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# Etch Rate Modification of $SiO_2$ by Ion Damage

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Increased etch rate for implanted oxide with boron, phosphorus, arsenic, and argon is characterized for aqueous and vapor hydrofluoric acid (HF). Destruction by implantation of Si-O bonds makes oxide more reactive to HF. Water being reaction product and catalyst for oxide etching, its amount controls the reaction kinetic. In aqueous solution selectivity of four between implanted and unimplanted oxide is reached but increases up to 200 in vapor HF. In the case of HF etching under vapor phase the generated water increases the etch rate. This technique opens many process possibilities such as etch stop layer development, etching of buried trenches, definition of MEMS anchors, etc.
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From the mid-1980s to the mid-1990s several research groups published[1-3] experimental results on etch rate modification of silicon dioxide by ion implantation. The mechanisms of etch rate modification are well understood. The collisions between implanted ions and the nuclei of the silicon dioxide target atoms disorganize the structure of the oxide and break the Si-O bonds. It has been shown that any kind of ions could be implanted to modify the structure of the oxide. Once the structure has been modified it becomes more reactive to HF wet etching solutions. The literature reports selectivity of five between implanted and unimplanted oxide.[3] The etch rate modification depends on the mass of the implanted ions, the implantation dose and the energy. Although this effect is of interest from a scientific point of view, it has mainly been considered as a parasitic effect that makes the etch rate of $SiO_2$ difficult to control. Because of the low etching selectivity ($\sim 5$) between implanted and unimplanted silicon dioxide, the implantation of $SiO_2$ has not been considered for developing patterned sacrificial or etch stop layers. In this paper we demonstrate that the enhancement of the etching selectivity up to a value of more than 200 could be reached using vapor HF instead of wet HF etchant. This result opens new interests in microelectronics and MEMS technology, making implanted oxide a perfect candidate for sacrificial layer or buried mask definition and conjointly unimplanted oxide a good etch stop layer.

## Experimental

3000 Å thermal oxide was grown in wet ambient at 1000°C on 3 in. p-type, ⟨100⟩ oriented silicon wafers. The oxide thickness was accurately measured by ellipsometry. A photolithography was done before the implantation defining implanted and unimplanted zones. Boron, phosphorus, argon and arsenic were implanted at different energies and doses in the oxide layer through the photoresist mask. The samples were cleaned in $H_2O_2/H_2SO_4$ solution and diced in 1 $cm^2$ pieces. The wet HF etching was done in 3% HF solution diluted in deionized (DI) water. The vapor HF etching was performed on a GEMETEC PAD-Fume, commercially available system for wafer cleaning that was adapted according to custom specifications to enable stiction-free surface micromachining. The gas flow (nitrogen bubbling through a 49% HF solution) was 1 L/min and the temperature was 38°C. Etchings were performed during time periods of 2 or 5 min, depending on the etch rate of the implanted oxide. The remaining thicknesses after etching of implanted and unimplanted oxide were measured by ellipsometry.

## Results and Discussion

*Wet etching*.— Previous studies[1-3] have shown that implanted oxide layer could be etched in buffered HF (BHF) or in diluted HF up till five times faster than unimplanted oxide. The enhancement of the etching rate is due to the higher reactivity of the Si-O bonds of oxide broken by the implantation. In our experiments, a 3000 Å thick oxide layer has been implanted by argon at an energy of 160 keV and a dose of $2 \cdot 10^{14}$ atom/$cm^2$. The etch rate in HF 3% was measured in function of the depth in the oxide layer measured from its top surface. Figure 1 superposes the argon concentration and the etching rate in function of oxide depth. Ar concentration was calculated with the software SRIM.[4] This simulation tool is based on an ion transport code that calculates quantities such as stopping and range of ions using a quantum mechanical treatment of ion-material collisions.

From the surface of the oxide layer to a depth of 2000 Å the etch rate has a constant value of 300 Å/min. From 2000 to 2600 Å, the etch rate drops abruptly to reach a value of 100 Å/min. The argon concentration, plotted in logarithmic scale, is roughly $1 \cdot 10^{17}$ atom/$cm^2$ close to the surface, and reaches a maximum of $1 \cdot 10^{19}$ atom/$cm^2$ around a depth of 1900 Å. From 2600 Å the argon concentration is still rather high at a value of $2 \cdot 10^{18}$ atom/$cm^2$ It is thus clear that there is no direct correlation between the argon concentration and the etch rate modification. Actually, Hiraiwa et al.[2] reported that the enhancement of the etch rate is due to the destruction of the Si-O bonds of the silicon dioxide. When an ion penetrates a material, it undergoes in collision with the atoms of the target until it loses its total amount of energy. Energy loss proceeds through collisions[5] with the nuclei (elastic process) and with the electron shell (inelastic process). Energy loss through collisions with nuclei depends on ions energy whether energy loss through collisions with electron shell depends on ion velocity. Thus, electronic energy loss dominates the stopping of an implanted ion at high ion energies (higher than roughly 1 keV per atomic mass unit). However, at low ion energy, or when the ion has slowed down sufficiently, nuclear energy loss becomes significant. As the destruction of the Si-O bonds is due only to target nuclei displacement, we consider as relevant parameter only the nuclear energy loss. To calculate the nuclear energy loss we performed simulations using the SRIM.[4] code. SRIM models collisions between ions and target nuclei using the Ziegler-Biersack-Littmark (ZBL) screened Coulomb potential, including electron shell effects and long-range interactions such as plasmons. We were able to simulate the nuclear energy loss per ion in function of the depth in the sample. The total damage that suffers the target is characterized by the nuclear deposited energy $E_n$ given by

$$E_n = \eta_n \cdot D \quad [1]$$

where $\eta_n$ is the nuclear energy loss and $D$ the implanted dose.

Figure 2 plots the nuclear deposited energy and the etch rate for as implanted and annealed samples in function of the depth into the $SiO_2$ layer. The nuclear deposited energy has a constant value of $8 \cdot 10^{23}$ eV/$cm^2$ from the surface to a depth of 1600 Å and then decreases logarithmically. The nuclear deposited energy and the etch rate curves of the as implanted sample perfectly superpose to each other. This result demonstrates that the destruction of the Si-O

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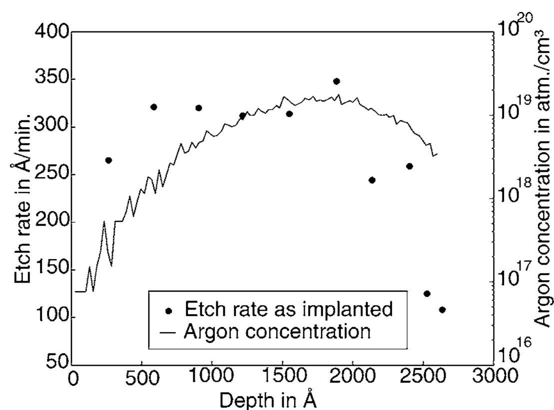


**Figure 1.** Etch rate in Å/min and argon concentration in atom/cm$^2$ vs depth in Å. The etching is performed in 3% aqueous HF.

bonds, characterized by the nuclear deposited energy is the mechanism responsible for the enhancement of the etching rate.

To check the validity of this hypothesis, the Ar implanted sample was annealed at 1000°C under a nitrogen flow of 1.5 L/min for 40 min. The plot of the measured etch rate after annealing does not show any dependence in function of the depth and the etch rate value is 80 Å/min, similar to the value obtained for unimplanted oxide. The annealing step of the implanted oxide samples reconstructs the Si-O bonds and the etching selectivity of four that was obtained between implanted and unimplanted oxide is lost.

As the etch rate of oxide is influenced by the amount of destructed Si-O bonds and not by the nature of the implanted ions, other species than argon, such as boron, phosphorus and arsenic were tested. SRIM simulations were performed to choose couples of dose and implantation energy for each species to get a constant nuclear deposited energy over the oxide film thickness. Six samples of each species were implanted at various doses to cover the nuclear deposited energy range from $1 \times 10^{22}$ to $1 \times 10^{26}$ eV/cm$^2$.

Table I gives the doses and energies at which were performed the implantations.

Figure 3 plots the nuclear energy loss for implantations of boron, phosphorus, argon and arsenic simulated with SRIM. After etching, the remaining oxide thickness was measured to check if the etched oxide had been implanted by comparing with the implantation range of Fig. 3.

Note that the lighter the ion is, the lower the nuclear energy loss is, thus the higher must the dose be to reach the same nuclear deposited energy. Lighter ions penetrates deeper in the oxide layer. In the case of phosphorus, argon, and arsenic, ~50% of the incident ion energy is dissipated through collisions with the target nuclei. The difference in nuclear energy loss is at first linked to the difference in incident ion mass. In the case of boron, for this range of implantation energy, the energy loss process through nuclear collision represents only 15% of the incident energy, which makes damage creation less efficient than with heavier ions, and it must be compensated for by increased dose.

**Table I. Implantation conditions for boron, phosphorus, arsenic, and argon.**

| Implanted species | Energy | Total Dose |
|---|---|---|
| Boron | 23% at 20 keV<br>77% at 90 keV | $1.8\times10^{13}$/cm$^2$ to $1.8\times10^{17}$/cm$^2$ |
| phosphorus | 16% at 50 keV<br>84% at 150 keV | $2.4\times10^{12}$/cm$^2$ to $4\times10^{16}$/cm$^2$ |
| Argon | 18% at 50 keV<br>82% at 150 keV | $1.9\times10^{12}$/cm$^2$ to $1.9\times10^{16}$/cm$^2$ |
| Arsenic | 100% at 150 keV | $7.7\times10^{11}$/cm$^2$ to $7.7\times10^{15}$/cm$^2$ |

Figure 4 plots the etch rate of oxide in HF 3% in function of the nuclear deposited energy for different implanted species. All of the measured etch rates presented in the graph are for points taken in the depth range where the nuclear deposited energy is constant. Figure 4 confirms that the type of implanted species has no influence on the etch rate. The only parameter to consider is the nuclear deposited energy. A nuclear deposited energy lower than $1 \times 10^{23}$ eV/cm$^2$ does not change the etch rate of oxide in HF 3%, i.e., 80 Å/min. Above $3 \times 10^{24}$ eV/cm$^2$, the etch rate saturates at an average value of 320 Å/min. Garrido et al.[6] have shown that not more than 15.5% of the Si-O bonds can be broken. Indeed, they demonstrated that above a certain concentration of nuclear deposited energy a steady state occurs between formation and breaking of Si-O bonds. The etch rate of implanted oxide can be enhanced by a factor 4 when etched in HF 3% whatever the type of implanted species.

*Vapor HF etching*.— Etching of implanted oxide has also been performed in vapor HF. Figure 5 plots the etch rate in function of the nuclear deposited energy for the boron and phosphorus implanted samples.

The increase in etch rate occurs for the same concentration of nuclear deposited energy as in the case of the wet etching, but the etching selectivity between implanted and unimplanted oxide which was around four in the case of wet etching is in the range of 200 for

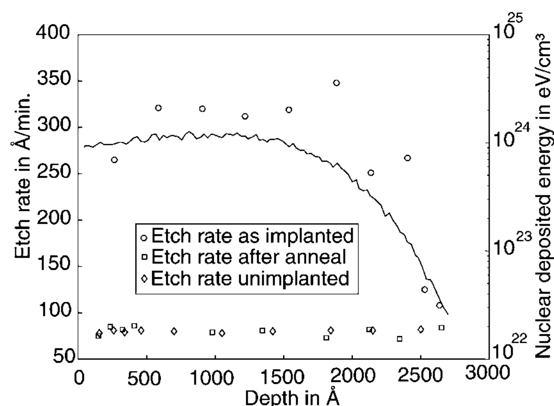


**Figure 2.** Etch rate in Å/min for as implanted and annealed oxide and nuclear deposited energy in eV/cm$^2$ vs depth in Å. The etching was performed in 3% aqueous HF.

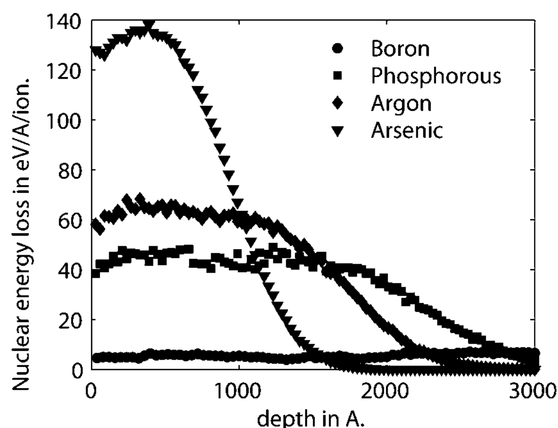


**Figure 3.** Simulated nuclear energy loss for boron, phosphorus, argon, and arsenic implantation in oxide. The implantation conditions are given in Table I.

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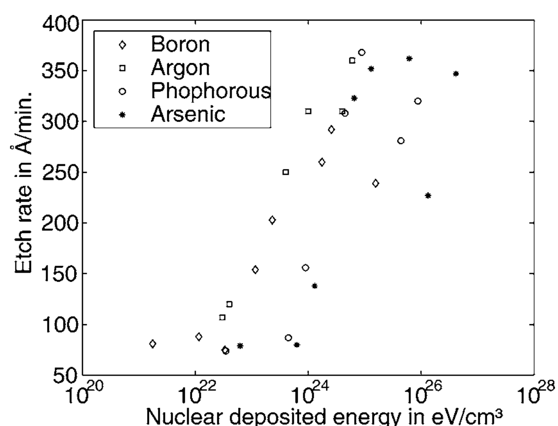



**Figure 4.** Etch rate in function of the nuclear deposited energy for various types of implanted species. The etching is performed in 3% aqueous HF.

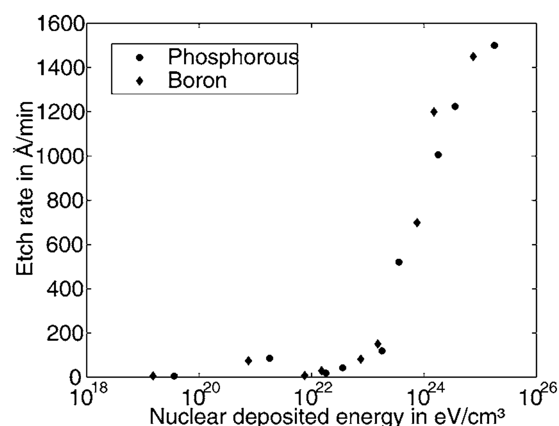



**Figure 5.** Etch rate of implanted oxide in function of the nuclear deposited energy for boron and phosphorus implanted oxide. The etching is performed in vapor HF.

vapor HF etching. The great etching selectivity difference between liquid and vapor HF can be easily explained knowing the etching mechanism of $SiO_2$ by HF.

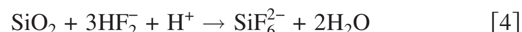
The etching of silicon dioxide in vapor HF has been well described in many publications.[7-9] Water plays a key role in the etching. Its presence is necessary to trigger the reaction. First, HF is decomposed into a $H^+$ ion and a $F^-$ ion thanks to $H_2O$ molecule

$$HF + H_2O \rightarrow F^- + H^+ \sim H_2O \quad [2]$$

The fluorine ion binds to HF

$$HF + F^- \rightarrow HF_2^- \quad [3]$$

$HF_2^-$ is the ion responsible for the oxide etching



$$SiO_2 + 3HF_2^- + H^+ \rightarrow SiF_6^{2-} + 2H_2O \quad [4]$$

The reaction produces water and fluosilicic acid. The fluosilicic acid undergoes the following reaction

$$2H^+ + SiF_6^{2-} \rightarrow H_2SiF_6 \quad [5]$$

$$H_2SiF_6 \rightarrow 2HF + SiF_4 \quad [6]$$

The $SiF_4$ evaporates and HF is re-used by the reaction.

Fluosilicic acid can also attack the oxide following the reaction

$$5SiF_6^{2-} + 4H^+ + SiO_2 \rightarrow 3(SiF_6 \times SiF_4)^{2-} + 2H_2O \quad [7]$$

However, $SiF_6^{2-}$ is easily recombined in presence of $H^+$ ions into $H_2SiF_6$ so that the last equation is of minor importance in the etching of silicon dioxide.

As described above, in vapor HF the etching mechanism needs water to initiate the reaction. Condensation must occur on the wafer surface to start the reaction. Once the reaction has started, water is produced by the reaction and immediately re-used for a new reaction cycle enhancing thus the etch rate by avalanche effect. The etch rate strongly depends on the amount of water produced by the etching. In the case of the wet etching, the quantity of water as product of the reaction is negligible in comparison to the water quantity of the solution and is immediately dissolved and therefore does not influence the kinetic of the reaction. The etch rate mainly depends on the HF, $HF_2^-$, and broken bonds concentration, but not on the reaction by-products. In the case of vapor etching, water is the limiting factor of the reaction kinetic. Water from the 49% HF solution condenses on the surface and initiate the reaction, but after a transition step the main origin of the water is as a reaction byproducts. The avalanche effect will thus be multiplied by the higher reactivity of the oxide due to the presence of broken bonds and the fact that more water is produced in the damaged zone than in the nonimplanted oxide. Selectivity of 200 can thus be achieved.

## Conclusion

The etch rate increase of implanted oxide has been verified in diluted HF for various implanted species. The parameter which controls the etch rate is the nuclear deposited energy, $E_n$ which depends on the atoms of the target, the mass and the dose of the implanted ions. For a nuclear-deposited energy lower than $1 \cdot 10^{23}$ eV/cm$^2$, the etch rate is not modified and for a nuclear-deposited energy larger than $3 \cdot 10^{24}$ eV/cm$^2$, the etch rate reaches its maximum value. Light or heavy ions can both be implanted. Heavy ions will have a shallow penetration while the light ions will penetrate deeper in the film. To reach the same level of nuclear deposited energy, higher dose must be considered for light ions as their nuclear energy loss is lower than for heavy ions. In the case of implantation through a silicon film, silicon or argon can be implanted to avoid contamination. The use of vapor HF etching instead of diluted HF increases the selectivity from 4 to 200. The dissolution of silicon dioxide in HF is an autocatalytic reaction which only requires water to be initiated. In vapor HF etching, the water produced by the reaction will be preponderant to the total amount of water taking part to the reaction yielding to an avalanche effect and a drastic increase of the etch rate. This very high selectivity opens very promising applications such as buried mask patterning in oxide and definition of sacrificial layers.

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## References


1. C. Dominguez, B. Garrido, J. Montserrat, J. R. Morante, and J. Samitier, *Nucl. Instrum. Methods Phys. Res. B*, **80-81**, 1367 (1993).
2. A. Hiraiwa, H. Usui, and K. Yagi, *Appl. Phys. Lett.*, **54**, 1106 (1989).
3. L. Liu, K. L. Pey, and P. Foo, *Tech. Dig. - Int. Electron Devices Meet.*, **1996** 17.
4. http:// www.srim.org
5. J. F. Ziegler, *The Stopping and Range of Ions in Solids*, Pergamon Press, Elmsford, NY (1985).
6. B. Garrido, J. Samitier, S. Bota, C. Dominguez, J. Montserrat, and J. R. Morante, *J. Non-Cryst. Solids*, **187**, 101 (1995).
7. D. F. Westonand and R. J. Mattox, *J. Vac. Sci. Technol.*, **1**, 466 (1980).
8. P. J. Holmes and J. E. Snell, *Microelectron. Reliab.*, **5**, 337 (1966).
9. C. R. Helms and B. E. Deal, *J. Vac. Sci. Technol. A*, **10**, 775 (1992).


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