A new charge-trapping nonvolatile memory based on the re-oxidized nitrous oxide

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Abstract

We report for the first time on feasibility of a re-oxidized nitrous oxide (N2O) as gate dielectric for charge-trapping nonvolatile memory. Ultra-thin oxide is grown directly on silicon substrate in a N2O ambient. The N2O oxide is then in situ re-oxidized in O2. This process is performed in a rapid thermal processor. After re-oxidation, the nitrogen distributions show two peaks, which consist of first peak at the initial Si–SiO2 interface and second peak at the growing Si–SiO2 interface. The second nitrogen peak is caused by diffusion of some of nitrogen toward the growing Si–SiO2 interface. The nitrogen incorporated in oxide bulk act as charge traps, and the nitrogen increased at the new Si–SiO2 interface improves interface stability. The re-oxidized N2O oxides show maximum memory window of about 0.55 V and the excellent dielectric breakdown. Oxide/nitrogen-rich layer/oxide structure can be applicable as gate dielectric for not only metal-oxide-semiconductor device, but also charge-trapping nonvolatile memory.

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1. Introduction

Nitrous oxide (N2O) has been intensively studied as an alternative gate dielectric for high-reliability metal-oxide-semiconductor (MOS) devices and flash electrically erasable and programmable read only memories (EEPROMs) [1,2]. A small amount of nitrogen incorporated at the silicon-oxide interface improves gate dielectric properties, such as a large charge-to-breakdown (QBD), high immunity to hot-carrier injection, and suppressed boron penetration [3,4]. Degradation characteristics on the tunnel dielectric of floating gate EEPROMs have also shown that the N2O oxide has better endurance...
than oxide tunnel dielectric [5]. On the other hand, the N₂O oxide may be degraded by nitrogen incorporation in the oxide bulk [6]. Vasquez and Madhukar [7] identified that the defects giving rise to the charge density responsible for the magnitude of the flat-band voltage shift have a spatial distribution which is correlated to, though not the same as, the nitrogen distribution, and postulated that the defects act as charge traps.

In this study, we propose for the first time a new nonvolatile memory that utilizes charge traps of the nitrogen-rich layer in a re-oxidized nitrous oxide (N₂O). For the purpose, thin oxide is grown directly on silicon substrate in a N₂O ambient. The N₂O oxide is then in situ re-oxidized in dry O₂ by rapid thermal processing (RTP). The nitrogen incorporated at the Si–SiO₂ interface is buried in oxide bulk by re-oxidation. Therefore, a new memory device with an “oxide/nitrogen-rich layer/oxide” structure can be produced via N₂O and O₂ oxidation by RTP. The incorporated nitrogen and new oxide grew at the Si–SiO₂ interface may play roles like memory nitride and tunnel oxide in polysilicon-oxide–nitride-oxide–silicon (SONOS) memory. The nitrogen peak concentration and the spatial distribution of the incorporated nitrogen may play a role as charge traps. A nitrogen concentration profiles are investigated as a function of the oxidation temperature and the oxidation time after N₂O oxidation. Nitrogen distributions are also investigated after re-oxidation of the N₂O oxide. In order to investigate memory characteristic of the re-oxidized N₂O oxide, flat-band voltages are measured as a function of the stress voltage. Finally, the reliability of the re-oxidized N₂O oxide is evaluated by current–voltage curve.

2. Experimental procedure

The starting materials were p-type (100) silicon wafers with resistivity of 17–21 Ω cm, which were cut into 1.0 × 1.0 cm². These samples were cleaned by a standard RCA method to remove organic substance contamination, and dipped into a diluted hydrofluoric acid solution of H₂O:HF (99:1) for 1 min to remove a native oxide film. Oxynitrides were grown directly on bare silicon at 950, 1000, and 1050 °C, respectively, in a ULVAC RH E-25P rapid thermal processor in an N₂O ambient. The purity of the N₂O gas used was 99.999%. The samples were then in situ re-oxidized in dry O₂ at 950 °C for 2 min to grow an additional oxide which may be used as a tunnel oxide. Thicknesses of the oxynitrides and the re-oxidized samples were determined using an ellipsometer with 1.46 for the index of refraction. Depth profiles for oxygen and nitrogen were obtained using a CAMECA ims-6f secondary ion mass spectroscopy (SIMS). Alumina gate MOS capacitors were fabricated to obtain both current–voltage (I–V) and capacitance–voltage (C–V) data with a HP4155B semiconductor parameter analyzer and a BOONTON-72BD capacitance meter. The gate electrode area of the MOS capacitors in this study was 0.785 mm².

3. Results and discussion

Fig. 1 show SIMS depth profiles for nitrogen and oxygen in N₂O oxides grown at: (a) 950 °C, (b) 1000 °C, and (c) 1050 °C for 6 min, respectively. The N₂O gas is introduced at a constant flow rate of 1.5 standard liters per minute (slm). Both Optical thickness and an oxygen concentration equal to 1/2 its value in SiO₂ are used to determine the location of the Si–SiO₂ interface. The depth scale of the SIMS profiles is obtained assuming a constant sputtering rate determined from the sputtering time and the measured insulator thickness. SIMS results show that the nitrogen peak concentration and the oxide thickness increase with increasing N₂O oxidation temperature. However, the nitrogen peak’s location with respect to the Si–SiO₂ interface does not show dependency of N₂O oxidation temperature. The nitrogen peak is always located at the Si–SiO₂ interface and its half-width is about 50 Å. This result is consistent with that reported previously [6,8]. Interfacial nitrogen pileup arises from interfacial strain due to structural mismatch between Si and SiO₂ [7].
Fig. 2 shows SIMS profiles of the RTP oxides which are grown directly from bare silicon in N\textsubscript{2}O at: (a) 950 °C, (b) 1000 °C, and (c) 1050 °C for 6 min, respectively. The solid lines indicate the Si–SiO\textsubscript{2} interface.

![SIMS profiles of RTP oxides](image)

We tried the N profile formed itself into a camel’s back in order to firstly apply a re-oxidized N\textsubscript{2}O oxide to gate dielectric for charge-trapping nonvolatile memory. The N\textsubscript{2}O gas is introduced at a constant flow rate of 1.5 slm. SIMS results show that the nitrogen peak concentration and the oxide thickness increase with increasing N\textsubscript{2}O oxidation time, however, the nitrogen peak is always located at the Si–SiO\textsubscript{2} interface.

![SIMS profiles of RTP oxides](image)

Fig. 2. SIMS profiles of the RTP oxides which are grown directly from bare silicon in N\textsubscript{2}O at 1000 °C for: (a) 3 min and (b) 6 min, respectively. The solid lines indicate the Si–SiO\textsubscript{2} interface.

crcreased from 32 to 62 Å by re-oxidation. SIMS result for re-oxidized N\textsubscript{2}O oxide is shown in Fig. 3. Re-oxidized N\textsubscript{2}O oxides showed a slight difference in the oxide thickness and the N profile. SIMS profile of Fig. 3 shows clearly the ONO-film in structure. SIMS profile of our sample shows the concentration of N in sputtering depth <1.5 nm is higher than that of the peak at sputtering depth = 2.5 nm. We think that the N in sputtering depth <1.5 nm is unexpected profile due to surface charging effect in SIMS analysis, N\textsubscript{2} purge in RTP, and oxide surface adsorption of nitrogen in the atmosphere. After re-oxidation, the nitrogen peak remains close to its original location in the oxide, but the peak is considerably reduced in magnitude. The nitrogen distributions show two peaks, which consist of first peak at the initial Si–SiO\textsubscript{2} interface and second peak at the growing Si–SiO\textsubscript{2} interface. The second nitrogen peak is caused by diffusion of some of nitrogen toward the growing Si–SiO\textsubscript{2}.
interface. We expect that if one apply the re-oxidized N$_2$O oxide with two N peak profiles to gate dielectric for charge-trapping nonvolatile memory, the first nitrogen peak incorporated in oxide bulk (sputtering depth = 2.5–3.0 nm) may play a role as memory charge trap, and the second peak at the new Si–SiO$_2$ interface (sputtering depth = 5.5–6.0 nm) improves the interface stability.

The result of Fig. 3 is inconsistent with that predicted in literature, where the position and shape of the original nitrogen profile are unchanged with respect to the top oxide surface by oxidation in dry O$_2$ [6,8]. In fact, however, SIMS profile reported by N.S. Saks is same as our SIMS profile. We think that he cannot only show even though the second N peak is, in fact present, because the N peak at the growing Si–SiO$_2$ interface is very small in magnitude. Other workers show this fact [9]. The nitrogen buried in oxide bulk may acts as charge traps. The re-oxidized N$_2$O oxide has unusually high (∼100%) hole trapping rates [10]. Hole traps in SiO$_2$ arise from oxygen vacancies [11]. A high density of hole traps could occur in the re-oxidized N$_2$O oxide because oxygen diffusion is retarded by the nitrogen-rich layer, causing oxide growth to occur under oxygen deficient conditions. Therefore, a new memory device with “oxide/nitrogen-rich layer/oxide” structure can be produced via N$_2$O and O$_2$ oxidation by RTP. We expect that the incorporated nitrogen and new SiO$_2$ may play roles like memory nitride and tunnel oxide structurally in charge-trapping SONOS memory.

In order to investigate memory characteristic of the re-oxidized N$_2$O oxide, flat-band voltages determined by $C–V$ method are measured as a function of the stress voltage. A stress voltages between −20 and 20 V are applied at every 2 V intervals for 1 s. Hysteresis characteristic of the re-oxidized N$_2$O oxide described in Fig. 3 is shown in Fig. 4. The maximum memory window obtained from the re-oxidized N$_2$O oxide is about 0.55 V. We demonstrated for the first time feasibility of a re-oxidized N$_2$O oxide as gate dielectric for charge-trapping nonvolatile memory. Nitrogen profile should be further optimized to improve memory characteristics of re-oxidized N$_2$O oxide. The first peak concentration of nitrogen buried in oxide bulk should not be decreased during re-oxidation because nitrogen peak concentra-

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**Fig. 3.** SIMS result for the re-oxidized N$_2$O oxide. The N$_2$O oxide is grown by rapid thermal oxidation at 1000 °C for 3 min followed by a re-oxidation in dry O$_2$ at 950 °C for 2 min. The N$_2$O gas is introduced at a constant flow rate of 0.5 slm. The solid lines and the dashed lines indicate the S–SiO$_2$ interface after N$_2$O oxidation and the new Si–SiO$_2$ interface after re-oxidation, respectively.
tion is correlated to charge trap density. We also think that the second N peak at the new Si–SiO₂ interface is very important in concentration. If the second N peak at the new Si–SiO₂ interface is high in concentration, the retention characteristic of charge-trapping nonvolatile memory may deteriorate, and if the second N peak at the new Si–SiO₂ interface is low in concentration, the reliability of gate dielectric may also deteriorate because new oxide grew at the Si–SiO₂ interface act as tunnel oxide.

Fig. 5 shows current–voltage curve of the MOS capacitor with the re-oxidized N₂O oxides, which has an ideal nitrogen profile for gate oxide in MOS devices. That is, the ideal nitrogen distributions in gate oxide should have a nitrogen peak.

Fig. 4. Hysteresis characteristic of the re-oxidized N₂O oxide.

Fig. 5. Current–voltage curve of the MOS capacitor with the re-oxidized N₂O oxide.
at the oxide/poly-Si interface to prevent boron penetration from p+-poly and some nitrogen at the Si–SiO₂ interface to improve the interface stability. As shown in Fig. 5, the breakdown electric field of the re-oxidized N₂O oxide is 36 MV/cm. Leakage currents are measured in accumulation mode (negative gate bias) and are between 10⁻⁸ and 10⁻⁹ A/cm². These are extremely good results for a dielectric of thickness 59 Å. The excellent dielectric breakdown obtained by the re-oxidized N₂O oxide is thought to be due to the accumulation of nitrogen at the Si–SiO₂ interface. Nitrogen accumulated at the new Si–SiO₂ interface is supposed to reduce the amount of distorted bonds by alleviating the strain in structural transition layer, thus improving the interface stability [6].

4. Conclusions

A new charge-trapping memory device with “oxide/nitrogen-rich layer/oxide” structure is able to fabricated by re-oxidation of N₂O oxide. The nitrogen buried in oxide bulk act as charge traps and some of nitrogen incorporated at the Si–SiO₂ interface improves dielectric’s reliability. The incorporated nitrogen and the new oxide grew at the Si–SiO₂ interface may play roles like memory nitride and tunnel oxide in SONOS memory. Oxide/nitrogen-rich layer/oxide structure can be applicable as gate dielectric for a charge-trapping nonvolatile memory as well as MOS device.

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References