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Radiation Effects in Oxynitrides Grown in N₂O

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ABSTRACT

We characterize the effects of ionizing radiation on oxynitrides furnace-grown in N₂O. Results are presented on hole trapping, interfacial trap creation, time-dependent hole annealing, and hole de-trapping using thermally-stimulated current analysis.

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Research over ^{the} past two decades has demonstrated that oxynitrides have several advantages over pure SiO₂ for use as a gate insulator in metal-insulator-silicon devices. Among their advantages are improved yield, reduced impurity diffusion, improved radiation hardness, and reduced hot carrier degradation. These oxynitrides are typically fabricated by growth of an SiO₂ layer, then nitridation in NH₃ at elevated temperatures (900-1200°C), and finally re-oxidation in O₂. This process usually requires a rapid-thermal annealing (RTA) system to obtain the high temperatures and short times required for optimized characteristics. Unfortunately, NH₃ oxynitrides also have several serious drawbacks, including high fixed oxide charge, increased electron trapping, and reduced inversion layer mobility. To date, these drawbacks have prevented the widespread use of oxynitrides in CMOS integrated circuits.

In the last several years, interest has grown in oxynitrides fabricated by nitridation in N₂O rather than NH₃ [1]. N₂O has several (potential) advantages. N₂O oxynitrides appear not to have high fixed insulator charge or reduced inversion layer mobility. Second, the insulator is not exposed to hydrogen during N₂O nitridation. (The presence of hydrogen during NH₃ nitridation has been shown to cause degradation in the insulator and is believed responsible for high electron trap densities.) Third, N₂O nitridation can be achieved in a standard oxidation furnace, without RTA, and thus is more compatible with mainstream CMOS manufacturing.

Here we report what we believe is the first comprehensive study of radiation effects in N₂O oxynitrides. In a first publication on radiation effects, Lo et al. [2] reported that N₂O oxynitrides show enhanced radiation hardness against both positive charge build-up and interface trap creation. Here we find no improvement in radiation hardness for positive charge trapping, but some improvement for interface trap creation. We also report thermally-stimulated current measurements of de-trapping of radiation-induced holes, electron spin resonance measurements, and measurements of time-dependent flatband voltage after pulsed irradiation to determine annealing rates of radiation-induced holes.

Oxynitrides have been fabricated by oxidation in N₂O in a conventional atmospheric-pressure oxidation furnace at 900-1000°C. A few principal process variations for a poly-gate capacitor process lot are shown in Table 1. Process variations (names in parentheses) include a control oxide grown in O₂ ("OX"), a nitrided oxide ("NO") obtained by nitridation in N₂O after growth of the same initial oxide in O₂, oxynitrides grown exclusively in N₂O at 900 or 1000°C ("OXY"), and finally an oxynitride fabricated by re-oxidation of NO in O₂ ("RNO"). Oxidation/nitridation in N₂O causes continued growth of the (mostly) SiO₂ layer, albeit at reduced rates compared to O₂ (see insulator thicknesses in Table 1).

In general, these oxynitrides have excellent electrical characteristics, including high yield, low fixed oxide charge, high breakdown fields (12-14 MV/cm), and high charge-to-breakdown Q_{bd} (~5-40 C/cm²). Detailed pre-irradiation characterization of these films is reported elsewhere [3]. SIMS profiles of the nitrogen, oxygen, and silicon concentrations of a typical NO film are shown in Fig. 1. There is a peak in the nitrogen concentration at the Si-SiO₂ interface (~0.5 at. %), with relatively little N in the remaining insulator. Similar N profiles are obtained for the "OXY" insulators grown exclusively in N₂O.

Oxynitride radiation response at 295K has been determined ^{estimated} using 10 keV x-rays or ⁶⁰Co. Densities of oxide trapped charge Q_{ot} and interface traps D_{it} were ~~determined~~ by measuring the mid-gap shift and stretch-out, respectively, of capacitance-voltage data on irradiated MIS capacitors. The efficiencies for generating (net) Q_{ot} and D_{it} (f_{ot} and f_{it}, respectively) were determined from the ratio of the post-irradiation change in density to the calculated density of holes created in the insulator by the

Efficiency data are quoted to remove effects of oxide thickness on ~~the~~ trapped charge density.

irradiation. Measured efficiencies for the oxynitrides are shown in Fig. 2 for a dose of 2 Mrad at $\approx +2$ MV/cm oxide field. The 10 nm control OX has a low f_{ot} of $\sim 3\%$, which is moderately radiation hard. In the oxynitrides (except for RNO), f_{ot} is not significantly changed due to the presence of nitrogen. This result is in disagreement with Lo *et al.* [2]. The difference probably arises because our starting oxide has a low f_{ot} which may be difficult to reduce further, whereas f_{ot} in Lo's 11.0 nm oxides is much higher (25% for a control oxide, 15% for the N_2O oxynitride). Note the f_{ot} for our N_2O oxide (3%) is also ~ 5 -times less than that of Lo *et al.*

Fig. 2 also shows the efficiencies f_{it} for creating radiation-induced interface traps D_{it} . Contrary to the hole trapping results, there is considerable reduction in f_{it} in the NO and OXY oxynitrides. The amount of improvement depends on the particular processing scheme used. The greatest reduction in f_{it} , about an order of magnitude, is obtained for OXY. However, this is still a smaller improvement in f_{it} than obtained in optimized NH_3 oxynitrides whose interfacial N concentration ($\sim 5\%$) is significantly higher than the N_2O oxynitrides here ($\sim 0.5\%$). For the RNO sample, both f_{ot} and f_{it} are more than an order of magnitude higher than the control. We speculate that this is due to the unusual N profiles in these oxides and unusual oxidation conditions during re-oxidation (to be described further at the conference). Finally, measurements of D_{it} creation after high field (Fowler-Nordheim) electron injection also show that D_{it} creation is smaller in the oxynitrides, which confirms the radiation results.

Thermally-stimulated current (TSC) measurements have been performed to determine if properties of the hole traps differ in the oxynitrides compared to pure SiO_2 . For TSC, large capacitors are irradiated at $25^\circ C$ to fill hole traps in the insulator. The capacitors are then warmed up to $T \geq 300^\circ C$ and the gate current, which arises from de-trapping of the radiation-induced trapped holes, is measured as a function of temperature [4]. Typical TSC data for the control OX (#1), NO oxynitride (#3), and OXY oxynitride (#11) are shown in Fig. 3. We find that the amount of hole de-trapping, and the energy of the hole traps (which is proportional to the temperature at the peak current), are almost identical in the OX and NO samples. Results are also similar for the OXY sample, except that the magnitude of the de-trapping is reduced (due to the smaller thickness of this insulator), and the peak is somewhat stretched out. These results qualitatively confirm the radiation results in Fig. 2 which show no significant differences in hole trapping among the various N_2O oxynitrides and the control OX. The amount of post-irradiation compensating electron trapping can also be determined from TSC measurements [4]. The ratio of electron to hole trapping, η_e , is found to be on the order of 25-50% for OX and NO samples, with no clear differences among them. η_e for OXY is smaller ($\sim 10\%$), but the analysis is more uncertain because of the thinness of this insulator. These results are consistent with reports of no increase in electron trapping in N_2O oxynitrides, contrary to results in NH_3 oxynitrides.

Electron spin resonance (ESR) measurements have been performed on oxynitrides grown on $\langle 111 \rangle$ silicon with the same process variations in Table 1. The primary result from this study is that the density of bridging nitrogen defects N_b is found to be approximately an order of magnitude lower in the N_2O oxynitrides compared to NH_3 oxynitrides. N_b are believed to be the source of electron traps in NH_3 oxynitrides [5]. This result suggests that N_2O oxynitrides do not suffer from significant electron trapping as do the NH_3 samples. We intend to confirm this result with future experiments on electron trapping using n-channel MOSFETs with N_2O oxynitride insulators currently in fabrication.

To measure hole transport and annealing, C-V flat-band voltage shifts have been determined as a function of time after pulsed irradiation. The radiation source is a Febetron 706 flash x-ray source with a short 3 ns radiation pulse. Results for a 16 nm control OX, and NO and OXY oxynitrides, are shown in Fig. 4 at liquid nitrogen temperature (normalized to 0.5 Mrad dose). For the control OX, about 50% of all holes created in the oxide by the radiation are still trapped in the insulator at the shortest measurement time. The subsequent OX anneal rate is consistent with de-trapping of holes by tunneling

at both interfaces [6]. The initial shift in the 7.2 nm OXY insulator is much smaller, because most holes can anneal by this tunneling mechanism even at short times in such a thin insulator. Unusual behavior is observed in the 14 nm NO sample. The initial shift represents about 70% hole trapping efficiency. However, the NO anneal rate is much larger than for the control OX, and cannot be explained by tunnel annealing. (This is not a spurious response caused, for example, by a rise in temperature due to the radiation pulse.) In a normal OX at 80K, holes form small polarons and do not transport appreciably at oxide fields below ~ 2 MV/cm. Significant hole transport does appear to occur in NO in Fig. 4. This result is surprising because the N concentration in NO is relatively low, and might not be expected to affect small polaron formation. These results are, however, at least qualitatively consistent with Boesch *et al.* [7] who observed enhanced anneal rates in 37 nm NH_3 oxynitrides at 78K.

In summary, we find that N_2O oxynitrides have somewhat improved characteristics compared to pure SiO_2 . N_2O oxynitrides do not show as much improvement in total dose response (or other characteristics) as NH_3 oxynitrides do, but the N_2O oxynitrides also do not have the same drawbacks. These results appear consistent with the lower N concentrations in the N_2O oxynitrides. The most unexpected result of this work is the abnormally high trapped hole annealing rate measured in the NO oxynitrides at liquid nitrogen temperature. If this result holds up (we have reproduced it in about 4 samples), these insulators may prove useful for hardened gate insulators for cryogenic CMOS applications, where room-temperature hardening approaches are ineffective. We thank the RAEE Office of the Defense Nuclear Agency, and the Office of Naval Research ^{and the Department of Energy} for their support of this work, and the NRL Nanoelectronics Facility for sample fabrication.

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PROCESS	wafer #	OXIDATION / NITRIDATION				t_{ox} (nm)
		(1) O_2 900C	(2) N_2O 900C 60'	(3) N_2O 1000C 60'	(4) O_2 900C 60'	
Control (OX)	1	X				10.0
Nitrided Ox (NO)	3	X	X			14.0
Re-ox NO (RNO)	4	X	X		X	20.2
N_2O (OXY)	11		X			7.2
N_2O (OXY)	12			X		7.1

Table 1 Key process variations for oxynitride growth.

Figure 1: SIMS profiles of N, O, and Si concentrations in an NO oxynitride.

Figure 2: Efficiencies of radiation-induced oxide trap creation (f_{ot}) and interface trap creation (f_{it}).

Figure 3: Thermally stimulated current measurements in control OX (w1), NO (w3), and OXY (w11) oxynitrides.

Figure 4: C-V flat-band voltage shifts as a function of time after pulse irradiation for control OX, and NO and OXY oxynitrides.

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