# Reaction Constant Versus
# Reaction Rate Constant

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The chemical etching of intrinsic polycrystalline silicon in $Cl_2$ environment is considered. The theoretically calculated dependences of poly-Si etching rate on pressure of $Cl_2$ molecules at different temperatures are compared with those experimentally measured. Reaction rate constants, found by fitting the experimental data, are converted into reaction constants. It is found that 99.99% of incident $Cl_2$ molecules are scattered from atomically clean Si surface at temperature 800 K. With the increase in pressure of $Cl_2$ molecules, the reaction constant monotonically decreases due to the increased surface coverage by $SiCl_2$ molecules.

topics: reaction constant, reaction rate constant, chemical etching

## 1. Introduction

The rate of chemical reaction is defined by a reaction rate constant. Theoretical physicists involved in the description of plasma etching processes benefit from the usage of chemical kinetics. Scientists create mathematical models that describe a specific plasma etching process and investigate how experimental parameters influence a theoretical etching rate. This type of analysis also yields information about the prevailing reaction mechanism. Meanwhile, the reaction constant is used exclusively by experimental physicists to describe properties of the investigated material. The black-box approach uses the flux of reactive particles to the surface being etched as the input parameter. The output parameter is the flux of the reaction product from the etched surface. This method of analysis is straightforward and does not require excellence in the chemical kinetics.

The reaction constant for the same substrate depends on a great variety of experimental parameters. During silicon etching in fluorine-based plasma, values of the reaction constant differ up to 2000 times [1]. This discrepancy arises due to different experimental conditions and different reaction constant calculation methods. When the corrected reaction constant was plotted as the function of F atom flux, the difference in the reaction constant decreased to 30 times. The reaction of F atoms with silicon was described in [2] by the single reaction constant in a wider range of concentrations. However, the fundamental difference between the

TABLE I

The dissociation parameters of halogen molecules [3]. BDE is the bond dissociation energy at standard conditions and $T_{D(1\%)}$ is the temperature at which 1% of halogen molecules dissociate.

| Halogen | $F_2$ | $Cl_2$ | $Br_2$ | $I_2$ |
|---|---|---|---|---|
| BDE [eV] | 1.63 | 2.51 | 1.99 | 1.57 |
| $T_{D(1\%)}$ [K] | 1040 | 1250 | 1050 | 850 |

reaction constant and the reaction rate constant limited a further extension of the concentration range in which the single reaction constant is valid.

In this work, the reaction constant is theoretically related to the reaction rate constant. In order to avoid artefacts, chemical etching of silicon in $Cl_2$ environment at elevated temperature is investigated. Molecular chlorine does not thermally dissociate due to strong bond energy, see Table I. Theoretical investigation is based on the already published experimental data. During the experiment [4], intrinsic poly-Si films were etched in $Cl_2$ environment. The poly-Si films were grown on the monocrystalline silicon substrates covered with a thermally grown 20-nm thick silicon oxide layer. The chemical etching of poly-Si was performed in a reactor consisting of a 30 cm long quartz tube with an inner diameter of 25 mm. During the etching process, the flow rate of $Cl_2$ gas varied from 10 to 15 sccm and the substrate temperature was in the range of 783–843 K. The surface area of poly-Si films was 4–9 $mm^2$. The etching rates were measured *in situ* using a laser interferometer.

## 2. Model

During silicon etching in $Cl_2$ environment, competition between formation and desorption of $SiCl_2$ molecules takes place. The $Cl_2$ molecules from the gas phase (g) react with Si atoms on the surface (s). This process is described schematically as
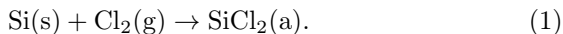
$$Si(s) + Cl_2(g) \rightarrow SiCl_2(a). \qquad (1)$$

The reaction consists of two elementary steps: (i) the dissociative chemisorption of $Cl_2$ molecules on the surface, i.e., $2Si(s) + Cl_2(g) \rightarrow 2SiCl(a)$, and (ii) the formation of $SiCl_2$ molecules as the final reaction product, i.e., $2SiCl(a) \rightarrow SiCl_2(a) + Si(s)$. According to the transition state theory described in [5], the reaction rate constant is equal to

$$k_r = A\nu_{TST} \exp\left(\frac{\Delta S}{k_B}\right) \exp\left(-\frac{\Delta H}{k_B T}\right), \qquad (2)$$

where $A$ is the average kinetic transmission coefficient, $\nu_{TST} = k_B T/h$ is the attempt frequency along the reaction coordinate, $h$ is the Planck constant, $k_B$ is the Boltzmann constant, $T$ is the temperature, $\Delta S$ is the activation entropy, $\Delta H = E_r - k_B T$ is the activation enthalpy and $E_r$ is the reaction activation energy. The mean reaction time is equal to $\tau_r = 1/(k_r p)$.

Diffusion of $SiCl_2$ molecules is taking place in the adsorbed layer until they eventually desorb [6, 7]. The first-order molecular desorption is described by the desorption rate constant

$$\omega = \nu_{TST} \exp\left(-\frac{E_d}{k_B T}\right), \qquad (3)$$

where $\nu_{TST}$ is equal to the lattice atom oscillation frequency [8] and $E_d$ is the desorption activation energy. The mean desorption time is defined by $\tau_d = \omega^{-1}$.

The $SiCl_2$ molecules, produced during a reaction on the surface, are included in the adsorbed layer of one-monolayer thickness. The relative concentration of $SiCl_2$ molecules in the adsorbed layer is equal to $c = [SiCl_2]/C$, where $[SiCl_2]$ denotes the concentration of $SiCl_2$ molecules in the adsorbed layer and $C = 1.36 \times 10^{19}$ m$^{-2}$ is the concentration of surface atoms. The following differential equation includes rate expressions of the processes mentioned earlier and describes the kinetics of concentration of $SiCl_2$ molecules in the adsorbed layer

$$\frac{dc}{dt} = \beta k_r p - \omega c, \qquad (4)$$

where $\beta = 1 - \Theta$ is the surface fraction not covered with the adsorbate, $\Theta = c$ is the surface coverage and $p$ is the pressure of $Cl_2$ molecules. The steady-state concentration of $SiCl_2$ molecules is equal to

$$c_{st} = \frac{k_r p}{k_r p + \omega}. \qquad (5)$$

The etching rate is equal to the desorption rate of $SiCl_2$ molecules, i.e.:

$$V_{st} = \frac{h_0 k_r p \omega}{k_r p + \omega}, \qquad (6)$$

where $h_0 = \left(\frac{M_{Si}}{\rho_{Si} N_A}\right)^{1/3} = 2.72$ Å is the monolayer thickness, $\rho_{Si}$ is the density of silicon, $M_{Si}$ is the molar mass of silicon and $N_A$ is the Avogadro constant.

The reaction constant shows how many Si atoms are removed from the surface by a single $Cl_2$ molecule. This quantity is given as

$$\varepsilon = \frac{\Phi(SiCl_2)}{\Phi(Cl_2)} = C \frac{k_r \omega \sqrt{2\pi m k_B T}}{k_r p + \omega}, \qquad (7)$$

where $\Phi(SiCl_2) = \omega[SiCl_2]$ is the flux of desorbing $SiCl_2$ molecules, $\Phi(Cl_2) = \frac{p}{\sqrt{2\pi m k_B T}}$ is the flux of $Cl_2$ molecules to the surface and $m$ is the mass of $Cl_2$ molecules. It is important to note that the reaction constant depends on pressure of $Cl_2$ molecules. At extremely low pressure, the reaction constant reaches its maximum value

$$\varepsilon_0 = C k_r \sqrt{2\pi m k_B T}. \qquad (8)$$

Ratio $\varepsilon/\varepsilon_0$ is equal to

$$\frac{\varepsilon}{\varepsilon_0} = \frac{\omega}{k_r p + \omega} = \beta. \qquad (9)$$

Surprisingly, ratio $\varepsilon/\varepsilon_0$ changes in the same way as the surface fraction not covered with the adsorbate.

## 3. Results and discussion

The experimentally measured dependences of intrinsic poly-Si etching rate on pressure of $Cl_2$ molecules at different temperatures [4] are used for detailed analysis of the etching process. The fitted experimental dependences are shown in Fig. 1. It is observed that with the increase in pressure of $Cl_2$ molecules, the influence of the desorption process on the etching rate becomes pronounced. As a result, the etching rate deviates from the linear increase and starts to approach the saturation regime. Reaction rate constants and desorption rate constants, found by fitting the experimental data,
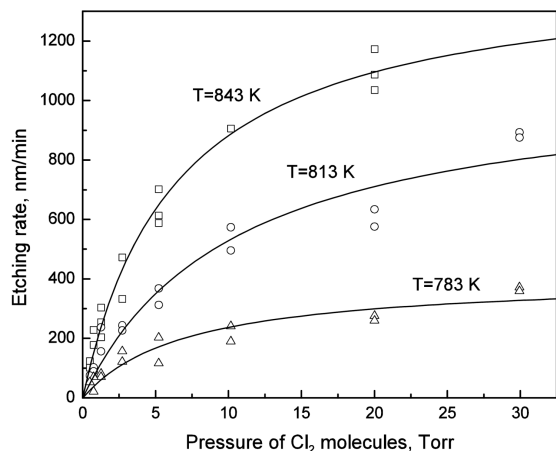


Fig. 1. Experimental [4] (points) and theoretical (curves) dependences of intrinsic poly-Si etching rate on pressure of $Cl_2$ molecules at different temperatures.
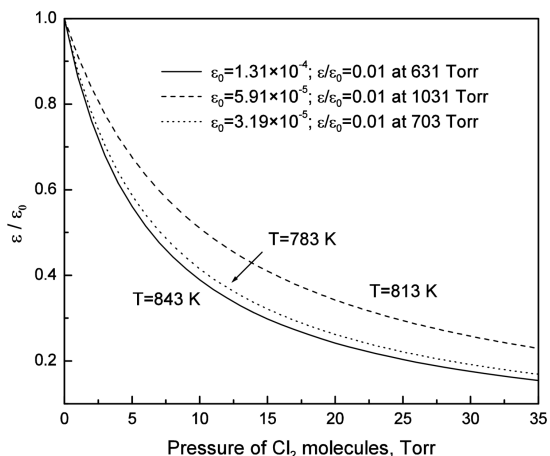
Fig. 2. The theoretical dependences of ratio $\varepsilon/\varepsilon_0$ on pressure of $Cl_2$ molecules at different temperatures. At constant pressure, ratio $\varepsilon/\varepsilon_0$ does not change monotonically with the increase in temperature because of the fitting errors which arise from the scattered experimental data.

TABLE II

The reaction rate constants and the desorption rate constants, found by fitting the experimental data. The reaction constants $\varepsilon_0$ are calculated using the reaction rate constants $k_r$ expressed in units of $Pa^{-1}$ $s^{-1}$.

| $T$ [K] | $k_r$ [Torr$^{-1}$ s$^{-1}$] | $\Delta k_r / k_r$ | $\varepsilon_0$ | $\omega$ [s$^{-1}$] | $\Delta \omega / \omega$ |
|---|---|---|---|---|---|
| 843 | 13.884 | 0.08 | $1.31 \times 10^{-4}$ | 88.53 | 0.05 |
| 813 | 6.357 | 0.16 | $5.91 \times 10^{-5}$ | 66.20 | 0.10 |
| 783 | 3.499 | 0.19 | $3.19 \times 10^{-5}$ | 24.84 | 0.10 |

are presented in Table II. The reaction rate constants $k_r$ are subsequently converted into the reaction constants $\varepsilon_0$ which yield additional information about the etching process. It is found that one $SiCl_2$ molecule desorbs after about $10^4$ collisions of $Cl_2$ molecules with the Si surface. This means that 99.99% of incident $Cl_2$ molecules are scattered from atomically clean Si surface. According to (9), ratio $\varepsilon/\varepsilon_0$ is equal to the surface fraction not covered with the adsorbate. The dependences of ratio $\varepsilon/\varepsilon_0$ on the pressure of $Cl_2$ molecules at different temperatures are shown in Fig. 2. It is observed that with the increase in pressure of $Cl_2$ molecules, ratio $\varepsilon/\varepsilon_0$ monotonically decreases. Two uncertainties, associated with the silicon etching rate at extremely high pressure, arise using the proposed model:

1. ratio $\varepsilon/\varepsilon_0$ is equal to zero;
2. maximum etching rate is equal to

$$V_{\max} = h_0 \omega. \qquad (10)$$

An attempt to address the uncertainties was made during the chemical etching of Ge(111) substrates in $Br_2$ environment. In the experiment [9],

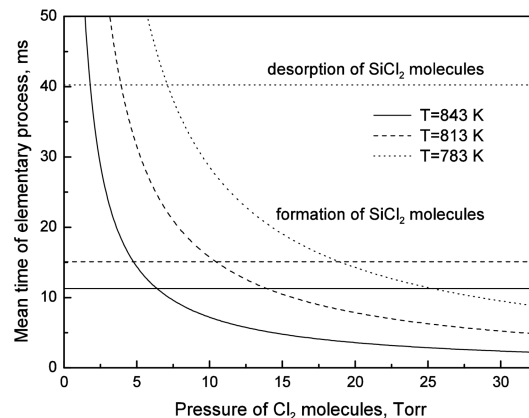

Fig. 3. The theoretical dependences of mean times of elementary processes on pressure of $Cl_2$ molecules at different temperatures.

isothermal dependences of the germanium etching rate on pressure of $Br_2$ molecules were measured. The maximum etching rate of germanium was achieved at pressure of about 3 Torr. It is important to note that with a further increase in the pressure of $Br_2$ molecules up to 200 Torr, the maximum etching rate did not change. The maximum etching rate of germanium in $Br_2$ environment increased only with the increase in temperature. This indicates that both uncertainties are valid during the chemical etching of germanium at high pressure of $Br_2$ molecules. These findings can be plausibly extended to the $Si/Cl_2$ system.

The mean times of elementary processes provide an additional insight into the chemical etching of silicon in $Cl_2$ environment. Theoretical dependences of the mean reaction time and mean desorption time on pressure of $Cl_2$ molecules at different temperatures are shown in Fig. 3. It is observed that the mean reaction time reciprocally decreases with the increase in pressure, while the mean desorption time does not depend on pressure. At low pressure of $Cl_2$ molecules, the formation of $SiCl_2$ molecules is the etching-rate limiting process. With the increase in pressure, the etching rate reaches half of its maximum value. At this point, the mean reaction time is equal to the mean desorption time [10]. At higher pressure of $Cl_2$ molecules, the desorption of $SiCl_2$ molecules becomes the etching-rate limiting process.

## 4. Conclusion

The chemical etching of intrinsic polycrystalline silicon in $Cl_2$ environment is investigated theoretically. The relationship between the reaction constant and the reaction rate constant is established using the chemical kinetics. It is shown that the reaction constant depends on pressure of $Cl_2$ molecules. At extremely low pressure, the reaction constant reaches its maximum value $\varepsilon_0$. With the increase in pressure of $Cl_2$ molecules, concentration

of $SiCl_2$ molecules in the adsorbed layer monotonically increases. The increased surface coverage limits the access of $Cl_2$ molecules to the Si surface and effectively reduces the reaction constant. Ratio $\varepsilon/\varepsilon_0$ is equal to the surface fraction not covered by the adsorbate. Meanwhile, the reaction rate constant does not depend on the surface coverage.

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