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Hygroscopic nature of Lanthanide oxide (Ln2O3) and its effect on electrical properties of Ln2O3

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1. Introduction
Recently, promising results of various lanthanide oxides (Ln2O3) were reported for MOS gate dielectric applications [1]. Lanthanide oxide materials with various advantages such as thermal stability based on thermodynamic analysis, moderately high dielectric constants, and high conduction band offset over 2eV are attractive candidates as an alternative to SiO2 [1-2]. However, considering conventional CMOS process, high reactivity with water is considered as a major problem of lanthanide oxide [3]. A couple of studies on water absorption of high-k gate dielectric such as Y2O3, and LaSi2O5 were reported [4-5]. However, comprehensive study on the origin of hygroscopic nature of various lanthanide oxides has not yet been reported.

In this paper, we report on hygroscopic nature of lanthanide oxide (Pr2O3, Sm2O3, Gd2O3, and Dy2O3) and its effect on electrical characteristics of Ln2O3.

2. Experimental
Various Ln2O3 samples were directly deposited by e-beam evaporation using oxide source. The hygroscopic nature of lanthanide oxide was characterized by means of x-ray photoelectron spectroscopy (XPS). The structure of Ln2O3, physical thickness of Ln2O3, and interfacial Si-O layer between Ln2O3/Si was characterized by XRD, XRR, and FTIR, respectively. For electrical characterization of oxide, MOS capacitors with Pt-electrode were fabricated using conventional process.

3. Results & Discussion
Fig. 1-2 shows O1s spectra of XPS and area ratio of OH. Fig. 3 shows electro-negativity and ionic radius of various elements. Among the prepared samples, Pr2O3 composed of Pr with larger ionic radius and lower electron-electron-negativity is the most reactive oxide with water, which readily forms high concentration of hydroxide (OH) in oxide. From Pr2O3 to Dy2O3, a reduction of hygroscopicity was observed which can be explained by different electron-electro-negativity of Ln metal ion [3].

Fig. 4 and 5 shows O1s spectra of Sm2O3, and Dy2O3 with sputtering time. Compared with Dy2O3, the OH peak intensity of Sm2O3 is insensitive to sputtering time which indicates relatively large OH concentration in the bulk of Sm2O3.

Fig. 6 shows the area ratio of Si-O to Si peak versus various Ln2O3, which explains the effect of hygroscopicity on the growth of interfacial SiO layer between Ln2O3 and Si.

Fig. 7 and 8 shows EOT and J-V characteristics of Pr2O3, respectively. As expected, EOT increases and leakage current decreases with increasing annealing temperature. It can be explained by the growth of interfacial Si-O layer as shown in FTIR data of Fig. 9.

Fig. 10 shows EOT vs. annealing temperature of various samples. Compared with other samples, the reduction of EOT values with increasing annealing temperature up to 600°C was observed for Gd2O3 and Dy2O3 samples which can be explained by significant densification of as-deposited sample. A significant densification of oxide layer with increasing annealing temperature up to 800°C was observed for relatively thick as-deposited sample as shown in Fig. 11. Fig. 12 confirmed that all samples were crystallized at annealing temperature of 700°C.

A different EOT behavior can be explained by the competition between the growth of interfacial Si-O layer and the densification of oxide bulk. Considering less hygroscopic nature of Gd2O3 and Dy2O3 which form relatively thin interfacial oxide (Si-O) layer, the reduction of EOT values with increasing annealing temperature up to 600°C can be explained.

4. Summary
We studied the hygroscopic nature of Ln2O3 and its effect on electrical characteristics of Ln2O3. Among the prepared lanthanide oxides, Pr2O3 shows highest reactivity with water, which can be explained by larger ionic radius and lower electron-electro-negativity of Pr. The difference of hygroscopicity of lanthanide oxide can be explained by different electron-electro-negativity of Ln elements in Ln2O3. A clear understanding on hygroscopic nature of high-k oxide and optimization of process flow to minimize the growth of interfacial Si-O layer are necessary for future high-k gate dielectric application.

Acknowledgments
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References

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Fig. 1. O1s spectra of XPS for various lanthanide oxides.

Fig. 2. Hydroxide/LnO peak area ratio based on O1s spectra of XPS in Fig 1.

Fig. 3. The dependence of element on ionic radius and electro-negativity.

Fig. 4. O1s spectra of XPS with sputtering time for water reactive Sm2O3.

Fig. 5. O1s spectra of XPS with sputtering time for less water reactive Dy2O3.

Fig. 6. Si-O/Si peak area ratio based on Si 2p spectra of XPS for various lanthanide oxides.

Fig. 7. EOT versus annealing temperature for Pr2O3.

Fig. 8. Leakage current density (J) versus gate bias with anneal temperature for Pr2O3.

Fig. 9. Peak area of Si-O layer with anneal temperature based on FTIR measurement for Pr2O3.

Fig. 10. EOT versus anneal temperature for various lanthanide oxides (EOT of as depo=18-23Å).

Fig. 11. Thickness of high K layer with anneal temperature, which was measured by XRR.

Fig. 12. X-ray long power scan of various lanthanide oxide annealed at 700°C.