Spring 2010

Interferometric Porosimetry of Porous Silicon with Radius Distribution Functions

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DOI: <https://doi.org/10.31979/etd.qtbu-5gqa>
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INTERFEROMETRIC POROSIMETRY OF POROUS SILICON WITH RADIUS
DISTRIBUTION FUNCTIONS

A Thesis

Presented to

The Faculty of the Department of Chemistry

San Jose State University

In Partial Fulfillment

of the Requirements for the Degree

Master of Science

by

Yu-Chun Lu

May 2010

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The Designated Thesis Committee Approves the Thesis Titled

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DISTRIBUTION FUNCTIONS

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ABSTRACT

INTERFEROMETRIC POROSIMETRY OF POROUS SILICON WITH RADIUS DISTRIBUTION FUNCTIONS

By

Yu Chun Lu

In this study a set of porous silicon (pSi) interferometric vapor sensor were made from p⁺ (~1 Ω-cm) and p⁺⁺ (~0.005 Ω-cm) B-doped Si. The pSi layers were prepared electrochemically, stabilized either by ozone oxidation or 1-octene derivatization, and then characterized. FTIR reflection spectroscopy, scanning electron microscopy, and x-ray spectroscopy of pSi layer cross sections confirmed the completeness of the ozone oxidation and 1-octene hydrosilation. The performance of the pSi layers as interferometric ethanol vapor sensors was assessed by constructing calibration curves of optical thickness change versus ethanol partial pressure and using these to assess the detection limits for ethanol vapor sensing. The interferometric calibration curves were analyzed by fitting them to a BET adsorption and capillary condensation model. The model fits the calibration curves using four parameters: two thermodynamic parameters describing physisorption, plus a mean radius and standard deviation describing the pore size distribution. Acceptable fits were obtained for the p⁺ Si only, and these fits yielded reasonable mean radii that clearly contracted in response to the octene hydrosilation.

ACKNOWLEDGEMENTS

I wish to thank all those who helped me. Without them, I could not have completed this project.

First, I thank my research advisor, Dr. Roger Terrill, who gave me so many suggestions to support me to finish the project and he also helped me to handle my course problems, writing and language issues. Working with him was interesting and I learned a lot from him both in academic and everyday life. There are no words I can use to explain how much I appreciate him.

Moreover, Dr. Joseph Pesek and Dr. John Logan gave me suggestions to modify the thesis. Dr. Michel Goedert and Dr. Anastasia Micheals from the department of chemical and materials engineering trained me to use AFM and SEM to study the surface of the samples. Mr. Mike Stephens helped us to finish the cell for our experiment. I thank them for their help with my experiments.

Also, to every teacher of the classes that I have taken - I thank them for the knowledge and understanding they gave me in the field of chemistry.

I appreciate my friends who encouraged and pushed me to finish the project.

Finally, I thank my parents. Without their financial support, I could not have finished the whole project.

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1. INTRODUCTION

1.1. Background

Thin films of porous silicon (pSi) on polished Si substrates can be generated during the anodic electrochemical or oxidative chemical etching of Si in contact with HF solutions. Depending on the conditions, the anodic porous layers can be prepared with a wide variety of topographies from arrays of independent cylindrical pores to dense networks of nm-dimension pores that may be branched or interconnected. A common attribute of pSi layers formed for technological applications is that their pores are just one to a few tens of nm in average radius but can be made many microns in length, penetrating deeply into the bulk of the Si substrate and with a depth and compositional uniformity sufficient to produce good optical qualities. These pores provide a large surface area for chemical partitioning or binding, and thus pSi films have generated much interest as a sensing medium. In their simplest sensor implementations pSi layers may directly transduce chemical partitioning into the pSi into an electrical signal via impedance modulation of the pSi phase¹, and as such has been used to detect volatile hydrocarbons^{2,3}, various organic vapors⁴, oxygen⁵, and NO₂⁶, CO₂, and H₂⁷. Similarly, the photoluminescence of suitably prepared pSi layers⁸⁻¹⁹ may also be sensitive, via a quenching effect, to the presence of various chemicals such as oxygen,⁵ and aliphatic alcohols²⁰. In this thesis, we explore the qualities of various pSi layers via their optical interferometric response (i.e., iridescence change) to ethanol vapor and subsequently analyze of the apparent pore size distribution pSi phase. Interferometric and related optical spectral analyses of the reflectivity of pSi have been shown to be highly sensitive to the chemical environment of the pSi layer.²¹ As

an additional benefit, freshly prepared pSi also presents a Si-H surface termination that is chemically reactive and allows covalent modification of the surface through hydrosilation, wherein olefins couple to the Si-H surface yielding direct covalent Si-C bonds.

Optimistically one might hope that judicious derivatization may yield pSi sensors with a degree of selectivity to particular analytes or analyte classes.

Optical detection in pSi can be performed in both the visible and infrared²² spectroscopic regimes. This paper focuses on the characterization of pSi layers via calibration to ethanol vapor concentration and analysis of the well-resolved Fabry-Perot interference patterns in the visible and secondarily using mid infrared spectroscopic analysis. These complimentary visible and IR detection modes permit a simple and convenient optical detection to be combined with a selective fingerprinting detection mode. Optical interferometric applications of pSi in chemical sensing have included organic vapor detection^{23,24} as well as studies of proteins such as immunoglobulin G.²⁵ Oxidized (ozone treated) pSi can also be used to detect extremely low concentrations of HF vapor via a simple interferometric transduction mechanism.²⁶

The present report is directed at characterizing pSi layers that can be prepared using electrochemical etches with a long term goal of making biosensors that employ mixed optical and infrared sensing modes. Experiments were performed using a matrix of samples) that characterized the responses of p⁺ and p⁺⁺ Si samples etched for a range of times and then modified for stability either by hydrosilation or ozonolysis. Each sample was characterized by FTIR reflection-absorption spectroscopy and interferometrically in the mid-visible using ethanol vapor of variable concentration. A subset of samples was

analyzed in cross section by scanning electron microscopy and with energy dispersive x-ray analysis in order to characterize the porous layer depth and composition.

1.2. Electrochemical Preparation of pSi Layers

The electrochemical method of pSi preparation was developed in 1958 by Uhliar²⁷ and 1965 by Turner.²⁸ In this method silicon is exposed to HF solution and a constant anodic current is applied. Within a fairly wide range of current density and total charge applied this treatment can yield a porous silicon layer with good optical interference and thickness uniformity. The mechanism of the pSi formation has been studied by Lenmann et al.²⁹ They propose a Si-etching mechanism wherein anodic current results in holes (h⁺) that attack the Si-H bond leaving it exposed to nucleophilic attack by fluoride ions and formation of Si-F bonds and ultimately the removal of Si as SiF₄. The reason for the extreme anisotropy of the etch, i.e., the propensity to form pores rather than etch uniformly, is not conclusively known, but numerous insights have been documented.³⁰ The dopant level in the Si substrate, the HF concentration and surface tension of the etch solution and the current density of the etch process are all important variables. Numerous systematic studies have been made of these parameters, but among the most definitive was the study by Sailor et al. wherein it was shown electrochemical etching of heavily B-doped (p⁺⁺⁺) Si yielded roughly columnar pore arrays of a diameters between roughly 2 and 500 nm that depended in a straightforward way on the etch rate employed.³¹ A more recent review covers a broad range of pore forming conditions.³⁰

1.3. Fabry-Perot Optical Interference by pSi Layers

Electrochemically generated pSi layers will exhibit well resolved Fabry-Perot interference fringes.³² **(Figure 1)** Fabry-Perot interference arises because of interference between light reflected at the air|pSi and pSi|Si interfaces as these rays recombine en-route to the detector. The Fabry-Perot equation describes the maxima in the reflection spectrum at wavelengths, λ , and corresponding to interference orders m , that are a function of the effective refractive index of the layer n and the pSi layer thickness L , which at normal incidence is described by:

Equation 1.
$$m\lambda = 2nL$$

Where m is an integer, λ is the light wavelength, n is the refractive index of the pSi layer, and L is the physical thickness of porous layer. The value n is often referred to as the effective refractive index (n_{EFF}) because the pSi layer is a heterogeneous composite of Si and the medium filling the pores which may be, for example, air, some condensed liquid such as water and perhaps a surface layer such as SiO_2 . The product of n_{EFF} and the physical thickness, L is termed the optical thickness (OT) and is the metric derived from the interferometer. Changes in effective refractive index (Δn_{EFF}) naturally manifest as shifts in the wavelengths ($\Delta\lambda$) of given fringes in the interferogram:

Equation 2.
$$m\Delta\lambda = 2\Delta n_{\text{EFF}} L$$

By recasting the spectral data as reciprocal wavelength ($\bar{\nu} = \frac{1}{\lambda}$, cm^{-1}), we see that maxima in the reflected light intensity (fringes) occur as m - $\bar{\nu}$ pairs that satisfy the equality for a given optical thickness ($n_{\text{EFF}}L$) product:

Equation 3.

$$m = 2n_{EFF} L \bar{\nu}$$

This is illustrated in **Figure 1**, an experimental reflectance spectrum of a thin pSi layer.

The lowest order ($m=1$) peak in the reflection spectrum occurs at the long wavelength (low wavenumber) side of the spectrum. When plotted as reflectivity versus wavenumber (R vs. $\bar{\nu}$), the reflectivity maxima have a frequency of $2n_{EFF}L$. A clear

illustration of how the optical fringe frequency changes with the pSi layer thickness is made in **Figure 2**, which shows the optical reflection spectra of a series of pSi films as a function of their etch time. As the etch time and hence L value increases the number of fringes (and their frequency) increases.

A further implication of Equation 3 is that changes in n_{EFF} of a given pSi layer will be reflected in a change in optical thickness $n_{EFF}L$. Therefore, if chemicals displace air within the pores, n_{EFF} and therefore the optical thickness will change, so optical thickness is proportional to the chemical content of the layer. In this work, the optical thickness of the layer is monitored using a data reduction scheme consisting of a discrete Fourier transform of the optical reflection spectrum (R vs. $\bar{\nu}$, cm^{-1}) as outlined by Sailor et al.³³ and described more fully below. When this transform, $F(R)$, is implemented, it yields a power spectrum with a peak centered on the OT of the pSi layer. The position of the peak along the Fourier x-axis is the average optical thickness. The CCD-spectrometer is capable of quasi-continuously streaming optical power spectra to the computer, which are in turn Fourier transformed in real time permitting us to track relative changes in the

Figure 1. Normal Incidence Optical Reflection Spectrum of pSi Layer. Raw intensity of optical signal is plotted versus wavelength of light. Interference peaks are labeled with interferometric order m.

Figure 2. PSi Interferograms for Series of Increasing Etch Times.

All samples were prepared at low (12 mA/cm^2) current density and were analyzed as prepared.

layer index n_{EFF} as a function of time (since L does not change). **Figure 3** illustrates this process for the case of a sensor chip that is exposed periodically to ethanol vapor and dry air. This figure qualitatively illustrates to important points: Firstly, it confirms that the pSi optical thickness may be derived from the Fourier transformed optical spectrum. This is further illustrated in **Figure 4**, a plot of the derived optical thickness as a function of the total pSi formation (etch) time (and hence charge for this constant current process) of the electrochemical etch that produces the porous layer. As expected, the optical thickness of the layer is a good linear function of the etch time. Secondly, the pSi layer optical thickness increases with exposure to the ethanol vapor (*vide infra*), which is clearly a function of ethanol condensation into the pSi layer that changes the layer's effective refractive index. Hence, the optical interferometric measurement may be used as a sensor for chemicals like ethanol vapor.

1.4. Physisorption and Capillary Condensation in Chemical Vapor Sensing

Two mechanisms contribute to the response of pSi to vapors such as ethanol – physisorption and capillary condensation. In each case, the surface of the pSi promotes the condensation of liquid, and this liquid is then detected as an optical shift. Physisorption may be observed at lower vapor pressures than capillary condensation and contributes a thin, sub to several monolayer thick layer of condensed vapor. The simple theory devised by Brunauer Emmet and Teller, now called BET theory³⁴, has been extremely broadly applied is often successful in describing the qualitative and semiquantitative aspects of such physisorption isotherms – often referred to as “t-curves”

Figure 3. Labview™ Interferometric Analysis Applied to Ethanol Vapor Sensing.

Figure 4. FFT-Derived Optical Thickness of pSi Layers Versus Etch Time.

P-type Si, etched at 12 mA/cm^2 , was used for these experiments and optical thicknesses were measured for chips as they were prepared and without surface modification.

since they describe the thickness of an adsorbed condensed layer as a function of the vapor pressure of the condensing gas. Strictly speaking, BET models describe non-interacting adsorbates and are most successful with non-polar systems such as low temperature dinitrogen adsorption. But the overall shapes of the t-curves are conserved for many condensing gasses, and a host of adaptations to BET theory have been proposed that parameterize in an approximate way these more complex systems. Below is a simple but successful semi-empirical model that describes physisorption in two parameters, c_{BET} and K .³⁵

Equation 4.

$$t = \frac{d_0 c_{BET} K \frac{P}{P_s}}{(1 - K) \left(1 + K (c_{BET} - 1) \frac{P}{P_s} \right)}$$

$$c_{BET} = e^{\left(\frac{\Delta H_{VAP} - \Delta H_{ADS}}{RT} \right)}$$

Where P/P_s is the adsorbate partial saturation pressure, d_0 is monolayer thickness, and K is scaling term. Note that in this model c_{BET} has its classical meaning from BET theory, based on the difference in the heat of adsorption (ΔH_{ADS}) and the heat of condensation (ΔH_{VAP}) of the gas. But, in part to allow for multi-layering, this model also employs a scaling term K that may be adjusted within reason to permit up to several multiples of the monolayer thickness d_0 to accumulate. On a surface where gasses adsorb, this model predicts a Langmuir-like t-curve that rises linearly with partial pressure and then levels off.

The second operative condensation phenomenon is capillary condensation. Nanometre dimension capillaries promote the condensation of gasses, and for very small

pores, this condensation phenomenon occurs below the equilibrium vapor pressures (dew point) of the bulk liquid. Micro-porous^a pSi such as was employed in these studies exhibits capillary condensation. Capillary condensation is driven by the surface energy of the incipient liquid phase and is described approximately for perfect cylindrical capillaries with near zero liquid contact angle by the Kelvin equation³⁶:

Equation 5.

$$r = \frac{-2\gamma V}{RT \ln\left(\frac{P}{P_0}\right)}$$

Where r is the critical capillary radius that promotes capillary condensation, γ is the surface tension of liquid, V is the molar volume of the liquid, R is the gas constant, T is the temperature, P_0 is the saturation vapor pressure of the gas over the bulk liquid, and P is the vapor pressure at which condensation is observed to occur in the capillary. Notably, for ethanol the surface tension is $\gamma_{EtOH} = 0.02227 \text{ N} \cdot \text{m}^{-1}$, yielding $\frac{2\gamma}{RT} = 1.0 \text{ nm}$. Hence, ethanol vapor is expected to condense into 1 nm pores when the relative vapor pressure is:

$$\frac{P}{P_0} \approx \frac{1}{e} \approx 0.4.$$

The capillary condensation phenomenon is well documented in the pSi literature and numerous pSi gas sensors have been described that attribute their sensitivity to capillary condensation.²⁴ In reports employing optical detection modalities, the condensation is detected by the increase it makes in the pSi layer effective refractive index. This increase is intuitive because the voids are originally filled with air, $n \sim 1.00$, and this air is displaced

^a IUPAC classifies pSi based on average pore radius as: micro ($r < 10 \text{ nm}$), meso ($10 < r < 50 \text{ nm}$) and

by, e.g. ethanol of $n \sim 1.35$ when capillary condensation takes place. The detailed proportionality between the pSi layer effective refractive index (n_{EFF}) and the volume fraction of ethanol is described by various models including the Bruggeman effective medium approximation (EMA).^{37,38} $\sum_i f_i \frac{n_i^2 - n_{\text{eff}}^2}{n_i^2 + (d-1)n_{\text{eff}}^2} = 0$ where n_i are the refractive indices of phases i , f_i are their volume fractions, d is the system dimensionality (3 for the microporous pSi used herein) and n_{eff} is the pSi phase effective refractive index. Importantly, this EMA, which has been employed for pSi characterization by a number of groups^{39,31} predict a nearly linear proportionality between n_{EFF} of the pSi layer and the volume fraction of the liquid filling the voids in the surface, and do so without an explicit pore size dependence within the long wavelength approximation of the EMA (i.e. when the optical wavelength is much greater than the pore size – easily satisfied for microporous pSi and visible light). Also, the proportionality between optical thickness shift and volume of condensed gas has been theoretically confirmed in a number of papers.^{40,41,42}

In experimental studies using interferometric, ellipsometric and other measurements of optical thickness or closely related phenomena, capillary condensation in pSi typically leads to quasi-linear, curving or sigmoidal calibrations of optical shift versus gas vapor pressure. This work aims to improve our understanding of the distribution of effective pore radii that result from different pSi preparation modes and to introduce a simple approximate method for deriving pore size distributions from interferometric data. The derivation of pore-radius distribution information from such calibration curves is made in the results and discussion section below.

macro-porous ($50 \text{ nm} < r$) pSi.

2. EXPERIMENTAL

2.1. PSi Sample Preparation

Two kinds of <100> oriented, B-doped p-type silicon wafers were used in experiments in this thesis; a heavily doped variety that we designate p⁺⁺, which has a resistivity of $\rho < 0.005 \text{ } \Omega\text{-cm}$ (Silicon Quest International Inc.) and a p⁺ one with $\rho \sim 1 \text{ to } 2 \text{ } \Omega\text{-cm}$ (donated by the San Jose State University Department of Materials Engineering).

Porous Si layers were prepared by electrochemical etching procedures as described by Sailor et al. (see for example Janshoff et al.³¹ and references therein). In this work, the back side of the Si wafer was coated with 25 nm of gold to increase the electrical conductivity and the quality of the electrical contact between the Si coupon and the aluminum anode contact of the etch cell. Gold coating was carried out with a Denton Vacuum DV-515 resistive evaporator operating at roughly 10^{-5} T .

After gold coating, Si wafers were cleaved into ~ 0.5 by 0.5 inch coupons for installation into the Teflon® electrochemical etch cell (**Figure 5**) that employs an o-ring contact that exposes approximately 0.5 cm^2 of Si surface to the cell. Etch processes were performed under constant current conditions and with an HF based electrolyte made from a 3:1 volume ratio of ethanol (anhydrous, 200 proof, Sigma-Aldrich 99.5%+) and 48% aqueous HF (Mallinckrodt). Constant current etches were performed with an EG&G PAR 273 potentiostat and M270 software. Samples were etched at either 12 mA/cm^2 or 300 mA/cm^2 . The main comparative data set uses the 300 mA/cm^2 protocol and 5, 10, 15 or 20 seconds of etch time⁴³. After etching, pSi coupons were rinsed with ethanol, dried in air, and promptly subjected to surface modification as described below.

Figure 5. Diagram of Teflon® Electrochemical Etch Cell.

Si coupon is placed between an aluminum block anode and a sealed to the cell with a Teflon-coated o-ring. The etch solution is comprised of 3:1 ethanol: 30% aqueous HF. The cathode is a coiled platinum wire. The etch is performed by applying a constant current to the cell.

2.2. Psi Sample Surface Modification

Porous Si surfaces formed in HF electrolytes are heavily terminated with Si-H (silicon hydride) that undergoes a slow oxidation process in air. In this work, stabilization of the as-formed pSi was carried out with either ozone, quickly yielding an oxidized, and polar SiO_x / SiOH surface, or with 1-octene, via hydrosilation as described below.

Hydrosilation is a reaction in which an olefin, in this case 1-octene, is coupled to silicon hydride yielding a Si-C bond to octane and yielding a hydrophobic interior surface. Hydrosilation, by similar means has been well documented in recent years on both H-terminated, planar⁴⁴ and electrochemically prepared porous Si surfaces⁴⁵. The 1-octene modification was carried out as follows: immediately following pSi formation pSi chips were put into 100 mL of neat 1-octene (98%, Aldrich Chemical Company, Inc.) to which 1000 μ L of H₂PtCl₄ solution (1% in isopropanol) had been added as a catalyst. The catalyst, 1-octene and pSi were held at 40 °C for 16 hours under nitrogen and using a 15° C condenser. Upon removal, pSi specimens were rinsed copiously with toluene and ethanol and dried in a N₂ stream.

Ozone was produced using O₂ and a low-pressure Hg penlamp (4 inch, 25 W, UVP Inc.) in a simple flow-system constructed from glass and Teflon. In this system, oxygen gas was passed at ~5 mL min⁻¹ over the penlamp housed in a 50 mL glass test tube and then following partial conversion to ozone, the mixed oxygen and ozone was directed to the pSi surface via $\frac{1}{16}$ inch O.D. Teflon tubing. In-situ measurements of ozonolysis via interferometry were made to confirm the time required to fully oxidize the pSi surface,

which appears to take approximately five minutes to complete (**Figure 6**).

FTIR analysis of these chips confirmed the presence of the octane moiety via the appearance of CH stretching intensity, the disappearance of Si-H intensity and the substantial suppression of oxide formation. A typical example of this result is illustrated in **Figure 7**.

Fourier transform infrared (FTIR) spectroscopy (Perkin Elmer System 2000) was used extensively to characterize the pSi layers. Because the more highly doped Si substrate is opaque to IR radiation, a specular-reflection geometry was used to acquire the absorbance spectra of the pSi layers. To do this we employed a Harrick Scientific Seagull® variable angle reflection accessory set to grazing (75° from normal) incidence. Three primary spectral regions were analyzed: 2100 cm^{-1} , where clear Si-H stretching modes can be seen, 3000 cm^{-1} where C-H stretching modes can be seen, and 1100 cm^{-1} where stretching modes attributable to the Si-O-Si linkage appear.⁴⁶ (See **Figure 7** and **Figure 8**)

2.3. Interferometer and Software

Visible wavelength (350-1000 nm) reflection spectra were acquired from the pSi layer in a flow cell setting as illustrated in **Figure 9**. In this system, light from a quartz

Figure 6. Real Time Optical Thickness Versus Ozone Exposure Time.

The pSi specimen was made by a 150 second etch at 12 mA/cm^2 . The specimen was then transferred to a gas flow cell under O_2 and at the indicated time an O_3 generation source was turned on initiating superficial oxidation of the pSi surface from SiH to SiO_2 .

Figure 7. FTIR Spectra Illustrating 1-Octene Hydrosilation.

This specimen was prepared using p++ Si with a 5 second etch time at 300mA/cm² current density and was derivatized in 1-Octene with H₂PtCl₄ catalyst 16 hours. a. SiC-H stretch, b. Si-Hx stretch x=1-3, c. possible Si-O-Si stretch, d. CH bend. FTIR spectra acquired with reflection mode at 75 degree.

Figure 8. FTIR Spectra Illustrating Ozonolysis.

This specimen was prepared from p+ Si for 150 s at 12mA/cm². Top curve is freshly prepared pSi, bottom follows 100 min. O₃ exposure. a. SiO-H stretch, b. Si-H_x stretch x=1-3, c. Si-O-Si/Si-OH stretch. FTIR spectra were acquired in external reflection mode at 75°.

Figure 9. Block Diagram of Interferometry System.

This system comprises a white light source coupled to a 400 micron optical fiber and bifurcated probe that directs the beam down to the pSi surface and collects the reflected light. The gas flow cell contains the pSi coupon. Reflected light is collected by the fiber optic probe and directed into a CCD-based spectrometer and computer. Light is reflected and undergoes Fabry-Perot interference within the pSi layer as indicated in the diagram on the lower right.

tungsten-halogen lamp is coupled into a 400 micron optical fiber and directed via a fiber-optic reflection probe into a gas flow cell containing the pSi specimen. The reflected light is directed into the CCD spectrometer (Ocean Optics USB650) and spectra are integrated (5 ms) and streamed into the computer for analysis. Analysis is achieved via a real-time fast-Fourier transform (FFT) following Anglin and Sailor.³³ This analysis entails the conversion of the wavelength axis from nanometers into wavenumbers (cm^{-1}), re-sorting the data into ascending wavenumber order, linear interpolation to generate a spectrum containing 4096 reflectivity points on an even cm^{-1} abscissa, a fast Fourier transform to generate a 2048-point power spectrum of light power with new abscissa in units of cm^{-1} . The power spectrum then naturally presents a peak centered on the frequency of the quasi-sinusoidal oscillation in light power comprising the Fabry-Perot interferogram, and hence at twice the pSi layer optical thickness, $2n_{\text{EFF}}L$. The algorithm we used to identify the exact position of the peak is a simple center-of-mass calculation which takes the average of the abscissa (cm^{-1}) values in the region of the peak weighted by their relative intensities (ordinate values proportional to light power). The result is a quasi-continuous monitor of optical thickness (OT) as a function of time that is clearly responsive to capillary condensation as illustrated for ethanol in **Figure 3**.

2.4. Ethanol Vapor Pressure Control System

In order to calibrate the pSi response, we built an ethanol vapor dilution system as illustrated in **Figure 10**. The apparatus uses two metering valves, serial ethanol vapor

Figure 10. Ethanol Vapor Dilution Apparatus.

Dry air is mixed in different proportions with ethanol vapor saturated dry air. Individual flow rates are measured using the floating ball flow meter and then the total flow is measured. A reproducible protocol for gas mixing was established and calibrated using transmission FTIR to accurately relate flow settings to ethanol vapor partial pressure.

saturation (bubblers) and a single floating ball flow meter. A flow of dry air at 15 pSi is split and directed to two metering valves. The valves are set to achieve the desired flow rates and regulate down to a pressure of 0-1 psi. One of the two flows is passed into a series of two ethanol vapor saturators before being rejoined to the first flow and passing into the cell. Protocol for establishing reliable ethanol vapor pressures is as follows: first ethanol saturated air flow is stopped with a cutoff valve and the dry air flow is established at half of the full scale of the flow-meter. Next the ethanol vapor flow is turned on and adjusted to the desired target value for the total flow. The nominal ethanol vapor saturation is then defined as the total flow rate minus the dry air flow rate ethanol saturated flow rate divided by the total flow rate:

Equation 6.
$$S_{NOM} = \frac{f_{TOT} - f_{DRY}}{f_{TOT}}$$

To then generate saturations greater than 0.5, the initial dry air flow is simply lowered incrementally to zero and the dry air flow f_{DRY} computed by difference. This protocol, which starts with dry air ($S_{NOM} = 0$) and ends with saturated vapor ($S_{NOM} = 1$), can then be reasonably well reproduced and results in a predictable nonlinearity in nominal saturation, S_{NOM} , that can be corrected and converted to relative saturation using a calibration curve that is constructed as follows. The calibration of S versus S_{NOM} was implemented by generating a series of gas flows at a series of S_{NOM} values using the above protocol and at each point recording the integrated IR absorbance between 2850 and 3100 cm^{-1} of the gas stream in a 10 cm path-length cell. Since the IR absorbance of the CH stretching region is expected to be linear for ethanol vapor, this value is used to compute the true relative

saturation S . A second-order polynomial was then fit to the curve that results from a plot of S versus S_{NOM} . Subsequent measurements employed this calibration curve, shown in **Figure 11**, to establish the true ethanol partial pressure.

It is very likely that some hysteresis exists in the capillary condensation response of the pSi samples used.⁴⁷ In other words, the uptake of liquid by the pSi from the vapor during a gradual increase in vapor pressure will likely be different functionally from the loss of vapor upon gradual reduction of contacting vapor pressure. Therefore, in this protocol, calibration curves are normally constructed while successively increasing the relative saturation.

2.5. Scanning Electron Microscopy and Energy Dispersive X-Ray Analysis

Cross sections of the cleaved Si coupons were imaged and analyzed using an FEI Quanta 200 scanning electron microscope. A beam energy of 10 keV was typically used and the angle incidence was typically within 5 to 10 degrees of the surface normal. Once identified in the SEM image, the pSi layer was analyzed in cross-section with an energy-dispersive x-ray system in order to quantify the relative atomic abundances of Si, O, C, and in some cases F as a function of depth within the pSi layer.

3. RESULTS AND DISCUSSION

3.1. Preparation of pSi Layers

Figure 2 contrasts the reflection spectra of a series of pSi layers prepared from p+ pSi and etched for increasing times but at the same current density ($12 \text{ mA}\cdot\text{cm}^{-2}$). The fringe-patterns clearly increase in frequency, and substantially more peaks are evident in the spectra of pSi layers etched for a longer time – an expected consequence of increasing pSi layer thickness. Beyond 240 s, a loss of finesse, i.e., peak-valley resolution, is observed, indicating that for these preparation conditions, there is very likely an optimal etch time that maximizes the sensor properties of the pSi layer (*vide infra*). **Figure 4** illustrates that the FFT-derived optical thicknesses of the pSi layers increases linearly with etch time, which is consistent with similar reports that the etching rate appears to be constant as the pSi layer thickens. The general phenomenon of interferometric fringing and its dependence on the pSi layer thickness can also be seen in the infrared wavelength reflections as is clearly evident in **Figure 12** and **Figure 13**, which contrast the 5,10,15, and 20 s etches for p+ and p++ pSi layers respectively. Also evident in these spectra are the Si-H stretching 2115 cm^{-1} and bending 915 cm^{-1} resonances⁴⁴ and additional complex bands in the $500\text{-}750 \text{ cm}^{-1}$ range that appear to increase in intensity as the etch time increases.

3.2. Electron Microscopic and X-ray Characterization of Oxidized pSi

Scanning electron microscopy (SEM) was performed on a substantial number of as-prepared and ozone oxidized pSi layer cross sections. In order to image the pSi layer

Figure 11. Ethanol Vapor Pressure Calibration Curve.

This curve was used to correct nominal saturation values from the flow mixing apparatus into true ethanol vapor pressures assessed using transmission FTIR absorbance spectroscopy.

Figure 12. FTIR Spectra Contrasting Etch Times for p⁺ Specimens.

Specimens were prepared from p⁺ Si and spectra were recorded in reflection mode at 75° of as-prepared pSi samples. Note the increase in Fabry-Perot oscillation frequency as the etch time increases. Samples were prepared at 300 mA/cm² current density.

Figure 13. FTIR Spectra Contrasting Etch Times for p++ Specimens.

brightness and hazier texture in the SEM image than the solid Si substrate. Sometimes, e.g., in **Figure 14**, these SEM images presented a bright line that cut across the pSi layer. In these cases we examined the idea that this line corresponded to the bottom of the pSi layer, but rejected it mainly because its shallow depth implies an unreasonably large n_{EFF} considering the interferometric measurement of OT, but also because the elemental composition (*vide infra*) of the cross section does not change abruptly at this point.

Rather, in **Figure 14**, the pSi layer appears to extend further into the Si and probably extends as deeply as the scalloping in the image. To further explore the physical depth of the pSi layer we used the SEM to measure the elemental composition of the pSi layer in a depth profile motif. This mapping was done using energy dispersive x-ray spectral (EDS) analysis of line scans taken parallel to the pSi surface but at increasing depth below the surface. For each scan the approximate relative elemental abundances of Si, C and O are plotted alongside the SEM image. The resulting depth profiles indicate by the loss of O and C signals that the depth of penetration of the pSi layer into the pSi surface is roughly five microns. Judging by the O- and Si-concentration profiles, the ozone-oxidation of the pSi layer appears to penetrate to the bottom of the pSi layer. As the pSi layer terminates the elemental composition changes to pure Si. The source of the carbon signal is unknown, but, one may surmise that the remaining material is SiO_2 since the atomic abundance of O is almost exactly twice that of Si.^{31,46} Comparison of the SEM-identified physical thickness, L , of the pSi layer to the optical thickness ($n_{\text{EFF}}L$) obtained from optical

interferometry affords a rough estimate of $n_{\text{EFF}} \sim 2.8$ for pSi as we prepare it herein.^b This is a reasonable value considering the constituents of the pSi layer and their respective refractive indices: Si ($n \sim 4$), SiO₂ ($n \sim 1.5$) and vacuum ($n=1$). The time evolution of the O-abundance profile within the pSi layer as a function of ozone exposure time can also be estimated using the EDS measurement.

Figure 15 illustrates a series of measurements made on identically prepared pSi layers that were ozone treated for the indicated times, cleaved and analyzed by SEM. In this case it is clearly evident that extensive ozone exposure time, at least up to 100 minutes, can increase oxidation within the pSi layer. It also appears, based on these measurements, that with time the O-profile deepens in such a way as to imply that oxidation of the pSi surface layer begins at the outermost part and evolves inward toward the pSi-Si interface over a time as long as 100 minutes.

3.3. FTIR Characterization of the Ozone Oxidation Process

Similarly, FTIR spectra (**Figure 16**) acquired from a freshly prepared pSi layer that is periodically removed from the spectrometer and ozone-treated corroborate this picture of oxidation but emphasize the relatively fast initial oxidation processes. The superficial SiH layer is destroyed quickly as evidenced by the almost immediate loss of

^b This value is derived from a simple calculation, for example, as follows: The optical thickness of a pSi layer formed at 12mA cm^{-2} and for 180 seconds was approximately 3.5 microns, (**Figure 15**) and the $OT = n_{\text{EFF}}L$ in our interferometer is $9.6\mu\text{m}$, hence $n_{\text{EFF}} \approx 2.8$.

Figure 14. Scanning Electron Micrograph of Cleaved Edge of pSi Layer.

Layer was electrochemically etched into p-Si and subsequently oxidized with ozone. The physical thickness of the pSi layer, inferred by the change in texture and shade, indicates a physical thickness of about 6 μm . The corresponding optical thickness ($n_{\text{EFF}}L$) was approximately 9 μm in dry air, hence the average effective refractive index was may be inferred to be approximately $n_{\text{EFF}} \sim 1.5$. Oxygen, silicon and carbon were evident in the x-ray emission spectra and their corresponding depth profiles are plotted on the left. It is not clear what the bright feature in the SEM image near two microns is, but optical interferometry and ozone oxygen penetration indicate that the porous layer is nearer to 5 or 6 microns.

Figure 15. SEM-EDS X-Ray Spectral Oxygen Depth Profiles.

The above oxygen depth profiles were acquired for a series of ozone treated pSi layers as a function of O_3 exposure time. pSi layers were prepared at 12 mA/cm^2 and for 180 seconds, ozone oxidized, cleaved and measured by SEM for the indicated times.

Figure 16. Reflection FTIR (75°) Analysis of Ozone Treatment Time.

In this study, p+ Si coupons were etched for 150s at 12mA/cm². Independently prepared pSi specimens were ozone oxidized for 0,2,3,5,10,20,30 and 40 minutes. The peak at ~1225 cm⁻¹ is attributable to Si-O-Si stretching modes and appears within two minutes of exposure to ozone. The peak at 2100 cm⁻¹ is attributed to the Si-H stretching mode and is gone after 5 minutes of ozone treatment.

SiH stretching mode intensity near 2100 cm^{-1} . These bands, strong in the as-prepared samples, are almost completely gone after the first two minutes and are clearly gone after three minutes of exposure. Si-O-Si stretching modes near $1200\text{-}1250\text{ cm}^{-1}$ are slower to evolve and appear to gradually increase in intensity for approximately the first 15 minutes of O_3 exposure.

3.4. In-Situ Interferometric Analysis of Ozone Oxidation

The optical interferometric measurement was also made *in-situ* during ozone exposure. **Figure 6** illustrates an experiment wherein a freshly prepared pSi sample was inserted into the optical reflection cell under a flow of dry O_2 . After approximately 60 s, the ozone generator was turned on and O_3 –oxidation was observed to commence at about 100 s. This measurement indicates that the O_3 oxidation is complete in approximately 300 s under these conditions. All subsequent O_3 treatments were therefore made for 300s anticipating that this should produce a stable SiO_2 surface where chemical measurements would be relatively unaffected by further growth of native oxide within the pSi layer.

3.5. FTIR Characterization of 1-Octene Modified pSi Layers

The 1-octene hydrosilation process was not similarly optimized. Instead we rely on the stability of the optical response of the octane-modified pSi as an assurance that the modification protocol is sufficiently complete, and the pSi layer sufficiently passivated, that ambient Si-oxidation is not important during subsequent measurements. FTIR

measurements like those **Figure 7** indicate that along with the incorporated octyl groups (as evidenced by the CH stretching modes near 3000 cm^{-1}) there is a complete loss of Si-H stretching intensity but no evidence of an oxide similar to that found in ozone-treated pSi since there is no appreciable Si-O-Si stretching evident near 1250 cm^{-1} . The origin of the broad band that appears near 1000 cm^{-1} in the hydrosilated pSi is unclear. It may be Si-O related, or it may possibly be associated with bound octane, but it does not appear in the liquid phase IR spectrum of neat octane, and similar bands are only weakly observed in small branched hydrocarbons such as 2-methylbutane. Weak modes near 1400 cm^{-1} in hydrosilated pSi may be attributable to CH bending along the hydrocarbon backbone. Overall, the rinse- and oxidation-resistant hydrocarbon bands in the IR suggest a successful covalent octyl modification on the pSi surface.

3.6. Calibration of Interferometric Response to Ethanol Vapor Condensation

One objective of this investigation was to optimize the performance of pSi interferometric vapor sensors by exploring the following pSi preparation parameters: layer thickness, surface modification (1-octene or ozone) and boron doping level in the Si (p+, $\sim 1\text{ }\Omega\text{-cm}$ vs. p++, $\sim 0.005\text{ }\Omega\text{-cm}$). The experimental design is illustrated in Table 1. The sixteen pSi specimens used in this final stage of the project were prepared homologously to those analyzed above and at $300\text{ mA}\cdot\text{cm}^{-2}$, assessed with FTIR (see **Figure 12** and **Figure 13**) and then surface modified and calibrated as ethanol vapor sensors. The ethanol vapor response was then analyzed in terms of the signal and noise magnitudes to assess a detection limit and the shape of the calibration curve of optical thickness change versus

ethanol vapor pressure to characterize the pore-size distributions.

3.7. Calibration Sensitivity, Noise Level and Limits of Detection

Our original prejudice was that a thicker pSi layer, with its anticipated larger change in optical thickness and larger capacity for uptake of liquid, would make a superior sensor. The following critique examines this assumption. Within the range of preparation conditions we found that the optical thickness change for saturated ethanol vapor exposure did indeed scale with the layer thickness (**Figure 17**, top), but that the relative change *did not* significantly change with layer thickness (**Figure 17**, bottom). Note that relative change, $\Delta OT\%$, is parameterized as follows:

Equation 7:
$$\Delta OT\% = 100\% \frac{OT - OT_0}{OT_0}$$

where OT_0 is the dry layer optical thickness and OT is the optical thickness at a given ethanol partial pressure. This may be interpreted to mean that the layers are reasonably uniform compositionally as they are etched deeper into the Si substrate. If this were not the case, for example if more extensive etching increased the average porosity of the layer substantially, then this it is unlikely that the relative change in optical thickness would be invariant to etch thickness. The largest relative increases in $\Delta OT\%$ were observed, in **Figure 17**, bottom, for the ozone-oxidized p+ layers. In these cases, the OT increased by ~14% upon exposure to ethanol vapor. The remaining samples, including octyl-p+ and p++ and ozone treated p++ layers, exhibited between 3 and 6% elevation in OT. Another conclusion that is evident in **Figure 17** is that octane modification appears to have a large negative impact on the responsiveness of the p+ layers, and a modest one on the p++ layers.

In order to understand why these differences exist we may consider the following. In general, the relative change in OT due to ethanol condensation must be due to the exchange of air ($n=1.00$) with ethanol ($n=1.36$) within the pores. This intuitive result is expressed in detail by effective medium approximations such as the Maxwell Garnett or Bruggeman expressions.³⁷ These have the form:

Equation 8:
$$0 = f_a \frac{\epsilon_a - \epsilon_{EFF}}{\epsilon_a + 2\epsilon_{EFF}} + f_b \frac{\epsilon_b - \epsilon_{EFF}}{\epsilon_b + 2\epsilon_{EFF}}$$

where f_a and f_b and ϵ_a and ϵ_b are the volume fractions and dielectric constants of mixed phases a and b, and ϵ_{EFF} is the effective dielectric constant of the mixture. For reasonable values of f_a , f_b , ϵ_a and ϵ_b , the resulting ϵ_{EFF} deviates by no more than 5% from an average of ϵ_a and ϵ_b weighted by f_a and f_b - a simple and intuitive result which can be expressed as: $\epsilon_{EFF} \approx f_a \epsilon_a + f_b \epsilon_b$. Let us consider phase a to be the solid part of the pSi (comprising Si, SiO₂ or octyl modified Si), and phase b to be the pore (comprising either air or condensed ethanol in this case). When ethanol displaces air in the pores, ϵ_b changes from 1.00 to 1.35 but the other terms affecting ϵ_{EFF} remain constant. In this form it is easy to see that, when comparing two pSi samples with identical ϵ_a and ϵ_b , then if f_a for the first sample is greater than f_a for the second sample then, then the first sample will give a larger change in ϵ_{EFF} , and hence in $\Delta OT\%$ when filled with ethanol. This simple conclusion is that a more porous layer should give a larger

Table 1. Experimental Design for pSi Preparation.

Si-type	Modification method	Etch time /s
p ⁺	Ozone	5
		10
		15
		20
	1-Octene	5
		10
		15
		20
p ⁺⁺	Ozone	5
		10
		15
		20
	1-Octene	5
		10
		15
		20

Figure 17. Maximum and Relative Changes in Optical Thickness versus Etch Time.

Maximum (top, ΔOT) and relative change in optical thickness (bottom, $\Delta OT \%$) for pSi layers upon exposure to saturated ethanol vapor in dry air were recorded for a series of p+ pSi specimens prepared for increasing etch time. Note that optical thickness change scales with etch time, but relative change does not.

maximum $\Delta OT\%$ signal. Similarly, when comparing two pSi layers, with different pSi compositions, i.e., different ϵ_a , then the layer with the smaller ϵ_a should be more sensitive to ethanol displacement of air as well since the invariant $f_a \epsilon_a$ term will be a smaller fraction of the total signal. Or, in other words, a lower index pSi layer will give a larger maximum $\Delta OT\%$ signal. The above rationales are consistent with the observations in **Figure 17** because it is likely that the oxidized phases are: **a.** lower index and **b.** more porous than the octyl phases. It is clear from **Figure 6** that oxidation decreases the pSi OT by roughly 5%, presumably because SiO₂ is much lower index (~ 1.46) than Si (~ 4.0) at visible wavelengths and this decrease offsets the additional mass added to the pSi layer by the oxygen. On the other hand, it seems highly likely that octyl modification will increase OT relative to as-prepared pSi since it simply adds octane to the surface of the as-formed pSi, and this addition surface mass may also reduce the effective pore sizes. Hence, the relatively more porous and lower-index oxidized p+ phase (**Figure 17, $\diamond$**) would be expected to give a larger $\Delta OT\%$ response. For the p+ samples, the strong attenuation in response due to octane modification (**Figure 17, $\diamond \rightarrow \square$**) is also reasonable considering the likely decrease in porosity that results from octane modification. The p++ samples were both less responsive on average than the p+ samples and less sensitive to surface treatment, indicating a lower overall porosity or a higher index (inclusively) for the p++ phases.

Based on the maximum signal magnitude alone, one might anticipate that p+ Si, etched for 20s and stabilized with ozone should result in the most sensitive detection of ethanol

vapor. A better question of course is which phase offers a lower detection limit (i.e. P_{MIN} the lowest detectable ethanol partial pressure) which we will define here, consistently with IUPAC as: $P_{MIN} = \frac{3\sigma_B}{m}$ where σ_B is the standard deviation of the blank signal and m is the calibration slope near zero. P_{MIN} values acquired under identical optical and signal averaging conditions across the set of pSi layers tested are presented in **Table 2**. These values clearly indicate a lower average detection limit for the p+ derived samples. P_{MIN} values for p+ and p++ samples were 0.19 ± 0.15 and 1.36 ± 0.54 T respectively and are distinct at the 99.9% confidence level. Given the spread in the values obtained it is not possible to say whether etch time or either the surface treatment nor the etch time are correlated to the detection limits. Please note that these detection limits are not intended to represent a best-case scenario for vapor detection using pSi as they have not been optimized with respect to the optical detection.

3.8. Vapor Response Calibration and Apparent Pore Size Distributions

Figure 18 presents calibrations curves and model fits of the optical interferometric response as $\Delta\%OT$ versus the supplied ethanol vapor pressure. The sixteen calibration curves are grouped by substrate type (p+, left side or p++ Si right) and surface stabilization (ozone oxidation, top or hydrosilation with 1-octene, bottom). While some differences in response magnitude do appear within these quadrants, the groupings generally preserve the qualitative aspects of the calibrations. The solid lines are least-squares fits using the

Table 2. Compiled Maximum Optical Shift and Detection Limits Results.

Si-type	Modification method	Etch time /s	Max Δ OT / μ m	Max Δ OT %	Detection limit / Torr
p ⁺	Ozone	5	0.12	14.1	-
		10	0.23	14.4	0.46
		15	0.29	13.5	0.15
		20	0.42	13.2	0.08
	Averages:			13.8	0.2
	1-Octene	5	0.03	2.9	-
		10	0.13	6.2	0.25
		15	0.20	7.0	0.05
		20	0.23	5.5	0.13
	Averages:			5.4	0.1
	p (ozone vs. octene):			0.0001	0.55
p ⁺⁺	Ozone	5	0.09	4.4	1.24
		10	0.15	4.3	2.28
		15	0.26	5.3	1.80
		20	0.42	6.3	1.63
	Averages:			5.1	1.7
	1-Octene	5	0.06	3.4	1.43
		10	0.15	4.2	1.11
		15	0.22	4.3	0.63
		20	0.30	4.2	0.80
	Averages:			4.0	1.0
	p (ozone vs. octene):			0.1	0.04

Detection limits are defined consistently with IUPAC standards ($C_M = \frac{3\sigma_B}{m}$) and using the standard deviation of the optical signal for blank (σ_B) and the calibration slope near zero signal (m). P-values are probabilities associated with the t-test (2-tailed, unpaired and assuming equal variance) for the equality of the means of the Max Δ %OT and the detection limits.

Figure 18. Δ OT% Interferometric Response Versus Ethanol Vapor Pressure.

Left column: p+ Si substrates. **Right column:** p++ substrates. **Top row:** Ozone oxidized layers. **Bottom row:** Octene modified layers. Lines are least-squares fits of the data to the log-normal distribution model.

Adsorption-condensation log-normal pore distribution model described below.

The **upper left** quadrant combines data for **oxidized, p+ samples**. These calibration curves are clearly similar to the Type IV adsorption isotherm as described by Brunauer et al.⁴⁸ In general these curves consist of two sigmoidal sections, one rising from zero and another rising at ca 30 T. In the **lower left** data for **octyl p+ samples** are shown. These data are quite similar to oxidized p+ ozone, comprising two distinct regions wherein the OT signal first rises and then plateaus. But, relative to oxidized pSi, octyl pSi signals are: **a.** attenuated, especially at low pressure and **b.** shifted to lower pressure, beginning to rise near 20 T.

The **upper right** quadrant combines data for **oxidized, p++ samples**. These data also exhibit two rising portions one from zero and one near 50 T (except for the 20 s etch, which rises more gradually and from 30 T), but are attenuated relative to p+ signals (note change in scale). In general these resemble the Type II p++. Oxidized p++ signals are similar to oxidized p+, but shifted down and to the right. The **lower right** panel shows data for **octyl p++ samples**, which most resemble the Type III isotherm. These data exhibit a single and much more gradual rise originating at zero and more gradually increasing in slope up to saturation. In aggregate, the p++ data are attenuated and shifted to higher pressure relative to the p+ data, and do not reach a plateau. The same data are re-plotted in **Figure 19** (p+) and (p++) on log-log scales for clarity and with lines that are simply guides to the eye. The p+ data all exhibit clear and distinct low pressure adsorption isotherms followed by a sharp rise due to capillary condensation. In some cases, the p++ data in

Figure 20 exhibit a weak adsorptive shoulder, but only within the ozone modified set. Most data and all hydrosilated examples exhibit only a monotonic rise.

In the following section we endeavour to fit these calibration curves to a model that includes both adsorption thermodynamic parameters and an approximate pore size distribution model describing the various pSi phases. As noted above, because of the connection between pore radius and partial pressure for capillary condensation, the mean of the radius distribution may be close to the Kelvin radius corresponding roughly to the inflection points in the rising response. Similarly, the radius distribution standard deviation is related to the widths of the rises.

Assuming as noted above that the interferometric optical response is in good linear proportion to the volume of adsorbed liquid, the interferometric calibration curves in **Figure 18** can be modeled using a model that accounts for physisorption and capillary condensation. In experimental studies using interferometric, ellipsometric, and other optical measurements of optical thickness or closely related phenomena, capillary condensation in pSi may lead to quasi-linear or more complex calibration curves of optical shift versus gas vapor pressure. In some cases a quasi-linear response may span many orders of magnitude in, e.g., ethanol partial pressures in the following range: $10^{-4} < P/P_0 < 10^{-1}$.^{24,49,50,51} But a consensus about these observations is that the optical shift is proportional to the *volume* of condensed gas within the microporous pSi, and, as noted in the introduction in connection with Bruggeman effective medium theory, this volume is, to within about 5%, in linear correspondence to the change in effective refractive index of the pSi phase.

Figure 19. Log-Log Plots of Calibration Data for p+ pSi Data.

Upper curves are for ozone-oxidized and bottom curves are for octene modified specimens. Data are plotted against apparent pore radius derived from Equation 5. Lines are simply cosmetic fits and are a guide to the eye. Average radii, standard deviation and amplitude information are summarized in **Table 2**.

Figure 20. Log-Log Plots of Calibration Data for p++ pSi Data.

Upper curves are log-log plots of calibration data for ozone-oxidized and lower curves are for octene modified (bottom) p++ pSi specimens. Data plotted against apparent pore radius. Lines are a cosmetic fit and are intended to be a guide to the eye only.

Hence our metric of optical response, $\Delta\%OT$, is a good surrogate for volume of condensed liquid within the above approximation and is used without any adjustment in the analysis below. At this juncture we wish to further highlight the simple fact that the rising shapes the calibration curves directly reflect the cumulative distributions of pore sizes within the pSi phase. To illustrate this, and ignoring physisorption for the sake of clarity, consider a fictitious pSi phase comprising identical pores of uniform radius. In this case, one would expect to observe all capillary condensation to occur just above a critical saturation threshold as indicated by the Kelvin equation. For a case in point, let us consider ethanol vapor and a hypothetical pSi phase with pores all of exactly 1.0 nm radius. In this case, in a hypothetical experiment wherein the ethanol vapor pressure above the pSi were gradually increased with time, the entire capillary condensation phenomenon would be expected to occur at a specific relative saturation, $\frac{P}{P_0} \approx e^{\frac{-2\gamma V}{rRT}} \approx 0.503$. In other words, for this hypothetical perfectly uniform pSi phase, the response to ethanol vapor would be expected to be nil below 0.503, and then reach a maximum constant value thereafter – an abrupt shift from zero to maximum. This is in clear contradistinction to the observed gradual increases in $n_{EFF}L$ as a function of volatile organic vapor partial pressure. In order to rationalize the gradual response, one may assume a distribution of pore radii ranging from very small pores that respond to very low vapor pressure and followed, for each incremental increase in vapor pressure, by a corresponding volume fraction of the next larger pores up to some maximum value beyond which the pSi no longer promotes capillary condensation. This relationship, wherein each incremental increase in partial

pressure triggers an incremental increase in the volume of condensed gas corresponding to a specific interval in pore radii, means that the optical signal directly translates the volume-weighted distribution of pore radii. This idea is not at all new – in fact the phenomenon of gradual capillary condensation has been well documented in terms of pore radius distribution, using gravimetric porosimetry, and described theoretically for materials such as silica, activated carbon and clays since the early 1950's.⁵²

In this study we use a model developed for gravimetric porosimetry and apply it to the interferometric data herein. Specifically, this analysis relates the n_{EFF} versus P/P_0 curves to an approximate pore size distribution function. The model was originally developed by Wheeler to derive pore radius information from N_2 adsorption isotherms. It's basic function is to consider the aggregate effects of both physisorption (which gradually constricts capillary radii) and capillary condensation (which abruptly fills capillaries with restricted radii below the Kelvin radius).⁵² Our model is a simple and transparent finite-integral approach to the well known Barrett-Joyner-Halenda (BJH) method for computing the pore radius distribution from the adsorption porosimetry curve.³⁶ The main difference in our approach is that we use the optical interferometric response rather than the mass as a metric of condensed liquid volume. The use of the optical ellipsometric response to measure condensed liquid volume within BJH computation is was recently applied to porous silicon by Barrett and Wongmanerod.⁵³ In the BJH model the capillary radius reduced by the thickness of the BET layer, $r_i - t(p)$, is used to evaluate the onset of capillary condensation. The volume of condensed liquid is derived from the sum of the BET layer volumes in the partially filled capillaries and the total volumes of the completely

filled capillaries.

Equation 9:

$$V_l(p) = \sum_i L(r_i) \pi (r_i^2 - \phi(r_i - t(p) - r_c(p)) (r_i - t(p))^2)$$

p = partial pressure of condensing vapor

$V_l(p)$ = volume of condensed liquid

$L(r)$ = distribution function for the total length of pores with radius r

$t(p)$ = thickness of BET layer

$r_c(p)$ = critical radius for capillary condensation

r_i = model pore radii array (250 radii from 0.025 to 10.000 nm by 0.040 nm)

$\phi(x)$ = Heaviside step function : if $x \leq 0$, $\phi(x) = 0$, else $\phi(x) = 1$

Equation 9 is a finite sum form of Wheeler model of condensed liquid volume function.

For each partial vapor pressure, p , the sum accounts for condensed liquid in each pore in order of radius (r). The radius distribution function $L(r)$ gives the total length (i.e. number) of pores of a given radius interval. For clarity, the parameters that are optimized in $L(r)$, i.e., the mean and standard deviation of the radius distribution function, and in $t(p)$, i.e., C_{BET} and K , are omitted.

Note that in the above equation, the Heaviside step function, ϕ , accounts for capillary condensation in the following way: If the argument of ϕ , $r_i - t(p) - r_c(p)$, is less than zero, then the inner capillary radius, $r_i - t(p)$, that is the radius reduced by the BET layer thickness, is below the Kelvin radius, and the pore is filled. In this case the ϕ function returns zero and the entire pore volume $L(r)\pi r^2$ is added to the sum. Otherwise, if the inner capillary radius is above the Kelvin threshold, then only the BET layer volume, $L(r)\pi r^2 - L(r)\pi(r - t(p))^2$, is added to the sum.

By scaling $V_l(p_S)$ to the $\Delta\%OT$ value at $p = p_S$, i.e. very near or at the saturation vapor

pressure, this model can be fit directly to the optical calibration curves in **Figure 18**. This scaling approach ignores the total porosity, but rather gives the radius distribution function for the pores that do exist however few or numerous they may be. If it is desired, the total porosity can subsequently be computed from the peak $\Delta\%OT$ given suitable estimates of the pSi layer optical constants. As noted above, this and assumes that the pSi effective dielectric function is a linear function of the volume of condensed vapor.

A novel aspect of this analysis is that it presupposes a model distribution for the pore radii – in this case we tried the lognormal and the normal distribution functions for comparison. This model-dependent approach is partly in response to the sensitivity to noise in analyses that back-calculate the detailed distribution and which proved unsatisfactory when applied to our data sets. Also, since the t-curve, that is the BET adsorption thickness versus pressure relation, for ethanol adsorption to silica and to octene-silica was not known, this approach is amenable to a least-squares fit which uses the overall adsorption curve to optimize parameters that describe the BET layer as well. To perform the least-squares fit requires the optimization of four parameters: two that describe BET³⁴ physisorption t-curve, (c_{BET} and K), see **Equation 9** above, and two that describe the radius distribution function, i.e., the mean and standard deviation in the pore radius, see Equation 10 and Equation 11 below. Our intent is to characterize the approximate pSi pore size distributions and to consider how Si type and modifications may change it.³⁶

The two pore radius distributions functions that we employed are the normal or lognormal distributions. The well-known functions are:

Equation 10. Normal Distribution:
$$L(r) = \varphi(r) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left(-\frac{(r-\bar{r})^2}{2\sigma^2}\right)$$

Equation 11. Log-Normal Distribution: $L(r) - \theta(r) = \frac{1}{r\beta\sqrt{2\pi}} \exp\left(-\frac{(\ln(r) - \alpha)^2}{2\sigma^2}\right).$

In the log-normal case the distribution mean $\bar{r} = \int_{-\infty}^{\infty} rP(r)dr$ and standard deviation $\sigma = \sqrt{\int_{-\infty}^{\infty} (r - \bar{r})^2 P(r)dr}$ of the distributions may be calculated from α and β using:

Equation 12: $\bar{r} = \exp\left(\alpha + \frac{\beta^2}{2}\right)$
and

Equation 13: $\sigma = \sqrt{[\exp(\beta^2) - 1][\exp(2\alpha + \beta^2)]}.$

The log-normal distribution is sensible in this case because a normal distribution would predict a finite density of pores with zero or negative radius, whereas the lognormal distribution goes to zero at $r = 0$. Similarly, the lognormal distribution is skewed to positive radii as illustrated below. In fact, broad pore distributions in porous Si do often resemble lognormals as was observed by Ghulinyan et al,⁵⁴ who note that this type of functional fit also permits the calculation of specific surface area. **(Figure 21)**

In this work, each of the 16 data sets were fit to both normal and log-normal distribution function using a Levenburg-Marquardt algorithm. The fit required optimization of four adjustable parameters. Because of the complexity and possibility of convergence on local minima, each fit was repeated roughly 250 times using random combinations of guess values taken from a generous but reasonable interval for the four initial parameters. Of these roughly 250 results, the 100 best (lowest ϕ^2 values) were analyzed. The derived parameter estimates are listed in **Table 3**. The parameters K,

C_{BET} , $\bar{r}$ and $\bar{\sigma}$ are weighted averages from the 100-best nonlinear least squares results.

The weights used to compute the results were the reciprocal χ^2 values. Please note that the standard deviations in $\bar{r}$ and $\bar{\sigma}$ are reflective of the distribution of results returned by the nonlinear least squares fitting routine. Hence they should not be interpreted as deriving from any sort of sample-to-sample variation, rather they should be interpreted as deriving from the relationship between the data and the model as well to the success of the Levenburg-Marquardt algorithm in finding a global minimum for the parameter estimates.

Figure 19 illustrates the quite satisfactory fits between this model and the adsorption curves for the p+ samples, and the clearly unsatisfactory fits to the p++ samples. In the latter case, the BJH model is simply not appropriate to the data implying a morphology quite different than the cylindrical pore system implied in the model. In the former, p+ case the model clearly followed both the low-pressure (adsorptive) and higher pressure (capillary condensation) regimes that are distinctive of the Type V isotherms. The full sets of best fit parameters for the p+ Si specimens are included in **Table 3** and **Table 4**.

Unfortunately interpretation of the physisorption parameters K and C_{BET} is impossible due to their extensive coupling between these two variables. This is illustrated by the plots of K versus C_{BET} for the 100-best optimizations to a well-fit data set illustrated in **Figure 22** (top).

Figure 21. Illustration of Normal and Lognormal Distribution Functions.

Normal distribution mean = 0.1 and standard deviation = 1. For the lognormal $\alpha=0.1$ and $\beta=1$. Note that the lognormal function goes to zero at $x=1$, and is skewed to positive values of the abscissa.

Table 3. Lognormal Modeling Results From 100-Best Fits to Sample Data.

Ln-normal Distribution Modeling Results

Si	modification	etch / s	CBET	K	mean of radius distribution / nm	standard deviation of distribution / nm	χ^2_v
P+	ozone	5	30 $\pm$ 21	0.09 $\pm$ 0.09	2.04 $\pm$ 0.26	0.62 $\pm$ 0.21	0.39
		10	32 $\pm$ 15	0.16 $\pm$ 0.06	1.93 $\pm$ 0.06	0.75 $\pm$ 0.05	0.04
		15	61 $\pm$ 25	0.18 $\pm$ 0.05	2.00 $\pm$ 0.07	0.62 $\pm$ 0.17	0.07
		20	32 $\pm$ 16	0.14 $\pm$ 0.06	1.88 $\pm$ 0.08	0.45 $\pm$ 0.06	0.23
	octene	5	57 $\pm$ 13	0.23 $\pm$ 0.04	1.75 $\pm$ 0.04	0.36 $\pm$ 0.02	0.01
		10	28 $\pm$ 18	0.08 $\pm$ 0.06	1.53 $\pm$ 0.05	0.30 $\pm$ 0.03	0.07
		15	34 $\pm$ 10	0.27 $\pm$ 0.05	1.57 $\pm$ 0.05	0.29 $\pm$ 0.03	0.03
		20	20 $\pm$ 13	0.20 $\pm$ 0.07	1.70 $\pm$ 0.08	0.21 $\pm$ 0.09	0.18
P++	ozone	5	169 $\pm$ 131	-0.12 $\pm$ 0.34	6.06 $\pm$ 5.50	17 $\pm$ 31	0.63
		10	6 $\pm$ 644	0.16 $\pm$ 0.13	8.72 $\pm$ 6.68	27 $\pm$ 36	0.75
		15	98 $\pm$ 28	0.21 $\pm$ 0.07	7.77 $\pm$ 1.45	24 $\pm$ 8	0.96
		20	24 $\pm$ 18	0.21 $\pm$ 0.11	3.50 $\pm$ 0.49	5.2 $\pm$ 1.4	0.97
	octene	5	22 $\pm$ 4	0.38 $\pm$ 0.03	3.37 $\pm$ 0.16	4.86 $\pm$ 0.43	0.19
		10	9 $\pm$ 3	0.26 $\pm$ 0.05	3.04 $\pm$ 0.16	3.84 $\pm$ 0.26	0.30
		15	17 $\pm$ 3	0.29 $\pm$ 0.04	2.80 $\pm$ 0.16	3.29 $\pm$ 0.24	0.23
		20	21 $\pm$ 5	0.29 $\pm$ 0.03	3.48 $\pm$ 0.19	5.33 $\pm$ 0.45	0.46

Note that CBET and K values are statistically dubious as is evident in their relative standard deviations. Mean and standard deviations of the radii distributions were computed from the lognormal distribution parameters α and β using formulae in text.

Table 4. Normal Distribution Modeling Results From 100-Best Fits to Sample Data.

Normal Distribution Modeling Results

Si	modification	etch / s	CBET	K	mean of radius distribution / nm	standard deviation of distribution / nm	χ^2_v
P+	ozone	5	13 $\pm$ 23	0.13 $\pm$ 0.08	1.16 $\pm$ 0.37	0.97 $\pm$ 0.21	0.57
		10	51 $\pm$ 9	0.07 $\pm$ 0.01	0.83 $\pm$ 0.20	1.24 $\pm$ 0.08	0.07
		15	106 $\pm$ 56	0.10 $\pm$ 0.04	1.53 $\pm$ 0.09	0.87 $\pm$ 0.37	0.10
		20	48 $\pm$ 15	0.06 $\pm$ 0.03	1.41 $\pm$ 0.22	0.72 $\pm$ 0.12	0.31
	octene	5	91 $\pm$ 37	0.16 $\pm$ 0.05	1.57 $\pm$ 0.11	0.46 $\pm$ 0.08	0.01
		10	24 $\pm$ 18	0.07 $\pm$ 0.07	1.29 $\pm$ 0.18	0.41 $\pm$ 0.08	0.09
		15	50 $\pm$ 16	0.18 $\pm$ 0.05	1.41 $\pm$ 0.10	0.37 $\pm$ 0.05	0.04
		20	37 $\pm$ 19	0.10 $\pm$ 0.07	1.48 $\pm$ 0.20	0.35 $\pm$ 0.14	0.07
P++	ozone	5	160 $\pm$ 95	0.29 $\pm$ 0.09	4.20 $\pm$ 1.47	4.03 $\pm$ 0.81	0.59
		10	158 $\pm$ 142	0.20 $\pm$ 0.13	4.64 $\pm$ 2.71	3.91 $\pm$ 1.03	0.58
		15	78 $\pm$ 68	0.36 $\pm$ 0.07	2.73 $\pm$ 1.63	4.44 $\pm$ 0.94	0.89
		20	56 $\pm$ 59	0.31 $\pm$ 0.11	3.14 $\pm$ 1.48	3.51 $\pm$ 0.57	0.83
	octene	5	39 $\pm$ 66	0.55 $\pm$ 0.03	2.97 $\pm$ 0.60	3.85 $\pm$ 0.55	0.17
		10	65 $\pm$ 86	0.29 $\pm$ 0.17	2.36 $\pm$ 1.21	3.45 $\pm$ 0.58	0.34
		15	21 $\pm$ 39	0.44 $\pm$ 0.14	1.83 $\pm$ 1.13	2.95 $\pm$ 0.38	0.29
		20	53 $\pm$ 77	0.37 $\pm$ 0.15	2.39 $\pm$ 1.37	3.27 $\pm$ 1.64	0.45

Note that CBET and K values are statistically dubious as is evident in their relative standard deviations. None of the P++ parameters data are considered significant.

Figure 22. Parameter Results From Best 100 Least-Squares Fits. Fits to isotherm for p^+ , 5s, ozone modified samples were chosen. In the top panel the open symbols are K and the closed symbols are C_{BET} values. In the bottom panel the open symbols are α and closed symbols are β values.

In this **Figure 22**, the K and C_{BET} , α and β results are plotted versus the RMS residuals (χ^2) for the fit. In this case the lognormal model was applied to the p+, 5s, ozone specimen. There is an order-of-magnitude range of K and C_{BET} values that satisfied the nonlinear LS algorithm along the χ^2 axis and the values did not converge clearly as the overall fit improved. This highly coupled and shallow error surface leaves a great degree of uncertainty as to what the true values of these parameters may be. The optimized values are listed in the tables for completeness, but it is our position in this thesis that the results of this aspect of the analysis are purely cosmetic and should not be otherwise interpreted. The weighted averages of the radii ($\bar{r}$) and standard deviations ($\bar{\sigma}$) of the lognormal model pore radii distributions appear to be well determined however. The error surfaces for the 100-best fits encompass a roughly 20% variation in α and β and these values converge nicely at the minimum of the χ^2 as illustrated in **Figure 22** (bottom). A more concise summary is made in **Table 5** where $\bar{r}$ and $\bar{\sigma}$ results are averaged across the 5-20s p+ data sets. A clear result is that the lognormal model fits to the p+-ozone specimens yielded tightly grouped $\bar{r} = 1.96 \pm 0.07$ nm, and $\bar{\sigma} = 0.61 \pm 0.12$ nm distributions. In this case, the ± 0.07 nm and ± 0.12 nm uncertainties *do* reflect sample-to-sample variations, across the four 5, 10, 15 and 20 s etch times. Application of the normal distribution model yielded significantly smaller $\bar{r} = 1.23 \pm 0.31$ and larger $\bar{\sigma} = 0.95 \pm 0.22$ nm values.^c

^c Despite these differences, the F-test applied to the χ^2 did not reveal significant differences between the goodness of the lognormal and normal fits, probably because of the interactions with the poorly determined C_{BET} and K .

Table 5. Summary of Results Averaged Across Etch Times For P+ Substrates.

Model	Si	Modification	average of $\bar{r}$ / nm			p	average of $\bar{\sigma}$ / nm			p
Lognormal	P+	Ozone	1.96	±	0.12	0.002	0.61	±	0.12	0.003
		Octene	1.64	±	0.06		0.29	±	0.04	
Normal	P+	Ozone	1.23	±	0.22	0.27	0.95	±	0.19	0.003
		Octene	1.44	±	0.15		0.40	±	0.09	

Note that $\bar{r}$ and $\bar{\sigma}$ are unweighted averages across the 5, 10, 15 and 20 s etch times. The confidence intervals (CI) correspond to the pooled, two-tailed t-tests comparing the ozone and octene modified radii and standard deviations. Octene hydrosilation yielded highly significant reductions in pore radius and radius distribution, except in the case of the normal distribution model results for $\bar{r}$.

Table 6. Review of Porosimetry Reports For Porous Si.

Author	Year	Doping	$\rho / \Omega\cdot\text{cm}$	Electrolyte	$J/\text{A}\cdot\text{cm}^{-2}$	$\bar{r}_p / \text{nm}$	Calc Method	Exp Method	Mod
Herino	1987	p+	1	1:1 HF:EtOH	25	< 2	BJH	N ₂ grav	none
		p++	0.01	3:1 HF:EtOH	10 to 240	2 to 9			
Kinoshita	2002	p+	1	HF Aq 25%	10	12.1	Anderson	H ₂ O grav	none
				HF Aq 30%		8.8			
				HF Aq 40%		7.3			
				HF Aq 55%		2.5			
Wongmanerod	2001	p++	0.01	2:3 HF:EtOH	65	5.0±0.5	BJH	H ₂ O ellipsom	air ox 300C
					150	5.5	BJH	N ₂ grav	
Sailor	1998	p+++	0.001	HF EtOH	300	11	-	AFM	ozone
					400	80			
					500	250			
					600	500			
Ruike	1996	p-	20	HF Aq 25%	10	3.1	BJH	N ₂ grav	none
				HF Aq 30%		3.4			
				HF Aq 37%		3.2			
				HF Aq 46%		2.3			
Grosman	2008	p+	not specified	3:1 HF:EtOH	20	13±5	not spec.	N ₂ , Ar, Kr grav	none
				3:1 HF:EtOH	20	10±3	-	TEM	
				1:1 HF:EtOH	50	25±5	-	TEM	
Lu	2010	p+	1	1:3 HF EtOH	12	2.0±0.6	BJH	EtOH	ozone
		p++	0.005	1:3 HF EtOH	300	>2	approx	interferom	

These studies used boron-doped Si of <100> crystallographic orientation. In some cases radii were estimated from graphs provided in the reports. Data are not necessarily comprehensive from each report.

It is noteworthy that the lognormal model yields significantly more precise $\bar{r}$ and $\bar{\sigma}$ values because the lognormal model function converged on a much narrower distribution of values examined across the range of etch times. It is also instructive to examine the effect on the derived parameters of the different stabilization methods – ozonolysis and octene hydrosilation. The p columns in **Table 5** give the two-tailed t-test results for the probability that the ozone and octene metrics are the same. The tighter lognormal fits permitted comparison of $\bar{r}$ and $\bar{\sigma}$ values between ozone and octene modified samples with a high degree of confidence, > 99.7%. In contrast the normal distribution model *did not* clearly distinguish the $\bar{r}$ between ozone and octene modifications (though it did distinguish the $\bar{\sigma}$ values). The lognormal model indicates that octene modification a. narrows the pores by ~0.3 nm and b. narrows the pore radius distributions by nearly the same amount. Overall these radii distributions are consistent with the lower end of the reported values for similar porosimetry results in the literature (**Table 6**). These reports seem, in general, to support the idea that the p+ Si made with relatively low current density yields these small, microporous phases. The closest matches to our preparation method for p+ samples were reported by Herino et al. who used a classical N₂ adsorption gravimetric method and applied the same BJH analytical method. These results included histograms of the pore size distributions that were sensitive in average radius (2-9 nm) and width (not quantified, but roughly between 0.2 and 2 nm) to dopant level, HF concentration and current density. The only other optical porosimetry method applied to porous Si was that done by Wongmanerod et al., but in this p++ Si and a high-temperature annealing method to oxidize the pSi phase were used.

4. CONCLUSIONS

Layers of pSi were electrochemically generated on the surface of p⁺ and p⁺⁺ Si <100> and stabilized by either ozone or hydrosilation with 1-octene and using a chloroplatinic acid catalyst. The resulting phases were then characterized SEM (in cross section) and by reflection FTIR spectroscopy and finally by examination of their optical interferometric response to ethanol vapor across a range of partial pressures in air. It was demonstrated that the BJH porosimetry model can be applied to the p⁺ porous silicon to calculate the pore radius distribution using only the interferometric optical response to estimate the volume of condensed ethanol as a function of ethanol vapor partial pressure. An approach to fitting the optical interferometric data to the BJH model was developed that utilized model distribution functions (normal and lognormal). This pore distribution model-dependent approach to analyzing the adsorption data was adopted in part because of the noise generated by the crude gas-mixing apparatus used to set the ethanol vapor partial pressure. These adsorption curves yielded apparently good estimates of the pore radius distributions and clearly detected a contraction in the pore radius that resulted from the 1-octene hydrosilation of the porous Si phases.

Future experiments will incorporate FTIR absorption measurements of the adsorbed gas volumes to corroborate the visible wavelength interferometric data as well as a superior method for setting the vapor partial pressure such as a vacuum system and pressure transducer.

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