La-based ternary rare-earth oxides as alternative high-κ dielectrics

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Abstract

Amorphous LaScO₃ and LaLuO₃ thin films have been grown by molecular-beam and pulsed-laser deposition on Si substrates, respectively. The depositions were performed at room temperature, 250 or 450 °C. Electrical characterization of the films reveal C-V curves with a small hysteresis and low leakage current densities. LaScO₃ and LaLuO₃ films prepared at room temperature show a dielectric constant of ~17. Much higher κ values of around 30 could be achieved when the films were deposited on heated substrates. We correlate this improvement to the achievement of an oxygen stoichiometry close to the nominal stoichiometric composition.

Keywords: alternative gate dielectrics; higher-κ; rare-earth oxides; LaScO₃; LaLuO₃

1. Introduction

Because of the continuing downscaling of metal oxide semiconductor field effect transistors (MOSFETs), the thickness of the SiO₂-based gate dielectric film is approaching its physical limit. Therefore, scaling of the gate oxide must end or an alternative material with a higher dielectric constant has to be used to replace the SiO₂ as a gate dielectric.

According to the International Technology Roadmap for Semiconductors [1], the implementation of high-κ gate dielectrics with a dielectric constant κ larger than 20 will be required in 2009, in order to meet both, low leakage current density and performance requirements.

Among several candidates, ternary rare-earth oxides (e.g.: LaScO₃, DyScO₃) have been identified as potential alternatives for such high-κ applications. Recent results for amorphous thin films reveal κ values of 20-23, large optical band gap (>5 eV) and band offsets (2-2.5 eV) to silicon, and stability during
thermal treatments up to 1000 °C (e.g.: GdScO₃, DyScO₃ or LaLuO₃) [2-5]. These crystallization onset temperatures are significantly higher than that observed for pure HfO₂ films (~500 °C) [6], and comparable to those observed for ternary Hf-based dielectrics such as HfSiOₓ and HfAlOₓ, which can retain their structure up to temperatures close to 1000 °C, but offer only a slightly higher κ value (≤ 20) [7,8]. In this contribution, we report results of two alternative high-κ dielectrics: LaScO₃ and LaLuO₃. We show that amorphous thin layers of these materials, grown on silicon substrates by molecular-beam deposition (MBD) and pulsed-laser deposition (PLD), can exhibit even higher κ values around 30.

2. Experimental procedure

Amorphous LaScO₃ and LaLuO₃ films were grown by MBD and PLD, respectively. RCA-cleaned p-type (100) Si with or without an HF-last surface were used as substrates. While the MBD LaScO₃ films were deposited by co-evaporating lanthanum and scandium from individual effusion cells in an O₂ background atmosphere (~1x10⁻⁶ mbar), the preparation of LaLuO₃ films by PLD made use of a ceramic target, produced from a stoichiometric mixture of Lu₂O₃ and La₂O₃ [5]. In this case, the deposition took place in an O₂ ambient of about 1×10⁻³ mbar. In order to investigate the effects of deposition temperature on the properties of the samples, the films were grown either at room temperature (RT) or at temperatures between 250 and 450 °C.

A combination of Rutherford backscattering spectrometry (RBS), cross-sectional transmission electron microscopy (XTEM), atomic force microscopy (AFM), X-ray reflectometry (XRR), and X-ray diffraction (XRD) were used to study the composition and microstructural properties of the films. For the electrical characterization, 70 nm thick Pt top-contacts were deposited by electron-beam evaporation through a shadow mask. Ohmic backside contacts were made by MBD deposition of 150 nm of Al, followed by a forming gas anneal (90% N₂ + 10% H₂) at 450 °C for 10 min to improve the Al backside contact to silicon. Capacitance-voltage (C-V) and the current-voltage (I-V) curves were measured using an impedance analyser (HP 4192A) and a semiconductor parameter analyser (HP 4155B), respectively.

3. Results and discussion

AFM analyses (not shown) reveal that films with a good surface morphology can be grown with both deposition techniques. Even for thicker layers (20-60 nm) the root mean square (RMS) and peak-to-valley roughness did not exceed 0.5 and 2 nm, respectively. Regarding the microstructure, XRD patterns show an amorphous structure for the films.

TEM observations confirm the amorphous structure of the films. Figure 1 illustrates a cross sectional image of a ~20 nm thick LaLuO₃ film deposited at 450 °C. The growth of an interfacial layer (I.L.) is visible, which has also been observed for LaScO₃ films deposited by MBD at high temperatures. The reduction in thickness of such an interlayer for values ≤1 nm could be achieved by depositing the films at RT on Si substrates with an HF-last surface.

Fig. 1. XTEM-micrograph of a ~20 nm thick LaLuO₃ film deposited on RCA-cleaned (100) Si at 450 °C. (I.L.: interfacial layer).

The composition of the LaScO₃ and LaLuO₃ films were investigated by RBS and their thicknesses measured with XRR. The RBS results show a stoichiometry with a ratio varying between 1:0.9 and
1:1.2 for the metallic elements (Sc:La or Lu:La) independent of the deposition temperature. On the contrary, the oxygen content is lower when heating is applied during deposition. Films deposited at RT are O-rich, containing 2±0.1 oxygen atoms per metal atom. By depositing at higher temperatures (250-450 °C), this value is 1.5±0.2, which is consistent with the stoichiometric composition. Combining the RBS atomic coverage per unit area with the XRR thicknesses, the atomic number density (atoms/cm²) on the films can be calculated. While the LaScO₃ films present a density of 81±5% of the single crystalline density, this value is 89±5% for the LaLuO₃ samples. Interestingly, in spite of the different oxygen amount and a slight variation in the thickness, the atomic density have shown to be independent of the growth temperatures used in this work.

Figure 2 shows C-V curves for LaScO₃ and LaLuO₃ films with different thicknesses deposited on p-type Si at high temperatures. The curves were recorded under forward and reverse bias sweeps at a frequency of 100 kHz and a hold time of 3 s for each measuring point. Curves with a small hysteresis and free of humps and irregularities were achieved, with the best results obtained for the LaLuO₃ films. Only a small shift in the flat band voltage is observed depending on the film thickness. Additionally, leakage current densities (not shown) lower than 10⁻⁴ A/cm² at a voltage of −1 V (for 6 nm thick films) were measured for these samples.

Figure 3 shows the capacitance equivalent thickness (CET) of the LaScO₃ and LaLuO₃ films, plotted as a function of the physical thickness as measured by XRR measurements. In contrast to the equivalent oxide thickness (EOT), the CET does not take quantum mechanical effects into account and can be described as:

\[ \text{CET} = \left( \frac{\kappa_{\text{SiO}_2}}{\kappa_{\text{high-}\kappa}} \right) t_{\text{high-}\kappa} + t_{\text{SiO}_2} \]  

where \( \kappa_{\text{SiO}_2} \) and \( \kappa_{\text{high-}\kappa} \) are the dielectric constants of the SiO₂ interfacial layer and the high-\( \kappa \) layer, while \( t_{\text{SiO}_2} \) and \( t_{\text{high-}\kappa} \) are their physical thicknesses, respectively. This equation is easily deduced by considering that the high-\( \kappa \) and the interfacial layers offer a effective series capacitance.

In this work, the CET values were calculated taking into account the capacitance in accumulation regime at −2 V. From the slope of the linear fit, it is possible to deduce the dielectric constant of the films excluding the contribution of the interface. The \( \kappa \) value obtained for the LaScO₃ and LaLuO₃ films grown on heated substrates are 28 and 32, respectively. These values are higher than those previously determined for other amorphous alternative high-\( \kappa \) oxide films (e.g., HfO₂ and HfAlOₓ) [2,3,8,9] exhibiting \( \kappa = 20-23 \). In agreement with TEM observations, the intersection between the CET axis and the linear fit indicates the existence of a lower-\( \kappa \) interfacial layer between the film and the Si substrate.

Although the formation of an interlayer can be avoided by depositing the LaScO₃ and LaLuO₃ films at RT, the dielectric constant deduced in those cases
were only around 17. These low $\kappa$ values may be related to its higher oxygen content as compared to the films deposited at higher temperatures. On the other hand, the achievement of a better stoichiometry regarding the oxygen content, and also an adjustment of the short-range order structure within the amorphous matrix may explain the higher $\kappa$ deduced for the layers grown on heated substrates. In fact, the same correlation between the dielectric constant and the oxygen content seems to exist for LaScO$_3$ films deposited at RT and further submitted to thermal treatments \[10\]. A detailed investigation taking into account all those different aspects is currently in progress.

4. Summary

In summary, we have shown results of two promising alternative dielectrics (LaScO$_3$ and LaLuO$_3$) that fulfill the demand of higher-$\kappa$ materials for future CMOS applications. Amorphous thin films of these oxides, grown on silicon substrates by molecular-beam deposition (MBD) and pulsed-laser deposition (PLD), exhibit $\kappa$ values around 30. Such high values surpass those previously determined for other amorphous alternative high-$\kappa$ oxide films deposited by different techniques. Additionally, well-behaved $C-V$ curves and low leakage current density levels were measured for these samples.

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References