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Influence of temperature on the formation of SiF_2 molecules

R. Knizikevičius [a,*], V. Kopustinskas [b]

[a] Department of Physics, Kaunas University of Technology, 73 K. Donelaičio St., LT-44029, Kaunas, Lithuania
[b] Institute of Materials Science, Kaunas University of Technology, 59 K. Baršausko St., LT-51423, Kaunas, Lithuania

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ABSTRACT

Chemical etching of silicon in SF_6 plasma is considered. Dependences of Si etching rate on pressure of reactive species are measured at two different temperatures. Atomic layer etching of silicon with F atoms is analyzed using theoretical results obtained by fitting the experimental data. It is found that at high pressure, the formation of SiF_2 molecules is the etching-rate limiting process. As a result, dependences of Si etching rate on pressure of reactive species have pronounced maxima. The increase in temperature during Si etching in SF_6 plasma shifts maximum etching rate to lower pressure. This phenomenon is caused by an increased chemisorption of F atoms on the surface.

1. Introduction

SiF_2 is known as high temperature molecule with unique properties. Unlike other silicon dihalides, silicon difluoride exhibits very low reactivity in the gas phase towards many reagents. Mean lifetime of gaseous SiF_2 molecules is 210 s [1]. However, when condensed, they react with a large variety of inorganic and organic compounds to yield novel compounds containing $(SiF_2)_n$ units [2]. They also disproportionate to $(SiF)_n$ and perfluorosilanes [3]. Properties and reactivity of gaseous SiF_2 and polymeric $(SiF_2)_n$ have been investigated for many years, but no stable compound is found.

SiF_2 molecules are primary reaction product during Si etching in fluorine-based plasmas. Reaction of F atoms with silicon is highly exothermic, and the reaction layer extends to near-surface region. Dissociative chemisorption of F_2 and XeF_2 molecules on Si surface saturates at approximately 1.5 monolayer surface coverage. Synchrotron photoemission investigation of fluorine on Si(111)-(2 × 1) surface shown that SiF radicals prevail in the adsorbed layer [4]. Concentrations of SiF_2 and SiF_3 radicals in the adsorbed layer are similar but much lower than concentration of SiF radicals. Meanwhile, atomic fluorine uptake extends saturation regime to several Si monolayers [5]. It is practically impossible to analyze atomic layer etching of silicon with F atoms using modern experimental equipment. Other halogens do not cause such problems during reaction with silicon.

In previous work [6], silicon etching in CF_4 plasma is simulated. It is determined that the formation of SiF_2 radicals is the etching-rate limiting process. However, chemisorption of F atoms on the surface and desorption of SiF_2 molecules was little investigated. In this work, chemical etching (CE) of silicon in SF_6 plasma is considered. Dependences of Si etching rate on pressure of reactive species are measured at two different temperatures. Atomic layer etching of silicon with F atoms is analyzed using theoretical results obtained by fitting the experimental data. It is found that at low pressure chemisorption of F atoms on the surface is the etching-rate limiting process.

2. Experimental

The single-crystal silicon substrates are oxidized in H_2O vapor at temperature of 1300 K. Aluminum is used as masking material for Si(100) substrates and SiO_2 films. CE rate depends on the mask geometry during etching of narrow trenches. The mask height 100 nm and the mask width 80 μm are used to avoid neutral shadowing. The CE of both materials is performed in the reactor PK-2430PD. During etching process the following parameters are kept constant: the flow rate of SF_6 gas 20 sccm, the discharge power density 0.25 W/cm^2. Temperature is varied from 293 to 400 K, and pressure is varied from 10 to 300 Pa. The trenches are etched on the overall exposed area of 25 mm^2. The etching rates are measured using multifunctional scanning probe microscope NT-206.

3. Modeling of chemical etching

3.1. Si etching

The CE of silicon in SF_6 plasma is simulated. It is measured experimentally that dependence of Si etching rate on pressure is not linear.

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[*] Corresponding author.
E-mail address: Rimantas.Knizikevicius@ktu.lt (R. Knizikevičius).

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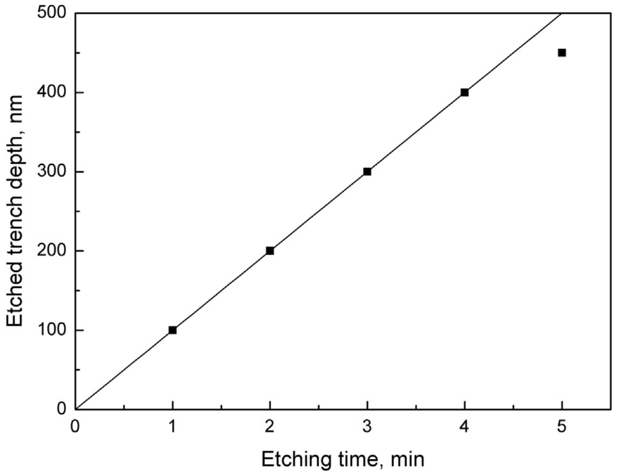

Fig. 1. Trench depth kinetics during Si etching in SF_6 plasma. The temperature is 293 K, and the pressure is 20 Pa.

Table 1
The rate constants found by fitting the experimental data. Desorption rate constants are subsequently analyzed using transition state theory.

Material	T, K	$\alpha, Pa^{-1}\ s^{-1}$	k_r, s^{-1}	ω, s^{-1}	$\nu_0, \times 10^{12}\ s^{-1}$	E, eV	ΔE, eV
Si(100)	293	1.00	160	41	6.11	0.650	0.016
Si(100)	400	1.57	182	52	8.33	0.889	0.017
SiO_2 film	293	0.30	550	18	6.11	0.670	0.037

This phenomenon is caused by slow formation of SiF_2 molecules [7]. During the etching process F atoms chemisorbed on Si surface:

$$Si(s) + F(g) \rightarrow SiF(a). \tag{1}$$

The chemisorption process is described by adsorption rate constant $\alpha = s\Phi/C$, where s is the sticking coefficient, $\Phi = n(kT/2\pi m)^{1/2}$ is the flux of F atoms, n is the concentration of F atoms in the plasma, k is the Boltzmann constant, T is the temperature, m is the atomic mass of F atoms, and C is the concentration of surface atoms ($C = 1.36 \times 10^{19} m^{-2}$). Mean chemisorption time is equal to $\tau_c = \alpha^{-1}$. SiF_2 molecules are formed during the following reaction:

$$2SiF(a) \overset{SV}{\rightarrow} SiF_2(a) + Si(s), \tag{2}$$

where SV is the surface vacancy. Concentration of SVs is proportional the substrate surface area not covered with adsorbate. The reaction process is described by reaction rate constant k_r. Mean reaction time is equal to $\tau_r = k_r^{-1}[SiF]^{-2}$. Desorption of formed SiF_2 molecules is described by desorption rate constant

$$\omega = \nu_0 \exp(-E_d/kT), \tag{3}$$

where $\nu_0 = kT/h$ is the lattice atom oscillation frequency, h is the Planck constant, and E_d is the desorption activation energy of SiF_2 molecules. Mean desorption time is equal to $\tau_d = \omega^{-1}$.

Components produced during reactions on the surface are included in the adsorbed layer of one-monolayer thickness. SiF and SiF_2 radicals exist in the adsorbed layer with relative concentrations $c_1 = [SiF]/C$ and $c_2 = [SiF_2]/C$, respectively. The following system of equations includes rate expressions of processes mentioned earlier and describes the kinetics of component concentrations in the adsorbed layer:

$$\begin{cases} \frac{dc_1}{dt} = \alpha\beta - 2\beta k_r c_1^2, \\ \frac{dc_2}{dt} = \beta k_r c_1^2 - \omega c_2, \end{cases} \tag{4}$$

where $\beta = 1 - \Theta$ is the fraction of the surface not covered with adsorbate and $\Theta = c_1 + c_2$ is the surface coverage. The etching rate is equal to desorption rate of formed SiF_2 molecules:

$$V = h_0 \omega c_2, \tag{5}$$

where $h_0 = 2.72$ Å is the monolayer thickness.

3.2. SiO_2 etching

The CE of silicon dioxide in SF_6 plasma is simulated. It is measured experimentally that SiO_xF_y layer is formed on the surface. During the etching process F atoms chemisorbed on SiO_2 surface:

$$SiO_2(s) + F(g) \rightarrow SiOF(a) + O(g). \tag{6}$$

The chemisorption process is described by adsorption rate constant α, where concentration of surface molecules is equal to $C =$

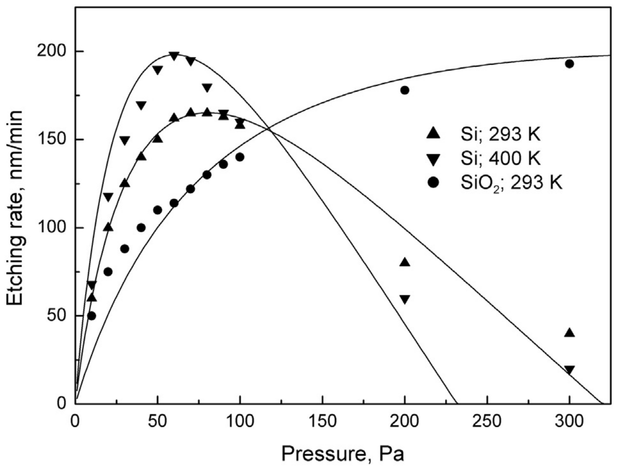

Fig. 2. Experimental and theoretical dependences of CE rate of silicon in SF_6 plasma on pressure at two different temperatures. Dependence of CE rate of SiO_2 in SF_6 plasma on pressure is inserted for comparison of Si and SiO_2 etching rates.

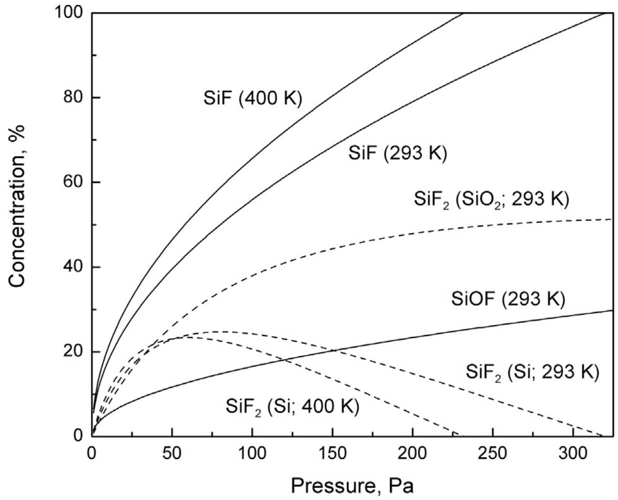

Fig. 3. Theoretical dependences of adsorbed layer components on pressure during Si and SiO_2 etching in SF_6 plasma.