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Stacking Fault Growth Kinetics during Thermal Oxidation of Silicon in N_2O at High Temperatures and Pressures

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An experimental study for the growth of oxidation-induced stacking faults (OISFs) during silicon oxidation in N_2O at high temperatures and pressures was developed. As the oxidation temperature increases, the OISF length increases, and as the pressure increases, the length diminishes. These dependences upon temperature and pressure are different from those for oxidation in O_2. The most important difference is associated to the faults reduction when the gas partial pressure is increased, which is an opposite behavior to the one observed during O_2 silicon oxidation. These differences are explained in terms of the N distribution close to the silicon-oxide interface and also in terms of the N/O ratio within the oxide which should change as a function of temperature and pressure during the N_2O silicon oxidation.

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Due to the continuous scaling of silicon device dimensions for very large scale integrated (VLSI) circuits, the gate dielectric of metal-insulator-semiconductor (MIS) based structures is becoming very thin (below 10 nm). Therefore, new problems may occur due to dopant (boron) penetration and to electron tunneling through the dielectric film, so that new materials with better diffusion barrier properties and higher dielectric constants than SiO_2 are needed.

Ultrathin silicon oxynitrides (SiO_xN_y) exhibit several properties superior to those of conventional thermal O_2 oxides.

1. Suppression of boron penetration from poly-Si gates.
2. The dielectric constant of oxynitrides increases linearly with the percentage of nitrogen in the film from $\varepsilon(SiO_2) = 3.8$ to $\varepsilon(Si_3N_4) = 7.8$.
3. Increased time for dielectric breakdown.
4. Improved hot electron endurance.
5. Reduced interface trap densities due to the accumulation of nitrogen at the Si-oxide interface.

For achieving some of these advantages over SiO_2 films, one of the most used materials is the thermal oxide grown in a N_2O ambient and therefore the knowledge of its properties and the growth kinetics are now very important.

For a better understanding of the growth kinetics of oxides obtained thermally in N_2O, we also need to know more on the kinetics of self-interstitial generation at the silicon-oxide interface during silicon oxidation. One way of observing this is by means of monitoring the growth of oxidation-induced stacking faults (OISFs).[1-3] In a previous work, Tsamis *et al.*[4] have made a study of point defect injection kinetics during N_2O oxidation of silicon in the high-temperature regime, but they have not determined a complete predictive model for this. Therefore, in this work we develop an empirical model for the growth of OISFs, taking into account the influence of temperature and N_2O pressure. Previously, Leroy[5] and other authors[6] obtained a similar model for the kinetics of stacking fault growth during oxidation of Si in a dry O_2 ambient. We show that the behavior for oxidation in N_2O is very different than for oxidation in O_2, due to the greater complexity of the oxidation process in N_2O as compared to oxidation in O_2.

Experimental

Silicon p-type (100) wafers were used. At first, all the wafers were implanted with boron (5×10^{13} cm^{-2}, 80 keV) in order to create nucleation sites where OISF will form. These parameters were selected to have a suitable density of faults for later measurements. Subsequently, all the wafers were oxidized in wet oxygen at 1100°C for 1 h with the aim of increasing the OISF to have an appropriate reference length. A schematic view of our system is shown in Fig. 1. After removing the thermal oxide with a 10% HF solution, the wafers were oxidized in an N_2O ambient with a constant flow rate of 1 slm, for various temperatures (1000-1200°C), various pressures (1-3 atm), and different growth times (1-8 h). The oxide film thickness was measured with an ellipsometer, assuming a bulk SiO_2 layer with a refractive index of 1.465.

For all the samples, the nitrogen-rich oxide (SiO_xN_y) was removed, and a group of six half samples was selected for studying the OISF reduction in a neutral ambient (Ar) at a flow rate of 1 slm at two temperatures (1100 and 1150°C) and various times (1-5 h). The defects in all the samples were revealed with Wright etch[7] and an optical microscope was used in order to measure the OISF lengths, taking an average from at least six measurements per sample.

Results

Transmission electron microscopy (TEM) analysis has shown that OISFs are two-dimensional extrinsic defects lying along the ⟨111⟩ planes and bounded by Frank dislocations.[1] The growth of OISFs consists of two regimes, commonly referred to as the growth and the retrogrowth regimes. During the growth regime, for short oxidations at low temperatures, the OISFs expand with time. During the retrogrowth regime, for long oxidations at high temperatures, the OISFs shrink. The shrinkage of OISFs is also observed when the wafers are annealed in a neutral ambient at high temperatures.[8,9] The shrinkage in both neutral and oxidizing ambients is similar and appears to be controlled by the same mechanism.[6] To explain both the growth and retrogrowth, it is considered that the Frank partial loop bounding the faults acts as a sink or a source of interstitials.

The growth/retrogrowth behavior of the OISF is of the form

$$L = L_o + \Delta L$$
$$\Delta L = \Delta L_G - \Delta L_R \qquad [1]$$

where L is the OISF length obtained after each process, L_o is the reference length from the faults previously grown (in our case it was 13.1 μm in average), ΔL_G is the growth part, and ΔL_R corresponds to the shrinkage part.

Retrogrowth of OISF during annealing in Ar.—For a neutral ambient or when the oxidation rate is small and the interstitial generation is negligible, the interstitial concentration in the bulk returns to

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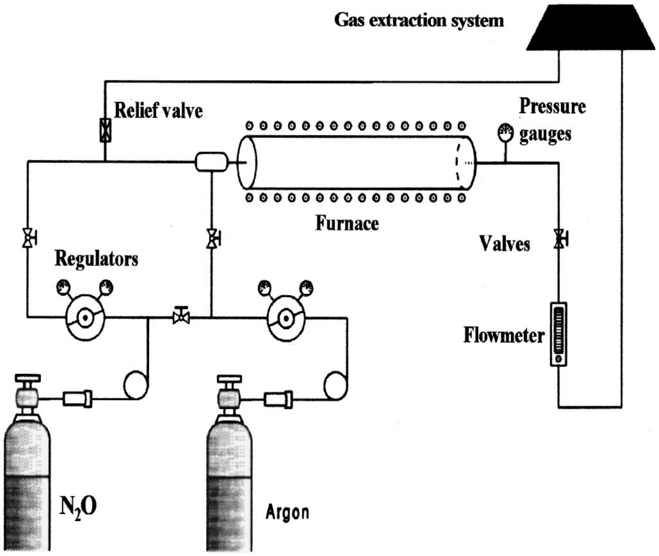

Figure 1. Schematic view of the thermal N_2O silicon oxidation system.

the equilibrium level, which is lower than the interstitial concentration in equilibrium with the faults. The dislocation then acts as a source of interstitials and the interstitials diffuse away from the faults, causing the faults to shrink. As explained previously, the retrogrowth process was measured by annealing in a neutral ambient (Ar), obtaining that the reduction behavior follows a linear dependence with time, as shown in Fig. 2. This behavior is described by

$$\Delta L_R = -C_R t \qquad [2]$$

where C_R depends upon the annealing temperature. When this model is fitted with an Arrhenius temperature dependence, we obtain

$$\Delta L_R = -5.82 \times 10^{17} t \ \exp\left(-\frac{4.8}{kT}\right) \qquad [3]$$

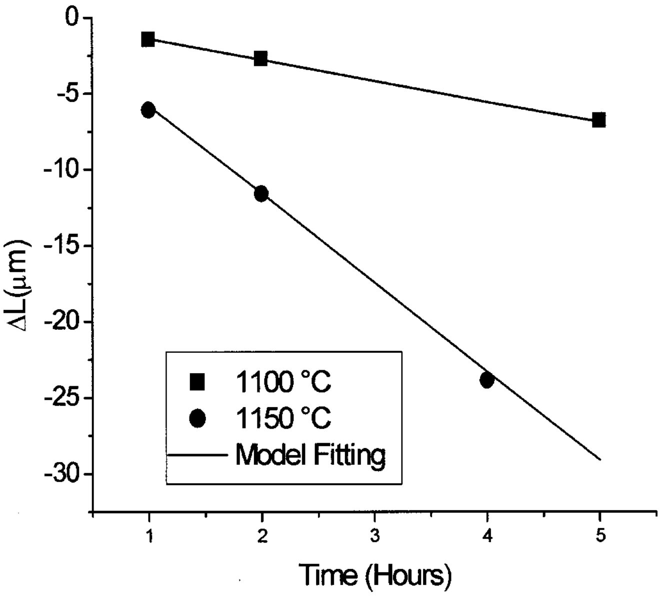

Figure 2. Reduction of stacking faults in silicon in an Ar ambient as a function of time for two different temperatures.

where ΔL_R is in µm, t in h, and kT in eV. This behavior is very similar to what other authors have obtained[6,8,9] with an activation energy in the range 4.78-5.02 eV.

Growth of OISF during oxynitridation in N_2O.—During oxidation, silicon interstitials are produced at the Si-oxide interface and diffuse quickly in the silicon, causing a higher interstitial concentration than the equilibrium concentration surrounding the stacking faults. The partial dislocations, acting as a sink, capture the interstitials within a certain radius and cause the faults to grow.

Figure 3 shows the OISF length as a function of oxidation time

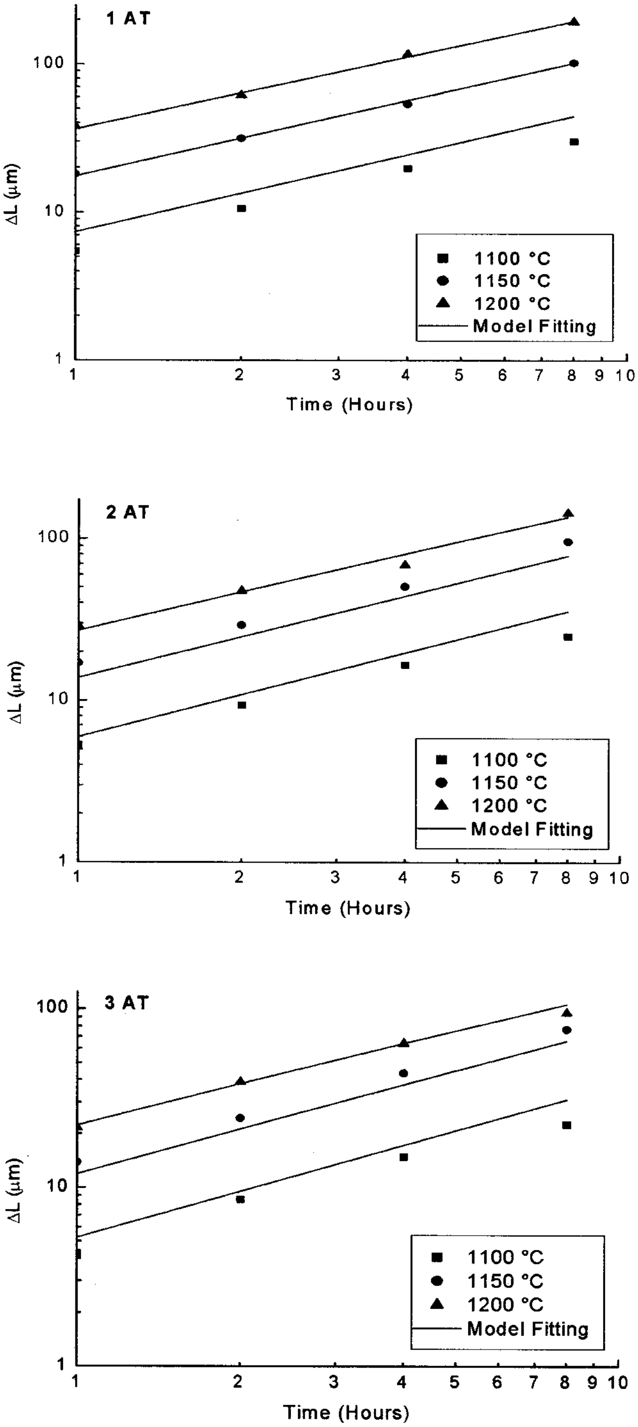

Figure 3. Increase of the OISF length for 1, 2, and 3 atm: (■, ●, ▲) experimental values and (——) the fitted model.

for the different temperatures and pressures used. We notice that the behavior is of the form

$$\Delta L = \alpha t^{\beta} - 5.82 \times 10^{17} t \ \exp\left(-\frac{4.8}{kT}\right) \qquad [4]$$

where β is almost independent of the temperature and pressure of the process, and nearly a constant value of 0.89 was obtained for all the samples. Notice that this value is a little higher than for oxidation in O_2 (0.75-0.8).[5,6] We have assumed that α has a dependence upon temperature and partial pressure of N_2O according to

$$\alpha = \alpha_0 p_{N_2O}^{\eta} \ \exp(-E_{gr}/kT) \qquad [5]$$

where E_{gr} is the activation energy associated to the growth of the stacking faults. When this model is fitted to the experimental data by least squares using a steepest descent method to find the optimum value of α_0, η, and E_{gr} we find

$$\Delta L = 1.2 \times 10^{13} t^{0.89} p_{N_2O}^{-0.25} \ \exp\left(-\frac{3.31}{kT}\right) - 5.82 \times 10^{17} t \ \exp\left(-\frac{4.8}{kT}\right) \qquad [6]$$

where ΔL is in μm, p_{N_2O} is in atm, t in h, and kT in eV. The fitted model to the experimental data is also shown in Fig. 3.

A similar model was obtained by Leroy[5] for the kinetics of OISFs during oxidation of (100)-oriented silicon in O_2

$$R = 3.528 t^{0.75} p_{O_2}^{0.25} \ \exp\left(-\frac{2.5}{kT}\right) - 1 \times 10^{7} t \ \exp\left(-\frac{5.02}{kT}\right) \qquad [7]$$

where R is one half of the OISF length in cm, t is in h, p_{O_2} in atm, and kT is in eV.

Although a similar model is used, the pressure, temperature, and time dependences are found to be different, which indicates that the mechanisms during N_2O and O_2 oxidation are not the same. For both processes the power dependences on time are close: around 0.89 for the N_2O process and 0.75-0.8[5,6] for the O_2 process. However, a big difference is noticed for the pressure and temperature dependences of both oxidation processes. For oxidation in O_2 the OISF length increases with the O_2 partial pressure, but for oxidation in N_2O the length decreases with the partial pressure. Also, the growth activation energy for oxidation in N_2O (3.3 eV) is much larger than for oxidation in O_2 (2.2-2.55 eV).[5,6,10]

Results and Discussion

Notice that the activation energy for the faults growth includes the energy for interstitial generation at the silicon-oxide interface in addition to the interstitial migration energy. From our results we may conclude that the generation energy in our case is different than for silicon oxidation in O_2, since we may assume that the migration energy should be the same in both cases. The difference of 0.8 eV should be related to the different oxidizing species for these two cases. The activation energy corresponding to retrogrowth involves the formation and migration energies of interstitials near the stacking faults. The total activation energy determined here (4.8 eV) is very close to the one obtained by Leroy,[5] *i.e.*, 5.2 eV.

From the distribution profiles of nitrogen through the oxide layer obtained by other researchers,[11,12] it is known that a peak of nitrogen is obtained inside the oxide near the oxide-silicon interface for oxidation in N_2O. In addition, it is known that interstitials generated at the oxide-silicon interface, during the oxidation process, tend either to diffuse into the oxide, reacting with the incoming material, to incorporate to the silicon regrowth at the interface, or to diffuse into the silicon bulk. In comparison with silicon oxidation in O_2,[4] the oxidation rate in N_2O is smaller (3-4 times) because the layer of incorporated nitrogen near the interface reduces the diffusion of the oxidizing molecules (NO,NO_2). In spite of this, a larger interstitial supersaturation is obtained for N_2O than O_2 silicon oxidation, because the nitrided layer at the oxidizing interface acts as a barrier for the diffusion of silicon interstitials back into the oxide, increasing the supersaturation of interstitials at the oxide-silicon interface.

Notice that as the oxidation temperature increases, the faults grow according to the above model. This dependence is due to two reasons: The first one, and the most important, is that at higher temperatures a larger quantity of the oxidizing species incorporates into the interface, generating a higher interstitial concentration. The second one is that at higher temperatures the quantity of nitrogen and oxygen may increase as well as the ratio of nitrogen/oxygen, because a higher NO percentage will be obtained from the N_2O decomposition in the gas phase.[11,12] Therefore, due to the higher quantity of nitrogen in the layer, a higher quantity of interstitials generated at the interface diffuse toward the stacking faults.

Notice also that as the gas pressure increases the faults length diminishes. Here it is proposed that this behavior is due to a smaller nitrogen/oxygen ratio, *i.e.*, the incorporation of oxygen might be favored and the relative nitrogen quantity decreased. This relative reduction of nitrogen may occur because the incorporation of nitrogen into the layer occurs simultaneously with its removal[13] caused by atomic oxygen, according to Carr *et al.*[14] Then, since the nitrogen barrier would be smaller, self-interstitials generated at the interface during the oxidation process should diffuse toward the faults, but also into the oxide, making the faults grow at a lesser extent.

Conclusions

1. We have obtained an experimental model for the growth and retrogrowth of OISFs during silicon oxidation in N_2O, at high temperatures and pressures. It obeys the form $\Delta L = \alpha t^{\beta} - \Delta L_R$, were $\beta \approx 0.89$ remains constant while α varies with both temperature and pressure. The activation energy for this process is 3.31 eV while the dependence upon pressure is of the form $p^{-0.25}$. These values are very different from silicon oxidation in O_2.

2. As the oxidation temperature increases, the OISF length increases due to a higher quantity of oxidizing species incoming into the film and to a larger nitrogen concentration in the film.

3. However, as the pressure increases, the faults length growth diminishes, because the nitrogen/oxygen ratio in the film could be decreasing. In other words, a higher quantity of oxygen and a smaller quantity of nitrogen should be incorporated into the oxide.

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