Electrical Characteristics of Rare Earth (La, Ce, Pr and Tm) Oxides/Silicates Gate Dielectric

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Abstract

Metal-oxide-semiconductor (MOS) capacitors with rare earth (La, Ce, Pr and Tm) oxides/silicates were fabricated to investigate the effective fixed charges density (Q_{fix}) in the gate dielectrics from the slope of EOT-V_{fb} plots. In the small EOT region, a diffusion of gate metal atoms caused to increase fixed charge at the interface between RE-oxide and RE-silicate. TmO_x/ Tm-silicate capacitors exhibit small Q_{fix} of -6.5×10^{12} cm^{-2} in the small EOT region.

Introduction

Downsizing has been the most effective way to improve the performance of Si-MOS devices, however, gate oxide has recently faced to its scaling limit with SiO_2 based gate dielectric [1]. This limit has been resolved with the introduction of high-k, which enables further reduction of the equivalent oxide thickness (EOT) and some leading-edge CMOS with Hf-based oxide was put into practical use.

In general, a SiO_2 interfacial layer is inserted between a high-k layer and a Si substrate to improve effective mobility and reliability [2]. However, to achieve an EOT down to 0.5 nm, which is the ultimate specification in ITRS roadmap [3], the high-k layer should be directly contacted on the Si substrate. It is reported the directly contact in Hf-based oxide is achived by a choice of proper metal electrode, improving effective mobility and reliability is necessary. On the other hand, rare earth (RE) oxides react with Si to form RE-silicate by annealing [4]. RE-silicate layers generally have dielectric constants more than 8, so that a directly contact structure can be easily achieved. However, mobility degradation of MOSFETs with La_2O_3/La-silicate in EOT below 0.5 nm has been one of the major issues [5]. The degradation is caused by fixed charges in high-k, and the correlation with a shift in flat band voltage is known. We consider there is a possibility of improving the interface properties by combining La-silicate and RE oxides.

In this report, the dependce of flat band voltage (V_{fb}) shift on EOT of MOS capacitors with RE (La, Ce, Pr and Tm) oxides/silicates were investigated.

Experimental

Figure 1(a) summarizes the device fabrication flow of MOS capacitors with La_2O_3, CeO_x, PrO_x, and TmO_x gate dielectrics. The capacitors were fabricated on *n*-type (100)-oriented Si substrates. The wafers were then cleaned by a mixture of H_2SO_4/H_2O_2 to remove all the resist-related organic contamination, followed by diluted HF cleaning. La_2O_3, CeO_x, PrO_x and TmO_x (x<2) films were deposited by e-beam evaporation in an ultrahigh vacuum chamber (~10^{-6} Pa). A gate electrode of tungsten (W) was *in-situ* deposited by sputtering and patterned by reactive ion etching (RIE) with SF_6 chemistry. Then, post-metallization annealing (PMA) was carried out in forming gas ambient (H_2:3%, N_2:97%) at 500^{o}C for 30 min. Capacitance-voltage (*C-V*) characteristics of the capacitors were measured at 100 kHz and EOT was calculated from the *C-V* characteristics.

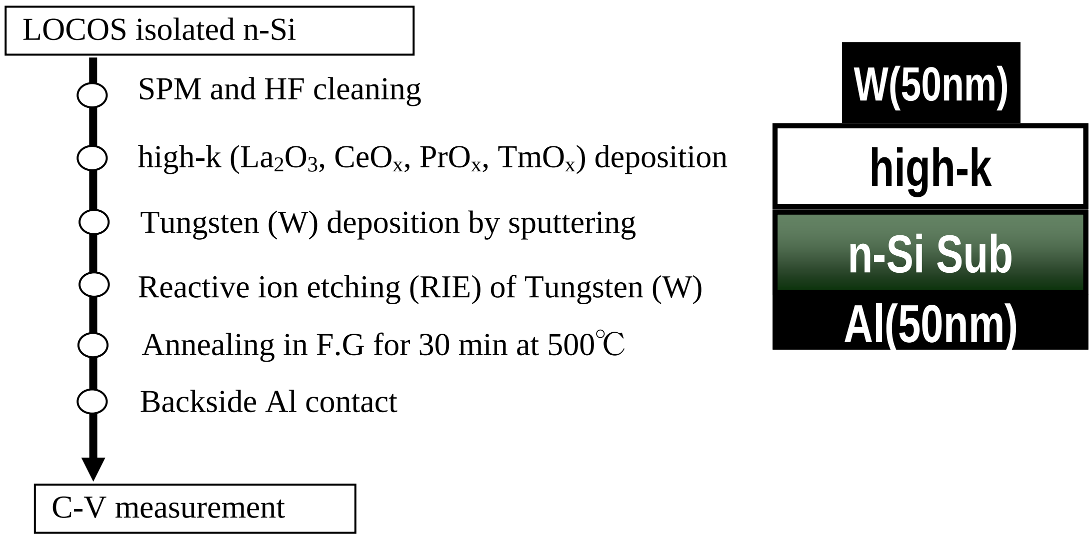

Figure 1. (a) Fabrication process flow of high-k gated n-MOS capacitor (b) Structure of fabricated MOS capacitor.

Results

V_{fb} dependence on EOT of the capacitor with La_2O_3

Figure 2 shows the dependence of V_{fb} on EOT for La_2O_3/La-silicate MOS capacitors. In this figure, two linear regions were observed. From the slope of the dependence of flatband voltage on EOT, the effective fixed charges density (Q_{fix}) at the interfaces of RE-oxide/RE-silicate and RE-silicate/Si can be extracted.

The EOT ranges from 0.9-1.3 nm, and 1.3-2 nm in La_2O_3/La-silicate samples exhibited the Q_{fix} of -2.2×10^{13} and -6.6×10^{12} cm^{-2}, respectively. At the cross-point of these linear regions, physical thickness is about 4 nm, and it is considered that a diffusion of tungsten atoms cause to increase fixed charges below this thicknesses.

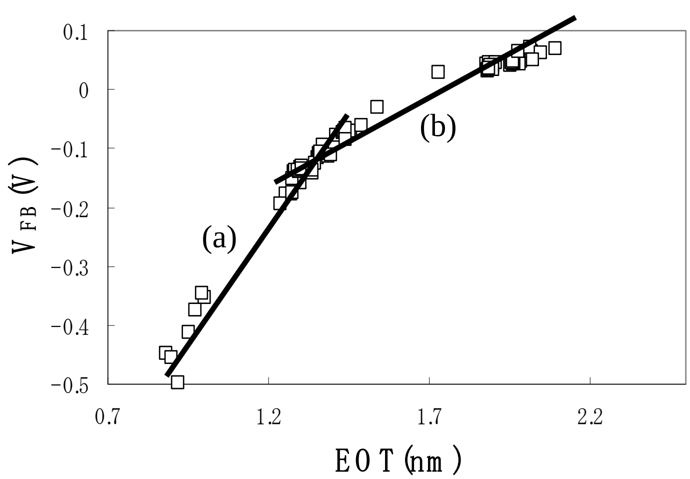

Figure 2. V_{fb} as a function of EOT for W/La_2O_3/Si capacitors after annealing at 500 ^{o}C

V_{fb} dependence on EOT of the capacitor with CeOx

Figure 3 shows the dependence of the V_{fb} on EOT for CeO_x/Ce-silicate MOS capacitors. In this figure, two linear regions were observed. The EOT ranges from 1.0~1.2, 1.2~1.4, and 1.4~1.6 nm in CeO_x/Ce-silicate samples exhibited the Q_{fix} of -6.6×10^{13}, $+6.1\times10^{12}$ and $+6.3\times10^{11}$ cm^{-2}, respectively. In EOT range below 1.2 nm, a diffusion of tungsten atoms might cause to increase fixed charges like the La_2O_3/La-silicate samples. In the EOT range over 1.2 nm, we consider that negative fixed charges in the CeO_x layer cause the flatband shift,. The smaller crosspoint than La_2O_3 is due to its higher dielectric constant. Fixed charges in CeO_x have much effect on V_{fb} shift

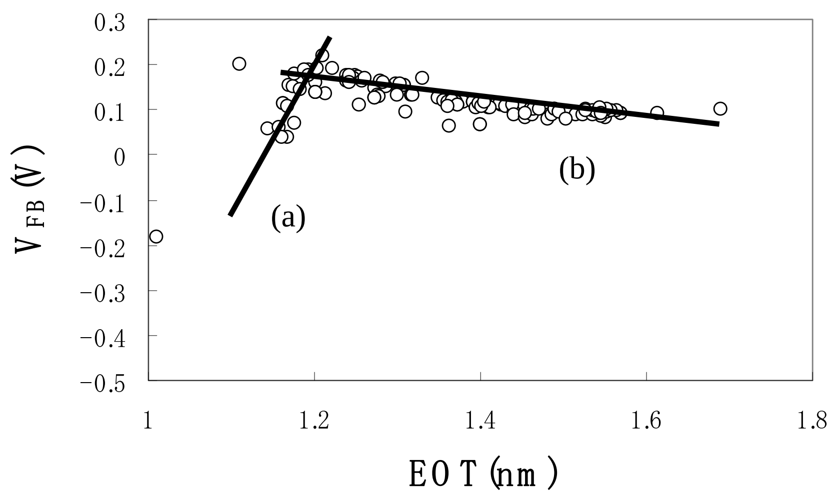

Figure 3. V_{fb} as a function of EOT for W/CeO_x/Si capacitors after annealing at 500 ^{o}C

V_{fb} dependence on EOT of the capacitor with PrO_x

Figure 4 shows the dependence of V_{fb} on EOT for PrO_x/Pr-silicate MOS capacitors. In this figure, two linear regions were observed. The EOT ranges from 0.7~1.2, 1.2~2.3 nm, PrO_x/Pr-silicate exhibited the Q_{fix} of -1.4×10^{13}, -2.7×10^{12} cm^{-2}, respectively. This result is similar to that of La_2O_3/La-silicate samples. Therefore, a diffusion of tungsten atoms probably causes to increase fixed charges like the La_2O_3 case.

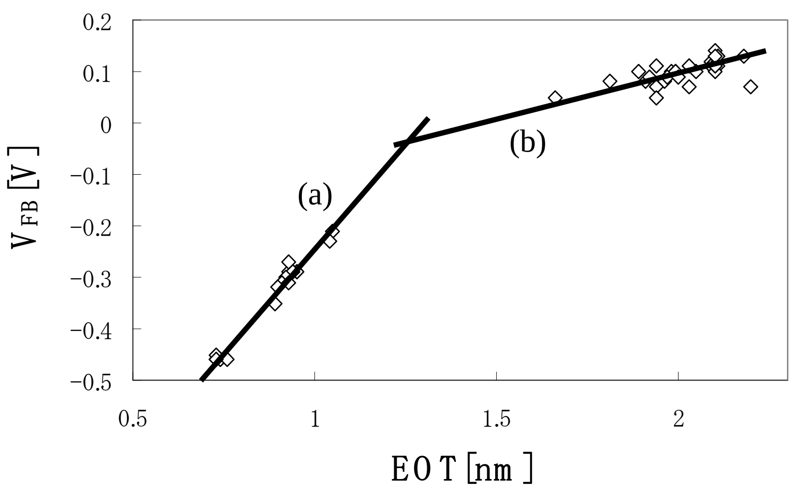

Figure 4. V_{fb} as a function of EOT for W/PrO_x/Si capacitors after annealing at 500 ^{o}C

V_{fb} dependence on EOT of the capacitor with TmOx

Figure 5 shows the dependence of V_{fb} on EOT in TmO_x/Tm-silicate MOS capacitors. In this figure, two linear regions were observed.

The EOT ranges from 0.6~1.8, and 1.8~3.0 nm in TmO_x/Tm-silicate samples exhibited the Q_{fix} of -6.5×10^{12}, and -3.3×10^{12} cm^{-2}, respectively. This behavior is also similar to that of La_2O_3/La-silicate samples. However, the value of the Q_{fix} was the lowest value among the samples of the current study.

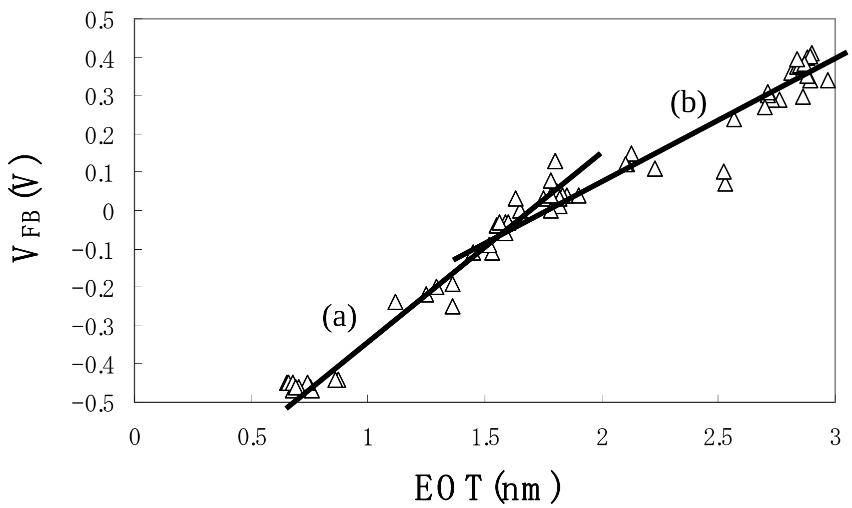

Figure 5. V_{fb} as a function of EOT for W/TmO_x/Si capacitors after annealing at 500 ^oC

Discussions

Figure 6 shows the schematic illustration of the location of fixed charges in La_2O_3, PrO_x and TmO_x. From the slope of (a) as shown in Figs. 2-5, the fixed charges at La_2O_3/silicate, CeO_x/silicate, PrO_x/silicate, and TmO_x/silicate interfaces are found to be negative, presumably because the tungsten (W) atoms are located near the interface and the diffusion of W atoms toward the interface is not negligible. However, in the region (b), the fixed charges at La_2O_3/silicate, PrO_x/silicate, and TmO_x/silicate interfaces decrease, because the distance from W electrode to these interface increases and the diffusion of W atoms to the interface is negligible.

Figure 7 shows the schematic illustration of the location of fixed charges in CeO_x layers. In the region (b) as shown in Fig 3, negative fixed charges in the CeO_x layer increase owing to the increase in CeOx layer thickness, while the negative fixed charges at CeO_x/silicate interface decreases. CeO_x can achieve the same EOT with physical thickness larger than those of La_2O_3, PrO_x and TmO_x owing to its high dielectric constant. Therefore, an amount of fixed charge in CeOx layer has much effect on V_{fb} shift.

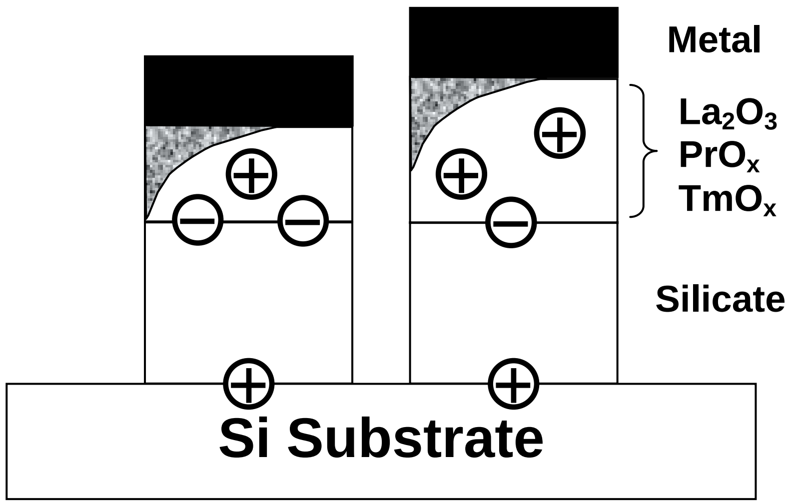

Figure6. Schematic illustration of fixed charges generation in the oxide and oxide/silicate interface for two thicknesses of La_2O_3, PrO_x and TmO_x layers.

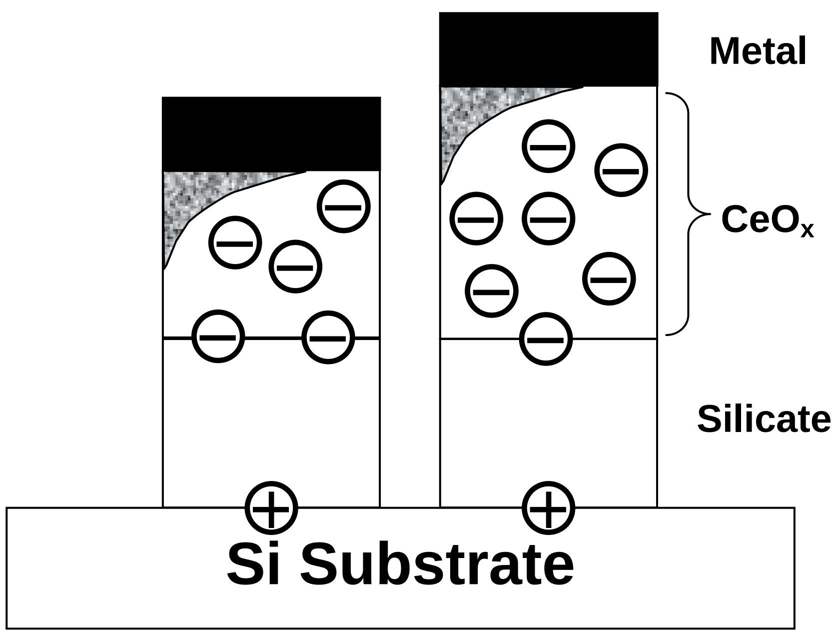

Figure 7. Schematic illustration of fixed charges generation in the oxide and oxide/silicate interface for two thicknesses of CeO_x layer.

Conclusion

Dependence of V_{fb} shift on EOT of MOS capacitors with rare earth (La, Ce, Pr and Tm) oxides/silicates are investigated. In the small EOT region, a diffusion of gate metal atoms from gate electrode increases fixed charge at the interface between RE-oxide and RE-silicate. With the increase in EOT, the effect of fixed charge in the RE-oxide film on V_{fb} shift increases. TmO_x/Tm-silicate capasitor exhibits small Q_{fix} of -6.5×10^{12} cm^{-2} in the low EOT region.

Acknowledgments

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