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Thermal stability of $GdScO_3$ and $LaLuO_3$ films prepared by liquid injection MOCVD

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A B S T R A C T

We have studied thermal stability of $GdScO_3$ and $LaLuO_3$ films prepared by liquid injection metal-organic chemical vapour deposition (MOCVD). In the present work, we report on the characterization of $LaLuO_3$ and $GdScO_3$ thin dielectric films by SIMS and capacitance–voltage (*C–V*) measurements. In both $GdScO_3$ and $LaLuO_3$ films, SIMS analysis revealed the presence of a silicate interfacial layer. The *C–V* characteristics were found to be shifted after thermal treatment to negative and positive voltages for $GdScO_3$ and $LaLuO_3$ films, respectively. Furthermore we have observed that $LaLuO_3$ films exhibit *C–V* characteristics more stable to annealing conditions compared with $GdScO_3$ films.

1. Introduction

The conventional semiconductor technology based on Si has reached its physical limits. Scaling the SiO_2 gate thickness down to 1.5 nm has led to high tunnelling leakage current [1] and, therefore continuous research has been done for alternative material development. One of the results is the suggested high permittivity (high-κ) oxides such as Al_2O_3, HfO_2, La_2O_3, $HfSiO_x$ and their alloys [2,3]. These high permittivity oxides can be prepared by various technological methods such as pulsed laser deposition (PLD), metal-organic chemical vapour deposition (MOCVD) or atomic layer deposition (ALD). Hafnium-based dielectrics were used for SiO_2 replacement as the first generation. Unfortunately hafnium-based materials do not have a stable amorphous phase at temperatures higher than 500 °C [4]. The next generation candidates are metal oxides, like the rare-earth oxides in an RE_2O_3 configuration. Among these the La_2O_3 oxide or its combination with addition of a second metal like Lu and Al to form $LaLuO_3$, $LaAlO_3$ is the most promising material [1,5,6]. Because of their good quality, high-κ value and especially thermal stability rare-earth based oxides ($GdScO_3$, $LaLuO_3$ and similar materials) are considered to be the next candidates for SiO_2 replacement [7,8].

One of the most important issues for high-κ materials is thermodynamic stability. Therefore great attention should be devoted to the growth of the dielectric layer on top of a silicon substrate with respect to thermal stability in different ambient conditions.

In this work thin dielectric $GdScO_3$ and $LaLuO_3$ films were grown by metal-organic chemical vapour deposition (MOCVD). We have studied the thermal stability of as-deposited and annealed in oxygen, nitrogen or ultra-high vacuum (UHV) films by secondary ion mass spectrometry (SIMS). In addition, we have evaluated the electrical properties of $GdScO_3$ and $LaLuO_3$ dielectrics in MOS structures.

2. Experimental details

$GdScO_3$ and $LaLuO_3$ films were grown by the TriJet™ liquid precursor delivery technology (AIXTRON) in a low-pressure hot-wall quartz MOCVD reactor. We used β-diketonates (2,2,6,6-tetramethyl-3,5-heptanedionato, thd) as precursor for each element. Gd $(thd)_3$ and Sc $(thd)_3$ or La $(thd)_3$ and Lu $(thd)_3$ were used on the top of (100) n-doped silicon substrates ($1 \times 1\ cm^2$ in size). The native SiO_2 layer was removed by dipping the substrate in diluted HF acid. The deposition temperature of $GdScO_3$ films was 500 °C. O_2 and Ar were used as reaction and carrier gases with flow rate of 50 ml/min and 60 ml/min, respectively. The growth rate was approximately 3.8 nm/min. $LaLuO_3$ films were deposited at 450 °C using O_2 as a reactive gas and Ar as a carrier gas with flow rates of 30 ml/min and 60 ml/min, respectively. The growth rate achieved was 0.8 nm/min at a total pressure of 1330 Pa.

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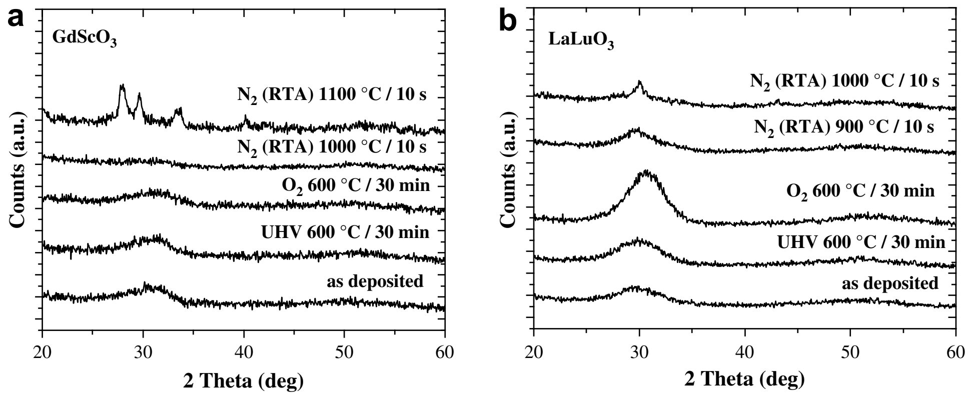

Fig. 1. XRD spectra of $GdScO_3$ (a) and $LaLuO_3$ (b) films after different heat treatment procedures.

After $GdScO_3$ and $LaLuO_3$ film deposition, the long lasting thermal treatments were performed in O_2 atmosphere and in UHV at 600 °C for 30 min. We have performed rapid thermal annealing as well (RTA, 10 s holding at set point) in N_2 ambient in the temperature range of 700 °C–1100 °C. For capacitance–voltage (*C–V*) measurements of as-deposited and annealed films, Ru electrodes were deposited using TriJet™ technology at 350 °C and patterned by standard optical lithography followed by Ar ion beam etching. We deposited an Ru metal gate after thermal treatment to suppress the effect of work-function change due to oxidation of the interface between Ru and oxides. After Ru electrode deposition and standard lithography application to achieve suitable electrodes for *C–V* measurements, Al back contacts were sputtered at the back-side of the substrate. Afterwards MOS structures were exposed to post-metallization annealing in forming gas (FGA, 10% H_2 + 90% N_2) at 450 °C for 30 min [9]. The *C–V* characteristics were measured using an Agilent 4284A LCR-meter. For determination of capacitance equivalent thickness (CET), the equation $CET = 3.9\varepsilon_0 A/C_{Ox}$ was used, where ε_0 is the vacuum permittivity; A is the contact area equal to 1.9×10^{-3} cm^{-2} and C_{Ox} is the capacitance at 2 V in accumulation regime.

The film structure was studied by X-ray diffraction (XRD) in grazing incidence mode. The thicknesses of the dielectric films were extracted from the X-ray reflectivity (XRR) measurements. In the study, we have employed a time-of-flight based SIMS instrument (Ion-TOF, SIMS IV) with high-energy Bi^+ primary source. For depth profiling, the high-energy pulsed primary gun is combined with the low energy sputter gun (Cs^+) [10].

3. Results

The crystallinity of the as-deposited $GdScO_3$ films was examined by XRD. The XRD spectrum in Fig. 1(a) shows the amorphous phase of the as-deposited film. $GdScO_3$ films remain amorphous under oxygen ambient and in UHV. The $GdScO_3$ films show a very good thermal stability, as the crystallization starts only after RTA annealing at 1100 °C in N_2 ambient, in comparison to $LaLuO_3$ films that stay amorphous up to 900 °C and crystallize above 1000 °C in N_2 atmosphere, Fig. 1(b).

In order to investigate the composition and the impurity content of the atomic layers, SIMS measurements were performed with as-deposited and annealed $GdScO_3$ films in oxygen ambient and in UHV as well as in N_2 (RTA) ambient. Typical depth profile of the $GdScO_3$ film is shown in Fig. 2(a). The depth profile reveals Gd and Sc elements coupled to O. According to the observations in Fig. 1(a) and in the SIMS analysis, we can consider the $GdScO_3$ structure as a mixture of Gd_xO_y and Sc_xO_y in an amorphous phase. At the interface with the Si substrate, silicate interfacial layers of ScSiO and GdSiO are observed. The intensity of the ScO signal raises one order of magnitude after annealing, which is a consequence of the changes in chemical bonds (not shown). The oxygen bonds to Gd and Sc metals are reorganized in the volume of the dielectric film.

A comparison of GdO profiles for different heat treatment procedures is shown in Fig. 3(a). This plot reveals the thermal stability of the GdO profile over the film. The ScO profile reaches the same thermal stability (not shown), however the surface and the interface parts are affected by the temperature and heat treatment

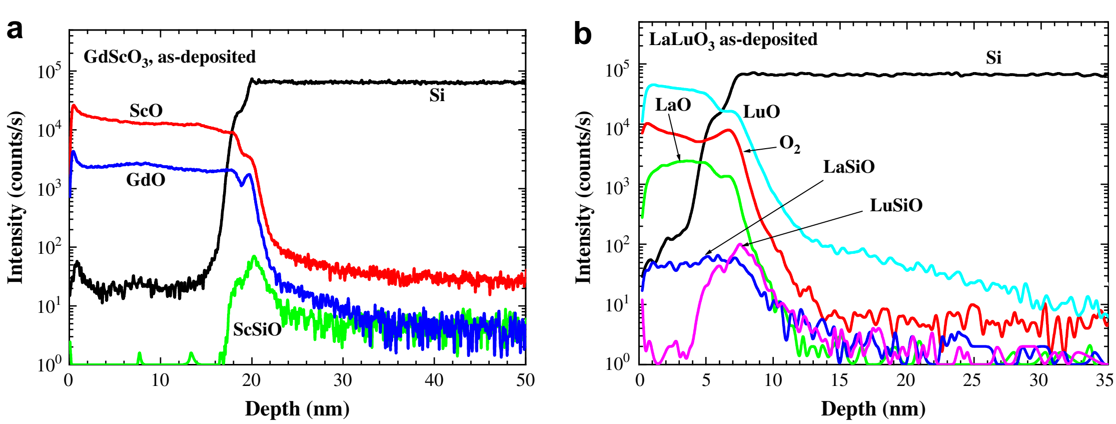

Fig. 2. SIMS depth profiles of as-deposited $GdScO_3$ (a) and $LaLuO_3$ (b) dielectric films.