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Growth of lanthanum oxide films for application as a gate dielectric in CMOS technology

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Abstract

We have investigated properties of insulating lanthanum oxide (La_2O_3) films in connection with the replacement of silicon oxide (SiO_2) gate dielectrics in new generation of CMOS devices. The La_2O_3 layers were grown using metal organic chemical vapour deposition (MOCVD) at 500 °C. X-ray diffraction analysis revealed polycrystalline character of the films grown above 500 °C. The X-ray photoemission spectroscopy detected lanthanum carbonate as a principal impurity in the films and lanthanum silicate at the interface with silicon. Density of oxide charge, interface trap density, leakage currents and dielectric constant (κ) were extracted from the $C-V$ and $I-V$ measurements. Electrical properties, in particular dielectric constant of the MOCVD grown La_2O_3 are discussed with regard to the film preparation conditions. The as grown film had $\kappa \sim 11$. Electrical measurements indicate possible presence of oxygen vacancies in oxide layer. The O_2-annealed La_2O_3 film had $\kappa \sim 17$.

Keywords: MOCVD; High-κ dielectric; Lanthanum oxide; MOS structure

1. Introduction

In the present time a lot of research effort is devoted to search for new alternative dielectric materials for CMOS technology. As the dimensions of MOS FET devices are scaled down, materials having higher dielectric constant should replace SiO_2 gate dielectric: high-κ materials. Lanthanum oxide, La_2O_3, could be considered as a candidate for CMOS gate application, since it has high dielectric constant close to 30 and enough large band gap equal to 4.3 eV [1,2]. However, the La_2O_3 films were reported to be hygroscopic and unstable in the air, forming carbonate and hydroxide impurities [3,4]. These impurities are harmful for a MOS FET device, since they create charges in the gate dielectric and consequently, result in large flat-band voltage shifts [5].

Thin lanthanum oxide films were already prepared by molecular beam epitaxy [4], vacuum evaporation [6–8], atomic layer deposition (ALD) [4] and by metal organic chemical vapour deposition (MOCVD) [9]. Even though the latter methods (ALD and MOCVD) exhibit enough

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flexibility for industrial application, they involve use of hydrocarbon-based precursors and an introduction of carbon impurities into the film is very likely. Therefore, thorough study of stability and impurities of the ALD and MOCVD grown La_2O_3 films should be carried out to justify their application as a MOS FET gate dielectrics.

In the present work we report on the chemical and physical characterization of MOCVD grown La_2O_3 thin films. The films were prepared by MOCVD technique using thermal evaporation of powder precursors. Detailed X-ray photoemission spectroscopy (XPS) analysis of as-deposited and UHV annealed films is discussed focusing on carbon contamination and properties of the film at the interface.

2. Experimental

Lanthanum oxide films were prepared by MOCVD. The powder precursor, $La(thd)_3$ triglyme is evaporated in the evaporation chamber of the MOCVD reactor. After evaporation, the metal organic vapours are mixed with oxygen and transported by argon into the deposition chamber. Lanthanum oxide films, presented in this study were grown at the deposition temperature $T_D = 500\,^\circ C$ on (1 0 0) phosphor doped n-type Si substrates with resistivity 3.5–6.5 Ω cm (ON Semiconductor Czech Republic). The chamber pressure during deposition was about 160 Pa. To remove native oxide, the Si substrates were etched before deposition in 10% HF solution at room temperature for 30 s.

The films were studied by the X-ray diffraction (XRD) in the Bragg–Brentano geometry using Cu Kα radiation. The thickness of the films (Table 1) was determined by Micropack NanoCalc 2000 using Ocean Optics/Mikropack micro-spectrometer working in a reflection mode. The thickness from Micropack NanoCalc 2000 measurement was calibrated against X-ray reflectivity (XRR) measurement. XRR was measured on a Stoe high-resolution diffractometer with Cu $K\alpha_1$ radiation ($\lambda = 0.15405$ nm). Reflectivity curves were simulated by the Fresnel optical computational code assuming an error function interface profile. XPS spectra were obtained in an ESCALAB 210 spectrometer, consisted of an analysis chamber and two separate independently pumped preparation chambers. Pressures in the range of 6×10^{-9} and 10^{-6} Pa were obtained in the analysis and preparation chambers, respectively. Non-monochromatized Mg Kα radiation was used as the excitation source. A depth profiling of the film was done by ion bombardment in the preparation chamber with Ar ions of 1 keV of kinetic energy. The composition of the films was calculated from the area of the bands in the XPS spectra. Annealing was done in the preparation chamber at the temperature 610 °C under the pressure of 10^{-7} Pa in the second preparation chamber.

Samples for electrical measurements were made by evaporating of Al dots and backside contact at room temperature to form $Al/La_2O_3/Si$ MOS structure. The samples for capacitance and current measurements were annealed in O_2 (atmospheric pressure) at 450 °C for 20 min and then in forming gas (90% N_2 + 10% H_2) (atmospheric pressure) at 420 °C for 20 min. Capacitance and leakage currents were measured as a function of voltage using an Agilent 4284A LCR meter and a Keithley 6517A Electrometer/High resistance meter.

3. Results and discussion

XRD were used to determine the crystallinity of as grown film. The measurements revealed that La_2O_3 films deposited at 500 °C were polycrystalline with slightly distorted cubic structure, with the (2 2 2) reflection as the strongest peak (Fig. 1). The XRR curve of the sample La22a in Fig. 2 revealed the smooth film surface with roughness ~1 nm.

Composition of the grown films was analysed by XPS. The most important part of the surface contamination of the as grown La_2O_3 films, revealed by the XPS analysis, were hydrocarbons, usually observed on the surface of the films kept in the air. After removal of the

Table 1

Parameters of as grown and annealed MOS capacitor samples with La_2O_3 film

Sample	Annealing	Thickness (nm)	κ	V_{FB} (V)	ΔV_{FB} (V)	N_f (cm^{-2})
La16b	—	70±2	10.50	−1.45	0.95	8.92×10^{11}
La16b	O_2	70±2	17.20	−0.96	0.3	5.92×10^{11}
La16b	Forming gas	70±2	17.09	−0.71	0.26	3.06×10^{11}
La23b	—	25±0.5	9.60	−3.90	1.1	7.63×10^{12}
La28a	—	50±1	12.20	−3.60	1.6	4.45×10^{12}
La24a	—	60±2	13.33	−4.00	1.9	4.54×10^{12}
La26b	—	75±2	11.22	−2.85	1.9	2.10×10^{12}
La27a	—	103±2	11.50	−2.80	1.9	1.54×10^{12}