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Molecular modeling of water diffusion in amorphous SiC

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The diffusion of water in amorphous SiC (*a*-SiC) was investigated by molecular modeling methods based on density functional theory. It was assumed that the structure of *a*-SiC at the molecular level can be described by a model that takes into account a distribution of cage structures which consist of SiC units forming *n*-member rings from a suitable precursor in a chemical vapor deposition process. Electronic structure calculations are then performed to determine the energy barrier that the water molecule encounters when it penetrates through SiC rings of various sizes. It has been found that along its diffusion path through the SiC network the water molecule neither breaks up nor attaches itself to the SiC network and the energy barrier for diffusion depends mainly on the local SiC ring topology. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1968439]

I. INTRODUCTION

Amorphous silicon carbide (*a*-SiC) and silicon-carbon alloy films are of great scientific and technological interests. Their applications may range from protective coatings against metallurgical tools' wear[1] to wide band gap semiconductors for window layers in solar cells,[2] visible-ultraviolet detectors,[3] and light emitting diodes (LEDs).[4] Water at the interface is often the main cause of corrosion, blistering, and debonding of the coating/substrate system. Consequently, transport of water from the environment to the coating/substrate interface is the subject of great interest in many technological applications. Besides, the recent developments of organic and polymer-based LEDs, especially for flexible displays, present applications for Si-containing protective coatings which require extremely low values for the water vapor transport rate (WVTR) to keep moisture from both, the cathode (usually Li or Ca metal, often overcoated with Al) and the organic or polymer layers.

Opila has studied the water-enhanced oxidation of silicon carbide at high temperatures.[5] But to our knowledge, no other study has ever considered diffusion of water in thin films of *a*-SiC. This may be due to the fact that the permeation of water in these films is insidious and is not readily detected. In this paper, we report the results of a theoretical study of diffusion of water in *a*-SiC using molecular orbital methods to calculate the interaction energetics between the diffusant and the network.

II. COMPUTATIONAL METHOD

Since the energetics of the system depend on the local bonding environment in an amorphous solid, the SiC network of *a*-SiC was simulated by a cluster model consisting of *n*-member SiC rings where *n* is the number of the SiC diatomic units forming a ring. The choice of the cluster model is justified by the fact that *a*-SiC has a short-range order,[6,7] for which the connectivity between nearest neighbors is characterized by that of its crystalline counterparts. The principal construction rules followed here are consistent with the Polk model for amorphous semiconductors,[8] which requires the atoms to be arranged in an approximately tetrahedral geometry with bond lengths and bond angles distributed about the corresponding values in the crystalline state.

Figure 1(a) shows the initial configuration of the three-member SiC rings, which represent the Si–C network in analogy to the zinc-blende crystalline structure.[9] The existence of higher-member rings in the SiC network is also taken into account by considering four-, five-, and six-member SiC rings in the calculations. We note that Monte Carlo calculations have shown that the medium-range order of annealed *a*-SiC is more open than the crystalline zinc-blende structure.[10] A recent molecular dynamics study also confirms the occurrence of two-, three-, four-, and five-member rings in amorphous SiC, which results in the material's low density as compared to the crystal phase.[7] The SiC cage structure considered here consists of two or more layers of *n*-member SiC rings (with $n=3,\ldots,6$) in which the dangling bonds were terminated by hydrogen atoms to suppress the so-called surface effects.[11]

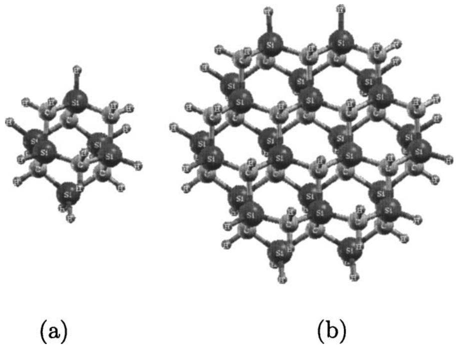

FIG. 1. Three-member (a) single-cage cluster (terminated by hydrogen atoms) and (b) extended cage structure (composed of seven single cages and connected by the same covalent bonds that make each ring).

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Geometry optimization without the symmetry constraint was performed for both the water molecule and the SiC network using the Austin Model 1 (AM1) semiempirical molecular orbital method[12] and the density functional theory (DFT) method using the B3LYP exchange[13] and correlation functional form[14] with the 6-31G* basis set for Si and C atoms.[15] Initial steps in the geometry optimization were performed using the AM1 method. The resulting configuration was reoptimized using the DFT method from which improvements in the accuracy of the calculated energy values are expected. The optimization was achieved with a gradient norm smaller than 10^{-4} hartree/bohr and an energy convergence of 10^{-6} hartree. For the water molecule, the calculated bond length $R_{\text{O–H}}$ is 96.9 (98.9) pm, and the bond angle $A_{\text{H–O–H}}$ is 103.6° (100.0°) at the DFT (AM1) level. These values are in very good agreement with the corresponding experimental values of 95.7 pm and 104.5° for an isolated water molecule.[16] The *n*-member SiC rings optimized by either the AM1 or DFT method also provide a realistic description of the SiC network in *a*-SiC. For example, in three-member SiC rings the maximum deviations from the experimental values[17] of bond lengths are about 1.4% (AM1) or 3.6% (DFT), and those of bond angles vary from −2.8% to +1.6% (AM1) or from −2.1% to +1.1% (DFT).

In order to further check the viability of our single-cage cluster model, an extended cage structure was also considered which consists of seven cages of three-member SiC rings, as shown in Fig. 1(b). The atoms in the center cage have three or four nonhydrogen neighbors in contrast to the hydrogen termination in the single-cage structure. The calculated results of the diffusion energetics using a single-cage structure and an extended cage structure are in good agreement with each other, supporting our choice of the cluster model in this study.

The interaction of the SiC network with a water molecule diffusing through the random maze of rings is idealized by treating the SiC rings as barriers through which the H_2O molecule penetrates. We note here that this particular mode of water transport is selected as the simplest transport mechanism in covalently bonded solids. This idea was first investigated by Anderson and Stuart by considering the interstices connected by "doorways" in their study of molecular diffusion and ionic conduction in silica glasses.[18] A similar approach was employed by Pernisz *et al.* to calculate the molecular water diffusion barrier in thin films of nondense silica derived from H-silsesquioxane.[19] More recently, Bakos *et al.* studied the diffusion of H_2O and O_2 molecules in amorphous SiO_2 on the same basis by considering ring-type structures which constitute the bottlenecks of different sizes in the diffusion channel.[20] It should, however, be pointed out that H_2O diffuses in SiO_2 by a hydrolysis-condensation reaction mechanism due to the existence of Si–O bonds,[20,21] which is not the case in SiC.

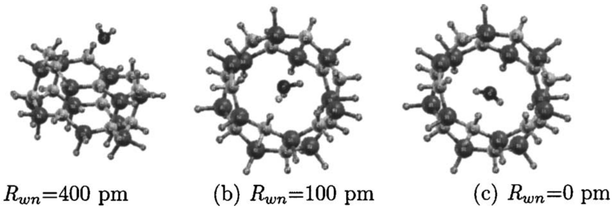
(a) R_{wn}=400 pm (b) R_{wn}=100 pm (c) R_{wn}=0 pm

FIG. 2. Diffusion of water through a six-member SiC cage structure simulating the *a*-SiC network. R_{wn} is the distance of water from the cage.

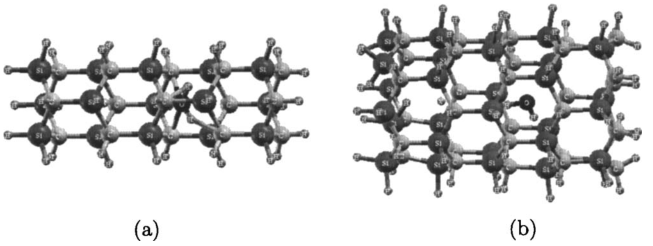

FIG. 3. Molecular permeation of water through (a) three-member and (b) six-member extended cages simulating the *a*-SiC network.

In our study, two processes were considered to simulate diffusion of H_2O in the network of *a*-SiC. In the first process, H_2O was moved directly from outside into the SiC network through the *n*-member surface ring, as shown in Fig. 2. In the second process, H_2O moves through the SiC network from a cage center to another neighboring cage center, as shown in Fig. 3. It simulates the permeation of molecular water through the SiC network. In both cases, the pathway is defined along the line that passes through the center of the *n*-member SiC ring and the reference point defined to measure R_{wn} (i.e., distance of H_2O to the SiC network). The reference point is taken to be the center of mass of the SiC cage structure.

III. RESULTS AND DISCUSSION

Figures 4(a) and 4(b) show the AM1 potential energy curve along the diffusion pathway for three- and six-member SiC cage structures, respectively. In these calculations, R_{wn} was varied from 400 pm down to zero with a step size of −20 pm. Since the orientation of the polar H_2O molecule is expected to be influenced by the SiC network as H_2O approaches toward the network, scans of all the possible orientations of H_2O were performed at each value of R_{wn}.

For all *n*-member SiC cage structures considered here, H_2O prefers the orientation with O pointing towards the network and H pointing away from the network for $R_{\text{wn}} > 250$ pm. As H_2O gets closer to the network, it rotates to make one OH bond perpendicular to the SiC ring. Once H_2O penetrates the ring, it takes the inverse orientation where O

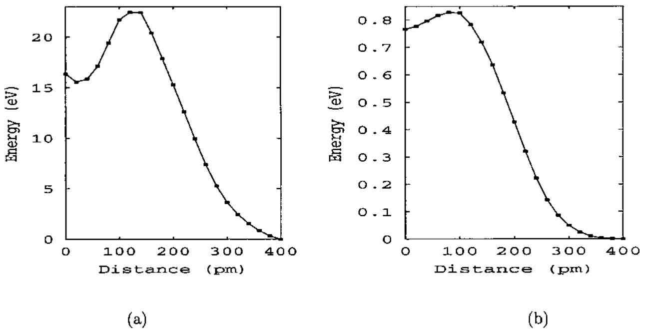

FIG. 4. The AM1 potential energy curve representing the diffusion of water through (a) three-member and (b) six-member cages simulating the *a*-SiC network.

TABLE I. The DFT apparent activation energy E_a^* for the direct penetration of water into the *n*-member SiC network.

Ring system	Diameter (pm)	E_a^* (eV)
Three-member	≃360	19.2
Four-member	≃460	5.1
Five-member	≃560	1.0
Six-member	≃660	⋯

again rotates toward the ring with H pointing away from the ring toward the center. As shown in Figs. 4(a) and 4(b), the total energy of the system increases continuously as H_2O approaches the SiC network achieving a maximum value when H_2O is close to the surface. It then decreases when H_2O approaches the reference point of the network (i.e., $R_{wn}=0$ pm). The maximum energy near the surface is expected, because when H_2O enters the network, a conformational change is required to alleviate the stress in the network. The apparent activation energy (E_a^*) for the direct penetration of water into the SiC network can then be defined as the difference between the maximum and minimum (near $R_{wn}=400$ pm) on the energy curve. Table I collects the calculated results of the apparent activation energy of the direct penetration of water into *n*-member SiC cage structures.

As indicated before, the apparent activation energy has a prominent dependence on the size of the SiC rings modeling the SiC network. The three-member SiC cage structure represents a basic building block of the zinc-blende crystal, which is highly compact and dense. The energy barrier for the direct penetration of water is around 19 eV, which is so high that it essentially disallows any possibility for H_2O diffusion into the SiC network dominated by cages built from three-member rings. This value is larger than the bond energy of 4.5 eV of the SiC diatomic molecule which implies that H_2O diffusion will not occur without a strong perturbation to the network. The energy barrier, however, drops abruptly as the size of the ring increases for higher-member cages, and becomes insignificant for the six-member cage structure.

In these calculations, we have simplified the computational problem by using a rigid SiC network since the relaxation of atoms is small in a tetrahedral covalently bonded network. However, in an attempt to explore the possible chemical reaction of H_2O with SiC, we have performed both partially and fully relaxed calculations of the three-member SiC cage structure together with a H_2O molecule near and inside the cage. For the rigid three-member cage structure, the strong steric interaction fragments the H_2O molecule into a H bonded to a C and an OH bonded to a Si. Nevertheless, in the optimization process in which both the SiC network and H_2O are fully relaxed, H_2O simply expands the ring and gets outside without breaking up. It should be pointed out that the three-member SiC cage structure is highly packed and the cavity inside is too small to contain a H_2O molecule. Thus, the observed dissociation of H_2O is simply driven by the strong steric interactions rather than any propensity for a chemical reaction between H_2O and SiC. This is supported by further relaxation calculations on the five-member SiC cage structures. Whatever the initial position and orientation of the H_2O molecule, when relaxed, it moves away from the nearest Si or C, showing no affinity to react. Depending on its initial position, the water molecule will relocate to either the cage center or outside of the cage. In contrast to the observation of H_2O dissociation on the reconstructed[22] or Si-terminated SiC surface,[23] the inertness of the SiC inner surface to H_2O is due to the saturation of all the dangling bonds in the present structure model. Further study of the effect of the dangling bonds on water diffusion is in progress.

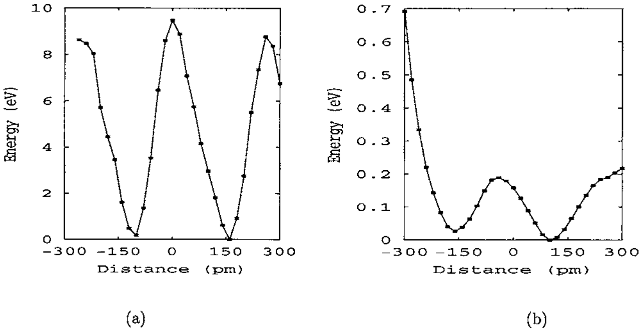

FIG. 5. The AM1 potential energy curve of molecular permeation of water through (a) three-member and (b) six-member cages simulating the *a*-SiC network.

We now mimic the permeation of molecular water through the network by considering multilayered cage structures to simulate the SiC network. The calculated (AM1) energy profiles for H_2O diffusion in five-layer SiC cage structures are shown in Figs. 5(a) and 5(b) for three- and six-member rings.

We can see that the total energy of the system varies periodically with R_{wn}, where the reference point is taken to be the center of the five-layer structure and at the geometric center of a ring in the middle layer. The energy surface shows a peak E_{max} when H_2O begins to penetrate through the center of one of the rings and drops to a local minimum E_{min} when H_2O goes into the interstices (i.e., cage centers in the network). The energy difference between these two values is identified as the activation energy E_a of the H_2O diffusion within the network.

Table II collects the DFT energy values of the activation energy, showing a strong dependence on the local ring size chosen to represent the network. However, the values of the activation energy are significantly lower compared to those given in Table I. We can, therefore, conclude that once H_2O has entered the network, it encounters a smaller energy bar-

TABLE II. The DFT activation energy E_a for molecular permeation of water through the SiC network.

Ring system	Diameter (pm)	E_a (eV)
Three-member	≃350	9.9
Four-member	≃440	2.2
Five-member	≃550	0.4
Six-member	≃650	0.02

rier for diffusion. The cause of the smaller activation energy for molecular permeation can roughly be traced to the high residual steric interaction in the interstitial sites relative to that outside of the network. The energy difference is called the incorporation energy E_{inc}. For an interstitial H_2O molecule in the cage center it can be calculated by considering the minimum total energy for the whole system $E_{\min}$ with respect to the energy of the undisturbed SiC network E_{SiC} and of the isolated H_2O molecule E_{H_2O} as

$$E_{\text{inc}} = E_{\min} - (E_{\text{SiC}} + E_{H_2O}). \quad (1)$$

Accordingly, the calculated DFT values of E_{inc} come out to be 12.4, 3.7, and 0.6 eV for three-, four-, and five-member rings, respectively. The rings show a drastic decrease in E_{inc} with increase of cage size and E_{inc} essentially vanishes for the six-member ring; the same behavior is observed for the diffusion of molecular O_2 in disordered SiO_2.[24] The incorporation energy is very high for the cage of three-member rings, which implies that the probability of finding the water molecule in such a cage is extremely small. It drops to a relatively low value for cages with five- and six-member rings. Due to this high incorporation energy, the H_2O molecule entering into the SiC network from outside experiences a larger activation energy (E_a^*) for penetration into the network than the H_2O molecule in the network diffusing through SiC rings of various sizes (E_a). However, due to the steep concentration gradient of H_2O at the interface of water vapor with the *a*-SiC thin film, we consider in the following the value of the activation energy E_a corresponding to the diffusion of H_2O within the network as the rate limiting factor for diffusion of water in the SiC network.

To obtain an estimate of the WVTR value, we consider exposing a 500 nm thick *a*-SiC thin film to highly saturated humid air. The saturation concentration of water vapor at $T = 300$ K is approximately 26 g/m^3. The water flux density (J) can be obtained, in steady state, in terms of the diffusion constant D and water concentration gradient, from Fick's First Law $J = -D(\partial n/\partial x)$. For a realistic estimate of the diffusion constant, the size distribution of the SiC rings needs to be taken into account as well as a model for the percolation path of water molecules through the large rings. This is, however, beyond the scope of the present study. Instead, we assume a highly simplified model which employs the Arrhenius expression $[D = D_0 \exp(-E_a/kT)]$ to obtain an estimate of the water flux from the thermally activated ring penetration of a water molecule considering each of the ring sizes individually. Here E_a is the activation energy introduced for this process before (see Table II). The prefactor D_0 can be estimated by using the Einstein relation[25] in the absence of a driving force, $D_0 = a^2 \nu z/6$, where a is the distance between adjacent sites normal to the ring plane, ν is a frequency-of-attempt value, and z is the number of possible jump sites which corresponds to the nearest-neighbor coordination number if only nearest-neighbor jumps are allowed. Thus the geometry-related factor $z/6$ is equal to 1 for the simple model in which vacant jump sites are available only in each of the six directions of the three-dimensional space. The site separation a is nearly the same for all ring size structures and has a value of 270 pm. An estimate of ν can be made from the vibrational frequencies of the SiC network. The peak around 1100 cm^{-1} in the IR spectrum represents a typical stretch mode; this corresponds to a frequency of $\nu = 3.3 \times 10^{13}\ \text{s}^{-1}$, so that D_0 is around $2.4 \times 10^{-2}\ \text{cm}^2/\text{s}$. The water flux densities are then calculated to be 1.4×10^{-39}, 2.4×10^{-9}, and $5.6 \times 10^{-3}\ \text{g/cm}^2\,\text{s}$ for the four-, five-, and six-member ring, respectively, using the DFT values. These are the upper limits since they were obtained without accounting for the solubility of H_2O in *a*-SiC which would make the concentration gradient, and thus the water flux density values calculated, several orders of magnitude smaller. The exercise shows, however, that adequate water barrier performance requires a material that avoids percolation paths consisting of six-member or larger ring sizes.

IV. SUMMARY

We have developed a cluster model by using single or multilayer cages to describe the amorphous SiC film structure. As a primary step, only tetrahedrally heteronuclear bonding networks were considered. Water diffusion in these films was simulated by molecular models using density functional theory. The dependence of the diffusion barrier on ring size is emphasized here.

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