Effects of Nitric Oxide Annealing of Thermally Grown Silicon Dioxide Characteristics

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Abstract—The effects of nitric oxide (NO) annealing on conventional thermal oxides are reported in this letter. The oxide thickness increase, resulting from NO annealing, is found to be only a few angstroms (<0.5 nm) and independent on the initial oxide thickness. Furthermore, both the electrical and physical characteristics are improved. This technique is expected to achieve sub-5 nm high quality ultrathin dielectric films for the applications in EEPROM's and ULSI.

I. INTRODUCTION

VERY thin dielectric films are needed for the gate dielectrics for scaled MOSFET's, EPROM's, and EEPROM's. For these devices, dielectric films should have low leakage characteristics and high dielectric strength. For gate oxide thickness less than 5 nm, the properties of conventional SiO₂ in these applications are not acceptable [1]–[3]. Currently, the search for an alternative gate dielectric film points towards the incorporation of nitrogen in the oxides. Thermal nitridation in ammonia (NH₃) and in a nitrous oxide (N₂O) ambient have recently been reported to lead to dielectrics of superior properties over conventional thermal oxides due to the incorporation of nitrogen in the vicinity of the dielectric–silicon substrate interface region [4]–[10]. However, the dielectric films which were nitrided in NH₃ showed large amounts of electron trapping and mobility degradation due to the incorporation of hydrogen atoms and “heavy” nitridation [4], [7], [8], whereas N₂O–oxynitridation showed insufficient nitrogen in the dielectric films to prevent boron penetration from the boron-doped polysilicon gates [11]–[13]. We have suggested the use of nitric oxide (NO) as a dielectric growth ambient to obtain high quality ultrathin dielectric films [14]–[16]. However, since the growth in NO ambient is self-limiting, due to the creation of strong Si–N bonds at the dielectric–silicon interface region, it is very difficult to obtain a dielectric film which is thicker than about 3.5 nm for reasonable growth times. In order to obtain high quality dielectric films of desired thicknesses, a two-step process may be necessary: an initial oxide grown in pure oxygen, and then annealed in an NO ambient. In this letter, we report the effects of NO anneal on conventional oxides of less than 5 nm.

II. EXPERIMENTAL

1.4–5.0 $\Omega \cdot \text{cm}$ n -type (100) silicon wafers were cleaned using both a H₂SO₄/H₂O₂ solution and RCA cleaning process. The wafers were then washed in 1% HF for 60 s immediately prior to dielectric film growth. The films were grown in an AG610 rapid thermal processing (RTP) unit. The initial oxides were grown in the RTP unit in an ultra-high purity oxygen ambient at 950°C for 30 s. Then, the samples were annealed in a nitric oxide ambient at 1000°C and 1150°C, both for 5 min. These samples are referred to as ON1 and ON2, respectively. Other samples were grown at 1000°C for 25 s in O₂ and then annealed in a nitric oxide ambient at 1150°C for 1 and 5 min. The purity of the nitric oxide gas used throughout this experiment was 99.0% (chemical pure grade). The RTP chamber was purged with ultra high purity N₂ prior to the introduction of O₂ or NO. Aluminum gate MOS capacitors (area = 0.01 cm²) were fabricated to evaluate the electrical characteristics.

XPS measurements were carried out on a Perkin–Elmer PHI model 560 electron spectrometer with an Mg X-ray source to determine the nitrogen concentration and distribution throughout the dielectric film. Thicknesses of the dielectric films in this work, including the pure oxides, were measured using ellipsometry with three angles of incidence (60°, 65°, and 70°). This method allows for the extraction of both the film thickness and the refractive index. The refractive index of those NO-grown or NO-annealed oxynitride is unknown, due to the incorporation of nitrogen. Moreover, the nitrogen distribution in the NO-annealed film is nonuniform inside the film. Thus, the single layer model for the calculation could result in inaccuracies, especially for such thin film. In this work, a two-layer model was used during the calculation, which necessitated at least two angles of incidence. We use three angles, and thus, three combinations, to get more accurate results. An HP4145B semiconductor parameter analyzer and an HP4284A LCR meter were used to obtain current-voltage (J-V), high frequency voltage-capacitance (C-V), and small-signal conductance (G-V) characteristics of MOS capacitors before and after positive gate bias Fowler–Nordheim constant-current tunneling stress.

III. RESULTS AND DISCUSSION

The thickness of the initial oxides of samples ON1 and ON2, grown in pure O₂ ambient at 950°C for 30 s, was 4.0 nm. The overall dielectric thicknesses were 4.4 nm for both 1000°C and 1150°C anneal in NO, with the top layer of 3.2 nm with refractive index $n = 1.49$ and the bottom layer of

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Fig. 1. XPS depth profiles for NO-annealed oxides ON1 (solid lines), which were annealed in NO at 1000°C for 5 min., and ON2 samples (dashed lines) which were annealed in NO at 1150°C for 5 min.

1.2 nm with $n = 1.56$ for ON1, and the top layer of 3.2 nm with refractive index $n = 1.49$ and the bottom layer of 1.2 nm with $n = 1.61$ for ON2. This result shows that the growth rate in NO is very low. Other experiments on the effects of growth kinetics show that the growth rate is also a very weak function of time for the samples with an initial oxide of 4 nm. Fig. 1 shows the Si, O, and N XPS distribution profiles for the NO annealed samples, ON1 (5 min at 1000°C) and ON2 (5 min at 1150°C). The nitrogen concentrations at the dielectric-silicon interface are 3.9% and 5.0% for ON1 and ON2, respectively, and drop to about 2% at the surface of the dielectric films. These nitrogen concentrations are much higher than those reported for annealing in N_2O ambient: the highest nitrogen concentration we have obtained using N_2O annealed oxides is around 1.4% (results not shown here) [15]. It can be seen from Fig. 1 that the nitrogen in NO-annealed samples piles up at the dielectric-silicon interface region; this is different from the case of the dielectrics grown directly in an NO ambient, where the nitrogen is distributed uniformly through the dielectric layer at about 5.3% [14], [15], [17]. The nitrogen profile of the NO-annealed samples is attributed to the reaction of the nitrogen from NO with the defect centers in the suboxide layer of the initial thermal oxide.

Fig. 2 shows the C-V and the I-V characteristics of aluminum gate MOS capacitors (gate area = 0.01 cm² made with the two samples (ON1 and ON2) which were annealed in a nitric oxide ambient at 1000°C and 1150°C, both for 5 min. Characteristics for the O_2 grown oxide (950°C for 30 s) are also shown for comparison. Fig. 2 shows that there is a kink in the high-frequency C-V curve of the initial oxide which is an effect already observed in thermal oxides [18]. Fig. 2 also shows that the annealing in NO removes this kink. The absence of this kink was also observed with the NO-grown samples [15], [17]. These results would indicate that interface defects giving rise to the kink are removed just as effectively

Fig. 2. C-V and I-V characteristic curves for initial oxide (950°C, 30 s) and its NO-annealed sample ON1 (annealed in NO at 1000°C for 5 min.) and ON2 (annealed in NO at 1150°C for 5 min.). The gate area of the MOS capacitors is 0.01 cm².

at 1000°C as at 1150°C (at least for the 5 min anneal time). A flat-band voltage shift has been observed when comparing the ON2 to ON1 and the control oxide. This shift indicates reduction of a positive trapped charge in the oxide during the annealing process in NO. The leakage current plots in Fig. 2 show a dramatic improvement provided by NO anneal, especially for the sample annealed at 1150°C. The I-V plots point to the fact that annealing temperature is a very sensitive parameter in the improvement of the quality of the dielectrics. From Figs. 1 and 2, it could be concluded that the quality of the dielectrics is directly proportional to nitrogen concentration in the bulk of the dielectrics. The mid-gap interface state density of the initial oxide was $6.26 \cdot 10^{11} \text{ cm}^{-2} \cdot \text{eV}^{-1}$ as measured using the conductance technique [19]. Annealing in NO at 1000°C and 1150°C, both for 5 min, reduced the mid-gap interface state densities to $1.49 \cdot 10^{11} \text{ cm}^{-2} \cdot \text{eV}^{-1}$ and $1.40 \cdot 10^{11} \text{ cm}^{-2} \cdot \text{eV}^{-1}$, respectively, which is a reduction by a factor of about 5. While the mid-gap interface state density of $1.5 \cdot 10^{11} \text{ cm}^{-2} \cdot \text{eV}^{-1}$ is one order of magnitude higher than the values expected from thicker gate dielectric films used in MOSFET devices, it is two to three times lower than that seen in ultrathin N_2O -grown or annealed oxide. Although the nitrogen concentration in the ON2 sample is higher, the mid-gap interface state densities in ON1 and ON2 samples are similar. This indicates that the nitrogen is mostly spent on neutralizing the oxide traps, as indicated by the above-mentioned flat-band voltage shift (Fig. 2).

We have also investigated the response of electrical characteristics in response to anneal time at constant anneal temperatures. The MOS capacitors for thermal oxide samples annealed at 1150°C for 1 min and 5 min were measured. Identical improvements compared to the initial oxide samples were observed for both samples (1 and 5 min of NO anneal) in both the high frequency C-V and the dc leakage current characteristics. Our XPS results show there is no significant nitrogen concentration difference in the NO-annealed oxides

which were annealed at 1150°C for 1 min and 5 min. These results suggest that the improvement is a reaction rate limited process in the bulk of the dielectric through the incorporation of nitrogen atoms in the dielectric. Overall, we speculate that the nitrogen incorporated reduces the number of dangling bonds in the bulk of the dielectric film, observed as trapped charges, as well as those at the dielectric, which mainly react with silicon dangling bonds at the interface region and the bulk of the film so as to reduce the interface state density and oxide trap density.

The charge-trapping behavior of the NO-annealed oxides (ON1 and ON2) was investigated using a positive gate bias Fowler–Nordheim constant-current stressing of $+5.0 \mu\text{A}/\text{cm}^2$ for 300 s. The change in gate voltage was monitored during stress, and G-V measurements were performed before and immediately after stressing, to determine the generation of the interface states (ΔD_{it}) resulting from the stress. During the stress, the changes of gate voltage (ΔV_g) needed to maintain the constant current were monitored. After the constant current stressing, the ΔD_{it} of ON1 and ON2 samples were 0.3 and $0.21 \cdot 10^{11} \text{ cm}^{-2} \cdot \text{eV}^{-1}$, respectively. The gate voltage shifts during the constant current stressing were negative for both ON1 and ON2 samples and the shifts saturated after 100 s stress. The maximum shifts for ON1 and ON2 samples were -0.11V and -0.13V , respectively, indicating positive charge buildup during stress. The results shown here indicate that the incorporation of nitrogen can improve the interface endurance against the hot carriers charge-trapping properties.

IV. CONCLUSION

The characteristics of NO-annealed oxides have been investigated in this letter. The results show that the NO annealing process not only introduces higher nitrogen concentration in the annealed oxides, but also leads to significant improvement in their electrical properties, such as lower intrinsic interface state density, and reduced interface state generation and lower trap generation rate in the bulk of the annealed oxides during electrical stress, while the thickness increase after the NO annealing process is less than 5 Å. A significant observation is that the improvement in dc leakage current through the thin (<5 nm) annealed oxide, and the improvement in its interface characteristics as observed via high frequency C-V and interface state density measurements, respond differently to anneal temperature. We attribute the difference in the

response to the incorporation of nitrogen in the bulk of the dielectric and at the interface during annealing.

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