Deposition Conditions and Post Treatment of High-k Praseodymium and Lanthanum Oxide Dielectrics

G. Lippert, J. Dąbrowski, P. Formanek, V. Melnik, R. Sorge, Ch. Wenger, P. Zaumseil, H.-J. Müssig
IHP, Im Technologiepark 25, D-15236 Frankfurt (Oder), Germany

The semiconductor technology roadmap predicts that high-k dielectric materials will substitute SiO_2 in Metal Oxide Semiconductor Field Effect Transistors (MOSFETs) and Metal Insulator Metal capacitors (MIMs). Pr and La oxides are among the prospective candidates for these alternative dielectrics. A problem typical for all the candidates considered so far is that the Equivalent Oxide Thickness (EOT) is limited by the formation of an interfacial layer with a lower K, and that the electrical properties of the film are deteriorated by the presence of electrically active defects and/or impurities.

This paper investigates the influence of the substrate (Si(001), TiN), the growth temperature, and the subsequent annealing procedure on the properties of the dielectric. The films are grown by Molecular Beam Epitaxy (MBE). Our analysis is based mostly on results of X-Ray Diffraction (XRD), X-Ray Photoelectron Spectroscopy (XPS), Cross Section Transmission Electron Microscopy (XTEM), Secondary Ion Mass Spectroscopy (SIMS), High Frequency Capacitance-Voltage measurements (HF CV), and ab initio total energy calculations. We show that the structural and electrical film properties are significantly influenced by the substrate material, by the growth and annealing temperatures, and by the presence of a capping Si layer. We propose mechanisms which may explain for the observed behavior. We also discuss the relevance of our results for the understanding of the properties of other lanthanide oxides.

XRD and XTEM data for Pr_2O_3/Si(001) indicate the formation of a thin amorphous interfacial layer by the interaction with air. Both layers can be suppressed by in situ capping with Si (Fig.1).

In Pr and La oxide films, XPS and SIMS reveal a strong OH signal in the uncapped area of the wafer (Fig 2). Annealing in vacuum removes the OH groups.

SIMS detected a temperature-dependent segregation of silicon from the substrate into crystalline Pr_2O_3 and La_2O_3 films. This occurs during the growth and results in the formation of a non-crystalline silicate at the interface. According to ab initio calculations, Pr silicate is thermodynamically stable with respect to separation into Pr_2O_3 and SiO_2. The silicate formation on a Si substrate is associated with the availability of oxygen. Water dissolved in the oxide facilitates the mixing process (Fig.3).

The frequency dependence of the film capacitance and conductivity is different for films grown on different substrates (Fig.4). The observed frequency dispersion may be explained by the differences in the dominant hopping mechanism in Pr_2O_3 and La_2O_3 films. We argue that a combined doping by H from water and by Si from the substrate is responsible for the observed deterioration of dielectric properties. For MIM applications, we could not detect OH groups in the film, and we achieved for the thinnest film an EOT of 0.57 nm. In thicker layers we obtained an ideal capacitive behavior in the investigated frequency range of 100 Hz to 1 MHz.

We conclude that Pr and La oxide films should be separated from the Si substrate and the air ambient by protective diffusion barriers.

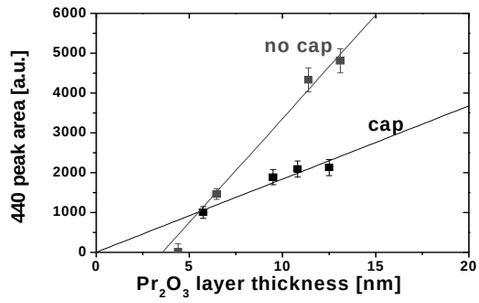

Fig.1: XRD data for uncapped Pr_2O_3/Si(001) indicate the formation of an amorphous interfacial layer.

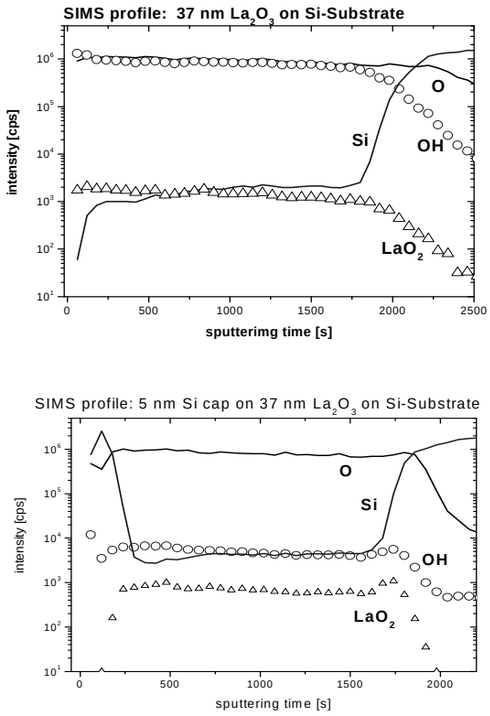

Fig.2: SIMS shows in the uncapped area of the wafer a OH signal 2 orders of magnitude higher as a capped area

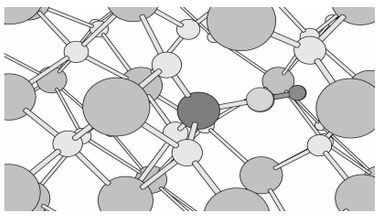

Fig.3: OH group dissolved in the Pr_2O_3 crystal

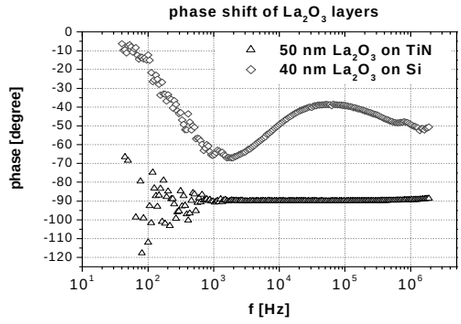

Fig.4: Frequency dispersion of phase shift of La_2O_3 films in MIM and MOS applications