving visible residues. To investigate the effectiveness of FC at the subnanometer level, we used variable-angle, spectroscopic ellipsometry (VASE) to measure sample top-layer thickness after repeated application/storage/removal cycles of standard (red) FC with three sample sets (CVD Si_3N_4 on Si, bare Si, and SiO_2 on Si). The samples were measured via VASE after every FC removal to understand contaminant thickness changes with "peel-off" count. Control samples were also measured at each iteration. Ellipsometric analysis revealed FC removed, during the first peel-off, impurity from the surface of samples treated with impure isopropyl alcohol. Linear regressions and t-tests comparing samples with and without FC were employed for evaluating changes with peel-off counts. There is evidence for the very slight build-up of material which is not removed by iterative FC application/removal cycles on these samples. It is slight, <0.1 nm after 17 iterations, in the case of native oxide on Si.

Keywords: Contamination Control, Variable-angle spectroscopic ellipsometry, First Contact Polymer, silicon nitride, native oxide, optical surfaces, surface cleanliness, cleaning

1. INTRODUCTION

Contamination on both the micron and the nanometer scale often is a significant issue for optical surfaces. As such, contamination control has become a field of marked importance for spacecraft, thermal control surfaces, lithography, and optical components such as, baffles, lens, mirrors and windows. As these fields increasingly require lower contamination levels, the need for techniques to produce and measure atomic level cleanliness increase. While chemical washing, plasma cleaning, and CO_2 snow are commonly used for cleaning surfaces, they require constant application in order to keep the surface clean.

First Contact (FC) Polymer™is a relatively new cleaning technology which has been shown to be effective on protecting and cleaning contamination susceptible surfaces.[1] Baozhu et al. showed by monitoring the absorption coefficients before and after FC application and finding that the absorption coefficients decreased after application that FC can clean optical thin films.[2] Baozhu et al. also found FC also cleaned handprints after application.[2] FC has also been compared with traditional cleaning methods, such as the "drag-wipe", also known as the drop-and-drag method which use solvents such as methanol or isopropyl alcohol (IPA) on lint-free wipes. As noted by the Laser Interferometer Gravitational-wave Observatory (LIGO), Phelps, Zhang, & Dannenburg used this method with methanol and compared it with cleaning using FC for use on optical surfaces. They found that surfaces cleaned by FC exhibited less diffuse scattering as measured by BRDF than those cleaned by drag wiping with methanol[3,4] .

While FC has been shown to be effective for surface cleaning, the effect of repeated applications of FC has not been well investigated. Since FC's beneficial action depends highly on the differential adhesion the polymer makes with the surface and with the contaminants, attention needs to be paid to atomic-level changes at surfaces.

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Contamination on the micron level is typically thought as particulate contamination, while on the nanometer level, it is thought as molecular contaminants. Common molecular contaminants include carbon and oxygen containing compounds (organics) adsorbed from the atmosphere. This is often referred to as adventitious carbon. Such contamination is often characterized via surface sensitive probes such as X-Ray Photoelectron Spectroscopy (XPS), Auger Electron Spectroscopy (AES), Fourier Transform Infrared (FTIR) methods, electron-beam x-ray fluorescence spectroscopy, and ellipsometry.

To investigate the effect of repeated application of red FC on surfaces, variable-angle, spectroscopic ellipsometry (VASE) was chosen, since it is a rapid, convenient, effective, way to investigate the effect of multiple FC peel-offs on a sufficiently large number of samples to make statistically significant comparisons possible. VASE has also been used many studies because of its reputability and effectiveness.[5,6,7] In interpreting the VASE measurements a fitting program is used which treats the studied material as a multiple layer stack. The top layer is assumed to contain the adventitious surface molecules, if any, and if the same spot is measured several times, changes in the ellipsometric spectra are interpreted as changes in the apparent thickness and/or composition of this layer, corresponding to increases or decreases of contaminants or FC-residue. We term this apparent thickness because the actual thickness of the layer is not the goal. The study aims at precision, measuring changes in the apparent thickness with treatments. Aspnes stated that SE is in principle capable of achieving a precision in Si oxide thickness on Si of less than 0.001 nm.[8]

As discussed below, in VASE a beam of polarized white light is caused to fall on the sample at a desired spot and at a given angle of incidence. After measurements are made at that angle the incidence angle is incremented via computer control and the process is iterated. Changes in the ratio between the p and s polarization amplitudes, r_p and r_s, in the reflected light are recorded as amplitude (Ψ) and phase (Δ) values for each wavelength and angle of incidence. Both the amplitude and the phase are related to the ratio of the Fresnel reflection coefficients of the p and s polarizations[9] as shown in the following equation:

$$\tan(\Psi)\, e^{i\Delta} = \frac{\tilde{r}_p}{\tilde{r}_s}$$

For a given sample measurement, thousands of values of Ψ and Δ are collected. The values are then used to fit the model parameters to the data using a least-squares method. Since the number of data vastly exceed the number of parameters the system is overdetermined. A 'mean square error' (MSE) is calculated by the J. A. Woollam, Inc. software which indicates how close the model fits the data. The closer to 1 the MSE is, generally the closely the fit is thought to describe the reflecting surface. The quest for low MSE is not absolute, however. As discussed elsewhere, the model needs to have as many thicknesses and composition constrained as knowledge of the sample can provide to avoid generating unrealistic parameter values.[6] Because an iterative process generates progressive data on the same sample(s) the statistical tools used answer the kinds of questions that deal with trends, such as these. To what degree of certainty can we say that there is a trend? How confident are we that a given trend with one group of samples is different than the trend with another set of samples such as the control or another sample treated in a slightly different? The statistical tools for addressing these are linear regressions, which generate R^2 and p-values used for analyzing trends, and t-tests, which generate separate p-values used for comparing two data sets. Error bars are also computed.

2. EXPERIMENT METHODOLOGY

2.1 Experimental Set-up

Three silicon-based sample sets were chosen which share two common features. First, the surface of each is primarily silicon dioxide, albeit a thin oxide in two sets, and second, the substrates for all are single-crystal silicon, (100) orientation. The roughly square samples- 13 to 26 mm on a side- were cleaved from the wafers. The first of these sample sets consisted of four samples of silicon with native oxide. The second consisted of four samples of c.a. 300 nm of CVD silicon nitride on silicon (Si_3N_4 on Si), and five samples of c.a. 400 nm thermal silicon dioxide on silicon (SiO_2 on Si) comprised the third set. Prior to the first measurements, the first two sample sets were treated with impure IPA, which provided a slightly contaminated surface with about 0.8 $\pm$ 0.2 nm of contamination as determined via VASE. The IPA was blown off the surface with dry N_2 before

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the samples were measured. The presence of the residue left from the IPA could be clearly seen in a fit to the ellipsometric data. Note the points at zero treatment on the left axis of Fig. 3 and 4. The preparation of the thermal silicon dioxide on silicon samples began as with the first two. However, after the nitrogen blow off, these samples were subjected to a low-pressure, RF, oxygen-containing (that is, an air) plasma for two minutes in a Herrick model PDC 1-HP Plasma Cleaner at high power before the application of FC. FC red, a version of the polymer designed by Photonic Cleaning Technologies[1] for glass and general applications, was the formulation used in these studies.

After sample preparation, the samples were measured via VASE from 50 to 80 degrees in 5 degree intervals. Here, angles are measured from normal incidence. The iterative process for repeatedly measuring FC-applied samples is as follows:

1. Apply FC to the sample surface.
2. Wait for FC to harden enough to place the samples in a sample-storage container. This was typically less than 30 minutes.
3. Place the samples in a desiccator for at least a day.
4. Remove the samples from the desiccator when the time for remeasurement comes.
5. Embed a piece of chemically inert mesh or unwaxed dental floss both provided in a FC kit by applying FC to the coated piece while the mesh or floss is on top of the already cured layer of FC. Wait until this new FC layer is finished curing so the mesh or floss is thoroughly embedded. This step can also be before step 4.
6. Peel off the FC using the embedded mesh or floss.
7. Measure the sample in at least three different spots via VASE and
8. Repeat the sequence starting at the first step for as many FC-application, storage, peel-off and measurement iterations as desired.

The samples were processed as a batch. Thus, they necessarily remained in open air (the lab environment) for anywhere from one half to three hours, based on how many samples were being measured that day. For all sample sets, there was a control sample to which FC was never applied. It was measured at the same time as the FC-applied samples were measured. Later, the VASE measurements of the FC-applied samples were compared with those of the control (non-FC-applied) sample to distinguish the effect of FC application and removal from other aging effects. The relative humidity for both the lab environment and the desiccator were 10%-15% for the majority of the measurements, however, this increased to 25%-30% during the last two peel-off iterations.

Removing First Contact- In most cases, FC peeled off easily. There were exceptions, however. These mostly occurred when floss was used instead of mesh and there was insufficient curing time. The floss could pull through the FC if the FC was not sufficiently cured. In such cases, additional floss and FC was applied and the sample was given sufficient cure time. Towards the latter end of the project, the procedure was amended to avoid the peeled spot on the sample if this were the case. However, this was only observed in a few exceptional measurements and not considered to be a significant effect on the thickness observed. It was observed that the PEEK Mesh was better suited for FC removal. We altered our procedure so that whenever possible, mesh was used instead of floss.

2.2 Sample-set variations

While all sample sets followed the steps described above, for some sets there were additional steps.

2.2.1 CVD silicon nitride on silicon

One of the five FC-applied samples was consistently left outside of the desiccator to see if the exposure to the lab environment would cause any significant differences from the samples stored in the desiccator.

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2.2.2 Thermal silicon dioxide on silicon

The thermal silicon dioxide on silicon samples were prepared later than the first two sample sets. Fewer measurements had, therefore, been made on them by the end of the study. In addition, as mentioned above, all members of this sample set were plasma cleaned *before the first VASE measurements*, so the amount of contamination which was removed by FC from a purposely contaminated thermal oxide sample was not measured.

2.3 Variable-angle, spectroscopic ellipsometry measurements

A J.A. Woollam model RC-2, variable-angle, spectroscopic ellipsometer was used for all VASE measurements. The instrument's light beam is approximately 1 mm diameter. It illuminates an ellipse, wider at low angles of incidence. For example, at 80° from normal the ellipse is almost 6 mm wide. The presence of crosshairs on the ellipsometer stage aided our placing the sample so that the beam hit the desired spot on the sample's surface. Three different spots were measured on each sample, usually one near the center and two closer to the corners along the diagonal. At the beginning of each measurement the sample stage tilt was realigned. No effort was made to measure precisely the same spot on a sample from one FC application, storage and removal iteration to the next. The computed thicknesses thus vary somewhat randomly from one iteration to the next.

2.3.1 VASE modeling and fitting

J. A. Woollam Inc.'s CompleteEase® program was used to fit the chosen model's free parameters to a given sample's ellipsometric measurements. As we built our models, CompleteEase utilized as inputs the optical constants of the material or materials in each layer and estimates of layer thicknesses. The optical constants used for this study are shown in Fig. 2. The user selects which parameters the program adjusts to achieve a best fit to the measured Ψ and Δ values for a given set(s) of measurements.

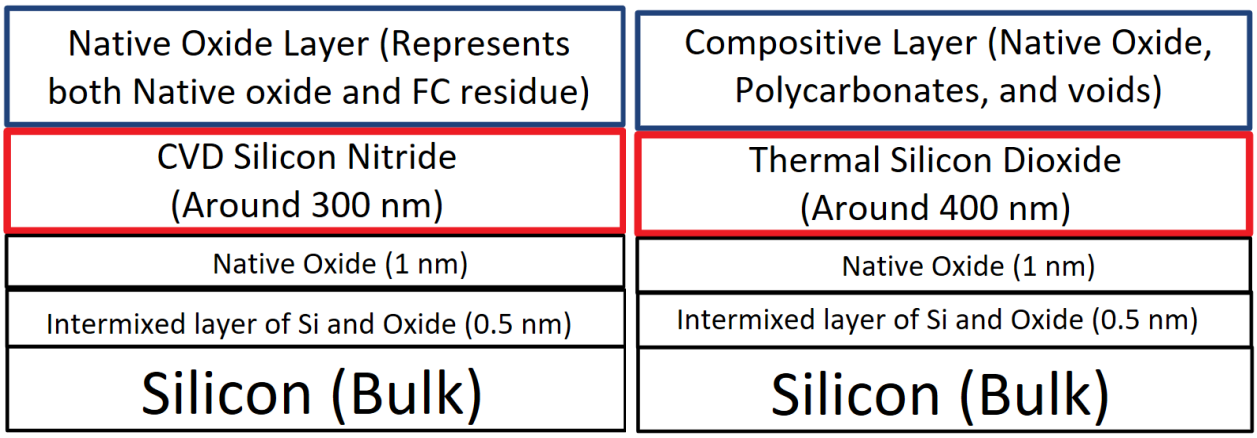
In this study, generally the parameters selected for fitting were layer thicknesses. The top-layer thickness was invariably fit since for the purpose of our study the top layer was a catch-all, containing the surface oxide, the contaminants, and FC residue (if any) lumped together. This is an important point. *For our studies there was no effort to compute the index of the topmost layer.* Generally, the oxide is the largest component of the layer. For the first two sample sets the optical constants of the native oxide that forms on silicon was used as the top layer's optical constants. For the third sample set- thermal silicon dioxide on silicon- the native oxide optical constants failed to fit this layer well. Instead, the top layer was a three-component, effective medium approximation (EMA) layer. In addition to the thickness, the fraction of each component were usually fit. All measurements were recorded for subsequent analysis according to the sample set and peel-off count they corresponded to.

Multi-Sample Analysis (MSA) is a useful feature CompleteEase offers. It allows batch fitting rather than individual datafile fitting. With MSA, thickness values for a given layer in a sample can be calculated either as a best fit for an ensemble of measurements on the sample or for each measurement file individually. For a given Si_3N_4 or SiO_2 sample, represented by Fig. 1, the thickness of the Si_3N_4 or SiO_2 should be the same for all measurements of that sample. MSA allowed us to find that one 'best fit' thickness. On the other hand, we expected the thickness of the topmost layer to change so we allowed the fit to optimize the thickness of that layer for each peel-off measurement. All other thicknesses are either held constant.

CompleteEase can fit every layer in a stack, but it often yields *nonsensical*, unphysical parameter values, if the model parameters are not sufficiently constrained. To obtain realistic thicknesses which are constant or change in a consistent manner from one iteration of applying and removing FC to the next, we found that CompleteEase functioned best when only one stack parameter was changed for a given data set. Therefore, the topmost layer was the layer whose thickness was always fit. It is observed that for a top-surface layer less than a few nanometers thick, VASE measurements can be fit reasonably well using one of variety of different mostly transparent materials. In this study specifically, fits to the measured data yield approximately the same optical thickness for the top layer using materials with an index in the visible range between about 1.4 (many metal fluorides and SiO_2) to about 1.7 (some plastics and aluminum oxide). Optical thickness is the refractive index times the physical thickness.

To properly represent the top layer constituents in CompleteEase, two optical constant variations were devised based on simplicity and MSE reduction. In the first and second sets, the constants used for the topmost layer

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(a) **(b)**

Figure 1. Cross-section diagrams describing the model used to fit the VASE data. a) Cross-section diagram describing the CVD silicon nitride sample set. The model utilizes the optical constants of native oxide for top layer. Both native oxide,contaminants and FC residue are lumped together. A single value of the CVD silicon nitride thickness was determined fitting the entire set of measurements. b) Cross-section diagram describing the thermal silicon dioxide sample set. The topmost layer is an effective medium (EMA) layer using the Bruggeman approximation[10] composed of native oxide,[11] polycarbonate, and void. The top layer thickness, as well as the percentages of each of the constituents, was calculated by CompleteEase for each measurement. As with nitride, the thickness for thermal silicon dioxide is a single value that was fit over the entire set of five samples and all peel-off counts. The roughness was constrained to be 1 nm.

were Woollam's NTVE_JAW2,[11] a "native oxide" layer, shown in Fig. 2a. It is the layer that forms on either silicon and silicon nitride in air over time. As mentioned earlier, we lump any FC residue and other materials into the layer. The layer of silicon nitride uses a Tauc-Lorentz model with a Gaussian at around 7.44 eV and has optical constants shown in Fig. 2b. However, in the case of thermal SiO_2 on Si, the MSE was consistently significantly higher using the constants of NTVE_JAW2. This was an indication that a "native-oxide layer" is not an adequate optical representation of what is on the samples' surface. The optical constants from a mixture of an organic polymer, native oxide, and void for the topmost layer was found to be more successful for this sample set. The organic layer that gradually builds up on surfaces in lab air is often termed 'adventitious carbon'. EDX shows it also contains some oxygen. Hydrogen is also likely present, as is some nitrogen. We selected from the Woollam polycarbonate(Cauchy) optical constant file for this organic material, since it is high index (1.585). In summary, we treated this layer as a composite and had CompleteEase focus on changing this layer's thickness and adjusting the relative fraction of the three components in the layer. The optical constants for these components are in Fig. 2a, d, and e.

To ensure consistency in the CompleteEase analyses from measurement-to-measurement, as well as to focus on the changes to the topmost layer, however subtle, various potential fit parameters were turned off or set to a constant. Roughness is the most important of these potential fit parameters we considered. In CompleteEase, the roughness is defined as an EMA layer composed of half of the topmost layer material and half void, that is, vacuum. Since the amount of roughness is not expect to vary much from measurement to measurement for a given sample, the roughness was held constant for the sample. For all bare Si samples, the roughness was constrained to be 0.5 nm. For all Si_3N_4 on Si and SiO_2 on Si models, the roughness was constrained to be 1 nm. The selection of these values were based on of past experience with of these samples, including atomic force microscope measurements. Bare silicon wafers are notably smoother than those with deposited (ex. Si_3N_4 on Si) or grown (thermal SiO_2 on Si) overlayers. The samples were also assumed to be "ideal" to reduce the fit quantities with CompleteEase. Ideal means that the thickness nonuniformity parameter and angle offset were set to zero in all analyses.

After the thicknesses of each top layer were calculated by the program, these numbers were entered into Excel so that plots could be prepared and statistical analysis could be performed.

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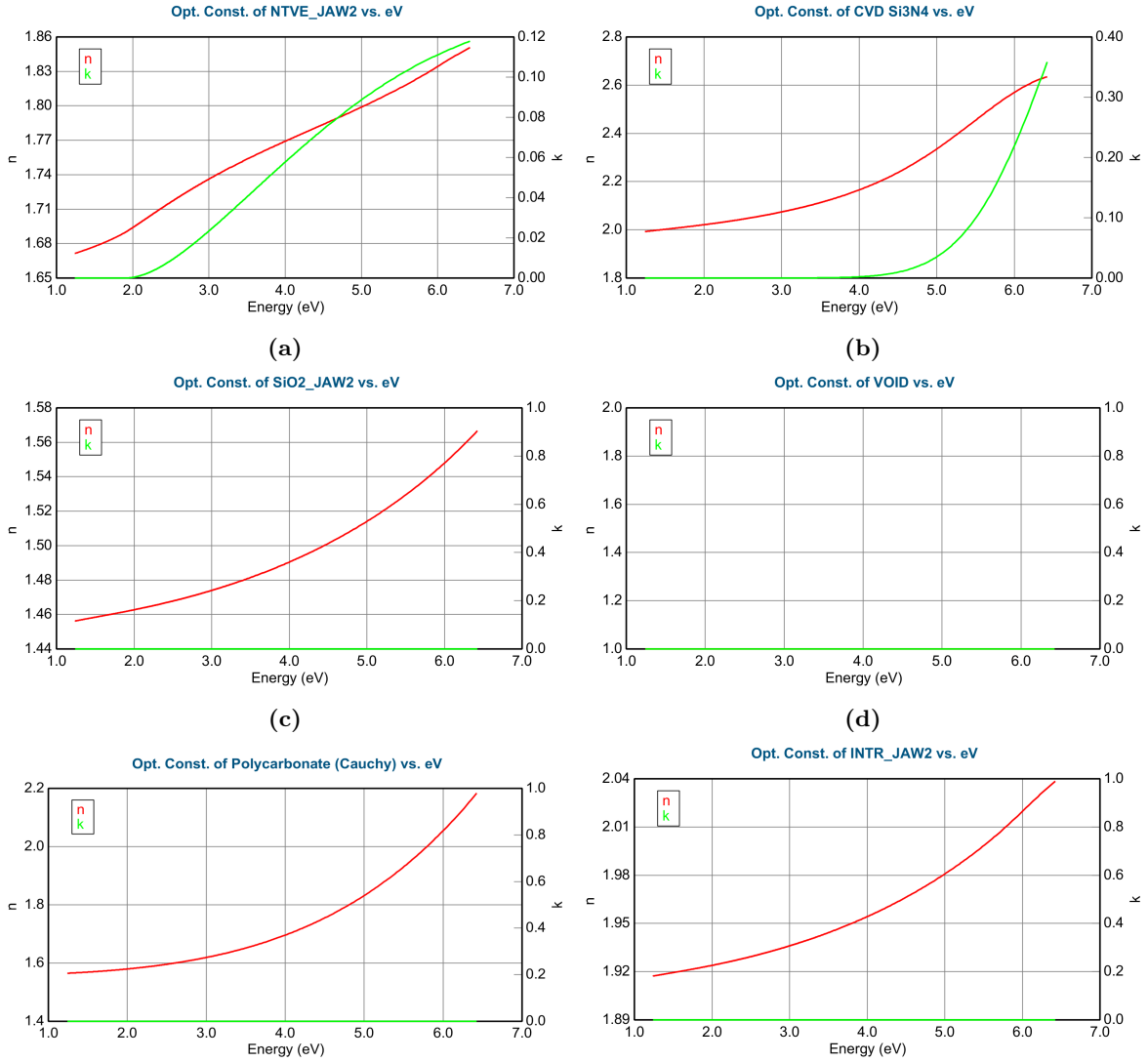


Figure 2. The optical constants of materials used in CompleteEase to create a model to fit the thickness of the samples' top layer. All except the CVD silicon nitride are from Woollam's database: (a) native oxide[11] (b) CVD silicon nitride (c) thermal silicon dioxide[11] (d) void (e) polycarbonate (Cauchy) (f) intermixed silicon dioxide/silicon layer.[11] Note that the top curve-red color-is n, the index of refraction, while the bottom (green) curve is k and its values are read on the right axis.

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2.3.2 Statistical Analysis on Excel

Once the top-layer thicknesses from CompleteEase were transcribed into a spread sheet (Excel), the thicknesses that corresponded to measurements at a specific peel-off count were averaged for each sample in the set. The averaged thicknesses of each FC-applied sample were then averaged together to obtain a quantity termed the sample's average thickness. Various statistical analysis functions were employed to better understand the thickness results. The standard error, which is the standard deviation of all the samples divided by the square root of the number of measurements, was used as the magnitude of the error bar for the measurements. For the control (i.e., no-FC) sample, a standard deviation of the measured thicknesses was calculated using Excel's STDEV.S function.

To determine if differences between samples sets are statistically significant various tests for performed. For example, a t-test comparing the thickness of the FC-applied average samples and the control (non-FC-applied) sample would answer the question if the differences between the two sample thickness distributions were statistically significant. To use the t-test to investigate if the changes to the thickness with peel-off count are statistically significant, we created two trendlines, one for the control sample and the other for the FC-applied samples. To use the t-test to analyze the difference between the FC-applied and the control, the difference of the y-intercepts was subtracted from the set with the larger values (typically the non-FC-applied samples) to create a new thickness value, which is only used for the t-test. If the p-value given by the t-test is less than 0.05, it can be considered statistically significant at the 2σ (95% confidence) level. However, if it is greater, the null hypothesis is refuted only at the level given and therefore the chance is larger that two sample are the same.

For each of the linear regressions for thickness as a function of peel-off counts, that is, for the FC-applied average thickness and for the control thickness, Excel gives an R^2 value and an analysis of how each variable affects the trend. This analysis calculates a p-value that correlates changes in the top layer thickness with the number of peel-offs. If that p-value is less than 0.05, then the null hypothesis, which is that the peel-off count does not affect the top layer thickness, can be rejected at the 95% confidence level. Confidence in the regression p-value relies on the coefficient of determination (R^2) generated from the regression. The R^2 value represents the fraction of the data that can be predicted by the regression model.[12] A low R^2 with a low p-value (< 0.05) indicates there is a large amount of variation with a potentially significant trend occurring.[13]

3. RESULTS

Following the procedure above starting from February 10th, 2023 for CVD Si_3N_4 on Si, February 14th, 2023 for bare Si, and April 17th, 2023 for thermal SiO_2 on Si, the samples were repeatedly measured. The last reported measurement for all samples was on June 16th, 2023.

3.1 FC Observations

The samples were accidentally left in the lab environment two times. These two measurements correspond with peel-off count 10 and 18. However, the value does not appear to differ much from the previous measurement, so it is not considered as significant for the purpose of this analysis.

3.2 Ellipsometric analysis

3.2.1 Bare Si

The application of FC on bare Si provided the most conclusive observations out of the three sample sets. The results are shown in Fig. 3. IPA was applied and blown off, but it left residue on the surface of the samples. This provided the opportunity to not only see the effect of the repeated application of FC, but also the cleaning of a contaminated sample surface at the angstrom level. The difference between the initial thickness of the topmost layer and the thickness of the topmost layer after the first application of FC was 0.9 nm - from 2.78 nm to 1.87 nm. Our interpretation of the difference was that FC was able to clean the contaminant off the sample with a single application. This dramatic difference in top layer thickness is evidence that FC can clean silicon wafers contaminated with impure solvent residue at the angstrom level.

After peel-off count 5, the control sample (no FC applied ever) was cleaved to compare the effect of plasma cleaning on the control sample. As shown in Fig. 3, the top layer thickness of the two control samples were fairly

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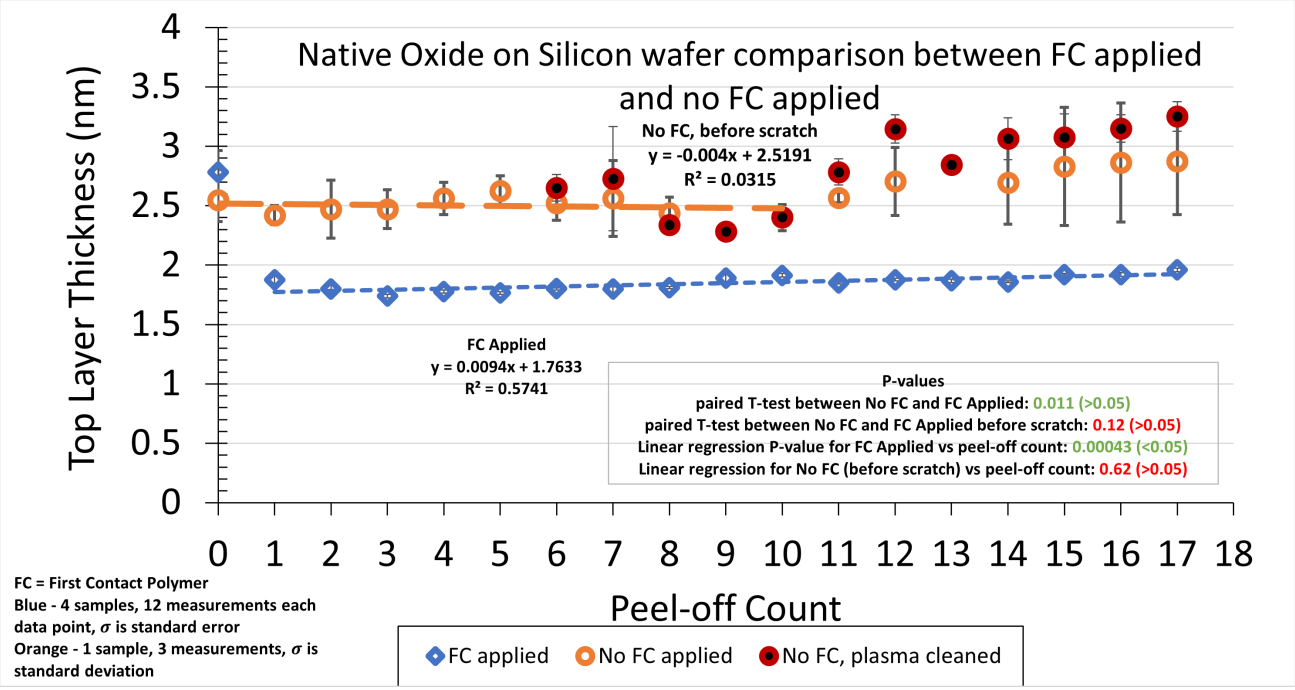


Figure 3. Top-layer thickness for native oxide on Si Tests. FC was applied to four Si wafer pieces. The blue diamonds correspond to the mean thicknesses calculated at each peel-off date. Two other samples were controls and had no FC applied. The orange open circles show the top-layer thicknesses for the IPA-contaminated control sample that had no FC applied. Red, filled circles plot thicknesses of a control sample, plasma-cleaned after the fifth iteration. Thickness uncertainties are within symbols if error bars are not visible. P-values from a paired t-test between FC-applied and the control as well as from the linear regression analysis are also noted. As shown, before FC application, the topmost layer was 2.78 nm while, after FC, the topmost layer was measured as 1.88 nm. The thickness of native oxide on aged Si wafer surfaces is often in this range. The difference of 0.9 nm is significant. The top layer thickness for the FC-applied samples increased very slightly (slope =0.0094) but significantly with peel-off count (P= 0.00043). Before the scratch, the FC-applied and the no-FC-applied control follow similiar trends but become statistically different overall after the scratch (paired t-Test p-value before scratch = 0.12 > 0.05, overall=0.011 < 0.05). The linear regression of the control (the no-FC-applied) sample before the scratch at peel-off count 11 with peel-off count showed no significant increase at the two-sigma level (p-value =0.62, and R^2 value =0.03). Some measurements with the control (no-FC) sample were not made, i.e., peel-off count 9 and 13. The error bars were calculated with the standard error (STDEV.S function in Excel of all the data points corresponding to the peel-off count divided by the square root of the number of data points) for the FC-applied samples. The standard deviations of the control (STDEV.S in Excel) are also displayed on the figure.

consistent until the samples were damaged by their falling on the ground after peel-off count 12. Particulates were then removed by nitrogen blow-off, but the sample was damaged enough to potentially compromise subsequent measurements. This can be observed in the 'No-FC-applied' data in Fig. 3 with the sudden increase after the 11^{th} measurement. We tried to measure around visible scratches. While the scratched area produced in the damage were not measured, the top-layer thickness values for the control sample exhibited a significant increase at this point. Also note that two of the measurements for the sample with-no-FC-applied are missing. The control was not measured on those specific dates due to alignment issues. This missing data does affect the trendline, but it is not expected to increase substantially at those points. From this data, as shown in Fig. 3, we were able to deduce that: 1. FC was able to clean the contaminant off the sample with a single application. 2. There is a significant, though very small, increase in the thickness of the top layer for the FC-applied samples with peel-off counts. This may be due to adventitious carbon.

3.2.2 Si_3N_4 on Si

The figures discussed in this section are 4, 5 and 6. A substantial decrease in the top layer thickness, from 2.06 nm to 1.45 nm was seen due to the initial application and removal of FC. See Fig. 4. This removal of contaminants

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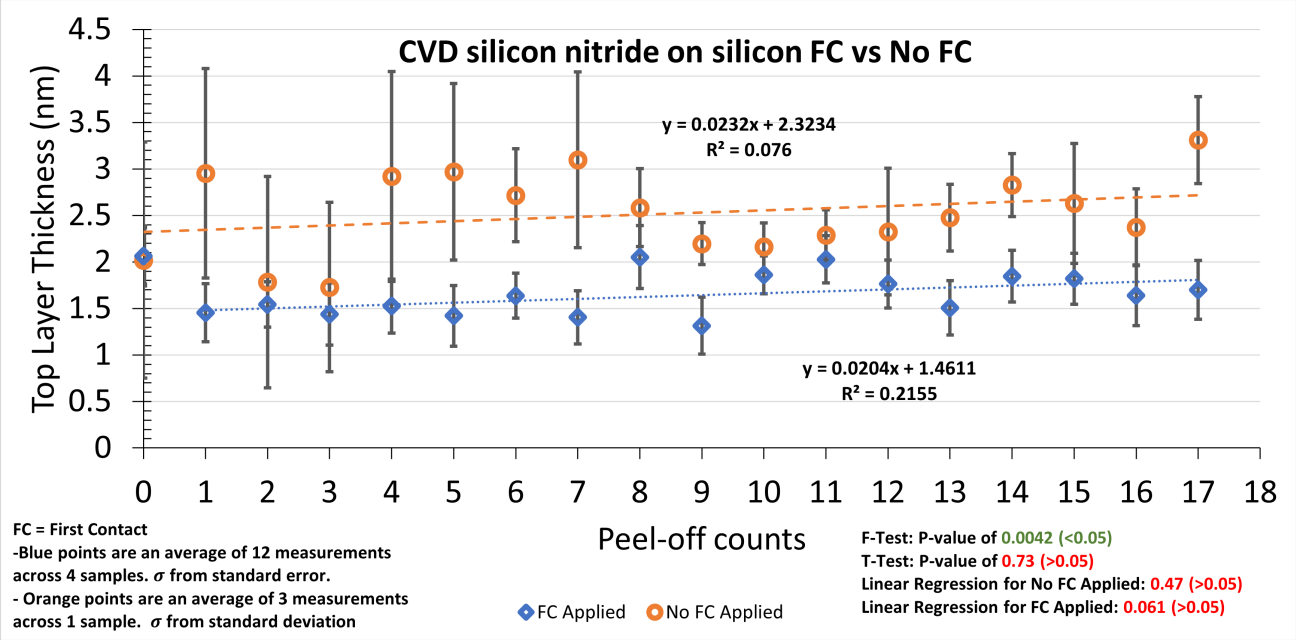


Figure 4. Si_3N_4 on Si The average thickness of four FC-applied CVD silicon nitride on silicon samples are the blue diamonds. The control (orange circles) is a CVD silicon nitride on silicon sample with no FC applied. Both FC-applied and control were stored in a desiccator. As the samples were not necessarily from the same wafer or portion of the same wafer, an F-test was performed to determine if the variances are unequal. The F-test returned a p-value less than 0.05, indicating that the variances are not equal. However, a t-test comparing two samples of unequal variances yielded a p-value of 0.73. Thus, the analysis indicates that the FC-applied samples were not statistically different than the control sample (no FC-applied). The linear regressions of the FC-applied samples measurements and the no FC-applied sample measurements have similar slopes. However, the statistical uncertainties do not support the apparent increase of 0.25 nm in the case of the control. The linear regression for FC-applied is significant at 94%. However, the R^2 value for both are sufficiently small to suggest that in neither case does the trend line fit the apparent increase very well.

at the nm scale was also seen for the native oxide on Si samples. Throughout the subsequent measurements, the top layer thickness increases from 1.45 nm to 1.7 nm. Is the increase significant? Perhaps. Performing a linear regression for the four FC-applied CVD silicon nitride on silicon samples with the independent variable being peel-off counts gives a p-value of 0.061. Thus, there is a 94% chance that it is significant. On the other hand, R^2 for the trend line is small. That is, the data does not follow the trend line well.

These samples were difficult to fit in the ellipsometry model. The MSE for typical fits were around 12. This relatively large MSE characteristic of having a sufficiently thick dielectric layer- CVD Si_3N_4 -on the Si substrate to produce several interference fringes. The parametric optical model for the nitride used in the analysis is not a perfect fit to the optical constants. In addition, not allowing layer thickness nonuniformity, as discussed in the previous sections makes a low MSE fit unlikely. As a result, as shown in Fig. 5, the computed Ψ and Δ functions sometimes failed to match the measured values, particularly at maxima of psi. See, for example, the maxima at about 2.7 eV. Nevertheless, statistical deductions are possible. For example, the p-value of the linear regression on the FC-applied sample data is 0.06 in Fig. 4. This means the top layer thickness increase associated with increasing number of FC-applications and peel-off or, alternatively, with increasing time, is at nearly the two-sigma level.

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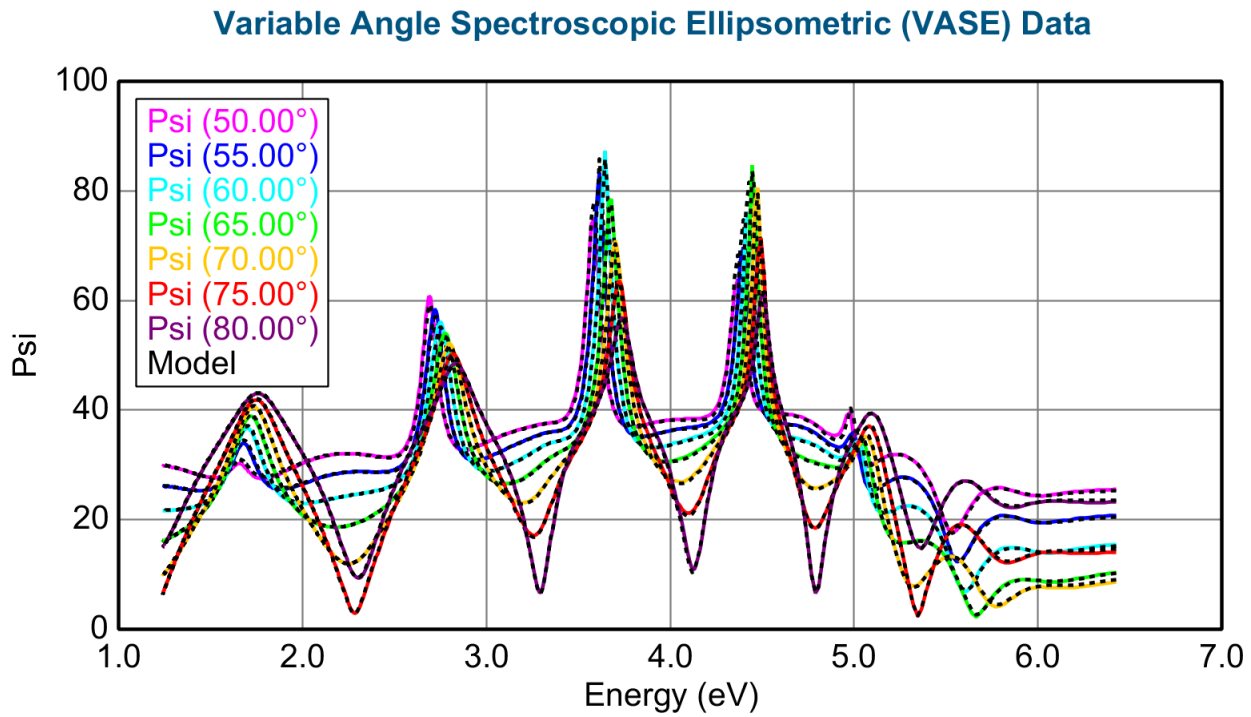


Figure 5. The Ψ values from measurement for the control (no FC applied) CVD silicon nitride sample for peel-off count 17. Note that the challenging of matching the psi values at the high, sharp peaks which may contribute to larger MSE values. The model from Fig. 1a was employed.

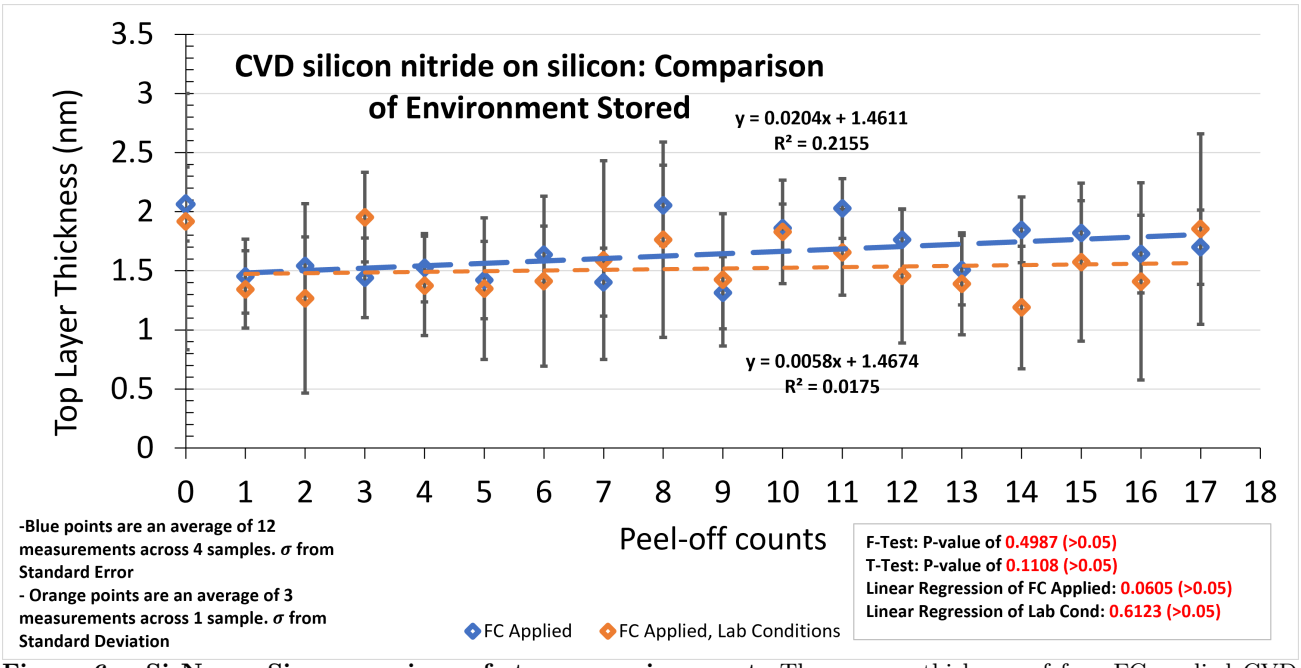


Figure 6. **Si_3N_4 on Si: comparison of storage environments** The average thickness of four FC-applied CVD silicon nitride on silicon samples stored in a desiccator and one FC-applied CVD silicon nitride on silicon sample stored in the lab environment. The p-value from the t-test indicates that there is only an 11% chance that the samples stored in the desiccator and the sample stored in the lab environment are still the same after the storage in the different environments.

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It should be noted that there were some times when the FC-applied average top-layer thickness jumped from 1.4 to 2 nm, but returned to the lower value on the following measurement.

Another issue which can be examined is: "Does the storage ambient make a difference on the changes to the FC-samples?" Shown in Fig. 6, a separate Si_3N_4 on Si sample was left in the lab environment and measured along with the samples kept in the desiccator. The sample measurements were statistically significant only at the 89% confidence level from the ones kept in a desiccator (P-value = 0.111). This indicates that the effect of the different storage environments were marginally similar and could warrant future study.

It is important to note that the control sample was cleaved between peel-off count 5 and 6 just as was the control sample of silicon with native oxide. Unlike the silicon with native oxide, however, fitting the silicon nitride thickness with CompleteEase required to split the batch fitting into two groups: before the cleaving and after the cleaving. The silicon nitride thickness before the cleaving was 298.79 nm while after the cleaving was 297.93 nm. Since this difference in thickness is not in the topmost layer, it is not seen in Fig. 4.

3.3 Thermal SiO_2 on Si

Thermal SiO_2 on Si could not be fit well using the optical constants of the native oxide model- MSE of 15-18. Using a three-component EMA layer where the fraction of each of the components as well as the overall thickness was fit worked better. The MSEs for MSA for the six samples were 9-11. The thickness shown in Fig. 7, 8, and 9 is determined by multiplying the calculated thickness of the topmost layer with the calculated fraction of the particular constituent. The calculated total thickness of the top layer is much larger than the top layers in the other two sample sets. It frequently in the range of 4.5 to 6.8 nm. This thickness is not physical but is an artifact of how the thermal SiO_2 layer thickness is computed. Nevertheless, it is useful to track change on the top of the sample with peel-off counts. As shown in Fig. 7, there is a slight increase in the effective thickness of the native-oxide component of the top layer for both FC and control sample with peel-off count. The t-test gives a p-value of 0.29, which means there is a 29% chance that the measurements are functionally the same.

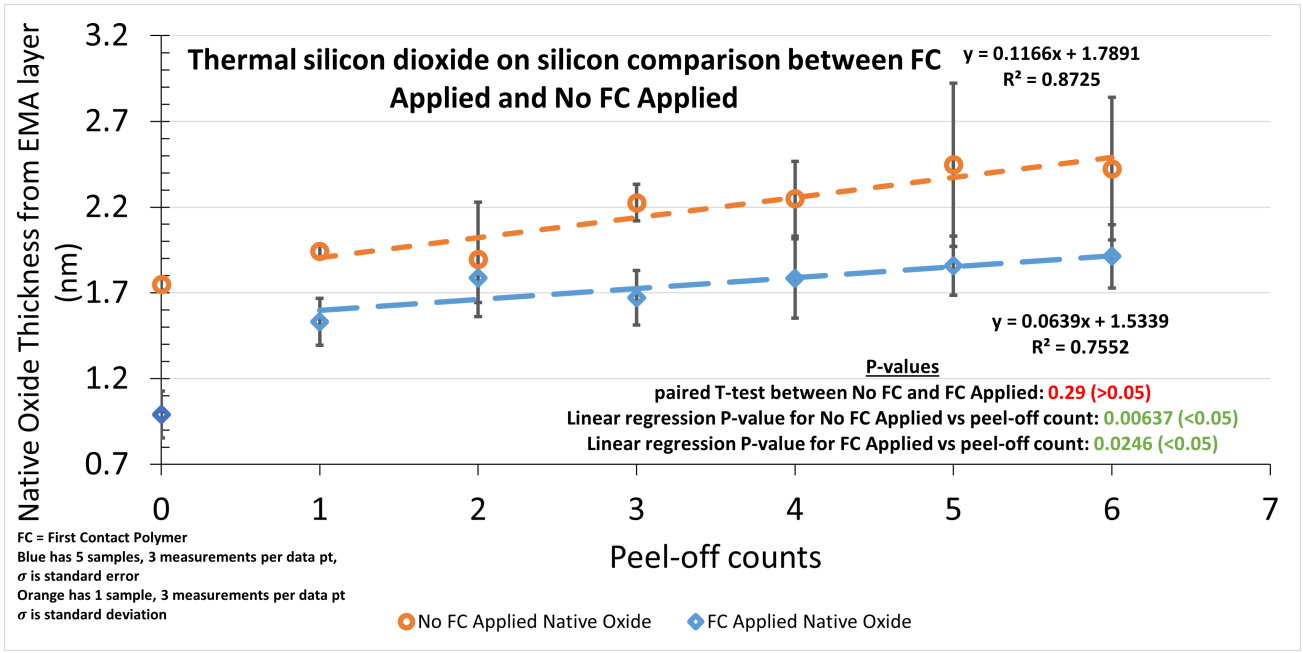


Figure 7. SiO_2 on Si Blue diamonds are the average effective thicknesses of the native oxide in the top layer of five FC-applied thermal silicon dioxide on silicon samples stored in a desiccator. The orange open circles are the thicknesses of the single thermal silicon dioxide on silicon sample with no FC applied stored in a desiccator. The linear regression p-values and R^2 for both FC-applied and control are statistical valid. A paired t-test gives a p-value of 0.29, or 29% chance the changes the samples experienced were functionally the same. Error bars are computed as discussed for the two other sets of samples.

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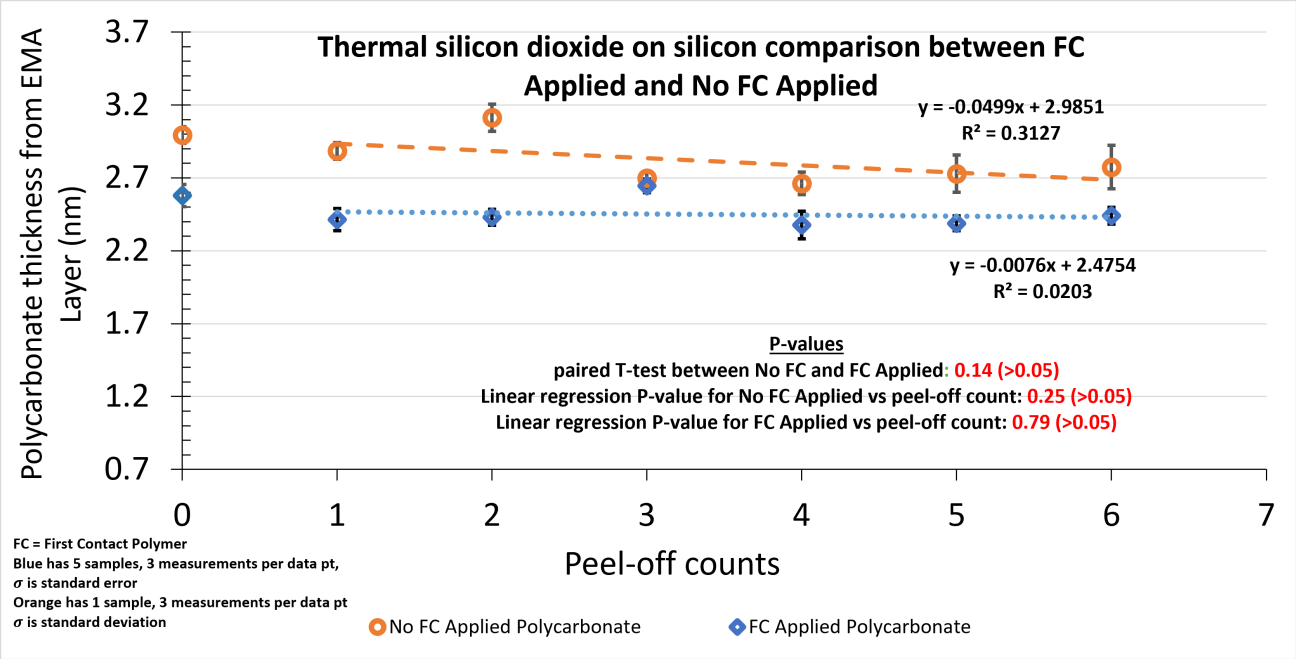


Figure 8. SiO_2 on Si The average 'polycarbonate' thickness (a stand-in for adventitious carbon) for five FC-applied thermal silicon dioxide on silicon samples (blue diamonds) and of one control (orange circles). The paired t-test between control (no FC-applied) sample and the FC-applied sample data was 0.14, or 86% chance that the changes the sample sets experienced were difference. However, the R^2 value for the FC-applied samples suggests there was no trend. Only 2% of these data follow the trend line.

The R^2 value for the FC- applied is 0.76, or 76% of the data follows the linear trend with peel-off counts. To confirm this trend, more data will need to be taken. The p-value from the analysis of the linear regression model suggests there is a 0.6% chance that peel-off counts are not associated with the increase. However, causality is not proven. Since the sample with no FC also increases, it most likely is due to a time increase instead of due to a residue increasing as the peel-off count increases.

The polycarbonate thickness calculated from the EMA layer does not appear to possess a statistically significant difference between the application of FC and the control. The R^2 value for the FC-applied samples is 0.02, which means only 2% of the data seem to follow the trendline. The paired t-test also indicate that there is only a 14% chance that the changes the effective polycarbonate thickness undergoes in the FC-applied sample is functionally the same as the polycarbonate changes seen in the control.

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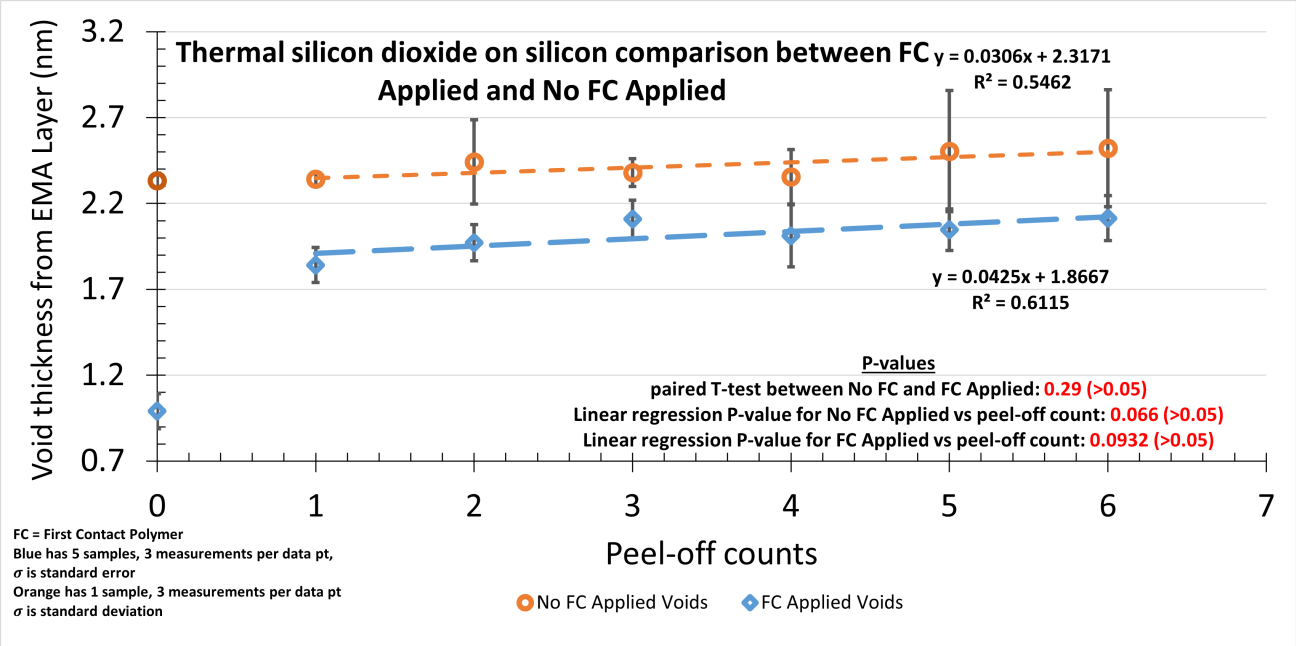


Figure 9. **SiO_2 on Si** The effective thickness of the void, comparing the average void thickness of five FC-applied thermal silicon dioxide on silicon samples and the single control. All were stored in a desiccator. The void thickness, in this case, is associated with porosity or layer roughness. The R^2 values for the FC-applied, and the control (no-FC-applied) are 0.61 and 0.55 respectively, which are large enough to be commentworthy. The p-value from the t-test (0.29) suggests that the changes the FC-applied samples experienced differed from the the control (no-FC-applied) sample only at the one-sigma level.

The R^2 value for voids for the FC-applied sample and control measurements is 0.61 and 0.55 respectively, which are large enough to be considered descriptive. That is 61% of the data points align with the regression model. Thus, in the model the void fraction increases with peel-off counts.

4. DISCUSSION

The MSEs of the three samples set were: approximately 2. (bare Si), 12 to 13(Si_3N_4 on Si), and 9 to 11 (SiO_2 on Si). As stated before, the closer to 1, the better the fit generally. While the fit for the native oxide on silicon set of samples was adequate, the MSE for other two sets are significantly higher than 1. Fig. 5 suggests this why these MSE values are nevertheless acceptable. When the thickness of the SiO_2 or Si_3N_4 films are in a range to produce a substantial number of interference fringes over the 1.24 to 6.5 eV energies of the measurements the effect of any inaccuracies in the optical consonants or small differences in oxide or nitride thicknesses are to produce large differences between measurement and fit values. In our MSA analyses, all measurements were fit by one thickness of the nitride or oxide layer, whereas in fact there are small variations from measurement-to-measurement. Only, the topmost layer was fit individually.

4.1 Bare silicon

There is still about 1.88 nm of native oxide after the first application of FC. This is probably pure native oxide rather than native oxide with contaminants. Further analysis with XPS could determine exactly how much organics are left.

For the repeated FC peel-off, the linear trendline in the FC-applied does increase. The R^2 of the FC-applied trendline is 0.57, as shown in Fig. 3, which means that 57% of the data can be represented by the linear trend with peel-off count. While not 100%, this means that the peel-off counts might influence the thickness. However, the increase was less than an angstrom, so, for many applications, this increase is negligible. Out of the three sample sets, this provides the highest confidence in the regression . The linear regression results of the FC-applied

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as a function of peel-off counts suggest that there was an increase due to peel-off counts. However, the increase was only 0.9 angstroms. The paired t-test also showed a significant difference between the FC-applied sample thicknesses and the no-FC-applied sample thicknesses, but, before the scratch, a paired t-test shows there is an 88% chance the differences are significant.

4.2 CVD silicon nitride on silicon

For the Si_3N_4 on Si samples shown in Fig. 4, the first application and removal of FC appears to have reduced the top-layer thickness by 0.61 nm. While not as much as the silicon wafers, this is a significant difference in thickness. This thickness is compatible with there being no contamination on the surface.

The linear increase in top-layer thickness for the FC-applied samples also continues to increase with increase FC peel-off count. However, it adds 0.25 nm instead of 0.09 nm, so there is a larger increase with peel-off counts. The R^2 is only 0.22, which is fairly low, suggesting that the peel-off counts only correspond with 22% of the increase, and that the peel-off counts most likely do not play a significant role in the increase of top-layer thickness. The p-values for the linear regressions, as shown on Fig. 4, are 0.061 for FC-applied and 0.47 for the control. The low R^2 combined with the p-value from the regression analysis of variation suggests that the sample's top layer thickness does not clearly increase with FC counts and differences may be random.

4.3 Thermal silicon dioxide on silicon

Unlike the previous two sample sets, the top layer of the thermal silicon dioxide on silicon model has three parameters: one thickness and two percentages- one for the native oxide fraction and the second for the void fraction. The resulting calculated thicknesses are presented in Figs. 7, 8, and 9. In contrast with the other two sets, these samples were plasma cleaned before tests began. With the plasma cleaning adsorbed organics and water were removed. That there was nothing that the FC could remove is seen is in Fig. 7. The native oxide effective thickness is 1 nm and jumps to 1.5 nm after first FC peel-off. The FC t-tests, for all constituents, showed that the changes the FC-applied samples experienced were similar to the corresponding control sample with no FC.

There were two trends exhibited in the EMA layer as peel-off count increased. For the native oxide and void constituents, there was a linear trend with R^2 values of 0.76 and 0.61 respectively. While it is shown that there is increase, the control also exhibits similar changes, so the changes may not be directly due to the FC application. In addition, neither this increase nor the apparent increase in native oxide is likely to be physical. Another model is required.

5. SUMMARY AND CONCLUSIONS

In summary, FC is shown to clean a silicon oxide surface contaminated with molecules from impure solvent. The top layer thickness of both bare Si and CVD Si_3N_4 on Si decreased by almost 1 nm due to the first FC peel-off. The VASE determined thickness for the the native oxide is what is expected for such materials in an atomically clean state, though this state was not proven. Statistical analysis suggests that repeated FC application can have a significant effect when compared with control samples (no FC). Statistical analysis of thickness as a function of peel-off count showed an apparent increasing in the top-layer thickness for the three sets. Only in the case of native oxide on Si is the case persuasive at the 2-sigma level and for it the increase is modest at best, smaller than 0.1 nm. The R^2 value was sufficiently large 0.57. Whether this increase is a FC residue or adventitious carbon buildup was not investigated. There is evidence that FC slows the build up of adventitious impurity on the surface of such samples. In the case of the silicon with native oxide, there was thickness increase with an R^2 value of 0.57, but the total increase was smaller than an angstrom. The Si_3N_4 on Si also saw an increase of top layer thickness, but the R^2 of the linear regression was modest (0.22). SiO_2 on Si could be modeled with an EMA top layer. However, due to the fact that three parameters were fit simultaneously, it is difficult to extract meaning from the trends. Thus, while the analysis of trend lines for other cases suggest that there may be and increasing top layer, it is not established that this is surface impurity nor that it is caused by FC application. Another model without voids will be required to make sense of the SiO_2 on Si sample set data.

Further research Using XPS on some of the FC applied samples after the final peel-off could be fruitful. XPS could check our results from VASE as well as show a better illustration of what is happening on the surface.

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Conflict of Interest

This work was partially supported by a grant from Photonic Cleaning Technologies, a company owned by one of the authors, professor Hamilton. Graduate student Joshua Vawdrey received partial support from Photonic Cleaning Technologies. In addition, First Contact Polymer kits provided by the company to perform the measurements.

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