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T. Singh

S. Pandey

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Citation: *J. Chem. Phys.* **131**, 034503 (2009); doi: 10.1063/1.3152846

View online: <http://dx.doi.org/10.1063/1.3152846>

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Kinetic Monte Carlo simulations of surface growth during plasma deposition of silicon thin films

Sumeet C. Pandey, Tejinder Singh, and Dimitrios Maroudas^{a)}

Department of Chemical Engineering, University of Massachusetts Amherst,
Amherst, Massachusetts 01003-3110, USA

(Received 14 March 2009; accepted 20 May 2009; published online 16 July 2009)

Based on an atomically detailed surface growth model, we have performed kinetic Monte Carlo (KMC) simulations to determine the surface chemical composition of plasma deposited hydrogenated amorphous silicon (*a*-Si:H) thin films as a function of substrate temperature. Our surface growth kinetic model consists of a combination of various surface rate processes, including silyl (SiH_3) radical chemisorption onto surface dangling bonds or insertion into Si-Si surface bonds, SiH_3 physisorption, SiH_3 surface diffusion, abstraction of surface H by SiH_3 radicals, surface hydride dissociation reactions, as well as desorption of SiH_3 , SiH_4 , and Si_2H_6 species into the gas phase. Transition rates for the adsorption, surface reaction and diffusion, and desorption processes accounted for in the KMC simulations are based on first-principles density-functional-theory computations of the corresponding optimal pathways on the H-terminated Si(001)-(2×1) surface. Results are reported for two types of KMC simulations. The first employs a fully *ab initio* database of activation energy barriers for the surface rate processes involved and is appropriate for modeling the early stages of growth. The second uses approximate rates for all the relevant processes to account properly for the effects on the activation energetics of interactions between species adsorbed at neighboring surface sites and is appropriate to model later stages of growth toward a steady state of the surface composition. The KMC predictions for the temperature dependence of the surface concentration of $\text{SiH}_{x(s)}$ ($x=1,2,3$) species, the surface hydrogen content, and the surface dangling-bond coverage are compared to experimental measurements on *a*-Si:H films deposited under operating conditions for which the SiH_3 radical is the dominant deposition precursor. The predictions of both KMC simulation types are consistent with the reported experimental data, which are based on *in situ* attenuated total reflection Fourier transformed infrared spectroscopy.

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I. INTRODUCTION

Hydrogenated amorphous silicon (*a*-Si:H) thin films are used extensively in the fabrication of large-area electronic and optoelectronic devices, such as thin-film transistors for active-matrix displays,¹ multiple-junction photovoltaic solar cells,¹ active pixels in x-ray imaging,² photoreceptors, and sensing devices.³ The growth of these *a*-Si:H thin films by plasma enhanced chemical vapor deposition has been studied widely both experimentally and computationally. The effects of plasma processing conditions on the quality of the films have been investigated experimentally through deposition of films at different plasma power densities and incident precursor fluxes and subsequent film characterization.⁴ It has been established that at low power densities and low pressures, the silyl radical (SiH_3) is the dominant deposition precursor leading to device-quality films.⁵ In spite of the substantial amount of information generated from such experiments, the growth models that have been proposed have been able to neither explain fully the complex growth process nor account

for the surface composition and its temperature dependence, as well as the relative roles of coordination defects in *a*-Si:H thin-film growth.

Several approaches have been taken to develop a growth model for the plasma deposition of *a*-Si:H thin films.^{6,7} Winer⁸ and Street⁹ proposed a thermodynamic model without considering detailed surface reactions. In this model, hydrogen equilibration during *a*-Si:H film deposition is invoked to explain the dependence of defect densities on the substrate temperature. Winer⁸ attributed the rate-limiting step for the dissociation of weak bonds to hydrogen diffusion, which leads to the formation of strong Si-H bonds and Si dangling bonds and facilitates an equilibrium distribution of Si-Si and Si-H bonds. Street⁹ based his description on the density of states and the chemical potential of hydrogen, which determine the hydrogen content at low-temperature growth. The first kinetic growth model was proposed by Gallagher,⁷ Perrin *et al.*,¹⁰ and Matsuda *et al.*^{11,12} (MGP) and assumes that the SiH_3 radical attaches to the surface in a weakly adsorbed state, forming a three-center Si-H-Si bond on hydrogenated Si surface sites (Si-H). In this model, the weakly adsorbed SiH_3 diffuses on the surface to either abstract a surface H or create a dangling bond and gaseous SiH_4 or attach to and passivate a surface Si dangling bond leading to film growth.

^{a)}Author to whom correspondence should be addressed. Electronic mail: maroudas@ecs.umass.edu.

The MGP model also included the possibility that two weakly adsorbed SiH_3 radicals interact to form gaseous Si_2H_6 ; however, desorption of SiH_3 was not considered to be important. This dangling-bond-based growth model has been used to explain the temperature independence of the surface reaction and sticking probabilities during $a\text{-Si:H}$ film growth. Nevertheless, a growth model based on these surface reactions cannot describe satisfactorily the surface defect densities and their impact on the growth process, as observed by *in situ* and real-time dangling-bond density measurements using electron spin resonance (ESR) by Yamasaki *et al.*¹³ and high-sensitivity evanescent wave cavity ring-down spectroscopy by Aarts *et al.*;¹⁴ according to these measurements, the dangling-bond creation rate is lower than the actual $a\text{-Si:H}$ growth rate.

In order to explain the faster growth rates during deposition at low surface dangling-bond densities, von Keudell and Abelson¹⁵ proposed that SiH_3 can insert into strained Si-Si bonds on the $a\text{-Si:H}$ surface and suggested this insertion reaction to be the dominant mechanism of Si incorporation leading to film growth. Using first-principles density-functional-theory (DFT) calculations, Bakos *et al.*¹⁶ computed a barrierless pathway for a similar SiH_3 insertion reaction into the Si-Si dimer bond on the $\text{Si}(001)\text{-(}2\times 1\text{):H}$ surface; SiH_3 insertion into surface Si-Si bonds also was observed during molecular-dynamics (MD) simulations of SiH_3 radical repeated impingement on surfaces of computationally grown $a\text{-Si:H}$ thin films.¹⁶ van de Sanden *et al.*¹⁷ demonstrated and explained an Eley-Rideal (ER) type of surface H abstraction reaction that creates dangling bonds, which can account for the temperature independence of growth and for the surface defect densities. Based on analysis of MD simulations, Ramalingam *et al.*^{18,19} reported an activation energy barrier of only 0.09 eV for such ER surface H abstraction reactions. Using first-principles DFT calculations, Bakos and Maroudas computed an athermal pathway for the same reaction on the $\text{Si}(001)\text{-(}2\times 1\text{):H}$ surface.²⁰

Based on their experimental observations, Kessels *et al.*²¹ proposed that H elimination is important during the growth process and postulated that dissociation of SiH_3 has important implications for the reduction of the grown films' hydrogen content as a function of temperature. They concluded that the $a\text{-Si:H}$ film growth mechanism was not fully revealed and that the atomic-scale mechanisms of dissociation reactions had to be studied further.²¹ Using *in situ* attenuated total reflection Fourier transformed infrared (ATR-FTIR) spectroscopy, Marra *et al.*²² investigated the surface silicon hydride composition and proposed a sequential dissociation reaction generating lower surface hydrides ($\text{SiH}_{3(s)} \rightarrow \text{SiH}_{2(s)} \rightarrow \text{SiH}_{(s)}$, where the subscript (s) denotes surface species). They also proposed that these dissociation reactions are promoted by surface dangling bonds.²² Using first-principles DFT calculations, Singh *et al.*^{23,24} computed the underlying atomic-scale mechanisms and the energetics of such surface hydride dissociation reactions, mediated either by surface dangling bonds (DBs) or by floating bonds (FBs), i.e., they examined the role in such reactions of both

surface undercoordination and surface overcoordination defects.

To obtain a fundamental understanding of the underlying atomic-scale mechanisms of radical-surface interactions and the resulting $a\text{-Si:H}$ film growth, Ramalingam *et al.*¹⁸ performed and analyzed MD simulations of repeated SiH_3 radical impingement on silicon crystalline and amorphous surfaces.¹⁹ Their analysis identified some of the key rate processes responsible for $a\text{-Si:H}$ film growth.^{18,19} For a better mechanistic and quantitative understanding of surface reactivity and Si incorporation that leads to growth of device-quality films, Bakos *et al.*²⁵⁻²⁸ conducted classical MD simulations of SiH_3 radical impingement on amorphous silicon surfaces in conjunction with first-principles DFT calculations of SiH_3 reactions and diffusion on the $\text{Si}(001)\text{-(}2\times 1\text{):H}$ surface.²⁵⁻²⁸ They analyzed the underlying physical mechanisms, computed the associated energetics, and assessed various proposed mechanisms; in addition, they established that the $\text{Si}(001)\text{-(}2\times 1\text{):H}$ crystalline surface provides for the incoming silyl radicals a local bonding environment similar to that of amorphous Si thin-film surfaces with similar optimal reaction and diffusion pathways.²⁵⁻²⁸ These findings enabled further detailed studies of reaction mechanisms on the $\text{Si}(001)\text{-(}2\times 1\text{):H}$ crystalline surface, as a representative model of local bonding environment of amorphous silicon thin-film surfaces. Along these lines, Singh *et al.*^{23,24} computed dissociative radical adsorption pathways on the $\text{Si}(001)\text{-(}2\times 1\text{):H}$ surface using DFT calculations and analyzed similar reactions on surfaces of $a\text{-Si:H}$ films identified in MD simulations. They proposed that surface coordination defects, DBs and FBs, mediate radical dissociation mechanisms on $a\text{-Si:H}$ film surfaces.^{23,24} Finally, Pandey *et al.*²⁹ examined further the importance of both DBs and FBs during surface silicon hydride dissociation reactions and found a possible reaction pathway connecting the two equilibrium configurations of chemisorbed SiH_3 onto the $\text{Si}(001)\text{-(}2\times 1\text{):H}$ surface; this enabled an essentially comprehensive list of possible elementary surface rate (reaction and diffusion) processes contributing to $a\text{-Si:H}$ thin-film growth.

In this article, we report the results of kinetic Monte Carlo (KMC) simulations that predict the surface composition of $a\text{-Si:H}$ thin films grown under conditions that make the SiH_3 radical the dominant deposition precursor. We simulate the very early stages of growth (at low surface coverage), as well as later stages where the growth-surface composition reaches steady state (monolayer coverage) and highlight the underlying growth kinetics. For the simulations of the early stages of growth, we use an *ab initio* database of transition probabilities for rate processes (reactions and surface diffusion events) on the $\text{Si}(001)\text{-(}2\times 1\text{):H}$ surface; this database is constructed based on DFT calculations of optimal pathways for these rate processes, all of which have been identified by MD simulation on $a\text{-Si:H}$ thin films. In order to simulate the growth surface at steady state, we account for the effect of the interactions between neighboring adsorbed radicals on the rates of surface reactions and diffusion events at higher surface coverages; this is done by DFT computation of the corresponding variation in binding energies due to

FIG. 1. (a) Si(001)-(2 $\times$ 1):H surface (only a small region of the actual simulation cell is depicted) used as the initial growth-surface configuration in the KMC simulations. Dark and white spheres are used to represent Si and H atoms, respectively. (b) Quasi-2D grid providing the simulation cell used in the lattice KMC simulations and consisting of 7260 adsorption, diffusion, and reaction sites. The cell dimensions are 22.6 $\times$ 23 nm². Each dark sphere corresponds to a Si atom at the first Si layer, second Si layer (in the trough), or third Si layer (in the trough) of the Si(001)-(2 $\times$ 1):H surface.

the presence of neighboring adsorbed radicals in all possible equilibrium configurations.

This paper is structured as follows. Our KMC model is described in detail in Sec. II. The surface kinetic processes (reaction and diffusion events) that are accounted for in the KMC simulations are listed and discussed in Sec. III. The KMC simulation results, both at early stages of growth and at steady state, are presented and discussed in Sec. IV, including their comparison with experimental measurements of surface species concentrations as a function of temperature. Finally, the most important conclusions of this study are summarized in Sec. V.

II. KINETIC MONTE CARLO MODEL

In our KMC simulations, the initial surface corresponds to a relaxed configuration of the Si(001)-(2 $\times$ 1):H substrate surface, depicted in Fig. 1(a); the surface configuration includes the H layer and the top, second, and third Si layers in a simulation cell that contains 14 460 Si and H atoms. This configuration is mapped onto a quasi-two-dimensional (2D) lattice as shown in Fig. 1(b), where the gray spheres represent the top- and second-layer Si atoms, as well as the third-layer Si atoms in the trough between adjacent dimer rows, identified as discrete sites on a grid and resulting in 7260 available lattice sites in the simulation cell for adsorption, reaction, and diffusion processes. This KMC simulation cell has dimensions of 22.6 $\times$ 23 nm²; periodic boundary conditions are applied in both (x and y) directions perpendicular to the impinging radical. We have implemented an on-lattice n -fold KMC propagator that keeps track of the coordination of surface Si atoms up to the next-nearest neighbor of each surface site in order to generate the lists of possible kinetic events at each time step. A variable time-step size is employed for time stepping as in an n -fold-way approach³⁰ and a linear search algorithm with grouping is employed for selecting a kinetic event from a dynamical list of possible events that is upgraded at each time step.³¹ The appropriate-

ness of an n -fold KMC algorithm and its equivalence to conventional Monte Carlo schemes has been demonstrated theoretically and numerically by Bulnes *et al.*³²

The transition probabilities for the various kinetic (adsorption, reaction, and diffusion) processes that are accounted for in our KMC simulations were determined based on DFT calculations of optimal pathways for the corresponding kinetic events on the Si(001)-(2 $\times$ 1):H surface. Forward and reverse pathways are considered for these kinetic events, which compete in order to determine the fate of an impinging SiH₃ radical on the surface. Our DFT calculations were conducted within the generalized gradient approximation (GGA) and employed slab supercells, ultrasoft pseudopotentials, and plane-wave basis sets as implemented in the VASP code.³³ To construct fully optimized pathways of the surface kinetic processes considered and obtain accurate saddle-point configurations and activation energy barriers, we implemented the nudged elastic band (NEB) method including a climbing image.³⁴ A detailed description of our DFT computational procedure for SiH₃ on Si(001)-(2 $\times$ 1):H has been given in Ref. 26.

The adsorption rate of a silyl radical on an unoccupied site is defined as a product of the impinging flux (at a flux of 7.3×10^4 radicals/nm² s) and the local sticking coefficient. We calculate the rate for radical adsorption, r_i^{ads} , based on the general expression for interaction rates between the surface and a gas-phase species (labeled i),³⁵

$$r_i^{\text{ads}} = f_i A_i \left(\frac{p}{\sqrt{2\pi m k_B T_g}} \right) \exp \left(\frac{-E_{a,i}^{\text{ads}}}{k_B T} \right). \quad (1)$$

In Eq. (1), m is the mass of the impinging radical, p is the partial pressure of silyl radicals in the gas phase, k_B is the Boltzmann constant, $E_{a,i}^{\text{ads}}$ is the activation energy barrier for radical adsorption along the corresponding minimum-energy pathway as computed by the DFT/GGA/NEB scheme described above, T and T_g are the substrate and gas-phase temperatures, respectively, A_i is the active area (in terms of available sites for that adsorption event type), and f_i is a reduction factor to account for reflection of impinging radicals, not traveling along the proper minimum-energy path.^{18,19} For radical desorption, the activation energy barrier, $E_{a,i}^{\text{des}}$, is related to the adsorption barriers through the expression³⁵

$$E_{a,i}^{\text{des}} = E_{a,i}^{\text{ads}} - E_{b,i}^{\text{cfg}}, \quad (2)$$

where $E_{b,i}^{\text{cfg}}$ is the binding energy for the radical in the adsorbed state (from which it desorbs) that is associated with a distinct equilibrium configuration. These binding energies have been calculated previously;²⁵ they are equal to 0.75 and 0.63 eV for SiH₃ inserted into the Si-Si dimer bond on the Si(001)-(2 $\times$ 1):H surface and for SiH₃ physisorbed onto the second-layer Si atom in the trough of this surface, respectively.

Rates for the rest of the surface reactions (using the term in a general sense to also include surface diffusion events), r_i^{sr} , were estimated based on the activation energy barriers

according to our DFT/GGA/NEB computations and invoking transition state theory within the harmonic approximation, i.e.,

$$r_i^{\text{sr}} = \nu_i \exp\left(\frac{-E_{a,i}^{\text{sr}}}{k_B T}\right). \quad (3)$$

In Eq. (3), $E_{a,i}^{\text{sr}}$ is the activation energy barrier for the reaction under consideration along the minimum-energy pathway and ν_i is the corresponding attempt frequency; this is given by $\nu_i = \prod_{j=1}^{3N} \nu_i^j / \prod_{j=1}^{3N-1} (\nu_i^j)^*$, where ν_i^j and $(\nu_i^j)^*$ are the eigenfrequencies of the $3N$ and $3N-1$ normal modes at the initial and transition state, respectively, with N being the number of atoms in the configuration under consideration. It should be mentioned that attempt frequencies depend on the local bonding environment and that their calculation demands significant computational resources. Ceriotti and Bernasconi³⁶ computed some of these attempt frequencies on the Si(001)-(2×1):H surface; specifically, they found the attempt frequencies for diffusion between two chemisorbed silyl states, diffusion between two physisorbed silyl states, and silyl desorption to be 28, 2, and 0.8 THz, respectively. Considering our long list of kinetic events and transition probabilities for the various reactions and various bonding configurations at the corresponding initial states, we make the following pragmatic assumption for the attempt frequencies: We take $\nu_i = 10^{12}$ Hz for transitions between physisorbed states and $\nu_i = 10^{13}$ Hz for transitions between chemisorbed states. This is a satisfactory assumption for our rate estimation purposes, i.e., using proper upper and lower bounds to these values give results well within the typical error margins for stochastic dynamical simulations.

At each time step of the KMC simulation, depending on the current growth-surface configuration, a grouped event list is generated and the corresponding transition probabilities are computed at each lattice site; the grouping is based on the process type and the set of possible kinetic events in accordance with microscopic reversibility. From this list of a maximum of 49 rate process types (groups ensuring dynamical hierarchy and detailed balance), one event is selected randomly to be executed at a specific site by drawing a random number from a uniform distribution, $\xi_1 \in (0,1)$, and picking a process type j out of groups i , with n_i^g number of events in the group and each such event having a rate r_i , according to the criterion

$$\frac{1}{R} \sum_{i=1}^{j-1} r_i^g \leq \xi_1 \leq \frac{1}{R} \sum_{i=1}^j r_i^g,$$

where

$$R = \sum_{k=1}^M r_k \quad (4)$$

and

$$r_i^g = n_i^g r_i.$$

In Eq. (4), M denotes the total number of events at all possible sites during that time step. After each execution of a

kinetic event, time is incremented by the stochastic time interval

$$\Delta t = \frac{-\ln(\xi_2)}{R}, \quad (5)$$

where $\xi_2 \in (0,1)$ is a random number drawn from a uniform distribution. The growth-surface configuration is updated and recorded, and the system is propagated in time until the desired surface coverage is achieved. We report results for surface hydride composition, DB coverage, and hydrogen content based on computations of ensemble-averaged growth-surface compositions from 20–50 different KMC trajectories.

For simulating the early stages of growth, we rely entirely on the strict DFT database of kinetic processes in terms of available configurations and corresponding energy barriers; none of these kinetic processes involve interactions beyond those of two adsorbed radicals that are either nearest or next-nearest neighbors. Hence, simulations of the early stages of growth are terminated when we run out of possible kinetic events available in our database, i.e., when there are no events left other than those for which initial and final configurations will involve more than two radicals becoming neighbors. These simulations are limited to submonolayer surface coverages, achieved in $\sim 10^7$ to $\sim 10^8$ KMC steps (depending on temperature) for each trajectory in an ensemble. At all temperatures, in order to eschew any unphysical kinetics and to preserve the DFT description within statistical errors, KMC simulations describing early stages of growth were terminated as soon as the atomistic rules of bonding configurations set by our DFT/GGA/NEB computations began to get violated. These DFT analyses were carried out to determine optimal pathways for diffusion and reaction processes in the absence of any other adsorbed radicals within the interaction range, as well as for radical-radical interactions between only two neighboring radicals. This DFT database can describe satisfactorily the surface growth dynamics at the dilute limit of low surface coverage, where the growth kinetics is not affected significantly by the presence of interacting adsorbed radicals.

In order to simulate surface growth beyond these very early stages, it is required to include effects on the reaction rates of adsorbed radical interactions at higher surface coverages. We addressed this requirement and improved our rate estimation method by following an approach similar to that by Smilauer *et al.*³⁷ Specifically, we included contributions to the activation energy barriers of all the kinetic processes considered due to neighboring radical interactions, resulting in the rate equation

$$r_{i \rightarrow f} = \nu_0 \exp\left\{-\frac{1}{k_B T} \left[E_{i \rightarrow f}^a + \sum_{n=1}^3 V_{b,n}(i) \right]\right\}. \quad (6)$$

In Eq. (6), $r_{i \rightarrow f}$ is the forward rate of transition from state i to f , ν_0 is the corresponding vibrational attempt frequency, over the range 10^{12} – 10^{13} s⁻¹ as discussed above, $E_{i \rightarrow f}^a$ is the activation energy barrier for transition from state i to state f , and $V_{b,n}(i)$ is the variation in binding energy due to the presence of radicals adsorbed at neighboring sites ($n=1, 2$, or 3) to that considered for the chosen event in state i . For a radi-

cal inserted into a Si–Si dimer and having a physisorbed radical as neighbor, the binding energy variation is computed within DFT/GGA to be 0.11 eV, while for a radical adsorbed onto a DB site in the vicinity of a physisorbed radical in the trough, the corresponding binding energy variation is computed to be 0.18 eV. We assume the rate expression of Eq. (6) to be valid at higher surface coverages, which allows for further simulation of surface evolution to attain monolayer coverage and reach a steady state in the surface chemical composition.

III. SURFACE KINETIC PROCESSES

Under plasma conditions of low power and low pressure, the SiH₃ radical is the most abundant radical species in the plasma phase.⁴ Therefore, it is considered to be the major growth precursor during deposition of device-quality *a*-Si:H thin films grown under such conditions. Consequently, surface growth is the outcome of SiH₃ radical-surface interactions, surface diffusion of the adsorbed radical, and adsorbed radical-radical interactions, as well as desorption, dissociation reactions, and disproportionation reactions. Table I provides a list of the kinetic events included in our KMC simulations that correspond to radical-surface interactions. Possible outcomes for an impinging SiH₃ radical on the surface include abstraction of surface hydrogen through an Eley–Rideal (ER) mechanism, chemisorption either by adsorbing onto a dangling bond, or by inserting into and breaking a Si–Si dimer bond, physisorption by adsorbing weakly onto the surface at the second Si layer in the trough between adjacent dimer rows, and reflection back into the gas phase. Adsorption and ER hydrogen abstraction processes are either barrierless or have very low activation energies. Such athermal radical-surface interactions account for the temperature independent surface reactivity of SiH₃.^{38,16}

Table II lists surface reactions undergone by the adsorbed radicals and surface migration (i.e., diffusion) processes that are included in our KMC simulations; the reported activation energies are for the forward reaction or migration pathways. These processes include thermally activated Langmuir–Hinshelwood (LH) and precursor-mediated (PM) surface H abstraction mechanisms; these constitute means of hydrogen removal from the growing surface (and creation of DBs) in addition to ER abstraction of surface H. The inserted SiH₃ on a surface Si–Si dimer bond can abstract H from either its nearest or second-nearest surface site, through LH pathways with activation energy barriers of 0.76 and 0.78 eV, respectively.²⁶ On the other hand, SiH₃ radicals that get weakly adsorbed onto the subsurface Si layer can abstract hydrogen through a PM pathway with an activation energy barrier of 0.39 eV.²⁶

Other surface kinetic processes listed in Table II include dissociation reactions of surface hydride species. Surface coordination defects play a critical role in the surface trihydride, SiH_{3(s)}, dissociation processes that contribute to *a*-Si:H thin film growth by Si incorporation. SiH_{3(s)} dissociates to surface dihydrides, SiH_{2(s)}, and monohydrides, SiH_(s), through both DB- and FB-mediated dissociation pathways. The range of activation energy barriers for different DB-

TABLE I. Surface kinetic (adsorption, abstraction, and reflection) processes and the associated atomic-scale mechanisms (only initial and/or final fully relaxed configurations are depicted from the corresponding DFT calculations) due to SiH₃ radical-surface interactions during plasma deposition of silicon thin films; the subscripts (s) and (g) are used to denote surface and gas-phase species, respectively. The listed processes either are barrierless or have very low activation energies. The numbers of different kinetic events associated with each set of forward reactions are provided in square brackets. In the depicted configurations, the numbers shown give interatomic distances in Å.

Surface Process	Physical Mechanisms
Eley-Rideal H abstraction ^a [1] SiH _{3(g)} + H _(s) → SiH _{4(g)} + DB	
Insertion into Si-Si dimer bond ^b [1] SiH _{3(g)} + HSi-SiH _(s) → HSi-SiH ₃ -SiH _(s)	
Adsorption onto DB ^c [1] SiH _{3(g)} + DB → SiH _{3(s)}	
Weak adsorption involving FB ^d [1] SiH _{3(g)} + Si _(s) → Si-SiH _{3(s)} SiH _{3(g)} + 2 Si _(s) → Si-SiH ₃ -Si _(s) (Si _(s) are 4-fold coordinated)	
Reflection ^e [1]	

^aReferences 17–20.

^bReference 16.

^cReference 20.

^dReferences 18, 19, and 25.

^eReferences 18 and 19.

mediated and FB-mediated SiH_{3(s)} dissociation pathways are 0.16–0.98 and 0.40–0.55 eV, respectively.^{23,24} SiH_{2(s)} species formed through FB-mediated dissociation reactions of SiH_{3(s)} dissociate further to SiH_(s) species through pathways with activation barriers of 0.25–0.27 eV.^{23,24} On the other hand, DB-mediated dissociation of stable SiH_{2(s)} is characterized by a high barrier of 1.04 eV. As opposed to inserted SiH₃ radicals, surface trihydrides in the form of SiH₃ radicals chemisorbed onto DBs are trapped in a deeper potential well and they transition to an inserted configuration before they tend to dissociate. Specifically, there is a pathway that connects the two equilibrium chemisorbed SiH_{3(s)} configurations (radical inserted and radical chemisorbed onto a DB). On this pathway, a SiH₃ inserted into a Si–Si dimer bond transfers an H atom to the nearest Si in the trough and reforms the Si–Si dimer bond, resulting in a SiH_{3(s)} configuration similar to a SiH₃ radical chemisorbed onto a DB. This process involves bond breaking and bond forming events. The activation energy barriers for the forward and reverse pathway are 0.45 and 0.49 eV, respectively.²⁹

TABLE II. Surface kinetic (reaction, diffusion, and desorption) processes and the associated atomic-scale mechanisms (only initial and final fully relaxed configurations are depicted from the corresponding DFT calculations) that involve adsorbed radicals and other surface hydride species during plasma deposition of silicon thin films; the subscripts (s) and (g) are used to denote surface and gas-phase species, respectively. In the case of diffusion, the corresponding migration paths are sketched. Activation-energy ranges in eV and the numbers of different kinetic events associated with each set of forward reactions are provided in parentheses and square brackets, respectively. In the depicted configurations, the numbers shown give interatomic distances in Å.

Surface Process	Physical Mechanisms
Langmuir-Hinshelwood H abstraction ^a [2] $\text{SiH}_{3(s)} + \text{H}_{(s)} \rightarrow \text{SiH}_{4(g)} + \text{DB}$ (0.76-0.78)	
FB- and DB-mediated surface hydride dissociation ^b [12] $\text{SiH}_{3(s)} + \text{SiH}_{(s)} \rightarrow 2\text{SiH}_{2(s)}$ $\text{SiH}_{3(s)} + \text{Si}_{(s)} \rightarrow \text{SiH}_{2(s)} + \text{SiH}_{(s)}$ DB (0.16-0.98): $\text{SiH}_{3(s)} \rightarrow \text{SiH}_{2(s)} + \text{H}_{(s)}$ FB (0.25-0.27): $\text{SiH}_{2(s)} \rightarrow \text{SiH}_{(s)} + \text{H}_{(s)}$ DB (1.04): $\text{SiH}_{2(s)} \rightarrow \text{SiH}_{(s)} + \text{H}_{(s)}$	
Diffusion ^c (0.18-0.89) [7]	
Disproportionation ^d (0.46-0.68) [2] $\text{SiH}_{3(s)} + \text{SiH}_{3(s)} \rightarrow \text{SiH}_{4(g)} + \text{SiH}_{2(s)}$	
Disilane formation ^d (0.08-0.46) [2] $\text{SiH}_{3(s)} + \text{SiH}_{3(s)} \rightarrow \text{Si}_2\text{H}_6(g)$	
Precursor-mediated H abstraction ^a (0.39) [1] $\text{SiH}_{3(s)} + \text{H}_{(s)} \rightarrow \text{SiH}_{4(g)} + \text{DB}$	

^aReference 26.

^bReferences 23 and 24.

^cReference 25.

^dReference 28.

The remaining surface processes listed in Table II include surface diffusion, disilane formation, and disproportionation reactions. The chemisorbed radical starting from the inserted configuration diffuses along (and on top of) the

dimer rows and across the dimer rows with energy barriers of 0.42 and 0.59 eV, respectively.^{25,27} Weakly adsorbed (and bond-reformed chemisorbed) radicals diffuse along the dimer rows in the trough with barriers of 0.18 and 0.25 eV and across the dimer rows in the trough with a high barrier of 0.89 eV.^{25,27} Two adsorbed and diffusing $\text{SiH}_{3(s)}$ on the film surface can react with each other to form either disilane (Si_2H_6) or $\text{SiH}_{2(s)}$ and silane (SiH_4) depending on the coordination of the (neighboring) surface Si atoms they are bonded to. When a SiH_3 radical weakly adsorbed onto a fivefold coordinated Si in the trough interacts with a chemisorbed $\text{SiH}_{3(s)}$ onto a fourfold coordinated Si, they can either form Si_2H_6 , which desorbs into the gas phase, or disproportionate to form a $\text{SiH}_{2(s)}$ species and a SiH_4 molecule that desorbs back into the plasma phase; both of the corresponding activation energy barriers are equal to 0.46 eV.²⁸ Furthermore, two SiH_3 radicals physisorbed in the subsurface layer can combine to either form a Si_2H_6 molecule or disproportionate into a $\text{SiH}_{2(s)}$ and a desorbing SiH_4 molecule; the corresponding activation barriers are 0.08 and 0.68 eV.²⁸ In summary, disproportionation reactions, disilane formation, as well as LH and PM abstraction reactions lead to desorption of surface Si species. Finally, for a weakly adsorbed radical bonded to two overcoordinated surface Si atoms in the trough, there exists a desorption pathway characterized by a very low barrier (0.08 eV).^{36,28}

IV. RESULTS AND DISCUSSION

A. Early stages of growth

Figure 2 shows the evolution of the surface concentration of various surface hydride species, expressed in terms of fractional surface coverage Θ , as predicted by our KMC simulations for the early stages of growth at various substrate temperatures. The simulations are restricted to transitions between configurations governed by atomic-scale mechanisms that include all of the kinetic processes listed in Tables I and II, where the corresponding activation energetics has been predicted by our first-principles DFT/GGA/NEB approach. At low substrate temperature T , barrierless SiH_3 radical chemisorption (onto a DB and through insertion into a Si-Si dimer bond), ER H abstraction by the SiH_3 radical, SiH_3 physisorption (weak adsorption onto second-layer Si), in conjunction with low-barrier pathways of surface diffusion of weakly adsorbed SiH_3 , as well as Si_2H_6 formation and desorption are crucial in determining the surface composition. Figure 2(a) shows the evolution of the growth-surface composition at $T=373$ K. DB-mediated dissociation reactions with activation energies $E_a=0.16-0.33$ eV causes some ($<20\%$) of the $\text{SiH}_{3(s)}$ species to dissociate into $\text{SiH}_{2(s)}$ and $\text{SiH}_{(s)}$, thus generating some lower surface hydrides; the growth surface, however, is predominantly covered by trihydrides at low temperature ($\Theta > 70\%$ for $\text{SiH}_{3(s)}$ at $T \leq 373$ K). Throughout the early stage of low-temperature growth, the $\text{SiH}_{3(s)}$ surface coverage is highest, while the $\text{SiH}_{2(s)}$ and $\text{SiH}_{(s)}$ coverages remain low. Figure 2(b) shows the evolution of the growth-surface composition at the intermediate substrate temperature $T=500$ K. At temperatures

FIG. 2. Evolution of averaged surface coverage, $\Theta(t)$, of surface silicon hydride species at various temperatures. Solid lines, circles connected with dashed lines, and triangles connected with dotted lines are used to represent $\text{SiH}_{3(s)}$, $\text{SiH}_{2(s)}$, and $\text{SiH}_{(s)}$ coverages, respectively. (a) $T=373$ K, (b) $T=500$ K, and (c) $T=640$ K.

near 500 K, the surface hydride concentrations are determined by the competition between radical surface diffusion and thermally activated trihydride dissociation. At the very early stages of growth, when the surface DB coverage is very low, $\text{SiH}_{3(s)}$ and $\text{SiH}_{2(s)}$ species compete to dominate the surface composition. However, the surface DB concentration increases rapidly due to H abstraction and SiH_4 and Si_2H_6 desorption. This allows DB-mediated $\text{SiH}_{3(s)}$ dissociation reactions ($E_a=0.16\text{--}0.33$ eV) to occur more frequently ($\sim 5\%$ of surface reactions, excluding diffusion and very-low-barrier adsorption, abstraction, and desorption processes) and bolsters the $\text{SiH}_{2(s)}$ concentration on the surface. Figure 2(c) shows the evolution of the growth-surface composition at the high substrate temperature $T=640$ K. At such high tempera-

tures, sufficient thermal energy is available to not only allow more sequential $\text{SiH}_{3(s)}$ dissociation to form $\text{SiH}_{(s)}$ through FB-mediated pathways but also make high-barrier DB-mediated $\text{SiH}_{2(s)}$ dissociation accessible. Specifically, FB-mediated $\text{SiH}_{3(s)}$ dissociation ($E_a=0.51$ eV) forms two surface $\text{SiH}_{2(s)}$ species per trihydride, which subsequently dissociate into $\text{SiH}_{(s)}$ ($E_a=0.25\text{--}0.27$ eV). In addition, the high-barrier DB-mediated $\text{SiH}_{2(s)}$ dissociation reaction ($E_a=1.04$ eV) contributes further $\text{SiH}_{(s)}$ species to the growth surface. Nevertheless, at high substrate temperatures ($T>640$ K), more $\text{SiH}_{(s)}$ species are formed due to both FB- and DB-mediated $\text{SiH}_{3(s)}$ dissociation reactions ($\sim 4:1$

FIG. 3. Surface configurations at early stages of growth predicted by KMC simulation. Large and light (yellow), small and light (green), and small and dark (purple) spheres are used to denote $\text{SiH}_{3(s)}$, $\text{SiH}_{2(s)}$, and $\text{SiH}_{(s)}$ species, respectively. (a) $T=373$ K, (b) $T=500$ K, and (c) $T=640$ K.

FIG. 4. Comparison of surface hydride concentrations of *a*-Si:H films predicted by our KMC simulations with those measured experimentally by *in situ* ATR-FTIR spectroscopy (Ref. 22). (a) Experiment at $T=373$ K; KMC simulations at $T=350$, 373, and 400 K. (b) Experiment at $T=500$ K; KMC simulations at $T=475$, 500, and 525 K. (c) Experiment at $T=640$ K; KMC simulations at $T=615$, 640, 665, and 715 K.

occurrences), than due to DB-mediated $\text{SiH}_{2(s)}$ dissociation reactions ($\sim 0.2\%$ of surface reactions occurring).

Figure 3 depicts growth-surface configurations from KMC simulations at three different temperatures. At $T=373$ K, Fig. 3(a), $\text{SiH}_{3(s)}$ is the dominant surface hydride species, followed by $\text{SiH}_{2(s)}$, while $\text{SiH}_{(s)}$ are present but at extremely low concentrations; the corresponding relative surface coverages are 68%, 28%, and 4% for $\text{SiH}_{3(s)}$, $\text{SiH}_{2(s)}$, and $\text{SiH}_{(s)}$, respectively. The relative surface coverage of a surface hydride species is defined as its surface coverage divided by the sum of the surface coverages of all three surface hydrides. At $T=500$ K, Fig. 3(b), the surface composition is dominated by dihydrides, with the rest of the surface covered by trihydrides and monohydrides at comparable concentrations; the corresponding relative surface coverages are 49%, 28%, and 23% for $\text{SiH}_{2(s)}$, $\text{SiH}_{3(s)}$, and $\text{SiH}_{(s)}$, respectively. Finally, at $T=640$ K, Fig. 3(c), surface monohydrides become the dominant surface hydride species, while the surface dihydride concentration is reduced and surface trihydrides are depleted substantially with respect to their intermediate-temperature concentrations; the corresponding relative surface coverages are 43%, 42%, and 15% for $\text{SiH}_{(s)}$, $\text{SiH}_{2(s)}$, and $\text{SiH}_{3(s)}$, respectively.

Figure 4 shows comparisons of the growth-surface composition predicted by our KMC simulations at ten different temperatures with the experimental data by Marra *et al.*²² over the temperature range of 40–370 °C. The experimental (steady-state) measurements were conducted by *in situ* ATR-FTIR and spectroscopic ellipsometry on *a*-Si:H films deposited in inductively coupled plasma reactors with silane [SiH_4 at 50 SCCM (SCCM denotes cubic centimeter per minute at STP)] feed gas in inert gas (1% Ar) without any hydrogen dilution.^{22,39} In Fig. 4(a), the experimentally mea-

sured surface composition at $T=373$ K is compared to our early-stage, low-temperature KMC simulation predictions at $T=350$, 373, and 400 K. The predicted $\text{SiH}_{3(s)}$ relative coverages are in good agreement with the experimental ones and decrease with increasing temperature, whereas the $\text{SiH}_{2(s)}$ and $\text{SiH}_{(s)}$ relative coverages increase with increasing temperature. Figure 4(b) compares intermediate-temperature KMC predictions with experimentally measured surface coverages at $T=500$ K; KMC results at $T=475$, 500, and 525 K are shown. The intermediate-temperature predictions are in very good agreement with the experimental data: $\text{SiH}_{2(s)}$ is the dominant surface hydride at a relative coverage of 49%, which does not change appreciably over the 50 K temperature range depicted. Finally, high-temperature KMC predictions are compared to experimental data for surface coverages at $T=640$ K. Although the KMC results are in qualitative agreement with the experimental data, the KMC predictions at $T=615$, 640, and 665 K show only a slight dominance of monohydrides; only after the temperature is raised to 715 K the $\text{SiH}_{(s)}$ coverage increases substantially. This is due to the added contribution ($\sim 0.4\%$ of surface reactions) from high-barrier DB-mediated $\text{SiH}_{2(s)}$ dissociation, which does not occur at lower temperatures.

According to our KMC simulations of the early stage of growth, the surface DB coverage is found to be practically independent of temperature; it remains fairly uniform at around 8×10^{-2} throughout the temperature range examined. This prediction is in agreement (i.e., of the order of magnitude of 10^{-2}) with ESR measurements,¹³ but it is higher than the DB coverage measured by Aarts *et al.*¹⁴ These surface DBs promote surface hydride dissociation reactions from $\text{SiH}_{3(s)}$ to $\text{SiH}_{2(s)}$ through low-barrier DB-mediated pathways ($E_a=0.16\text{--}0.33$ eV), but their surface coverage is low dur-

FIG. 5. Evolution of averaged surface coverage, $\Theta(t)$, of silicon hydride species leading to a steady-state surface composition at (a) $T=313$ K, (b) $T=433$ K, (c) $T=503$ K, and (d) $T=643$ K. Diamonds connected with a solid line, circles connected with a dotted line, and triangles connected with a dashed line are used to represent $\text{SiH}_{3(s)}$, $\text{SiH}_{2(s)}$, and $\text{SiH}_{(s)}$ coverages, respectively.

ing α -Si:H growth throughout the temperature range of interest. The role of DBs in promoting hydride dissociation and sequential dissociation reactions has also been inferred based on experiments.²² However, DB-mediated $\text{SiH}_{3(s)}$ dissociation does not depend strongly on substrate temperature (as DBs are created mostly by impinging SiH_3 radicals through barrierless ER H abstraction), whereas FB-mediated dissociation reactions (through thermally activated pathways) show a strong temperature dependence.

B. Steady-state composition of growth surface

For KMC predictions of the growth-surface composition at steady state, in addition to the DFT-generated database outlined in Tables I and II, the effects on thermal activation energetics of the interactions between adsorbed species at neighboring sites needs to be accounted for as described in Sec. II. Here, we show results of our KMC simulations with such effects incorporated into the rate calculations, which enables the KMC propagation of the surface growth process to steady state. Figure 5 depicts the evolution of the ensemble-averaged surface silicon hydride coverages $\Theta(t)$ at $T=313$, 433, 503, and 643 K. Due to our simulation initial conditions and the many fast rate processes involved, the incorporation of hydride species on the surface is fast during the early stages of growth. Subsequently, the rate of surface occupation decreases with time and the surface composition attains eventually a steady state, where the averaged surface coverage of the surface silicon hydrides remains constant over time. In Figs. 5(a)–5(d), the symbols shown correspond to ensemble-averaged compositions that are also time averaged over several thousands of KMC steps at the late stages of growth. At $T=313$ K, Fig. 5(a), the steady-state surface

composition is dominated by $\text{SiH}_{3(s)}$ species; $\text{SiH}_{2(s)}$ and $\text{SiH}_{(s)}$ species are formed from low-barrier DB-mediated dissociation reactions, but their concentrations are considerably lower than that of the surface trihydrides. However, at $T=433$ K, Fig. 5(b), the surface coverages of $\text{SiH}_{2(s)}$ and $\text{SiH}_{(s)}$ increase substantially due to the increased rates of DB- and FB-mediated $\text{SiH}_{3(s)}$ dissociation reactions. Notably, FBs are formed during the course of these surface reactions due to bonding of the radical with fully (fourfold) coordinated surface Si atoms, thus making possible the (FB-mediated) dissociation of $\text{SiH}_{3(s)}$ even without the availability of surface DBs. Over the temperature range $313 \text{ K} < T < 500 \text{ K}$, $\text{SiH}_{3(s)}$ dissociation reactions compete with adsorption and surface diffusion events for determining the chemical state of the growth surface. At $T > 500 \text{ K}$, FB-mediated dissociation plays an increasingly important role in determining the surface composition, resulting in $\text{SiH}_{2(s)}$ and $\text{SiH}_{(s)}$ coverages higher than that of $\text{SiH}_{3(s)}$; the evolution of the various surface hydride coverages at $T=503 \text{ K}$ is shown in Fig. 5(c). At high temperatures ($T > 600 \text{ K}$), there is enough thermal activation for even DB-mediated $\text{SiH}_{2(s)}$ dissociation reactions ($E_a=1.04 \text{ eV}$) to compete with other surface rate processes, but $\text{SiH}_{3(s)}$ desorption events tend to slow down the growth rate at very early growth stages; the evolution of the surface composition at $T=643 \text{ K}$ is shown in Fig. 5(d). As high-temperature growth proceeds beyond its early stage, an increased growth rate is observed due to contributions to Si incorporation into the growth surface from both DB- and FB-mediated $\text{SiH}_{3(s)}$ dissociation reactions. It should be mentioned that DB creation does not depend strongly on temperature (ER H abstraction is barrierless) and, thus, the occurrence of low-barrier DB-mediated $\text{SiH}_{3(s)}$ dissociation

FIG. 6. Surface configurations at steady state predicted by KMC simulation. Large and light (yellow), small and light (green), and small and dark (purple) spheres are used to denote $\text{SiH}_{3(s)}$, $\text{SiH}_{2(s)}$, and $\text{SiH}_{(s)}$ species, respectively. (a) $T=313$ K, (b) $T=503$ K, and (c) $T=643$ K.

events is almost constant over the temperature range $503 \text{ K} < T < 643 \text{ K}$. On the other hand, the rate of FB-mediated hydride dissociation reactions increases at high temperatures leading to surfaces dominated by monohydrides at $T > 600 \text{ K}$. The combined effects of DB- and FB-mediated hydride dissociation reactions play an important role in determining the temperature dependence of the surface concentration of silicon hydrides. Surface configurations at steady state are shown in Figs. 6(a)–6(c) for $T=313$, 503, and 643 K, respectively.

The KMC simulation predictions for the temperature dependence of the growth-surface composition at steady state are shown in Fig. 7 over the temperature range $313 \text{ K} \leq T \leq 643 \text{ K}$. $\text{SiH}_{3(s)}$ is the major surface hydride species at low temperatures ($T < 400 \text{ K}$), while $\text{SiH}_{2(s)}$ is the dominant surface hydride at $433 \text{ K} \leq T \leq 503 \text{ K}$, and $\text{SiH}_{(s)}$ becomes the most abundant surface species at higher temperatures ($T > 573 \text{ K}$). The $\text{SiH}_{3(s)}$ coverage decreases monotonically with increasing temperature, while the $\text{SiH}_{(s)}$ coverage increases monotonically with rising temperature. On the other hand, the temperature dependence of the $\text{SiH}_{2(s)}$ coverage exhibits a maximum near 500 K. The error bars on the plot of Fig. 7 do not correspond to statistical errors; our ensemble and time averaging have reduced the variance of the simulations and the statistical error is comparable to (or smaller

than) the size of the symbols in the plot. Instead, the error bars indicate the dependence of the average surface hydride concentration on the impingement rate of the SiH_3 radical, with a maximum and minimum deviation from the result shown at a given temperature corresponding to a surface composition for growth at impingement rates of ten times faster and ten times slower, respectively, than the one that yielded the result shown by each symbol. Decreasing the radical impingement rate (i.e., decreasing the radical adsorption rate) increases the surface coverages of the lower hydrides ($\text{SiH}_{(s)}$ and $\text{SiH}_{2(s)}$), whereas increasing the radical impingement rate increases the concentration of surface trihydrides. Most importantly, there is a transformation in the composition of the growth surface: From a surface dominated by higher hydrides at low temperatures to one dominated by lower hydrides at higher temperatures. This predicted trend is in excellent qualitative agreement and good overall quantitative agreement with the experimental findings for *a*-Si:H film composition reported by Marra *et al.*²² and shown by the dashed lines in Fig. 7.

The predicted surface hydrogen concentration on the surfaces grown by our KMC simulations decreases drastically from 2.0×10^{15} to $1.5 \times 10^{15} \text{ cm}^{-2}$ as the temperature increases from 300 to 500 K, but then remains practically constant at around $1.4 \times 10^{15} \text{ cm}^{-2}$ for temperatures up to 640 K. Figure 8 illustrates this trend and compares the KMC simulation predictions with experimental measurements of

FIG. 7. Temperature dependence of surface silicon hydride concentrations predicted by KMC simulation (solid lines) and determined experimentally (dashed lines) from *in situ* ATR-FTIR measurements (Ref. 22). Open diamonds, squares, and triangles are used to denote $\text{SiH}_{3(s)}$, $\text{SiH}_{2(s)}$, and $\text{SiH}_{(s)}$ coverages, respectively.

FIG. 8. Temperature dependence of surface hydrogen concentration predicted by KMC simulation (open diamonds) and determined experimentally (open circles) from *in situ* ATR-FTIR measurements (Refs. 22 and 39).

hydrogen content in *a*-Si:H films.^{22,39} The agreement is very good quantitatively at low temperatures and overall very good qualitatively, i.e., the experimental measurements indicate a saturation of the H content as the temperature increases. The quantitative differences in H content between simulation predictions and experimental measurements at high temperatures may be attributed to the greater population of undissociated higher surface hydrides, SiH_{3(s)} and SiH_{2(s)}, predicted in the simulations. At low temperature, the quantitative discrepancy in the surface H content between the experimental data and the simulation predictions is ascribed to low-barrier SiH_{3(s)} dissociation into lower surface hydrides that occupy sites that would be available for radical (carrying three H atoms) adsorption on the surface. Another important surface property is the steady-state coverage of surface dangling bonds. Our KMC simulations predict a DB coverage of 0.01–0.05 over the entire temperature range examined (313 K ≤ *T* ≤ 643 K) with a weak temperature dependence. This prediction is in agreement (of the same order of magnitude) with surface DB coverages reported in experimental studies of surface composition of *a*-Si:H films grown under conditions consistent with our simulation conditions.¹³

V. CONCLUSIONS

This computational study focused on predicting growth-surface composition during plasma deposition of *a*-Si:H thin films from a silane feed gas without hydrogen dilution at low plasma power densities and low pressures, i.e., under conditions that make the SiH₃ radical the dominant deposition precursor. We reported results of dynamical simulations based on an on-lattice, *n*-fold KMC propagator; these KMC simulations rely on transition probabilities predicted from first-principles-based construction of optimal pathways for the various surface rate processes that constitute the film growth process. These processes include insertion of SiH₃ radicals into surface Si–Si bonds and chemisorption onto DBs created by ER abstraction of surface H, interaction of adsorbed and rapidly diffusing SiH₃ radicals leading to disproportionated dihydrides on the surface, and, most importantly, SiH₃ radical dissociative adsorption reactions, which constitute Si incorporation processes that govern the overall temperature dependence of the silicon film surface composition. The KMC simulations of the very early stages of growth (submonolayer coverage) are based on a strictly *ab initio* rate database. Later growth stages, toward a steady state in the composition of the growth surface, are based on approximate rates that take properly into account effects on the activation energetics of interactions between adsorbed species at neighboring surface sites. The KMC simulations predict important surface properties of grown *a*-Si:H films, such as surface hydride concentrations, surface H content, and surface DB coverage, which determine the grown films' quality and stability.

Our KMC simulations account for the experimentally measured surface hydride composition of plasma deposited *a*-Si:H thin films under deposition conditions that are consistent with our simulation conditions. The agreement between our KMC predictions and the experimental data is good

quantitatively and excellent in terms of the qualitative trends captured; these include the monotonic decrease and increase, respectively, in the concentrations of surface trihydrides and monohydrides with increasing temperature and the appearance of a maximum in the surface dihydride concentration at an intermediate (around 500 K) growth temperature. Furthermore, our study explains adequately the critical roles of surface coordination defects (both dangling bonds and floating bonds) during *a*-Si:H film growth and their relative contributions to the growth process over a broad range of substrate temperatures.

ACKNOWLEDGMENTS

Fruitful discussions with M. S. Valipa are gratefully acknowledged. This work was supported by the NSF through Award Nos. CTS-0417770, CMMI-0531171, and CBET-0613501.

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