

The role of fluorine-containing ultra-thin layer in controlling boron thermal diffusion into silicon

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Abstract—We have investigated the influence of silicon dioxide reactive ion etching (RIE) parameters on the composition of the polymer layer that is formed during this process on top of the etched layer, and finally, the role of this layer in high-temperature thermal diffusion of boron into silicon. The polymeric layer formed on the etched surface appeared to consist of fluorine and silicon fluoride (SiOF and SiF). Concentration of these components changes depending on the parameters of RIE process, i.e., rf power, gas pressure and etching time. The composition of this polymeric layer affects, in turn, boron thermal diffusion into silicon. With increasing rf power, the depth of boron junction is increased, while increasing time of etching process reduces boron diffusion into silicon.

Keywords—fluorine, reactive ion etching, silicon fluoride, boron thermal diffusion, fluorocarbon plasma.

1. Introduction

When silicon dioxide or silicon are exposed to fluorocarbon plasma (e.g., CF_4) during reactive ion etching (RIE), an ultra-thin polymer layer consisting of fluorine and silicon fluoride (SiOF and SiF) is formed on the etched surface. In fact, etching and polymer deposition take place in parallel (e.g., [1, 2]). It is reasonable to expect that concentration of these components depends on the RIE process parameters, e.g., rf power, gas pressure and etching time.

On the other hand, for the past few years, fluorine and its chemical compounds have been investigated as a means to reduce boron thermal diffusion into silicon.

In this work we try to find correlations between the parameters of RIE applied to silicon dioxide, the chemical composition of the polymer layer and the rate of high-temperature boron diffusion into silicon through that polymer layer.

2. Experiment

N-type, phosphorus-doped (100)-oriented silicon wafers with resistivity of 4–10 Ωcm were cleaned using standard procedures prior to oxidation. After that 150 Å thick thermal oxide was formed.

In the next step, this oxide layer was etched off at constant room temperature by RIE in CF_4 (50 sccm) under various process conditions: rf power, gas pressure and etching time. Boron thermal diffusion was studied afterwards at two temperatures: 1000°C and 1100°C. The matrix of experiments is shown in Table 1.

The chemical composition of the thin polymer layer, formed on the etched surface of silicon dioxide during RIE in fluorocarbon plasma, has been evaluated by ultra-low-energy secondary ion mass spectrometry (ULE-SIMS). Ellipsometry was used to obtain the thickness of this layer.

Table 1
The matrix of experiments

Experiments	RIE parameters		Diffusion parameters		
	Time [min]	Power [W]	Pressure [mTr]	Temperature [°C]	Time [min]
1	1	80	200	1100	30
2	2	80	200	1100	30
3	7	80	200	1100	30
4	10	80	200	1100	30
5	10	120	200	1100	30
6	10	180	200	1100	30
7	2	80	200	1000	30
8	7	80	200	1000	30
9	10	80	200	1000	30
10	10	80	100	1000	30
11	10	180	200	1000	30

The depth of boron diffusion into silicon was determined by grooving and staining. Boron profiles in samples 1 to 6 were measured by means of high-energy secondary ion mass spectrometry.

3. Results and discussion

It has already been established (e.g., [1, 2]) that an ultra-thin polymer layer is formed on the etched surface of silicon dioxide or silicon during RIE process in fluorocarbon plasma. Surface chemical reactions during RIE process, depending on the etching process parameters, are responsible for this situation.

When SiO_2 surface is irradiated with CF_4 atoms, free fluorine ions penetrate the bulk of the oxide, displace atoms in dangling bonds and form new compounds like SiOF or SiF. Fluorine is accumulating in the polymer layer as free ions, too [3]. Da Zhang observed that during oxide etching the bombarding fluorine ions break O-Si-O bounds.

Dangling and unsaturated Si-O and Si bonds are formed on the surface. As a result of free fluorine ions reacting with broken bonds, SiOF and SiF species appear on the surface as chemical components of the polymer layer formed [3].

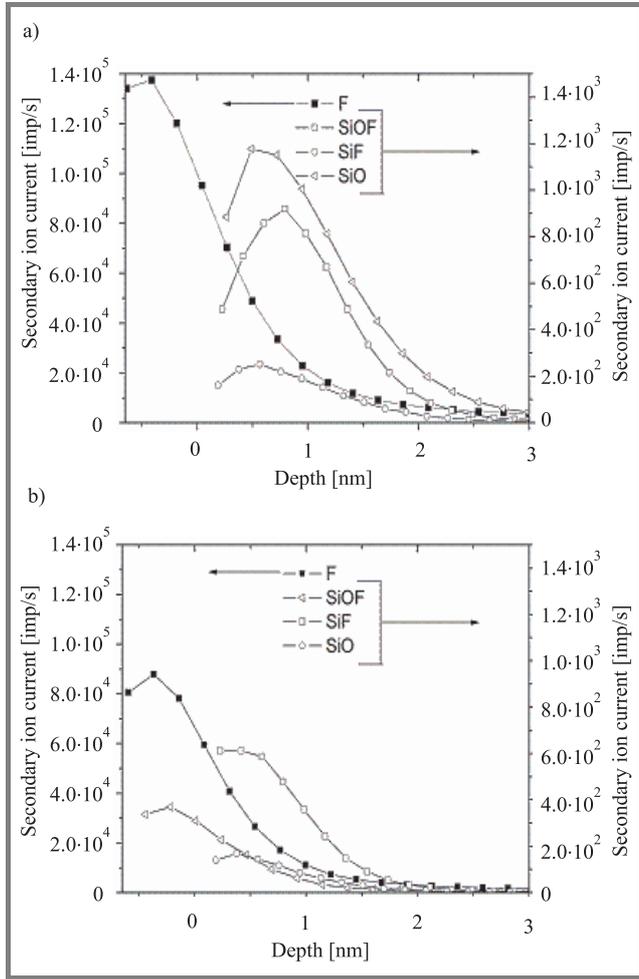


Fig. 1. Profiles of chemical components of the polymer layer (determined by ULE-SIMS) for two samples: (a) $CF_4 = 50$ sccm, $p = 200$ mTr, $P = 80$ W, $t = 2$ min; (b) $CF_4 = 50$ sccm, $p = 200$ mTr, $P = 80$ W, $t = 7$ min.

The results of ULE-SIMS obtained for two samples are presented in Fig. 1. It is clear that the surface of the silicon substrate is covered by a layer containing SiO_2 , SiOF and SiF species with the thickness of a few nanometers. The chemical composition of this polymer layer has been measured by ULE-SIMS, which yields relative concentrations of chemical components only.

The SiOF concentration in ultra-thin polymer layer is constant with increasing etching time (compare Fig. 1 or see Fig. 2c) and is increased very strongly with increasing rf power and gas pressure (Fig. 2a and 2b).

The fluorine concentration in polymer layer is varying with RIE process parameters too, but in a different way. Fluorine concentration increases only with increasing etching time (compare Fig. 1 or see Fig. 2c).

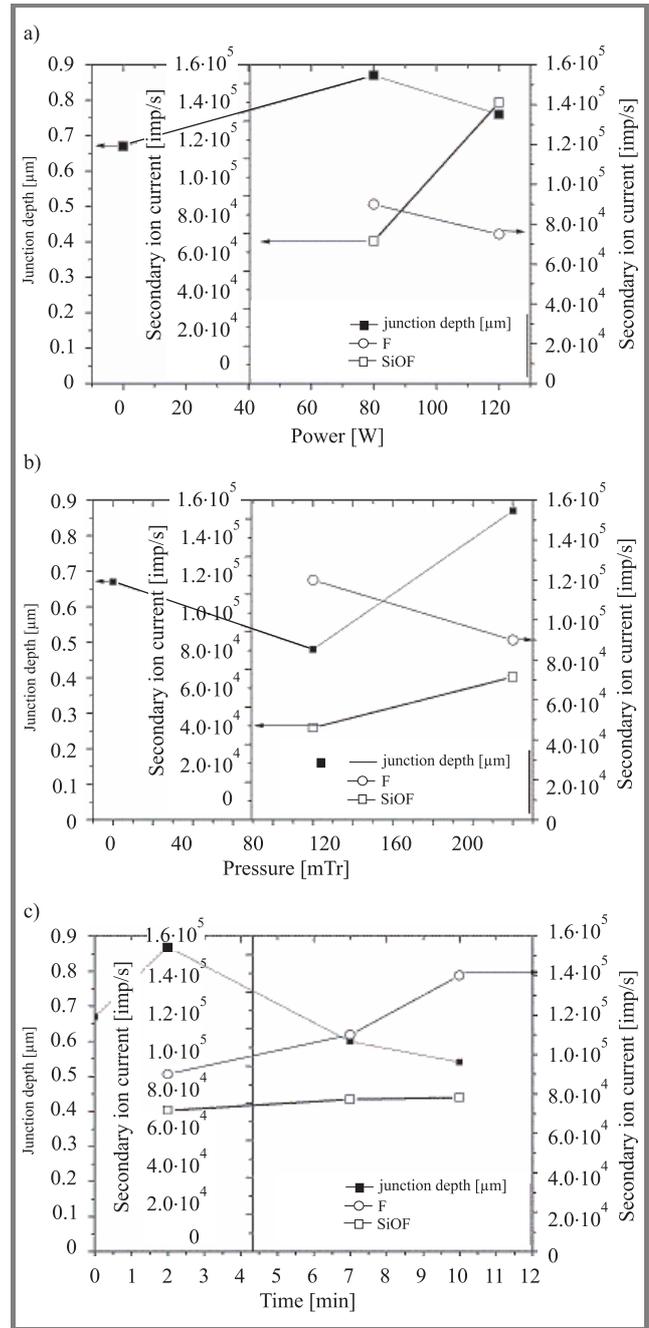


Fig. 2. Concentration of SiOF and F in the polymer layer formed on etched surface during RIE of silicon dioxide: (a) at constant etching time of 2 min, gas pressure of 200 mTr and rf power varying between 80 W and 120 W; (b) at constant rf power of 80 W, etching time of 2 min and gas pressure varying between 100 mTr and 200 mTr; (c) at constant rf power of 80 W, gas pressure of 200 mTr and etching time varying between 2 min and 10 min.

Figure 1 indicates that SiF concentration changes similarly to fluorine concentration. The amount of SiF in the layer increases with increasing etching time. For a short etching time (1 min or 2 min) and low rf power (80 W), SiOF concentration in the polymer layer is higher than that of SiF (see Fig. 1a). This may be due to the fact that many

more broken Si-O bonds exist at the etched surface than Si bonds.

This situation changes with increased etching time (7 min or 10 min). In this case, the concentration of SiF in the polymer layer increases, and is higher than the concentration of SiOF (see Fig. 1b). This is probably caused by reduced density of broken Si-O bonds and increased density of dangling and unsaturated Si and SiF bonds. Reduction of broken Si-O bond density is obtained at a certain moment, when the whole SiO₂ layer is already etched off and silicon etching begins. Free fluorine ions react then with broken Si bonds of the silicon substrate and form SiF species.

On the other hand, variation of rf power (from 80 W to 120 W – for longer etching time – 10 min) makes SiOF concentration increase (see Fig. 2a). This is probably due to high concentration of Si-F bonds existing at the etched surface for higher rf power. As it has already been established in [3] SiF species does not have preferable energetic structure. Therefore, exposing the sample to the air causes spontaneous reaction of this species with free oxygen, both from air and SiOF species, the energetic structure of which is much more stable [3]. Consequently, an increase of SiOF concentration is observed in the polymer layer.

As it can be seen in Table 2, the thickness of polymer layer depends on RIE process parameters. As expected, the thickness decreases with increasing etching time, while

Table 2
The relationship between SiOF layer thickness and RIE process parameters

Experiments	RIE parameters			Polymer layer thickness [Å]
	Time [min]	Power [W]	Gas pressure [mTr]	
1	1	80	200	98
2	2	80	200	50
3	7	80	200	24
4	10	80	200	4
5	10	120	200	8
6	10	180	200	12

increasing rf power makes it increase. The effects described by Da Zhang in [3] are probably responsible for these results. Da Zhang observed that the deposited polymer is simultaneously etched off by oxygen released from broken Si-O bonds during silicon dioxide etching. Free oxygen diffuses through silicon dioxide to the interface and etches the deposited polymeric layer from underside. This is why the layer formed on the etched surface is very thin (about 4 Å) [3]. Deposition and etching of the polymer layer take place in parallel.

As we can see in Table 2, with increasing rf power (from 80 W to 120 W) the thickness of the polymer layer in-

creases from 4 Å to 10 Å – 12 Å. This is probably due to spontaneous oxidation of unsaturated bonds that replaced etching of the deposited polymer by oxygen (as described by Da Zhang in [3]).

F/SiOF concentration ratio decreases with increasing values of rf power or process pressure and increases with increasing time of etching (see Fig. 2).

In Fig. 3 boron profiles (obtained from SIMS measurements) resulting from thermal diffusion at 1000°C and

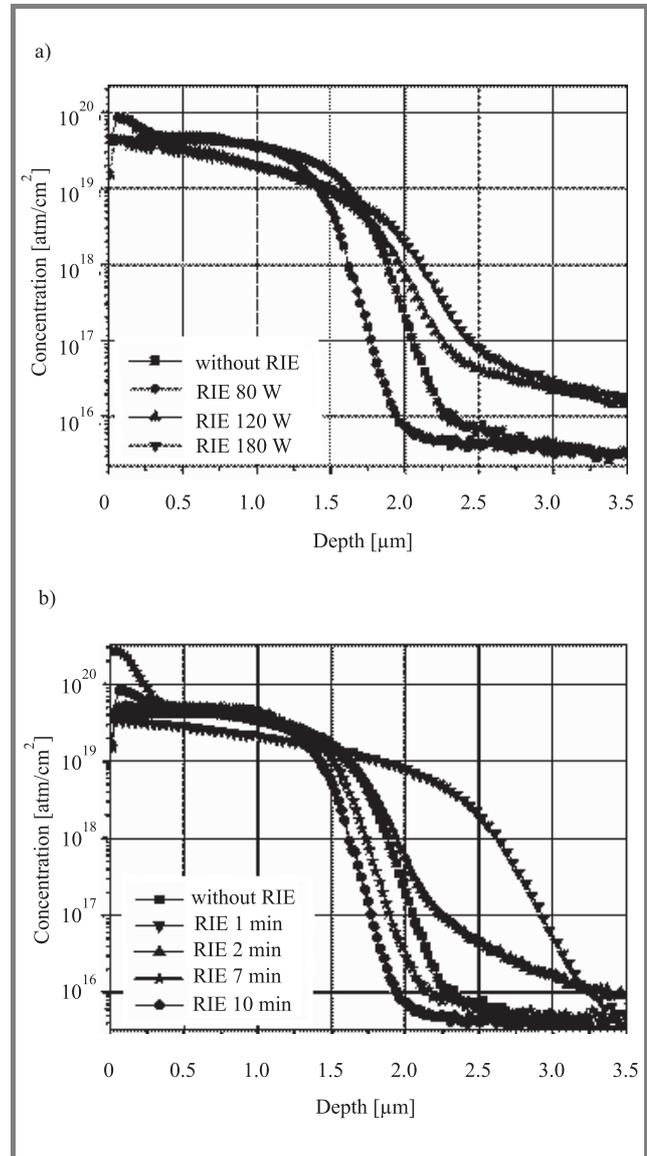


Fig. 3. Boron profiles for different: (a) rf power; (b) etching time.

1100°C are presented. For the sake of clarity, the reference profile of a sample not exposed to any RIE process is also shown. It is visible that both, the junction depth and the whole dopant profile, depend on the parameters of RIE.

If we compare all the obtained results, i.e., polymer layer composition, polymer layer thickness and the depth of boron thermal diffusion with RIE parameters, the depen-

dence of boron junction depth on the rf plasma power used during RIE is simple. The higher the rf power, the deeper the junction (Fig. 3a). It is, however, surprising to see the reference profile between these obtained at 80 W and 120 W of rf power. Surface modification during RIE process could possibly explain this result.

There is a significant difference between the reference samples and those that underwent RIE of thermal oxide. The silicon surface of the former ones is clean, while the latter ones the polymer layer on top of silicon. This layer obviously creates an additional barrier for boron thermal diffusion. Its thickness depends on RIE parameters, as has already been discussed above.

Intuitively one would expect that boron junction to deepen with thinner polymer layers. The results obtained at different rf power demonstrate that this simple relation does not hold true (see Fig. 3).

Our results show that boron thermal diffusion depends on the chemical composition of the polymer layer. Thinner layers, formed at low rf power, happen to have low SiOF concentration and high concentration of F species (Fig. 1b). As we know from [4] high concentration of F may reduce boron diffusion into silicon. This is probably why we get shallower junctions for thinner layers with high concentration of fluorine (compare Figs. 1b and 3a). In thicker layers the situation is opposite. High concentration of SiOF, obtained in polymer layers formed at high rf power, accelerates boron diffusion into silicon [5], therefore we get deeper junctions.

As we can see in Fig. 3b, with increasing time of etching, the depth of boron diffusion is decreased. Also in this case the reference profile is placed between these for short (1 min and 2 min) and long (7 min and 10 min) etching times. The hypothesis relating the boron profile depth to the composition of the layer may also be used in this case. For longer times of etching the concentration of SiOF in the polymer layer was lower and the concentration of SiF and F was higher (Fig. 1). Therefore, for short times of etching (1 min and 2 min), the depth of boron junction is higher than for clean silicon, and for long times of etching (7 min and 10 min), the depth of boron junction is lower than for clean silicon (see Fig. 3b).

A comparison of the obtained results indicates that boron profile depth depends on the relative concentration of SiOF and F in the polymer layer.

High F/SiOF concentration ratios slow down boron thermal diffusion into silicon and shallower junction is formed (Fig. 2). It seems reasonable to conclude that SiOF increases the diffusion rate, while F reduces it.

4. Conclusion

In this study, the influence of RIE parameters on the chemical components of polymer layer and depth of boron thermal diffusion was investigated. The obtained results show

that the chemical composition of the polymer layer depends on RIE parameters and this, in turn, affects the depth of boron diffusion.

It is visible that RIE parameters determine the thickness and chemical composition of the polymer layer and the depth of boron diffusion into silicon. From the obtained results it becomes clear that the depth of boron thermal diffusion does not depend on the thickness of the polymeric layer formed on the silicon surface during RIE process in fluorocarbon plasma, but on its chemical composition. Each of polymer layer chemical components plays a different role during thermal diffusion of boron into silicon. SiOF accelerates boron diffusion into silicon, while SiF and F slow it down. The final conclusion is that RIE parameters determine the depth of boron thermal diffusion.

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Romuald B. Beck – for biography, see this issue, p. 7.

Michał Ćwil – for biography, see this issue, p. 8.