INFLUENCE OF TEMPERATURE ON THE FORMATION OF ALTERED LAYER DURING SILICON ETCHING IN CF_2Cl_2 PLASMA

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Reactive ion etching of silicon in CF_2Cl_2 plasma is considered. During the experiment, silicon substrates are etched in CF_2Cl_2 plasma at temperatures of 320 and 390 K. Thickness of formed altered layers is measured using an X-ray photoelectron spectrometer. The thickness of the altered layer decreases with the increase in temperature. Extrapolation of experimentally measured concentrations of Si atoms in the altered layer is used to determine processes that influence the decrease of the thickness of the altered layer at a higher temperature. It is determined that the thickness of the altered layer decreases with the increase in temperature due to slowdown of the chemical reaction of CF_2 radicals with Si atoms and intensified desorption of formed SiF_4 molecules.

Keywords: CF_2Cl_2 plasma, silicon, reactive ion etching, altered layer

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1. Introduction

Isolation technology using silicon grooves is employed in high-speed integrated circuits. Important steps in a groove isolation process are: (i) reactive ion etching (RIE) of narrow and deep grooves in silicon, (ii) removal of the etching mask and cleaning of the grooves, (iii) refilling with dielectric materials, and (iv) planarization of the surface. The task of etching the grooves consists of finding an etch process with not only high anisotropy and high selectivity to the mask but also with high silicon etching rates and good compatibility with the other steps in the groove isolation process [1].

CF_2Cl_2, Cl_2 molecules have high polarization as compared to CF_x ($x \leq 2$) [2], and atomization energy of C–Cl species is much lower than C–F [3], as a result, the concentrations of CF_2 and Cl are increased in the bottom of a groove. CF_2 and CF radicals produce a polymeric layer on the surface, and $SiCl_2$ due to a high desorption activation energy [4] decreases the etching rate. The polymeric layer formed on the sidewalls becomes charged with the increase of groove depth, distorts trajectories of ions, and decreases the ion current density [5, 6]. This effect is especially pronounced in narrow grooves [7]. When molecules and radicals arrive at such a narrow groove they are polarized and, during the interaction with the surface, decompose into chemically active fragments that significantly change the rates of etching and polymerization reactions. These processes increase the etching anisotropy in shallow grooves and suppress etching in deep grooves.

The deposition rate decreases with the increase of the substrate temperature, and it is proportional to the volume of adsorbed particles. Less bondings of C atoms with F atoms exist in polymers deposited on a high-temperature substrate, in a low-pressure plasma, and at a high discharge power density [8]. CF_2 radicals are a build-up material for polymeric layer during RIE of silicon in CF_2Cl_2 plasma.

In this work, one-dimensional RIE of silicon in CF_2Cl_2 plasma at different temperatures is investigated. The structures of the polymeric layer and the near-surface region are determined. Thickness of formed altered layers is measured using an X-ray photoelectron spectrometer. It is determined that the thickness of the altered layer decreases with the increase in temperature.

2. Experimental

The single-crystal silicon substrates (111) are etched in CF_2Cl_2 plasma. Prior to the etching silicon substrates were cleaned in a buffered HF solution. Alu-

minum masks of 100 nm thickness were deposited by electron beam evaporation. The etching process is performed in the asymmetric diode system PK 2420 RIE. The frequency of discharge is 13.56 MHz, the flow rate of CF_2Cl_2 gas is 24 sccm, the discharge power density is 0.9 W/cm^2, the pressure is 26.7 Pa, the energy of incident ions is 400 eV, the temperature is 290–390 K, the etchable surface area is 25 mm^2, and the etching time is 10 min. The temperature of substrates is varied with an electrical heater. After etching the substrates are left for 20–40 min in the reactor to reach steady-state conditions and transferred through the air into the measurement chamber. The etching rate is measured using a scanning electron microscope JSM-25S. The composition of the near-surface layer is analysed using an X-ray photoelectron spectrometer 800 Kratos Analytical XPS.

3. Model

The RIE of the silicon substrate in CF_2Cl_2 plasma is simulated. The main products of dissociation of CF_2Cl_2 molecules are CF_2Cl, CF_2 radicals, and Cl atoms [9]. In order to reduce the number of frequency probabilities that are freely chosen, only CF_2 radicals are considered. CF_2 radicals present in the plasma adsorb on the substrate surface:

$$CF_2(g) \rightarrow CF_2(ads). \tag{1}$$
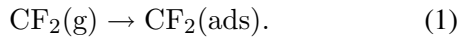
This process is characterized by frequency probability of adsorption $\alpha = \alpha_0 N_{CF_2}$, where α_0 is the sticking coefficient and N_{CF_2} is the concentration of CF_2 radicals in the plasma. Adsorbed CF_2 radicals are activated by ion bombardment:
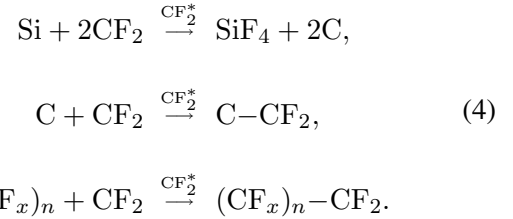
$$CF_2(ads) + A^+ \rightarrow CF_2^*(ads) + A^+. \tag{2}$$
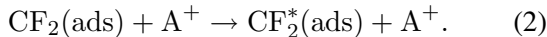
This process is characterized by the frequency probability of activation

$$G = \frac{gI_0}{C_0}, \tag{3}$$

where g is the activation constant, I_0 is the ion flux, and C_0 is the concentration of surface atoms ($C_0 = 1.36 \cdot 10^{19}$ m^{-2}). The activated CF_2 radicals are more likely to chemisorb species reaching the surface from the plasma and to change the kinetics of silicon etching rate and the thickness of the altered layer. The main

reactions taking place in the adsorbed layer are as follows:

$$Si + 2CF_2 \overset{CF_2^*}{\rightarrow} SiF_4 + 2C,$$

$$C + CF_2 \overset{CF_2^*}{\rightarrow} C-CF_2, \tag{4}$$

$$(CF_x)_n + CF_2 \overset{CF_2^*}{\rightarrow} (CF_x)_n-CF_2.$$

These reactions are characterized by frequency probabilities of reactions $R_1 = k_1 N_{CF_2}^2$, $R_2 = k_2 N_{CF_2}$, and $R_3 = k_3 N_{CF_2}$, respectively, where k_i is the reaction rate constant of the ith reaction. The activated CF_2 radicals relax: $CF_2^* \rightarrow CF_2$. This process is characterized by the frequency probability of relaxation $R_r = 1/\tau$, where τ is the mean relaxation time.

The removal of the adsorbed layer components is characterized by the frequency probability of removal ω_i, which consists of frequency probabilities of desorption and sputtering

$$\omega_i = \omega_{i,d} + \omega_{i,s}$$

$$= \nu_0 \exp\left(-\frac{E_{i,d}}{kT}\right) + \frac{Y_i I_0}{C_0}, \tag{5}$$

where ν_0 is the frequency of oscillation of atoms in the solid, $E_{i,d}$ is the desorption activation energy of the ith component, k is the Boltzmann constant, T is the temperature, and Y_i is the sputtering yield of the ith component. The removal of surface components is characterized by frequency probabilities of sputtering $\omega_{i,s}$. Let us assume that the temperature of the altered layer is equal to the substrate temperature in the bulk.

C atoms produced during reaction of CF_2 radicals with Si atoms (the first reaction in Eq. (4)) stick on the surface. The sticking processes of C atoms on Si and C atoms present on the surface are characterized by the sticking coefficients κ_{46} and κ_{47}, respectively. As the processes of deposition and removal take place simultaneously, the stochastic mixing between monolayers (ML) occurs. When C atom is adsorbed on the surface, an atom of the kth monolayer is transferred into the $(k + 1)$th monolayer. In this way, an altered layer with an elemental composition different from the bulk composition is formed. Reaction $Si + 2Cl \rightarrow SiCl_2$ increases the etching rate at an elevated temperature, however, it does not influence the thickness of the altered layer. The influence of reaction $Si + 4F \rightarrow SiF_4$ on the etching rate is negligible.

It follows that five components exist in the adsorbed layer: SiF_4, CF_2, CF_2^*, C, $(CF_x)_n$, with relative con-

centrations $c_1 = [\mathrm{SiF_4}]/C_0$, $c_2 = [\mathrm{CF_2}]/C_0$, $c_3 = [\mathrm{CF_2^*}]/C_0$, $c_4 = [\mathrm{C}]/C_0$, and $c_5 = [(\mathrm{CF}_x)_n]/C_0$; two components exist in the near-surface region: Si and C, with relative concentrations $c_6 = [\mathrm{Si}]/C_0$ and $c_7 = [\mathrm{C}]/C_0$. The relative concentrations of components in the near-surface region must fulfill the following condition: $c_6 + c_7 = 1$. It was found that only a model including physical and chemical processes in the adsorbed layer describes the silicon etching process in $\mathrm{CF_2Cl_2}$ plasma. The following system of equations includes rate expressions of different processes [10, 11] and describes the kinetics of component concentrations in the adsorbed layer and in the near-surface region:

$$\frac{dc_1}{dt} = R_1 \beta c_3^2 c_6 - \omega_1 c_1,$$

$$\frac{dc_2}{dt} = \alpha \beta - G c_2 + R_r c_3 - \omega_2 c_2,$$

$$\frac{dc_3}{dt} = G c_2 - R_r c_3 - \omega_3 c_3,$$

$$\frac{dc_4}{dt} = 2 R_1 \beta c_3^2 c_6 - R_2 \beta c_3 c_4$$
$$- \kappa_{46} c_4 c_6^{(1)} - \kappa_{47} c_4 c_7^{(1)} - \omega_4 c_4, \tag{6}$$

$$\frac{dc_5}{dt} = R_2 \beta c_3 c_4 - R_3 \beta c_3 c_5 - \omega_5 c_5,$$

$$\frac{dc_6^{(1)}}{dt} = -\kappa_{46} c_4 c_6^{(1)} + c_6^{(2)} \omega_7 c_7^{(1)},$$

$$\frac{dc_6^{(k)}}{dt} = V_A \left(c_6^{(k-1)} - c_6^{(k)} \right),$$

where $\beta = 1 - \Theta$ is the fraction of the surface not covered with adsorbate, $\Theta = \sum_{i=1}^{5} c_i$ is the surface coverage, and $V_A = \kappa_{46} c_4 c_6^{(1)} - \kappa_{47} c_4 c_7^{(1)}$ is the deposition rate. The etching rate is proportional to the difference of removal and deposition rates:

$$V = h_0 (V_S - V_A), \tag{7}$$

where $h_0 = 2.72$ Å is the monolayer thickness and $V_S = \omega_1 c_1$ is the removal rate.

4. Results and discussion

During RIE of silicon in $\mathrm{CF_2Cl_2}$ plasma due to the presence of halocarbon radicals, deposition takes
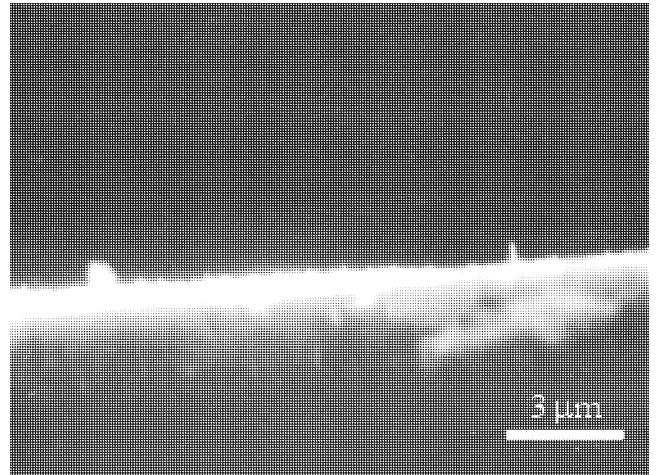

Fig. 1. The interface formed during silicon etching in $\mathrm{CF_2Cl_2}$ plasma at the temperature $T = 320$ K.

place. At a high energy of bombarding ions nonvolatile species are sputtered from the surface, however, at a low energy only the prevailing type of bonds changes. When concentrations of nonvolatile species with strong bonds approach steady-state values, the polymeric layer is formed. The presence of the polymeric layer on the surface reduces the etching rate of silicon. Composition of the polymeric layer depends on the energy of bombarding ions and etching time. The thickness of this layer is few nanometres.

The surface subjected to ion bombardment is in a thermodynamically unstable state, therefore, the formation of mechanical stresses and defects in a near-surface region (up to 15 nm) takes place [12]. In this region, due to the penetration of bombarding ions and diffusion, the interface with increased concentrations of Si–C, Si–F, and Si–Cl species is formed (Fig. 1). SiC inclusions of different sizes exist under the polymeric layer in the near-surface region. These inclusions, defects, and mechanical stresses change electrical properties of a near-surface region. The thickness of the layer with altered electrical properties depends on the energy of bombarding ions and temperature, and extends up to 7 μm [13]. On the other hand, with the increase of temperature in the reactor, intensive reemission of adsorbed particles takes place. The etchant products ($\mathrm{SiF_4}$, $\mathrm{SiCl_2}$, etc.) dissociate in the plasma and deposit on the surface. In this way, an α-Si layer is formed.

The extrapolation of experimentally measured concentrations of Si atoms in the altered layer was used to determine processes that influence the decrease of thickness of the altered layer at a higher temperature. Experimentally measured and theoretically calculated
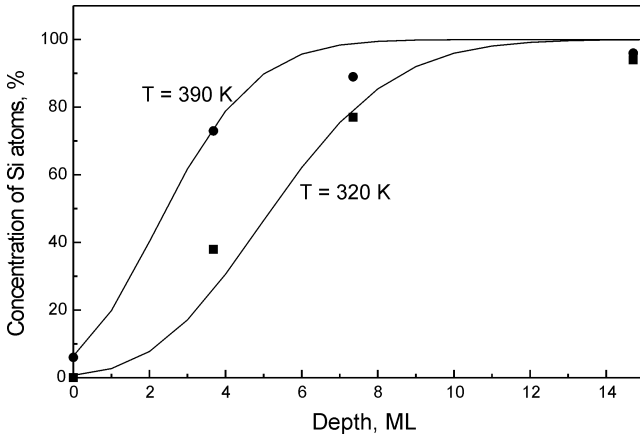
Fig. 2. Experimental (points) and theoretical (curves) concentrations of Si atoms in the altered layer at different temperatures.

using Eq. (6) concentrations of Si atoms in the altered layer are shown in Fig. 2. The following values of frequency probabilities were found by extrapolation:

$$\alpha(320, 390 \text{ K}) = 1.0 \text{ s}^{-1},$$

$$R_1(320 \text{ K}) = 1.15 \cdot 10^4 \text{ s}^{-1},$$

$$R_1(390 \text{ K}) = 1.15 \cdot 10^3 \text{ s}^{-1},$$

$$R_2(320, 390 \text{ K}) = 0.25 \text{ s}^{-1},$$

$$R_3(320, 390 \text{ K}) = 0.10 \text{ s}^{-1},$$

$$G(320, 390 \text{ K}) = 8.5 \cdot 10^{-5} \text{ s}^{-1},$$

$$R_\text{r}(320, 390 \text{ K}) = 0 \text{ s}^{-1},$$

$$\omega_1(320 \text{ K}) = 1.0 \cdot 10^3 \text{ s}^{-1},$$

$$\omega_1(390 \text{ K}) = 1.0 \cdot 10^4 \text{ s}^{-1},$$

$$\omega_2(320, 390 \text{ K}) = 0.40 \text{ s}^{-1},$$

$$\omega_3(320, 390 \text{ K}) = 2.5 \cdot 10^{-4} \text{ s}^{-1},$$

$$\omega_4(320, 390 \text{ K}) = 100 \text{ s}^{-1},$$

$$\omega_5(320, 390 \text{ K}) = 4.0 \cdot 10^{-3} \text{ s}^{-1},$$

$$\omega_7(320, 390 \text{ K}) = 0 \text{ s}^{-1},$$

$$\kappa_{46}(320, 390 \text{ K}) = 4.0 \text{ s}^{-1},$$

$$\kappa_{47}(320, 390 \text{ K}) = 5.0 \text{ s}^{-1},$$

with $t = 3600$ a.u. The theoretically calculated desorption activation energy of SiF$_4$ molecules [14] was used to evaluate the frequency probabilities of desorption ω_1 at different temperatures. The values of frequency probabilities of sticking κ_{46} and κ_{47} were

found by extrapolation from the experimental data. The values of other frequency probabilities were found from the analysis of etching rate kinetics of silicon in CF$_2$Cl$_2$ plasma at different energies of bombarding ions [11]. The thickness of the altered layer decreases with the increase in temperature due to slowdown of the chemical reaction of CF$_2$ radicals with Si atoms (the first reaction in Eq. (4)) and intensified desorption of formed SiF$_4$ molecules. The decrease of the thickness of the altered layer at a higher temperature was observed in the experiment [8]. During the experiment the composition of polymeric layers formed in different halocarbon plasmas was analysed. XPS measurements showed that the concentrations of C–C, C–CF$_x$ species increased and that of CF$_x$ radicals decreased with the increase in temperature.

5. Conclusions

1. During RIE of silicon in CF$_2$Cl$_2$ plasma a polymeric layer exists on the top of the substrate. SiC inclusions of different sizes exist under the polymeric layer in the near-surface region.

2. The thickness of the altered layer decreases with the increase in temperature due to slowered chemical reaction of CF$_2$ radicals with Si atoms and intensified desorption of formed SiF$_4$ molecules.

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TEMPERATŪROS ĮTAKA PAKEISTO SLUOKSNIO SUSIDARYMUI, ĖSDINANT SILICĮ CF_2Cl_2 PLAZMOJE

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Santrauka

Išnagrinėtas reaktyvus joninis silicio ėsdinimas CF_2Cl_2 plazmoje. Eksperimento metu silicio bandiniai ėsdinti CF_2Cl_2 plazmoje 320 ir 390 K temperatūroje. Susidariusių pakeistų sluoksnių storiai išmatuoti Röntgen'o fotoelektronų spektrometru. Pakeisto sluoksnio storis mažėja, didėjant temperatūrai. Eksperi-

mentiškai išmatuotos Si atomų koncentracijos pakeistame sluoksnyje naudotos išaiškinti procesams, įtakojantiems pakeisto sluoksnio storio sumažėjimą aukštesnėje temperatūroje. Paaiškėjo, kad didėjant temperatūrai pakeisto sluoksnio storis mažėja dėl sulėtėjusios CF_2 radikalų reakcijos su Si atomais ir suintensyvėjusios susidariusių SiF_4 molekulių atvirkštinės gerties.