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

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Abstract

Amorphous $LaScO_3$ and $LaLuO_3$ 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. $LaScO_3$ and $LaLuO_3$ 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; $LaScO_3$; $LaLuO_3$

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1. Introduction

Because of the continuing downscaling of metal oxide semiconductor field effect transistors (MOSFETs), the thickness of the SiO_2-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 SiO_2 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.: $LaScO_3$, $DyScO_3$) 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

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thermal treatments up to 1000 °C (e.g.: $GdScO_3$, $DyScO_3$ or $LaLuO_3$) [2-5]. These crystallization onset temperatures are significantly higher than that observed for pure HfO_2 films (~500 °C) [6], and comparable to those observed for ternary Hf-based dielectrics such as $HfSiO_x$ and $HfAlO_x$, which can retain their structure up to temperatures close to 1000 °C, but offer only a slightly higher κ value ($\leq$ 20) [7,8]. In this contribution, we report results of two alternative high-κ dielectrics: $LaScO_3$ and $LaLuO_3$. 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 $LaScO_3$ and $LaLuO_3$ 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 $LaScO_3$ films were deposited by co-evaporating lanthanum and scandium from individual effusion cells in an O_2 background atmosphere (~$1x10^{-6}$ mbar), the preparation of $LaLuO_3$ films by PLD made use of a ceramic target, produced from a stoichiometric mixture of Lu_2O_3 and La_2O_3 [5]. In this case, the deposition took place in an O_2 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% N_2 + 10% H_2) 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 $LaLuO_3$ film deposited at 450 °C. The growth of an interfacial layer (I.L.) is visible, which has also been observed for $LaScO_3$ 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.

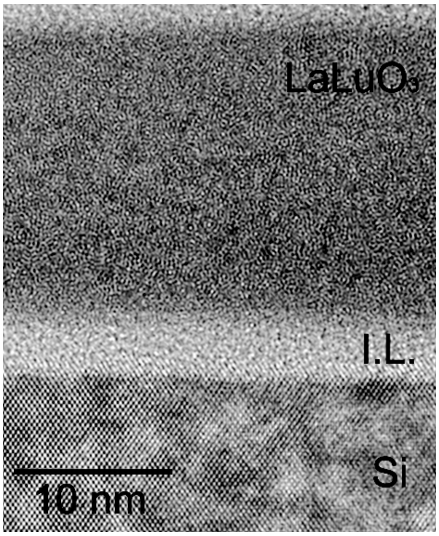

Fig. 1. XTEM-micrograph of a ~20 nm thick $LaLuO_3$ film deposited on RCA-cleaned (100) Si at 450 °C. (I.L.: interfacial layer).

The composition of the $LaScO_3$ and $LaLuO_3$ 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/cm^3) on the films can be calculated. While the $LaScO_3$ films present a density of 81±5% of the single crystalline density, this value is 89±5% for the $LaLuO_3$ 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 $LaScO_3$ and $LaLuO_3$ 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 $LaLuO_3$ 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/cm^2 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 $LaScO_3$ and $LaLuO_3$ 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:

$$CET = (\kappa_{SiO_2} / \kappa_{high-\kappa}) t_{high-k} + t_{SiO_2} \quad (1)$$

where κ_{SiO_2} and $\kappa_{high-\kappa}$ are the dielectric constants of the SiO_2 interfacial layer and the high-κ layer, while t_{SiO_2} and t_{high-k} are their physical thicknesses, respectively. This equation is easily deduced by considering that the high-κ 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 κ value obtained for the $LaScO_3$ and $LaLuO_3$ films grown on heated substrates are 28 and 32, respectively. These values are higher than those previously determined for other amorphous alternative high-κ oxide films (e.g., HfO_2 and $HfAlO_x$) [2,3,8,9] exhibiting κ = 20-23. In agreement with TEM observations, the intersection between the CET axis and the linear fit indicates the existence of a lower-κ interfacial layer between the film and the Si substrate.

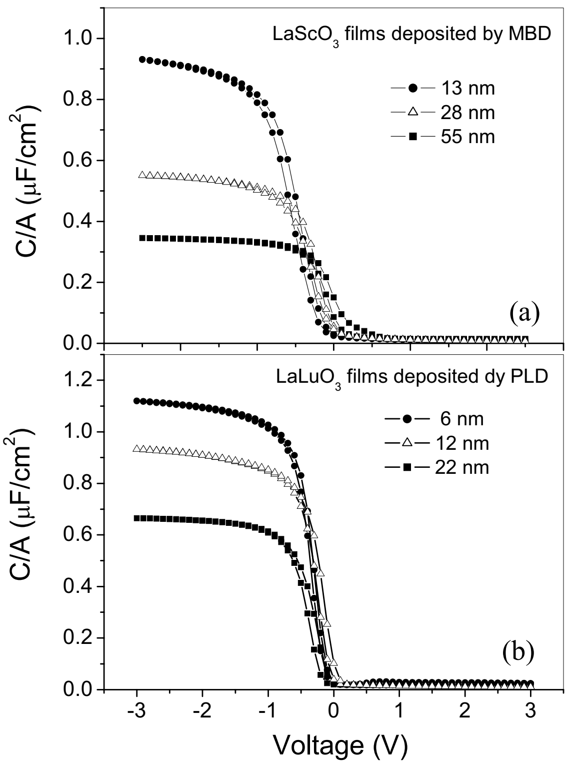

Fig. 2. *C-V* curves for Pt/high-κ/*p*-Si capacitor stacks measured at 100 kHz for (a) $LaScO_3$ films deposited at 250 °C and (b) $LaLuO_3$ films deposited at 450 °C.

Although the formation of an interlayer can be avoided by depositing the $LaScO_3$ and $LaLuO_3$ films at RT, the dielectric constant deduced in those cases were only around 17. These low κ 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 κ 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.

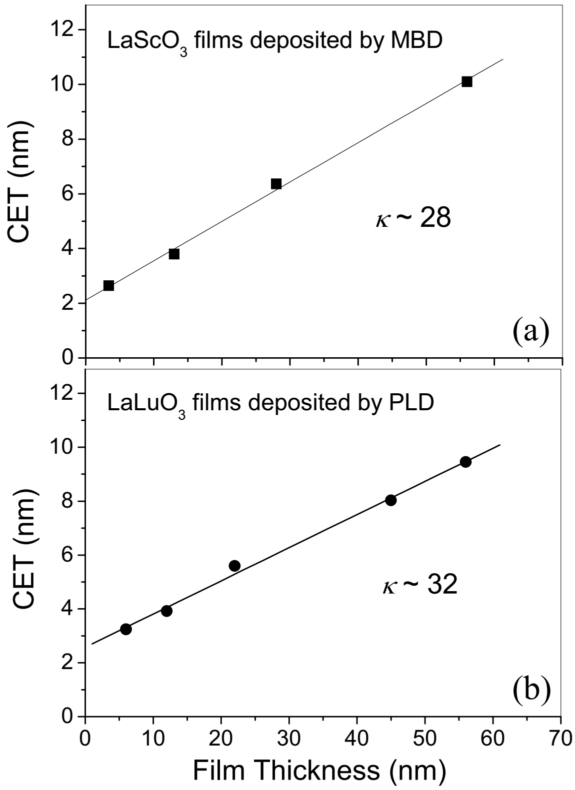

Fig. 3. CET plotted as a function of the XRR thickness for (a) $LaScO_3$ films deposited at 250 °C and (b) $LaLuO_3$ films deposited at 450 °C.

4. Summary

In summary, we have shown results of two promising alternative dielectrics ($LaScO_3$ and $LaLuO_3$) that fulfill the demand of higher-κ 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 κ values around 30. Such high values surpass those previously determined for other amorphous alternative high-κ oxide films deposited by different techniques. Additionally, well-behaved *C-V* curves and low leakage current density levels were measured for these samples.

Acknowledgements

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