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Precursor mechanism for interaction of bulk interstitial atoms with Si(100)

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In the same way that gases react with surfaces from above, solid-state point defects such as interstitial atoms can react from below. Little attention has been paid to this form of surface chemistry. Recent bulk self-diffusion measurements near the Si(100) surface have quantified Si interstitial annihilation rates, and shown that these rates can be described by an annihilation probability that varies by two orders of magnitude in response to saturation of surface dangling bonds by submonolayer gas adsorption. The present work shows by modeling that the interstitial annihilation kinetics are well described by a precursor mechanism in which interstitials move substantial distances parallel to the surface before incorporation.

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I. INTRODUCTION

In the same way that gases approach surfaces from above, other reactive species can approach and react from below. Examples include bulk point defects such as interstitial atoms and vacancies. Little attention has been paid to this form of surface chemistry. To our knowledge, point defect annihilation rates at surfaces have never been quantified experimentally aside from our work detailed below.

Such rates are important to know, however, because point defects govern many aspects of bulk material behavior. For example, defects typically serve as the primary mediators of solid-state diffusion.[1–3] Thus, the rates of defect creation and annihilation at surfaces can in principle become controlling factors of solid-state diffusion rates—especially when surface-to-volume ratios are high. Defect diffusion governs the behavior of solid-state electrolytes such as ZrO_2 in sensor applications.[4] Defect creation, destruction, and diffusion near surfaces play an important role in thermal catalysis by metal oxides, such as vanadia[5,6] for partial oxidation and selective catalytic reduction. The interaction of defects with surfaces strongly affects doping processes for integrated circuits by thermal[7] or implantation[8] methods. Point defect concentrations play a role in photocatalysis and photostimulated power generation by semiconductors, since the defects serve as unwanted electron-hole recombination centers.[9]

There is good reason to believe that surfaces differ markedly in their ability to annihilate defects. For example, adsorption should exert significant effects, as suggested by recent quantum calculations[10,11] by Kirichenko *et al.* An atomically clean surface that possesses dangling bonds can annihilate interstitial atoms by simple addition of the interstitials to the bonds. However, if the same surface becomes saturated with a strongly bonded adsorbate, annihilation requires the insertion of interstitials into existing bonds. Such insertion should have a higher activation barrier and a correspondingly reduced probability of occurrence. A schematic diagram of this idea appears in Fig. 1.

Using diffusion measurements near the Si(100) surface, this laboratory has recently discovered how to vary interstitial generation and annihilation rates controllably over several orders of magnitude through submonolayer nitrogen adsorption.[12] In other words, gas-surface chemistry was used to control defect-surface chemistry. Interstitial annihilation can be thought of as the rough analog of adsorption in gas-surface chemistry.

The annihilation rates for self-interstitials were examined in the greatest detail, and were quantified through an annihilation probability *S*—defined as the probability that an interstitial encountering the surface actually incorporates there and is removed from the bulk.[13] Thus, the annihilation probability is loosely analogous to the sticking probability commonly used to describe adsorption rates in gas-surface chemistry.[14] Several different regimes of behavior were observed for *S* depending upon adsorbed nitrogen concentration.[12]

The present work seeks to develop a kinetic model for surface annihilation of silicon interstitial under influence of nitrogen adsorption. The annihilation kinetics are well described by a precursor mechanism in which interstitials move substantial distances parallel to the surface before incorporation. Rate parameters and associated confidence intervals for elementary steps in the precursor model are determined by Maximum Likelihood estimation.

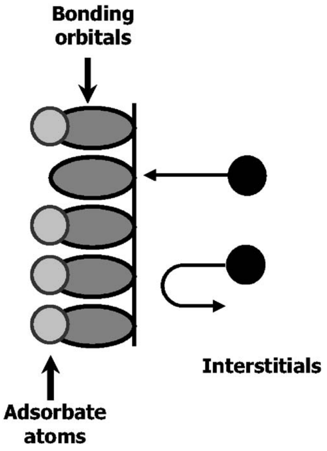

FIG. 1. Schematic diagram showing how bulk interstitials can react easily with surface dangling bond sites, but less easily with sites saturated by a strongly bonded adsorbate.

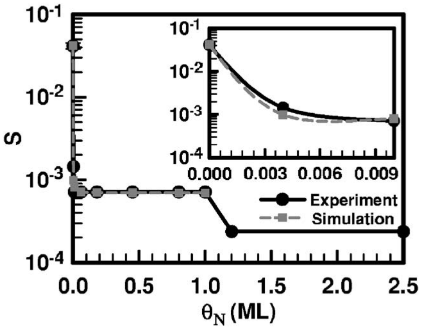

FIG. 2. Experimental and simulation data for annihilation probability S as a function of nitrogen coverage θ_N. For clarity, the inset diagram reproduces data at very small coverages.

II. MODEL FORMULATION

A. Simple expression for annihilation probability

The annihilation probability S can be defined as the probability that an interstitial encountering the surface is annihilated there and does not return to the bulk. S can be a function of the adsorbate coverage θ and other variables such as temperature T. Experimental results show that the self-interstitial annihilation probability on Si(100) depends strongly on the coverage of adsorbed nitrogen. S is insensitive to nitrogen coverage for $0.01 < \theta_N < 1$ (Fig. 2), where θ_N refers to the fraction of first-layer saturation. Such weak coverage dependence is observed for the sticking probability in a number of gas adsorption systems,[15–17] and follows from a precursor-mediated mechanism[14,18] in which impinging gas molecules enter a weakly bound precursor state and diffuse along the surface before chemisorption or desorption back into the gas [Fig. 3(a)]. By analogy, we propose that interstitials can enter a weakly bonded precursor state and diffuse parallel to the surface before annihilation at the surface or desorption back into the bulk [Fig. 3(b)]. Curiously, however, the experimental annihilation probability decreased strongly with coverage for $\theta_N < 0.01$. Such behavior is not commonly observed for gas-phase precursor-mediated adsorption.

We envision the interstitial precursor state to lie just under the surface plane. Although we do not know the exact geometry, there is evidence from quantum calculations that neutral vacancies can be trapped in the third subsurface layer[10] of Si(100). There is no such evidence for neutral interstitials, though the calculations suggest that self-interstitials in $(110)_{\parallel}$ at the second subsurface layer have formation energies only 0.2 eV above those of surface adatoms.[10] We do not know the charge state of the subsurface interstitials; Si self-interstitials can exist in several such states, and the ionization levels are poorly known.[19–22] In a related vein, tight-binding molecular-dynamics simulations,[23,24] and quantum calculations[25] of bulk interstitial-vacancy recombination in Si suggest that interstitials do not recombine easily with vacancies as might otherwise be expected. Instead, there exists a metastable interstitial-vacancy complex with an annihilation energy barrier of 0.3–1.1 eV owing to the local distortion around the $\langle 110 \rangle$ dumbell interstitial towards the vacancy.

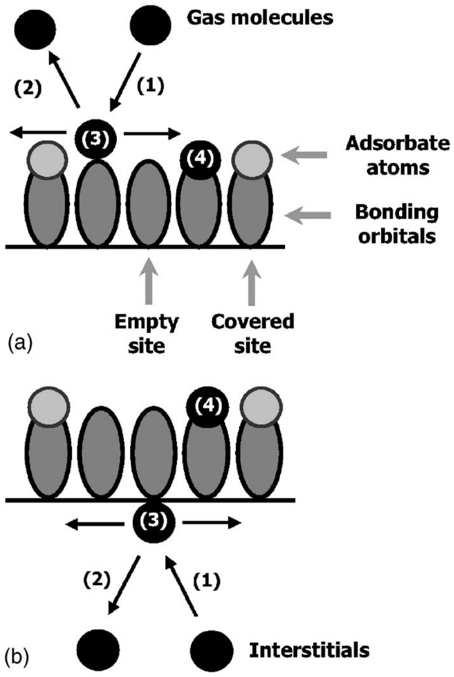

FIG. 3. (a) Schematic diagram of a typical precursor mechanism for gas adsorption and (b) analogous model for interstitials annihilation showing (1) bulk atoms entering into the precursor state, (2) desorption of precursor back into the bulk, (3) precursor diffusion along the surface, and (4) surface annihilation of precursors by chemical bond formation.

It is clear that a subsurface precursor state is at least plausible, and in any case, the precursor state is almost certainly not a surface adatom. As we will show, desorption of the precursor back down into the bulk is quite likely, and is affected strongly by the presence of surface nitrogen. It is difficult to envision Si adatoms behaving in this fashion.

Figure 4 diagrams the precursor mechanism proposed to explain this behavior, with the following rates defined (in units such as atom/cm^2 s):

r_{enter}-rate at which atoms enter precursor state
r_{des}-rate of desorption from precursor state into bulk
r_{ann}-rate of annihilation at a surface site
r_{hop}-rate of hop to adjacent site

With the precursor model, S can be calculated as

$$S = \frac{\text{number (or rate) of atoms annihilated}}{\text{number (or rate) of atoms entering precursor state}} = \frac{r_{\text{ann}}}{r_{\text{enter}}}. \tag{1}$$

To develop a mathematical expression for the annihilation

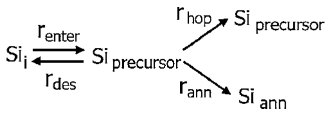

FIG. 4. Reaction network representing the precursor mechanism for interstitial annihilation.

probability S, we make the following assumptions:

(a) Atoms do not accumulate in the precursor state. That is, all precursors are short lifetime species that ultimately either annihilate at the surface or desorb back into the bulk. An equivalent sort of steady-state assumption is often employed in modeling precursor-mediated gas adsorption.[16,26]

(b) The rate r_{enter} of interstitials entering the precursor state is specified. In gas adsorption, the impinging flux can be calculated from the kinetic theory of gases. In the present case of defect annihilation, the impinging flux comes from a solid-state diffusion equation.[13]

(c) Surface sites remain independent, meaning that occupation of one site by nitrogen does not influence the annihilation probability at neighboring sites. This assumption also finds widespread use in modeling gas-surface interactions to simplify the key rate expressions, though it sometimes breaks down in that application. For a similar reason of simplification, we employ the assumption here, though in principle long-range lattice strain or electronic interactions could complicate matters.

(d) Elementary steps obey first-order kinetics. For precursor annihilation, we are therefore neglecting the concentration of annihilation sites as well as the possibility of sites having intrinsically different annihilation rates (apart from whether the sites are saturated with adsorbate). Although the first-order assumption could be incorrect, it simplifies the rate expressions and has good analogies in gas-surface chemistry.

A mass balance on the precursor state yields

$$r_{\mathrm{enter}} = r_{\mathrm{des}} + r_{\mathrm{ann}} \text{ (at steady state)}. \tag{2}$$

Substitution of Eq. (2) into Eq. (1) yields

$$S = \frac{r_{\mathrm{ann}}}{r_{\mathrm{enter}}} = \frac{r_{\mathrm{ann}}}{r_{\mathrm{ann}} + r_{\mathrm{des}}}. \tag{3}$$

With the assumption of first-order kinetics

$$r_{\mathrm{ann}} = k_{\mathrm{ann}} C_{\mathrm{prec}} \quad \text{and} \quad r_{\mathrm{des}} = k_{\mathrm{des}} C_{\mathrm{prec}}, \tag{4}$$

where C_{prec} is the concentration of precursor state (atom/cm^2) and k_{ann} or k_{des} is the relevant first order rate constant (s^{-1}). Combining Eqs. (3) and (4) yields

$$S = \frac{k_{\mathrm{ann}}}{k_{\mathrm{ann}} + k_{\mathrm{des}}}. \tag{5}$$

Unfortunately, the form of Eq. (5) is such that k_{ann} and k_{des} cannot be uniquely determined from data for S alone. These parameters can be determined only to within a multiplicative constant.

B. Refinement through estimation of interstitial lifetime

The lifetime and consequent diffusion length may be helpful for estimating the multiplicative constant in k_{des} and k_{ann}. One simple way to derive the lifetime is to consider a thought experiment in which the supply of atoms entering the precursor state is suddenly shut off. An unsteady-state mass balance on the precursor atoms yields

$$\frac{d[C_{\mathrm{prec}}]}{dt} = - r_{\mathrm{des}} - r_{\mathrm{ann}}. \tag{6}$$

Rearrangement and substitution for r_{des} and r_{ann} gives

$$\frac{d[C_{\mathrm{prec}}]}{dt} + (k_{\mathrm{ann}} + k_{\mathrm{des}}) C_{\mathrm{prec}} = 0. \tag{7}$$

With a step-function initial condition, the precursor concentration decays exponentially with lifetime according to

$$\tau = \frac{1}{(k_{\mathrm{ann}} + k_{\mathrm{des}})}. \tag{8}$$

The average number of hops N before annihilation or bulk desorption is the product of the precursor lifetime and the hopping frequency r_{hop}

$$N = r_{\mathrm{hop}} \tau = \frac{r_{\mathrm{hop}}}{(k_{\mathrm{ann}} + k_{\mathrm{des}})}. \tag{9}$$

The hopping frequency can be expressed in terms of diffusivity D and hop length λ

$$r_{\mathrm{hop}} = \frac{D}{\lambda^2} = \frac{D_0}{\lambda^2} \exp\left(\frac{-E_{\mathrm{diff}}}{kT} \right), \tag{10}$$

where E_{diff} denotes the activation energy for diffusion of the precursor, and D_0 is the preexponential factor. The average diffusion length L of an interstitial in the precursor state can be written as

$$L = N^{1/2} \lambda \tag{11}$$

$$= \frac{\lambda r_{\mathrm{hop}}^{1/2}}{(k_{\mathrm{ann}} + k_{\mathrm{des}})^{1/2}} = \left[\frac{D}{(k_{\mathrm{ann}} + k_{\mathrm{des}})} \right]^{1/2}. \tag{12}$$

Since λ and r_{hop} can be estimated by independent means, a determination of L permits calculation of the multiplicative constant in k_{ann} and k_{des}.

C. Effects of nitrogen adsorption

The effects of nitrogen adsorption can be included by writing the individual rate constants k_{ann} and k_{des} as weighted sums of the corresponding rate constants for the nitrogen-covered surface and the atomically clean surface

$$k_{\mathrm{ann}} = k_{\mathrm{ann,N}} \theta_{\mathrm{N}} + k_{\mathrm{ann,o}} (1 - \theta_{\mathrm{N}}), \tag{13}$$

$$k_{\mathrm{des}} = k_{\mathrm{des,N}} \theta_{\mathrm{N}} + k_{\mathrm{des,o}} (1 - \theta_{\mathrm{N}}), \tag{14}$$

where the subscripts "N" and "o" refer to nitrogen-covered and atomically clean, respectively. These expressions assume independent surface sites as discussed above. Substitution of Eqs. (13) and (14) into Eq. (5) gives

$$S = \frac{k_{\mathrm{ann,N}} \theta_{\mathrm{N}} + k_{\mathrm{ann,o}} (1 - \theta_{\mathrm{N}})}{k_{\mathrm{ann,N}} \theta_{\mathrm{N}} + k_{\mathrm{ann,o}} (1 - \theta_{\mathrm{N}}) + k_{\mathrm{des,N}} \theta_{\mathrm{N}} + k_{\mathrm{des,o}} (1 - \theta_{\mathrm{N}})}. \tag{15}$$

For a specified nitrogen coverage, S depends upon the four parameters $k_{\mathrm{ann,N}}$, $k_{\mathrm{ann,o}}$, $k_{\mathrm{des,N}}$, and $k_{\mathrm{des,o}}$. S has no explicit dependence upon the precursor concentration C_{prec} or the hopping rate r_{hop}. However, the present derivation implicitly assumes that r_{hop} is large enough to keep sites with very fast annihilation or desorption rates supplied with interstitials. If r_{hop} decreases sufficiently, the fast sites simply become depleted and make little contribution to S.

One major difference between the present model and those developed for precursor-mediated gas adsorption is that in the latter case, the impinging species itself acts as a site blocker that prohibits further adsorption on occupied sites. The rate of gas chemisorption r_{ad} therefore depends upon both gas flux and adsorbate coverage. As one example particularly relevant to the present case, Takaoka and Kusunoki[27] have developed a precursor-mediated model for the adsorption of ammonia on Si(100). The low-coverage sticking probability has exactly the same form as the one in Eq. (5). However, since further ammonia adsorption cannot take place at occupied sites, the coverage dependence of sticking probability follows a classical Kisliuk model[18] with a convex S vs θ curve

$$\frac{S(\theta)}{S_o} = \frac{1}{1 + \dfrac{K\theta}{1-\theta}} \quad \text{where } K = \frac{k_{\text{ad}} + k_{\text{des}} + k_{\text{hop}}}{k_{\text{ad}} + k_{\text{des}}}. \tag{16}$$

By contrast, addition of a self-interstitial to a dangling bond does not normally destroy the dangling bond. For example, if the new surface atom remains at the annihilation site, it may offer its own dangling bond(s) in place of those it has saturated. The new surface atom may also cause local reconstructions that actually increase the total number of dangling bonds. Also, the newly created surface atom may surface-diffuse away from the annihilation site to a kink site, keeping the total number of dangling bonds constant. This last phenomenon has been investigated for Si(001) after ion bombardment by scanning tunneling microscopy.[28] Images showed that the areal density of adatom like defects (adatoms, ad-dimers, and adatom clusters) increase by a factor of roughly three as temperature increases from 130 K to 180 K due to migration of bulk interstitials to the surface. Further heating to 294 K decreases the surface defect density owing to surface diffusion of adatoms and related healing processes.

D. Effects of temperature

Equations (5) and (15) predict a temperature dependence in S, most likely through k_{des} (if annihilation is not activated, as a dangling-bond addition model might suggest). The effective activation energy of S depends upon the relative magnitudes of k_{ann} and k_{des}, but generally S should decrease with increasing T. Data for the temperature dependence of S do not yet exist. However, since S is only about 0.05 at $\theta_{\text{N}}=0$ and decreases considerably as θ_{N} increases (Fig. 2), it follows that $k_{\text{ann}} \ll k_{\text{des}}$. Thus, effectively $S=k_{\text{ann}}/k_{\text{des}}$, and the effective activation energy E_S equals $E_{\text{ann}}-E_{\text{des}} \approx -E_{\text{des}}$ assuming that annihilation has no energy barrier. Since k_{des} and therefore E_{des} depend upon coverage, the temperature dependence of S also contains a dependence on θ_{N}, with experiments at 0 and 1 ML, respectively yielding the parameters connected with the "o" and "N" subscripts.

In a like manner, the diffusion length L has a temperature dependence, although the effective activation energy depends on the relative magnitudes of k_{ann} and k_{des} as well as on E_{diff}.

III. METHOD FOR PARAMETER ESTIMATION

Maximum Likelihood estimation proved useful to determine the rate parameters $k_{\text{ann,N}}$, $k_{\text{ann,o}}$, $k_{\text{des,N}}$, and $k_{\text{des,o}}$ from data for S. Maximum Likelihood estimation finds widespread use in applications such as heat and mass transfer,[29–31] batch crystallization[32,33] and biological reaction engineering,[34] and is especially useful for quantifying rate parameters extracted from data sets that are described by models incorporating numerous elementary kinetic steps.[35,36] This approach also yields rigorous estimates for the confidence intervals of the derived parameters.

In the present case, four parameters were to be determined from S, the only measured variable. The general equations for Maximum Likelihood estimation then simplify to minimizing the following functional Φ with respect to the parameter set:[35,36]

$$\Phi(k_{\text{ann,N}},k_{\text{ann,o}},k_{\text{des,N}},k_{\text{des,o}}) = \sum_{i=1}^{N_d} w_i (S_i - \tilde{S}_i)^2, \tag{17}$$

where S_i and $\tilde{S}_i$ are the measured and simulated annihilation probability for the i^{th} value of nitrogen coverage, and the corresponding weighting factor w_i for each of the N_d data points equals the inverse of the measurement error variance

$$w_i = \frac{1}{\sigma_i^2}, \tag{18}$$

where σ_i is the standard deviation in the measured annihilation probability of the i^{th} value of nitrogen coverage. The values of S and the corresponding confidence intervals were themselves obtained by rigorous systems methods described elsewhere.[13]

IV. RESULTS AND DISCUSSION

Table I shows the Maximum Likelihood estimates of $k_{\text{ann,N}}$, $k_{\text{ann,o}}$, $k_{\text{des,N}}$, and $k_{\text{des,o}}$, with $k_{\text{des,N}}$ arbitrarily set equal to 1 s^{-1} to account for the indeterminate multiplicative constant. The fit these parameters provide for the experimental data is quite good (Fig. 2). In all cases the confidence intervals are rather narrow, and in fact are quite narrow for some parameters. Such narrow confidence intervals suggest a very good fit.

A primary success of the expression for S in Eq. (15) is its prediction of the strongly concave shape of the S vs θ_{N} curve. Simple Langmuir-like models predict a linear or modestly concave shape, and standard precursor models (that focus on adsorbate site-blocking rather than adsorbate-influenced desorption into the bulk) predict a convex curve.

A. Determination of the multiplicative constant

Estimation of the average number of hops N and average diffusion length L provides a means for reducing the range of

TABLE I. Rate parameters for Si interstitial annihilation assuming $k_{\mathrm{des,N}}=1\ \mathrm{s}^{-1}$.

Parameter	Value[a] (s^{-1})
$k_{\mathrm{ann,N}}$	$(6.945\pm0.001)\times10^{-4}$
$k_{\mathrm{ann,o}}$	$(1.20\pm0.16)\times10^{-6}$
$k_{\mathrm{des,N}}$	1.00 ± 0.01
$k_{\mathrm{des,o}}$	$(2.73\pm0.82)\times10^{-5}$

[a] 95% confidence at 1253 K.

TABLE II. Rate parameters for Si interstitial annihilation from lifetime estimates.

Parameter	Value[a] (s^{-1})	
	Lower limit	Upper limit
$k_{\mathrm{ann,N}}$	$(5.13\pm0.14)\times10^{5}$	$(1.19\pm0.03)\times10^{6}$
$k_{\mathrm{ann,o}}$	$(8.84\pm1.19)\times10^{2}$	$(2.04\pm0.28)\times10^{3}$
$k_{\mathrm{des,N}}$	$(7.39\pm0.17)\times10^{8}$	$(1.71\pm0.04)\times10^{9}$
$k_{\mathrm{des,o}}$	$(2.02\pm0.60)\times10^{4}$	$(4.66\pm1.39)\times10^{4}$

[a] 95% confidence at 1253 K.

the indeterminate multiplicative constant (and therefore of the parameters themselves) to a relatively narrow window. Upper limits for the rate parameters can be estimated by determining the minimum average diffusion length for interstitial precursors. For a well-defined precursor state to exist, we expect N to be at least roughly unity throughout the entire range of nitrogen coverages. That is, a precursor interstitial must make at least one hop before desorbing or annihilating. With $N=1$, Eqs. (9) and (10) then can be used to determine τ, since the parameters in r_{hop} can be estimated independently. Values of D_0 and E_{diff} have been estimated previously as $10^{-3}\ \mathrm{cm}^2/\mathrm{s}$ and 0.72 eV, respectively.[37] The parameter λ was estimated as the atomic nearest neighbor distance in silicon (2.73 nm), and S was measured at $T=1253$ K.

Lower limits for the rate parameters can be estimated by determining the maximum average diffusion length for interstitial precursors. One possible determinant of the maximum diffusion length is the presence of a second kind of site that is more active for annihilation or desorption than a typical terrace site. Surface defects such as steps or kinks could play such a role. Such defects typically bond gaseous adsorbates more strongly than terrace sites, and often provide the primary pathway for gas adorption and desorption, especially when the sticking probability for a perfect surface is low.[38] It is therefore reasonable to suppose that steps or kinks play analogous roles for the annihilation of interstitials, and influence the annihilation kinetics embodied in Fig. 2.

Yet the proposed model fits the data quite well with the assumption of only a single type of site, not two types having significantly differing activity. Indeed, a two-site model has difficulty explaining both the strong concavity of the S vs θ_{N} curve for $\theta_{\mathrm{N}}<0.01$ and the constancy of S for $\theta_{\mathrm{N}}>0.01$. Thus, we infer that steps and kinks do not participate strongly in interstitial annihilation, though interstitials reaching them might be annihilated very efficiently. It then follows that the average diffusion length L in the precursor state is significantly less than the average distance between a precursor interstitial and a step or kink. If we assume the sample has a miscut angle of 0.1°, then the average spacing between S_{B} steps is given by $[2\times1.36\times10^{-8}\ \mathrm{cm}/\tan(0.1\pi/180)]\approx156$ nm,[39] where 1.36×10^{-8} cm is the height of a single layer step. The average diffusion length of precursor at $\theta_{\mathrm{N}}=0$ cannot be larger than roughly half this distance, i.e., $L_{\max}=78$ nm. Lower limits for the rate parameters can be determined by this constraint together with Eq. (12).

The approach described above assumes that the diffusion parameters for subsurface precursors match those of interstitials in the bulk. This assumption may not be correct, as quantum calculations suggest that pathways and energetics for subsurface vacancy diffusion can differ from those in the bulk.[10] For example, such calculations indicate that vacancies in the third subsurface layer of Si(100) diffuse parallel to the surface with an energy barrier of 0.6 eV, but diffuse perpendicularly up toward the surface with a lower barrier of 0.4 eV. Such anisotropy is not observed in the deep bulk. With the deep bulk assumption, however, Table II shows revised values and associated confidence intervals for the parameters composing S. The upper and lower parameter limits vary by less than an order of magnitude.

The parameters in Tables I and II show that nitrogen enhances both the annihilation and bulk desorption pathways for interstitials to leave the precursor state. The biggest effect is on k_{des}, which increases by nearly five orders of magnitude as θ_{N} increases in the range $0\le\theta_{\mathrm{N}}\le0.01$. Coupling between the surface and the interstitials can take place by means of direct electrostatic interaction or by subsurface strain effects. Adsorption can modify both mechanisms, though adsorbate-induced changes in strain seems more likely if the precursor lies two to three layers beneath the surface. Strains near an adsorbed atom could destroy the energy barrier that traps a precursor atom, making desorption into the bulk much more likely.

The enhancement of k_{ann} by nitrogen, though modest, is more difficult to rationalize. The simple dangling bond model depicted in Fig. 1 does not predict enhancement of interstitial annihilation upon N adsorption because of the needed insertion into the strong Si-N bond. Indeed, quantum calculations of H and Cl adsorption on Si(100) suggest that adsorbate passivation should impede annihilation.[11] These calculations examined only formation energies, though, not kinetic activation barriers for annihilation. However, nitrogen adsorption may instead induce other changes in surface bond structure that alter the mechanism for annihilation.

Such changes can be inferred from studies of nitrogen adsorption on Si(100), which has been studied in great detail.[40–46] The atomically clean Si(100)2×1 reconstruction is fully saturated. The dimer rows are kept together by σ and π interactions between the dimer atoms that leave no dangling bonds. Addition of an interstitial is presumably rather difficult as a consequence. Quantum calculations suggest that insertion of the NH group into a Si-Si dimer bond offers the lowest energy barrier to the initial growth of silicon nitride.[46] The insertion of an NH group into the dimer bond induces localized rearrangements that create a dangling bond and presumably increase k_{ann}. There is some debate about this process, however. Some reports[40,41,45] suggest that ammonia adsorbs dissociatively as H and NH_x at room temperature. Others[42] suggest that only hydrogen stays at the surface, while nitrogen rests in subsurface sites. For both cases, further ammonia adsorption is not possible until desorption of hydrogen at higher temperatures (330–530 °C).

Unfortunately, very little literature[40] focuses on conditions of high substrate temperature (~800 °C) and low gas exposure (~5 L) as in the present case. It is clear, however, that temperatures of 630–930 °C initiates the growth of true silicon nitride, in the form of nitride islands surrounded by regions of clean silicon.[43–45] However, at low exposures (<5 L), insufficient nitrogen exists to create a true nitride (with Si atoms all surrounded by N atoms).[44] Under such conditions where H has desorbed, each nitrogen atom seeks to fill its bonding capacity by bonding to three silicon atoms. This odd number means that some silicon atoms may be unable to dimerize, thereby becoming dangling-bond sites for interstitial annihilation and increasing k_{ann}.

S is essentially constant for $0.01 \leq \theta_{\mathrm{N}} \leq 1$. The reason is that the contribution of $k_{\mathrm{des,o}}$ and $k_{\mathrm{ann,o}}$ to S becomes negligible in this range of θ_{N}, since $k_{\mathrm{des,N}} \gg k_{\mathrm{des,o}}$ and $k_{\mathrm{ann,N}} \gg k_{\mathrm{ann,o}}$. S can therefore be approximated as

$$S \approx \frac{k_{\mathrm{ann,N}}\theta_{\mathrm{N}}}{k_{\mathrm{ann,N}}\theta_{\mathrm{N}} + k_{\mathrm{des,N}}\theta_{\mathrm{N}}} = \frac{k_{\mathrm{ann,N}}}{k_{\mathrm{ann,N}} + k_{\mathrm{des,N}}}. \tag{19}$$

Thus, the ratio of the rate constants for annihilation and bulk desorption become largely independent of θ_{N} when $0.01 \leq \theta_{\mathrm{N}} \leq 1$.

The present study has not examined the coverage dependence of S for $\theta_{\mathrm{N}} > 1$. S decreases further for $1 < \theta_{\mathrm{N}} < 1.2$, and stays fairly constant for $\theta_{\mathrm{N}} > 1.2$. This behavior can be interpreted as a repetition of the trend for $0 < \theta_{\mathrm{N}} < 1$. Structural changes of the adlayer (e.g., formation of bilayer, nitride islands, etc.) probably take place as θ_{N} rises just above unity, resulting in a high sensitivity of S to θ_{N} in this range. A true nitride layer begins to form at higher coverages, with negligible changes in S.

V. CONCLUSION

The annihilation kinetics of self-interstitials at the Si(100) surface are well described by a precursor mechanism in which interstitials move substantial distances parallel to the surface before incorporation. Kinetic analysis shows that nitrogen adsorption enhances the rates of both desorption and annihilation of interstitial precursors, indicating that nitrogen may induce local structural rearrangements that foster escape from the precursor state. The present model fits the data quite well, but studies now underway regarding the temperature dependence of S will provide further insights. Studies on different crystallographic orientations will also be obvious avenues to examine to determine whether precursor mechanisms are a common feature of defect-surface interactions.

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