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Characterization of lanthanum lutetium oxide thin films grown by atomic layer deposition as an alternative gate dielectric

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ABSTRACT

$LaLuO_3$ thin films have been deposited with atomic layer deposition on Si substrates using β-diketonate compounds for the rare earth metals and ozone as the oxygen source. Subsequently, the films were investigated regarding their chemical composition, morphology, and electrical characteristics. The as deposited films are amorphous, uniform, and smooth but reveal an excess of oxygen and a low κ-value of ~17. Oxygen annealing of the films at 800 °C for 5 min leads to a reduction of the oxygen content and a dramatic increase of the permittivity to ~30 but also to a crystallization of thick films.

1. Introduction

In order to satisfy the demand for higher integration density in microelectronics, the scaling of MOSFETs becomes more and more aggressive. As the leading manufacturer of integrated circuits recently announced to introduce hafnium based high-κ dielectrics in their next CMOS generation [1] research focuses now on so- called "higher-κ" materials with a dielectric constant of 30 and above in order to satisfy the demands for future CMOS applications.

A promising class of materials for high-κ applications are the rare earth based oxides due to their favorable material properties. For example, rare earth scandates ($RE ScO_3$, *RE* = Dy, Gd, La, etc.) show superior electrical properties including suitable band offsets to silicon and κ-values typically above 20 [2,3]. Recently, also the deposition of high quality rare earth scandate films ($YScO_3$ [4], $GdScO_3$ [5,6]) with atomic layer deposition (ALD) as the favorite deposition method for industrial use has been demonstrated. Another member of the rare earth based ternary oxides – lanthanum lutetium oxide ($LaLuO_3$) – shows as good electrical behavior as the scandates but an even higher dielectric constant of 32 for films deposited by pulsed laser deposition (PLD) [7]. In this contribution, we describe the deposition of amorphous $LaLuO_3$ thin films with ALD and show detailed investigations on their morphology, chemical composition, and thermodynamic stability.

2. Experimental details

Samples with thicknesses ranging from 6 nm to 72 nm were deposited in a commercial flow-type hot-wall ALD-reactor (F-120 by ASM Microchemistry Ltd.) using β-diketonate compounds $M(thd)_3$ (M = La, Lu; thd=2,2,6,6-tetramethyl-3,5-heptanedionato) as metal-containing precursors and ozone as the oxygen source. The depositions were carried out at a substrate temperature of 300 °C and a pressure of 2–3 mbar. The substrate material was p-doped silicon (1–10 Ωcm). Prior to the high-κ deposition the samples were HF dipped in order to remove the native oxide from the surface. After the deposition the films were characterized either as deposited or annealed in oxygen for different times and temperatures (10 min at 600 °C, 5 min at 700 °C, 5 min at 800 °C). Different characterization methods were employed to investigate the structure, composition, and thermal stability of the films such as Rutherford backscattering spectrometry (RBS), X-ray diffration (XRD), X-ray reflectivity (XRR), transmission electron microscopy (TEM), atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS). For the electrical characterization capacitor structures were prepared by deposition of 70 nm Pt through a shadow mask for the top electrodes and 120 nm Al for the back side contacts. All the samples were post metal annealed in forming gas at 400 °C for 10 min prior to the electrical characterization on a measuring station equipped with an impedance analyzer (HP 4192A) and a semiconductor parameter analyzer (HP 4155B).

3. Results and discussion

The coverage of the substrate surface with atoms of La and Lu was determined using Rutherford backscattering spectrometry. The stoichiometry of the films is close to the nominal composition of $LaLuO_3$. The ratio La:Lu lies between 1:0.99 and 1:1.03 for the thin films. Fig. 1 shows a TEM micrograph of an as deposited $LaLuO_3$ film. The film is amorphous and an interfacial layer of about 1 nm thickness is formed between the dielectric and the silicon substrate. AFM measurements reveal a surface rms

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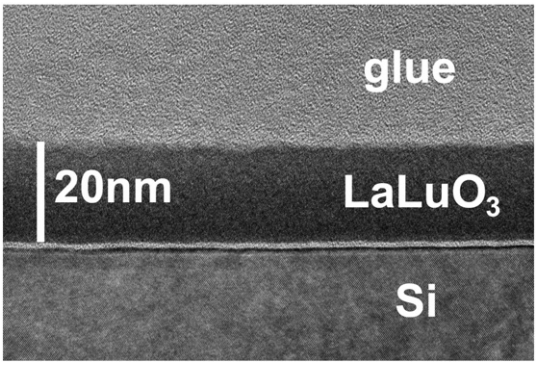

Fig. 1. TEM micrograph of an as deposited $LaLuO_3$ film. There is no sign of crystallization. An interfacial layer of ~1 nm thickness between the dielectric and the silicon can be measured.

roughness ranging from ~0.3 nm for a 6.3 nm thick film up to ~0.8 nm for a 72 nm thick film (not shown). To investigate the thermal stability of the $LaLuO_3$ films, X-ray diffraction (XRD) patterns of a ~17 nm thick film after annealings in nitrogen ambient for 10 s at different temperatures were recorded (Fig. 2). The measurements verify that the film remains amorphous up to 1000 °C. After 1100 °C annealing the onset of crystallization is observed, indicated by the arrow, which is consistent with the value measured for films deposited by PLD [6]. Fig. 3 displays C–V curves of $LaLuO_3$ films with different thicknesses annealed in oxygen at 600 °C for 10 min after deposition. The curves are featureless, smooth, and free of any hysteresis. Only a small shift in the flatband voltage depending on the film thickness is observed. The inset shows leakage current measurements for the thinnest film (d_{XRR}=6.3 nm, CET=3.1 nm). At −2 V a leakage current density below 1 μA/cm^2 is measured.

Looking at CET plots drawn with values taken from the film capacitance in the accumulation regime at −2 V and XRR measurements for the physical film thickness (Fig. 4) one can deduce only a rather low κ-value of ~17 from the slope of the linear fit. Oxygen annealing of the films at 600 °C and 700 °C results only in minor changes of the κ-value. But after annealing at 800 °C for 5 min the CET of the thin films increase due to the growth of an interfacial layer and the extracted κ-value also increases to ~25. However, the most obvious change appears for the thick film. The inset of Fig. 4 displays a XRD pattern measured for this film at the bottom together with a curve above corresponding to orthorhombic $LaLuO_3$ [8]. All the peaks can be perfectly correlated with this orthorhombic phase of $LaLuO_3$ proving that the film is polycrystal-

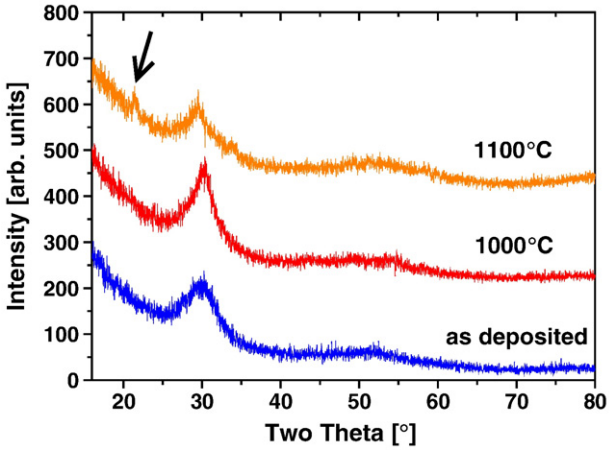

Fig. 2. XRD patterns of a ~17 nm thick $LaLuO_3$ films after annealing in nitrogen for 10 s at different temperatures. The amorphous phase is stable up to 1000 °C. Only at 1100 °C the onset of crystallization can be observed as indicated by the arrow.

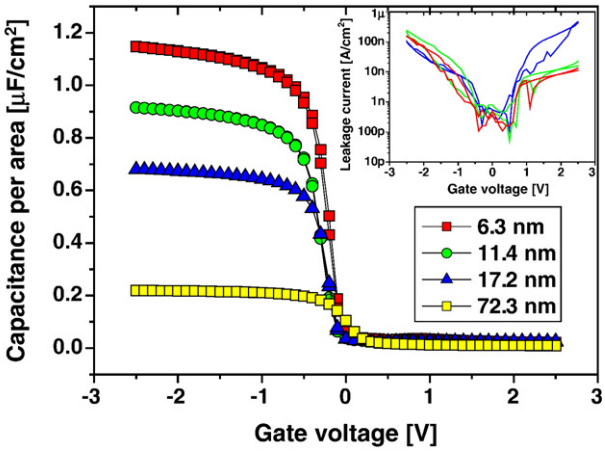

Fig. 3. C–V curves of $LaLuO_3$ films with different thicknesses annealed in oxygen at 600 °C for 10 min showing no irregularities and no hystereses. The inset displays leakage current measurements for the thinnest film (d_{XRR}=6.3 nm, CET=3.1 nm). At −2 V a leakage current density of <1 μA/cm^2 is achieved.

line. Assuming conservatively an interfacial layer of ~1 nm of SiO_2 the CET plot results in a κ-value of ~30. To elucidate this behavior further RBS spectra of the thick film before and after annealing were recorded (Fig. 5). Fitting of the measured curve of the as deposited sample provides a composition of $LaLuO_{5.2}$ which means that the film contains excessive oxygen probably preventing a near range order necessary for a high κ-value to be established. During annealing the composition changes to $LaLuO_{3.6}$ which is a reasonable value for single crystalline films. At the same time the physical thickness of the film measured by XRR is reduced by ~16% while maintaining the same density as deduced by comparison of XRR and RBS measurements. A similar behavior was observed for $LaScO_3$ deposited with MBD [9]. To confirm a loss of oxygen in the films XPS measurements on films before and after annealing were performed. Indeed, due to the annealing a significant change of the oxygen signal towards the single crystalline case is found (not shown).

4. Conclusions

In summary, the deposition of $LaLuO_3$ thin films with atomic layer deposition using β-diketonate compounds and ozone was demonstrated. The as deposited films are smooth (rms roughness ~0.3 nm) and

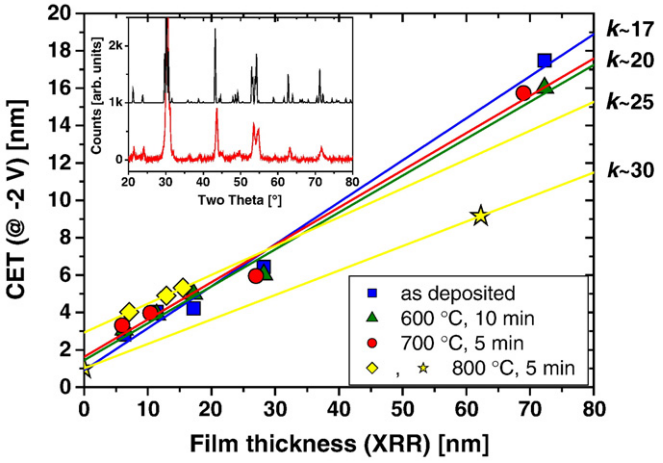

Fig. 4. CET plots of several series of $LaLuO_3$ samples annealed in oxygen at different temperatures and times. For the thick film annealed at 800 °C for 5 min an interfacial layer of 1 nm is assumed for the CET plot. The inset shows a XRD pattern of this film (at the bottom) together with one of orthorhombic $LaLuO_3$ (at the top) taken from [8]. Obviously the film has crystallized into the orthorhombic phase.

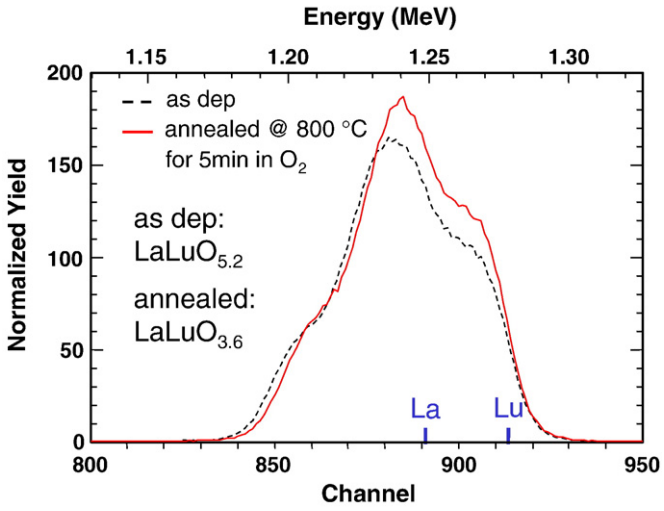

Fig. 5. RBS spectra of a 72.3 nm thick $LaLuO_3$ films as deposited and after annealing in oxygen at 800 °C for 5 min. The energies for the elements La and Lu are marked. From the simulations of the curves a significant decrease of the oxygen content can be derived. Simultaneously, the physical thickness is reduced by ~16%.

thin films remain amorphous up to 1000 °C. The ratio of the metals is close to 1:1 but excessive oxygen is found. The C–V curves are nearly ideal and the leakage current densities are low, but the κ-value of the as deposited films amounts to only ~17. After oxygen annealing of the films the oxygen content can be reduced to a value of a nominal composition and the κ-value of the thick film rises up to ~30, however, the film crystallizes. The next challenge will be to synthesize by ALD thin films of $LaLuO_3$ that are amorphous and exhibit a high κ-value as shown for PLD films.

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