Effect of Alternating Ar and SF_6/C_4F_8 Gas Flow in Si Nano-Structure Plasma Etching

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ABSTRACT:

Si is very reactive to normal plasma etchants such as fluorine (F) based chemicals and the reactions are inherently isotropic. To fabricate small and/or high aspect ratio nanoscale structures in Si, an anisotropic etching process is necessary. SF_6 combined with C_4F_8 has been demonstrated as a good gas combination for anisotropic Si etching. In this study, Ar gas was introduced into the etching chamber to improve Si etching rate. In addition to mixing Ar with F etching gases directly, an alternating Ar and F gas flow process is proposed. It is interesting to see that not only Si etching rate but also etching selectivity are improved by alternating Ar bombardment and SF_6/C_4F_8 etching steps. The Si etching rate is determined by the Ar treatment step in this new alternating Ar and F two step process.

Keywords: Plasma, Etching, Silicon

Introduction:

A plasma is a gas that contains equal numbers of positive and negative charges, as well as neutral atoms, radicals, and molecules. The reactive and high energy species in a plasma etch away materials such as resist, dielectrics, or metals by physical and chemical interactions. For normal etching processes, the plasma species adsorb on the materials surface, there is a chemical reaction and/or physical bombardment, and then the final products desorb from the surface. Plasma processes have been widely used to etch substrates in many industries. The advantage of plasma etching is its accurate profile control capability. Small and high aspect ratio structures have been successfully demonstrated by plasma etching technology. The applications include semiconductor fabrication, micro-electromechanical systems (MEMS), magnetic storage, flat panel displays, opto-electronic devices, polymer surface modification and so on [1-5].

Silicon has been widely used in semiconductor device fabrication, photovoltaic manufacturing, microelectronics and MEMS industries. Si can be etched by both wet chemicals and dry plasma. However, Si is very reactive to normal plasma etchants such as F based chemicals and the reactions are inherently isotropic. This isotropic profile prevents the miniaturization of Si structures down to nanometer scale and the integration of Si based components to achieve better performance. To fabricate a small and/or high aspect ratio structures in Si, side-wall protection is necessary [6, 7]. Several gas combinations, such as SF_6/O_2 [6] and SF_6/C_4F_8 [7] have been used to protect Si sidewall during the trench etching. In addition to add the passivation layer at room temperature, cryogenic wafer cooling is also used to condense the polymer protection layer on the sidewall [8]. Since a sidewall protection is required in F based Si etching, Cl and Br gases were used for etching Si directly [4]. Recently, nano-scale Si structures have been etched successfully by $BCl_3/Cl_2/Ar/O_2$ [9], HBr [10] and the other similar gas combinations. Other than reactive etching gases, neutral beam, such as Ar neutral species in plasma, also has been used to etch nano-Si structures recently [11]. The Si etching profile and etching rate have also been studied in detail [12].

In this study, C_4F_8 was mixed with SF_6 etching gas as a sidewall protection gas to control the Si etching profile. Ar was introduced as the ion source to improve the etching rate. It has been demonstrated that the etching rate is a synergism between the fluxes of ions and neutrals. The total etch rate is greater with both ions and neutrals than with either alone [12]. In the past, the ions were added with neutrals in the same process step. Here, we separate the ions and the neutrals in different steps. An alternating Ar physical bombardment and F chemical etching process was proposed and the impact of the separated Ar ions on the etching rate was studied. It was found that by alternating Ar physical bombardment and F chemical etching steps, not only Si etching rate but also etching selectivity were improved.

Experimental

SF_6 combined with C_4F_8 is one of the demonstrated Si etching gas combination, in which C_4F_8 was used to protect Si sidewall while SF_6 was used to etch Si [13]. During etching, the sample is, in general, negatively biased with respect to the plasma so that positive ions directly strike the bottom surface only by means of an external power supply. With direct ion bombardment on the bottom Si surface, SF_6 removes the bottom polymer coating and chemically reacts with Si to generate a vertical etching profile.

In our experiment, polymer resists (ZEP 520 and S1813) were used as etching masks. ZEP 520 was exposed by E-beam lithography and then developed by Hexyl Acetate while S1813 was exposed by UV light and then developed by MF-312. The Si etching process was carried out in an inductively coupled plasma etching system. A SF_6 and C_4F_8 gas mixture was used. The gas flow ratio of SF_6/C_4F_8 was kept at 25.0 cm^3/min and 50.0 cm^3/min respectively. The plasma etching chamber pressure was kept at 3.3 Pa. The SF_6/C_4F_8 ratio and the chamber pressure were optimized to achieve the best vertical and smooth sidewall profile. Ar gas was introduced into the etching process by alternating with the F gases as a separate step. The process was divided into physical Ar surface bombardment and SF_6/C_4F_8 chemical etching steps and repeated in cycles (one Ar followed by one SF_6/C_4F_8 step). For each cycle, the etching time was fixed at 10 s, while the Ar and SF_6/C_4F_8 step times were varied. The time ratio of Ar to SF_6/C_4F_8 in each step was from 0 to 4.0. Mixing Ar with SF_6/C_4F_8 in one step was also studied as a comparison. For the Ar mixture process, the volume fraction of Ar was varied from 0 to 34.8 %. The etching results, e.g. etching rate and profile were monitored by scanning electron microscopy (SEM).

The etching selectivity was defined as the ratio of Si etching rate over the photo-resist etching rate. The SEM measurement error is normally less than 3.0 % as given by the manufacturer.

Instruments and materials are identified in this paper to describe the experiments. In no case does such identification imply recommendation or endorsement by the National Institute of Standards and Technology (NIST). The results may vary depending on the tool, tool condition, material and structure.

Results and Discussion

A good chemical combination is important to achieve anisotropic etching. In this paper, C_4F_8 was introduced to protect the Si sidewall while SF_6 was used to etch Si. C_4F_8 plasma free radicals can form a polymer which creates a protective barrier that blocks chemical attack on the side of the features. Two mechanisms have been proposed to explain this sidewall protection. The first mechanism is that the coating plasma species induces the growth of a protective film, whose composition and thickness prevent the etchant species from interacting with the Si sidewall. The second mechanism is that adsorption of radical changes the chemical reactivity of the sidewall and promotes recombination processes, which deactivate the incoming etchant species [14]. With ion bombardment on the bottom Si surfaces in the biased plasma, SF_6 can remove the bottom polymer coating and chemically react with Si to generate a vertical etching profile.

In addition to a well balanced chemical combination, plasma density and chamber pressure are critical parameters in minimizing collisions of the energetic ions with the feature's sidewall, thus enabling an anisotropic sidewall. A smooth and straight anisotropic Si etching profile has been achieved (as shown in Figure 1).

However, the etch rate is about 8.0 nm/min which is too slow for deep trench etching. To increase the Si etch rate, Ar was added to the gas mixture to provide an additional ion source. As mentioned before, the sample is negatively biased with respect to the plasma so positive Ar ions can enhance the strike on the bottom surface. The combination of the neutral Ar ions with the reactive ions significantly enhance the Si etch rate. The kinetic scrubbing action of the Ar ions on the surface being etched enables a much faster Si reaction rate. It was found that the combined effect of active neutral species and ion bombardment is more efficient than the sum of the individual processes [15].

In this study, Ar was introduced into the plasma chamber with SF_6 and C_4F_8 etching gases either directly or separately. Mixing Ar with etchant gases was tested first. Ar concentration was varied from a volume fraction of 0.0 % to 34.8 % while the chamber pressure was held constant at 3.3 Pa. Figure 2 shows that with a volume fraction of 6.3 % of Ar inside the chamber, the Si etch rate increases as expected. However, as the Ar concentration continues to increase, the etching rate decreases. Overall, mixing Ar with F etching gases gives very limited or no improvement on the Si etching rate. This “abnormal” behavior is due to the dilution of Ar in the etchant species (SF_6 and C_4F_8) in the chamber. To keep the etchant concentration, we then tried to add Ar separately from the chemical etchants. The process was divided into physical Ar surface bombardment and SF_6/C_4F_8 chemical etching steps and repeated in cycles (one Ar plus one SF_6/C_4F_8 step). For each cycle, the etching time was fixed at 10 s, while the Ar and SF_6/C_4F_8 step times were varied. Figure 3 shows the impact of Ar bombardment time in each cycle on the Si etch rate. In contrast to Figure 2, increasing the Ar step time in each etch cycle continuously increases the etching rate in our experimental range. The Si etch rate can be improved up to a factor of 4 when the Ar to SF_6/C_4F_8 step time ratio is increased to 4. The basic energy transport from the Ar plasma to the Si surface and the F interaction on the Si surface after Ar plasma bombardment have been studied by simulation [16]. The results indicate that the impact of Ar ions on silicon surfaces will render the top atomic layers amorphous. The thickness of this amorphous layer is primarily a function of ion energy. As the surface is impacted with more and more Ar, the atoms in the amorphous layer are seen to mix vigorously, while atoms in the crystalline layer remain more or less stationary [16]. Silicon atoms in the amorphous region are in a less stable configuration and are more likely to move around when energy is deposited nearby, compared to the atoms in more stable crystalline configurations. When F reacts with the Si surface, F atoms are only adsorbed on the amorphous silicon surface. More surface adsorption sites are generated by Ar surface bombardment on an amorphized silicon [17]. In our alternating Si etching process, the Ar bombardment step can modify the top Si morphology and roughen the surface while F etchant can absorb and remove Si from the surface. Since the Si etching rate increases with the Ar step time and does not decrease with the SF_6/C_4F_8 step time, it is clear that the etching rate is determined by the Ar bombardment step. This result also indicates that physical Ar bombardment step is much slower than the chemical F etching step.

Introducing Ar ions can also affect etching profile and mask selectivity. As mentioned above, the Si etching profile is based on surface polymer protection. The removal of this coating by Ar bombardment is directional because the ion flux on the lateral sidewall of the feature is negligible. With Ar ion bombardment, SF_6 reacts with the bottom exposed Si to achieve anisotropic profile no matter if the Ar flow is continuous or paused. Figure 4 shows the Si profile etched by paused Ar process. Comparing with Figure 1, the sidewall is straighter and the bottom tends to be flat. Etching selectivity is defined by Si etching rate over mask etching rate. In our experiment, the etching rate on polymer mask tends to increase by either adding the Ar process step or mixing Ar in the process chamber. However, the trends for Si etching rate is different as discussed before. Therefore the impact of Ar ions on mask etching selectivity is process dependent. Figure 5 shows that the etching selectivity by alternating Ar and SF_6/C_4F_8 gases is higher than that by mixing Ar into etchant gases. By using no Ar gas process as a reference, etching selectivity tends to increase in alternating Ar and SF_6/C_4F_8 gas flow process (Figure 5a) but decrease in continuous Ar flow process except at very low Ar concentration (Figure 5b).

Conclusions

In conclusion, smooth and straight Si sidewall etching profile has been achieved by using SF_6, C_4F_8 and Ar plasmas. Ar plays an important role for etching profile, etching rate and selectivity. By alternating Ar bombardment and SF_6/C_4F_8 etching steps, the concentration of F chemical etchant in each etching step can stay constant while the efficiency of the Ar in physical bombardment step can be improved. The impact of the Ar bombardment step on Si etching rate is significant and can increase the etching rate up to 4 times. The impact of the Ar step on the polymer mask is less than on Si, so the etching selectivity of Si over polymer mask can also be improved.

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Figure legends

Figure 1. Si with ZEP as mask etched by 300W ICP plasma (SF_6: 25.0 cm^3/min.; C_4F_8: 50.0 cm^3/min.; Pressure: 3.3 Pa for 10 min.)

Figure 2. Si etching rate v.s. continuous Ar gas mixed with SF_6 and C_4F_8

Figure 3. Effect of Ar etch step time fraction in each cycle on Si etching rate

Figure 4. Si etching profile with ZEP as mask after alternating Ar/SF_6 process for 10min.

Figure 5. Effect of Ar ion bombardment on etching selectivity (Si/S1813) (a: Continuous Ar flow; b: paused Ar flow)

Figure 1

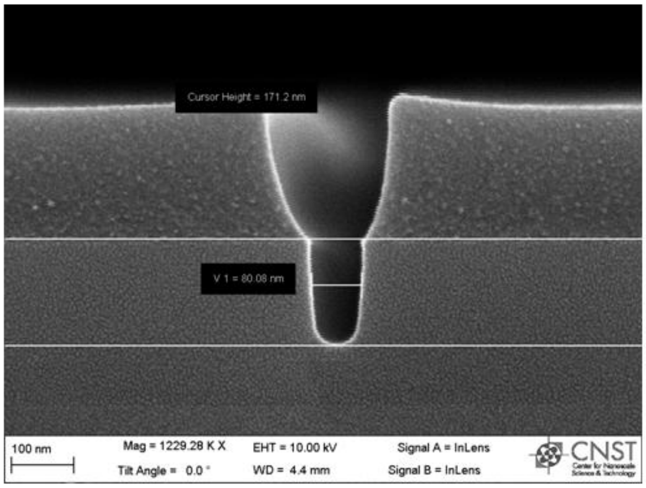
Cursor Height = 171.2 nm
V 1 = 80.08 nm
100 nm
Mag = 1229.28 K X
Tilt Angle = 0.0 °
EHT = 10.00 kV
WD = 4.4 mm
Signal A = InLens
Signal B = InLens
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Figure 2

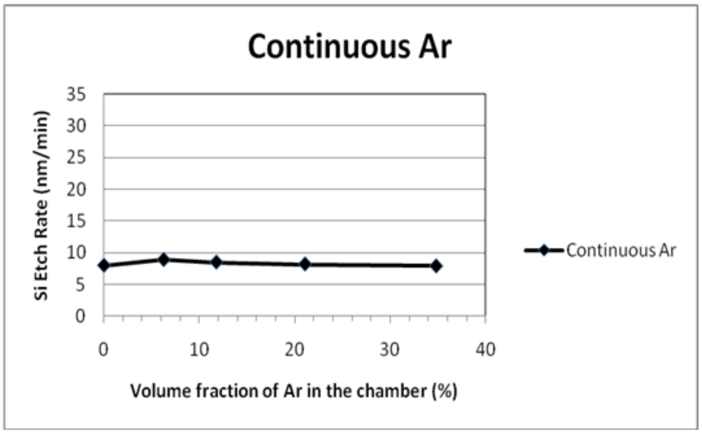
Continuous Ar
Si Etch Rate (nm/min)
35
30
25
20
15
10
5
0
0
10
20
30
40
Volume fraction of Ar in the chamber (%)
Continuous Ar

Figure 3

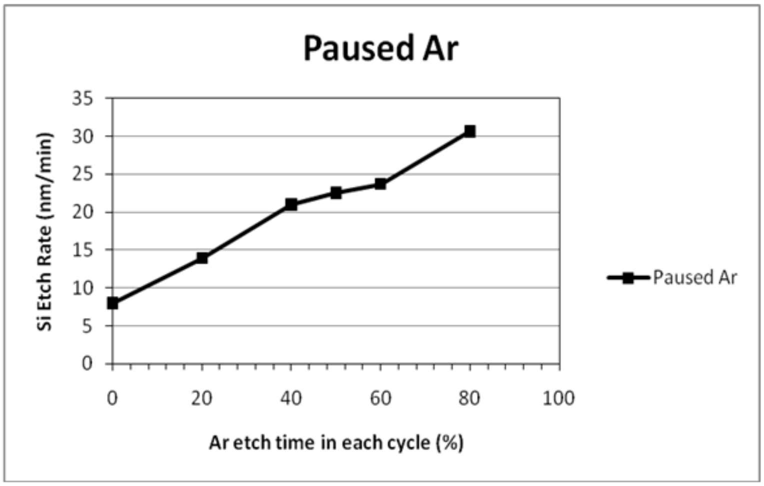
Paused Ar
Si Etch Rate (nm/min)
35
30
25
20
15
10
5
0
0
20
40
60
80
100
Ar etch time in each cycle (%)
Paused Ar

Figure 4

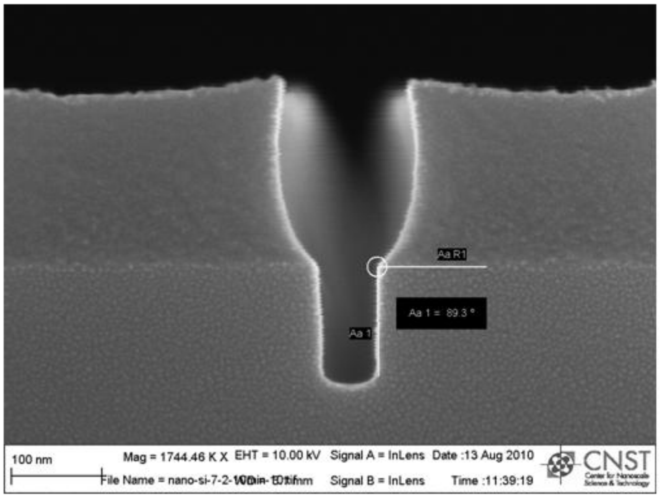
Aa R1
Aa 1 = 89.3 °
Aa 1
100 nm
Mag = 1744.46 K X
EHT = 10.00 kV
Signal A = InLens
Date :13 Aug 2010
File Name = nano-si-7-2-10Win-101.tifmm
Signal B = InLens
Time :11:39:19
CNST
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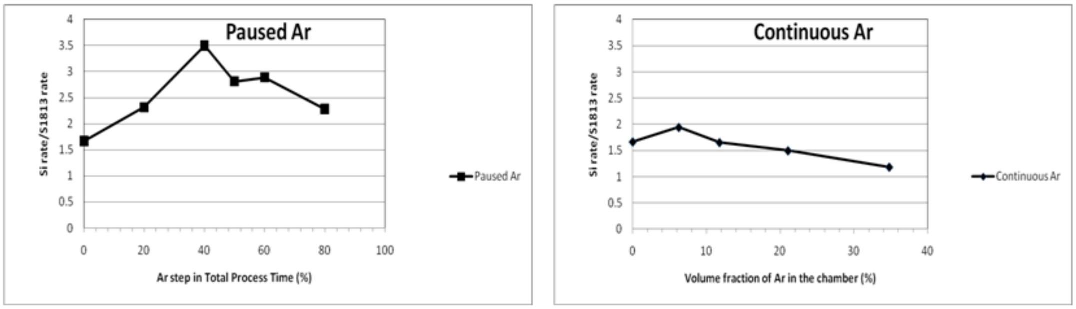
Figure 5


Paused Ar
Si rate/S1813 rate
4
3.5
3
2.5
2
1.5
1
0.5
0
0
20
40
60
80
100
Ar step in Total Process Time (%)
Paused Ar
Continuous Ar
Si rate/S1813 rate
4
3.5
3
2.5
2
1.5
1
0.5
0
0
10
20
30
40
Volume fraction of Ar in the chamber (%)
Continuous Ar

(a)

(b)