

# Charged defects reduction in gate insulator with multivalent materials

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## Abstract

A novel method of controlling the number of charged defects in high-k gate dielectric for Metal Oxide Semiconductor Field-Effect Transistor (MOSFET) with high-k gate dielectric has been proposed. As shown Fig.1, the amount of charged defects, either interstitial oxygen atoms or vacancies, depends on the process ambient. These cause flatband voltage ( $V_{fb}$ ) instability (Fig.2, 3)[1-2]. On the other hand, oxides with multivalent materials release or absorb oxygen atoms by changing the valence number of anion atom, to fix the chemical potential to a constant value. With the use of multivalent oxide material as a capping layer for gate dielectric, the chemical potential of the adjacent high-k can be kept constant so that the amount of charged defects in the high-k layer can be controlled. First-principles calculation has revealed that  $CeO_x$  capping on  $La_2O_3$  or  $HfO_2$  layer fixes the chemical potential to a value where lowest number of charges in the high-k can be achieved and is effective among other multivalent oxide materials. As shown Fig4, the valence number transition triggered by reduced or oxidation process has been confirmed by x-ray photoelectron spectroscopy (XPS). Multivalent material capping is a useful way to fix the oxygen chemical potential for future ionic oxide material applications.

## Introduction

$La_2O_3$  is known as the most promising gate insulating oxide to achieve the effective oxide thickness below 0.5 nm. However, the oxygen concentration in the high-k materials including  $La_2O_3$  is very sensitive to the oxygen partial pressure in process ambient, and thus oxygen-related defects are easily form in the oxide layer. These defects are usually charged, which results in  $V_{fb}$  shifts. In fact,  $V_{fb}$  shifts have been observed as changing the external oxygen atmosphere. Controlling ambient oxygen pressure might be effective for decreasing the intrinsic charged defects. However, it is hard to adjust the ambient oxygen pressure in the entire process of the MOSFET fabrication. Thus, an alternative solution has been awaited.

In this study, we report a novel method for the reduction in the charged defects using multivalent materials. From a theoretical study using first-principles calculation, the propriety of this technique has been confirmed.

## Experiment

In the theoretical calculation, the charge defects are calculated by using the first-principle method. Two intrinsic defects, a single oxygen vacancy at 4-fold oxygen site,  $V_O^{2+}$  and oxygen interstitial at 6-fold oxygen site,  $I_O^{2-}$  (Fig.5) are investigated. The stabilities of these defects were compared in terms of the formation energy defined by  $E_f(X^Q) = E_{tot}(X^Q) - E_{tot}(bulk) - n_O \mu_O + Q(\epsilon_F + \epsilon_i + \Delta V + E_{corr})$ , (1) where  $E_{tot}(X^Q)$  and  $E_{tot}(bulk)$  are the total energy of a defect X ( $V_O$  or  $I_O$ ) with charge Q (2+ or 2-) and the bulk  $La_2O_3$ .  $n_O$  is the number of oxygen atoms removed from the perfect

crystal.  $\mu_O$  is the oxygen chemical potential, this is only the variable in Eq.(1).

## Results and Discussions

The density of charge defect:  $n_{cd}$  is calculated from  $n_{cd} = N_{site} / (1 + \exp(E_f / k_B T))$  where  $N_{site}$  is the number of defect sites available in a unit volume. Fig.6 shows that the total charge density has a minimum at the -4.2 eV. Therefore, it's preferable that  $\mu_O$  is fixed at near this value. By using multivalent materials,  $\mu_O$  may be fixed. As shown in Fig.6, if the oxide has two phases associated with different valence in the material,  $\mu_O$  value can be uniquely determined. Fig.6(a) shows the  $\mu_O$  of Ce-oxide is closest to the minimum point of the density of charged defects in  $La_2O_3$ . Therefore, it's expected that the combination of  $La_2O_3$  and Ce-oxide has an effect on reducing the fixed charge in  $La_2O_3$ . The same can be said the  $HfO_2$  case (Fig.6(b)). Therefore, Ce-oxide capping can be considered as effective in charged defects reduction.

Fig. 7 shows the mechanism of fixed chemical potential in high-k. (a) shows  $La_2O_3$  single layered case. When a process with reducing ambient is performed, oxygen atoms were taken out to produce oxygen vacancies, so that oxygen chemical potential changed. On the other hand, when oxidizing process is performed, oxygen atoms will be taken in to compensate the oxygen vacancies. As the result, oxygen vacancies are reduced. However, interstitial oxygen atoms will be generated in the film, if excess oxidation is performed. Therefore, the oxygen chemical potential fluctuates by device process ambient. So, a way to fix the chemical potential against process ambient is essential.

(b) shows  $CeO_x$  capped on  $La_2O_3$  case. At reduction ambient, if only high-k film, many oxygen vacancies are generated. However, when  $CeO_x$  is capped on high-k,  $CeO_x$  released oxygen atoms to compensate the oxygen vacancies in the high-k by increasing the ratio of  $Ce_2O_3$ . On the other hand, at oxidizing process, if only high-k film, interstitial oxygen atoms are generated. But the case of  $CeO_x$  is capped, oxygen atom are absorbed into  $CeO_x$  to suppress the interstitial oxygen atoms by increasing the ratio of  $CeO_2$ . For both conditions, the chemical potential of  $CeO_x$  and the high-k is kept constant.

## Conclusion

In this paper, we proposed a novel method for reduction of the charge defects in film by using multivalent materials. We demonstrated the effectiveness's the proposed method using both of the theoretical calculation and experiment. It was shown that capping with Ce-oxide has great potential for reduction of the charge defects in  $La_2O_3$  and also in  $HfO_2$ .

## Reference

- [1] E. Cartier *et al.*, Symposium on VLSI 2005, p.203
- [2] K. Ohmori *et al.*, J. Appl. Phys. **101** 084118 (2007)

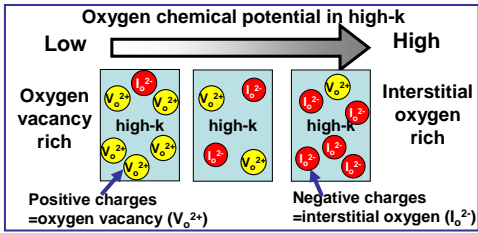


Fig.1 Positive charges due to oxygen vacancy and negative charges due to interstitial oxygen both are inside high-k gate oxide. The number of charges are dependent on the oxygen chemical potential in high-k.

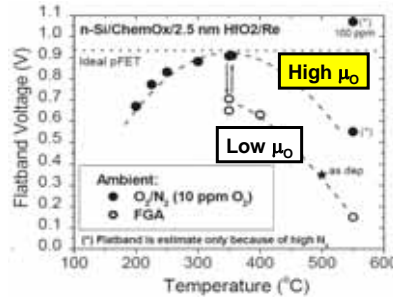


Fig.2 the flatband voltage instability of HfO2. Annealing in oxygen ambient moves the flatband voltage to positive direction and reducing ambient negatively shifts, (Ref [1]).

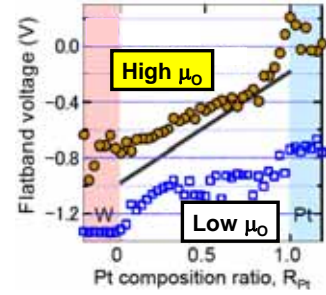
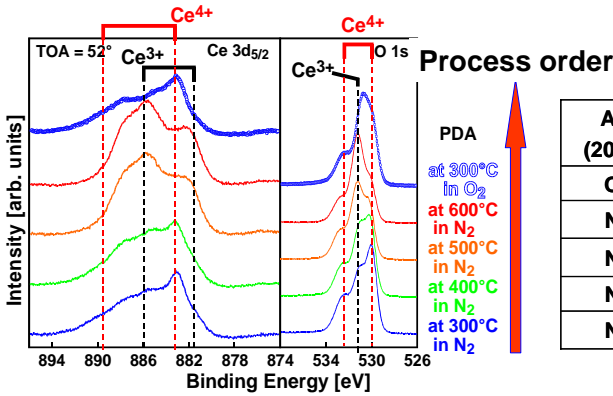


Fig.3 Flatband voltage instability of La2O3 case (Ref[2]).



Annealing (20min 1Torr)	Ce <sub>2</sub> O <sub>3</sub> (%)
O <sub>2</sub> 300 °C	40
N <sub>2</sub> 600 °C	69
N <sub>2</sub> 500 °C	61
N <sub>2</sub> 400 °C	48
N <sub>2</sub> 300 °C	40

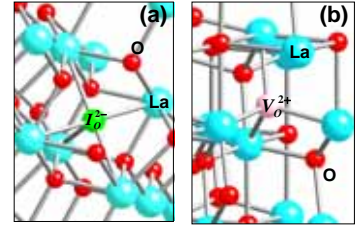


Fig.5 (a) Oxygen interstitial at 6-fold oxygen site (b) Oxygen vacancy at 4-fold oxygen site in a 50-atom supercell of hexagonal La<sub>2</sub>O<sub>3</sub>.

Fig.4 XPS spectra from Ce-oxide layer in Ce-oxide/La<sub>2</sub>O<sub>3</sub> capacitor structure. The ratio of Ce<sup>3+</sup> and Ce<sup>4+</sup> changes with the temperature and ambient. Both Ce<sup>3+</sup> and Ce<sup>4+</sup> states co-exist at the same time

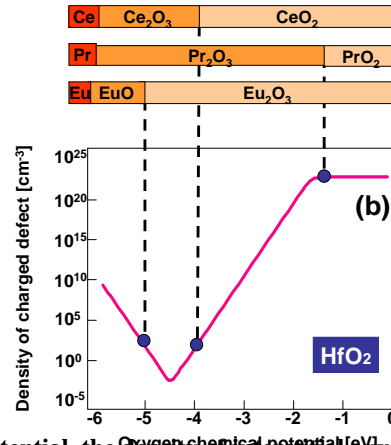
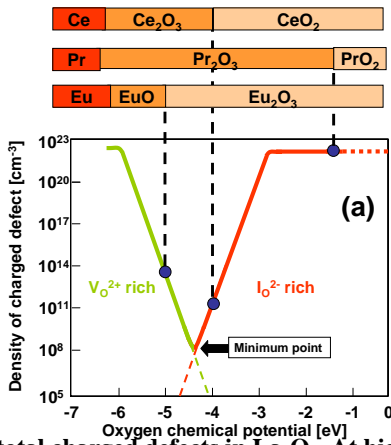


Fig.6 (a) The total charged defects in La<sub>2</sub>O<sub>3</sub>. At high oxygen chemical potential, the density of interstitial oxygen high. When the oxygen chemical potential decreases, the density of interstitial oxygen decreases and the density of oxygen vacancies increases. At a certain value of oxygen chemical potential, the number of oxygen vacancies exceeds to that of interstitials, oxygen vacancies become dominant. (b) HfO<sub>2</sub> is also the same as the La<sub>2</sub>O<sub>3</sub>

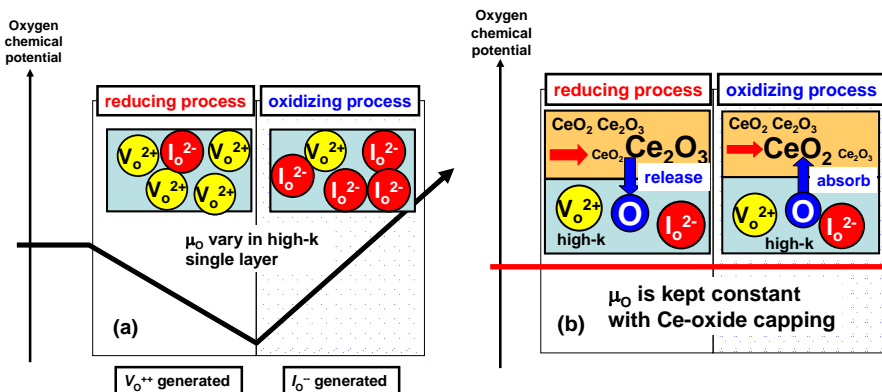


Fig.7 The mechanism of fixed oxygen chemical potential in host high-k. (a) single high-k layered case. (b) CeOx capped on high-k case.