

Models for Thermal Dissociation of Silane on a Polysilicon Surface

Tapio T. Rantala

Microelectronics and Material Physics Laboratories, University of Oulu,
SF-90570 Oulu, Finland

Received 13 April 1989/Accepted 8 September 1989

Abstract. Simple models for the thermally activated dissociation reaction of silane and silicon growth on a polycrystalline silicon surface are presented. The models are fitted to recent experimental molecular beam scattering data for the low-pressure reactive sticking coefficient. Thermally activated few-step models fit the data reasonably well, and thus, we are able to explain the temperature and pressure dependencies of the observed deposition rate.

PACS: 68.55, 82.65

Chemical vapor deposition (CVD) is one of the standard processes for thin film manufacture in microelectronics [1], and silicon as a deposit or a substrate is one of the most important materials due to its applicability in wide range of purposes in realisation of both active and passive components. For silicon deposition, the usual choice of the growth gas is silane (SiH_4), which is used to deposit both pure and doped silicon on various substrates. However, the reaction mechanisms of silane dissociation and silicon growth in the deposition process are not fully understood even for the common substrates in standard processing [1–3]. The importance of understanding the detailed reaction mechanisms has increased together with the development of new processing techniques, such as local laser-induced CVD (LCVD) [2–3], where a much larger local reaction rate is often required as compared to the conventional CVD. Although, a locally laser-induced reaction may have its special features, the pyrolytic LCVD might involve much the same surface reactions as the thermal CVD. This should be the case if direct interaction between the laser light and growth gas (photolysis) is not present and the preceding gas phase reactions can be eliminated [3–5].

Under the usual processing conditions, conventional silane CVD process obviously includes several gas phase reactions preceding the surface reaction of Si deposition and growth [4]. However, in low-pressure

molecular beam scattering deposition the gas phase precursors can largely be eliminated [5], which then allows one to examine the direct silane surface reaction only. The overall reaction rate of the direct silane dissociation on silicon surfaces has been examined in various conditions [5–9], and the measured thermal activation energies vary from zero to about 50 kcal/mol depending on the experimental technique and silicon substrate orientation; see summary in [5]. It seems obvious that the overall reaction cannot be described by a single activation energy, and furthermore, such factors as growth gas pressure (flux) and surface orientation noticeably effect the deposition rate.

Here we decompose the reaction $\text{SiH}_4(\text{g}) + \text{Si-substrate} \rightarrow \text{Si-deposit/Si-substrate} + 2 \text{H}_2(\text{g})$ into a few steps: adsorption, desorption and dissociation, or alternatively, precursor formation and subsequent dissociative adsorption. To each of these steps we assign a thermal activation energy and a constant prefactor, which define the temperature dependent reaction rate of the step. However, one should note that these steps are not necessarily the elementary ones but they might be further decomposed to precursor or intermediate migration, various energy exchange processes and nucleation, for example. Also, surface site interactions might be involved. In fact, the parameters above could be assigned to any model

with the equivalent number and type of thermally activated steps.

In this paper we present some fits of the parameters of two- or three-step models to the experimental data of Buss et al. [5], measured from the low-pressure molecular beam deposition of Si from silane gas on a polycrystalline silicon substrate. In the first section we define the models and give their solutions; Sect. 2 contains the results and discussion, and conclusions are given in the last section.

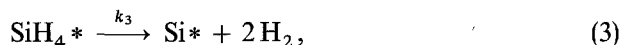
1. Models

In the experimental studies of silane dissociation on silicon substrates, the (111) surface of silicon has been most widely considered. Farrow [6] found a linear pressure dependence of the dissociation and suggested a first-order unimolecular surface reaction. He also detected disilane (Si_2H_6) production and assigned it to the silane desorption. Farnaam and Olander [7] found an activation energy of 17 kcal/mol for the dissociation at the surface but zero activation energy for the preceding adsorption through $\text{SiH}_4 \rightarrow \text{SiH}_2 + \text{H}_2$. Experiments with two different hydrogen isotopes did not reveal atomically adsorbed hydrogen. Donahue and Reif [8] pointed out the substrate orientation dependence of the reaction. They obtained activation energies of 9 and 51 kcal/mol for the high temperature and low temperature dissociation, respectively. In very recent low temperature experiments Gates et al. [9] found zero activation for adsorption and temperature independent reaction rate in some conditions. From the low initial sticking coefficient they also concluded the existence of very few but active sites at the Si(111)-(7 × 7) surface.

The experimental data of Buss et al. [5] are obtained from low pressure measurements for the polycrystalline silicon surface, and consist of the temperature and pressure (flux) dependencies of the reactive sticking coefficient (RSC) in about 30 measurements. The RSC is defined by the number of silicon atoms deposited per number of silicon atoms (silane molecules) impinging on the surface in the silane molecular flux Φ . In our studies of the reaction kinetics, it turned out that these experimental data are probably not sufficient to reveal the detailed reaction mechanism, and models with too many free parameters might give several good fits resulting in an ambiguous physical picture of the reaction. Therefore, we restrict ourselves to the simple two and three reaction step models, where only one activation energy and pre-factor are assigned to each reaction step. Thus, our models are not sophisticated, but rather, they are of general nature. These models also include those pre-

sented by Buss et al. [5], but fitting to the data revealed new aspects to the thermal activation and the role of the surface coverage.

The three reaction steps considered first are defined by the following equations



where $*$ represents the surface site of the substrate. Here, Si^* can be regarded equivalent with $*$ during the deposit growth. From the silicon atomic mass 28.1 g/mol and density 2.33 g/cm³ an average value $[*] = 1.36 \times 10^{15}$ sites/cm² for the surface site density is obtained. This is a somewhat larger value than the surface site density of the well-defined silicon surfaces, which are relatively open structures. Therefore, we expect this value to be a good average for a polycrystalline surface during the deposition.

The Adsorption-Dissociation (AD) model includes the reactions (1) and (3) only. Application of the steady condition for the adsorbate concentration $[\text{SiH}_4^*] = \theta[*]$ leads to

$$k_1[\text{SiH}_4](1 - \theta)[*] - k_3\theta[*] = 0, \quad (4)$$

where θ is the adsorbate (or precursor) coverage on the surface. For convenience, we use, instead of the reaction rate k_1 , the initial sticking coefficient σ , defined as the probability of adsorption for those molecules which impinge at an unoccupied surface site. This is given by

$$\sigma = k_1[*][\text{SiH}_4]/\Phi. \quad (5)$$

With this notation we may solve for the coverage

$$\theta_{\text{AD}} = \frac{\sigma\Phi}{\sigma\Phi + k_3[*]} \quad (6)$$

and for the reactive sticking coefficient $k_3\theta[*]/\Phi$ we obtain

$$\text{RSC}_{\text{AD}} = \frac{\sigma k_3[*]}{\sigma\Phi + k_3[*]}, \quad (7)$$

which is also the quantity experimentally measured by Buss et al. [5].

The Adsorption-Desorption-Dissociation (ADD) model consists of the AD model above with the addition of desorption, i.e. the ADD model consists of the equations (1–3). In analogy to the above, we derive for the coverage

$$\theta_{\text{ADD}} = \frac{\sigma\Phi}{\sigma\Phi + (k_2 + k_3)[*]} \quad (8)$$

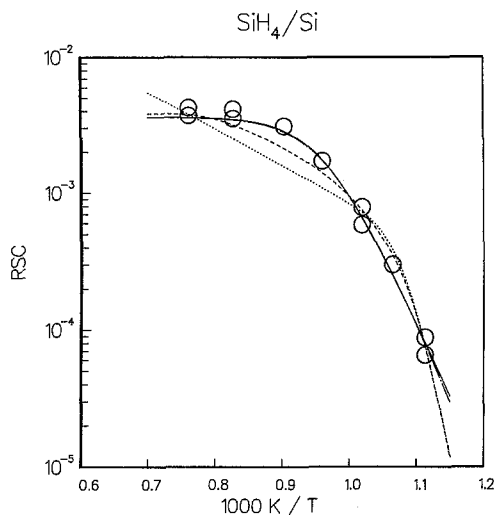


Fig. 1. Temperature dependence of the reactive sticking coefficient (RSC) of silane at a silicon surface for the flux $\Phi = 5.9 \times 10^{17} \text{ cm}^{-2} \text{ s}^{-1}$ ($P = 2 \times 10^{-3} \text{ mbar}$). Open circles are experimental observations [5]. Dotted, solid, dash-dotted, and dashed curves are the fits to the models, labeled as AD, ADD₁, ADD₂, and AD θ , respectively. See text for details

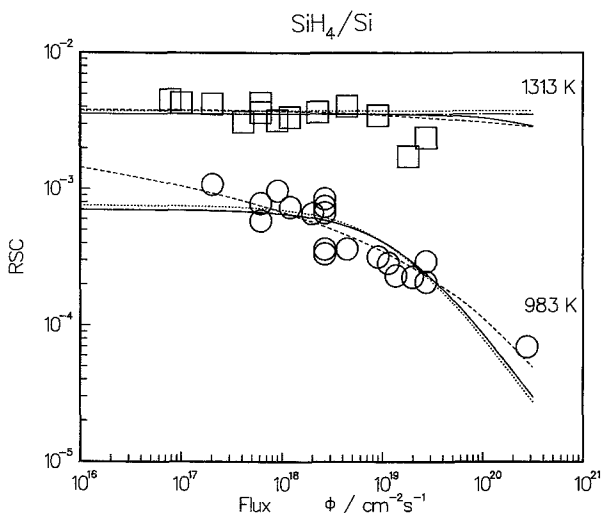


Fig. 2. Pressure (flux) dependence of the RSC. Experimental data are given for temperatures 1040°C (1313 K, open squares) and 710°C (983 K, open circles). The fitted models are shown with the same symbols as in Fig. 1. For pressure use: $P [\text{mbar}] = 3.6 \times 10^{-21} \Phi [\text{cm}^{-2} \text{ s}^{-1}]$

and for $k_3\theta[*]/\Phi$ we obtain

$$\text{RSC}_{\text{ADD}} = \frac{\sigma k_3[*]}{\sigma\Phi + (k_2 + k_3)[*]}. \quad (9)$$

We now assume the reactions to be thermally activated by the surface temperature T_s and write for the reaction rates

$$k_i(T_s) = v_i e^{-E_i/k_B T_s}, \quad (10)$$

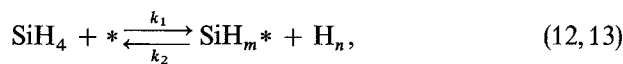
where the parameters, prefactor v_i and activation energy E_i are to be determined for each step i .

In order to compare with the models given in [5], we consider one more model, which we call AD θ . It is basically the AD model defined above but now with a surface-coverage (or precursor) dependent activation energy

$$E_3(\theta) = E_a + E_b\theta. \quad (11)$$

With this form of activation energy substituted into the reaction rate k_3 in (10), we find that (6) and (7) apply for the AD θ model, too.

Finally, we want to note that the parameters defined above are actually from a more general model:



where $m+n=4$. The adsorbed intermediate SiH_m^* in the equations above can be interpreted as a precursor, as well. Hence, the discussion in the next section should also be considered from this, more general, point of view.

The fitting was done by minimizing the least squares sum of the model deviations from all the experimentally measured data shown in Figs. 1 and 2. The computations were performed using a suitable NAG [10] subroutine. Although fitting of four, six, and five parameters of the models AD, ADD, and AD θ should, in principle, be simple; due to the functional dependencies in (10), proper transformations for the parameters before fitting had to be done. Furthermore,

Table 1. Parameters fitted to the models, given in the order of increasing goodness of the fit (the best fit being the last line). Note that $\sigma(T_s) = v_1 \exp(-E_1/k_B T_s)$, cf. (10). Activation energies are given in kcal/mol

Model	v_1	E_1	$v_2 [\text{s}^{-1}]$	E_2	$v_3 [\text{s}^{-1}]$	E_3
AD	0.44	12			3.3×10^{24}	107
ADD ₃	3.9×10^{-3}	0	1.1×10^{18}	74	4.4×10^{24}	107
ADD ₂	3.6×10^{-3}	0	5.1×10^7	28	2.3×10^{17}	74
ADD ₁	3.6×10^{-3}	0	30	0	3.8×10^{11}	48
AD θ	3.8×10^{-3}	0			3.1×10^{27}	153–35 θ

the fitting procedure resulted in more than one local minimum for the ADD model, see Table 1. It should also be noted that it is possible that we have not found all local minima or even the absolute minima for the present models.

2. Results and Discussion

Starting from the simplest case we first consider the AD model. The fit to the temperature dependence is poor as seen in Fig. 1 and the fit to the pressure dependence data in Fig. 2 does not essentially differ from that of the ADD model. In this model, at high temperatures the coverage is extremely low, see Figs. 3 and 4, implying an adsorption- or precursor-limited reaction rate. Along with the pressure increase at lower temperature the coverage saturates to unity and the reaction becomes dissociation limited. In both temperature ranges the slope of the fit in Fig. 1 is obviously too large leading to overestimation of the activation energies given in Table 1, although an experimental high temperature activation energy of 9 kcal/mol is reported elsewhere [9], too.

For the ADD model the fitting procedure resulted in three local minima for the least squares sum. They are given separately in Table 1. These three fits are almost equally good and much better than the fit of the AD model. The largest differences between these three fits are seen in the coverage dependencies, Figs. 3 and 4. The ADD₃ is found least satisfactory in the temperature dependence, following close to the AD θ model.

The best fit to the temperature dependence, ADD₁, suggests activation free adsorption and desorption, and 48 kcal/mol activation energy for dissociation. The latter is close to the experimental LCVD value 43.5 kcal/mol of Doppelbauer and Bäuerle [11], who measured the apparent activation energy for the pyrolytic Si rod growth from silane gas at pressures from 50 to 300 mbar. In our model and fit the silane coverage is relatively low for low pressure and low temperatures, see Fig. 3, as a consequence of rapid desorption. With increasing pressure, however, the desorption-limited reaction converts to dissociation limited mechanism with saturated coverage, see Fig. 4. At higher temperatures, the adsorbing silane dissociates directly resulting in a low coverage and adsorption-limited reaction rate.

The other two fits, ADD₂ and ADD₃, of this model also suggest activation free adsorption but activated desorption and dissociation, and therefore, the silane coverage dependencies are very different from ADD₁ and also from each other. The ADD₃ is much like the AD with probably too high an activation energy for dissociation. The ADD₂, in contrast, follows very

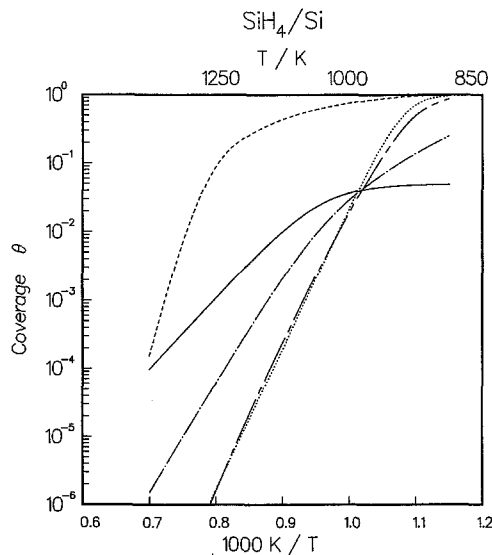


Fig. 3. Temperature dependence of the silane coverage on the silicon surface in various models for the fits shown in Fig. 1 ($P = 2 \times 10^{-3}$ mbar). The symbols are the same as in Fig. 1, with the additional chain curve for ADD₃.

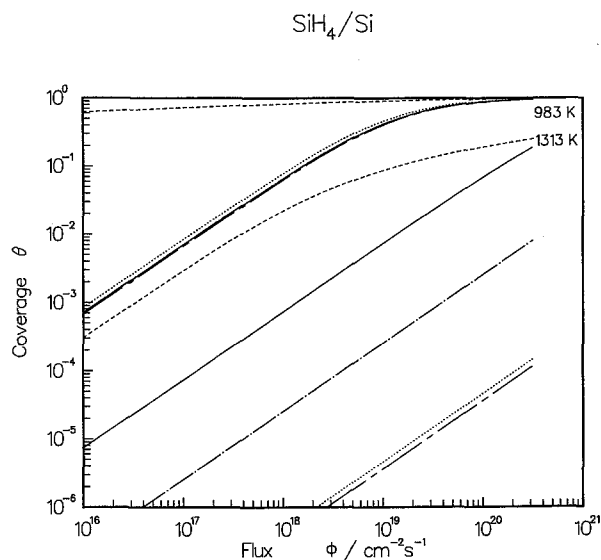


Fig. 4. Pressure dependence of the silane coverage for the fits shown in Fig. 2. The upper and lower curves correspond to 710°C (983 K) and 1040°C (1313 K), respectively. The symbols are the same as in Fig. 3.

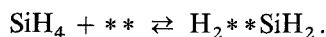
closely to the ADD₁ in Figs. 1 and 2, and it has non-zero activation energy for desorption as is reasonable. The desorption energy, 1.2 eV (28 kcal/mol), should be interpreted in terms of the general model (12–14), which involves various species with desorption energies ranging to the Si desorption energy which is about 1.6 eV. Also, it should be noted that the hydrogen desorption is included into the adsorption or

dissociation reaction in our models. The common crossing point of the curves in Fig. 3 coincides with the lower temperature (983 K), where the pressure dependence data is fitted, and thus, it may be an artifact arising from too few experimental temperatures.

The AD θ model should be the same as that used to fit the data in [5]. However, our fit is not identical to theirs but, in our opinion, slightly better except for the low temperature pressure dependence. In this model the silane coverage is always much higher compared to the other models; this is a consequence of the coverage dependence of the activation energy of dissociation. In this case we interpret the result as due to an overestimation of the activation energy that is partly canceled by the overestimation of adsorbate interactions, i.e. coverage dependence. The cancellation is not complete, however, as seen by the too large slope at the low temperature end of the fit in Fig. 1.

All of our models suggest zero activation energy for adsorption, except AD which gives a small value of 12 kcal/mol. The non-activated adsorption is also supported by several experiments [5–7, 9], leading us to conclude that the initial sticking coefficient is surface temperature and silane pressure independent. There remains, however, the possible silane gas temperature dependency which is not examined here. As pointed out by Buss et al. [5], a small gas temperature dependent adsorption barrier would explain the low RSC at high temperatures. From our room-temperature initial sticking coefficient $\sigma = 0.0036$ we calculate a barrier of 0.15 eV or 3.4 kcal/mol, which might be a consequence of a precursor state or of a molecular distortion necessary during the adsorption. Therefore, heating of the silane gas should increase the reaction rate considerably, and an experimental test of this would be worthwhile.

The “best” model of Buss et al. [5] differs from the model ADD both in the adsorption and desorption mechanism. They assume dissociative adsorption and desorption involving two adjacent surface sites, i.e.,



We note however, that in the high coverage limit in an analytical treatment of adsorption kinetics it is not straightforward to correctly take into account the correlation of the two free surface sites required for adsorption. In the low coverage limit, on the other hand, a similar use of the law of mass action and $[*]^2$ -dependency for desorption would require high mobility of H_2 molecules on the surface. Such mechanisms involving surface site correlations can be examined most conveniently by using the Monte Carlo type methods as is done for the present reaction by Kotecki and Herman [12] or for hydrogenated silicon growth by other authors [13].

Comparing the “best” model of Buss et al. with our models we note that it corresponds to our fit ADD₂ with essentially the same desorption energy, which is not very much different from the Si desorption energy, as pointed out above. In our opinion the ADD₂ fit to the data is the better of the two but they are both less successful than the fit ADD₁. We emphasize, however, that due to the simplicity and generality of the models, each of the different fits may have found some of the many activation energies possibly present in the whole reaction. Therefore, they may give complementary information about the reaction, rather than merely alternatives for the reaction mechanism. This assumption also receives some support from recent experiments on hydrogen desorption from the silicon surface by Sinniah et al. [14]. Their interpretation of the results is based on a multistep mechanism that, of course, cannot be taken into account in our few-step models, but however, if correct, might be reflected in the fitted energies.

3. Conclusions

The available experimental data are too few to develop a complete picture for the silane low-pressure dissociation at silicon surface. With relatively simple models, however, we are able to predict activation-free adsorption with an initial sticking coefficient of about 0.004 and activated dissociation at the surface. The resulting value of the initial sticking coefficient, constant in these conditions, may depend on the silane gas temperature rather than the surface temperature and gas pressure. In the present case it leads to an adsorption (or precursor formation)-limited reaction rate at high surface temperature. At low temperatures the reaction converts from desorption limited to dissociation limited as the pressure increases. However, the role of desorption remains unclear and our models are obviously too simple to account for it completely.

The several local minima found in the fitting procedure, and particularly, the variation of the activation energies of dissociation and desorption, might be reflections of the more complex structure of these single steps in our models. In particular, the reaction may include desorption of various species and SiH_4 dissociation in several steps with different activation energies. Therefore, we suggest that the different fits and resulting activation energies should be regarded as complementary information about the reaction rather than alternatives for the reaction mechanism.

Acknowledgements. The Academy of Finland is acknowledged for financial support. The author also wants to thank Prof. S. Leppävuori, Dr. J. Lenkkeri, and Mr. T. S. Rantala for their interest in this work.

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