Effects of N_2O Anneal and Reoxidation on Thermal Oxide Characteristics

Zhihong Liu, *Member, IEEE,* Hsing-Jen Wann, Ping K. Ko, *Member, IEEE,*
Chenming Hu, *Fellow, IEEE,* and Yiu Chung Cheng, *Senior Member, IEEE*

Abstract—**The effects of post-oxidation N_2O anneal on conventional thermal oxide are studied. The oxide thickness increase resulting from N_2O anneal is found to be self-limiting and insensitive to initial oxide thickness, which makes the thickness of the resulting oxide easy to control. The N_2O anneal leads to increased resistance against injection-induced interface-state generation and to reduced hole trapping. No further quality improvement is found when the N_2O-annealed oxide is subject to an additional reoxidation. This finding confirms that nitrogen incorporation in the absence of hydrogen is responsible for improving the quality of the conventional oxides.**

I. INTRODUCTION

THERMAL nitrioxide grown in N_2O ambient has recently been reported to have superior qualities over conventional thermal oxide due to the incorporation of nitrogen in the vicinity of the oxide–silicon substrate interface [1], [2]. Since the growth is self-limiting, higher temperature ($\geq$ 1100°C) is required and rapid thermal processing (RTP) is used in order to grow nitrioxide thicker than 50 Å. However, high-temperature procedures are not desirable and the thickness uniformity of the nitrioxide grown by RTP is rather poor [3]. Alternatively, a two-step process may be used to achieve a thicker oxide; the oxide is initially grown in pure oxygen and then further nitrided in N_2O [2], [4]. However, very limited data are available for this process. Furthermore, some optimum nitridation conditions seem to occur for nitrided oxides grown previously using different technologies [1], [5]–[8]; it is thus important to relate the qualities of the N_2O-nitrided oxide to the nitridation parameter of this two-step process. The effects of reoxidizing the N_2O-nitrided oxides must also be studied since an additional reoxidation procedure is found to be necessary to improve the quality of NH_3-nitrided oxide [5], [8].

In this work, the effects of N_2O-anneal (nitridation) and subsequent reoxidation on conventional oxides with thicknesses of 50 to 100 Å are studied. All processes were done in a conventional furnace in order to achieve thickness uniformity.

II. SAMPLE PREPARATION

Devices used in this study were polysilicon-gate MOS capacitors fabricated on ⟨100⟩ p-Si 10–20-Ω · cm wafers. After the field isolation oxide was etched back, conventional thermal oxides were first grown in dry O_2 at 850°C to thicknesses of 55 to 100 Å and then annealed (nitrided) in atmospheric N_2O at either 900 or 950°C for 10 to 80 min. Some of the N_2O-annealed samples were further reoxidized in O_2 at 900°C for 10 to 40 min. A post-oxidation anneal was performed in N_2 for 15 min. Determined both by ellipsometry measurement (reflection index = 1.46) and by capacitance measurement (permittivity = 3.9), the final gate oxide thicknesses, which are equivalent to those of conventional thermal oxides, were in the range of 70 to 120 Å. After the deposition of the *in-situ* phosphorous-doped polysilicon, gate patterns were defined and aluminum contacts were formed. To preserve the inherent properties of the oxide–Si interface, forming-gas anneal was not carried out. The gate area is 80 μm × 80μm. For the high-field stress experiments, a constant current injection was performed by applying a negative voltage to the gate.

III. RESULTS AND DISCUSSION

Good film thickness control as a result of the self-limiting growth kinetics has been promoted as one of the main advantages of pure N_2O oxidation [1]. For the two-step process, the thickness increase resulting from N_2O anneal is also self-limiting, as shown in Fig. 1. Compared with results of one-step N_2O oxide [1], this nitridation-induced oxide growth is much slower since an initial oxide exists. However, as seen in Fig. 1, this thickness increase is insensitive to initial oxide thickness. For oxides with initial thicknesses of 50 to 100 Å, the thickness will increase by 15 Å after 20-min annealing at 900°C, or 20 Å at 950°C. This makes it relatively easy to project the final film thickness after N_2O anneal.

The observed self-limiting growth kinetics are usually explained by nitrogen incorporation into the oxide, which in turn blocks further oxidation of the silicon substrate. Evidence of this can be seen in oxidation-resistant characteristics of the N_2O-annealed oxides shown in Fig. 1. For comparison, the thickness of control oxide is shown in the same figure as a function of oxidation time. In the case of the nitrided oxide, the oxidation rate is much lower than that of pure thermal oxide. The reoxidation rate is compa-

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Z. Liu, H.-J. Wann, P. K. Ko, and C. Hu are with the Department of Electrical Engineering and Computer Science, University of California, Berkeley, CA 94720.

Y. C. Cheng is with The Directorate, City Polytechnic of Hong Kong, Hong Kong.

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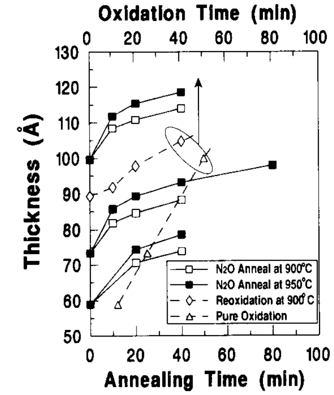

Fig. 1. The kinetics of N_2O anneal for oxides with three different initial thicknesses (solid lines). Two N_2O-annealing temperatures, 900°C (open markers) and 950°C (filled markers), are used. Note that the growth rate for different initial oxides is similar. Also shown in the same figure is the thickness increase versus oxidation time for post-N_2O-anneal reoxidation and conventional dry oxidation (dashed lines). For the first case, the initial 75-Å oxide was N_2O-annealed at 950°C for 20 min, then reoxidized in dry O_2 at 900°C. For the second case, bare Si was oxidized in dry O_2.

rable to the growth rate of N_2O nitridation at the beginning and then increases gradually with increasing reoxidation time.

The interface endurance of the oxides against Fowler–Nordheim (F–N) stress is examined by measuring quasi-static and 1-MHz *CV* curves before and after constant current stress. The typical interface-state density (D_{it}) distribution in the energy bandgap before and after 0.1-C/cm^2 injection for N_2O-annealed, reoxidized N_2O-annealed, and control oxides is shown in Fig. 2. The nitridation procedure suppresses the interface-state generation induced by F–N injection, especially in the upper-half energy bandgap where most of the degradation occurs. As will be mentioned later, this improved interface hardness for the N_2O-annealed oxides is correlated with reduced hole trapping. Additional reoxidation does not further improve the interface hardness. Instead, excessive reoxidation (e.g., 950°C, > 20 min for as-grown N_2O-annealed oxides) will degrade the superior interface obtained by the N_2O anneal.

The interface-state density at midgap (D_{itm}) is depicted in Fig. 3 as a function of N_2O-annealing time for two N_2O-annealing temperatures. Although all of the N_2O-annealed samples show comparable initial D_{itm} (not shown) and suppressed interface-state generation induced by injection, this suppression does not monotonically increase with increasing N_2O-annealing time. This can be readily explained by the fact that the nitrogen incorporated at the oxide–silicon substrate interface is a stronger function of the annealing temperature than that of the annealing time [1]. Consequently, continuously increasing annealing time will increase oxide thickness (see Fig. 1) and lead to degradation of interface hardness. Even though oxides with different annealing time and temperature may have the same thickness, the ones annealed at 950°C for shorter time always show less ΔD_{itm} than those annealed at 900°C for longer time. We speculate that more nitrogen can be incorporated at higher temperature and the interface-state generation induced by injection will reduce continuously as nitrogen incorporated at the interface increases [5]. This observation suggests that to optimize the N_2O-anneal process, higher annealing temperature and shorter annealing time would be preferable so that more nitrogen can be incorporated before the thickness increases too much.

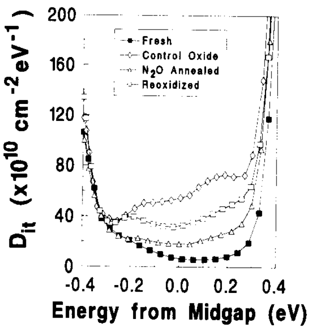

Fig. 2. Interface-state density D_{it} versus energy from midgap for devices with control oxide, N_2O-annealed (nitrided) oxide, and reoxidized N_2O-annealed oxide after 0.1-C/cm^2 injection. The electrons are injected from the gate at a current density of 0.1 mA/cm^2. Since D_{it} for all fresh devices is comparable, only one set of fresh data is plotted. The oxide thickness is about 100 Å. The N_2O anneal was performed at 950°C for 40 min; reoxidation was performed at 900°C for 20 min.

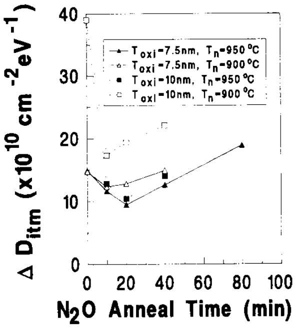

Fig. 3. The increase of midgap interface-state density ΔD_{itm} induced by 0.1-C/cm^2 injection for devices with different N_2O-anneal conditions. The N_2O-annealing temperature T_n is 950°C, and the initial oxide thickness T_{oxi} is 75 and 100 Å. The injection current density is 0.1 mA/cm^2.

Hole trapping in oxides has long been considered as the cause of injection-induced interface-state generation [9], [10]. To evaluate the effects of N_2O anneal on hole trapping, both the shift of midgap voltage [12], ΔV_{mid}, and gate voltage shift during constant current injection, ΔV_g, are plotted in Fig. 4. To reduce injection-induced electron-trap generation, the injection current density is kept at a low level of 10 μA/cm^2 [11]. According to this figure, both ΔV_{mid} and ΔV_g are greatly reduced by N_2O nitridation, indicating the suppressed hole trapping. Consistent

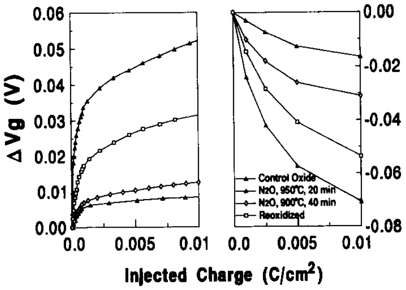

Fig. 4. Midgap voltage shift ΔV_{mid} [12] and gate voltage shift ΔV_g versus injected charge density under 10-μA/cm^2 injection. Both negative shift of ΔV_{mid} and positive shift of ΔV_g ($|\Delta V_g|$ reduction for $-V_g$ stress) indicate hole trapping. The N_2O anneal was performed at 900°C for 40 min or 950°C for 20 min; the reoxidation was performed to the 950°C, 20-min nitrided oxide at 900°C for 20 min. The thickness of these oxides is about 90 Å.

with the observations for ΔD_{itm}, the oxide annealed at 900°C has more hole trapping than the oxide annealed at 950°C. Yet, reoxidation does not further decrease hole trapping, although charge trapping reduction by reoxidation has been frequently observed for NH_3-nitrided oxides [5], [8]. One possible interpretation of these results is that reoxidation can effectively reduce hydrogen-related species induced during NH_3 nitridation, which are believed to be responsible for the increase of charge-trapping in NH_3-nitrided oxides [5]. Since no hydrogen-related species exist during N_2O nitridation, reoxidation has no effect in improving the quality of the film. This result clarifies that the incorporation of nitrogen but not hydrogen or oxygen leads to a reduction of hole trapping, and hence increases the interface stability.

IV. SUMMARY

Post-oxidation N_2O anneal can effectively reduce hole trapping and increase interface hardness against high-field F–N injection. However, since this improvement does not increase monotonically with increasing N_2O-annealing time and temperature, an optimized annealing condition should be adopted. Unlike it does for NH_3-nitrided oxides, reoxidation does not further improve the qualities of N_2O-annealed oxides.

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