

Nonequilibrium Activated Dissociative Chemisorption: SiH₄ on Si(100)

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Received: November 10, 2004; In Final Form: December 6, 2004

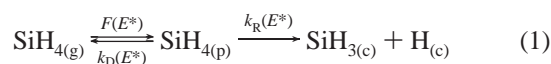
A three-parameter local hot spot model of gas–surface reactivity is employed to analyze and predict dissociative sticking coefficients for SiH₄ incident on Si(100) under varied nonequilibrium conditions. Two Si surface oscillators and the molecular vibrations, rotations, and translational energy directed along the local surface normal are active degrees of freedom in the 15 dimensional microcanonical kinetics. The threshold energy for SiH₄ dissociative chemisorption is found to be 19 kJ/mol, in quantitative agreement with recent GGA-DFT calculations. A simple scheme for increasing the rate of chemical vapor deposition of silicon from SiH₄ at low surface temperatures is modeled.

The activated dissociation of polyatomic molecules at surfaces can be rate limiting for many technologically important catalytic¹ and chemical vapor deposition² processes. Oftentimes such dissociative chemisorption reactions are run under nonequilibrium conditions that rule out kinetic analysis using thermal rate constants of the familiar Arrhenius form.³ A three-parameter physisorbed complex-microcanonical unimolecular rate theory (PC-MURT) model of gas–surface reactivity was recently shown to accurately predict dissociative sticking coefficients for CH₄ incident on the smooth Pt(111)⁴ and Ni(100)⁵ metal surfaces for a broad range of thermal equilibrium, nonequilibrium, and molecular eigenstate-resolved experiments that span roughly 10 orders of magnitude variation in sticking and pressure. The PC-MURT provides a statistical description of the surface reaction dynamics, recovers canonical transition state theory and Arrhenius sticking coefficients for thermal systems, and provides a baseline against which nonstatistical behavior^{6,7} can be identified when it occurs. In this manuscript, we extend the PC-MURT to treat SiH₄ reactivity at the corrugated Si(100) semiconductor surface and explicitly calculate sticking coefficients for the most commonly encountered nonequilibrium situation where the temperature of the impinging gas differs from that of the surface. Our simple modeling provides a unified framework for understanding a large number of disparate experiments and yields a 19.3 kJ/mol apparent threshold energy for SiH₄ dissociation that may serve as a benchmark for electronic structure theory calculations.

Chemical vapor deposition (CVD) of silicon from low-pressure SiH₄ gas is one of the most widely applied technologies for the fabrication of modern microelectronic devices. Interest in obtaining a molecular level understanding of semiconductor CVD processes stems from the need to engineer devices at ever smaller nanoscale dimensions. The single-crystal Si(100) wafers used by the semiconductor industry reconstruct to expose Si(100)–(2 × 1) surfaces with parallel rows of Si atom dimers. Silane CVD on Si(100) at low pressures (<10⁻² mbar) and

surface temperatures less than 873 K can be rate limited by H desorption, but SiH₄ dissociative chemisorption is rate limiting at higher temperatures.² Xia et al.⁸ explored the angular variation of SiH₄ sticking from molecular beams on Si(100) and found that sticking scales with the local normal translational energy averaged over the surface unit cell, $\langle E_{t,\perp} \rangle = E_t \Theta(\Delta, \vartheta)$ where the universal scaling function $\Theta(\Delta, \vartheta) = (1 - \Delta) \cos^2 \vartheta + 3\Delta \sin^2 \vartheta$ depends on the surface corrugation factor Δ and angle of incidence ϑ .⁹ The experimentally determined corrugation factor of $\Delta = 0.151 \pm 0.09$ for the SiH₄/Si(100) system⁸ relates to the corrugation of the reactive potential energy surface⁹ and contrasts to the value of $\Delta = 0$ found for the dissociative chemisorption of many small molecules on smooth metal surfaces where in-plane corrugation of the reactive potential is negligible.

Gates et al.¹⁰ employed static secondary ion scattering to show that the primary step in SiH₄ chemisorption on Si(100) is dissociation to yield chemisorbed SiH₃ and H fragments. We assume the silane dissociative chemisorption kinetics on Si(100) can be described microcanonically as⁴



where the E^* zero of energy occurs with silane at infinite separation from the surface when all species are at 0 K. Silane incident on the surface from the gas phase is assumed to form a transient gas/surface collision complex consisting of a molecule, in the neighborhood of the physisorption potential well minimum, that interacts with a few immediately adjacent surface atoms. Energy within these collisionally formed “physisorbed complexes” (PC) or “local hot spots” is assumed to become microcanonically redistributed in a collision ensemble averaged sense. Diffusion of energy away from the PCs and into the Si(100) bulk is limited by the ultrafast time scale for desorption at reactive energies. PCs formed at some total energy E^* can go on to desorb or react dissociatively with the surface to yield chemisorbed fragments with RRKM rate constants

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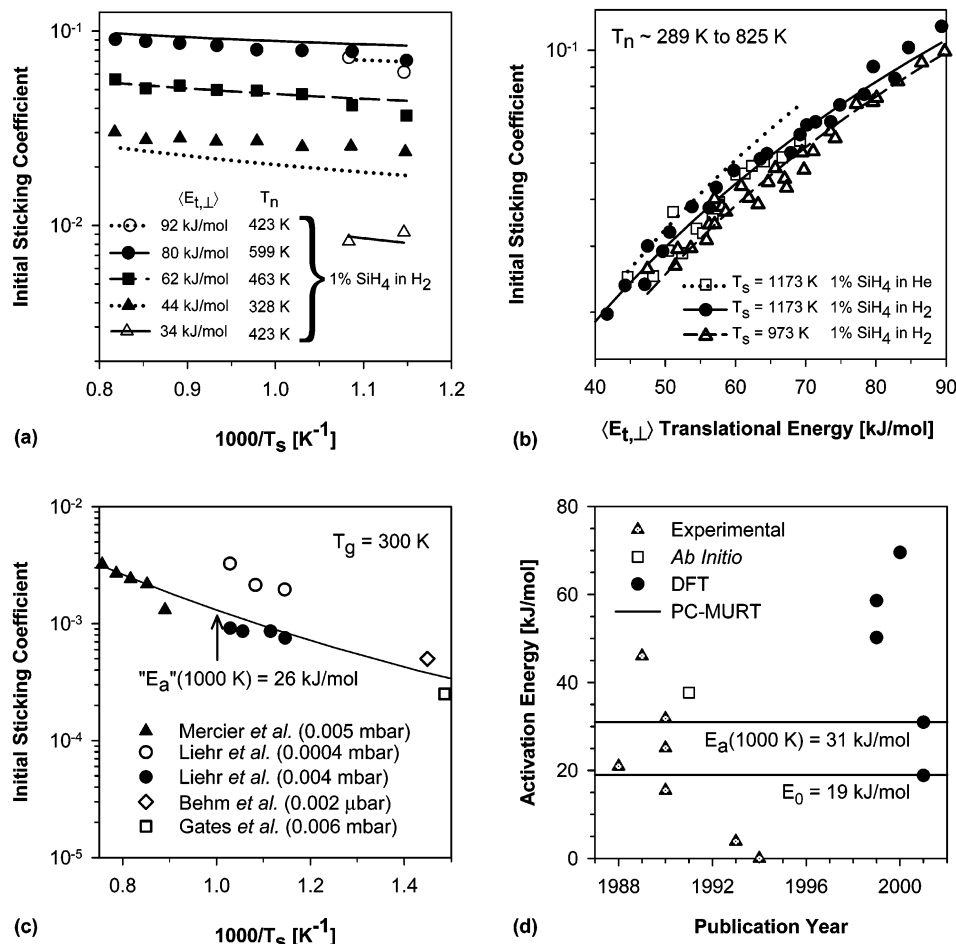


Figure 1. Comparison of experimentally derived dissociative sticking coefficients (points) for SiH₄ impinging on Si(100) with the theoretical predictions of the PC-MURT (lines) with parameters { $E_0 = 19.3$ kJ/mol, $\nu_D = 230$ cm⁻¹, $s = 2$ }. (a) Sticking from molecular beams as a function of surface temperature T_s at given average local normal translational energies $\langle E_{t,\perp} \rangle$ and nozzle temperatures T_n . Solid data points are from Xia et al.⁸ Open data points from Mullins *et al.*¹³ have been multiplied by 2.0. (b) Sticking from molecular beams as a function of $\langle E_{t,\perp} \rangle$ at various T_s , T_n , and seeding gas mixtures from Jones *et al.*¹² (c) Low-pressure dissociative sticking from a 300 K ambient gas.^{21–24} (d) Activation energies for SiH₄ dissociative chemisorption derived experimentally as "E_a" with $T_g = 300$ K^{21,22,25–28} and apparent threshold energies E_0 ($=E_a$ at 0 K) derived from ab initio¹⁷ or density functional theory^{14,16,18} electronic structure calculations are compared to the thermal equilibrium E_a predictions of the PC-MURT.

$k_D(E^*)$ and $k_R(E^*)$. The steady-state approximation applied to the SiH_{4(p)} coverage of eq 1 yields

$$S = \int_0^\infty S(E^*)f(E^*) dE^* \quad (2)$$

where

$$S(E^*) = \frac{W_R^\ddagger(E^* - E_0)}{W_R^\ddagger(E^* - E_0) + W_D^\ddagger(E^*)} \quad (3)$$

is the microcanonical sticking coefficient, W_i^\ddagger is the sum of states for transition state i , E_0 is the apparent threshold energy for dissociation, and

$$f(E^*) = \int_0^{E^*} f_t(E_t) \int_0^{E^* - E_t} f_v(E_v) \int_0^{E^* - E_t - E_v} f_r(E_r) f_s(E^* - E_t - E_v - E_r) dE_r dE_v dE_t \quad (4)$$

is the probability distribution for creating a PC at $E^* = E_t + E_v + E_r + E_s$. The $f(E^*)$ is formed by convolution over the various SiH₄ energy distributions and the surface energy distribution for s oscillators vibrating at the mean silicon phonon frequency, $\nu_s = (3/4)k_b\theta_{\text{Debye}}/h = 335$ cm⁻¹.

Discounting parallel molecular translational energy as a spectator or inactive form of energy over the course of the reactive gas–surface collisions, we assume that only $\langle E_{t,\perp} \rangle$ will contribute to E_t in the expressions above (i.e., set $E_t = \langle E_{t,\perp} \rangle$ alone). Following common practice, we further assume that in molecular beam experiments the nozzle temperature, T_n , sets the vibrational and rotational temperatures of the beam molecules as $T_v = T_n$ and $T_r = 0.1T_n$, respectively.

The desorption transition state is taken to occur when SiH₄ is freely rotating and vibrating in the gas phase, far from the surface. The dissociation transition state is characterized by the nine vibrational modes of SiH₄ in the gas, s vibrational modes of the Si surface oscillators, four vibrational modes at a single lumped frequency ν_D representative of the three frustrated rotations and the vibration along the surface normal of silane at the dissociation transition state, and one of the triply degenerate antisymmetric Si–H stretching vibrations ($\nu_3 = 2190$ cm⁻¹) of SiH₄ is sacrificed as the reaction coordinate. The resulting PC-MURT has only three adjustable parameters, E_0 , ν_D , and s , that can be fixed by comparative simulation to varied experimental data.

The three parameters of the PC-MURT were optimized by simulating the solid data points of Figure 1a–c derived from experiments conducted at surface temperatures greater than 873

K where Si(100) should remain clean and free from any possible H passivation² that might complicate our analysis. A minimum in the average relative discrepancy (ARD) between theory and experiment of 9.8% was achieved for PC-MURT parameters $\{E_0 = 19.3 \text{ kJ/mol}, \nu_D = 230 \text{ cm}^{-1}, s = 2\}$. Another parameter set of $\{E_0 = 14.5 \text{ kJ/mol}, \nu_D = 270 \text{ cm}^{-1}, s = 1\}$ gave an ARD only slightly higher at 10.3% but did not predict nearly so well the relatively high dynamic range thermal nonequilibrium sticking experiments of Figure 1c. Parameter sets with $E_0 > 20 \text{ kJ/mol}$, $E_0 < 13 \text{ kJ/mol}$, $\nu_D > 290 \text{ cm}^{-1}$, $\nu_D < 220 \text{ cm}^{-1}$, or $s > 2$ all had ARDs greater than 12%. On physical grounds, it is likely that the reactive mechanism involves two Si atoms (i.e., $s = 2$; vide infra) and the ν_D frequency should be close to the 218 cm^{-1} value calculated by Xia et al.⁸ for vibration along the surface normal of SiH₄ on Si(100). As a consequence, the ARD minimum parameter set is believed to best represent the SiH₄/Si(100) transition state characteristics within the framework of the PC-MURT and the existent experimental data that span less than 3 orders of magnitude variation in sticking coefficient.

PC-MURT sticking predictions using the $\{E_0 = 19.3 \text{ kJ/mol}, \nu_D = 230 \text{ cm}^{-1}, s = 2\}$ parameter set are given for the varied experiments of Figure 1a–c. The overall ARD for PC-MURT predictions of both the closed and open data point experiments is 14.5%. The nozzle temperatures for Engstrom's molecular beam experiments were calculated according to his equations⁸ using specific heat ratios given by Larsen et al.¹¹ and calibrated against the two specific examples discussed in detail by Jones et al.¹² In Figure 1a, the Mullins et al.¹³ molecular beam sticking data were multiplied by a factor of 2.0 that was chosen for best agreement with the PC-MURT predictions and to restore consistency with the Engstrom data. The Mullins rescaling seems appropriate because accurate calibration of absolute sticking coefficients is undoubtedly very difficult to achieve^{5,11} and otherwise the Mullins sticking coefficients for a $\langle E_{t,\perp} \rangle = 92 \text{ kJ/mol}$, $T_n = 423 \text{ K}$ beam would fall virtually on top of those for the $\langle E_{t,\perp} \rangle = 44 \text{ kJ/mol}$, $T_n = 328 \text{ K}$ beam reported by Jones et al.,¹² a seemingly unphysical result. Ultimately, rescaling the Mullins data by a single global factor leads to low ARD PC-MURT predictions for all four Mullins experimental sticking coefficients.

The PC-MURT predictions appear to quite faithfully replicate the nonequilibrium experimental sticking as a function of surface temperature and $\langle E_{t,\perp} \rangle$. The largest discrepancies occur for the He seeded molecular beam data in Figure 1b and the lower pressure Liehr et al. ambient gas data in Figure 1c. A modest kinetic isotope effect (KIE) of 1.1–1.6 for SiH₄/SiD₄ sticking was measured in He seeded molecular beams¹² under conditions where the PC-MURT predicts a KIE of 4.5. The relatively high KIE predicted by the PC-MURT stems primarily from the smaller rotational constants for SiD₄ as compared to SiH₄ which leads to relatively more open desorption channels [i.e., $W_D^\ddagger(E^*)$] that compete with reactive channels for SiD₄ (see eq 3). Importantly, the ability of the PC-MURT to accurately predict the nonequilibrium sticking in Figure 1c from a random gas incident from all angles to the surface provides additional support for the validity of Engstrom's analysis⁹ and molecular beam finding¹² that the sticking coefficient scales with the average local normal translational energy, $\langle E_{t,\perp} \rangle$. In addition, the Figure 1c PC-MURT predictions are consistent with energy in all of the molecular vibrational and rotational degrees of freedom being fully exchangeable within the reactive transition state. The influence of rotational energy on dissociative sticking is much smaller in supersonic beam experiments because of substantial rotational cooling, $T_r \sim 0.1T_n$. Indeed, because the

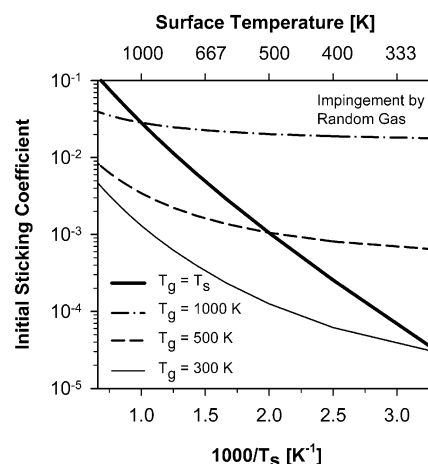


Figure 2. PC-MURT predictions of SiH₄ dissociative sticking on Si(100).

average local normal translational energies of the Figure 1 molecular beam experiments are considerably higher than E_0 even the effects of varying T_s and $T_n (=T_v)$ are relatively modest.

Figure 1d illustrates the range of activation energies E_a proposed for SiH₄ dissociative chemisorption on Si(100) over time. Although dissociative sticking is exponential in E_a , there has been remarkably little consensus on its value. The PC-MURT, informed by the many nonequilibrium experiments of Figure 1a–c, indicates that the apparent threshold energy for reaction is $E_0 = 19.3 \text{ kJ/mol}$ which is in excellent agreement with the 18.8 kJ/mol value predicted by Musgrave's density functional theory (DFT) calculations¹⁴ using a new KMLYP functional.¹⁵ This functional was tested on 74 transition state barriers and had an absolute mean deviation from experiment of only 3.8 kJ/mol .¹⁵

The PC-MURT parameter of $s = 2$ surface oscillators is consistent with a reactive transition state involving 2 adjacent Si atoms in either an intra- or interdimer mechanism as proposed by Gates.¹⁰ Musgrave's¹⁴ and Doren's¹⁶ DFT calculations support an intra-dimer mechanism, whereas an ab initio¹⁷ and Lin's¹⁸ DFT calculations support an interdimer mechanism with considerably higher barriers. Although the initial activated dissociative chemisorption of H₂ on Si(100) has recently been shown by scanning tunneling microscopy to involve an interdimer mechanism,¹⁹ our analysis of the SiH₄ dissociative sticking provides support for Musgrave's transition state and an intradimer mechanism.

Figure 2 contrasts predictions for SiH₄ dissociative sticking from a random gas under thermal equilibrium and under nonequilibrium conditions where $T_g \neq T_s$. Clearly, surface science experiments exposing Si(100) to gas at $T_g = 300 \text{ K}$ will measure quite different sticking coefficients and "activation energies" than will equilibrium experiments employing an isothermal UHV–CVD reactor. There are other variants of UHV–CVD reactors, some with hot walls and some with cold walls, where the gas may not be in equilibrium with the surface. It is quite likely that some of the apparent experimental contradictions in the literature occur simply because two-parameter Arrhenius sticking expressions measured under one set of nonequilibrium conditions are not transferable to another. Recognizing that both molecular and surface degrees of freedom can supply energy to surmount the barrier to dissociation, the three-parameter PC-MURT model is able to accurately predict both equilibrium and nonequilibrium dissociative sticking in a simple unified manner.

Our analysis indicates that CVD deposition rates could be significantly enhanced by raising T_g while maintaining the silicon growth surface at relatively modest T_s limited only by the ongoing needs to desorb H and diffuse the new Si adatoms into epitaxial crystalline growth registry. Such a simple scheme for CVD growth of semiconductor at low surface temperatures might be usefully and easily integrated into the fabrication of modern microelectronic devices and integrated microsensors.²⁰

Acknowledgment. This work was supported by the National Science Foundation and by the Donors of the American Chemical Society Petroleum Research Fund.

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