Diffusion dynamics of small molecules from mesoporous silicon films by real-time optical interferometry

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Time-dependent laser reflectometry measurements are presented as a means to rigorously characterize analyte diffusion dynamics of small molecules from mesoporous silicon (PSi) films for drug delivery and membrane physics applications. Calculations based on inclusion of a spatially and temporally dependent solute concentration profile in a one-dimensional Fickian diffusion flow model are performed to determine the diffusion coefficients for the selected prototypical polar species, sucrose (340 Da), exiting from PSi films. The diffusion properties of the molecules depend on both PSi pore size and film thickness. For films with average pore diameters between $10^{-3}$ nm and film thicknesses between $300-900$ nm, the sucrose diffusion coefficient can be tuned between approximately 100 and $550 \mu m^2/s$. Extensions of the real-time measurement and modeling approach for determining the diffusivity of small molecules that strongly interact with and corrode the internal surfaces of PSi films are also discussed. © 2011 Optical Society of America

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1. Introduction

Porous silicon (PSi), a material characterized by controllable, well-aligned, and densely distributed nanometer-scale pore channels [1,2], has rapidly gained attention in recent decades for diverse applications including chemical and biological sensing [3–5], passive photonics components [6,7], and active optoelectronic devices [8,9]. PSi has also been explored for use in drug delivery and controlled release applications [10–12], owing to its biocompatibility [10,13,14] and exceptionally large internal surface area that enables its large drug-loading capacity. In addition to its advantageous morphology, PSi also exhibits simplicity in its fabrication and compatibility with existing silicon electronics processing technology. The ease with which the porosity and mean pore size of PSi films can be varied over a wide range by adjusting the anodic etching parameters facilitates many of the aforementioned applications.

Although many of the attributes of PSi films have been well characterized [1,15,16], there remains a need to accurately and easily characterize the diffusion properties of molecular species through such films. While several studies have experimentally evaluated the rate at which certain molecular species are released from porous films and particles for specific applications [12,17–20], an experimentally simple optical approach for rigorously characterizing the physical diffusion dynamic of small molecules in PSi films has not been reported. The focus of the effort here is to exploit a straightforward real-time optical interferometric measurement technique, along with numerical modeling based on Fickian diffusion dynamics, to characterize the outdiffusion of molecules from PSi as a function of PSi pore size and film thickness. A key target application of our approach is the engineering of PSi films from which particles can be fabricated and exploited as drug-delivery vehicles.
With a strong quantitative knowledge of the diffusion characteristics of PSi films, it will be possible to tailor porosity profiles of both PSi films and particles derived from PSi films [10,12,21] to achieve customized release profiles for drugs. While this effort was aimed specifically at drug-delivery applications as a motivation of the technique, the method itself complements the existing body of studies of such phenomena.

In this work, the mathematical principles of diffusion measurement by time-dependent laser reflectometry are first established. A model is introduced specifically as it is applicable to tailoring molecule outdiffusion in porosity tuned PSi films. The experimental aspects of the diffusion measurements by reflectometry are then described. Determination of effective diffusion coefficients as a function of film pore size by this method is presented for the model polar species, sucrose. Finally, extensions of the method are discussed and limitations of the specific analytical model are exemplified by the case of outdiffusion of the amphiphilic molecule, sodium-dodecyl sulfate (SDS). The release rate of SDS, which exhibits dynamics not described by simple Fickian diffusion, is nonetheless shown to be tunable over nearly 1 order of magnitude by tuning PSi porosity.

2. Theory

Diffusion physics is a diverse and fundamentally important field that is central to the study of many phenomena ranging from groundwater filtration and pollutant seepage [22,23] to the diffusion of carriers in solid-state devices. Of interest in this work are the mechanisms of solute diffusion out of mesoporous films with nanoscale pore diameters. The dependence of diffusion properties upon film porosity or pore size is important not only in drug-delivery applications but also in membrane physics [18,20,24–26] and gas or vapor sensing applications [27,28]. The experimentally simple, but rigorously quantitative, method to optically measure diffusion coefficients in mesoporous films presented here is applicable to a variety of porous films that meet sufficient minimum transparency, smoothness, and homogeneity requirements. The technique may also be readily extended to different physical scenarios involving diffusion phenomena in such films.

Diffusion dynamics measurements are accomplished by real-time monitoring of the reflectance of monochromatic light from a PSi film during solute diffusion out of the film. Temporal variation in the reflectance amplitude occurs because changes in the solute concentration distribution in the PSi layer cause changes in the effective refractive index profile, \( n_{\text{eff}}(x, t) \), of the film. The changing film refractive index in turn alters the relative phase of the multiple internal reflections occurring within the film that contribute to the total reflected beam intensity, resulting in a time-varying reflected amplitude. The mathematical description of this behavior is an extension of the well-known matrix formulation often used for modeling thin-film spectral properties [29]. Application of this model allows for a mathematical prediction of the temporal reflectance curve to be made, which can then be fitted to the measured data using a standard parameter-search error-minimization approach. Therefore, if all the relevant physical parameters of the film are known, the diffusion coefficient can be determined with good accuracy. The basic theory of thin-film reflectance is briefly reviewed for completeness, followed by its extension to the specific physical scenario considered in this work.

The film (or each film, \( j \), in the case of multilayer structures) is represented by a transmission matrix \( L_j \), while each interface is represented by a reflection matrix \( H_j \) [29]:

\[
L_j = \begin{bmatrix}
\exp(i\beta_j) & 0 \\
0 & \exp(-i\beta_j)
\end{bmatrix},
\]

\[
H_j = \frac{1}{r_j} \begin{bmatrix} 1 & r_j \\ r_j & 1 \end{bmatrix},
\]

where \( r_j \) and \( r_j \) are the Fresnel transmission and reflection coefficients, respectively. Matrices are concatenated multiplicatively to form a system matrix. Centrally important is the phase acquired by light traversing a film, \( \beta \). In a homogeneous film with light at normal incidence, this phase is simply \( (2\pi/\lambda)nL \), where \( L \) is the film thickness and \( n \) is the complex refractive index of the layer. However, during the dynamic process of solute diffusion out of or into a porous membrane, the effective refractive index of the porous layer will be a function of the solute concentration profile within the membrane, and it will therefore be a function of depth in the film.

During the process of solute diffusion out, the effective refractive index of the porous layer is assumed to be a spatially weighted average (also called the parallel effective medium approximation) of the silicon regions and the porous void regions, described by the following relation [30]:

\[
n_{\text{eff}}(x, t) = n_{\text{Si}}(1 - p) + n_p(x, t)p,
\]

in which \( p \) is the film porosity, \( n_{\text{Si}} \) is the refractive index of silicon, and \( n_p \) is the refractive index of the pore regions that contain air, water, or solution. Other effective medium models, such as the Bruggeman or Maxwell–Garnett effective medium approximations, could also be applied depending on the particular morphology of the porous film and the details of the solute concentration gradient within the film [31]. During the process of solute diffusion, the refractive index of the solution-containing pore regions is that of the solution, \( n_s(x, t) \), and it is a function of depth in the porous film. The temporally varying refractive index of the solution, which depends linearly upon solute concentration [32], is calculated as a function of depth in the porous region from
\[ n_p(x, t) = n_v + (n_f - n_v)C(x, t), \quad (4) \]

where \( n_v \) is the solution refractive index when it is vacant of solute, \( n_f \) is that of the solution when it is maximally full of solute, and \( C(x, t) \) is the normalized, spatial, and temporally dependent solute concentration profile. The acquired phase of normally incident light traversing the layer may be expressed at any time \( t \) as

\[ \beta = \left( \frac{2\pi}{\lambda_0} \right) \left[ n_{\text{eff}, v}L + (n_{\text{eff}, f} - n_{\text{eff}, v}) \int_0^L C(x, t)dx \right], \quad (5) \]

in which \( n_{\text{eff}, v} \) is the effective refractive index of the film when vacant of solute, and \( n_{\text{eff}, f} \) is that of the film when full of solute. The integral in Eq. (5) represents the total fraction of solute remaining (in the case of outdiffusion) in the film at time \( t \). By this equation, the temporal behavior of the reflectance can be accurately modeled if the time-varying concentration profile is correctly ascertained. The necessary concentration profile of the solute within the porous structure can be obtained, in general, by either analytical or numerical modeling.

In this study, the concentration profile is obtained by applying Fick’s diffusion equation for homogeneous media in which the temporal variation of the concentration, \( C \), is dictated by its spatial gradient and the spatially invariant diffusion coefficient \( D \) [33]:

\[ \frac{\partial C(x, t)}{\partial t} = D \frac{\partial^2 C(x, t)}{\partial x^2}. \quad (6) \]

The boundary conditions for the scenario under consideration are dictated by the initial concentration of solute within the film (assumed to be uniform throughout the film), the closed-ended geometry of the on-substrate PSi film, and the tendency of the film solute concentration toward zero as time increases:

\[ C(x, 0) = C_0, \quad 0 \leq x < L, \quad (7a) \]

\[ C(x, t \to \infty) = 0, \quad x > 0, \quad (7b) \]

\[ \frac{\partial}{\partial t} C(x, t \leq 0) = 0, \quad x > 0. \quad (7c) \]

The analytical solution for these conditions may be found by application of an appropriate Green's function (among other methods) [33,34]:

\[ C(x, t) = \frac{1}{2} C_0 \left[ \text{erf} \left( \frac{L - x}{2\sqrt{Dt}} \right) + \text{erf} \left( \frac{L + x}{2\sqrt{Dt}} \right) \right], \quad (8) \]

where \( L \) is the film thickness. This phenomenological model is employed for its simplicity, and its applicability is well supported by the data-fitting results presented herein. It is noted that the general approach presented in this work can be extended to different physical scenarios, such as diffusion of molecules into a closed-ended porous film [27,28], diffusion through open-ended porous media/films [25,35–37], and diffusion of solute through multilayer porous media with spatially varying diffusion coefficient [22,23], so long as proper boundary conditions are enforced and a valid concentration profile is employed. Refinements such as inclusion of concentration dependence or spatially varying diffusion coefficient may also be studied with proper analytical solutions of the concentration function. Furthermore, numerical simulations of diffusion phenomena, such as those based upon the Crank–Nicholson finite-difference time-domain approach, are also a valid and accessible means of obtaining the necessary temporally varying concentration profile.

3. Nanoporous Film Fabrication and Characterization

PSi samples were fabricated by anodic electrochemical etching in electrolyte solution consisting of 15% hydrofluoric acid in ethanol. Silicon substrates used were 500 ± 25 μm in thickness, p-type, boron doped, (100)-orientation, with resistivities of 0.005–0.01 Ω·cm (Silicon Valley Microelectronics). Selection of these silicon substrate parameters ensured PSi film characteristics necessary for the diffusion studies, including densely packed pores with a relatively large range of porosities and pores that propagate parallel to the surface normal. Additionally, note that for drug-delivery applications, PSi particles formed from similarly specified silicon substrates have been demonstrated to be biocompatible. From full wafers, individual rectangular silicon samples of approximately 2 cm × 2 cm were scribed. Prior to etching, these samples were submersed in a buffered-oxide etch for 3–5 min to remove the native oxide on the substrate surface. One porous film was then etched into each of the silicon samples in a Teflon electrochemical etch cell. The porosity of each film was dictated by specifying the current density through the films with a Keithley 2425 source meter. Samples of uniform porosity were etched, each with a fixed current density, and these ranged between 5 and 40 mA/cm², in 5 mA/cm² increments. For each etch current, porous films of nominal thickness of 300, 600, and 900 nm were produced, for a total of 24 samples, which comprise the main sample set for the sucrose diffusion experiments. Films were allowed to partially oxidize in ambient conditions for 24 hours, such that only a thin (<1 nm) native oxide layer is expected. It is important to note that the degree of oxidation was found to strongly affect diffusion characteristics and that highly oxidized films generally did not exhibit significantly hindered diffusion, as did the natively oxidized (nominally unoxidized) samples. Thus, for this study, the latter was of greater interest.

Samples were characterized by scanning electron microscopy (SEM, Hitachi S-2400) for thickness (cross-sectional view) and pore size and distribution (top view). Spectral reflectometry was carried out...
(J. A. Woolam M-2000 spectroscopic ellipsometer) on selected samples for testing the consistency of film optical properties throughout experimentation. Determination of pore size (Feret diameter) distributions and average pore diameter were made by applying a MATLAB-based image processing algorithm to the top-view SEM images. Film porosity values were calculated as follows. A fast-Fourier transform of the measured reflectance spectrum was performed to determine the film optical thickness \[38\]. Using this optical thickness, the effective refractive index was derived using the known physical thickness of the film, as measured by SEM. From the calculated effective refractive index, the film porosity was determined from Eq. \((3)\), in which \(n_p\) is simply that of air, 1.

4. Experiment
A custom-made diffusion chamber was utilized for time-dependent optical reflectometry measurements of film diffusion and degradation processes. As shown schematically in Fig. 1, the diffusion apparatus consists of two rigid polystyrene chambers separated by a barrier wall with a 3 mm diameter aperture that serves both as the solute flow channel and as an optical aperture to the sample surface. On one side of the channel, an O-ring seal joins the aperture to the sample surface, which is held securely in place by tensioned plastic fixture (backing). Prior to beginning a diffusion measurement, in a separate container, samples are immersed in 20 ml of the solution under investigation for an appropriate amount of time (0.5–6h, depending on the solute and film thickness). Upon removing the PSi sample from the initial loading-solution, a thin (\(~0.07\ mm\) transparent polypropylene sheet is placed in intimate contact with the full surface of the PSi sample to serve as a barrier, or gate, such that diffusion cannot occur prior to its removal. The sample and gate are then placed in the diffusion apparatus with the gate firmly secured between the sample and the O-ring. With the sample and gate both in place in the apparatus, the ambient medium (water) is then added to the larger frontal chamber. The incident laser beam is aligned prior to gate withdrawal, and at commencement of the measurement, the gate is removed and solute outdiffusion is allowed to transpire while optical measurement is in progress. The concentration of the sucrose solution used in the experiments presented here was 1.2 g/ml (54.5% by mass), and that of the SDS solution was 0.1 g/ml (9%). The pH of both solutions was approximately that of deionized water, 7.0.

A visible laser (He–Ne, 632.8 nm wavelength, 5 mW) is chosen for ease of use and alignment. Figure 2 shows the optical system layout used for the experiments. The laser beam is guided through an optical chopper and a splitter. The reflection from the splitter (20%, or \(500 \mu\text{W, including chopper loss}\)) is guided to a detector (\(D_{\text{ref}}, \text{Newport 71581}\)) to act as a reference arm, while the transmitted arm illuminates the PSi sample surface through the front, larger chamber of the diffusion apparatus. The reflected beam from the sample surface is detected by a separate detector (\(D_{\text{samp}, \text{Newport 818}}\)). After reflection losses in the diffusion chamber and absorption loss from the samples, the reflected beam intensity typically ranged from 50–200 \(\mu\text{W}\). Both detectors are then fed to a lock-in amplifier (Stanford Research Systems 830) as a ratio, which thereby corrects for variations in laser output due to slow changes in the ambient room temperature. The optical chopper triggers the lock-in amplifier and is operated at a nominal modulation frequency of 275 Hz, which is sufficiently fast to observe the temporal variations in the reflected beam intensity. Measurement values were acquired in approximately 40–60 ms intervals.

![Fig. 1. (Color online) a) Schematic of the diffusion chamber apparatus used for measurement of optical reflectance during film diffusion. b) Magnified side view of the pre-experiment arrangement of a porous film under interrogation. Note that dimensions and spacing are exaggerated in the image and that the gate, film, and tensioned backing are all in intimate contact prior to experiment execution.](image1)

![Fig. 2. Optical and instrumentation setup for diffusion measurements utilizing the diffusion-chamber apparatus.](image2)
by a computer linked to the lock-in amplifier, facilitated by a LabView virtual instrument. To fit the collected temporally varying reflectance data to the model described in Eqs. (1)–(8), a parametric search was performed using code written in Mathematica, which numerically models the reflectance phenomenon and evaluates a fitting error for measured data as compared to the theoretical temporal reflectance curve. By minimizing the error between measured and theoretical reflectance curves, the diffusion coefficient was extracted. Parameters that were allowed to vary in the fitting included diffusion coefficient, film thickness (within the uncertainty of the SEM side profile, approximately ±10 nm), loss due to optical absorption or scattering, and angle of incidence (within the accuracy of its measured value, 8 ± 1°).

5. Results

A. Porous Silicon Characterization

Figure 3 shows SEM images of a typical PSi sample. Measurement of film thickness and assessment of average pore diameter can be determined from the cross-sectional and top-view images, respectively. The cross-sectional image of the film in Fig. 3a) shows well-defined and relatively straight pore walls. In general, the pores become more branched for lower porosity (smaller pore radius) films, and this morphology may play a very significant role in the effective diffusion coefficients of solute molecules within the films. Top-view SEM images, such as Fig. 3b), clearly show unobstructed, closely spaced pore openings in the silicon matrix that allow solute infiltration and release. A typical pore-diameter distribution generated based on SEM image analysis is shown in Fig. 3c). The average pore Feret diameter, \( d_{\text{avg}} \), is taken to be the independent variable in evaluating diffusion coefficients, although the distribution of pore widths and shapes also plays a role and may account for imperfections in theoretical fits to experimental data. For this PSi material system, the porosity and pore size are correlated, so the diffusion coefficient may therefore be associated with film porosity as well. Figure 4 provides a summary of the mean pore diameter, derived porosity, and etch rate of the PSi films as a function of formation etch-current density.

B. Sucrose Diffusion

In general, the measured temporal reflectance variations observed in sucrose outdiffusion were fit well by the mathematical model and enabled determination of diffusion coefficients. Figure 5 shows measured and fitted curves for sucrose outdiffusion from three films of different thicknesses, but the same average pore diameter and porosity (16.3 nm and 58%, respectively). The variation in behavior between the samples is evident, and the total evacuation time (time to reach signal steady-state) increases with increasing film thickness, as expected. In addition, the total change in reflected amplitude increased with increasing film thickness as a result of the greater change in optical path length of these films during sucrose evacuation. The slight deviation of the best-fit curve from the model can be accounted for qualitatively by considering the pore distribution and error in measurements of thickness or porosity. Importantly, the fitted diffusion coefficients shown on the graph increase with decreasing film thickness. This trend was found to be consistent across the sucrose diffusion data for all pore diameters. Figure 6 gives the fitted diffusion coefficient for the entire PSi sample set as a function of mean pore diameter. The diffusion coefficient also increases with increasing pore size. Thus, the diffusion coefficient of the thinnest and highest porosity films approach, and become approximately equal to, the bulk diffusion

Fig. 3. Typical SEM images of PSi films used to characterize film thickness and average pore Feret diameter. a) Cross-sectional image of a PSi film shows well-defined nanometer-scale pores terminating at a uniform depth. b) Top-view image of the same film shows clear, unobstructed pore openings. c) The pore-size distribution, as derived from a larger field of view top-view image (0.5 \( \mu \text{m} \times 0.75 \mu \text{m}) indicates an average pore diameter of approximately 26 nm.
coefficient for sucrose in water. This trend is explained by considering that diffusion is hindered by interactions of the molecules with the pore walls, which are essentially scattering events. Hence, a molecule diffusing out of a thicker film will have more opportunity to interact with the pore walls, which slows the release rate. Conversely, for pore diameters that are large relative to the pore length, a physical scenario may occur in which a particle will interact with the wall, on average, less than one time. In such a case, the effective diffusion coefficient is expected to approach that of the solute in only water. The diffusion coefficients that appear to exceed that of sucrose in water in Fig. 6 may be associated with either concentration-dependent diffusion (not considered here) or a simple error in data fitting.

C. Extensions of Measurement and Modeling Approach

The diffusion of sucrose from much thicker PSi films was also examined. For thicker films, a substantially greater total change in $\beta$ will result in oscillation of the reflected beam intensity as the relative phase of internally reflected beams vary between constructive and destructive conditions (i.e., temporal “fringes”); this is in contrast to the monotonic temporal changes in reflectance observed for thinner films. To test the applicability of the laser reflectometry and diffusion method for such thicker films, several PSi films with thickness $>5 \mu m$ and relatively high porosity ($>65\%$) were prepared. In order to reduce evacuation time, these films were thermally oxidized (at 800 °C for 30 min). As mentioned previously, diffusion through oxidized films was found to not be significantly hindered. Accordingly, the diffusion model applied with the known diffusion coefficient of sucrose in water ($540 \mu m^2/s$) was fit to experimental data with good agreement. Figure 7 shows the modeled reflectance

![Graph](image1)

![Graph](image2)

![Graph](image3)

![Graph](image4)

![Graph](image5)

![Graph](image6)

![Graph](image7)
curve as fit to the measured data of the sucrose outdiffusion from an 11.5 μm film. Good agreement between the model and experiment is evident, with the exception of two limitations of the method. First, with the rapid diffusion of relatively large quantities of high-concentration sucrose solution out of the pores, there is an immediate clouding effect near the sample surface, which reduces the intensity of the signal. This is shown by the lower magnitude of the first measured oscillation (peak at \( \sim 0.35 \) s). The scattering of the beam is visibly evident during experimentation, and typically persists for 0.5–3 s, depending on film thickness. The second limitation is in the data acquisition method (lock-in amplification), which requires some finite integration time (set between 30 and 100 ms for all measurements here), and it thereby limits the minimal temporal resolution needed to achieve a good signal-to-noise ratio. Thus, the earliest predicted oscillation (dashed curve) would not be resolved, even if clouding was not present. More precisely timed implementations could readily circumvent this latter challenge.

The second extension of the laser reflectometry and diffusion modeling method considered is the diffusion of the amphiphilic molecule, SDS. A key difference between sucrose and SDS is that the latter is likely to form energetically favorable surface structures on the interior surface of pores. Such aggregations are physically similar to micelle formations, and the stability of these structures is strongly dependent on pore geometry and size. Simple ancillary investigations involving the extended exposure of PSi films to SDS solution revealed that the release of SDS by PSi also involves the degradation of the silicon matrix, which does not occur with sucrose solution. Thus, fitting a simple Fickian diffusion coefficient to the reflected data is not physically valid. Consequently, it is important to recognize that the model presented in this work is not sufficient to extract the diffusion coefficient of SDS released from PSi films without further modification to include the degradation contribution. However, the experimental data for the SDS sample set did exhibit a distinct and interesting dependence upon the average pore diameter, which suggests that properly engineered PSi films can be used to tune the diffusion rate of SDS molecules. Figure 8 shows four such data sets for films of the same nominal thickness (300 nm) and varying mean pore diameter. The films of lower mean pore diameter show significantly increased evacuation time as compared to those films of greater pore diameter. This slower solute evacuation implies more stable adsorbed phases of the molecule on the pore walls for these films. The greater change in reflectance amplitude also indicates an increased degradation (or a greater quantity of total silicon mass lost during evacuation) during the outdiffusion of the SDS molecules. It is therefore noted that amphiphilic molecules may be more stably loaded into a PSi matrix of smaller mean pore size. Thus, while the simplistic diffusion model presented here does not accurately predict the measured temporal reflectance curves, useful quantitative information such as total evacuation time is nonetheless easily measured by this method.

Although it is beyond the scope of this work to include a comprehensive model of such degradation dynamics, a simple degradation model was applied to the SDS outdiffusion from a single PSi film to demonstrate that this phenomenon can also be quantitatively studied by this method. In particular, a linear change in the refractive index as a function of time, which is consistent with a fixed degradation rate \([16]\), was modeled to account for multiple oscillations observed in the measurement of the early time SDS outdiffusion from a 695 nm thick film. Figure 9 shows the interferometry measurement and modeled fit for the first 400 s of the experiment.
Note that the uniform rate of oscillations during the first 400 s is in direct contrast to the reflectance profile observed for films in Fig. 5. The simple degradation model shows good agreement with experiment in Fig. 9, and corresponds to a linear increase in porosity of approximately 0.25% over the 400 s period. After this initial period, the degradation (and therefore outdiffusion of SDS) slows, as expected, with a diminishing solute concentration within the film. Modeling of this later period would require inclusion of both degradation and diffusion mechanisms. A comprehensive model that takes into account both degradation and diffusion mechanisms, which vary in their relative contributions appropriately over time, will be the subject of continued future investigations.

6. Conclusion

A simple but highly quantitative means of assessing solute diffusion dynamics from PSi films by real-time laser interferometry was presented. The experimental procedure and apparatus used were described, along with the relevant mathematical formulation needed to predict measured results. By fitting measured reflectance variations with a model of Fickian outdiffusion, the effective diffusion coefficients of sucrose from PSi films of varying pore diameter and thickness were obtained. The effective diffusion coefficient of sucrose from PSi films was shown to be tunable over the range 100–550 μm²/s, and showed a direct dependence on pore size or porosity. Evaluation of SDS outdiffusion from films of different pore diameters was also made to examine the effect of the molecule’s amphiphilic property on hindered diffusion. The release behavior of SDS was found to be complicated by degradation processes occurring during outdiffusion and therefore not described by Fickian dynamics. By tuning the average pore size over the range 10–30 nm, however, the release rate of SDS could be varied over nearly 1 order of magnitude for 300 nm thick films, suggesting the possibility to greatly alter the release rate of amphiphilic drug molecules by selecting film porosity or mean pore diameter. The extension of this technique to drug delivery and other technologies was emphasized, and suggestions for application of the method to other physical scenarios were discussed.

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References and Notes

31. We note that the use of the Bruggeman approximation rather than the parallel approximation presented in Eq. (3) resulted in calculated diffusion coefficients that were within the expected error range of the technique (approximately ±50 μm²/s), as compared to the results presented. Additionally, there is no qualitatively different trend evident from use of the Bruggeman approximation, implying that the error of the technique is not sufficiently low to resolve the diffusion coefficients yielded by the different approximations.