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Furnace gas-phase chemistry of silicon oxynitridation in N_2O

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During furnace N_2O-based silicon oxynitride growth, the total concentration of NO_x species varies strongly with the flow rate of N_2O. At low flow rates the N_2O decomposes at least partially in the cooler region of the furnace near the gas inlet. This results in lower than expected NO_x $(x=1,2)$ concentrations in the oxidizing ambient. At high flow rates, the exothermic decomposition of N_2O can heat the inlet region of the furnace, resulting in decomposition at a temperature above the nominal furnace temperature and higher than expected NO_x concentrations. These effects can lead to a substantial variation in the concentration of N in the oxynitride as a function of N_2O flow. © *1996 American Institute of Physics.* [S0003-6951(96)05012-X]

The use of N_2O in the growth of gate oxides dates to 1990, when it was discovered that oxidation in N_2O results in the enhancement of electrical properties of metal-oxide-semiconductor field-effect transistors (MOSFETs).[1] This benefit has been linked to the position and bonding state of incorporated nitrogen.[2] X-ray photoelectron spectroscopy (XPS) measurements indicate that when N is incorporated within 20 Å of the interface, it is triply bonded to Si, and appears to be responsible for suppressing latent interface states. N further from the interface, where it is doubly bonded to Si, appears to play no such role. It has also been shown that the presence of N in the oxide is useful in suppressing the indiffusion of B from p^+-polysilicon in p-MOSFET devices.[3]

One of the concerns associated with N_2O furnace growth of gate oxides is the variation of N concentration with the N_2O flow rate.[4] This was recently attributed by Tobin *et al.*,[5] to the influence of reaction (1),

$$2NO+O_2 \leftrightarrow 2NO_2, \tag{1}$$

which results in the gradual conversion of NO, previously produced during the decomposition of N_2O, into NO_2.[4] However, it is well-established that NO_2 dissociates rapidly and completely into NO and O_2 above 600 °C.[5,6] Meaningful amounts of NO_2 will therefore never accumulate in the furnace. Additionally, in the model of Tobin *et al.*,[4] flow rate had a negligable effect on NO_x $(x=1,2)$ concentrations. However, here we present evidence that the total concentration of NO_x species in a furnace oxidation process changes with flow rate. In light of this discovery, we have developed a new model for the furnace gas-phase chemistry of N_2O oxidation, one which leads to the possibility of greater control over nitrogen incorporation.

The basis of this model is an observation by Briner *et al.*,[7] who studied N_2O decomposition in a fundamentally different type of reaction vessel. They found that the amount of NO produced during decomposition increases with temperature. The nature of this effect is not precisely known, as it involves competition between several reaction pathways. This temperature dependence provides a mechanism by which the flow rate can have a direct effect on the NO concentration. At lower flow rates, the N_2O decomposes at least partially in the cool inlet of the furnace, resulting in lower NO concentrations and less N incorporated into the oxide. At higher flow rates, the exothermic decomposition of N_2O can heat the inlet, resulting in greater NO production and an increase in the amount of N incorporated into the oxide. As a test of this model, we have studied the temperature profile and exhaust gas NO_x concentration $(x=1,2)$ as a function of flow rate for a small tube furnace. We have also directly measured the N content in oxides grown at different flow rates in a conventional gate oxidation furnace.

The furnace used in this study was a 1 in. (ID) quartz furnace tube, resistively heated along 15 in. of its length. Although the furnace diameter was obviously much smaller than that typically used for growing gate oxides, the reaction mechanisms involved in N_2O decomposition have been shown to be independent of surface effects.[8] Thus, we anticipate that most of our observations will scale with furnace size. However, we acknowledge that heat dissipation and turbulence effects will not scale with furnace size. We also identify the gas flow velocity, in cm/s at standard temperature and pressure, as the most fundamental measure of flow rate.

In discussing the composition of the oxidation ambient for such a furnace, we note that in most cases the gas residence time is significantly greater than the lifetime of N_2O at the oxidation temperature, estimated at 2 s at 900 °C.[4] From this we can conclude that the oxidation takes place entirely in the decomposition products of N_2O. The first step in this decomposition is the unimolecular dissociation of N_2O, represented in reaction (2). The atomic oxygen generated in this process reacts rapidly through one of the reactions (3)–(7), which with reaction (1) give rise to O_2, NO, and N_2 as decomposition products:[9]

$$N_2O \rightarrow N_2+O, \qquad \Delta H^0=38.3 \text{ kcal/mole}, \tag{2}$$

$$O+O \rightarrow O_2, \tag{3}$$

$$O+N_2O \rightarrow 2NO, \tag{4}$$

$$O+N_2O \rightarrow N_2+O_2, \tag{5}$$

$$O+NO \rightarrow NO_2+h\nu, \tag{6}$$

$$NO_2+N_2O \rightarrow N_2+O_2+NO. \tag{7}$$

Note that the NO_2 generated by reaction (6) decomposes immediately into NO and O_2.[5] The relative amounts of the three decomposition products, N_2, O_2, and NO, depends upon pressure, the presence of inert species, and most importantly the temperature at which the process occurs.[7,10] Since NO is the species responsible for N incorporation into the oxide,[11] and the amount of N incorporated into the oxide can be linked to the growth rate,[12] we can expect both the N content and the growth rate of the oxide to vary directly with the NO/O_2 ratio.

The temperature dependence of the NO concentration, coupled with the short life time of N_2O, raises the possibility that the temperature profile at the gas inlet plays an important role in determining the NO concentration. If the gas heat-up time, i.e., the time required to bring the gas from room temperature to the nominal furnace temperature, is long compared to the lifetime of N_2O at these temperatures, then the NO concentration will be below the expected isothermal value. On the other hand, the exothermic nature of reaction (2) raises the possibility that at sufficiently high flow rates enough heat will be generated in the inlet to raise the gas temperature beyond the nominal furnace temperature, resulting in higher NO concentrations. This exothermic heating phenomenon has been noticed previously.[13]

To examine these possible thermal effects, we measured the NO_x concentrations in the exhaust gas using a technique loosely based on one developed in Ref. 11. We used an evacuated flask to draw a sample of the furnace exhaust gases. We introduced H_2O into the flask, and allowed the system to come to equilibrium. The NO_2 in the exhaust gas underwent a slow oxidation-reduction reaction with the H_2O, resulting in the generation of nitric acid.[14] Since this reaction was complete, the net result was one mole of HNO_3 for each mole of NO or NO_2 in the furnace gas. With a standard volumetric titration we determined the amount of HNO_3 in the flask, and therefore the concentration of NO_x species in the furnace gas. Knowing the amount of NO_x species drawn into the flask, and the total volume of exhaust gas involved, we calculated the NO concentration inside the furnace, assuming that all NO_x species were in the form of NO.

We measured the furnace NO concentrations in this manner at two temperatures, 900 and 1000 °C. We also measured the temperature of different furnace gases as a function of distance into the furnace, by placing a thermocouple in the gas stream. For these temperature profiles, we made measurements for both N_2 and N_2O, to isolate the heating effect of decomposition. As shown in Fig. 1(a), at 1000 °C with N_2O flowing into the furnace, the gas at the inlet was heated by as much as 200 °C above the temperature observed for N_2. We attributed this heating to the exothermic nature of N_2O decomposition. The hot region in Fig. 1, at about 5 cm into the furnace, corresponded to the location of a white flame, visible to the naked eye. We attributed this flame to the chemiluminescence of reaction (6).[9] In Fig. 2, for the same temperature we show the measured NO concentration as a function of flow rate. The concentration varied from 4% NO at the lowest flow velocity, to a maximum of 19% NO at flow velocities above 1.5 cm/s. This was consistent with data from Briner *et al.*,[7] who observed a NO concentration of 5.9% for an isothermal decomposition process at 1000 °C.

We found that the temperature profile at 900 °C differed qualitatively from the profile for 1000 °C, as shown in Fig. 1. The gas inlet was heated by at most 10 °C above the furnace wall temperature, and correspondingly we did not observe chemiluminescence in the furnace tube. This indicated that decomposition took place over a region at least several cm in length. As a consequence of the lack of significant exothermic heating the NO concentration varied over a smaller range, from 2.2% to 4.4%, for a variation in flow velocity of 0.15–2.25 cm/s. This was consistent with a concentration of 2.7% observed by Briner *et al.*,[7] for an isothermal decomposition process.

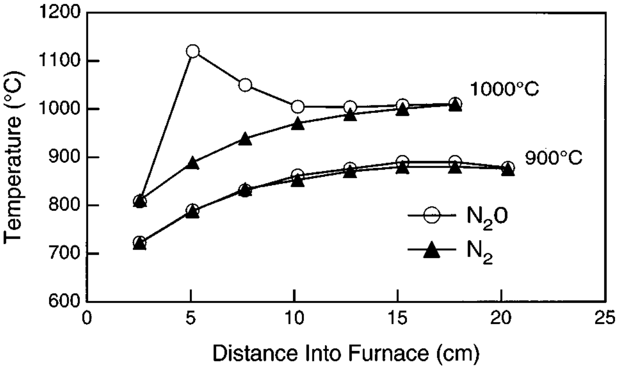

FIG. 1. Temperature profiles for the 1 in. furnace at 900 and 1000 °C. The 1000 °C data were taken at a flow velocity of 1.5 cm/s. The 900 °C data were taken at a flow velocity of 0.65 cm/s.

If we assume that the NO concentrations scale with furnace size, our observations lead to the conclusion that under standard operating conditions we can vary the NO concentration by up to a factor of two. For a standard 3 in. diffusion furnace, flow velocities are typically 0.15–0.6 cm/s, or 1–4 standard liters per minute (SLM). At 1000 °C this corresponds to a NO concentrations of 3.5%–7.5%. At 900 °C, we predict that the NO concentration should change from 2.2%–4%.

To directly examine the consequences of such a variation in NO concentration, we grew a series of gate oxides in a standard 3 in. diffusion furnace. We grew all of the oxides on 3 in. Si⟨100⟩ wafers, following a recipe employed by Saks *et al.*,[15] consisting of a 5 min O_2 step, 30 min N_2O, 30 min O_2, and 30 min N_2O, all at 900 °C. Our motivation for using this particular protocol was to produce oxides with a bimodal nitrogen distribution. We grew three of these oxides, at flow

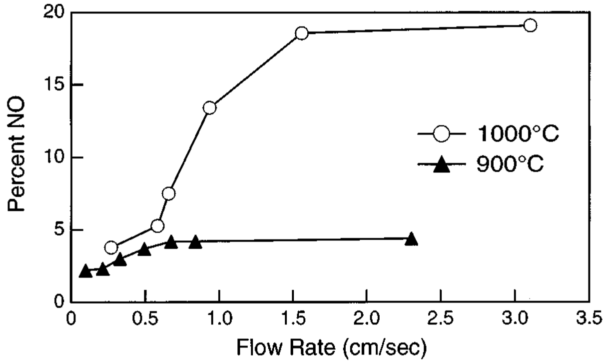

FIG. 2. NO concentration as a function of flow velocity for a 1 in. furnace at 900 and 1000 °C. The expected values for an isothermal decomposition process are 2.7% and 5.9%, respectively, from Ref. 7.

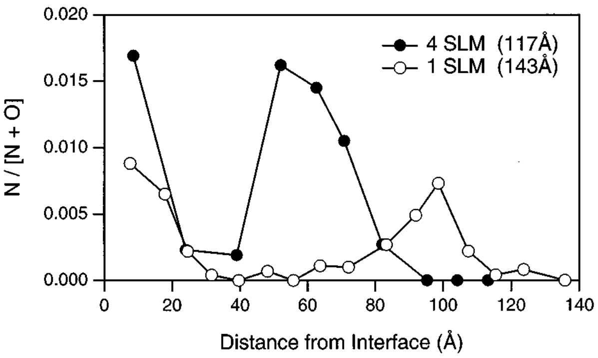

FIG. 3. N depth profile for two furnace N_2O gate oxides, showing the effect of flow rate on N concentration. The oxides were grown at 1 and 4 SLM, corresponding to flow velocities of 0.15 and 0.6 cm/s, at a temperature of 900 °C, in O_2 (5 min), N_2O (30 min), O_2 (30 min), and N_2O (30 min).

rates of 1, 2, and 4 slm, corresponding to flow velocities of 0.15, 0.3, and 0.6 cm/s. The oxide thicknesses were 143, 139, and 117 Å, respectively, as measured ellipsometrically with $n=1.462$. A comparison of the N profiles of the 1 and 4 slm oxides is given in Fig. 3. These N profiles were obtained by an XPS etchback process described elsewhere.[2] The integrated N concentration of the 4 slm oxide was twice that of the 1 slm oxide.

It is important to note that the wafers grown by Saks *et al.*,[15] had nitrogen exclusively at the interface, while our oxides clearly showed a bimodal nitrogen distribution. This difference appears to be due solely to a change in the flow rate. Their observation was that nitrogen which is incorporated during the initial N_2O oxidation step is removed during the final N_2O step. This was attributed by Saks *et al.*, to the removal of N through a reaction with NO. Since NO is also clearly present during the growth of our oxides, and action by O_2 was ruled out by Saks,[15] we suggest that the species responsible for N removal is atomic oxygen. It has been shown previously, with low pressure O_3 annealing, that atomic oxygen is capable of scavenging N from an oxide.[16] Under sufficiently high flow rates, atomic oxygen from reaction (2) may survive to reach the wafer. The short residence time used by Saks, reported as less than 10 s, is longer than the calculated N_2O lifetime of 2 s;[4] however, given the unknown time required to heat the gas to 900 °C, and the possibility of thermal inhomogeneities, we suspect that some N_2O survived to decompose near the wafer, resulting in exposure of the wafers of Saks *et al.*, to atomic oxygen.

We conclude that the variation of flow rate presents an important tool for optimizing nitrogen incorporation. It also brings to the surface several concerns regarding N_2O processing. Principally, this variation leads to some difficulty in comparing oxides grown in different furnaces, as growth recipes often do not include sufficient information on flow velocity and gas residence time. This effect has been known for some time.[4] However, our work suggests that at 900 °C the variation of oxide properties with flow velocity is far greater than might be anticipated from higher temperature studies. We also acknowlede that, because of our neglect in dealing with turbulence and the details of heat transfer, there may be other factors influencing furnace performance which prevent the scalability of our NO concentration measurements. Most notably, the shape of the furnace inlet and its size in comparison with the rest of the furnace may have secondary effects on the decomposition process. However, the mechanism by which these factors and the flow velocity influence the nitrogen incorporation are identical: the NO concentration at the wafer depends directly upon the temperature profile of the gas near the inlet. These changes in the temperature profile can arise from finite gas heat-up time, or can be produced by heat liberated during the decomposition of N_2O.

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