

Plasma-Deposited Hydrogenated Silicon Films: Multiscale Modeling Reveals Key Processes

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1. Detailed description of the model

A. Plasma Sheath Model

This section presents a multi-fluid model of the plasma sheath structure and a kinetic model of the plasma-surface interaction. Figure 1 shows a sketch of silicon film surface subjected to the incident neutral and ion fluxes from a reactive ICP plasma of Ar/H₂/SiH₄ mixture. The key species participating in the a-Si:H film surface interactions are SiH₃ and H reactive radicals and Ar⁺ ions.

To investigate the structure of plasma sheath and to obtain the fluxes of the ions and reactive radicals on the film surface, a conventional fluid model is proposed [1, 2]. In this model, for electrons and ions, the effects of ionization and collisions with neutrals are considered. However, the electron-ion collisions are neglected. It is assumed that the electrons and positive ions have constant temperature throughout the sheath, and radicals have the same temperature as the ions. In the multi-fluid approach, the density and velocity of the charged particles are described by the continuity equations

$$\nabla \cdot (n_i v_i) = \nu_{\text{ion}}^i n_e, \quad (1)$$

$$\nabla \cdot (n_e v_e) = \sum_i \nu_{\text{ion}}^i n_e, \quad (2)$$

momentum equations

$$m_i v_i \frac{dv_i}{dz} = -e \nabla \phi - \frac{T_i}{n_i} \frac{dn_i}{dz} - m_i \nu_g^i v_i, \quad (3)$$

$$0 = e \nabla \phi - \frac{T_e}{n_e} \frac{dn_e}{dz} - m_e \nu_g^e v_e, \quad (4)$$

and the Poisson's equation

$$\nabla^2 \phi = 4\pi \left[e \left(n_e - \sum_i n_i \right) \right], \quad (5)$$

which relates the densities of charge particles to the electric sheath potential . Here, $i = \text{Ar}^+, \text{SiH}_3^+, \text{H}^+$. Also, n_j is the number density, m_j is the mass and v_j is the fluid velocity of the particle species. Moreover, ν_{ion}^i , ν^e , and ν_g^i are the ionization frequency and the collision frequencies of the electrons and positive ions with neutrals, respectively.

The set of Eqs. (1)-(5) describes the dynamics of plasma sheath formed near the substrate. In order to determine the energy and flux of the positive ions and the flux of the reactive radicals at the substrate, the sheath governing equations are numerically solved in one dimension (z direction) [1, 2].

B. Ion/Radical-Surface interaction Model

To simulate Si:H film deposition process in a $\text{Ar}/\text{H}_2/\text{SiH}_4$ mixtures discharge, it is assumed that the substrate is exposed to the incoming radicals (SiH_3 , and H) and positive ions (Ar^+ , SiH_3^+ , and H^+) fluxes from the plasma sheath. The important species, namely Ar^+ and SiH_3^+ ions and SiH_3 and H radicals, can contribute into the film growth due to transport processes unique to PECVD.

These processes, as shown in Fig. 1 are the adsorption and desorption of SiH_3 radicals on the film surface, H abstraction by incoming SiH_3 and H radicals from plasma sheath, addition of incoming SiH_3 and H radicals to the dangling bond sites, hopping of adsorbed SiH_3 on the hydride sites, ion sputtering of Si and H atoms from the film, and chemisorption of adsorbed SiH_3 on the dangling bond sites. In the following section, the surface transport processes are formulated, described and exemplary results for variation of these processes with film temperature are presented:

1. Adsorption-desorption

The following Eqs. (6) and (7), respectively accounts for the adsorption and desorption of radicals on the Si surface,

$$J_{\text{ads}} = s_1 \theta_{\text{SiH}} j_{\alpha}, \quad (6)$$

$$J_{\text{des}} = \theta_{\text{SiH}_3} \nu v_0 \exp\left(\frac{-E_d}{k_B T_s}\right), \quad (7)$$

Here, α stands for SiH_3 and $j_{\alpha} = n_{\alpha} (kT_i/2\pi m_i)^{1/2}$ is the flux of the impinging SiH_3 species. The parameters s_1 , θ_{SiH} , and θ_{SiH_3} are the probability of adsorption reaction, surface coverage of monohydric sites (SiH) and physisorbed SiH_3 species, respectively. $v_0 = 1.4 \times 10^{15} \text{cm}^{-2}$ is the number of adsorption sites per unit area [3], $\nu = 1 \times 10^{13} \text{s}^{-1}$ is the thermal vibration frequency, and E_d is the adsorption barrier energy of physisorbed radicals.

2. Abstraction of H and physisorbed SiH_3 radicals

Silyl and hydrogen radicals may directly abstract a surface H thus creating a dangling bond on the surface through an Eley-Rideal mechanism [4–6]. The related expression is

$$J_{a1}^{\alpha} = \nu_{a\alpha} \theta_{\text{SiH}} j_{\alpha}, \quad (8)$$

where, $\nu_{a\alpha} = A_{\alpha} \exp\left(\frac{-E_{a\alpha}}{k_B T_s}\right)$ is the rate constant and $E_{a\alpha}$ is the energy barrier of Eley-Rideal H abstraction reaction by radical α ($\alpha = \text{SiH}_3$ and H). According to the density function theory (DFT) calculations, when H and SiH_3 radicals impinge on a H-terminated silicon surface, the H radicals are much more likely to abstract surface H (and hence create dangling bond sites) than SiH_3 radicals with energy barrier 0.4 eV and 0.2 eV for the SiH_3 and H radicals, respectively [7].

Also, the impinging SiH_3 radicals may also land upon a physisorbed radical. The result is formation of Si_2H_6 molecule that goes back to the gas phase making another hydride site available on the surface:

$$J_{a2} = s_2 \theta_{\text{SiH}_3} j_{\text{SiH}_3}, \quad (9)$$

where a probability of $s_2 \approx 0.1$ ($= 0.25 \times 0.4$) is assigned to this reaction since the dangling bond on the incident radical has to point towards the physisorbed radical (≈ 0.25) and can only attack the surface bond of the physisorbed radical from the sides, i.e., fractional area (≈ 0.4).

3. Addition of SiH₃ and H radicals to DBs

The incident H and SiH₃ radicals may directly chemisorbed on a dangling bond (Reaction A) forming a surface mono- and tri-hydride, respectively. This elementary addition reaction is barrier free and is assigned a probability of $s_0 = 0.25$ corresponding to the approximate fraction of surface area of a dangling bond on a SiH₃ radical. Then, the loss rates of dangling bond sites due to addition process can be defined as follows:

$$J_{add} = s_0 \theta_{db} j_\alpha, \quad (10)$$

where θ_{db} is the surface coverage of dangling bonds.

4. Hopping of adsorbed SiH₃ on the hydride sites

Once the silyl radical gets into a stable physisorbed on the surface, there are several possible surface reactions. It could hop onto another surface site, including hopping onto a dangling bond or from one hydride to another. The consumption flux of an adsorbed neutral participating in an adsorbed-layer reaction is given by,

$$J_h = \theta_{SiH_3} (1 - \theta_{db}) \nu v_0 \exp \left(\frac{-E_h}{k_B T_s} \right), \quad (11)$$

where, E_h , the apparent barrier for the hopping reaction, has been measured using surface roughness evolution to be $\approx 0.2\text{eV}$ [8–11].

5. Chemisorption of adsorbed SiH₃ onto DB

Physisorbed SiH₃ radicals can participate in the film growth due to hopping of SiH₃ onto the dangling bonds. The chemisorption flux is

$$J_s = \theta_{SiH_3} \theta_{db} \nu v_0 \exp \left(\frac{-E_s}{k_B T_s} \right), \quad (12)$$

where E_s is the barrier for hopping onto a dangling bonds.

6. Ion Sputtering

The ions can play an important role in the creation of surface dangling bonds in plasma deposition by physical sputtering of the mono-hydride sites with a flux that is described by:

$$J_{\text{sp}} = y_{\text{sp}}(E_i)\theta_{\text{SiH}}J_i, \quad (13)$$

where $y_{\text{sp}}(E_i)$ is the sputtering yield which is a function of ion energy (E_i). All surface processes included in the model and the corresponding functions are presented in Table 1. The overall site balance equation is used to describe the site-specific surface reactions. Three types of sites are considered on the growth surface, including dangling bonds (θ_{db}), physisorbed SiH_3 radicals (θ_{SiH_3}) and mono-hydrogen (θ_{SiH}) sites. These fractional coverages are constrained to satisfy

$$\theta_{\text{db}} + \theta_{\text{SiH}_3} + \theta_{\text{SiH}} = 1. \quad (14)$$

Having identified the key surface reactions in a-Si:H deposition, two additional independent equations, required to obtain the solution for the individual coverages of the different surface species, can be derived from the surface site balance for the dangling bonds and physisorbed SiH_3 radicals. The surface coverage of different species (θ_{db} , θ_{SiH} and θ_{SiH_3}) is expressed in terms of a set of coupled non-linear time-dependent differential equations that accounts for the generation and consumption of these sites. If we assume a steady state ($d\theta_i/dt = 0$) growth, these differential equations reduce to a set of non-linear algebraic equations. The steady-state site balances for θ_{db} , θ_{SiH} and θ_{SiH_3} are obtained in the next steps.

1. Dangling bond balance

Dangling bonds can be created by several distinct mechanisms: i) H abstraction reactions by incident SiH_3 (R_3); ii) H abstraction reactions by incident H radicals (R_4); and iii) Ion sputtering of surface hydrogen H (R_{10}). Dangling bonds are in turn consumed through

addition and chemisorption reactions (R_6 , R_7 and R_9). Hence the steady state balance for the dangling bonds is given by

$$\nu_{a\alpha}\theta_{\text{SiH}}j_{\alpha} + y_{sp}(\theta_{\text{SiH}})J_i - s_0\theta_{db}(j_{\text{SiH}} + j_{\text{SiH}_3}) - v_0\nu_s\theta_{db}\theta_{\text{SiH}_3} = 0. \quad (15)$$

2. Physisorbed Radical Balance

The physisorbed radical site balance involves creation through physisorption of incident SiH_3 radicals on the surface (R_1), and removal through; i) abstraction by incident SiH_3 (R_5); ii) thermal desorption (R_2); and iii) hopping onto a dangling bond (R_9):

$$s_1\theta_{\text{SiH}}j_{\text{SiH}_3} - s_2\theta_{\text{SiH}_3}j_{\text{SiH}_3} - v_0\nu_s\theta_{db}\theta_{\text{SiH}_3} = 0. \quad (16)$$

Equations (14)-(16) form a complete set of 3 independent non-linear algebraic equations that may be solved simultaneously for 3 independent variables (θ_{db} , θ_{SiH} and θ_{SiH_3}) as a function of substrate temperature and plasma parameters. Substitution of Eq. (14) in Eqs. (15) and (16) yields a system of two linear equations which gives the surface coverages of dangling bond and SiH_3 radicals. Then from Eq. (14) the surface coverage of mono-hydride surface SiH can be derived. The total hydrogen content on the surface (c_H) is further related to the SiH and SiH_3 fractions designated as follows:

$$c_H = 0.75\theta_{\text{SiH}_3} + 0.25\theta_{\text{SiH}} \quad (17)$$

This equation states that if, for example, the surface is completely covered by trihydride units, i.e., $\theta_{\text{SiH}_3} = 1$, then $c_H = 0.75$ and each Si atoms on the surface has three out of four available bonds as Si-H bonds.

The growth rate is calculated from the reaction rates resulting in the formation of a Si-Si bond between a precursor and the surface Si atoms. These include direct addition of impinging SiH_3 radicals and chemisorption of physisorbed SiH_3 radicals on a surface dangling bond

$$R_t = a_{si}[(s_0\theta_{db}/v_0)j_{\text{SiH}_3} + \nu_s\theta_{db}\theta_{\text{SiH}_3}]. \quad (18)$$

where a_{si} is the atomic distance between two Si atoms.

2. Additional results of numerical simulations:

- Figure S1. Different fluxes participating in plasma-surface processes
- Figure S2. The growth rate and the surface coverage

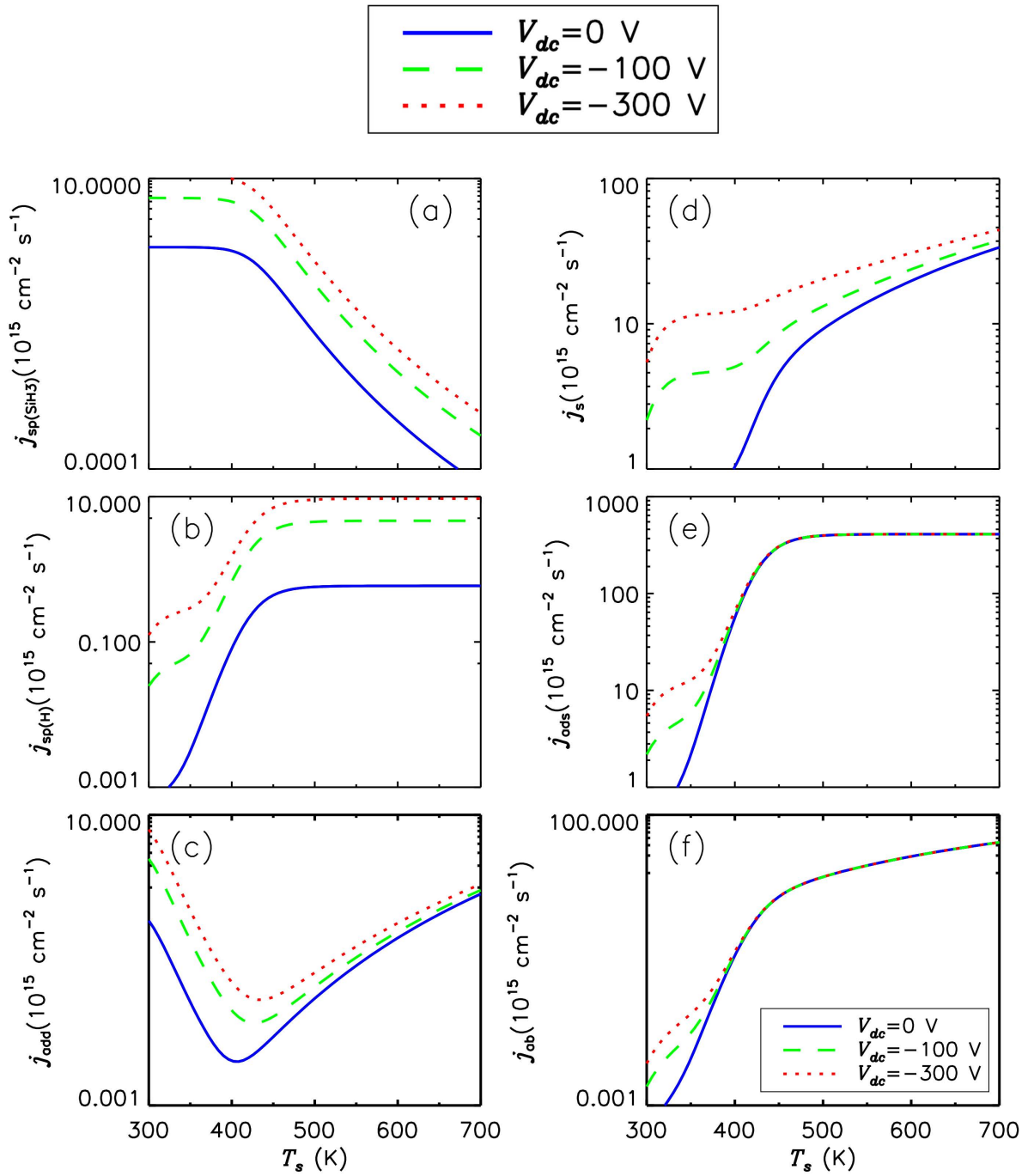


Figure S1. Different fluxes participating in plasma-surface processes as functions of substrate temperature for three different bias voltages. (a) ion sputtering flux of SiH₃, (b) ion sputtering flux of H, (c) addition flux, (d) chemisorption flux, (e) adsorption flux, and (f) abstraction flux. Other parameters are the same as in Table I.

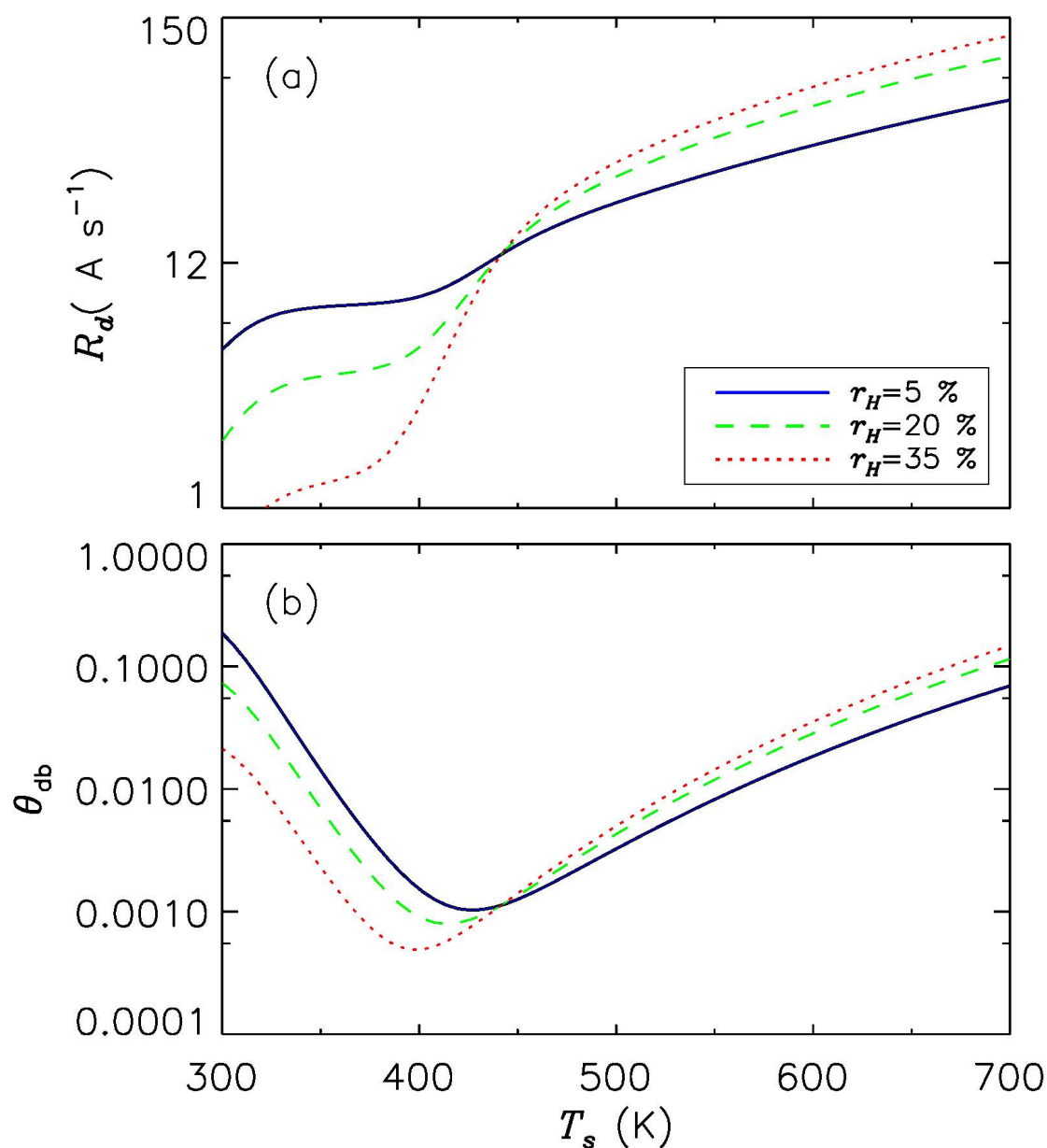


Figure S2. The growth rate and the surface coverage of dangling bonds as functions of substrate temperature for three different percentage of incoming hydrogen radicals from the plasma sheath. Other parameters are the same as Table I.

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