Interactions of Fluorine Redistribution and Nitrogen Incorporation with Boron Diffusion in Silicon Dioxide

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Abstract— **This work investigates the effect of composition of gate dielectric on boron diffusion. Gate oxides were grown with nitrogen contents varying from 0 to 1.4%. A series of SIMS measurement were carried out to measure the depth profile of incorporated nitrogen and fluorine. Capacitance voltage measurements were used to determine the amount of boron penetration. Also, to better understand the role of fluorine, experiments were carried out to investigate the redistribution of fluorine in the poly/SiO_2/Si system. Finally a model is proposed that accounts for diffusion of boron as a function of local impurity concentration in gate dielectric.**

I. Introduction

Advanced metal-oxide-semiconductor field effect transistors (MOSFETS) need gate oxides which are less than 80nm thick. In the fabrication of p^+-polysilicon gate, a major concern is the diffusion of boron through gate oxides. Boron penetration from the p^+-polysilicon gate can cause fluctuations in flat band voltage (V_{FB}) [1] which is accompanied by increases in electron charge trapping and inverse subthreshold slope [2].

The diffusivity of boron can be modified by many factors. Increased boron diffusivity is observed when fluorine or hydrogen is introduced in the oxide [3]. In contrast, incorporation of nitrogen in SiO_2 layers is known [4], [5] to reduce boron diffusivity in the SiO_2.

In order to help address these issues we have conducted a set of experiments where both boron diffusivity as well as the composition of oxide were studied.

II. Experimental Procedure

MOS capacitors were fabricated on 4″ (100) silicon wafers, with background phosphorus doping of 2-4 Ω-cm. A field oxide of 0.6μm was grown and etched to define active areas (100×100 μm^2). Gate dielectrics were grown at 870 and 910°C in pure O_2, pure N_2O or an N_2O/O_2 mixture. Undoped polysilicon was deposited at 625°C following gate dielectric growth. The polysilicon was implanted to a dose of 5×10^{15} cm^{-2}, using P^+ at 40 keV, BF_2 or B^+ at 25 keV. A low temperature cap oxide of 0.5 μm was deposited at 425°C to avoid out diffusion of boron. Wafers were annealed at 950 and 1000°C for various times to insure boron penetration. After removal of cap oxide, gate electrodes were patterned and etched.

Capacitors were evaluated using high frequency capacitance-voltage (C-V) measurements (see Figure 1). In addition, SIMS measurements were carried out to quantify the amount of nitrogen and fluorine incorporation in the gate oxides as well as in the polysilicon and substrate.

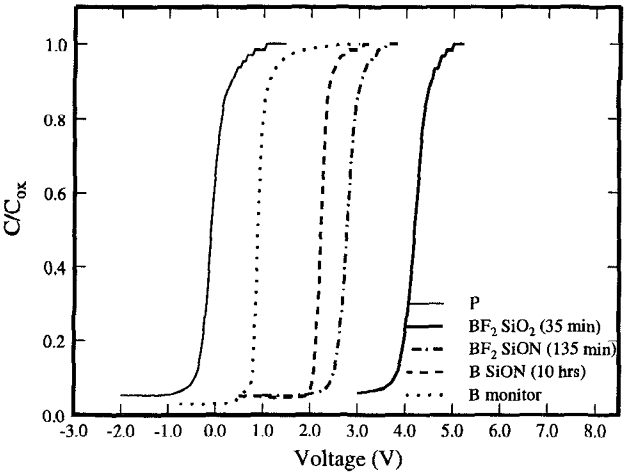

Fig. 1. Capacitor-Voltage measurement results for samples with different gate dielectrics annealed at 950°C

III. Modeling and Results

Figure 2 shows the extracted boron diffusivity versus temperature. Also shown is the extracted diffusivity from Aoyama [3]. It may be noted that boron diffusivities reported in this work agree very well with data obtained from Aoyama. The diffusivity parameters in this work were extracted by optimizing the boron diffusivity in oxide in a SUPREMIV simulation which was then fed into PISCES to simulate the CV curves obtained experimentally. Diffusivity of boron depends strongly on the composition of gate dielectric. When fluorine is present in the oxide the diffusivity of boron is enhanced (only 35 min. anneal is require for boron penetration at 950°C).

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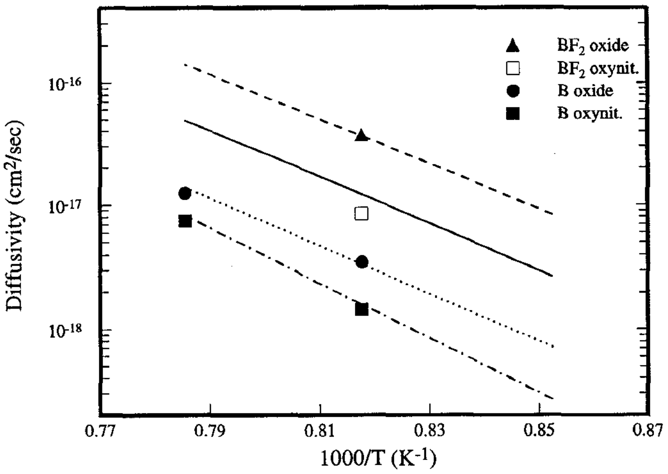

Fig. 2. Extracted boron diffusivity as function of temperature compared to data from Aoyama [3].

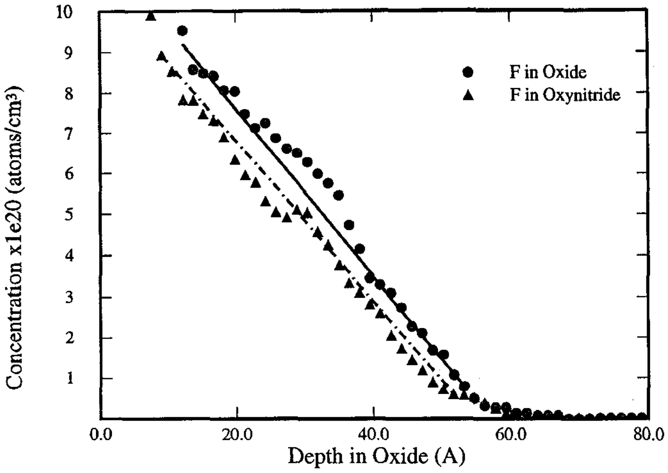

Fig. 4. Comparison of incorporated F in gate dielectric grown in pure O_2 and N_2O, both annealed at 950°C.

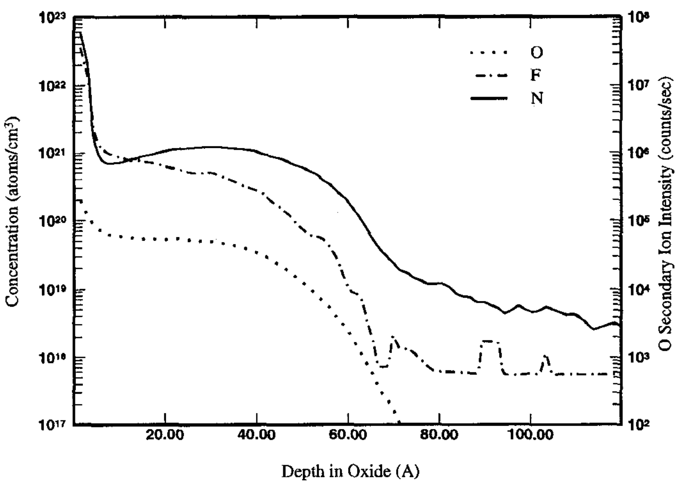

Fig. 3. SIMS profiles of nitrogen, fluorine and oxygen in oxynitride annealed for 120 minutes in N_2 at 950°C.

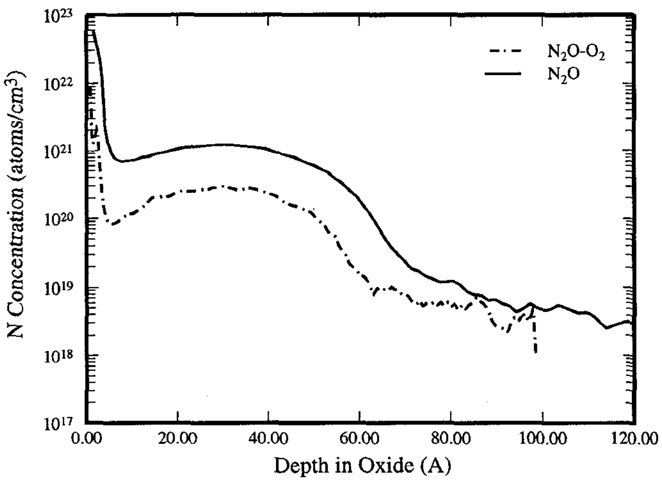

Fig. 5. Incorporated nitrogen concentration in the oxide for dielectric grown in pure N_2O and 20% N_2O/O_2.

However, when sufficient amount of nitrogen is incorporate in the gate dielectric boron diffusivity is reduced (the samples were annealed for 10 h to insure boron penetration).

SIMS profiles of fluorine and nitrogen in the oxide were measured for the same samples. Figure 3 shows an example for an N_2O grown oxide with a $5 \times 10^{15}\text{cm}^{-2}$ BF_2 implant in the polysilicon. While the nitrogen concentration is relatively uniform throughout the film, the fluorine shows a linear behavior (see Figure 4), suggesting that fluorine is diffusing through the thin dielectric to the substrate. This linear behavior is also seen for dielectrics grown in a pure O_2 ambient. Figure 4 shows a comparison of fluorine profile in oxides grown in 100% O_2 versus dielectrics grown in 100% N_2O. It can be observed that oxide grown in an N_2O ambient appeared to incorporate a lower level of fluorine. This behavior can be attributed to a difference in segregation of fluorine to oxides vs oxynitrides.

To investigate the effect of nitrogen incorporation on boron diffusivity, we fabricated gate dielectrics with different amounts of incorporated nitrogen. Figure 5 shows the comparison of two gate dielectrics grown in 100% N_2O and 20/80% N_2O/O_2.

The corresponding percent nitrogen content for the samples are 1.4% and 0.2% respectively. Extraction of boron diffusivity for these samples showed that a certain amount of nitrogen incorporation (on the order of 1% or more) is required to significantly reduce boron penetration compared to that of a oxide grown in pure O_2. The extracted boron diffusivity as a function of nitrogen content is shown in Figure 6. Close inspection of Figure 6 reveals that the effect of nitrogen is more pronounced when fluorine is present in the system. In the case of BF_2 implants the boron diffusivity in oxynitride is reduced by a factor of 4.3 compare to that of oxide grown in pure O_2, while when boron is implanted in polysilicon, this factor is only 2.4 times.

Although B diffusion is expected to depend locally on the oxide structure and composition, modeling to date has been generally limited to determining an effective average diffusivity as a function of processing conditions [5], [7].

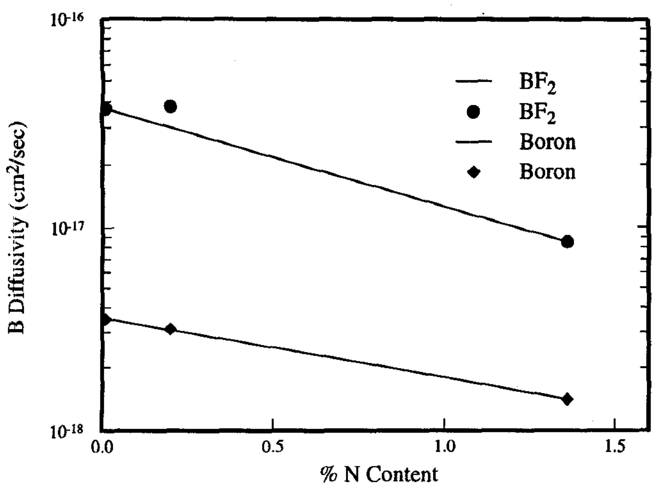

Fig. 6. Comparison of Boron Diffusivity in gate dielectric as a function of nitrogen content. Samples are annealed at 950°C

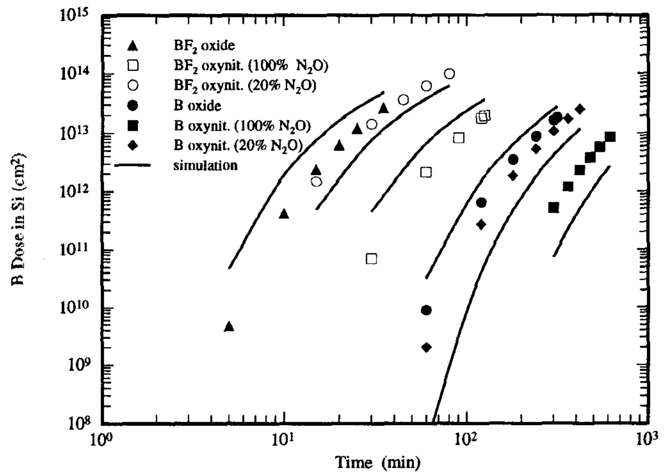

Fig. 7. Comparison on simulation vs data of penetrated boron dose in Si vs time for various processing conditions (all anneals at 950°C)

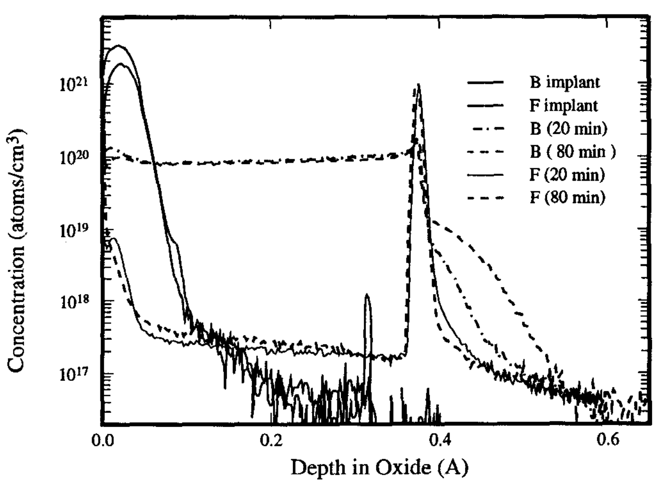

Fig. 8. SIMS profile of boron and fluorine in poly/SiO_2/Si system for 20 and 80 minutes anneal at 950°C.

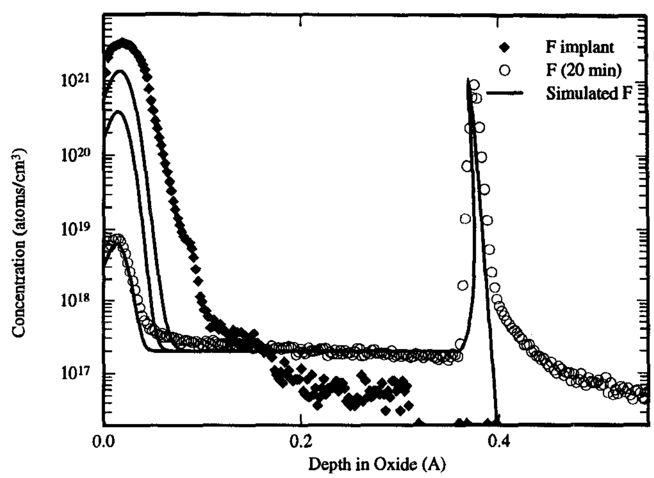

Fig. 9. Comparison of model for fluorine redistribution with SIMS data of oxide grown in 100% O_2 and BF_2 implanted polysilicon annealed for 20 min at 950°C.

To generate a predictive model, it is necessary to consider the underlying oxide composition and structure that gives the observed diffusivity.

Due to the high solubility and low diffusivity of boron in the oxide, one can model the system in terms of continuity equations:

$$\frac{\partial C_{\mathrm{B}}}{\partial t} = \frac{\partial}{\partial x} D_{\mathrm{B}} \frac{\partial C_{\mathrm{B}}}{\partial x} \tag{1}$$

where C_{B} is boron concentration and D_{B} is boron diffusivity in the oxide. Boron diffusivity is then modeled as a function of local composition and structure.

$$D_B(N,F) = D_{B0}\frac{(1+\alpha C_F)}{(1+\beta C_N)} \tag{2}$$

where D_{B0} is the diffusivity of boron in oxide grown in pure O_2 and C_F and C_N are the concentration of fluorine and nitrogen in oxide.

Figure 7 shows penetrated boron dose, extracted from shift of flat band voltage (V_{FB}) versus anneal time (boron dose of 2.6×10^{13} gives a V_{FB} shift of about 3V for an oxide of 55Å) . Also shown is the result of above simulation for the same conditions. The extracted parameters for above model are $\alpha = 7.3\times10^{-20}$ cm³, β=5.4×10^{-21} cm³ and D_{B0} =4.4×10^{-18} cm²/sec.

It is also known [10] that fluorine has a low solubility and very fast diffusion in both silicon and polysilicon and segregates strongly to oxides. The fluorine distribution in oxide is determined by the concentration in the poly combined with the interface segregation. To investigate the redistribution of fluorine in the poly/SiO_2/Si system, we carried out experiments where implanted BF_2 in the polysilicon are annealed for 20 and 80 minutes. SIMS profiles of fluorine and boron are shown in Figure 8. To account for the fluorine behavior we modeled F redistribution in poly/SiO_2/Si by assuming a fast diffusion of F in both polysilicon and silicon. We implemented a one moment clustering model [11] for fluorine diffusion in polysilicon. When fluorine concentration is larger than the solid

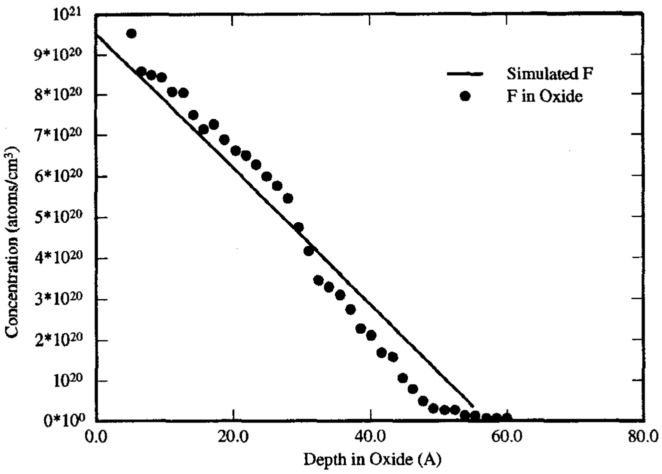

Fig. 10. Comparison of simulated fluorine with SIMS data in oxide grown in 100% O_2 and BF_2 implanted polysilicon annealed for 20 min.

solubility limit (2×10^{17}) clusters form and grow. When fluorine concentration is below the solid solubility clusters dissolve and diffuse. Fluorine profile in oxide is determined by diffusion and segregation at both interfaces. Figure 9 shows the simulation result in polysilicon compare to SIMS data. Figure 10 shows the profile of fluorine in oxide for the same simulation.

The shortcoming of above model is that it predicts a fast dissolution of aggregated fluorine in polysilicon. However, close inspection of Figure 8 shows that even after 80min anneal the fluorine aggregates are still present. One may conclude that a ripening model should be implemented to account for this behavior.

IV. Conclusions

To investigate the role of fluorine and nitrogen, we conducted a series of experiments using both B and BF_2 implanted into polysilicon and diffused through dielectrics grown in pure O_2, pure N_2O and N_2O/O_2 ambient. The extracted boron diffusivities were measured via threshold voltage shifts. SIMS analysis were performed to obtain the profiles of fluorine and nitrogen in the dielectric for the same samples. The results show that significant amount of incorporated nitrogen (order of 1% or more) is required to significantly reduce boron diffusion in the gate dielectric.

To account for the experimental data we presented a model where boron diffusion in oxide depends on the local incorporated impurity concentration. The model parameters (α and β) are optimized using data extracted from Capacitor-Voltage measurements.

We have also investigated the role of fluorine redistribution in the poly/SiO_2/Si system. Although nitrogen incorporation is fairly uniform in the gate dielectric, the profile of fluorine shows a linear behavior. This suggests that fluorine diffuses though the gate oxide. Its distribution in the oxide depends on the segregation from poly to oxide and it concentration in the poly. We proposed a one moment clustering model for diffusion of fluorine in polysilicon and compared results with experimental data.

A. References

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