Ion-Implanted Epitaxially Grown Gd$_2$O$_3$ on Silicon with Improved Electrical Properties

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The effects of nitrogen incorporation by high-dose ion implantation in epitaxial gadolinium oxide (Gd$_2$O$_3$) films on Si (111) followed by annealing have been investigated. The nitrogen content in the oxide layer was changed by altering the implantation dose. The presence of nitrogen incorporation on the Gd$_2$O$_3$ layer was studied using Auger electron spectroscopy. Nitrogen incorporation is believed to occur by filling the oxygen vacancies or by removing hydroxyl group ions in Gd$_2$O$_3$. A maximum concentration of 11% was obtained for nitrogen in the interface between the silicon dioxide and Gd$_2$O$_3$ layer and the implanted areas of the Gd$_2$O$_3$ oxide layer after sputter depth profiling. The nitrogen distribution in the layer was found to be non-uniform. Nitrogen incorporation sharply reduced the leakage current and effectively suppressed the hysteresis. Leakage current was two orders lower compared with the pure Gd$_2$O$_3$.

Key words: Ion implantation, nitrogen concentration, epitaxial growth, oxynitrides, leakage current

INTRODUCTION

Due to high direct tunnelling current, silicon dioxide thinner than 1.5 nm cannot be used for the gate dielectric of complementary metal oxide semiconductor (CMOS) devices. High-dielectric-constant (high-$k$) oxides offer an alternative to silicon dioxide (SiO$_2$) in very-large-scale integrated (VLSI) devices. The basic concept of using high-dielectric-constant materials is increasing the film thickness to reduce the tunnelling leakage current and improve reliability, while scaling the capacitance equivalent oxide thickness (CET) below the direct tunnelling limit of SiO$_2$. Rare earth oxides (REOs) have received much attention due to their many advantages, including high dielectric constant, sufficiently high breakdown strength, extremely low leakage current, and well-behaved interface properties. REOs such as La$_2$O$_3$ and Gd$_2$O$_3$ have been studied in detail. Also, the epitaxial growth of crystalline Gd$_2$O$_3$ on silicon in the cubic bixbyite structure has been widely investigated. This material has a large band gap of about 6 eV and nearly symmetrical band offsets, as well as a low lattice mismatch of about $-0.4\%$ to Si. Layers grown by an optimized process can display a sufficiently high-$k$ value to achieve equivalent oxide thickness (EOT) values below 1 nm, combined with ultra-low leakage current densities, excellent reliability, and high electrical breakdown voltages. A variety of metal oxide semiconductor (MOS) devices have been fabricated based on these layers.

The current field of research into rare earth nitrides (RENs) is rapidly expanding, driven by the material needs of proposed electronic and spintronic devices. The importance of RENs has been established due to their semiconducting and ferromagnetic properties. The present enthusiasm for the capability of spintronic devices has increased the
urgency of investigating intrinsic ferromagnetic semiconductors, of which the RENs offer a rich arrangement of illustrations. It is exciting to explore more about the transition between these two materials (i.e. REOs and RENs), which form rare earth oxynitrides. Only a few research publications about gadolinium oxynitrides are available, and the concentration of nitrogen has not been studied in detail.

In addition, ionic oxides generally have abundant oxygen vacancies (VOs). Considering different high-$k$ oxides (e.g., HfO$_2$, ZrO$_2$), ab initio calculations suggest that the presence of V$_{O}$ is associated with the degradation of electrical properties. Different methods have been suggested to enhance the electrical properties of high-$k$ oxide thin films, among which dopant incorporation has been found effective. It is reported that the inclusion of nitrogen significantly improves the electrical properties in various oxides.

In this work, we fabricated gadolinium oxynitride layers using high-dose nitrogen implantation into Gd$_2$O$_3$ layers grown by molecular beam epitaxy (MBE). The obtained layers were characterized structurally using x-ray diffraction (XRD), transmission electron microscopy (TEM), and Raman spectroscopy. The nitrogen incorporation and the impact on band structure were evaluated using x-ray photoelectron spectroscopy (XPS) and have been reported. We aimed to determine the nitrogen concentration in the layer using sputter depth profiling in an Auger electron spectroscopy (AES) system and investigated the changes in the electrical properties of the layer due to nitrogen incorporation.

EXPERIMENT

The samples were prepared using the MBE technique. The process flow of sample preparation, nitrogen ion implantation, and the conditions were elaborated in a previous publication. To perform electrical characterization, platinum (Pt) metal contacts were deposited on the implanted layers. The samples were characterized electrically by measuring their room temperature leakage current versus voltage ($I-V$) characteristics using a semiconductor parameter analyzer (Agilent 4156C). The hysteresis of the samples was studied by capacitance–voltage ($C-V$) measurements using an impedance analyzer (Agilent 4294A).

An AES technique, in conjunction with ion sputtering, was used to obtain elemental concentrations in high-dose nitrogen-implanted samples. For the depth profiling process, we used a high-dose ($2 \times 10^{17}$ atom/cm$^2$) nitrogen-implanted sample with 20 nm SiO$_2$ and 120 nm Gd$_2$O$_3$, which was annealed at 800°C in N$_2$ ambient for 1 min.

Sputtering details: Ion: Ar+, Energy: 4 keV, Angle: 38.8° angle of incidence to the surface normal, Beam current: $\sim 1 \mu$A.

RESULTS AND DISCUSSION

In this section, we summarize our findings for the samples obtained after different processing steps. XRD measurements were employed first. XRD data do not exhibit additional phases, but we observed a drop in the intensity and broadening of the oxide peak after implantation, which may be attributed to the reduction in the thickness of the crystalline oxide layer (Fig. 1). The strain effects in the Gd$_2$O$_3$ layer may also be a reason for peak broadening, which reduces after rapid thermal annealing (RTA).

The TEM image in Fig. 2 shows a very rough surface, and strong implantation effects are observed in the upper portion of the oxide layer, whereas the effects are comparatively weak near the substrate. These findings agree well with the stopping range of ions in matter (SRIM) implantation profile and with the structure of GdN reported by McKenzie et al. We observed the presence of an interfacial layer of thickness $\sim 7$ nm which formed due to annealing after implantation.

The concentration of nitrogen in the interface between the SiO$_2$ and Gd$_2$O$_3$ layer and the implanted areas of the Gd$_2$O$_3$ oxide layer after sputter depth profiling is summarized in Table I. The atomic percentages of all elements were obtained from the Auger spectra, depicted in Fig. 3. Because the sputtering rate for Gd$_2$O$_3$ is not known, we plotted the depth distribution as a function of sputtering time, illustrated in Fig. 4.

The quantitative Auger method calculations are on the assumption that:
Fig. 2. TEM bright-field image analysis of the sample with the highest implantation dose.

Table I. Concentration of Gd, O and N at different sputtering time

| Sputtered region | Sputtering time (s) | Gd (at.%) | O (at.%) | N (at.%) | Ar (at.%) |
|------------------|---------------------|-----------|----------|----------|-----------|
| SiO₂             | 360                 | 54.7      | 39.9     | 5.2      | –         |
| Gd₂O₃            | 36                  | 54.1      | 39.8     | 3.8      | 2.3       |
|                  | 72                  | 50.7      | 40.2     | 6.9      | 2.2       |
|                  | 144                 | 49.5      | 37.2     | 11.0     | 2.2       |
|                  | 216                 | 48.9      | 39.9     | 8.5      | 2.7       |

Numbers in bold indicate maximum nitrogen concentration obtained.

Fig. 3. Auger spectra after 72 s sputtering of the Gd₂O₃ layer. Elements present in the layer are marked in bold letters.

Fig. 4. Graph-sputtering time versus nitrogen concentration.
\[ I_A = S_A N_A, \]  
where \( I_A \) is the measured Auger current from element \( A \), \( S_A \) is the Auger sensitivity factor of element \( A \), and \( N_A \) is the number density of atoms of type \( A \).

If the sample contains two elements \( A \) and \( B \), the expression gives the number density \( N_A \) of \( A \):

\[ N_A = \frac{I_A}{S_A} \frac{S_A}{S_A + S_B} \frac{I_B}{S_B}. \]  

We calculated the elemental concentration using Eq. 2.

To find out nitrogen concentration \( N_{\text{nitro}} \):

\[ N_{\text{nitro}} = \frac{I_{\text{nitro}}}{S_{\text{nitro}}} \frac{S_{\text{nitro}}}{S_{\text{nitro}} + I_{\text{oxy}} + I_{\text{Ar}}} \]  

The main observation during sputter depth profiling is that the nitrogen distribution in the oxide layer is non-uniform. It takes 360 s to remove 20 nm SiO\(_2\). The sputtering rate of SiO\(_2\) is 3.33 nm/min. The concentration of nitrogen on the surface of the Gd\(_2\)O\(_3\) layer seems to be around 5 at.%. Going deeper into the Gd\(_2\)O\(_3\) layer, we obtain a maximum nitrogen concentration of 11 at.%. According to the SRIM ion distribution profile, the ion range is at 46.7 nm.\(^2\) The concentration of oxygen decreases with increasing nitrogen content, which can be explained as a result of preferential oxygen sputtering.\(^2\)

**Electrical Characterization**

The effect of nitrogen ion implantation on the dc leakage conduction of the epitaxially grown Gd\(_2\)O\(_3\) thin films was investigated by standard \( I-V \) measurements shown in Fig. 5. At applied electric fields below 1 MV/cm, the leakage current density of the high-dose nitrogen-implanted epitaxially grown Gd\(_2\)O\(_3\) samples were found to be about two orders of magnitude lower than the Gd\(_2\)O\(_3\) samples grown under similar oxygen partial pressure (PO\(_2\)). A previous publication from the same group reports that Gd\(_2\)O\(_3\) layers grown at PO\(_2 \sim 5 \times 10^{-6}\) mbar show leakage current of the order 10\(^{-2}\) A/cm\(^2\), whereas the same partial pressure in nitrogen ambient growth (PN\(_2\)O \sim 5 \times 10^{-6}\) mbar) gave leakage current in the range of 10\(^{-3}\) A/cm\(^2\). For our high-dose nitrogen-implanted sample (Fig. 5), leakage current density reduced sharply to 1.8 \(\times 10^{-4}\) A/cm\(^2\).

To elucidate the enhanced electrical properties of nitrogen-implanted Gd\(_2\)O\(_3\) layers, we have to take into account the effect of nitrogen in the electrically active defects present in Gd\(_2\)O\(_3\). In complex oxides grown at a higher temperature, V Os are the dominant electrically active defect sites.\(^2\) Reports show that the presence of V Os that induce an electron conduction path and the migration of V Os in the large electric field are the two main reasons for the enhanced leakage current density in complex oxides.\(^1\) When nitrogen is incorporated in the oxide layer, nitrogen atoms occupy the oxygen vacant sites and therefore change their energy levels and also immobilize the V Os, which may successively reduce the leakage current due to the movement of the V Os.\(^3\)

Further, we investigated the impact of nitrogen incorporation on the C–V behaviour of the nitrogen-implanted epitaxially grown Gd\(_2\)O\(_3\) layers. Figure 6 depicts the C–V hysteresis characteristics of high-dose nitrogen-implanted Gd\(_2\)O\(_3\). Reports show that C–V of a pure Gd\(_2\)O\(_3\) sample grown at lower PO\(_2\) (\(~ 2 \times 10^{-7}\) mbar) exhibits strong hysteresis.\(^4\) As shown in Fig. 6, nitrogen implantation in Gd\(_2\)O\(_3\) already results in nearly ideal dielectric behaviour because of the possibility to reduce the effect of mobile oxide charges formed from the V Os.

**CONCLUSION**

Nitrogen concentrations in high-dose-implanted samples were obtained using AES, in conjunction with ion sputtering. By conducting sputter depth

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**Fig. 5.** Room temperature leakage current density of nitrogen-implanted Gd\(_2\)O\(_3\).

**Fig. 6.** C–V hysteresis of nitrogen-implanted epitaxial Gd\(_2\)O\(_3\).
proliferation, we obtained a maximum concentration of 11 at.% nitrogen in the Gd$_2$O$_3$ layer, which was not in complete agreement with the SRIM implantation profile. Ion implantation caused damage to the layer, and there were no other prominent structural changes in XRD. For uniform nitrogen distribution in the oxide layer, we need further work on implantation parameters.

Nitrogen ion implantation is an effective method for reducing leakage current and enhancing the electrical behaviour of rare earth oxides.

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CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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