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Effect of incorporated nitrogen on the kinetics of thin rapid thermal N_2O oxides

M. L. Green, D. Brasen, and L. C. Feldman
AT&T Bell Laboratories, Murray Hill, New Jersey 07974

W. Lennard and H.-T. Tang
University of Western Ontario, London, Ontario N6A 3K7, Canada

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We have grown ~10 nm O_2 and N_2O-oxides on Si(100) by RTO (rapid thermal oxidation) over the temperature range 800–1200 °C. Although the growth rates of both oxides exhibit Arrhenius behavior over the entire temperature range, the N_2O-oxides exhibit a large change in the Arrhenius preexponential factor for oxidation temperatures greater than 1000 °C. Above this temperature, N_2O-oxides grow a factor of 5 slower than O_2 oxides. Below this temperature, N_2O-oxide growth rates approach those of O_2-oxides. This growth rate inflection can be explained in terms of N incorporation, which increases with increasing oxidation temperature. The equivalent of one monolayer of N coverage is achieved at about 1000 °C, coincident with the inflection. The incorporated N retards the linear growth of the thin N_2O-oxides either by occupying oxidation reaction sites or inhibiting transport of oxidant species to the vicinity of the interface. © *1995 American Institute of Physics.*

The incorporation of N (nitrogen) into SiO_2, i.e., oxynitridation, significantly retards boron penetration through the resultant Si–O–N dielectric.[1,2] Therefore, oxynitrides are potentially important gate dielectrics for ultralarge scale integration, where dielectric thicknesses will be ⩽7 nm. In the absence of N, boron, the P^+ polycrystalline silicon gate electrode dopant can diffuse through the thin SiO_2 layer during postgate dielectric growth processing, causing unacceptable shifts in device threshold voltage.[3,4] The simplest and most manufacturable of the many oxynitridation chemistries is the direct oxynitridation of Si in N_2O, which has been extensively studied with respect to processing,[5,6] electrical properties,[3,7,8] and reliability.[3] In N_2O-oxides, the incorporated N is closely confined to the Si/SiO_2 interface.[3,6,9] Further, the amount of N incorporated in RTO (rapid thermal oxidation) N_2O-oxides is small, but has been found to increase with increasing oxidation temperature[3,10,11] and oxide thickness.[5,9,12] For example, the equivalent of about one monolayer of N on Si(100), 7×10^{14} N/cm^2, is incorporated in a 10 nm N_2O-oxide grown at 1000 °C.[10] Other N incorporation data from the literature has been summarized in Ref. 10. The small amount of incorporated N has a large effect in retarding the kinetics of N_2O-oxide growth.[13–15] In this letter we report the relationship between oxidation kinetics of RTO O_2 and N_2O-oxides and incorporated N content for oxides of current technological importance, i.e., ~10 nm thick. We show that retardation of N_2O-oxide kinetics is due to the effect of incorporated N content on the Si/SiO_2 interfacial oxidation reaction constant.

RTO O_2 and N_2O-oxides ~10 nm thick (actual range 8.5–11.2 nm), were grown at temperatures ranging from 800 to 1200 °C in pure ambients and at atmospheric pressure. All oxides were grown on *p*-type (10–20 Ω cm, boron), 125 mm, Si(100) substrates. The N_2O-oxides are the same sample set whose incorporated N contents were reported in Fig. 1 of Ref. 10. Oxide thickness was determined by ellipsometry, with the index of refraction of the N_2O-oxides assumed to be that of the O_2-oxides, 1.459. The validity of this assumption has been confirmed by independent ion scattering measurements, and is consistent with the small amount of N in the oxides.

Figure 1(a) is an Arrhenius plot of average oxidation rate R_{O_2} or R_{N_2O}, where R_{O_2} and R_{N_2O} are defined as the oxide thickness divided by the time at oxidation temperature to reach ~10 nm thickness, for O_2 and N_2O-oxides, respectively. The O_2-oxide data obey an Arrhenius relationship that yields an activation energy of 2.1 ± 0.1 eV. In contrast, the N_2O-oxide data appear to only obey an Arrhenius relationship between about 1000 and 1200 °C, with activation energy equal to 1.9 ± 0.1 eV. In this temperature range, the N_2O-oxide growth rate is about five times slower than the O_2-oxide growth rate. Below 1000 °C, the N_2O-oxide growth rate exhibits an inflection and approaches the O_2-oxide growth rate, nearly equaling it below 850 °C.

The N_2O-oxide growth rate inflection can be seen more clearly in Fig. 1(b), where the ratio of the N_2O to O_2-oxide average growth rates, R_{N_2O}/R_{O_2}, is plotted as a function of oxidation temperature. The presence of the inflection in $R_{N_2O}R_{O_2}$, which can be clearly observed, is indicative of an abrupt transition in N_2O-oxide growth rate with respect to O_2-oxide growth rate. It has been shown,[10] for the present N_2O-oxide sample set, that incorporated N content increases approximately linearly in the oxidation temperature range 800–1200 °C, and that at 1000 °C, its value is 7×10^{14} N/cm^2, the equivalent of about one monolayer. Therefore, we can correlate the abrupt transition in R_{N_2O}/R_{O_2}, Fig. 1(b), with the increase in N content previously observed in Ref. 10. In Fig. 2 we have plotted R_{N_2O}/R_{O_2} as a function of N content, and it can be seen that the incorporation of a mono

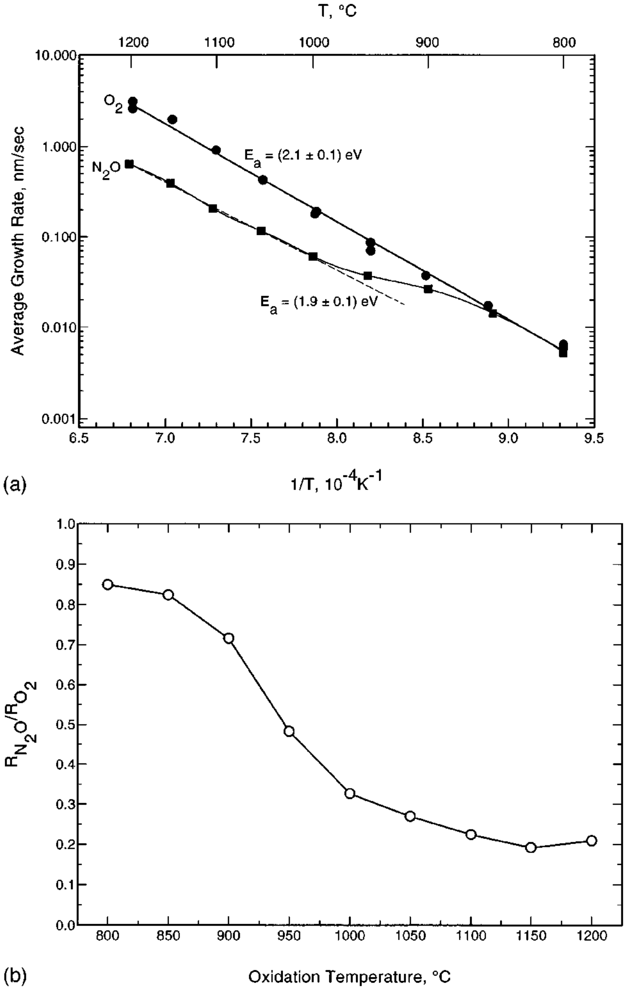

FIG. 1. (a) Arrhenius plot of average growth rate for ~10 nm thick O_2 and N_2O-oxides, over the temperature range 800–1200 °C, and (b) the ratio of the N_2O to O_2-oxide average growth rates as a function of oxidation temperature.

layer equivalent of N saturates the retardation of N_2O-oxidation kinetics.

Figure 1(a) also suggests that the growth of ~10 nm O_2 oxides occurs in the linear regime (as defined by Deal–Grove),[16] since the derived activation energy, 2.1±0.1 eV, is in excellent agreement with the 2.0 eV Deal–Grove value for their linear growth rate parameter. Other researchers have observed activation energies of 2.26 eV[17] and 2.0 eV[18] for the linear rate parameter for thin RTO O_2-oxides. Further, since the N_2O-oxides of Fig. 1(a) also show an activation energy of 1.9±0.1 eV for $T > 1000$ °C, within error equal to the Deal–Grove value, we assume that in this temperature range the N_2O-oxides grow in the linear regime. This must also be true for the N_2O-oxides grown below 1000 °C, since in that temperature range the N_2O-oxide growth rates approach the O_2-oxide growth rates. The apparent deviation from Arrhenius behavior exhibited by the N_2O-oxides is therefore probably due to a change in the pre-exponential factor. The activation energy, reflective of the oxide growth mechanism, appears to be unchanged for oxidation in either O_2 or N_2O ambient.

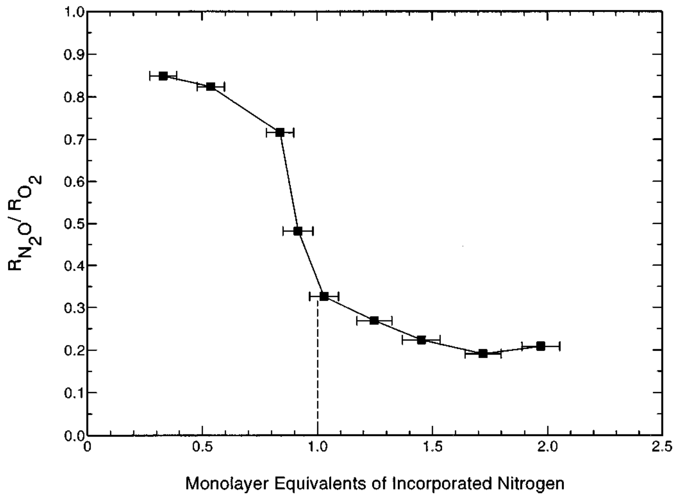

FIG. 2. The ratio of the N_2O to O_2-oxide average growth rates as a function of nitrogen content of the N_2O oxides. The nitrogen data come from Fig. 1 of Ref. 10.

The N incorporation/growth rate ratio data of Fig. 2 can be rationalized with linear, i.e., reaction controlled, oxide growth. It is known that the N is concentrated very close to the Si/SiO_2 interface.[3,6,9] We propose that as the N concentration increases with increasing temperature up to one monolayer equivalent, it continuously retards further oxidation by one of two mechanisms. If one assumes a pure interface oxidation reaction model,[16] then the N might be occupying oxidation reaction sites at the interface, as has been previously suggested.[19] This model suggests that N exists as a monolayer specifically bound to Si/SiO_2 interface sites. Alternatively, in a reactive layer model,[20] the N may be inhibiting transport of the oxidant species through the reactive layer, thereby retarding the interfacial reaction. In this way, the N acts to mask the approximately one monolayer of Si available to react at the interface. Either model is consistent with our finding of linear growth.

In summary, we have grown ~10 nm O_2 an N_2O-oxides by RTO over the temperature range 800–1200 °C and have found that growth is dominated by linear, i.e., Si/SiO_2 interfacial reaction kinetics. The N_2O-oxide growth rate decreases as N incorporation increases, due either to oxidation site occupation by N, or inhibition of oxidant transport through the reactive layer, again by N. At an N content equivalent to one monolayer on Si(100), the effect of the incorporated N on the N_2O-oxide kinetics saturates.

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