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We report on the effect of carbon doping on electrical properties of epitaxial Gd₂O₃ grown on Si substrates. The incorporation of small amounts of carbon (0.2-0.5 vol. %) into epitaxial Gd₂O₃ has been found to be very useful in improving the electrical properties especially by reducing the leakage current behavior. The doping has a negligible impact on the structural quality of the oxide layer. We show that the very often found adverse effect of oxygen vacancy induced defects in oxides grown at higher temperature can be eliminated by moderate amount of carbon doping during growth. © *2011 American Institute of Physics*. [doi:10.1063/1.3646104]

Functional oxides with higher dielectric constant have already been implemented as new gate dielectrics into the new generation complementary metal oxide semiconductor (CMOS) based devices to continue the scaling path driven by Moore's law.[1] However, the replacement of the very robust Si-based oxide by complex oxides has never been so easy owing to their very different electronic, structural, and thermodynamic properties.[2] While thermal stability of these oxides and their interfaces with Si substrates and metal electrodes have been a great obstacle, retaining their compositional stoichiometry during preparation and typical CMOS process steps is one of the most difficult challenges, the technologists are facing.[3,4] Crystalline rare earth oxides have been regarded as potential alternatives due to their higher dielectric constant, superior thermal and thermodynamic stabilities, larger band gap, and band offset with respect to Si substrate.[5] However, most of these oxides suffer from inferior reliability due to number of defects generated during either the preparation or typical CMOS process steps. One kind of such very often found defects are oxygen vacancies (V_o), which have been the most vulnerable defects in ionic oxides, degrading their electrical properties.[6]

There have been many post growth treatments attempted to improve the device performance of these oxides by annihilating those defects. However, such treatments, e.g., high temperature annealing, sometime degrades overall electrical properties due to the formation of an interfacial layer with much lower dielectric constant.[7,16] In contrast, *in-situ* treatment prior to or during oxide growth seems to be more effective in improving overall electrical performance of the devices.[8,9]

In the present work, we investigate the effect of carbon (C) incorporation on the dielectric properties of epitaxial lanthanide oxide, e.g., Gd₂O₃ thin films, especially leakage current, breakdown voltage, etc. There are mainly two reasons to focus on this subject. First, epitaxial Gd₂O₃ has been regarded as a suitable material for future gate dielectric in

CMOS devices.[5] It is often observed that inadequate oxygen during growth introduces V_o into the layer, while excess oxygen forms SiO_x like interfacial layer, degrading the overall electrical properties.[10,11] Therefore, maintaining an optimum growth condition remains to be very critical. A possible way to widen the processing window could be incorporation of foreign atoms into the growing layer, without having significant impact on structural properties. First principles calculation showed that C doping into ZrO₂ has a significant impact on its dielectric properties.[12] C incorporation in thick amorphous Ta₂O₃ films (~70 nm) in the range up to 2% was found to be helpful in reducing the leakage current (J_{leak}) compared to the undoped layers. However, no influence was found for thin layers below 10 nm.[13] Furthermore, in a similar study, it was reported that nitrogen incorporation into Hf-based dielectrics could improve the J_{leak} significantly by deactivating the oxygen vacancy (V_o) related gap levels.[14] Therefore, it would be worth to know the influence of C incorporation into very thin crystalline oxides on their structural and electrical properties. The second crucial aspect of the present work is to provide an insight into the effect of unintentional background C doping on the electrical properties of high-k oxides that occurs during preparation using industry's preferred growth techniques such as chemical vapor deposition (CVD), metal-organic CVD, and/or atomic layer deposition, where mostly C-based precursors are used.[15–17]

The epitaxial Gd₂O₃ layers with thicknesses between 6 and 7 nm were grown at substrate temperature of 650 °C on p-type Si (0.5-0.75 Ω cm) substrates using solid source molecular beam epitaxy.[9] The stoichiometric Gd₂O₃ pieces were co-evaporated using electron beam heating together with elemental C, which was evaporated using an effusion cell (SUKO). The detailed growth procedure of epi-Gd₂O₃ layers and surface treatments prior to the oxide growth could be found elsewhere.[9,18] To control the C doping into oxide layer, evaporation rate of both oxide and C sources were calibrated individually prior to co-deposition. Pt metal contacts were evaporated using electron beam heating in a different chamber without leaving the vacuum to fabricate

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MOS structure. The structural evolution of the epitaxial oxide was monitored *in situ* by reflection high-energy electron diffraction (RHEED). The layers were further investigated by x-ray photoelectron spectroscopy (XPS) measurements again without leaving the vacuum. Finally, Pt/C-doped Gd_2O_3/Si MOS capacitors were evaluated electrically using capacitance-voltage (C-V) and leakage current (J-V) measurements.

The RHEED pattern of the Gd_2O_3 layer surfaces on Si(111) as well as Si(001) obtained for different C doping levels up to 2% do not show any difference compared to undoped samples, inferring no change of the oxide surface and layer morphology by C doping.[17] The streaky patterns for the layers grown on Si(111) and Si(001) substrates (not shown) imply two-dimensional growth of epitaxial Gd_2O_3 layer.[17] Figure 1 shows the impact of C doping on valence band spectra of epitaxial Gd_2O_3. The oxide valence band (VB) offset with respect to Si remains sufficiently high ($>2.0\,eV$) for the layers with C concentration below 1%. However, the VB edge moves significantly upward thus reducing the offset value ($\sim1.4\,eV$) for the layers with $>2\%$ C. This behavior will be discussed in detail later in the text. The layers with and without C doping were further characterized electrically. Figure 2 compares the C-V hysteresis of epitaxial Gd_2O_3 layers grown under three different conditions on Si(001) substrates. The epi-Gd_2O_3 layer prepared under excess oxygen with partial pressure (P_{ox}) of 5×10^{-7} mbar shows negligible hysteresis and flat band voltage shift (Fig. 2(a)),[9] whereas the same prepared under inadequate oxygen supply ($\sim1 \times 10^{-7}$ mbar) exhibits remarkable shift in flat band voltage (Fig. 2(b)) towards negative voltage accompanied by a large hysteresis in C-V behavior after the first sweep. Such behavior can be attributed to the presence of large number of mobile oxide charges present in the layers, resulting from the V_o originated due to inadequate oxygen supply. During the first voltage sweep, some of the oxide charges become fixed near the interface hence, permanently shifting the C-V curve towards negative along the voltage axis. Incorporation of only 0.6% C into the oxide layer during growth results in restoring nearly ideal-like dielectric properties (Fig. 2(c)), where despite the layer prepared under reduced P_{ox} (1×10^{-7} mbar), no hysteresis in C-V sweep and flat band instability were observed. The adverse effects resulting from the presence of V_o seem to be compensated by small amount of C doping even in the very thin layers.
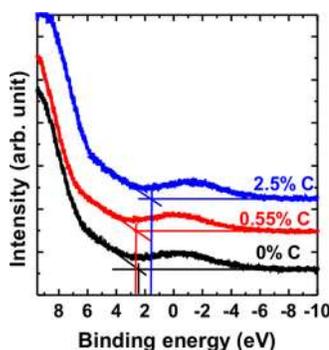

FIG. 2. C-V hysteresis of epitaxial Gd_2O_3 layer grown at different P_{ox} and condition. (a) 5×10^{-7} mbar, no carbon, (b) 1×10^{-7} mbar, no carbon, and (c) 1×10^{-7} mbar, 0.6% carbon.

The impact of C doping as well as P_{ox} on the electrical properties of thin Gd_2O_3 layers with thicknesses of 6.5 ± 0.5 nm is even more pronounced in the leakage current behavior (Fig. 3(a)). The current density measured at an applied electric field of 1 MV/cm has been increased by more than 2 orders of magnitude for the layer grown under reduced oxygen partial pressure ($\sim1 \times 10^{-7}$ mbar) as compared to that grown in standard condition (5×10^{-7} mbar). Furthermore, the break down voltage was also seen to decrease significantly for the oxide layer prepared under reduced oxygen partial pressure. On the other hand, the J_{leak} for the C-doped layer grown under reduced O_2-pressure is comparable to the one grown without C under standard oxygen pressure.

Figure 3(b) summarizes the effect of C doping on the dielectric constant and J_{leak} density of epi-Gd_2O_3 layers grown on Si(001) substrates with P_{ox} of 5×10^{-7} mbar. With increasing C content up to 0.4%, the dielectric constant increases monotonically. Further increase of C doping results in a continuous drop and finally reaches a constant value for C concentration above 1.5%. The J_{leak} decreases sharply with increasing C content up to 0.5% from where it remains nearly constant up to 2.5% C. Further increase of C incorporation results in a strong increase in J_{leak}.

To analyze the observed behavior, we presume that C atoms into the oxide lattice may either occupy V_o position

FIG. 1. (Color online) VB spectra of Gd_2O_3 layers as function of C doping. The layer is prepared at substrate temperature of $650\,°C$ with P_{ox} of 5×10^{-7} mbar on Si(001) substrates.
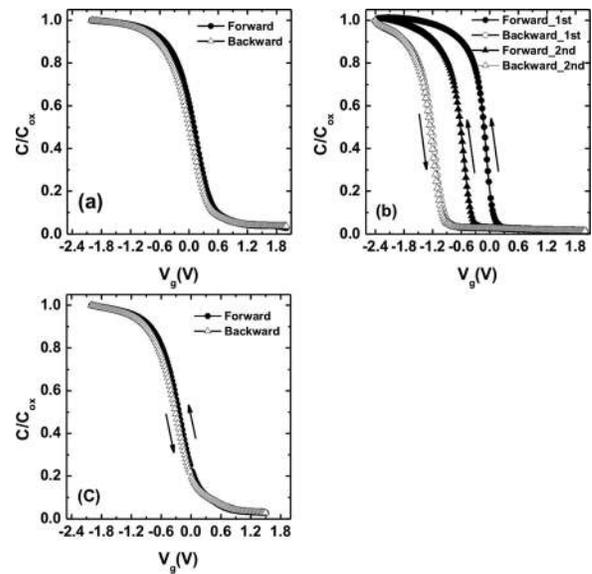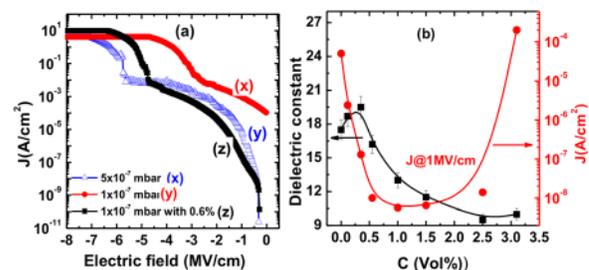

FIG. 3. (Color online) (a) Leakage current (J_{leak}) behavior of epi-Gd_2O_3 layers prepared under different conditions. (b) Dielectric constant and J_{leak} density measured at an electric field of 1 MV/cm as a function of C doping. Epi-Gd_2O_3 layers on Si(001) substrates were grown at P_{ox} of 5×10^{-7} mbar.

or/and substitute oxygen atoms, leading to secondary phase formation for higher concentration.[19,20] It is now well known that V_o are the most dominating defects in complex oxides grown at higher temperature.[6,21] Reduction of the oxygen chemical potential due to insufficient oxygen supply during oxide growth results creation of V_o into the oxides and formation of metal silicides at the interface.[11] These vacancy induced defects introduce new energy states within the oxide band gap and that eventually act as leakage paths for charge carriers.[14,20] However, what is not known is that whether these V_o induced oxide charges behave as either fixed or mobile charges? When a MOS capacitor with such large number oxide charges is subjected to an external electric field, one observes a large shift of entire C-V curve toward the negative side, implying that a large number of positive charges accumulate near the interface between oxide and Si substrate (Fig. 2(b)). Looking more closely into Fig. 2(b), one could arrive at a conclusion that there are two types of oxide charges present in the Gd_2O_3 layer, prepared under inadequate oxygen supply. The fixed oxide charges are those which permanently shift the entire C-V curve towards negative side after first voltage sweep, and it cannot be restored to the original position by applying a reverse bias. The number of fixed charges for this particular sample was estimated to be $8.6 \times 10^{12} \, cm^{-3}$. The second type of charges that are mostly mobile, causing large hysteresis in C-V sweep and their number was estimated to be $9 \times 10^{12} \, cm^{-3}$. One may conclude that these oxide charges are created due to the V_o as no hysteresis was observed for the layers grown under optimum P_{ox} (Fig. 2(a)). The detailed description about oxide charges and their nature can be found elsewhere.[22] Various processes mostly *ex situ* heat treatments in different ambient have been carried out in order to passivate these defects; however, such *ex situ* treatment some time turns out to be detrimental to the final electrical properties owing to the formation of interfacial layer.[17] An alternative way to compensate these defects could be doping these oxides with another element that has similar chemical properties (e.g., electronegativity) as oxygen.

In the present work, crystalline oxide (Gd_2O_3) has been doped with C. In an extreme situation Gd bonded with only C forms a stable phase like lanthanide sesquicarbide (Ln_2C_3) structure.[23] The occurrence of stable Gd–C bonds was also confirmed by recent XPS investigation.[24] Further, C incorporation into oxygen vacancy positions would result in a local strain within the Gd_2O_3 unit cell caused by the shorter Gd-C bond length compared to Gd–O. Such strain might lead to an increase of the dielectric constant. This has indeed been observed in the present investigation (shown in Fig. 3(b)) where the dielectric constant was found to increase for low C doping (upto 0.4%). We can, therefore, infer that for low doping (≤0.4%) C mainly couples with oxygen vacancy sites. Another possibility with higher C concentration (>2%) might be the substitution of Gd atoms by C (cation doping) which would result in a carbonate like phase formation, exhibiting completely different structure.[25] As we do not observe any change of layer structure, substitution of gadolinium atoms by C can be nearly excluded.

To understand the effect of C incorporation into lanthanide oxide, the present work can be attributed to the atomistic effect of nitrogen (N) atoms doped into Hf based gate dielectrics as studied using first principles calculation.[14] Umezawa *et al.*[14] reported that N atoms exhibit intrinsic effect that reduces the J_{leak} through HfO_2 significantly by deactivating V_o related gap states, where two N atoms occupy nearest neighbor O sites to V_o, consequently forming electric dipoles due to transfer of two electrons into the two N atoms. Similar effect can be ascribed to the present investigation where C atoms couple favorably with V_o in Gd_2O_3 and modify the charged state of V_o. Furthermore, N in HfO_2 has the strong effect on band gap narrowing by bringing the VB states up. Similarly, in the present investigation, the VB edge was shifted up significantly for higher C concentration (≥2 vol. %) in Gd_2O_3 as shown in Fig. 1.

In summary, we have shown that the incorporation of small amounts of C (0.2-0.5 vol. %) into epitaxial Gd_2O_3 layer can significantly improve its electrical properties, especially by reducing leakage current conduction. We also show that C doping can effectively compensate the electrically active defects induced by V_o into epi-Gd_2O_3. The incorporated C amount should be below 1% as higher C concentrations (>2%) into Gd_2O_3 degrades the electrical properties by forming additional type of defects.

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