

Vapor Adsorption in Thin Silicalite-1 Films Studied by Spectroscopic Ellipsometry

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Received: October 17, 1997; In Final Form: January 28, 1998

Thin films of silicalite-1 grown on silicon substrates were studied by spectroscopic ellipsometry. Analysis of spectra using an optical model consisting of a single porous layer on silicon yielded average film thicknesses of 84 and 223 nm for films synthesized for 10 and 30 h. Void fraction for the films was 0.32–0.33. Vapor adsorption from a nitrogen carrier gas at room temperature was monitored by ellipsometry. Isotherms for different adsorbates were obtained by analysis of spectra taken at different vapor concentrations using an optical model where the void volume was filled with both nitrogen and condensed vapors. Quantification of the condensed vapor amount was based on the changes in refractive index when adsorbates replaced nitrogen in the pores. Adsorbate volumes for water, toluene, 1-propanol, and hexane were 0.12, 0.12, 0.15, and 0.17 cm³ liquid g⁻¹ film, respectively.

Introduction

Thin films and membranes of porous inorganic materials have been the subject of advanced materials research for a number of years. Special attention has been given to films of porous silicon made by anodic etching of silicon in aqueous hydrofluoric acid. The discovery of visible photoluminescence at room temperature from porous silicon¹ has led to considerable research in its optoelectronic properties.² Another class of porous materials is zeolites which, although widely used in powder form, have also been fabricated as films and membranes with potential applications in the sensor and gas separation areas.^{3–7}

Properties of thin, porous inorganic films can often be investigated with the same instrumental techniques used for powder materials such as X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR). Even surface area and pore volume determinations by gas adsorption are possible but are made difficult by the relatively small surface areas available in thin films. Pore size distributions in porous silicon samples ranging from the micro- to mesopore region based on nitrogen adsorption–desorption experiments have been reported.⁸ Liquid penetration into porous silicon has been investigated calorimetrically.⁹ For such studies a large sample area, often consisting of several pieces, is required with the result that only average properties for the films under study are obtained.

Materials prepared in thin film form often have interesting optical properties which can be investigated by a number of techniques. Ellipsometry has historically been used to study the growth of thin films on solid surfaces such as oxide growth¹⁰ or vapor adsorption¹¹ on silicon. Wetting of a number of substrates by physisorption from the gas phase has been reported.^{12,13} With the advent of spectroscopic ellipsometry, together with effective medium methods,¹⁴ it has become possible to perform detailed analysis for fractions of constituents in single-layer or multilayer film structures such as moisture penetration into amorphous diamond-like carbon¹⁵ and water

vapor condensation in porous silicon dioxide.¹⁶ We report here adsorption studies on thin silicalite-1¹⁷ films using spectroscopic ellipsometry. For a transparent, porous material like silicalite-1, the optical properties depend on the degree of porosity and the refractive index of the substance filling the pores which makes it possible to determine the quantity of condensed liquids. In addition, since the ellipsometry light beam reflects from a film area of only a few mm², no large sample areas are required, and even thin films can be investigated.

Experimental Section

Films of silicalite-1 were prepared as described previously.¹⁸ Polished (100) p-type silicon wafers (0.8 × 4 cm) were treated with a cationic polymer (Berocell 6100, Akzo Nobel AB). Colloidal tetrapropylammonium (TPA) silicalite-1 crystals¹⁹ with an average crystal size of 45 nm were adsorbed as a monolayer on the polymer-coated substrate surfaces. The samples were calcined at 698 K for 10 min prior to film crystallization. Thin films were obtained by placing the substrates with adsorbed seeds in a synthesis solution at 373 K for 10 h, and thicker films were obtained after 30 h. A final calcination was done at 873 K to remove the template molecules and open the 5–6 Å silicalite-1 channels.

XRD data from the films were collected with a Siemens D5000 diffractometer equipped with thin film accessories working at an incidence angle of 1° and a detector 2θ scan between 5° and 50°. A Philips XL 30 scanning electron microscope (SEM) equipped with a LaB₆ emission source was used for studies of surface morphology and film thickness. Krypton adsorption isotherms on the films were obtained at liquid nitrogen temperature using a Micromeritics ASAP 2010 sorption instrument. The samples were degassed at 573 K prior to measurement. Film thickness was calculated using the Langmuir equation with the surface area and density (600 m² g⁻¹, 1760 kg m⁻²) of pure silicalite-1 as a reference. The calculations were based on an area of 21 Å² per adsorbed krypton molecule, in order to take account of an appreciable degree of localized adsorption.²⁰ Pore volumes were calculated using the density of liquid krypton at the boiling point. The

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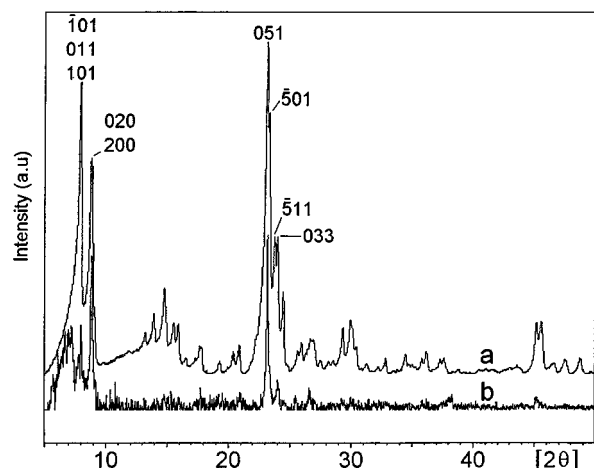


Figure 1. XRD data from a silicalite-1 powder (crystal size 150 nm) (a) and from a 213 nm thick silicalite-1 film (b). The intensity scale is linear in both diffractograms, but the intensity scale in the powder diffractogram is compressed 20 times. The background has been subtracted from both diffractograms.

saturation pressure for krypton was taken as the vapor pressure of the supercooled liquid.

Ellipsometric measurements were performed at room temperature on a variable angle spectroscopic ellipsometer (VASE) from J.A. Woollam Co. Spectra were taken in the 250–1000 nm region, and monitoring of adsorption and desorption kinetics was done at selected wavelengths. Silicalite-1 samples were dried at 573 K and sealed in a cell of about 8 mL volume positioned in the ellipsometer at a 68° angle of incidence so that the light beam was perpendicular to the cell walls. Dry nitrogen was flowed into the cell through a tube in the lid. Solvents were analytical grade from Merck GMBH, and the deionized water used had a resistivity of 18 MΩ cm. Vapor concentrations were controlled by varying the flow rate of nitrogen gas which first passed through two gas washing bottles containing the solvent under study (held at 298 and 288 K) and then into the carrier gas to the cell. Total flow was maintained at 100 mL min⁻¹. Relative pressures were calculated from the saturated pressures, p^0 , of the liquids²¹ at 288 and 293 K.

Results and Discussion

XRD, SEM, and Krypton Adsorption Studies. Figure 1 shows XRD data from a 213 nm silicalite-1 film. For comparison, the diffraction pattern from colloidal silicalite-1 powder (crystal size 150 nm) is also shown in the figure. The relative intensities of the peaks in the pattern from the film were shifted compared to the pattern from the powder. The major peaks in the film pattern were the (020) peak and the (051) peak, indicating a preferred orientation of the (0*h*0) planes of the crystals parallel to the substrate surface. However, the XRD data confirmed that the films consisted solely of silicalite-1. The films had a rough, uneven surface as shown in Figure 2, and film thicknesses obtained from cross-sectional SEM micrographs are listed in Table 1. Thicknesses obtained from krypton adsorption measurements are also included in the table.

Ellipsometry Applied to Silicalite-1 Films. Since ellipsometry is not a technique normally employed to study zeolites, a brief description of the basic principles and how they were applied to obtain the experimental results is given below.

The measured quantity in ellipsometry is the complex reflectance ratio ρ , which is defined as $\rho = R_p/R_s$ where R_p and R_s are the reflection coefficients for light polarized parallel and

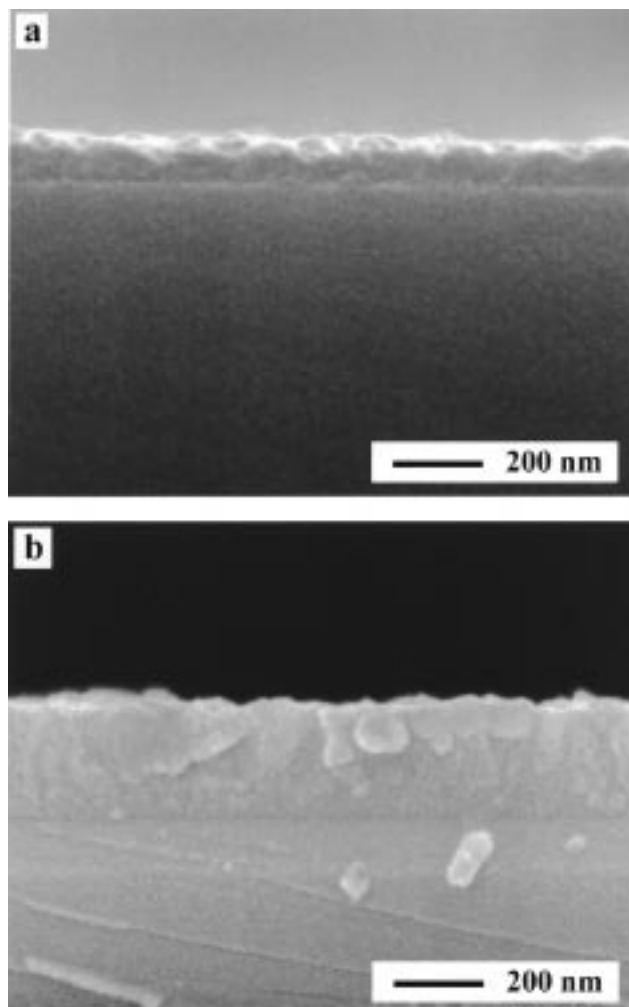


Figure 2. Cross-sectional SEM micrographs of silicalite-1 films synthesized for 10 h (a) and 30 h (b).

normal to the plane of incidence.¹⁰ Usually ρ is written in polar form as $\rho = \tan \psi \exp(i\Delta)$. Since the experimental quantity $\tan \psi$ is an amplitude ratio, ellipsometry is insensitive to the intensity of the light source in the instrument. The phase difference between the p- and s-directions, Δ , is measured as a mechanical angle or an electrical phase. Both ψ and Δ are easy to measure very accurately which gives ellipsometry a high sensitivity.

Ellipsometry is an indirect technique, and to fully utilize the information contained in ellipsometric data an optical model has to be developed. For studies of thin films a three-phase model, defined as ambient-film-substrate, is often used. In a three-phase system, the complex refractive index of a film can be determined from a measurement of ρ_{exp} at a specific angle of incidence and wavelength if the film thickness d and the refractive indices of the ambient and substrate are known. The general procedure in the analysis is to minimize the difference between the measured value ρ_{exp} and the calculated value ρ_{calc} using some standard mathematical inversion method such as the Newton–Raphson procedure. Silicalite-1 is a porous material which is transparent in the 250–1000 nm region. For sufficiently thick films the ψ and Δ spectra contain a number of interference oscillation peaks, and the films have a real-valued refractive index allowing both thickness and refractive index to be determined. However, since the main objective in this study was measurement of vapor adsorption in the films, the optical model was developed from optical constants available

TABLE 1: Void Fraction, Thickness, and Adsorbate Volume for Silicalite-1 Films

void fraction ^a	thickness, ^a nm	thickness, ^b nm	thickness, ^c nm	water ^d	toluene ^d	propanol ^d	hexane ^d
0.324	83	100	60	0.11	0.12	0.14	0.17
0.321	85	100	70	0.13	0.12	0.14	0.17
0.329	234	260	200	0.12	0.12	0.16	0.17
0.325	213	200	190	0.11	0.13	0.16	0.18

^a From ellipsometry, average of four measurements at different points. ^b From SEM. ^c From krypton adsorption. ^d In cm³ liquid g⁻¹ film.

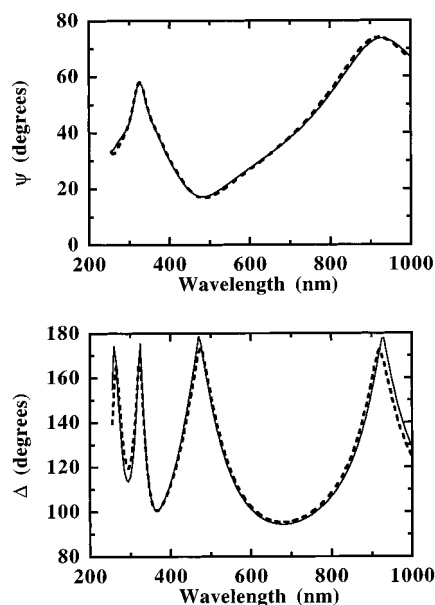


Figure 3. Experimental (dashed curves) and modeled (solid curves) ψ and Δ spectra for a 234 nm thick silicalite-1 film synthesized for 30 h on a silicon substrate.

in the literature. Since silicalite-1 is a crystalline silica, the optical properties for quartz (called type α , crystalline SiO₂ in Palik²²) were used in the model. The optical properties of quartz have been determined for both the ordinary index of refraction, n_o , for light with its electric field perpendicular to the optic axis and for the extraordinary index, n_e , for light parallel to the optic axis. With known optical properties for the substrate and silica, the unknown parameters for each film were the pore volume percent (void fraction) and film thickness.

In practice, one generally works explicitly with ψ and Δ to fit parameters of interest by minimizing a mean-squared error (MSE) function defined previously.¹⁶ Figure 3 shows a typical fit obtained by using the WVASE32 software (J.A. Woollam Co.) to obtain the thickness and void fraction of a silicalite-1 film. A model consisting of a single layer of quartz (ordinary index of refraction)²² and void on a silicon²³ substrate was used to represent the film. The effective refractive index for the layer was calculated using the Bruggeman effective medium approximation which describes aggregate topology for randomly mixed components.¹⁴ The fit to the model returned a film thickness of 234 ± 1 nm and void fraction 0.323 ± 0.003 with a MSE = 8.1. The limits correspond to the 90% confidence intervals.

The measured quantity ρ is very sensitive to both film thickness and changes in the refractive index of the film. Both these properties can be altered by vapors adsorbing or condensing in and on the film. Figure 4 shows spectra for the same film described above in nitrogen and in hexane ($p/p^0 = 0.76$). The peaks for both ψ and Δ were shifted to longer wavelengths when the hexane vapor condensed in the film. Analysis of the spectra using an optical model where the void was filled with a mixture of nitrogen and liquid hexane (refractive index as a

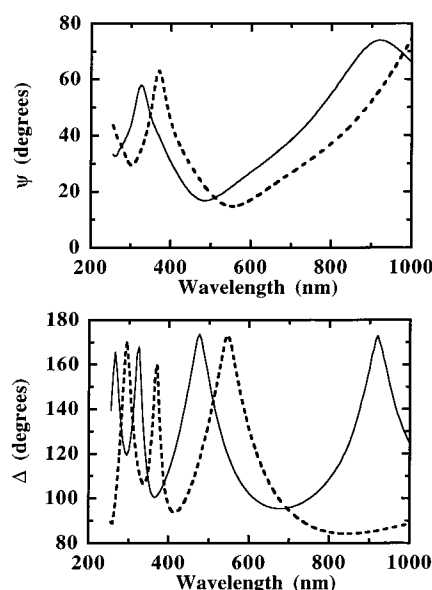


Figure 4. Experimental spectra for the silicalite-1 film in Figure 3 in nitrogen (solid curves) and in hexane (dashed curves), $p/p^0 = 0.76$.

function of wavelength taken from ref 24) yielded the result that hexane filled 0.297 ± 0.004 of the film volume (MSE = 8.4). In the analysis, a three-constituent (quartz, void, and hexane) effective medium approximation was used, and the layer thickness and quartz volume fraction ($1 - 0.323 = 0.677$) were held constant at the values determined in nitrogen. Analysis of spectra taken at different vapor concentrations made it possible to construct adsorption and desorption isotherms for the different vapors. In addition, the changes in ψ and Δ at selected wavelengths, for example on slopes of the interference peaks shown in Figure 3, were used to monitor adsorption and desorption kinetics. Adsorption times based on the leveling off of the ellipsometric angles at the lowest vapor concentration used, $p/p^0 = 0.009$, were < 1 min for hexane and 1-propanol, approximately 5 min for toluene, and 30 min for water.

Since interpretation of ellipsometric data is very dependent on the choice of optical model used in the analysis, some consideration of possible errors is in order. Studies of optical properties of aluminosilicate zeolites have shown that refractive indices are very sensitive to slight changes in crystal structure and composition, especially with regard to the exchangeable cations.²⁵ Since silicalite-1 consists of only crystalline silica possessing no cation-exchange properties, it was a logical choice to use quartz as the model substance to represent the silica in the films studied. Although quartz is anisotropic, its birefringence is small ($n_e - n_o = 0.091$ at 589.3 nm), and using n_e instead of n_o in the model had little effect on the results. Using amorphous SiO₂ to represent the silica in the films led to significantly lower void fractions, about 0.24, but film thicknesses were the same as when quartz was used in the model. The lower void fractions led to correspondingly lower adsorbate volumes for the vapors condensing in the films since less of the total film volume was available for condensation in the

a-SiO₂ model. Since the use of quartz in the model yielded the 33% porous volume determined for silicalite-1,¹⁷ it was deemed a better choice for the silica component in the films than a-SiO₂.

Determination of Thickness and Total Pore Volume.

Analysis of spectra taken for films in nitrogen was done in order to determine the thickness and volume porosity in the absence of adsorbed vapors. Table 1 shows parameters returned from fitting spectra calculated from a single-layer model consisting of quartz and void on a silicon substrate to the experimental curves. The MSE values for the curve fitting were in the range 5–10. The void fractions determined for the films, 0.32–0.33, were in excellent agreement with the reported total micropore volume of 0.19 cm³ g⁻¹ (corresponding to a void fraction of 0.33) obtained from saturation capacity.¹⁷ Film thicknesses were roughly in agreement with the synthesis times used in preparing the thinner and thicker films. There was also reasonably good agreement in thicknesses obtained from ellipsometry as compared to those measured by SEM and krypton adsorption. The films exhibited a considerable surface roughness (Figure 2) which made it difficult to estimate the thicknesses for the thinner films by SEM. Since the film thicknesses obtained from krypton adsorption were mean values of the whole film, the good agreement with the ellipsometry values, which were determined for a few mm² area, seemed to indicate uniform film thicknesses.

Since ellipsometry is an indirect measurement technique, some caution must be exercised in using ellipsometry to study complex systems. Optical models used to analyze ellipsometric data are based on several simplifying assumptions. The film and substrate are assumed to have plane, parallel boundaries and to be homogeneous and optically isotropic. The refractive index is assumed to change abruptly across each interface. Real films seldom meet all these requirements, but simple models can often produce adequate descriptions even for complex systems. Making the model more complicated can sometimes improve curve fitting, but this does not necessarily lead to more information. An example for silicalite-1 films is trying to model the surface roughness observed by SEM. For a transparent film the interference oscillation peaks calculated from an idealized model have their maxima near 180° for Δ spectra, as shown in Figure 5. The actual surface of the silicalite films was nonuniform, as shown in Figure 2, and a better fit could be obtained by including a surface nonuniformity factor in the fitting procedure. This is shown in Figure 5 where a surface nonuniformity of 10% yielded a better fit to the single interference oscillation peak than was obtained from the model based on a smooth surface. However, the differences in the thickness and void fraction obtained from the two models were less than the 90% confidence limits, and the inclusion of the nonuniformity parameter in the analysis of the data was judged to be unnecessary.

Sorption Measurements. Exposing silicalite-1 films to different concentrations of vapors caused shifts in the spectra as shown in Figure 4. When adsorbate molecules replaced nitrogen in the films, the total polarizability in the void fraction increased. This caused a change in the interference oscillations which shifted the ψ and Δ curves to longer wavelengths. These shifts were used to obtain the quantity of adsorbates filling the void fraction in the films for different vapor concentrations. Typical isotherms for hexane and water constructed from these results are shown in Figure 6. As expected, hexane exhibited a type I, nearly rectilinear isotherm¹⁷ whereas water exhibited a more gradual change with increasing partial pressure. Very

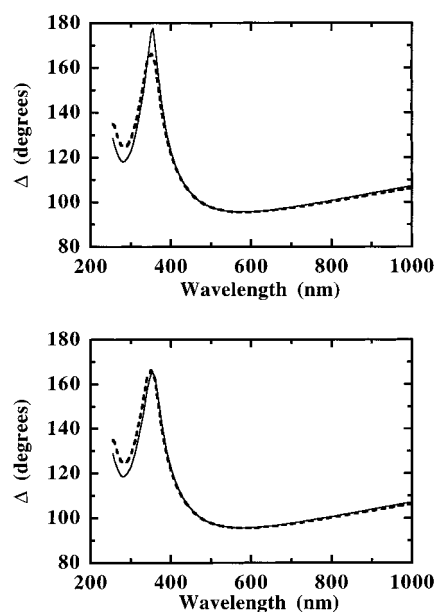


Figure 5. Experimental Δ spectra (dashed curves) for a 83 nm silicalite-1 film synthesized for 10 h compared with spectra (solid curves) calculated from models having a smooth (upper figure) and a 10% nonuniform surface (lower figure).

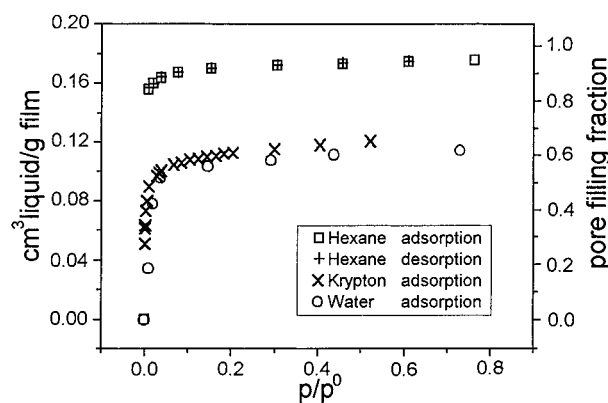


Figure 6. Isotherms for hexane at 293 K, water at 293 K, and krypton at 77 K on a 213 nm thick silicalite-1 film. A pore filling fraction = 1 for hexane and water corresponds to total filling of the 0.325 void fraction in the film.

little hysteresis was observed in the adsorption–desorption isotherms. For comparison, a krypton adsorption isotherm at 77 K is shown. The krypton adsorption was done on a film with a geometrical area of 5.2 cm², considerably larger than what was investigated by ellipsometry. Krypton adsorption is a localized process,²⁰ which explains why less krypton was adsorbed as compared to hexane. The right-hand axis in Figure 6 has been designated the pore-filling fraction in order to emphasize that spectroscopic ellipsometry makes possible the determination of both the filled and unfilled pore volume in the silicalite-1 films. Table 1 lists condensed vapor amounts for water, toluene, 1-propanol, and hexane in units of cm³ liquid g⁻¹ silicalite-1.

Good agreement with adsorption studies on powder samples was observed for hexane, 0.17–0.18 cm³ liquid g⁻¹ film, as compared to 0.199 cm³ liquid g⁻¹ powder reported by Flanigen et al.¹⁷ and 0.185 cm³ g⁻¹ reported by Wu et al.²⁶ However, the mean value obtained for water in this study, 0.12 cm³ g⁻¹ film, did not agree well with results obtained on powder samples. Flanigen et al. reported 0.047 cm³ g⁻¹ silicalite-1,¹⁷ and Sano

et al. observed an adsorption of $0.026 \text{ cm}^3 \text{ g}^{-1}$ for silicalite-1 synthesized at $T > 433 \text{ K}$ at autogenous pressure and $0.044 \text{ cm}^3 \text{ g}^{-1}$ from synthesis at $T = 363 \text{ K}$ under atmospheric pressure.²⁷ The films studied in the present investigation were grown from seed crystals of approximately 45 nm diameter adsorbed onto the substrate surface. Upon further crystallization these crystals grew to form a continuous film. However, the seeds did not grow into a monocrystal of silicalite-1, but rather formed a polycrystalline film of intergrown discrete crystals as can be seen in Figure 2b. It is possible that a high concentration of silanol groups at the interfaces between these crystals resulted in larger adsorbed water quantities than was observed in the previous studies on silicalite-1 powders.

Of general interest is the comparison of the properties of thin film materials with the corresponding bulk form. A remarkable feature of the adsorption-desorption isotherms for the microporous silicalite-1 films (shown for hexane in Figure 6) is the almost total absence of a hysteresis loop. Although the existence of a hysteresis loop is characteristic for mesoporous materials showing a type IV adsorption isotherm rather than microporous ones resulting in a type I adsorption isotherm,²⁰ some hysteresis is generally observed when analyzing zeolite powder samples by nitrogen adsorption-desorption. Zeolite crystals are relatively small and possess a significant external surface area. When forming a powder, a system of pores in the mesoporous region develops, having a pore size dependent on the crystal size and the packing of the powder. In nitrogen adsorption-desorption measurements these pores result in a type IV isotherm superimposed on the type I isotherm emanating from the adsorption in the zeolite pores and cause the hysteresis observed for zeolite powder samples. In a continuous zeolite film consisting of intergrown crystals, the secondary pore system is greatly reduced, a fact which most likely explains the absence of hysteresis effects. The ellipsometric data support this picture of a continuous morphology for the silicalite-1 films since a large number of experiments yielded void fractions attributed only to the zeolite pores. Measurement areas containing a large number of cracks were easily identified by their abnormally high void fractions and adsorption isotherms that did not level off at higher partial pressures. A detailed study of inter- and intraparticle surface areas for mesoporous thin films of silica formed from tetramethoxysilane has recently been reported.²⁸ The films were deposited on a surface acoustic wave device so that nitrogen sorption at 77 K could be studied. Despite the crack-free morphology of the films, a tremendous inter- and intraparticle porosity was observed which gave ready access to the intraparticle pores.

There are a number of assumptions in the optical model pertaining to vapor adsorption which should be commented on. Adsorption of molecules on silicalite-1 occurs through volume filling of micropores by physical adsorption at relatively low pressures. Since quantitative determination of the volume filling by ellipsometry is dependent on the refractive index of the adsorbate, some justification of the use of the liquid refractive indices²⁴ is required. Previous studies using ellipsometry to study vapor adsorption on silicon used refractive indices for the liquids to obtain adsorbed layer thicknesses^{11,13} even though there is usually a discrepancy between the refractive index of a material in a thin film and the bulk refractive index.¹⁰ The assumption that the adsorbate resembles the normal liquid is also employed in using liquid densities to calculate pore volumes from adsorption capacity in conventional adsorption studies.¹⁷ Also of some concern is the fact that the model is a rigid structure with the total void fraction and thickness being

set equal to the values obtained for the films in nitrogen. It is well-known that adsorbent deformation often accompanies gas adsorption.²⁹ Studies by XRD on porous silicon having 3–10 nm diameter pores formed by electrochemically etching silicon have recently shown that a lattice contraction occurs during low-pressure vapor adsorption and expansion upon total wetting.³⁰ The contraction observed was believed to be caused by attractive van der Waals interactions induced by vapor adsorption in nanometer-sized pores. Even zeolites have been observed to undergo deformation during interaction with gases.³¹ Thus, a more realistic model for the silicalite-1 films during vapor adsorption might be to include the thickness and total void fraction as fitting parameters. However, for the one-layer model used, these additional fitting parameters were observed to result in significant parameter correlations, and the rigid model was judged to be a more realistic description of the system.

Although the present study has dealt with vapor adsorption, it should also be possible to utilize spectroscopic ellipsometry to investigate zeolite films in contact with liquids. Systems of interest are the selective adsorption of organic molecules from aqueous solution³² and the liquid-phase, selective oxidation of organics by hydrogen peroxide over titanium silicalite-1.³³ Basic data analysis should be similar to that previously employed for surfactant adsorption in porous silicon,³⁴ with the selective oxidation system providing the opportunity to study both adsorption and chemical reaction in the film.

Acknowledgment. The work reported here was supported by a grant from Carl Trygger's Foundation for Scientific Research.

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