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Epitaxial multi-component rare earth oxide for high-K application

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Abstract

We studied the growth and electrical properties of single crystalline mixed $(Nd_{1-x}Gd_x)_2O_3$ (NGO) thin films and compared the results with those of the binary Gd_2O_3 and Nd_2O_3 thin films, respectively. Epitaxial ternary NGO thin films were grown on Si(100) substrates using modified solid state molecular beam epitaxy. The films were characterized physically using various techniques. The capacitance equivalent oxide thickness of a 4.5 nm NGO thin film extracted from capacitance–voltage (C–V) characteristics was 0.9 nm, which is lower than all values reported earlier for other crystalline oxides. The leakage current density and the density of interface traps were 0.3 mA/cm^2 at $|Vg-V_{FB}|=1$ V and 1.4×10^{12}/cm^2, respectively. These excellent electrical properties of NGO thin films demonstrate that such ternary oxides could be one of the promising candidates for gate dielectrics in the upcoming generations of complementary metal oxide semiconductor (CMOS) devices.

Keywords: High-K; Oxide; Epitaxy; MBE

1. Introduction

The scaling of complementary metal oxide semiconductor (CMOS) devices with silicon-based oxide as gate dielectric will soon reach the limit [1]. The effort to replace the conventional gate dielectrics with a suitable alternative material with higher dielectric constant has been started almost a decade ago. Several materials with relatively higher dielectric constant than conventional SiO_2 and $SiO_xN_{(1-x)}$ have been investigated so far. The common approach is involved with an amorphous material with higher dielectric constants, e.g. metal oxides and their silicates. Among these oxides, amorphous HfO_2 and $LaAlO_3$ (LAO) have attracted much attention due to their relatively higher dielectric constant (~25), larger band gap (5.7 eV), and thermodynamic stability on Si substrate.

However, both HfO_2 and LAO exhibit thermal instability during high temperature post-deposition processing [2,3]. Crystallization occurs below typical processing temperatures, leading to surface and/or interfacial roughness and increased leakage current due to the formation of grain boundaries. Therefore, the solution for a suitable material is still a matter of research. The problems associated with structural instability could be eliminated if one could use an epitaxial insulator. The International Roadmap for Semiconductor (ITRS) predicts perovskite $LaAlO_3$ for future epitaxial oxide [1]; however, recent calculations raise serious doubts whether $LaAlO_3$ can be used as an epitaxial gate dielectric or not [4]. Rare earth binary metal oxides, especially lanthanide oxides, have been found to be thermodynamically very stable on Si even at high temperatures [5]. They exhibit relatively higher dielectric constants (ranging between 15 and 35) depending on their structure, compositions and partly on the thickness of the layer. In addition, these lanthanide oxides (LnO) could be grown epitaxially on Si substrate due to the structural similarity with Si. Hence, the effect of grain boundaries could at least be eliminated in epitaxial thin films. Among the several LnOs, Gd_2O_3 and Nd_2O_3 have been found to be most suitable because of several reasons: From thermodynamic point of view these oxides should be stable ($2M_2O_3+3Si=4\ M+3SiO_2$, $\Delta G>100$ kJ) on Si up to 1000 °C [5]. Single valency of both Gd and Nd metal (+3) ions offers an additional advantage as they produce only one single oxide (Ln_2O_3) while reacting with oxygen. The dielectric constants of these two oxides are larger than 20. The conduction and valence band offsets of both Gd_2O_3 and Nd_2O_3 to Si are around 2 eV [6,7]. The lattice parameters of Gd_2O_3 and Nd_2O_3 in their *bixbyite* phase are 1.081 nm and 1.108 nm, respectively. While Si has a lattice constant (a_{si}) of 0.545 nm,

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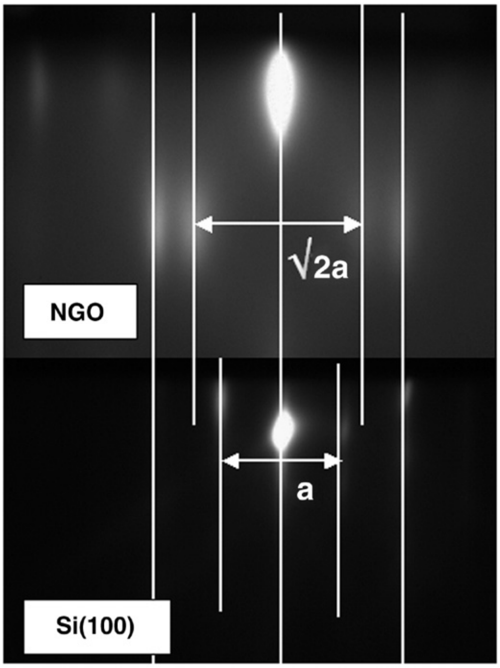

Fig. 1. RHEED images of 4.5 nm thick NGO thin films grown on Si(001) substrates and bare Si(001) surface.

$2a_{si}$ is 0.4% larger than Gd_2O_3 and 0.6% smaller than Nd_2O_3, respectively. Therefore, a combination of these two oxides would create a system exhibiting perfect lattice matching with Si especially at deposition temperature. Such a ternary system would provide much more flexibility in selecting the epitaxial high-K oxide for next generation CMOS devices. Recently, there were few attempts to use ternary metal rare earth oxide for high-K application to preserve their amorphous phases during post deposition high temperature annealing [8,9].

We studied the growth and electrical properties of epitaxial $(Nd_{1-x}Gd_x)_2O_3$ (NGO) thin films and compare the results with those of the binary Gd_2O_3 and Nd_2O_3 thin films, respectively.

2. Experimental

The films were grown on Si(100) (1–20 Ωcm) substrates in an integrated multi chamber ultrahigh vacuum system (*DCA instrument*) using solid source molecular beam epitaxy (MBE). Substrates were wet chemically cleaned using as the last step diluted (1:100) HF etch followed by a dilution rinse. Immediately after cleaning, the wafers were loaded into a vacuum chamber (load lock) attached to the main deposition chamber. After bake out at 150 °C in the load lock, the wafers were transferred to the deposition chamber and subsequently annealed so as to transform the initially hydrogen passivated (1 × 1) surface into the (2 × 1) surface superstructure, which indicates a clean and well-ordered surface. Commercially available granular Gd_2O_3 and Nd_2O_3 were evaporated simultaneously using independent electron-beam heating. The substrate temperature during deposition was varied between 650 °C and 750 °C. Since electron-beam evaporated LnO layers are usually oxygen deficient, the layers were subjected to additional molecular oxygen during growth that was introduced into the growth chamber using a piezo leak valve to adjust an oxygen partial pressure of $5.0 \cdot 10^{-7}$ mbar [10].

The crystalline structures of the films were characterized by reflection high-energy electron diffraction (RHEED), X-ray diffractions (XRD) and transmission electron microscopy (TEM). The chemical bonding and composition in the bulk and at the interface between the film and Si substrate were investigated using X-ray photoelectron spectroscopy (XPS) where the wafers were transferred into the XPS analysis chamber without leaving the UHV environment. Non-monochromatized Al Kα radiation ($h\nu = 1486.6$ eV) was used for the excitation of photoelectrons. The details of XPS measurement are described elsewhere [6]. Electrical evaluation such as *C–V* and *I–V* measurements were performed using a HP impedance analyzer and a semiconductor parameter analyzer, respectively.

3. Results and discussion

3.1. Structural characterization

Essential conditions for epitaxial growth on a clean surface require matching in symmetry and atomic spacing. It also involves two-dimensional arrangement of initial adatoms deposited onto the single crystal substrate. Such arrangement of the adatoms could usually be obtained under certain thermodynamic conditions. This implies that at suitable thermodynamic condition such as temperature and partial pressure in MBE chamber, the adatoms adsorbing onto the substrate should encounter other adsorbed adatoms and form dimers, trimers and larger cluster due to their mutual interaction before they are attached at the substrate. In our study, the growth of initial layers was carefully investigated by Reflection High Energy Electron Diffraction (RHEED). Fig. 1 shows the RHEED image of NGO layer grown at 650 °C with an oxygen partial pressure of 5×10^{-7} mbar. The image reveals interesting informations about

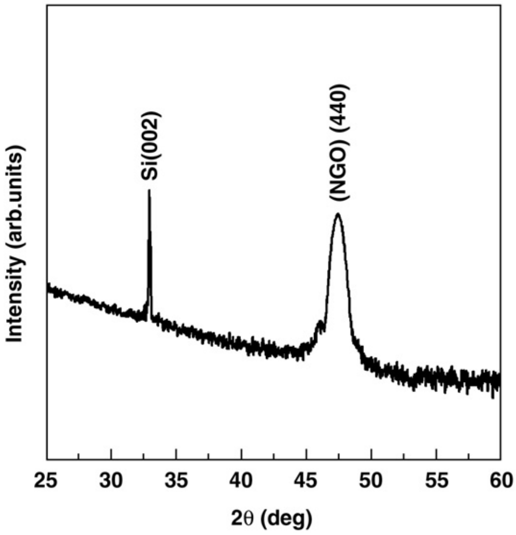

Fig. 2. Typical X-ray diffraction pattern of NGO/Si(001) structure confirming the epitaxial growth at 650 °C substrate temperature.