

## Improving dielectric properties of epitaxial Gd<sub>2</sub>O<sub>3</sub> thin films on silicon by nitrogen doping

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## Improving dielectric properties of epitaxial $\text{Gd}_2\text{O}_3$ thin films on silicon by nitrogen doping

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We report about the effect of nitrogen doping on the electrical properties of epitaxial  $\text{Gd}_2\text{O}_3$  thin films. Epitaxial  $\text{Gd}_2\text{O}_3\text{:N}$  thin films were grown on Si (111) substrates by solid source molecular beam epitaxy using nitrous oxide as the nitridation agent. Substitutional nitrogen incorporation into the dielectric layer was confirmed by secondary ion mass spectroscopy and X-ray photoelectron spectroscopy analysis. Substantial reduction of the leakage current density and disappearance of hysteresis in capacitance-voltage characteristics observed in the  $\text{Gd}_2\text{O}_3\text{:N}$  layers indicate that nitrogen incorporation in  $\text{Gd}_2\text{O}_3$  effectively eliminates the adverse effects of the oxygen vacancy induced defects in the oxide layer. © 2013 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4775688>]

Epitaxial rare earth oxide (REO) thin films have been widely investigated for their potential applications as alternative gate dielectrics in complimentary metal oxide semiconductor (CMOS) based devices to continue their downscaling following Moore's law.<sup>1</sup> REOs offer several advantages such as high dielectric constants, large band gap, and band offset to Si, superior thermal and thermodynamic stabilities which make them attractive for integration in Si-based technologies.<sup>2,3</sup> In addition, modern sophisticated growth techniques, such as molecular beam epitaxy (MBE), enable the fabrication of high quality epitaxial REO layers on Si with atomically sharp interfaces.<sup>3</sup> However, despite their supreme structural qualities, most of the epitaxial REOs grown on Si exhibit poor electrical properties, such as instability in the threshold voltage, high leakage current density, and poor reliability owing to the number of defects generated during either layer growth or post growth typical CMOS process steps.<sup>4</sup> One kind of very commonly found electrically active defects in such ionic oxides are the omnipresent oxygen vacancies ( $V_{\text{Os}}$ ). In case of various high- $\kappa$  oxides (e.g.,  $\text{HfO}_2$ ,  $\text{ZrO}_2$ , etc.), *ab-initio* calculations suggested that the  $V_{\text{Os}}$  give rise to degradation of electrical properties by inducing localized energy states in the band gap.<sup>4-7</sup>

In order to improve the electrical properties of epitaxial high- $\kappa$  oxide thin films, much attention has been paid to reduce the density of  $V_{\text{Os}}$  and/or compensate their detrimental effects by using different processing techniques. It has been demonstrated in case of MBE grown REO thin films that adequate oxygen supply during growth often facilitates reduction of  $V_{\text{Os}}$ .<sup>3,8</sup> However, a monotonic increase in oxygen supply does not ensure complete elimination of the  $V_{\text{Os}}$  in such oxide layers.<sup>8</sup> Various post growth processing techniques have been attempted to compensate those defects in ionic oxides. However, post growth processing which often involves annealing at high temperature sometimes degrades

the overall electrical properties due to the formation of interfacial layers with inferior dielectric constants.<sup>9,10</sup> Incorporation of dopants has been found to be a suitable alternative route to improve the electrical properties of different oxides by reducing the influence of oxygen vacancies. First principle calculations suggested that nitrogen (N) incorporation in Hf based dielectrics can reduce the leakage current conduction by effectively deactivating the  $V_{\text{Os}}$  related gap states.<sup>11</sup> In a similar study, Li *et al.* discussed the defect compensation by various dopant atoms in  $\text{LaAlO}_3$ .<sup>12</sup> Substantial improvement of the electrical properties has been reported for  $\text{HfO}_2$  thin films doped with fluorine, nitrogen, or La.<sup>13-15</sup> Similarly, carbon doping in different oxides was found to be helpful in improving their dielectric properties and reducing leakage current densities.<sup>16,17</sup> However, the impact of dopant incorporation on the electrical properties of epitaxial REOs has not been widely investigated. In a recent investigation, small amount of carbon incorporation was found to improve the dielectric properties of epitaxial  $\text{Gd}_2\text{O}_3$  thin films by deactivating the  $V_{\text{Os}}$  related defects.<sup>18</sup> Other dopants such as N (having chemical properties e.g., atomic radius, electronegativity comparable to oxygen) are also expected to have similar impact on  $\text{Gd}_2\text{O}_3$  in accordance to the theoretical calculations for related oxides.<sup>12</sup> However, Liu *et al.* demonstrated recently that N incorporation in amorphous gadolinium oxide thin films using  $\text{NH}_3$  renders the oxide as a charge storage layer.<sup>19</sup> In their report, an improvement in the memory window of gadolinium oxide has been attributed to a large quantity of electron traps generated by N incorporation. Although N incorporation can indeed give rise to charge traps in oxide layers,<sup>20</sup> the profound effect of hydrogen on trap generation cannot be ruled out when  $\text{NH}_3$  is used as a nitridation agent. It is known for  $\text{SiO}_2$  that nitridation using  $\text{NH}_3$  renders inevitable hydrogen related electron trapping problems.<sup>21,22</sup> Incorporation of hydrogen also reduces the reliability of the oxides,<sup>23</sup> whereas nitridation using alternative N sources (e.g.,  $\text{N}_2\text{O}$ ) can significantly improve the

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electrical properties of silicon oxide.<sup>24</sup> Therefore, it will be interesting to investigate the effect of N incorporation on the electrical properties of epitaxial REOs utilizing a hydrogen free nitridation agent.

In this study, we report on nitridation of epitaxial  $\text{Gd}_2\text{O}_3$  thin films using  $\text{N}_2\text{O}$ . We address the effect of  $\text{N}_2\text{O}$  partial pressure during growth on the dielectric and leakage current properties of N doped epitaxial  $\text{Gd}_2\text{O}_3$  layers.

The epitaxial  $\text{Gd}_2\text{O}_3$  films of thicknesses ranging between 5.5 and 6 nm were grown at substrate temperature of  $650^\circ\text{C}$  on p-type Si (111) ( $0.2\text{--}0.4\ \Omega\ \text{cm}$ ) substrates using a multichamber solid source molecular beam epitaxy system (DCA Instruments) which includes a metallization chamber and a X ray photoelectron spectroscopy (XPS) analysis chamber connected through an UHV transfer system. The stoichiometric granular  $\text{Gd}_2\text{O}_3$  pieces were evaporated by electron beam heating. The detailed procedure of  $\text{Gd}_2\text{O}_3$  growth and Si surface preparation prior to the epitaxial oxide layer growth can be found elsewhere.<sup>25,26</sup> For nitridation of the  $\text{Gd}_2\text{O}_3$  layers, molecular  $\text{N}_2\text{O}$  was introduced into the chamber during growth. The partial pressure of  $\text{N}_2\text{O}$  ( $P_{\text{N}_2\text{O}}$ ) was controlled using a piezo leak valve. A set of samples were grown under various  $P_{\text{N}_2\text{O}}$  ranging from  $2 \times 10^{-7}$  to  $5 \times 10^{-6}$  mbar. For comparison, several control  $\text{Gd}_2\text{O}_3$  samples were grown under various  $\text{O}_2$  partial pressures ( $P_{\text{O}_2}$ ) in the similar range. After the growth, the samples were transferred to another chamber without leaving the vacuum, where Pt metal contacts were deposited using electron beam evaporation through a shadow mask to form MOS structures. The structural evolution of the epitaxial layers was monitored *in-situ* by reflection high energy electron diffraction (RHEED). After the growth, the layers were investigated by using non-monochromatized Al  $K\alpha$  radiation ( $h\nu = 1486.6\ \text{eV}$ ). X ray diffraction and X ray reflectivity (XRR) (Bruker, D8 discover) investigations were performed *ex-situ* to characterize the crystalline quality and the thickness of the samples. The nitrogen profiles were determined by secondary ion mass spectroscopy (SIMS) using  $\text{Cs}^+$  ions (measured at CiS Forschungsinstitut für Mikrosensorik und Photovoltaik GmbH, Erfurt). Room temperature dielectric properties of the samples were studied

by capacitance-voltage (C-V) measurements using an impedance analyzer (Agilent 4294A). DC leakage current density of the samples as a function of applied voltage (J-V) was measured using a semiconductor parameter analyzer (Agilent 4156C).

All the  $\text{Gd}_2\text{O}_3$  layers exhibited well developed streaky RHEED pattern (not shown) irrespective of the ambient gas type ( $\text{N}_2\text{O}$  or  $\text{O}_2$ ) and pressure during growth. This observation indicated that N incorporation in  $\text{Gd}_2\text{O}_3$  layers does not affect the oxide growth behaviour significantly. Furthermore, analysis of the XRR patterns (not shown) indicated that all the samples grown under different partial pressures of  $\text{N}_2\text{O}$  and  $\text{O}_2$  possess sharp interface with the Si substrate without formation of any interfacial layer. The SIMS profile of a representative nitrided  $\text{Gd}_2\text{O}_3$  ( $\text{Gd}_2\text{O}_3:\text{N}$ ) sample shown in Figure 1(a) clearly demonstrates a uniform N concentration across the layer thickness. SIMS profiles obtained for samples grown under different partial pressures of  $\text{N}_2\text{O}$  exhibited similar uniform distribution of N concentration. The presence of N in the oxide layers was further confirmed by XPS measurements. Figure 1(b) shows the XPS Gd  $4d$  core level spectra of two representative  $\text{Gd}_2\text{O}_3:\text{N}$  samples in comparison with a control  $\text{Gd}_2\text{O}_3$  sample. All samples exhibited a prominent peak accompanied by a shoulder at higher binding energy resulting from the Gd  $4d_{5/2}$  and Gd  $4d_{3/2}$  splitting. Compared to the undoped sample, the Gd- $4d$  spectra of the nitrided samples display a shift towards lower binding energy. The shift indicates bonding of Gd with an element having lower electronegativity compared to oxygen, which in the present case is N. This becomes clearer after Gaussian deconvolution of the Gd- $4d$  peak. In case of N doping, a second component appears due to Gd-N bond formation, which is more prominent in the Gd- $4d_{5/2}$  peak. In Figure 1(b), the deconvoluted peaks corresponding only to Gd- $4d_{5/2}$  states have been shown for clarity. The Gd- $4d_{5/2}$  states related to Gd-O and Gd-N bonds have been denoted as 1 and 2, respectively. The relative intensity ratio of peak 2 with respect to peak 1 has been found to increase with increasing  $P_{\text{N}_2\text{O}}$  during growth. Such change in the peak intensity ratios could be attributed to the increase in number of Gd-N bonds with

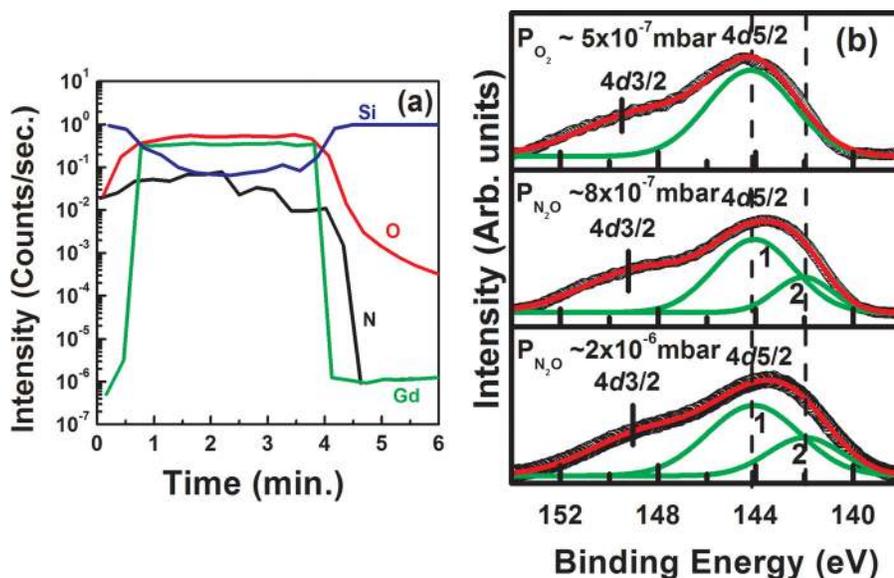


FIG. 1. (a) The SIMS depth profile of Gd, O, N, and Si elements of a representative  $\text{Gd}_2\text{O}_3:\text{N}$  sample as a function of etching time. (b) Core level XPS spectra of Gd- $4d$ , for a control  $\text{Gd}_2\text{O}_3$  sample and two representative  $\text{Gd}_2\text{O}_3:\text{N}$  samples.

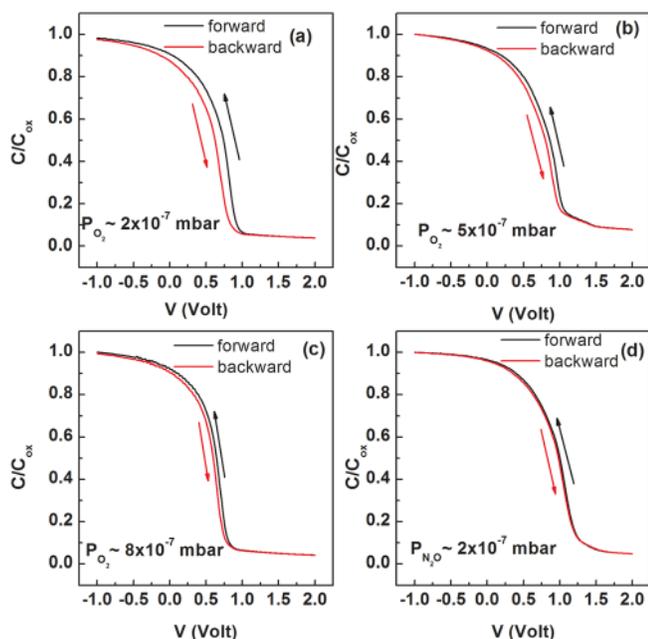


FIG. 2. (a)-(c) C-V hysteresis of epitaxial  $\text{Gd}_2\text{O}_3$  samples grown under different  $P_{\text{O}_2}$ . (d) C-V hysteresis of a representative epitaxial  $\text{Gd}_2\text{O}_3:\text{N}$  sample grown under  $P_{\text{N}_2\text{O}} \sim 2 \times 10^{-7}$  mbar.

increasing chemical potential of N corresponding to higher  $P_{\text{N}_2\text{O}}$ . However, increasing  $P_{\text{N}_2\text{O}}$  beyond  $2 \times 10^{-6}$  mbar did not result in further significant change in the relative intensities of the peaks 1 and 2, inferring saturation in the concentration of N incorporated into  $\text{Gd}_2\text{O}_3$ .

Further, we investigated the impact of N-doping on the C-V and I-V behaviour of the nitrated  $\text{Gd}_2\text{O}_3$  layers. Figure 2 compares the C-V hysteresis characteristics of a  $\text{Gd}_2\text{O}_3:\text{N}$  sample grown under low  $P_{\text{N}_2\text{O}}$  with three control samples grown under different  $P_{\text{O}_2}$ . C-V of an undoped  $\text{Gd}_2\text{O}_3$  sample grown at lower  $P_{\text{O}_2}$  ( $\sim 2 \times 10^{-7}$  mbar) exhibits a strong hysteresis (Figure 2(a)). Such hysteresis in C-V behaviour can be attributed to the presence of large number of mobile oxide charges resulting from  $V_{\text{Os}}$ .<sup>8,18</sup> From the hysteretic shift of the flat band voltage ( $\sim 140$  mV), a mobile charge density ( $Q_{\text{m}}$ ) of  $\sim 2 \times 10^{12} \text{ cm}^{-2}$  was estimated for the sample. Figures 2(b) and 2(c) clearly demonstrate that hysteresis in the C-V behaviour of epi- $\text{Gd}_2\text{O}_3$  layers reduces with increasing  $P_{\text{O}_2}$  during growth. However, some observable hysteresis ( $>30$  mV, corresponding to  $Q_{\text{m}} \sim 6-7 \times 10^{11} \text{ cm}^{-2}$ ) has been evident in the samples grown even under higher  $P_{\text{O}_2}$ , which does not comply with the requirement for reliable transistor operation.<sup>27</sup> In contrary, hysteresis in C-V was nearly vanished ( $<10$  mV) in case of N doping, which corresponds to a  $Q_{\text{m}} < 1 \times 10^{11} \text{ cm}^{-2}$ . As shown in Figure 2(d), nitridation of  $\text{Gd}_2\text{O}_3$  at lower  $P_{\text{N}_2\text{O}}$  already results in a nearly ideal dielectric behaviour. These results indicate that N doping of the epi- $\text{Gd}_2\text{O}_3$  layers can possibly compensate the effect of mobile oxide charges resulting from the  $V_{\text{Os}}$ .

The impact of N doping on the electrical properties of the epi- $\text{Gd}_2\text{O}_3$  layers is further demonstrated with respect to the dielectric constant and dc leakage current densities ( $J_{\text{leak}}$ ). Figure 3 shows the dielectric constant and the  $J_{\text{leak}}$  at 1 V ( $V_{\text{FB}}-1$ ) for different nitrated and control  $\text{Gd}_2\text{O}_3$  samples as functions of ambient gas ( $\text{N}_2\text{O}$  and  $\text{O}_2$ ) partial pressures during growth. The dielectric constants estimated from the

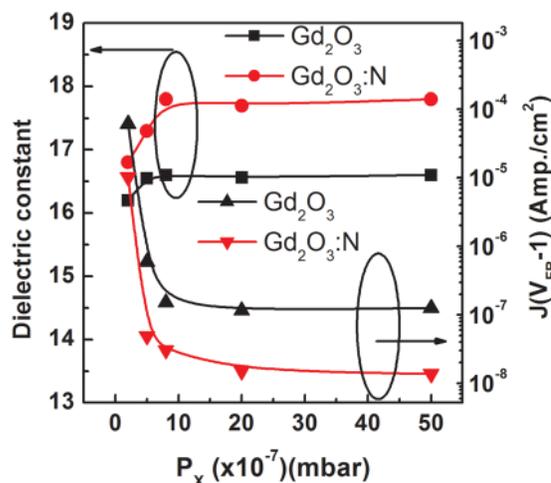


FIG. 3. Dielectric constants and dc leakage current densities measured at 1 V for different  $\text{Gd}_2\text{O}_3$  and  $\text{Gd}_2\text{O}_3:\text{N}$  samples as functions of ambient gas partial pressure ( $P_X$ ) during growth. X represents  $\text{O}_2$  in case  $\text{Gd}_2\text{O}_3$  and  $\text{N}_2\text{O}$  in case of  $\text{Gd}_2\text{O}_3:\text{N}$  layers. The lines are to guide the eyes.

accumulation capacitance of  $\text{Gd}_2\text{O}_3:\text{N}$  samples grown under different  $P_{\text{N}_2\text{O}}$  were found to be higher compared to the undoped  $\text{Gd}_2\text{O}_3$  samples. In analogy to N doped  $\text{HfO}_2$  thin films, such increase in the dielectric constant could possibly be attributed to the higher polarizability of Gd-N bonds over Gd-O bonds.<sup>28</sup> With increase in  $P_{\text{N}_2\text{O}}$ , the dielectric constant increases continuously followed by saturation after  $P_{\text{N}_2\text{O}} \sim 8 \times 10^{-7}$  mbar. Furthermore, profound effect of N doping has been observed for the leakage current density. With increasing  $P_{\text{N}_2\text{O}}$ , the leakage current density decreases sharply up to  $P_{\text{N}_2\text{O}} \sim 2 \times 10^{-6}$  mbar followed by saturation. The leakage current densities in all the  $\text{Gd}_2\text{O}_3:\text{N}$  samples were found to be more than one order of magnitude lower compared to the undoped  $\text{Gd}_2\text{O}_3$  samples.

The observed superior electrical properties of  $\text{Gd}_2\text{O}_3:\text{N}$  layers can be explained in terms of the impact of nitrogen on reducing the influence of electrically active defects in  $\text{Gd}_2\text{O}_3$ . It is well known that  $V_{\text{Os}}$  are the most dominating electrically active defect sites in complex oxides grown at higher temperatures.<sup>4,29</sup> In analogy, it can be expected that  $V_{\text{Os}}$  are the dominant defects also in REOs. As demonstrated both by experiment and *ab-initio* calculations, these  $V_{\text{Os}}$  can create electron conduction paths in complex oxides which gives rise to an increased leakage current.<sup>30-33</sup> In case of high- $\kappa$  oxides, this is due to the  $V_{\text{Os}}$  induced energy states within the band gap which are occupied by two electrons for the neutral vacancy ( $V_{\text{O}}^0$ ).<sup>4</sup> The gap states which are localized strongly on the orbitals of the adjacent metal ions result in an increase in the current conduction.<sup>4,11,12</sup> Further, if these  $V_{\text{Os}}$  are mobile, they can also give rise to hysteretic C-V behaviour when a MOS capacitor is subjected to an external electric field.<sup>8,18</sup> From our experiments, the dependence of C-V hysteresis on  $P_{\text{O}_2}$  during growth strongly indicates the presence of mobile  $V_{\text{Os}}$  in the undoped  $\text{Gd}_2\text{O}_3$  layers.

Further, our experiments revealed that the C-V hysteresis can be completely suppressed in N-incorporated  $\text{Gd}_2\text{O}_3$  (Figure 2(d)) which implies that nitrogen immobilizes the  $V_{\text{Os}}$ .<sup>11</sup> Moreover, in view of the low leakage current, this can happen only if a N- $V_{\text{Os}}$  complex is formed or if N atoms occupy the  $V_{\text{Os}}$  positions. First principle calculations of N

incorporation in different oxides suggested that two N atoms occupy the nearest neighbour O sites to  $V_{Os}$  in a minimum free energy configuration.<sup>11,12</sup> Each N atom extracts one electron from the neutral  $V_O$  sites to form a closed shell electronic configuration. As a consequence, neutral  $V_{Os}$  transform into positively charged  $V_O^{2+}$  forming electric dipoles, which effectively elevates the  $V_O$  related gap states above the conduction band of these oxides.<sup>4,11</sup> Elimination of  $V_O$  related gap states due to N incorporation leads to significant reduction in the leakage current. In the present study, the reduction in  $J_{leak}$  due to N incorporation in  $Gd_2O_3$  could be ascribed to a similar mechanism when N atoms couple favourably to  $V_O$  sites in  $Gd_2O_3$  and modify their charge states.

In summary, we have demonstrated the incorporation of N into MBE grown epitaxial  $Gd_2O_3$  layer using  $N_2O$  as nitridation agent. N doping effectively improves the overall electrical properties of the epi- $Gd_2O_3$  layers especially by reducing the C-V hysteresis and leakage current density. Combined with the previously reported *ab-initio* calculations, our experimental results suggest that N incorporation in a doping level can improve the electrical properties of various complex oxides, where  $V_{Os}$  are the dominant electrically active defects.

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