

Diffusion of Water Molecules in Amorphous Silica

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Abstract—The diffusive penetration of atmospheric water vapor into amorphous silica (a-SiO₂) degrades the performance of electronic devices. In this letter, we calculate the range of activation energies for water diffusion in a-SiO₂ such that the diffusion time through, for example, a 0.5- μm protective layer is on the order of the decadal time scale, as required in typical applications. We find that for all practical purposes, silica composed of n -member rings is impenetrable to water vapor for $n \leq 5$. Thus, we conclude that the distribution of n -member rings in a-SiO₂ and, specifically, the $n > 5$ fraction is the critical parameter for predicting device performance.

Index Terms—Amorphous silica (a-SiO₂), diffusion, thin film, water vapor.

I. INTRODUCTION

AMORPHOUS silica (a-SiO₂) is ubiquitous in electronic devices. Since the devices are exposed to water vapor in ambient conditions, the performance of devices coated with a-SiO₂ protective thin films is limited by water-vapor diffusive penetration [1], causing, for example, puzzling film corrosion [2]. Therefore, it is desirable to render such silica films impermeable to water-vapor molecules.

a-SiO₂ has a network structure characterized by rings of n members (i.e., silicon atoms), where n typically ranges from three to nine with $n = 6$ being the most frequently occurring ring size [3], [4]. The reactions of water molecules with such silica ring networks were recently investigated in [5], while activation energy calculations for the diffusion of water in silicon carbide (SiC) were presented in [6]. Here, we address the “impermeable-design” problem via diffusive scaling combined with the calculations of ring barrier energies based on first-principles methods. Specifically, we ask the following questions: 1) What is the range of activation (barrier) energies such that the diffusion time through, for example, a 0.5- μm protective layer is about several years (as required in typical applications)?, and 2) how sensitive is the diffusion time to changes in ring-energy-barrier estimates? Both a-SiO₂ and amorphous silicon carbide (a-SiC) are considered as they share

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the ring-based network structure and industrial applications as protective coatings [6].

II. DIFFUSIVE SCALING ESTIMATES

The mean diffusion time through a distance L is given by

$$t \approx \frac{L^2}{D} \quad (1)$$

where D is the diffusion coefficient, t is the mean (averaged over the molecules) or characteristic time scale, and L is the desired diffusion distance [7].

The diffusion coefficient is

$$D = D_0 e^{-E_a/kT} \quad (2)$$

where the prefactor $D_0 = a^2 \nu z / 6$, with a as the distance (normal to ring plane) between adjacent sites, ν as the IR vibrational frequency, and $z/6 = 1$ for the geometric model of a simple ring [6].

To express the activation energy as a function of time, we substitute and rearrange as follows:

$$t = \frac{L^2}{D_0} e^{E_a/kT} \rightarrow e^{E_a/kT} = \frac{D_0}{L^2} t \rightarrow \frac{E_a}{kT} = \ln(t/\tau)$$

yielding

$$E_a = kT \ln(t/\tau) \quad (3)$$

where $\tau = L^2/D_0 = 1/\nu(L/a)^2$ is the characteristic time.

To gain an intuitive feeling for the magnitudes of required barrier energies, for SiC [6], we set $a = 2.7 \text{ \AA}$ and $\nu = 3.3 \times 10^{13} \text{ s}^{-1}$ (taken from an IR spectrum peak near 1100 cm^{-1}), yielding $D_0 = a^2 \nu \simeq 2.4 \times 10^{-2} \text{ cm}^2/\text{s}$. For SiO₂, $a = 1.6 \text{ \AA}$ and $\nu = 3.3 \times 10^{13} \text{ s}^{-1}$ (taken from an IR spectrum peak near 1100 cm^{-1} [8]); hence, $D_0 = a^2 \nu \simeq 8.4 \times 10^{-3} \text{ cm}^2/\text{s}$. At room temperature, $E_a = (0.026 \text{ eV}) \ln(t/\tau)$, and therefore, a thickness of $L = 0.5 \text{ }\mu\text{m}$ yields $\tau = 1.0 \times 10^{-7} \text{ s} = 3.3 \times 10^{-15} \text{ year}$ for SiC and $\tau = 3.0 \times 10^{-7} \text{ s} = 9.4 \times 10^{-15} \text{ year}$ for SiO₂.

In Fig. 1, we present the required SiO₂ and SiC activation energies for various diffusion lengths L and times t . The activation energy required for a penetration time of five years through a SiO₂ layer of $0.5 \text{ }\mu\text{m}$ is about 0.88 eV. Note the sensitivity of diffusion time to small changes in energy: A penetration time of one year requires 0.84 eV, while two years corresponds to 0.86 eV. Recently, Lechenault *et al.* [2] estimated the water diffusion coefficient in silica as $D \sim 10^{-21} \text{ cm}^2 \cdot \text{s}^{-1}$ at room temperature. They did so by extrapolating experimentally the results of Tomozawa and Davis [9]. This corresponds to an effective activation energy of about 1.1 eV for SiO₂.

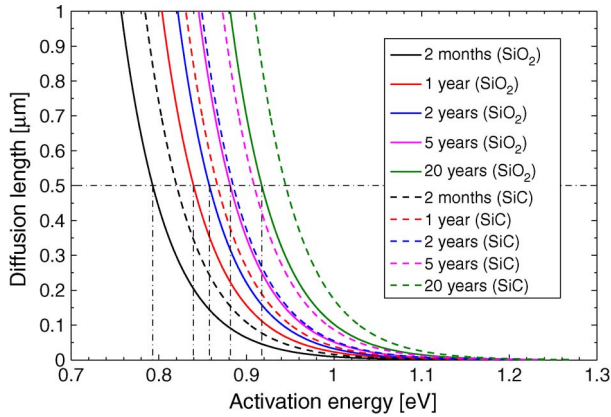


Fig. 1. Diffusion scaling versus activation energy. For example, water vapor penetration through a 0.5- μm SiO₂ layer in two years corresponds to an E_a of 0.86 eV.

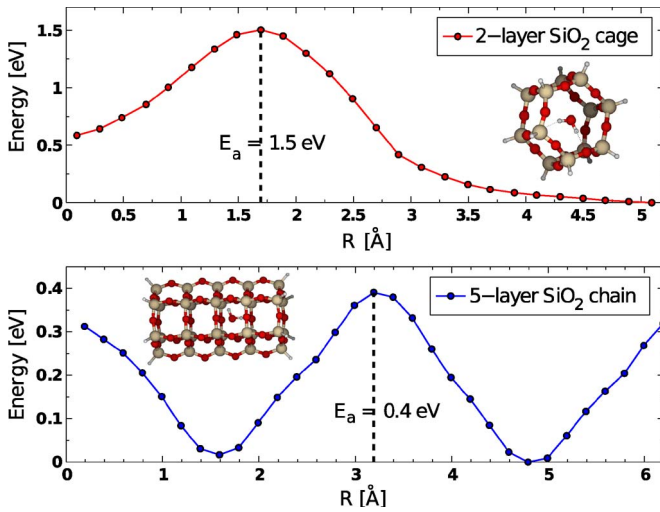


Fig. 2. Activation-energy-versus-distance results. (Top panel) Bilayer silica cage. (Bottom panel) Five-layer silica chain.

III. CALCULATIONS

Activation energies for water-vapor penetration and diffusion into a-SiO₂ and a-SiC were calculated using the Gaussian program [10]. As in [6], the structures of the water molecule and SiO₂ networks were first optimized by the Austin Model 1 (AM1) semiempirical molecular method [11] and then refined with density functional theory using the B3LYP exchange [12] and 6-31G* basis set [13]. Good agreement with the experimental values of structural properties (within a few percent) was obtained. For example, deviations from experimental values for the water molecule were 1.3% in the O–H bond length and 0.9% in the H–O–H bond angle.

Two variants of SiO₂ networks were optimized: a bilayer cage (see inset in the top plot of Fig. 2) and a five-layer chain (see inset in the bottom plot of Fig. 2). Silicon atoms in the outermost rings were terminated by hydrogen atoms [6].

We proceeded to calculate the activation energies of water diffusion and penetration into silica ring networks using a fixed potential energy scan with the AM1 method. (As will shortly become apparent, greater accuracy in calculating barrier energies using other methods, e.g., B3LYP, is unnecessary.)

TABLE I
BILAYER n -MEMBER RING CAGES: ACTIVATION ENERGY (E_a) VERSUS DIAMETER (D). FOR COMPARISON, RESULTS FOR SiC ARE ALSO GIVEN [6]

| number of ring members n | SiO ₂ | | SiC | |
|-------------------------------|------------------|------------|---------|------------|
| | D (Å) | E_a (eV) | D (Å) | E_a (eV) |
| 3 | 3.4 | 37.7 | 3.6 | 19.2 |
| 4 | 4.4 | 21.0 | 4.6 | 5.1 |
| 5 | 5.2 | 5.1 | 5.6 | 1.0 |
| 6 | 6.4 | 1.5 | 6.6 | ... |
| 7 | 7.2 | 0.3 | ... | ... |

TABLE II
FIVE-LAYER n -MEMBER RING CHAINS: ACTIVATION ENERGY (E_a) VERSUS DIAMETER (D). FOR COMPARISON, SiC RESULTS FROM [6] ARE ALSO GIVEN

| number of ring members n | SiO ₂ | | SiC | |
|-------------------------------|------------------|------------|---------|------------|
| | D (Å) | E_a (eV) | D (Å) | E_a (eV) |
| 3 | 3.4 | 41.7 | 3.5 | 9.9 |
| 4 | 4.3 | 9.6 | 4.4 | 2.2 |
| 5 | 5.3 | 2.0 | 5.5 | 0.4 |
| 6 | 6.3 | 0.4 | 6.5 | 0.02 |
| 7 | 7.2 | 0.01 | ... | ... |

Unlike [5], devoted to hydrolysis reactions, no bonds were broken during the scan while determining activation energies. In the potential energy scan, the water molecule travelled along and rotated about the silica cage's central axis in order to obtain the minimum energies at each distance R , where R is the distance between the oxygen atom of the water molecule and the center of mass of the cage structure.

IV. RESULTS AND DISCUSSION

Examples of the resulting energy curves versus R for selected n are given in Fig. 2. In the top panel are the “exterior” data of bilayer n -member rings (for modeling the penetration of water molecules into the outermost layer of the thin film). It is “exterior” in the sense that the energy scan began with the water molecule *outside* the cage which was then brought inside the cage (i.e., penetration). The bottom panel presents “interior” data, modeling a water molecule that had already penetrated and was situated inside a multilayer network (i.e., diffusion). Exterior and interior data for SiC and SiO₂ are given in Tables I and II, respectively.

The sensitivity of diffusion times to activation energy puts these ring energies in a different perspective, as shown in Fig. 3. It can be seen from the figure that differences in activation energies for different n 's are enormous, even when compared to differences in the diffusion times of two months and 20 years. Uncertainties in the estimates of a , e.g., 2.7 versus 1.8 Å, are minuscule by comparison. However, because E_a is linear in T , the activation energy is sensitive to changes in environmental temperature. For example, the temperature of a microchip's surroundings may increase as a computer heats up, and for a

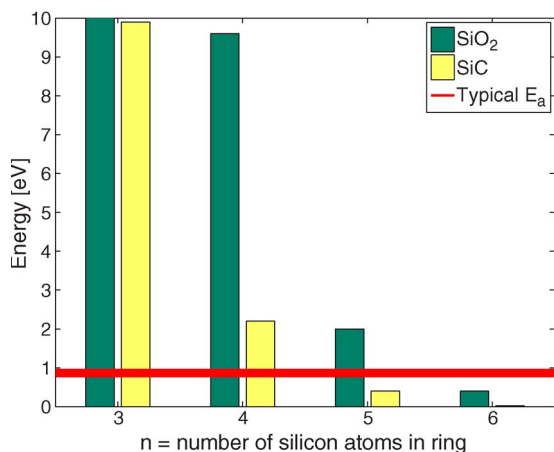


Fig. 3. At what n do n -member rings become permeable “holes”? The horizontal red line represents a range of typical E_a for $L = 0.5 \mu\text{m}$: The lower bound is 0.79 eV ($t = 2$ months for SiO_2); the upper bound is 0.94 eV ($t = 20$ years for SiC). Note that the activation energies of 0.82 (corresponding to $t = 2$ months for SiC) and 0.92 eV (corresponding to $t = 20$ years for SiO_2) fall within this range. The green and yellow bars are interior energies for SiO_2 and SiC , respectively. For all practical purposes, silica devices are impenetrable to water vapor when $n \leq 5$; for SiC , $n \leq 4$.

diffusion time of $t = 5$ years and length $L = 0.5 \mu\text{m}$ in silica, a 10% increase in kT from 0.026 to 0.0286 eV (an increase in operating temperature from about 27°C to 59°C) increases the activation energy from 0.88 to 0.97 eV , yet these differences are still smaller than those in E_a for different n 's.

Assuming a relatively constant temperature, for both SiO_2 and SiC , differences in E_a between different n 's are large compared to the smaller-than- 0.1-eV difference in E_a for varying diffusion times (e.g., from five years to two months). The horizontal diffusion time lines in Fig. 3 give rise to an unambiguous cutoff value for the desired number of ring members. “Holes,” or ring sizes responsible for water permeation, can therefore be clearly identified by their number of ring members n , as shown in Fig. 3. For example, by Fig. 3, we know that SiC rings no larger than four-member rings are desired in order to prevent water diffusion. Similarly, we see that a- SiO_2 should be composed of rings with five or fewer members. Thus, such plots show at what n rings become permeable pathways for water molecules.

Protective thin films can be fabricated by plasma-enhanced chemical vapor deposition as was shown in [14]. The reliable fabrication of impermeable (no-“hole” pathways) a- SiO_2 will require further investigation into the growth kinetics of thin films. Recent work suggests that there exists a weak coupling between the structure of bilayer a- SiO_2 films and that of their substrates (e.g., ruthenium in [3] and graphene in [15]). This may provide a platform for growing a- SiO_2 thin films with preferred ring-size distributions.

V. CONCLUDING REMARKS

Given the results of Fig. 3, we see that the question shifts from the precise evaluation of ring barrier energies (e.g., AM1 versus B3LYP calculations) to the estimates of the fraction and

network topology of water-permeable “holes,” the latter being defined by the activation energy corresponding to the desired diffusion time and length. Plots such as Fig. 3 yield a definite value of n at which n -member rings become holes (i.e., gates for water molecules to diffuse). In a- SiO_2 , n -member rings with $n > 5$ are holes; in a- SiC , this condition yields $n > 4$. Thus, for all practical purposes, silica devices are impenetrable to water vapor for $n \leq 5$; for silicon carbide devices, $n \leq 4$. In view of these results, we propose that a layer of a nonreactive amorphous-silicon-based compound, composed of rings of $n \leq 5$, would serve as a water-vapor-impermeable protective coating on the decadal time scale. Note that the fraction of holes need not be zero; rather, holes must be isolated so that a percolation path for water molecules cannot form.

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