Desorption Activation Energy of $SiBr_2$ Molecules according to Steady-State Approximation

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The chemical etching of intrinsic and n-type polycrystalline silicon in Br_2 ambient is considered. The theoretically calculated dependences of silicon etching rates on pressure of Br_2 molecules at different temperatures are compared with experimentally measured ones. The reaction and desorption activation energies are evaluated. It is found that activation energy of $Si + Br_2 \rightarrow SiBr_2$ reaction for intrinsic silicon is equal to (1.82 ± 0.24) eV, and decreases to (1.45 ± 0.24) eV when n-type silicon films are used. Desorption activation energy of $SiBr_2$ molecules for intrinsic silicon is equal to (1.94 ± 0.17) eV, and decreases to (1.51 ± 0.17) eV when n-type silicon films are used. Desorption of $SiBr_2$ molecules is an etching-rate limiting process at high pressure of Br_2 molecules.

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1. Introduction

The reactive ion etching of silicon in bromine-containing plasmas is used in integrated circuit manufacture. Ion bombardment assists in achieving the etching anisotropy due to the synergism of chemical etching and ion beam etching processes. Although Br_2 molecules dissociatively adsorb on single-crystal silicon at room temperature, they do not etch the surface in the absence of ion bombardment. Surface studies of silicon (100) substrates under these conditions show the stable SiBr configuration [1, 2]. When the temperature is raised to 600 K, the formation of $SiBr_2$ molecules takes place, and these molecules are the major etching product [3]. Silicon etching rate increases with the increase of free electron carrier concentration in the substrate. Activated n-type carriers raise the Fermi level and reduce the energy barrier for charge transfer to chemisorbed bromine. In the absence of ion bombardment, the etching rate is easily be enhanced by factor of 125 with moderate phosphorus doping levels [4, 5]. Many authors describing their experimental measurements assume that the $SiBr_2$ molecules that formed immediately desorb. This assumption is valid when desorption activation energy of formed species is much lower than reaction activation energy.

However, during silicon etching with Br_2 molecules reaction and desorption activation energies are comparable because dependence of silicon etching rate on concentration of Br_2 molecules is not linear [6]. Activation energies for these two processes can be determined using single dependence of silicon etching rate on concentration of Br_2 molecules. Reaction activation energy influences the overall etching rate at low concentration of Br_2 molecules. Meanwhile, at high concentration of Br_2 molecules the influence of desorption activation energy on overall etching rate becomes pronounced.

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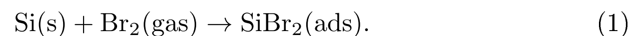
In this work, activation energy of $Si + Br_2 \rightarrow SiBr_2$ reaction and desorption activation energy of $SiBr_2$ molecules are evaluated using transition state theory (TST). In the chosen experiments [7], intrinsic and phosphorus-doped polycrystalline silicon films were etched in Br_2 ambient. The silicon films were grown on single-crystal silicon substrates covered with a thermally grown 20 nm thick silicon oxide layer. The chemical etching of silicon was performed in the reactor consisting of 40 cm length quartz tube with inner diameter of 25 mm. During the etching process the flow rate varied from 12 to 15 sccm, the surface area of silicon films was in the range $(4 \div 9)$ mm^2. The etching rates were measured using a laser interferometer. It is found by extrapolation from experimental results that desorption of $SiBr_2$ molecules is an etching-rate limiting process at high pressure of Br_2 molecules.

2. Model

The experimentally measured dependences of silicon etching rates on pressure of Br_2 molecules [7] are used to calculate reaction and desorption activation energies. Br_2 molecules from the gas phase adsorbed on the surface and reacted with Si atoms



$$\mathrm{Si(s)} + \mathrm{Br_2(gas)} \rightarrow \mathrm{SiBr_2(ads)}. \quad (1)$$

This resultant reaction includes the dissociative chemisorption of Br_2 molecules on the surface and formation of $SiBr_2$ as the final reaction product. The reaction rate constant, according to TST [8–10], is equal to

$$k_\mathrm{r} = B\tilde{\nu}_\mathrm{TST} \exp\left(-E_\mathrm{r}/kT\right), \quad (2)$$

where $\tilde{\nu}_\mathrm{TST} = \frac{kT}{h} \exp\left(\frac{\Delta S}{k}\right)$ is the pre-exponential factor. The neutral situation in which the entropy of the transition state does not notably differ from that of the reactants in the ground state ($\Delta S \approx 0$) yields the standard pre-exponential factor $\nu_\mathrm{TST} = kT/h$, which is of the order of 10^{13} s^{-1}, k is the Boltzmann constant, T is the temperature, h is the Planck constant, E_r is the reaction activation energy, and the reciprocal of molar concentration $B = 1$ m^3 mol^{-1} is used to fix the units

mismatch. $SiBr_2$ molecules present in the adsorbed layer desorb. The desorption rate constant is equal to

$$\omega = \nu_{\mathrm{TST}} \exp\left(-E_{\mathrm{d}}/kT\right), \qquad (3)$$

where E_{d} is the desorption activation energy.

$SiBr_2$ molecules produced during reaction on the surface are included in the adsorbed layer of one-monolayer thickness. The relative concentration of $SiBr_2$ molecules is equal to $c = [\mathrm{SiBr_2}]/C$, where C is the concentration of surface atoms ($C = 1.36 \times 10^{19}$ m^{-2}). The following equation includes rate expressions of the processes mentioned earlier and describes the kinetics of concentration of $SiBr_2$ molecules in the adsorbed layer

$$\frac{\mathrm{d}c}{\mathrm{d}t} = (1 - \Theta) k_{\mathrm{r}} [\mathrm{Br_2}] - \omega c, \qquad (4)$$

where $\Theta = c$ is the surface coverage. The steady-state concentration of $SiBr_2$ molecules is equal to

$$c_{\mathrm{St}} = k_{\mathrm{r}} [\mathrm{Br_2}] \,/\, (k_{\mathrm{r}} [\mathrm{Br_2}] + \omega). \qquad (5)$$

The etching rate is proportional to the desorption rate of formed $SiBr_2$ molecules. According to Eq. (5), the etching rate at the steady-state regime is equal to

$$V_{\mathrm{St}} = h_0 \omega c_{\mathrm{St}} = \frac{h_0 k_{\mathrm{r}} [\mathrm{Br_2}] \, \omega}{k_{\mathrm{r}} [\mathrm{Br_2}] + \omega}, \qquad (6)$$

where h_0 is the monolayer thickness, which is estimated using expression $h_0 = (M_{\mathrm{Si}}/\rho_{\mathrm{Si}} N_{\mathrm{A}})^{1/3} = 2.72$ Å, where M_{Si} is the atomic mass of silicon, ρ_{Si} is the density of silicon, N_{A} is the Avogadro constant.

3. Results and discussion

The experimentally measured dependences of Si etching rates on pressure of Br_2 molecules at different temperatures [7] are used to determine desorption activation energy of $SiBr_2$ molecules. The experimental and theoretical dependences of intrinsic and n-type polycrystalline silicon etching rates on pressure of Br_2 molecules at different temperatures are shown in Fig. 1. Totally, 24 dependences of etching rate on pressure of Br_2 molecules at different temperatures for various silicon films are measured experimentally. As a result, 24 different desorption rate constants are found by fitting the experimental data. TST is used to calculate the pre-exponential factor, desorption activation energy, and absolute error in desorption activation energy.

The constant values, found by fitting the experimental data and subsequent TST analysis, are presented in Table I. Averaged desorption activation energy of $SiBr_2$ molecules for intrinsic silicon is equal to $E_{\mathrm{d1}} \pm \Delta E_{\mathrm{d1}} = (1.94 \pm 0.17)$ eV, and decreases to $E_{\mathrm{d2}} \pm \Delta E_{\mathrm{d2}} = (1.51 \pm 0.17)$ eV when n-type silicon films are used. The desorption activation energy decreases due to the heating of the adsorbed layer by exothermic reaction. Determined values of desorption activation energy of $SiBr_2$ molecules are in good agreement with experimental measurements [11]. Desorption activation energy of $SiBr_2$ molecules determined *in situ* using surface reflectivity spectrometer is equal to $E_{\mathrm{d}} \pm \Delta E_{\mathrm{d}} = (1.8 \pm 0.4)$ eV.

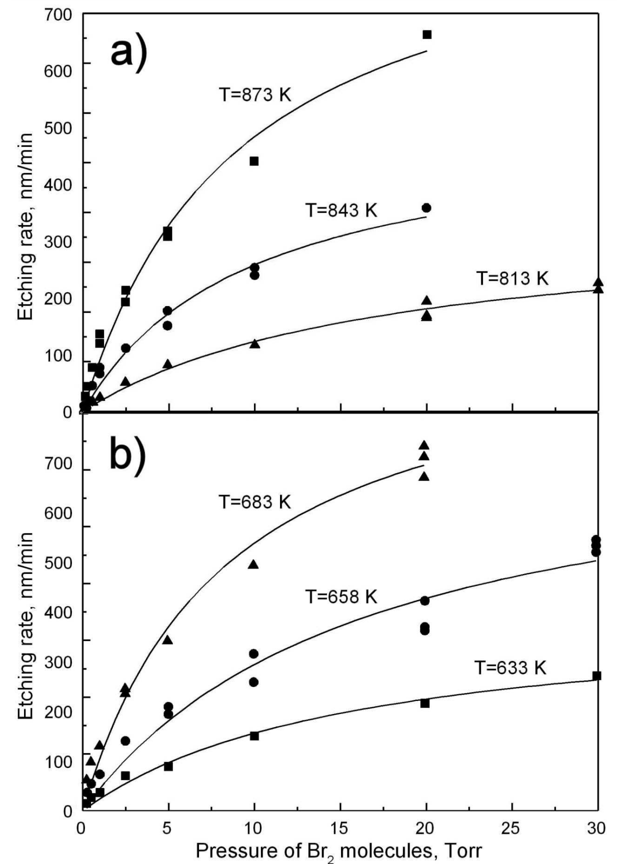


Fig. 1. Experimental [7] (points) and theoretical (curves) dependences of silicon etching rates on pressure of Br_2 molecules at different temperatures: (a) intrinsic poly-Si, (b) n-poly-Si.

24 different reaction rate constants are found by fitting the experimental data as well. TST is used to calculate the reaction activation energy and absolute error in reaction activation energy. Let us assume that pre--exponential factors at given temperature are the same in both reaction and desorption rate constants, $\tilde{\nu}_{\mathrm{TST}} = \nu_{\mathrm{TST}}$. The constant values, found by fitting the experimental data and subsequent TST analysis, are presented in Table II. Averaged reaction activation energy for intrinsic silicon is equal to $E_{\mathrm{r1}} \pm \Delta E_{\mathrm{r1}} = (1.82 \pm 0.24)$ eV, and decreases to $E_{\mathrm{r2}} \pm \Delta E_{\mathrm{r2}} = (1.45 \pm 0.24)$ eV when n-type silicon films are used. The reaction activation energy is lowered by doping but is independent of phosphorus doping level. Evaluation of activation energy of $\mathrm{Si} + \mathrm{Br_2} \rightarrow \mathrm{SiBr_2}$ reaction is more complicated than desorption activation energy of $SiBr_2$ molecules because of different number of elementary steps involved in the processes. At high temperatures more accurate values of reaction and desorption activation energies are found using polycrystalline films instead of single-crystal silicon substrates.

TABLE I

The constant values for desorption of $SiBr_2$ molecules found by fitting the experimental data and subsequent TST analysis.

Ref. [7]	Substrate	T [K]	ω [s^{-1}]	$\Delta\omega/\omega$	ν_{TST} [$\times 10^{13}$ s^{-1}]	E_d [eV]	ΔE_d [eV]
Fig. 3.1	intrinsic poly-Si	793	13.76	0.07	1.65	1.90	0.12
		783	10.10	0.09	1.63	1.90	0.18
		773	7.70	0.11	1.61	1.89	0.20
Fig. 3.5	intrinsic poly-Si	793	13.52	0.07	1.65	1.90	0.12
		773	10.45	0.09	1.61	1.87	0.18
		749	2.36	0.06	1.56	1.91	0.20
Fig. 3.12	intrinsic poly-Si	873	64.46	0.09	1.82	1.98	0.17
		843	35.57	0.10	1.76	1.96	0.20
		813	23.66	0.11	1.69	1.91	0.20
Fig. 3.10	intrinsic Si(100)	853	21.38	0.10	1.78	2.02	0.20
		838	18.86	0.13	1.75	1.99	0.26
		823	11.24	0.11	1.71	1.99	0.21
		813	7.26	0.05	1.69	2.00	0.10
		803	5.84	0.07	1.67	1.98	0.13
		793	5.93	0.08	1.65	1.96	0.16
Fig. 3.14	n-poly-Si 5×10^{18} cm^{-3}	683	52.81	0.07	1.42	1.55	0.10
		658	41.84	0.12	1.37	1.50	0.18
		633	21.48	0.10	1.32	1.48	0.15
Fig. 3.15	n-poly-Si 5×10^{19} cm^{-3}	683	48.15	0.08	1.42	1.55	0.12
		658	32.50	0.11	1.37	1.52	0.17
		633	20.37	0.13	1.32	1.48	0.19
Fig. 3.7	n-poly-Si 8×10^{19} cm^{-3}	673	49.96	0.11	1.40	1.53	0.17
		648	19.47	0.15	1.35	1.52	0.22
		623	11.65	0.17	1.30	1.49	0.25

TABLE II

The constant values for $Si + Br_2 \rightarrow SiBr_2$ reaction found by fitting the experimental data and subsequent TST analysis.

Ref. [7]	Substrate	T [K]	k_r [$Torr^{-1}$ s^{-1}]	k_r [m^3 mol^{-1} s^{-1}]	$\Delta k_r/k_r$	E_r [eV]	ΔE_r [eV]
Fig. 3.1	intrinsic poly-Si	793	1.636	81.08	0.12	1.78	0.22
		783	0.984	48.18	0.14	1.79	0.26
		773	0.778	37.59	0.18	1.78	0.32
Fig. 3.5	intrinsic poly-Si	793	1.338	66.32	0.11	1.79	0.19
		773	0.813	39.26	0.10	1.78	0.18
		749	0.822	38.48	0.10	1.73	0.18
Fig. 3.12	intrinsic poly-Si	873	7.125	388.9	0.09	1.85	0.17
		843	3.665	193.1	0.11	1.83	0.20
		813	1.353	68.79	0.13	1.84	0.24
Fig. 3.10	intrinsic Si(100)	853	2.502	133.4	0.16	1.88	0.31
		838	1.399	73.27	0.17	1.89	0.32
		823	1.247	64.17	0.18	1.87	0.33
		813	1.007	51.16	0.10	1.86	0.18
		803	0.762	38.23	0.12	1.85	0.22
		793	0.605	29.99	0.15	1.85	0.28
Fig. 3.14	n-poly-Si 5×10^{18} cm^{-3}	683	6.368	271.9	0.11	1.45	0.16
		658	2.533	104.2	0.15	1.45	0.21
		633	1.372	54.30	0.12	1.43	0.18
Fig. 3.15	n-poly-Si 5×10^{19} cm^{-3}	683	5.773	246.5	0.09	1.46	0.13
		658	2.271	93.44	0.14	1.46	0.20
		633	1.129	44.69	0.15	1.44	0.22
Fig. 3.7	n-poly-Si 8×10^{19} cm^{-3}	673	4.683	197.0	0.13	1.45	0.18
		648	2.028	82.14	0.28	1.44	0.40
		623	0.870	33.87	0.25	1.43	0.36

Theoretical dependences of concentration of $SiBr_2$ molecules in the adsorbed layer on pressure of Br_2 molecules at different temperatures for intrinsic and n-type polycrystalline silicon are shown in Fig. 2. It is observed that concentration of $SiBr_2$ molecules in the adsorbed layer increases with the increase in temperature. This indicates that the formation of $SiBr_2$ molecules is faster process than desorption. The statement is confirmed by reaction and desorption activation energies for intrinsic and n-type silicon. At low pressure of Br_2

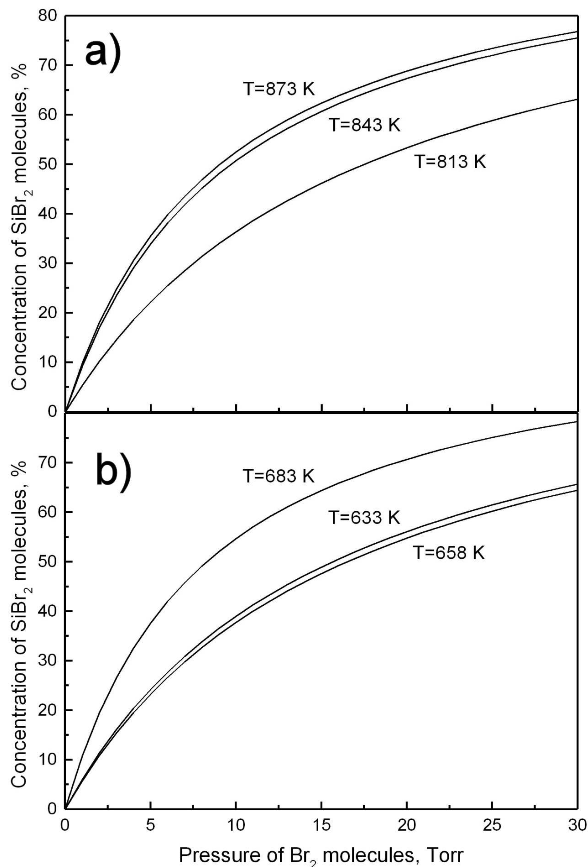


Fig. 2. Theoretical dependences of concentration of $SiBr_2$ molecules in the adsorbed layer on pressure of Br_2 molecules at different temperatures: (a) intrinsic poly-Si, (b) n-poly-Si. The dependences are calculated using rate constants found by fitting the experimental data.

molecules, formation of $SiBr_2$ molecules is the etching-rate limiting process. Concentration of $SiBr_2$ molecules in the adsorbed layer is very low, and slower desorption process does not affect the overall etching rate. With further increase in pressure of Br_2 molecules, concentration of $SiBr_2$ molecules in the adsorbed layer increases. The increased concentration of $SiBr_2$ molecules in the adsorbed layer suppresses the etching rate, and desorption of $SiBr_2$ molecules becomes the etching-rate limiting process at high pressure of Br_2 molecules.

4. Conclusions

Concentration of $SiBr_2$ molecules in the adsorbed layer increases with the increase in temperature because activation energy of $Si + Br_2 \to SiBr_2$ reaction is lower than desorption activation energy of $SiBr_2$ molecules. Activation energy of $Si + Br_2 \to SiBr_2$ reaction for intrinsic silicon is equal to (1.82 ± 0.24) eV, and decreases to (1.45 ± 0.24) eV when n-type silicon films are used. Meanwhile, desorption activation energy of $SiBr_2$ molecules for intrinsic silicon is equal to (1.94 ± 0.17) eV, and decreases to (1.51 ± 0.17) eV when n-type silicon films are used.

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