Thin Gate Oxides over Nitrogen Implanted Silicon

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Abstract- Here we study the effects of implanting nitrogen (N^+) into the substrate prior to thermal oxidation. We found that for implant doses higher than $1x10^{14}$ /cm^2 the oxidation rate is reduced between 10% and 75%. Also, the oxide thickness uniformity across the substrates was found to be degraded after the implantation, even though better uniformity was expected. Oxide characterization will be performed to compare the implanted areas to bare Si regions. The reported benefits of incorporating nitrogen into Si make this an interesting study for future generations of gate oxides.

I. INTRODUCTION

As VLSI devices continue to be scaled-down in size, they require thinner gate oxides. These are expected to be about 40-45Å in less than fifteen years.

Recent studies show that direct thermal nitridation of Si and thin SiO2 appears to be a viable alternative method of growing a good quality dielectric film in this very thin regime. [1]

Thermally grown films of silicon-nitride have a number of advantages over SiO2, including: a) they tend to have self-limiting growth kinetics and therefore their thickness is easily controllable; and b) they are effective barriers to impurity diffusion [1]. Furthermore, incorporating nitrogen in gate oxides has been shown to improve the hot-carrier resistance of submicrometer MOSFET's. Previously, silicon nitride and silicon dioxide layers have been prepared by implanting large doses (10^{16}/cm^2 to $2x10^{18}$/cm^2) of nitrogen or oxygen into Si substrates. However, due to damages in the Si substrates, the nitride or oxide layers could not be used as MOS dielectrics.

Recently it was discovered that light N^+ doses of $5x10^{13}$ – $5x10^{14}$/cm^2 were enough to reduce oxidation rates [2].

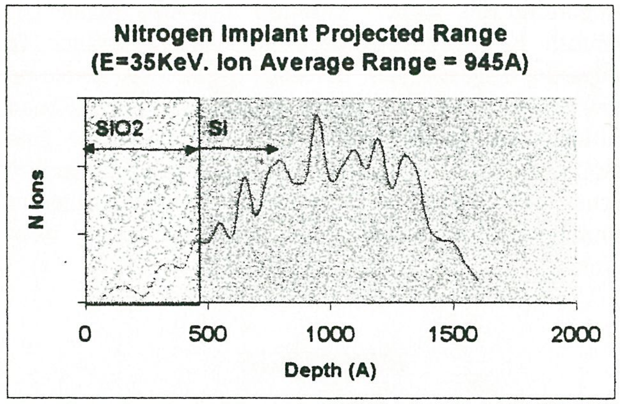

Figure 1. - Projected range for nitrogen with 400A screen oxide, and 35keV implant energy.

II. EXPERIMENTAL RESULTS

Nitrogen was implanted into the (100) p-type Si substrates at 35KeV through a 400Å screen oxide. This oxide was grown in a dry O_2 ambient (5 lpm) at 1000°C for 25 minutes. Figure 1 shows the projected range of the nitrogen as simulated by SRIM. The nitrogen was expected to be close to the Si surface. In this case the simulations shows the peak of the implant to be at about 500Å below the surface.

The implantation step was performed as follows: first, half of the Si substrates was covered with photoresist and a dose of nitrogen was implanted; second, the photoresist was removed and the wafers went through a blanket implant. By doing this we have to different doses on the same substrate. These doses were 0, $2x10^{13}$, $5x10^{14}$, and $9x10^{14}$ /cm^2.

Once the implantation step was complete the screen oxide was removed in BOE (Buffered Oxide Etch) for one minute. Then a standard RCA clean was performed, and finally a quick HF dip for 20 seconds prior to thermal oxidation.

At the same time the oxidation furnace was being prepared, and a trichloroethane (TCA) clean with a subsequent nitrogen purge was performed. Then the substrates were introduced, and the oxidation took place

at two temperatures (975 or 1050°C), for three possible soaking times (15, 30 or 120 minutes).

The oxide thickness was then measured by ellipsometry (λ=632.8 nm) on 40 sites of half of each Si wafer.

TABLE I. - OXIDE THICKNESS FOR VARIOUS NITROGEN DOSES AT 975C

	15 min	*30 min*	*120 min*	*Rate Reduction*
0	172	274	656	Reference
$2x10^{13}$	169	274	659	1%
$1.1x10^{14}$	155	246	629	8%
$4x10^{14}$	83	160	554	45%
$9x10^{14}$	37	43	269	75%

Table 1 shows the average oxidation rate reduction for several nitrogen doses at 975°C. It can be observed the increase in the reduction rate with an increase of implant dose. The results are also illustrated on Figure 2.

When we plot the oxidation rate versus the thickness, Figure 3, it can be observed that for doses below $1x10^{14}/cm^2$ the oxidation rate remains the same. At higher doses the initial oxidation rate is reduced compared to bare Si, and tends to remain almost constant. Thinner oxide growth would be easier to control because of this. Also, a shift to the left can be observed in Figure 3, as the dose is increased. This indicates the formation of thinner oxides after same oxidation times for different nitrogen doses.

Uniformity across the samples was measured as shown on Figure 4. This is based on 40 sites across half of a 4" Si wafer. The graph shows that there is an unexpected increase in oxide thickness difference for higher doses of nitrogen. Previous work in this area had demonstrated an improvement on uniformity, so we think that the non-uniformity effect observed in our case could be due to the implantation profile. If the nitrogen is not evenly distributed across the sample, only certain areas would show a retardation on the oxidation growth.

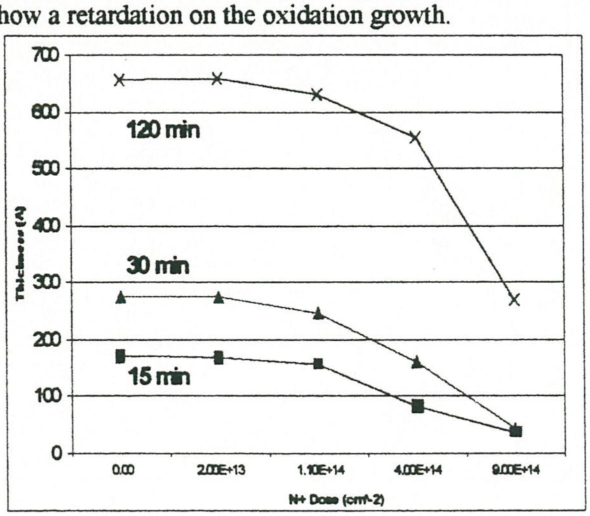

Figure 2. – Oxide thickness as a function of implant dose for 15, 30 and 120 min oxidation at 975°C.

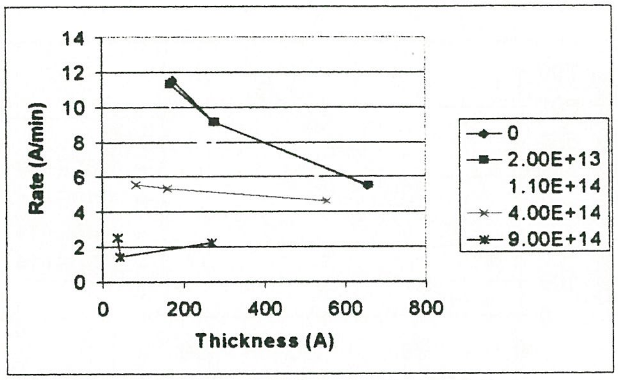

Figure 3. - Oxidation rate as a function of oxide thickness (T=975C).

If we take a look at the oxide thickness as a function of the oxidation time for a fixed oxidation temperature, as in Figure 5, we can extract a relationship for this particular temperature and predict the oxidation growth for different nitrogen doses:

$$X = a\,t^{b}$$

Where X is oxide thickness, and t is soak time.

TABLE II. CONSTANT VALUES DETERMINED FROM FIGURE 5.

	0	*$2x10^{13}$*	*$1.10x10^{14}$*	*$4x10^{14}$*	*$9x10^{14}$*
a	30.631	29.313	24.915	7.0763	1.9677
b	0.6407	0.6515	0.6742	0.9119	1.0041

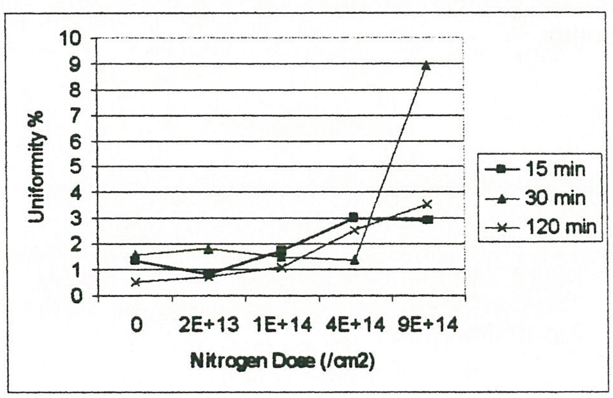

Figure 4. – Uniformity variation as a function of nitrogen dose for different oxidation times at 975°C.

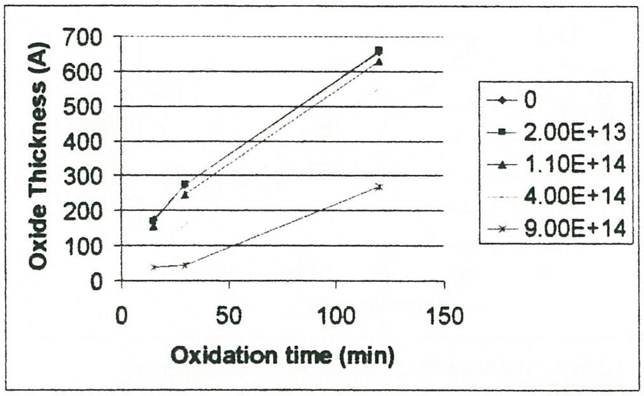

Figure 5. - Oxide thickness as a function of oxidation time (T = 975 ° C).

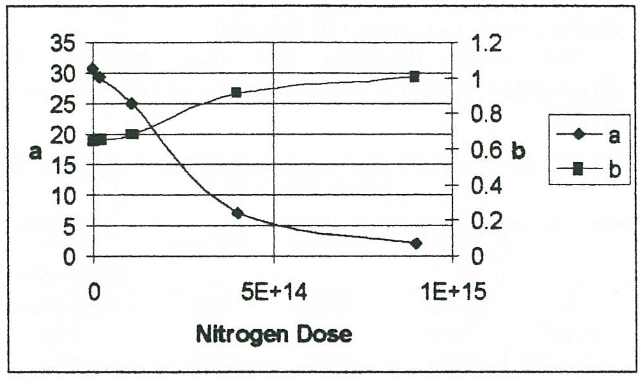

Figure 6. - Constants a and b for oxidation growth prediction at T=975°C. (See Table II).

III. Summary

Oxidation rate reduction for thermal oxidation was observed with the incorporation of nitrogen into the substrates prior to the oxidation step. The nitrogen was implanted 500Å below the Si surface, and it was incorporated into the oxide. The oxide thickness uniformity was degraded as a result of the implant. The implant profile is suspected to be responsible for this non-uniformity.

At last a relationship between oxidation time and temperature was calculated to predict oxide thickness for different nitrogen doses.

ACKNOWLEDGEMENTS

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