

SIMULATION OF SILICON ETCHING IN CF_2Cl_2 PLASMA

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Received 7 March 2005

The reactive ion etching of silicon in CF_2Cl_2 plasma is considered. The profiles of etched trenches are calculated as the functions of mask dimensions, flux of CF_2 radicals, and parameters of ion bombardment. The processes of adsorption, activation, chemical reactions, relaxation, desorption, and sputtering are included in the proposed model. During one-dimensional etching, F/C ratio of adsorbed layer decreases with the intensification of reaction of CF_2 radicals with Si atoms and of the sputtering of polymer and SiC molecules. The values of frequency probabilities, found by extrapolation from the experimentally measured one-dimensional silicon etching rate in CF_2Cl_2 plasma, are used for the calculation of the real dimensions of etched trenches. During two-dimensional etching, F/C ratio in the trench bottom depends on the fluxes of neutrals and ions. F/C ratio at the sidewalls is equal to 2. Special attention is given to the etching anisotropy and lateral etching. The influence of the ratio of concentration of CF_2 radicals and concentration of CF_2^+ ions in the plasma on an etched trench profile is considered. The conditions under which anisotropic etching prevails are found.

Keywords: CF_2Cl_2 plasma, silicon, reactive ion etching

PACS: 52.77.Bn, 82.35.Gh, 82.65.+r

1. Introduction

Isolation technology using silicon trenches is employed in high-speed integrated circuits. Important steps in a trench isolation process are: (1) reactive ion etching (RIE) of narrow and deep trenches in silicon; (2) removal of the etching mask and cleaning of the trenches; (3) refilling with dielectric materials; and (4) planarization of the surface. The task of etching the trenches consists of finding an etch process with not only a high anisotropy and a high selectivity between the silicon and the mask material but also with the high silicon etching rates and good compatibility with the other steps in the trench isolation process [1]. Main products of dissociation of CF_2Cl_2 molecules are CF_2 radicals and Cl atoms [2]. CF_2 radicals lead to the deposition of a polymeric layer during RIE of silicon. The deposition rate is proportional to the volume of adsorbed particles. The deposition rate decreases with the increase of discharge power density, substrate temperature, and energy of bombarding ions [3].

Sputtering and activation of adsorbed precursors or condensed species are significant effects in ion-assisted processes. In experiment [4], the polymer growth on a grounded silicon surface by a CF_2 beam coincident with an Ar microwave plasma was investigated. It was

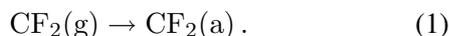
found that the polymer deposition rate is low when only the CF_2 beam is applied and that the deposition rate significantly increases with the addition of the Ar plasma. In experiment [4], the enhancement of polymer formation by ions has been observed at low ion energy (≈ 10 eV). At ion energy > 100 eV ion bombardment leads to sputtering of the polymer. In work [5], the enhancement of silicon etching rate in XeF_2 ambient was explained by the presence of activated polymer on the surface. The activated sites in the polymer film are dangling bonds.

In this work, RIE of silicon in CF_2Cl_2 plasma is considered. The simulation is based on the experimentally measured one-dimensional silicon etching rate in CF_2Cl_2 plasma [6, 7]. The values of frequency probabilities, found by extrapolation from one-dimensional etching rate, are used for the calculation of the real dimensions of etched trenches. It is found that activated polymer is more likely to chemisorb species reaching the surface from the plasma and changes the silicon etching rate. Low energy ion bombardment (100 eV) is suitable for anisotropic RIE of silicon in CF_2Cl_2 plasma.

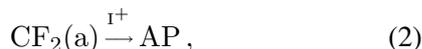
2. Modelling of Si etching in CF₂Cl₂ plasma

2.1. One-dimensional etching

The one-dimensional etching of Si substrate in a CF₂Cl₂ plasma is considered. Main products of dissociation of CF₂Cl₂ molecules are CF₂ radicals and Cl atoms [2]. In work [8], CF₂ radical density was measured in radio-frequency CF₂Cl₂ plasma using infrared absorption spectroscopy. It was found that the partial pressure of CF₂ is about 5% of the total pressure. In order to reduce the number of frequency probabilities that are freely chosen, only CF₂ radicals are considered. CF₂ radicals present in the plasma adsorb on the surface:



This process is characterized by frequency probability of adsorption $\varkappa = \alpha N_{\text{CF}_2}$, where α is the sticking coefficient and N_{CF_2} is the concentration of CF₂ radicals in the plasma. Adsorbed CF₂ radicals are activated by incident ions:



where I⁺ represents ion species and AP represents activated sites in the polymer film. The activated sites are more reactive and chemisorb the species reaching the surface from the plasma. Surface-adsorbed CF₂ radicals are activated even without ion bombardment [9]. The activation process is characterized by frequency probability of activation

$$G = g I_0 / N, \quad (3)$$

where g is the activation constant, I_0 is the ion flux, and N is the concentration of surface atoms ($N = 1.36 \cdot 10^{19} \text{ m}^{-2}$). The activated polymer relaxes: AP → P, where P represents non-activated sites in the polymer film. This process is characterized by frequency probability of relaxation $R_r = 1/\tau$, where τ is the mean relaxation time.

The main reactions taking place in the adsorbed layer are the following:

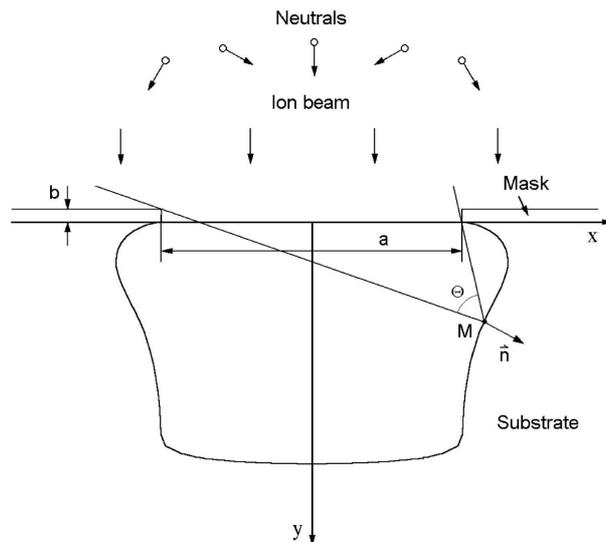
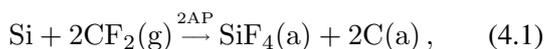


Fig. 1. Schematic presentation of RIE through the mask.

C atoms produced during reaction (Eq. (4.1)) exist in the adsorbed layer. Reaction rates are characterized by frequency probabilities of reactions $R_1 = k_1 N_{\text{CF}_2}^2$, $R_2 = k_2$, $R_3 = k_3 N_{\text{CF}_2}$, $R_4 = k_4 N_{\text{CF}_2}$, where k_i is the reaction rate constant of i th reaction. The influence of reactions $\text{Si} + 4\text{F}(\text{g}) \rightarrow \text{SiF}_4(\text{a})$ and $\text{Si} + 2\text{Cl}(\text{g}) \rightarrow \text{SiCl}_2(\text{a})$ on the etching rate is negligible, because these reactions reach steady-state regime within milliseconds. Let us assume that the polymer formed during reactions (Eqs. (4.3) and (4.4)) is much slower activated than the adsorbed CF₂ radicals. The components of adsorbed layer desorb and are sputtered by incident ions. The frequency probability of removal of i th adsorbed layer component ω_i consists of frequency probabilities of desorption and sputtering:

$$\omega_i = \omega_{i,d} + \omega_{i,s} = \quad (5)$$

$$\nu_0 \exp(-E_{i,d}/(kT)) + Y_i I_0 f(\alpha) N,$$

where ν_0 is the frequency of oscillation of atoms in the solid, $E_{i,d}$ is the desorption activation energy of i th component, k is the Boltzmann constant, T is the temperature, Y_i is the sputtering yield of i th component, and $f(\alpha) = \cos^{0.5} \alpha$ is the sputtering yield dependence on the incident ion angle α measured from the surface normal \mathbf{n} [10]. Sputtering of activated polymer, polymer, Si atoms, and SiC molecules is characterized by frequency probabilities of sputtering $\omega_{i,s}$ (Eq. 5).

Components present in the plasma and produced during reactions on the surface are included in the adsorbed layer of one-monolayer thickness. Five components exist in the adsorbed layer: SiF₄, CF₂, C, AP, P, with relative concentrations $c_1 = [\text{SiF}_4]/N$,

$c_2 = [\text{CF}_2]/N$, $c_3 = [\text{C}]/N$, $c_4 = [\text{AP}]/N$, and $c_5 = [\text{P}]/N$; two components exist on the surface: Si, SiC, with relative concentrations $c_6 = [\text{Si}]/N$ and $c_7 = [\text{SiC}]/N$. The relative concentrations of surface components must fulfil the condition $c_6 + c_7 = 1$. The following system of equations includes rate expressions of processes mentioned earlier [11] and describes the kinetics of component concentrations in the adsorbed layer and on the surface:

$$\left\{ \begin{array}{l} \frac{dc_1}{dt} = R_1\beta c_4^2 c_6 - \omega_1 c_1, \\ \frac{dc_2}{dt} = \alpha\beta - Gc_2 + R_r c_4 - \omega_2 c_2, \\ \frac{dc_3}{dt} = 2R_1\beta c_4^2 c_6 - R_2 c_3 c_6 - R_3 c_3 c_4 - \omega_3 c_3, \\ \frac{dc_4}{dt} = Gc_2 - R_r c_4 - \omega_4 c_4, \\ \frac{dc_5}{dt} = R_3 c_3 c_4 + R_4\beta c_4 c_5 - \omega_5 c_5, \\ \frac{dc_6}{dt} = -R_2 c_3 c_6 + \omega_7 c_7, \end{array} \right. \quad (6)$$

where $\beta = 1 - \Theta$ is the fraction of the surface not covered with adsorbate, and $\Theta = \sum_{i=1}^5 c_i$ is the surface coverage. The system of equations (6) has two peculiarities related to the chemical reactions taking place in the adsorbed layer: (1) two activated sites in the polymer film are required during reaction of CF_2 radicals with Si atoms (Eq. (4.1)); (2) the growing polymer occupies surface sites not covered with adsorbate. The etching rate is proportional to the sum of removal rates of SiF_4 and SiC molecules:

$$V = h_0(\omega_1 c_1 + \omega_7 c_7), \quad (7)$$

where $h_0 = 0.272 \text{ nm}$ is the thickness of monolayer.

2.2. Two-dimensional etching

The two-dimensional etching of Si substrate in a CF_2Cl_2 plasma is considered. Plasmochemical etching (PCE) is almost isotropic and produces etching in the vertical and horizontal directions [12]. Fluxes of species to the surface depend on the position of an arbitrary point $M(x, y, t)$ (Fig. 1). The part of primary flux of i th type species to the surface at point $M(x, y, t)$ is equal to $S_i(x, y)/S_{i,0} = N_i(x, y)/N_{i,0}$. Let us assume that ions and neutrals do not collide in the trench being etched, the angular distribution of particles in the

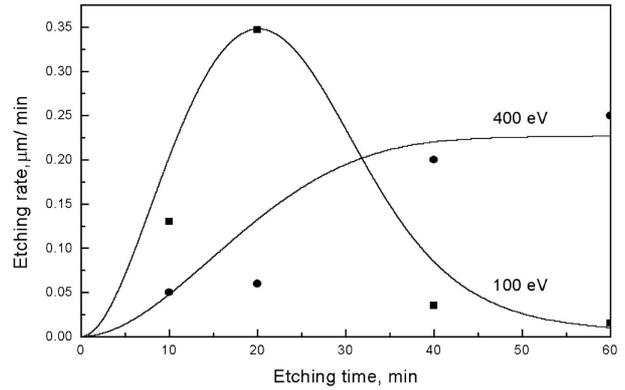


Fig. 2. Experimental [6] (points) and theoretical (curves) time dependence of silicon etching rates in CF_2Cl_2 plasma at 100 and 400 eV energies of bombarding ions.

plasma is isotropic, and the concentration of species at the surface is equal to $N_i(x, y) = N_{i,0}\Theta(x, y)/\pi$, where $N_{i,0}$ is the concentration of the i th plasma component and $\Theta(x, y)$ is the limiting angle in radians. It follows that the rates of reactions (Eqs. (4.1)–(4.4)) depend on the position of the arbitrary point $M(x, y, t)$ on the surface. Ion bombardment during RIE enhances chemical processes in the trench bottom and removes the reaction products. It increases the etching rate in vertical direction and the etching anisotropy. Frequency probabilities of sputtering of adsorbed layer components $\omega_{i,s}$ in the trench bottom depend on the surface orientation (Eq. (5)).

According to Eq. (7), the etching rate V is proportional to the sum of removal rates of SiF_4 and SiC molecules. Knowing the surface concentrations of components from the solutions of Eq. (6), the etching rate as a function of coordinate and time is obtained. The point $M(x, y, t)$ after time interval Δt will take position $M'(x + \Delta x, y + \Delta y, t + \Delta t)$, where $\Delta x = Vn_x\Delta t$ and $\Delta y = Vn_y\Delta t$, n_x and n_y are the components of the surface normal \mathbf{n} (Fig. 1). In this way, the trench profile as a function of time is obtained. Processes of particle reflection on the trench surface, redeposition of etchant products and sputtered mask material are not included in the model as they less influence the trench profile.

3. Results and discussion

3.1. One-dimensional etching

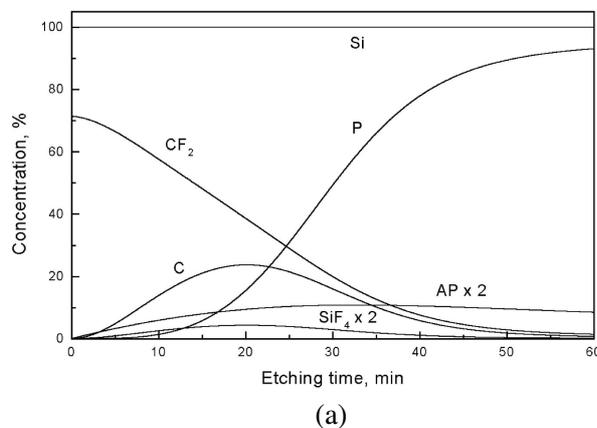
The experimentally measured silicon etching rates in CF_2Cl_2 plasma [6, 7] are used for the calculation of chemical compositions of adsorbed layer and surface. The etching process was performed in the reactor PK

Table 1. List of values of frequency probabilities found by extrapolation from experimental data.

Frequency probability, s^{-1}	Trench bottom, $E = 100$ eV	Trench bottom, $E = 400$ eV	Sidewalls, $E = 0$ eV
α	1.0	1.0	1.0
G	$8.5 \cdot 10^{-5}$	$8.5 \cdot 10^{-5}$	$8.5 \cdot 10^{-5}$
R_r	0	0	0
R_1	$6.3 \cdot 10^4$	$1.15 \cdot 10^4$	100
R_2	0	$5.0 \cdot 10^{-4}$	0
R_3	0.016	0.016	0.016
R_4	0.25	0.25	0.25
ω_1	1000	1000	500
ω_2	0.40	0.40	0.20
ω_3	180	180	90
ω_4	$2.5 \cdot 10^{-4}$	$2.5 \cdot 10^{-4}$	0
ω_5	$2.5 \cdot 10^{-5}$	$4.0 \cdot 10^{-3}$	0
ω_6	0	0	0
ω_7	0	$4.0 \cdot 10^{-3}$	0

2420 RIE. The frequency of discharge was 13.56 MHz, the flow rate was 24 sccm, the pressure was 26.6 Pa, and the discharge power density was 0.9 W/cm². The experimental procedure was described in more detail in [6]. The experimental and the theoretically calculated (using Eqs. (6) and (7)) silicon etching rates are shown in Fig. 2. The values of frequency probabilities found by extrapolation from experimental data are presented in Table 1. It is important to note that the value of frequency probability of removal of C atoms is very high as compared to other carbon-containing species. It is a result of two different phenomena: (1) C atoms are weakly bounded to the surface; (2) C atoms form clusters that occupy less surface area. Second phenomenon is confirmed experimentally [13].

The time dependence of concentrations of adsorbed layer and surface components during RIE of silicon in CF₂Cl₂ plasma at 100 eV energy of bombarding ions



is shown in Fig. 3(a). The concentration of C atoms at first increases due to the reaction of CF₂ radicals with Si atoms (Eq. (4.1)). As the concentration of C atoms approaches the maximum value, the reaction of CF₂ radicals with C atoms (Eq. (4.3)) starts. Later, the concentration of C atoms begins to decrease in proportion to the amount of formed polymer. The time dependence of concentrations of adsorbed layer and surface components during RIE of silicon in CF₂Cl₂ plasma at 400 eV energy of bombarding ions is shown in Fig. 3(b). In this case the concentration of C atoms approaches the maximum value at later stages of the etching process. CF₂ radicals prevail in the adsorbed layers at initial stages of the etching process. The formation of polymer is more pronounced at later stages of the etching process. Activated sites in the polymer film intensify the reactions taking place in the adsorbed layer and enhance the etching rate of silicon in CF₂Cl₂ plasma. The time dependence of F/C ratios of adsorbed layers at two different energies of bombarding ions is shown in Fig. 4. It is found that F/C ratios of adsorbed layers decrease with the intensification of reaction of CF₂ radicals with Si atoms (Eq. (4. 1)) and of the sputtering of polymer and SiC molecules.

3.2. Two-dimensional etching

The values of frequency probabilities, found by extrapolation from one-dimensional silicon etching rate kinetics in CF₂Cl₂ plasma, are used for the calculation of the real dimensions of etched trenches. The reactive species from the plasma reach the surface in the form of neutrals and ions. The coefficient η , which is equal to the ratio of concentration of CF₂ radicals to concentration of CF₂⁺ ions in the plasma ($\eta = N_{CF_2}/N_{CF_2^+}$), is used for the evaluation of influence of bombarding ions on the shape of etched trenches. The profiles of etched

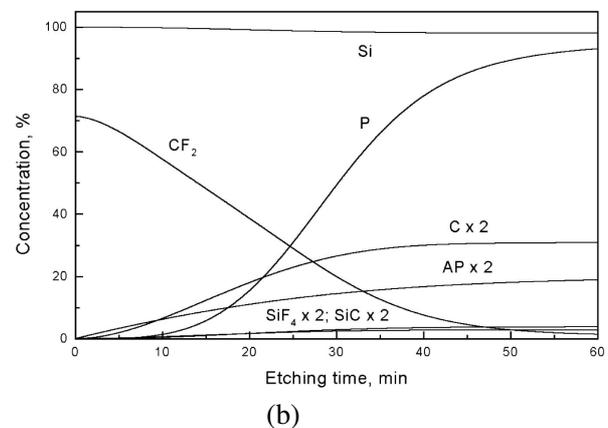


Fig. 3. The time dependence of concentrations of adsorbed layer and surface components at different energies of bombarding ions: (a) 100 eV, (b) 400 eV.

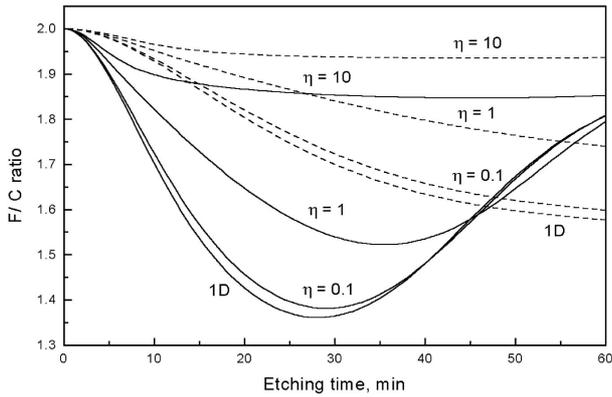


Fig. 4. The time dependence of F/C ratios of adsorbed layers during one- and two-dimensional RIE of silicon in CF_2Cl_2 plasma at different energies of bombarding ions (100 eV, solid curves; 400 eV, dashed curves). During two-dimensional etching, F/C ratios are calculated in the trench bottom ($x = 0$). The mask width is $0.4 \mu\text{m}$ and the mask height is $0.1 \mu\text{m}$.

trenches at different values of coefficient η are shown in Fig. 5. The depths of etched trenches at 100 and 400 eV energies of bombarding ions differ little when the etching process is ion-driven. The depths of etched trenches decrease with the increase of coefficient η .

The time dependence of F/C ratios of adsorbed layers in the trench bottom at different energies of bombarding ions is shown in Fig. 4. It is observed that decrease of F/C ratio is more pronounced at 100 eV energy of bombarding ions. F/C ratio at the sidewalls is equal to 2. The difference in the composition of adsorbed layers formed on the sidewalls and on the trench bottom enables anisotropic etching. The sidewall passivating film reduces etching rate in the horizontal direction, while ion bombardment maintains etching in the vertical direction.

The aspect ratio $y_{\text{max}}/(2x_{\text{max}})$ describes the shape of the etched trenches. The dependences of the aspect

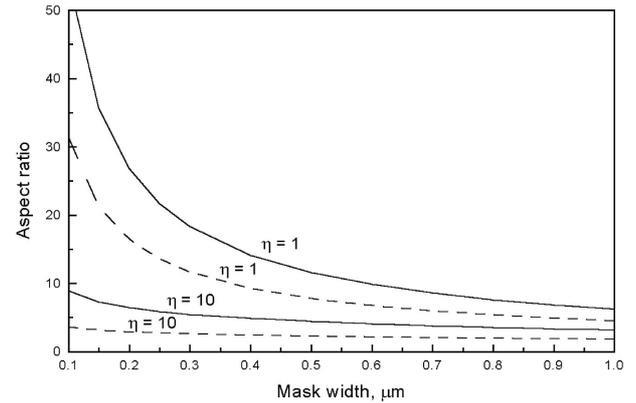
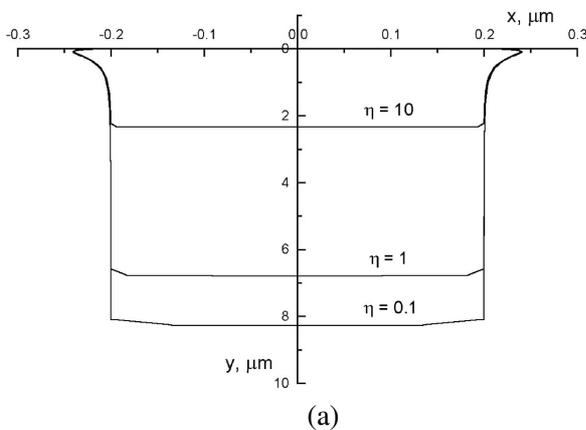


Fig. 6. The dependences of the aspect ratio on mask width at different energies of bombarding ions (100 eV, solid curves; 400 eV, dashed curves). The mask height is $0.1 \mu\text{m}$ and the etching time is 60 min.

ratio on mask width at different energies of bombarding ions are shown in Fig. 6. The aspect ratio at low values of mask width is quite high. As mask width increases, the aspect ratio decreases due to increased PCE. The etching anisotropy is equal to the ratio of etching rates in the vertical and horizontal directions (y_{max}/δ , where δ is the lateral undercutting). The dependences of the etching anisotropy on mask width at different energies of bombarding ions are shown in Fig. 7. It is observed that the trenches with a high value of etching anisotropy are etched at low values of mask width. When etching process is neutral-driven ($\eta = 10$), etching anisotropy slightly increases with the increase of mask width due to sidewall passivation. Low energy ion bombardment (100 eV) is suitable for anisotropic RIE of silicon in CF_2Cl_2 plasma.

In integrated circuit manufacture it is required to determine the etching time needed to etch a fixed trench depth. The dependences of the etching time on mask width at different values of coefficient η are shown in

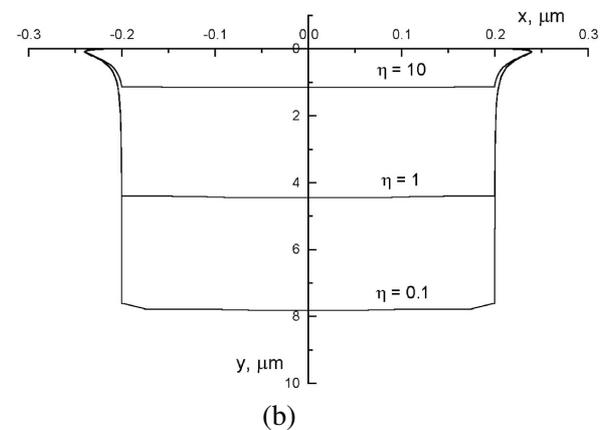


Fig. 5. The profiles of etched trenches at different energies of bombarding ions: (a) 100 eV, (b) 400 eV. The mask width is $0.4 \mu\text{m}$, the mask height is $0.1 \mu\text{m}$, and the etching time is 60 min.

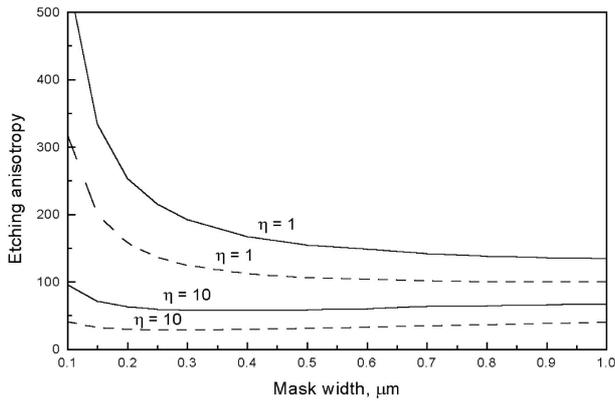


Fig. 7. The dependences of etching anisotropy on mask width at different energies of bombarding ions (100 eV, solid curves; 400 eV, dashed curves). The mask height is $0.1 \mu\text{m}$ and the etching time is 60 min.

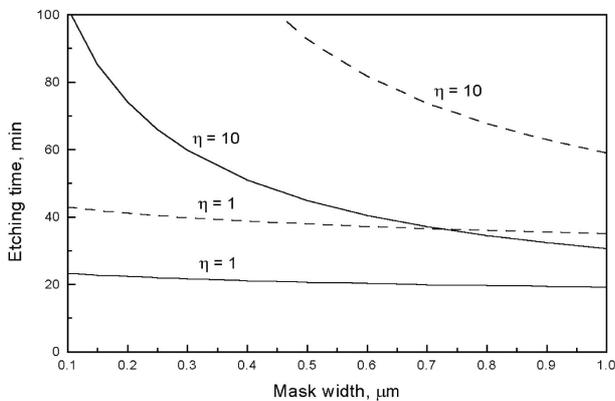


Fig. 8. The dependences of etching time needed to etch a fixed trench depth on mask width at different energies of bombarding ions (100 eV, solid curves; 400 eV, dashed curves). The trench depth is $2 \mu\text{m}$ and the mask height is $0.1 \mu\text{m}$.

Fig. 8. At low values of coefficient ($\eta \leq 1$) the etching process is ion-driven, and the etching time needed to etch the fixed trench depth is almost constant. When etching process is neutral-driven, narrow trenches are etched very long.

The presented model allows one to calculate the real dimensions of etched trench profiles from the experimentally measured one-dimensional silicon etching rate kinetics in CF_2Cl_2 plasma at 100 and 400 eV energies of bombarding ions. It is a useful tool for the prediction and control of the shape of etched trenches.

4. Conclusions

1. Low energy ion bombardment (100 eV) is suitable for anisotropic RIE of silicon in CF_2Cl_2 plasma.
2. The formation of polymer is more pronounced at later stages of the etching process. Activated sites

in the polymer film intensify the reactions taking place in adsorbed layer and enhance the etching rate of silicon in CF_2Cl_2 plasma.

3. F/C ratio of adsorbed layer decreases with the intensification of reaction of CF_2 radicals with Si atoms and of the sputtering of polymer and SiC molecules.

References

- [1] G. Wöhl, M. Matthes, and A. Weisheit, Reactive ion etching of deep trenches in silicon with CF_2Cl_2 and O_2 , *Vacuum* **38**(11), 1011–1014 (1988).
- [2] W.W. Stoffels, E. Stoffels, M. Haverlag, G.M.W. Kroesen, and F.J. de Hoog, The chemistry of a CCl_2F_2 radio frequency discharge, *J. Vac. Sci. Technol. A* **13**(4), 2058–2066 (1995).
- [3] S. Arai, K. Tsujimoto, and S. Tachi, Deposition in dry-etching gas plasmas, *Jpn. J. Appl. Phys.* **31**(6B), 2011–2019 (1992).
- [4] M. Inayoshi, M. Ito, M. Hori, T. Goto, and M. Hiramoto, Surface reaction of CF_2 radicals for fluorocarbon film formation in SiO_2/Si selective etching process, *J. Vac. Sci. Technol. A* **16**(1), 233–238 (1998).
- [5] R. Knizikevičius, Enhancement of silicon etching rate in XeF_2 ambient in the presence of activated polymer, *Appl. Surf. Sci.* **228**(1–4), 227–232 (2004).
- [6] Ž. Rutkūnienė and A. Grigonis, Formation of polymeric layers using halogen-carbon plasmas, *Vacuum* **68**(3), 239–244 (2003).
- [7] Ž. Rutkūnienė and A. Grigonis, Analysis of bonds influencing etching of silicon by CF_2Cl_2 plasma, *Lithuanian J. Phys.* **42**(1), 41–47 (2002).
- [8] M. Haverlag, E. Stoffels, W.W. Stoffels, G.M.W. Kroesen, and F.J. de Hoog, Measurements of radical densities in radio-frequency fluorocarbon plasmas using infrared absorption spectroscopy, *J. Vac. Sci. Technol. A* **12**(6), 3102–3108 (1994).
- [9] D. Zhang and M.J. Kushner, Investigations of surface reactions during C_2F_6 plasma etching of SiO_2 with equipment and feature scale models, *J. Vac. Sci. Technol. A* **19**(2), 524–538 (2001).
- [10] K. Ono and M. Tuda, Profile evolution during cold plasma beam etching of silicon, *Jpn. J. Appl. Phys.* **36**(7B), 4854–4865 (1997).
- [11] M.A. Lieberman and A.J. Lichtenberg, *Principles of Plasma Discharges and Materials Processing* (Wiley, New York, 1994).
- [12] R. Knizikevičius, Influence of reemission of neutrals on the shape of etched grooves, *Vacuum* **72**(4), 481–484 (2004).
- [13] V.N. Popov, Carbon nanotubes: Properties and application, *Mater. Sci. Eng. R* **43**(3), 61–102 (2004).

SILICIO ĖSDINIMO CF₂Cl₂ PLAZMOJE MODELIAVIMAS

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Išnagrinėtas reaktyvus joninis silicio ėsdinimas CF₂Cl₂ plazmoje. Išėsdintų kanalų profiliai apskaičiuoti kaip kaukės matmenų, CF₂ radikalų srauto ir joninio apšaudymo parametrų funkcija. Pasiūlytame modelyje atsižvelgta į įgerties, aktyvavimo, cheminių reakcijų, relaksacijos, atvirkštinės gerties ir dulkejimo vyksmus. Vienmačio ėsdinimo metu įgerto sluoksnio F/C santykis mažėja, intensyvėjant CF₂ radikalų reakcijai su Si atomais, polimero ir SiC molekulių dulkejimui. Dažniųjų tikimybių vertės, rastos ekstra-

poliuojant eksperimentiškai išmatuotas silicio vienmačio ėsdinimo spartas CF₂Cl₂ plazmoje, panaudotos išėsdintų kanalų realiams matmenims skaičiuoti. Dvimačio ėsdinimo metu F/C santykis kanalo dugne priklauso nuo neutralių ir joninių srautų. F/C santykis šoninėje sienelėje lygus 2. Atkreiptas dėmesys į ėsdinimo anizotropiją ir šoninį ėsdinimą. Tirta CF₂ radikalų ir CF₂⁺ jonų koncentracijų santykio plazmoje įtaka išėsdinto kanalo profiliui. Rasta, kojomis sąlygomis vyrauja anizotropinis ėsdinimas.