Simultaneous Etching and Deposition Processes during the Etching of Silicon with a Cl₂/O₂/Ar Inductively Coupled Plasma

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In this article, surface processes occurring during the etching of Si with a Cl₂/O₂/Ar plasma are investigated by means of experiments and modeling. Cl₂-based plasmas are commonly used to etch silicon, while a small fraction of O₂ is added to protect the sidewalls from lateral etching during the shallow trench isolation process. When the oxygen fraction exceeds a critical value, the wafer surface process changes from an etching regime to a deposition regime, drastically reducing the etch rate. This effect is commonly referred to as the etch stop phenomenon. To gain better understanding of this mechanism, the oxygen fraction is varied in the gas mixture and special attention is paid to the effects of oxygen and of the redeposition of non-volatile etched species on the overall etch/deposition process. It is found that, when the O₂ flow is increased, the etch process changes from successful etching to the formation of a rough surface, and eventually to the actual growth of an oxide layer which completely blocks the etching of the underlying Si. The size of this etch stop island was found to increase as a function of oxygen flow, while its thickness was dependent on the amount of Si etched. This suggests that the growth of the oxide layer mainly depends on the redeposition of non-volatile etch products. The abrupt change in the etch rate as a function of oxygen fraction was not found back in the oxygen content of the plasma, suggesting the competitive nature between oxidation and chlorination at the wafer. Finally, the wafer and reactor wall compositions were investigated by modeling and it was found that the surface rapidly consisted mainly of SiO₂ when the O₂ flow was increased above about 15 sccm.

Introduction

Shallow trench isolation (STI) is a widely used technique for the fabrication of integrated devices in the micro-electronics industry.[1] In this process, narrow trenches are etched in the silicon substrate, which are later filled with an
isolating material (such as SiO$_2$) to isolate active areas on the wafer. It is important to have a good understanding of this process so that the fabrication of these trenches with continuously decreasing dimensions can be well controlled.

Ar/Cl$_2$/O$_2$ plasmas are commonly applied for the selective etching of silicon in STI. Chlorine is known to react with a silicon surface to form SiCl$_4$, which is a volatile etch product. Since this chemical process is isotropic, a small fraction of O$_2$ is added to the gas mixture to protect the sidewalls from lateral chemical etching in order to increase the anisotropy. Indeed, oxygen will react with silicon to form a SiO$_2$ layer which can not be chemically etched by chlorine. In this way, the sidewalls of the trenches are protected from further chemical etching while the bottom is still etched properly due to the strongly directional sputtering of the SiO$_2$ layer by ions. However, if the O$_2$ fraction exceeds a certain value, the etch rate will be drastically reduced due to more oxidation and less chlorination of the Si. Since SiO$_2$ cannot be etched chemically by chlorine, the etch rate drops significantly, stopping the etching process completely. This phenomenon is therefore often referred to as etch stop.

The etch stop problem originated as a reproducibility problem. It was found that, during the STI etching of several wafers after each other, the etch rate dropped significantly after a few wafers even if the operating conditions were kept the same. It was concluded by Shamyrian et al. that the gradual heating of the top dielectric window was the origin of the problem. When the top dielectric window gradually heats up during the etch experiments, evaporation of (previously deposited) low-volatile etch products from this window due to sputtering is enhanced. At the same time, the wafer is deposited low-volatile etch products from this window due to the formation of passivation layers on feature surfaces. However, their investigation was limited to the formation of passivation layers only at the sidewalls of the trenches (at relatively low oxygen content). Moreover, two papers by McNevin report experimental results on the etching of Si by modulating the O$_2$/Cl$_2$ gases, altering the etching process and improving Si/SiO$_2$ etch selectivity. In addition, in our previous paper, etching of Si with an Ar/Cl$_2$/O$_2$ plasma was investigated by means of modeling under varying operating conditions, including a variation of the oxygen flow.

Experimental Section

Experiments were performed in a Lam Research 2300 Versys Kiyo 300 mm wafer reactor with a planar coil on top of the chamber. However, the quartz dielectric window was replaced by a ceramic material of which the temperature can be controlled. To increase the uniformity and reproducibility of the etching processes, the chamber walls were coated with a SiCl$_4$O$_2$ layer before each etching experiment. Indeed, wall loss of Cl (mostly to form Cl$_2$) is much lower on the coating compared to the clean reactor, increasing the uniformity of the Cl density in the plasma and hence the uniformity of the etch process. Moreover, by introducing a new coating before each new etch experiment, process control and reproducibility are increased in general.

The wafers consisted of 200 nm amorphous Si (α-Si) on a 100 nm SiO$_2$ layer. The thickness of the layers was measured with an ellipsometer (KLA-Tencor FS) at different points on a straight line across the wafer before and after the etch process to calculate the etch rate or the deposition rate.

The blanket α-Si wafers were etched under the following operating conditions: 40 mTorr total gas pressure, 600 W coil power, −500 V dc bias on the substrate, 13.56 MHz applied separately to both the coil and the substrate, 300 K gas temperature, 60°C window, walls and wafer temperature, 100 sccm Cl$_2$, 12 sccm Ar and a varying flow of O$_2$ between 0 and 100 sccm. Also the etch time was varied to a maximum of 60 s.

Description of the Model

To investigate the etching and deposition processes by means of modeling, three different models were applied. To calculate the general plasma properties, a two-dimensional hybrid fluid—Monte Carlo model developed by Kushner and coworkers was used. In addition, a surface Monte Carlo model, also developed by Kushner et al. was applied to describe surface processes such as etching and deposition, and to calculate the surface composition and returning
fluxes to the plasma. Finally, a separate Monte Carlo feature profile model was introduced after the plasma calculation to calculate nanoscale trench profiles during the etching of Si. More details about the latter model can be found in reference.\[9\]

The plasma model treats electrons in a Monte Carlo module and the heavy plasma species in a fluid module. In the fluid module, fluxes of the plasma species toward the wafer and the reactor walls are calculated and used as input in the surface model. Based on a surface chemistry set, etch rates, surface composition, and returning fluxes to the plasma are calculated. The returning fluxes are used again as input for an updated plasma simulation and the general calculation cycles between these two models until convergence is reached. Finally, after the plasma simulation, fluxes, energy distributions, and angle distributions to the wafer or walls are used as input in a Monte Carlo feature profile model to calculate the etch profile as a function of time.

To describe the plasma chemistry of a Cl\textsubscript{2}/O\textsubscript{2}/Ar plasma in contact with a SiCl\textsubscript{x}O\textsubscript{y} coating and a α-Si wafer, two extensive reaction sets were created, one for the plasma chemistry and one for the surface chemistry. These sets contain a large number of reactions between all plasma species, including etch products such as SiCl\textsubscript{0−4} and SiO\textsubscript{1,2}. A detailed description and explanation of the reaction sets can be found in our previous paper on the effect of chamber wall coating in this kind of systems.\[10\] In the surface reaction set, the following processes are taken into account: (i) chlorination of Si and SiCl\textsubscript{x} layers to volatile SiCl\textsubscript{4}, (ii) oxidation of Si and SiCl\textsubscript{x}O\textsubscript{y} layers, (iii) redeposition of non-volatile and low-volatile etch products, and (iv) physical sputtering, chemical sputtering, and sputter deposition. A summary of the most important reactions for the surface processes is presented in Table 1.

The reaction probabilities for chemical etching of Si with chlorine are adopted from literature\[3,10\] and the energy dependent sputter yields defined in the model are fitted to experimental results. The sensitivity of the results to these reaction probabilities was investigated in a previous paper\[7\] and it was found that the final results were most sensitive to the probabilities for chemical etching due to the relatively large flux of Cl and Cl\textsubscript{2}.
Results and Discussion

Etch and Deposition Processes as a Function of O₂ Flow

The etch stop phenomenon is illustrated in Figure 1, where the measured and calculated etch rates at the center of the wafer are plotted as a function of O₂ flow.

At low O₂ flow (from 0 to about 10 sccm), α-Si is being etched successfully by chlorine at a rate of about 300 nm min⁻¹. At very low oxygen content (i.e., less than 10 sccm), the isotropic chemical etching of α-Si by chlorine neutrals (Table 1, reactions 1.1 and 1.2) creates undercutting effects, as seen in Figure 2(a), which is a result obtained from the Monte Carlo profile model. When the oxygen fraction is increased to 12 sccm, a protective oxide layer is formed (Table 1, reactions 2.1–2.4) on the sidewalls to increase the anisotropy, as illustrated in Figure 2(b). This profile looks like a nearly ideal etch profile. The chemical etching of the formed SiClₓOᵧ sidewall layer has a very low rate and is negligible. This oxide layer can therefore only be removed by sputtering (Table 1, reactions 4.1 and 4.2), hence the formation of a narrow and deep trench.

When the oxygen flow is increased even more to values of 15 sccm, the thickness of the remaining α-Si layer could not be measured properly by the ellipsometer, hence the bouncing datapoints in the experimental result of Figure 1. This occurs when the remaining layer after the etch process is rough, not allowing a well-resolved ellipsometry measurement. The formation of a rough layer is most probably due to a balanced competition between etching and redeposition of non-volatile etch products. Indeed, the formation of a rough layer was also predicted by the model as shown in Figure 2(c). Finally, when the oxygen fraction is above 20 sccm, oxidation of the α-Si is dominant, reducing the etch rate to a value close to zero, as is obvious from Figure 1. Indeed, no α-Si is etched and, in addition, non-volatile products deposit, so an oxide layer is actually growing, as illustrated in Figure 2(d).

In addition to the simulated etch profiles that illustrate the different etch regimes, Figure 3 shows two SEM pictures where the transition of normal etching to roughness, and eventually to full etch stop, is visible. Although most experiments were performed on blanket silicon wafers, we used a patterned wafer to clearly see the transition when taking SEM pictures. In Figure 3a, the left side shows a normal etching regime, clearly visible due to the patterning. In the middle, a small roughness layer is visible, and eventually a full etch stop is observed at the right side of the figure. Figure 3b is a close up of the rough transition layer. This layer is smaller in size compared to the roughness on the blanket Si wafers because the actual area of etching is decreased due to the patterning. The region where a rough layer is formed has indeed a very low total etch rate, and a rough surface comparable to the simulation result.

The reason why there is redeposition of non-volatile etched species [Figure 2(d)] is because the formation of this etch-blocking SiO₂ layer occurs first in the center of the wafer, while simulta-
neously, α-Si is still etched at the edge of the wafer (as is illustrated in Figure 5 below). This is probably attributed to three effects: First, in this particular reactor geometry, the gas nozzle is located in the center of the top window right above the center of the wafer (see Figure 4 below). In order to maintain the (ultra) high vacuum in the chamber, the nozzle size is usually very small, like a needle. Therefore, to obtain the desired overall gas flow of more than 100 sccm, the gas must be injected through the nozzle at very high speeds. For this reason, the jet-like gas flow will directly arrive at the center of the wafer, creating a higher flow of neutral oxygen in this central area. Second, the maximum ion density is not found in the center of the chamber but it is characterized by a torus shape following the geometry of the coil. This results in a slightly higher ion flux and hence a higher sputter rate at the edge of the wafer, reducing the probability for formation of an oxide layer. This is illustrated in Figure 4(a) where the calculated density profile and flux lines for the ions are shown. For sake of simplicity, the sum of all ions present in the plasma is presented. Third, atomic oxygen has a much higher affinity to oxidize Si than O$_2$, and since O will stick to the walls and recombine to O$_2$, the density of atomic oxygen is slightly higher in the center of the chamber, allowing for a higher flux of O to the center of the wafer and hence a higher oxidation rate in the center of the wafer. This is illustrated in Figure 4(b) where the density profile of atomic oxygen is presented, as well as the flux lines. Indeed, all three effects increase the probability for the formation of an etch stop layer in the center of the wafer rather than at the edge.
The formation of an etch-stopping layer in the center of the wafer is clearly visible from the experimental results presented in Figure 5(a). In this plot, the etch rates on a straight line across the wafer are shown, for different oxygen flows. From this figure it can be concluded that, at 10 sccm of O₂, there is no formation of an oxygen island and Si is being etched successfully at a rate of ca. 300 nm/min. However, at 12 sccm O₂, there is a minor local decrease in the etch rate in the center of the wafer, due to the deposition of a small SiO₂-containing layer. This can be deduced from Figure 5(b) where the thickness of the deposited oxide layer is plotted for exactly the same conditions. Furthermore, at 15 sccm O₂, a significant SiO₂ island is formed of about 13 nm in thickness (after 20 s), blocking the etching of the α-Si almost completely.

The formation of this etch-stopping oxide layer occurs when the deposition rate of non-volatile etch products is higher than the sputter rate, resulting in the actual growth of a SiClₓOᵧ-containing layer which has a composition close to SiO₂ as will be discussed later in Section 4.3. Indeed, the growth of this layer is clearly dependent on the redeposition rate of etch products, as can be seen in Figure 5(b) when comparing the film thickness at 15 sccm to the thickness at 100 sccm. At 15 sccm, the thickness is about 13 nm after 20 s, compared to only 10 nm at 100 sccm O₂. This is due to the fact that at 15 sccm O₂, there is still α-Si being etched at the edge of the wafer [see Figure 5(a)] and therefore, there is a source of non-volatile etch products that can redeposit on the oxide island. On the other hand, at 100 sccm O₂, the complete wafer is oxidized, and almost no α-Si can be etched anymore [see Figure 5(a)], hence no etched species are launched in the plasma and the oxide layer therefore does not increase in thickness as rapidly. Indeed, from the simulation results can be concluded that the total etch product density decreases roughly two orders of magnitude going from 15 sccm O₂ flow to 100 sccm, as will be discussed later in Section 4.3. Please note that only the non-volatile etch products will account for redeposition (listed in reaction 3.1 from Table 1) where the most abundant etch products SiCl₂, SiCl₃, and SiCl₄ are more volatile and have wall loss probabilities close to zero (reaction 3.2 in Table 1). So, in the case of 15 sccm O₂, both etching and deposition occur simultaneously on the wafer. At the edge, Si is being removed while in the center a SiClₓOᵧ layer is being grown (with a composition close to SiO₂) due to the redeposition of the etched species.

The measured size of the etch stop area, or more specifically defined as the fraction of the total wafer area, is plotted as a function of O₂ flow in Figure 6, together with the calculated wafer averaged SiO₂ surface coverage.
fraction. In general, reasonable agreement is reached between the measured and calculated results. Please note that at low oxygen flow (1–10 sccm) there was no experimental evidence of an etch stop island in the center of the wafer, see dashed line. However, most likely there is already a fraction of the wafer surface oxidized (as can be seen from the calculated plot), but simply not with a significant thickness to be measured experimentally.

**Etch and Deposition Processes as a Function of Time**

Another way to verify whether the growth of this oxide layer is indeed due to the redeposition of etched species, is to study the etch rate at different etch times for 15 sccm O₂. Indeed, in our experiments, wafers of 200 nm α-Si on SiO₂ were utilized; hence we should expect that the growth of this oxide island stops after the etching of the 200 nm α-Si. Indeed, this can be concluded from Figures 7(a–d). In Figure 7(a) the removed α-Si is plotted as a function of time at 15 sccm O₂. At the edge of the wafer, the amount of α-Si etched increases linearly with time during the first 30 s, as expected. After about 30 s, the 200 nm α-Si is completely removed, hence the etched amount of α-Si remains constant after this time. In the center of the wafer, almost no α-Si is etched due to the formation of the etch stop layer, as mentioned before.

Figure 7(b) presents the thickness of the etch stop oxide layer as a function of etch time in the center of the wafer. It is clear that this layer increases in thickness during the time that α-Si is removed at the border of the wafer. After 30 s, this layer is no longer growing, but it decreases in thickness due to sputtering. These results suggest that the growth of the oxide layer is indeed dependent on the redeposition rate of non-volatile etch products.

Figures 7(c,d) shows similar results, but for a complete cross section of the wafer, at 15 sccm O₂, for different etch times. It is obvious from Figure 7(c) that the etching of Si at the edge of the wafer increases linearly as a function of time until 30 s, and then remains constant, whereas virtually no etching is observed in the center. Likewise, in Figure 7(d) it is illustrated that the thickness of the deposited SiOₓ layer at the center increases as a function of time until 30 s, after which it starts to decrease again due to sputtering.

**Correlation Between Etch Rate and Plasma Composition**

The abrupt change in the etch rate at varying O₂ flow, as was observed in Figure 1, is not found back in the oxygen content of the plasma itself, as illustrated in Figures 8(a,b) showing the volume averaged densities of most species as a function of O₂ flow. Indeed, the densities of oxygen containing species steadily increase, as expected. The steady increase of O₂ gas fraction and the abrupt change in etch rate suggest the competitive nature between chlorination and oxidation of the silicon surface. However, the most significant change is the total etch product density in the plasma which changes abruptly together with the etch rate. The highest etch product density (∼10¹⁴–10¹⁵ cm⁻³) is expected at low oxygen content where the etch rate is highest (∼300 nm). SiCl₂, SiCl₃, and SiCl₄ are the main etch products with comparable densities, although SiCl₂ always has a slightly higher density. As the oxygen content steadily increases, the etch product density in the plasma decreases abruptly to a value in the order of 10¹¹ cm⁻³.

Moreover, as the densities of the plasma species and their fluxes toward the wafer are strongly correlated, the fluxes of the (non-volatile) etch products toward the wafer show the...
same trends as a function of oxygen flow, as is clear from Figure 9(a,b). Indeed, at 15 sccm, where the formation of an etch stop layer occurs due to dominant oxidation over chlorination, the total flux of (non-volatile) etch products to the wafer is in the order of $10^{18}$ cm$^{-2}$s$^{-1}$, whereas at 100 sccm it is about two orders of magnitude lower ($10^{15}$–$10^{16}$ cm$^{-2}$s$^{-1}$). As mentioned before in Figure 5(b), the growth of the etch stop layer is highest at 15 sccm which also suggests that the formation of this layer is mainly based on redeposition of etch products as mentioned before. Although SiCl$_2$ and SiCl$_3$ are considered to be quasi-volatile, with a low deposition probability of 0.05, they are the most important species for deposition since their flux is roughly three orders of magnitude higher than the low-volatile species (compared to Si, SiCl, SiO, and SiO$_2$). Technically these species are easily sputtered again from the surface, but if they are oxidized before being sputtered, they are trapped in the oxy-chloride layer which is sputtered more slowly, resulting in actual layer growth.

At low oxygen content, the ions that account most for sputtering of the wafer surface are SiCl$^+$, SiCl$_2^+$, and SiCl$_3^+$, with fluxes in the order of $10^{15}$ cm$^{-2}$s$^{-1}$, with SiCl$^+$ always being slightly higher. The reason why SiCl$^+$ is the highest is due to electron impact dissociative ionization of SiCl$_2$ (to SiCl$^+$ + Cl), which is the most important species at low oxygen fraction. As mentioned before, at higher oxygen content, the etch product density decreases significantly and hence this applies also to the corresponding ions. Therefore, at high oxygen content and etch stop, the most important ions for sputtering become Cl$_2^+$, ClO$^-$ and O$_2^-$.

*Figure 8.* Reactor averaged densities of the various neutral species (a) and charged species (b) as a function of oxygen flow.

*Figure 9.* Radially averaged fluxes toward the wafer of the relevant neutral species (a) and charged species (b) as a function of oxygen flow.
Surface Composition on the Wafer and Reactor Wall

Finally, the calculated surface compositions of the wafer and the reactor wall as a function of O₂ flow are illustrated in Figures 10(a,b). At low oxygen fraction (i.e., below 10 sccm), the wafer surface is mainly chlorinated (SiCl₃) which is expected at 40 mTorr gas pressure. At this pressure, the fluxes of Cl and Cl₂ are at least 100 times higher than the ion fluxes, so the wafer surface will always be strongly chlorinated during the etching process. Therefore, the fraction of bare Si is only in the order of 10⁻³. On the other hand, when more oxygen is added to the gas mixture, the fraction of SiOₓ on the surface tends to rapidly increase, as expected, and at 20 sccm, the wafer surface is already predominantly composed of SiOₓ, as is clear from Figure 10(a). It should be noted that in this particular chemistry, SiClₓ layers can be oxidized to SiClₓO layers and eventually to SiO₂, replacing chlorine from the layer by oxygen.[11] On the other hand, a SiClₓOₓ or SiOₓ layer will not be chlorinated since the Si–O bond is stronger than the Si–Cl (110 kcal mol⁻¹ bond enthalpy compared to 90 kcal mol⁻¹, respectively). For this reason, the formation of a SiOₓ layer is favored compared to a SiClₓ layer. When the amount of oxygen in the plasma is increased, it is, therefore, expected that the surface of the wafer and the reactor walls rapidly tend to be covered with SiO₂. Moreover, since the SiO₂ layer cannot be removed chemically, it can only be removed by physical sputtering. For this reason it is expected that the fraction of SiO₂ is even higher on the reactor walls due to limited sputtering, as is indeed obvious when comparing Figure 10(b) with Figure 10(a).

The chemical composition of the deposited SiClₓOₓ layer, at 15 sccm O₂, was investigated experimentally by TOF-SIMS, and the result is illustrated in Figure 11. The intensity of the sputtered chlorine from this layer is much lower in signal compared to the oxygen containing species (O and SiO₂), proving that the deposited layer is indeed mainly composed of SiO₂. This again suggests the dominant oxidation over chlorination in this chemical system, where SiClₓ surface species are gradually converted into SiO₂ (Table 1, reaction 2.4). Please note that the intensities do not represent the composition in an exact way due to a different sensitivity and sputter yield for the different species. After about 400 s, the SiClₓOₓ passivation layer was completely removed. From here, only Si is sputtered and the signals converge to zero.
Conclusion

The growth mechanism of an etch-stopping oxide layer during the etching of silicon with an Ar/Cl₂/O₂ plasma, as applied in STI, is investigated by means of experiments and modeling. The oxygen gas fraction was varied and different etching or deposition regimes were observed. At very low oxygen content (below 10 sccm), silicon was found to be etched successfully, however, with undercutting effects due to the predominant isotropic chemical etching by chlorine neutrals. When the fraction of oxygen was increased slightly (up to about 12 sccm under the stated operating conditions), silicon is still etched successfully and the trench sidewalls are protected by an oxide layer, resulting in a desired anisotropic etch process.

However, if the fraction of oxygen is increased even more (to about 14 sccm), the resulting wafer surface was found to be very rough, suggesting a competition between oxidation and chlorination of the silicon. At even higher oxygen flow (15 sccm), an etch-stopping oxide layer was formed in the center of the wafer, which increased in thickness during the etch experiment. Simultaneously, at the border of the wafer, silicon was still etched successfully. At very high oxygen content (e.g., 100 sccm), the etch stop layer covered the complete wafer, but the layer did not increase in thickness as much as in the case of 15 sccm. This suggests that the growth of the etch stop layer depends on the redeposition of non-volatile etch products. The same could be concluded when investigating the etch rate and the formation of an SiO₂ layer as a function of the etch time. Indeed, when all 200 nm a-Si was etched from the border of the wafer, the growth of the central oxide layer decreased again due to sputtering and the lack of redepositing etch products.

The abrupt change in etch rate on the wafer as a function of O₂ flow was observed both in the experimental and simulation results, but it was not found back in the oxygen content of the plasma, suggesting that the strong change in etch rate is indeed a consequence of the competitive nature between chlorination and oxidation of silicon. The most important effect here was the significant drop in etch product density at increasing O₂ content. For this reason, the growth rate of the oxide layer decreased with increasing oxygen fraction, suggesting that the layer formation is indeed based on etch product redeposition. At low oxygen fraction, the most important ions were the ionized etch products SiCl⁻, SiCl₂⁺, and SiCl₃⁺, whereas at higher oxygen content Cl₂⁻, ClO²⁻, and O₂⁻ were the dominant ions.

The surface composition was investigated by means of modeling and it was found that when the oxygen flow is increased, the composition on wafer and walls quickly became mainly SiO₂ due to the fact that, in this chemical system, a silicon chloride layer can be oxidized, while a silicon oxide layer cannot be chlorinated.

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