Impacts of Annealing Conditions on the Flat Band Voltage of Alternate La$_2$O$_3$/Al$_2$O$_3$ Multilayer Stack Structures

Xing-Yao Feng, Hong-Xia Liu*, Xing Wang, Lu Zhao, Chen-Xi Fei and He-Lei Liu

Abstract

The mechanism of flat band voltage ($V_{FB}$) shift for alternate La$_2$O$_3$/Al$_2$O$_3$ multilayer stack structures in different annealing condition is investigated. The samples were prepared for alternate multilayer structures, which were annealed in different conditions. The capacitance-voltage (C-V) measuring results indicate that the $V_{FB}$ of samples shift negatively for thinner bottom Al$_2$O$_3$ layer, increasing annealing temperature or longer annealing duration. Simultaneously, the diffusion of high-$k$ material to interfaces in different multilayer structures and annealing conditions is observed by X-ray photoelectron spectroscopy (XPS). Based on the dipole theory, a correlation between the diffusion effect of La towards bottom Al$_2$O$_3$/Si interface and $V_{FB}$ shift is found. Without changing the dielectric constant $k$ of films, $V_{FB}$ shift can be manipulated by controlling the single-layer cycles and annealing conditions of alternate high-$k$ multilayer stack.

Keywords: Flat band voltage, La$_2$O$_3$/Al$_2$O$_3$ multilayer, Dipoles, Diffusion effect, Interface layer

Background

High dielectric constant (high-$k$) materials have been extensively used to substitute conventional SiO$_2$ gate oxides for its prominent properties such as small equivalent oxide thickness (EOT) and low leakage current. During the past years, researchers have paid lots of attentions to high-$k$ materials, such as hafnium oxide (HfO$_2$), yttrium oxide (Y$_2$O$_3$), zirconium oxides (ZrO$_2$), lanthanum oxide (La$_2$O$_3$), aluminum oxide (Al$_2$O$_3$), and other transition-metal oxides. Among them, La$_2$O$_3$ is considered a remarkable candidate because of its high dielectric constant (approximately 25) and large band gap (approximately 5.8 eV). However, the application of high-$k$ materials also cause lots of new problems and challenges [1, 2]. Recently, the properties of La$_2$O$_3$ and Al$_2$O$_3$ gate stacks have been studied by many researchers, and much promotion has been made in restraining leakage current and suppressing the formation of parasitic interface [3–5].

Furthermore, flat band voltage has been regarded as one of the most critical parameters for the design and fabrication of semiconductor devices. Earlier researchers claimed that the fixed charges are the main factor for flat band voltage ($V_{FB}$) shift [6]. However, Dr. Wang pointed out there was no correlation between $V_{FB}$ and fixed charges because the film Hf$_x$La$_{1-x}$O$_y$ keep the same $V_{FB}$ for different film thicknesses [7, 8]. Researchers also revealed that the main origin of $V_{FB}$ is the dipoles between high-$k$/interface layer [9, 10]. Besides, the atomic mechanism of $V_{FB}$ shifts for different high-$k$ gate stacks is also discussed specifically by Lin and Robertson [11, 12]. However, the influence of the film structure and annealing conditions on $V_{FB}$ has not been fully investigated. In this study, firstly, a model of $V_{FB}$ including the interfaces of metal/high-$k$ and high-$k$/Si was introduced. Then, alternate La$_2$O$_3$/Al$_2$O$_3$ multilayer stacks were prepared with different single-layer cycles by atomic layer deposition (ALD) and annealed in different temperatures and duration. The electrical and physical characteristics of the samples were investigated. Based on the theory of dipoles and diffusion effect, the mechanism of $V_{FB}$ shift was studied.
Methods
Firstly, p-type Si(100) wafers were washed in deionized water and chemically etched with diluted HF for 3 min to remove the native oxide. Then, alternate La$_2$O$_3$/Al$_2$O$_3$ multilayer high-$k$ stacks with different single-layer cycles were deposited on Si wafers by ALD reactor (Picosun R-150, Espoo, Finland) in 300 °C. La($i$-PrC$_{p}$)$_3$ and trinethylmumium (TMA) were used as precursors of La and Al, respectively. Besides, O$_3$ was used as oxidant, and ultra-high purity nitrogen (N$_2$, 99.999 %) was employed as carrier and purge gas. After deposition, the rapid thermal annealing (RTA) process was carried out at different temperatures for different duration in N$_2$ ambient. For further analysis, annealed La$_2$O$_3$/Al$_2$O$_3$ film thickness (without metal gate) was examined by Woollam M2000D (Woollam Co. Inc., Lincoln, NE, USA) spectroscopic ellipsometry (SE). X-ray photoelectron spectroscopy (XPS) was used to examine the bonding structures and chemical quantitative composition of the films. C1s peak from adventitious carbon at 284.6 eV [13] was used as an internal energy reference during the analysis. Besides, 100-nm-thick Al was deposited by magnetron sputtering as electrode, and then, capacitance-voltage (C-V) measurement was carried out using Agilent B1500A semiconductor analyzer at the frequency of 100 kHz.

Results and Discussion
Taking into consideration of fixed charges and interfacial dipoles, the $V_{FB}$ of conventional metal/SiO$_2$/Si metal oxide semiconductor (MOS) structure can be expressed as [14]:

$$V_{FB} = \frac{q}{q} - \frac{Q_0}{\varepsilon_0 \varepsilon_{ox}} + \left( \Delta_{metal/SiO_2} + \Delta_{SiO_2/Si} \right),$$

where $\varphi_{ms}$ is the work function difference between metal and Si substrate and $Q_0$ represents the fixed charges located in oxide layer. $\Delta_{metal/SiO_2}$ and $\Delta_{SiO_2/Si}$ are dipoles located in the interface of metal/SiO$_2$ and SiO$_2$/Si.

In this work, SiO$_2$ is substituted by high-$k$ materials Al$_2$O$_3$ and La$_2$O$_3$, so the $V_{FB}$ of samples with alternate high-$k$ dielectric gate stacks can be expressed as:

$$V_{FB} = \frac{q_{ms}}{q} - d_0 \left( \frac{Q_0}{\varepsilon_0 \varepsilon_{Al_2O_3}} \right) - d_1 \left( \frac{Q_1}{\varepsilon_0 \varepsilon_{La_2O_3}} \right) + \left( \Delta_{metal/high-k} + \Delta_{high-k/Si} + \Delta_{La_2O_3/Al_2O_3} \right).$$

In this equation, $Q_0$ and $Q_1$ represent the fixed charges in Al$_2$O$_3$ and La$_2$O$_3$ films, respectively. As shown in Fig. 1, all dipoles can be separated into three kinds. They are the dipoles between the alternate high-$k$ films, the dipoles at interfaces of metal/La$_2$O$_3$, and dipoles at interfaces of Al$_2$O$_3$/Si. Between the alternate high-$k$ layers, the dipoles La–O–Al and Al–O–La have reverse sequence which can cancel out each other. So these dipoles do not create net dipole.

Furthermore, some researches have proved that the contribution of dipoles at metal/high-$k$ interface to the $V_{FB}$ shift can be neglected [10, 15, 16]. For inspecting this point of view, two samples were prepared with different high-$k$ films, and then, the RTA process was carried out at 600 °C for 60 s in N$_2$ atmosphere. Their simplified schematic structures and C-V curves are shown in Fig. 2. It should be noted that the two films show approximately the same $V_{FB}$: 1.49 V (without La$_2$O$_3$ inserted layer) and 1.47 V (with La$_2$O$_3$ inserted layer). The insensitiveness of $V_{FB}$ values to the kind of dipoles at metal/high-$k$ interface clearly indicates the metal/high-$k$ interface is not one of the origin of $V_{FB}$ shift. Therefore, in this work, the fixed charges $Q_0$ and $Q_1$ and the dipoles at interface of Al$_2$O$_3$/Si need to be examined on the next step.

Fig. 1 The schematic of three kinds of dipoles in La$_2$O$_3$/Al$_2$O$_3$ high-$k$ dielectric stacks.
Samples S1–S5 were deposited for different structures in an identical annealing condition (annealed at 600 °C for 60 s in N₂ atmosphere). The schematic of alternate high-k films S1–S5 is shown in Fig. 3. For each of the samples S1–S4, 40-cycle La₂O₃ and 40-cycle Al₂O₃ were deposited with different single-layer cycles (from S1 to S4 are 40, 20, 10, and 1 cycle of single layer). In order to investigate the influence of fixed charges on V FB as shown in Fig. 3b, e, the sample S5 was deposited with the same single-layer cycles but double number of layers as S2. The structures and thicknesses of samples S1–S5 are listed in Table 1.

Figures 4 and 5 show the C-V curves and V FB shifts of samples S1–S5. Samples S1–S4 have very close accumulation capacitance. The EOTs of samples S1–S5 are extracted by NCSU CVC program [17], which are 2.21, 2.20, 2.21, 2.29, and 4.16 nm, respectively. The dielectric constants are 12.46, 12.44, 12.34, 12.89, and 12.56, respectively. The V FB of samples S1–S5 are 1.45, 1.30, 0.60, 0.25, and 1.30 V, respectively. For 80-cycle pure Al₂O₃ and 80-cycle pure La₂O₃ films deposited and annealed in the same condition with S1–S5, V FB are 1.49 and −0.32 V, which is shown in Fig. 5. We notice that V FB become smaller shifting from the V FB of pure Al₂O₃ film to the pure La₂O₃ direction for a thinner single layer (from 40 to 1 cycle). In a recent report [10], a negative V FB shift is observed for a thicker La₂O₃ inserted layer at HfO₂/Si interface which comes to a similar conclusion with our work. Furthermore, V FB is the same for samples S2 and S5, which indicates the Al₂O₃ and La₂O₃ films have few fixed charges. Therefore, the fixed charge Q₀ and Q₁ in Eq. 2 can be neglected for studying V FB shift. As discussed, the V FB shifts of S1–S4 have no relevance to the dipoles between alternate high-k layers and dipoles at metal/high-k interface. Therefore, it is clear that such a shift (from 1.45 to 0.25 V) is supposed to be relevant to the variation of dipoles at Al₂O₃/Si interface.

For further investigation about the mechanism of V FB shift for high-k gate stacks, different annealing conditions were employed after the ALD deposition. As shown in Table 2, samples S2 and S6–S10 were deposited for identical structure and then annealed at different temperatures (600, 700, and 800 °C) for different duration (30, 60, 90, and 120 s) in N₂ atmosphere. The correlations between C-V curves and annealing conditions of samples S2 and S6–S10 are shown in Fig. 6. The EOTs of samples S2 and S6–S10 extracted by NCSU CVC program [17] are 2.20, 2.23, 2.29, 2.20, 2.20, and 2.20 nm, respectively, and the dielectric constant k can be figured out as 12.44, 12.61, 12.26, 12.55, 12.53, and 12.62, respectively. As shown in Fig. 7, the V FB of samples S2 and S6–S10 are 1.3, 0.75, 0.5, 1.33, 1.28, and 1.22 V, respectively, which have a remarkable negative shift with increasing annealing temperature and a slight negative shift with increasing duration. Similar trend of V FB shift (approximately 1 to 0.6 V) was also reported for HfO₂ and Al₂O₃ stacks at different annealing temperature (400 and 1000 °C, respectively) [9].

Then, XPS was employed to examine the variation of bonding structure. Figure 8 shows the O1s XPS spectra of annealed samples S1–S4, and each of the spectra was fitted with four peaks Si–O–Al (532.5 eV), Al–O–Al (531.5 eV), Al–O–La (530.9 eV), and La–O–La (528.75 eV). It is found that La–O–Al peaks become larger while Al–O–Al and La–O–La peaks become smaller from S1 to S4. That is attributed to more La₂O₃/Al₂O₃ interface layers formed with decreasing single-layer cycles. As we discussed above, the dipoles La–O–Al and Al–O–La can cancel each other, so the variation of these peaks makes no contribution to V FB shift.

Figure 9 show the O1s XPS spectra of samples S2, S6, and S7. More Al–O–La bonds and less Al–O–Al and La–O–La bonds are observed from S2 to S7, which indicates more Al₂O₃ and La₂O₃ diffuse into each other and form LaAlO₃ at Al₂O₃/La₂O₃ interface at higher annealing temperature. The value of diffusion coefficient mainly depends on the kinds of diffusion substance and diffusion medium as well as the diffusion temperature.

### Table 1 The structures and thicknesses of annealed samples S1–S5

| Sample | Film structures | Thickness (nm) |
|--------|----------------|---------------|
| S1     | 1 × (40-cycle Al₂O₃ + 40-cycle La₂O₃) | 7.06 |
| S2     | 2 × (20-cycle Al₂O₃ + 20-cycle La₂O₃) | 7.02 |
| S3     | 4 × (10-cycle Al₂O₃ + 10-cycle La₂O₃) | 6.99 |
| S4     | 40 × (1-cycle Al₂O₃ + 1-cycle La₂O₃) | 7.57 |
| S5     | 4 × (20-cycle Al₂O₃ + 20-cycle La₂O₃) | 13.4 |

The samples were annealed at 600 °C for 60 s.
So this trend is due to the larger diffusion coefficient obtained at higher temperature.

In both Figs. 8 and 9, we notice that there is only small amount of Si–O–Al bonds which show a slight decrease for thinner single layer or higher annealing temperature. Thinner single layer means a thinner bottom Al₂O₃ layer, which leads to more La₂O₃ diffusing into Al₂O₃/Si interface and replacing the Si–O–Al with Si–O–La bonds. Based on the theory of diffusion, more La₂O₃ can diffuse through the bottom Al₂O₃ layer forming Si–O–La bonds at higher annealing temperature. Similarly, increasing annealing duration can also cause more La₂O₃ diffusing into Al₂O₃/Si interface. That is why, the amount of Si–O–Al bonds declines. This diffusion effect of high-k material after annealing process is also proved in report [9], which shows HfO₂ and Al₂O₃ stacks diffusing into each other and into the metal/high-k/highbottom Al₂O₃ layer after annealing process at different temperatures.

On the other hand, Si–O–Al and Si–O–La bonds are located at the interface of high-k/Si. According to the dipole theory discussed above, this substitution of La for Al should be responsible for the negative V_
FB shift. Therefore, we should also discuss how the increasing La–O–Si bonds at Al₂O₃/Si interface influences the V_
FB. La has weaker electronegativity than Al (La ~ 1.11, Al ~ 1.61). When Al is substituted by La, compared with Al, electrons will be further from La and move towards O. So the dipole La–O presents a larger polarity compared with dipole Al–O. It means a larger electrostatic potential, which can increase the band offset and finally cause the V_
FB shift. It is concluded that the more Al is substituted by La at Al₂O₃/Si interface the closer to blue dotted line, the V_
FB will be. Moreover, the V_
FB shift in
different annealing temperatures is much bigger compared with different duration. It can be explained by the exponential relationship between the temperature and diffusion coefficient. Therefore, a feasible way to modulate the $V_{FB}$ of alternate high-$k$ multilayer stack gate is to control the single-layer cycles and annealing conditions.

In addition, we should notice that the diffusion should be bidirectional, meaning the Al$_2$O$_3$ should also diffuse into the metal/La$_2$O$_3$ interface. But the experiment in our work shows no relevance between the metal/high-$k$ interface and the $V_{FB}$ shift. In fact, some researchers hold the contrary opinions to our work by investigating the high-$k$ inserted layer at metal/high-$k$ interface. However, in these reports [18, 19], the high temperature annealing (1000 °C) and thin high-$k$ films (approximately 4 nm) may lead to the non-negligible diffusion of inserted layer material to the high-$k$/Si interface and result in $V_{FB}$ shift. Furthermore, the reason that dipoles at metal/high-$k$ and high-$k$/Si interface present distinct effect on $V_{FB}$ shift is supposed to be relevant to the different properties of bonds. Unlike La–O–Si or Al–O–Si,

---

**Table 2** The annealing conditions and thicknesses of samples S2 and S6~S10

| Sample | Temperature (°C) | Duration (s) | Thickness (nm) |
|--------|------------------|--------------|----------------|
| S2     | 600              | 60           | 7.02           |
| S6     | 700              | 60           | 7.21           |
| S7     | 800              | 60           | 7.20           |
| S8     | 600              | 30           | 7.08           |
| S9     | 600              | 90           | 7.07           |
| S10    | 600              | 120          | 7.12           |

Samples S6~S10 have the same film structure with S2: 2 x (20-cycle Al$_2$O$_3$ + 20-cycle La$_2$O$_3$)

---

the bonds between metal gate and high-$k$ material are ionic bonding (La–O–Al or Al–O–Al), which may result in distinctly different electrical properties of dipoles. However, further work is still underway towards a more specific explanation about that.
Conclusions
The C-V curves and XPS results of alternate La₂O₃/Al₂O₃ multilayer stacks are investigated in the paper. It is concluded that the main factor of V_FB shift is the dipoles at high-k/Si interface. Furthermore, the V_FB of samples shifts negatively and varies from the V_FB of pure Al₂O₃ to the pure La₂O₃ direction for thinner bottom Al₂O₃ layer, increasing annealing temperature or longer annealing duration. In such a condition, more La₂O₃ can diffuse into the Al₂O₃/Si interface and form La–O–Si bonds. Because of a weaker electronegativity of La, dipole La–O has stronger polarity than dipole Al–O. It leads to the band offset and negative V_FB shift. As a result, a feasible way to modulate V_FB without changing the dielectric constant k of films is proposed.

Acknowledgements
This research is supported by the National Natural Science Foundation of China (Grant Nos. 61376099 and 61434007) and the Foundation for Fundamental Research of China (Grant No. JSZL2016110B003).

References
1. Zhao Y, Kita K, Kyuno K et al (2009) Band gap enhancement and electrical properties of La₂O₃ films doped with Y₂O₃ as high-k gate insulators. Appl Phys Lett 94:042901
2. Cao D, Cheng X, Yu Y et al (2013) Competitive Si and La effect in HfO₂ phase stabilization in multi-layer (La₂O₃)ₓ(HfO₂)₁₋ₓ films. Appl Phys Lett 103:081607
3. Wang X, Liu HX, Fei CK et al (2015) Silicon diffusion control in atomic-layer-deposited Al₂O₃/La₂O₃/Al₂O₃ gate stacks using an Al₂O₃ barrier layer. Nanoscale Res Lett 10:1–6
4. Lee WJ, Ma JW, Bae JM et al (2013) The diffusion of silicon atoms in stack structures of La₂O₃ and Al₂O₃. Curr Appl Phys 13:633–639
5. Kim Y, Woo S, Kim H et al (2010) Effects of an Al₂O₃ capping layer on La₂O₃-deposited by remote plasma atomic layer deposition. J Mater Res 25:1898–1903
6. Lee JH, Koh K, Lee NI et al (2000) Effect of polysilicon gate on the flatband voltage shift and mobility degradation for ALD-Al₂O₃ gate dielectric. In: International Electron Devices Meeting, pp 645–648
7. Wang XP, Li MF, Ren C et al (2006) Tuning effective metal gate work function by a novel gate dielectric HfLaO for nMOSFETs. IEEE Electron Device Lett 27:31–33
8. Wang XP, Lim EJ, Yu HY et al (2007) Work function tunability of refractory metal nitrides by lanthanum or aluminum doping for advanced CMOS devices. IEEE Transact Electron Devices 54:2871–2877
9. Kombilm L, Meyler B, Cytermann C et al (2012) Investigation of the band offsets caused by thin Al₂O₃ layers in HfO₂ based Si metal oxide semiconductor devices. Appl Phys Lett 100:062907
10. Kakushima K, Okamoto K, Adachi M et al (2008) Origin of flat band voltage shift in HfO₂ gate dielectric with La₂O₃ insertion. Solid-State Electr 52:1280–1284
11. Lin L, Robertson J (2009) Atomic mechanism of flat-band voltage shifts by La₂O₃ and Al₂O₃ in gate stacks. Appl Phys Lett 95:012906
12. Lin L, Robertson J (2009) Atomic mechanism of flat-band voltage shifts at La₂O₃, Al₂O₃ and Nb₂O₅ capping layers. Microelectron Eng 86:1743–1746
13. Pelloquin S, Saint-Girons G, Baboux N et al (2013) LaAlO₃/Si capacitors: comparison of different molecular beam deposition conditions and their impact on electrical properties. J Appl Phys 113:034106
14. Kaliski V, O’Sullivan B, Poulois G et al (2006) Estimation of fixed charge densities in hafnium-silicate gate dielectrics. IEEE Transact Electron Devices 53:2627–2633
15. Yamamoto Y, Kita K, Kyuno K et al (2007) Study of La-induced flat band voltage shift in metal/HfLaO₃/SiO₂/Si capacitors. Japanese J Appl Phys 46:7251–7255
16. Iwamoto K, Kamimura Y, Ogawa A et al (2008) Experimental evidence for the flatband voltage shift of high-k metal-oxide-semiconductor devices due to the dipole formation at the high-k/SiO₂ interface. Appl Phys Lett 92:132907
17. Hauser J (2000) NCSU CVC software, version 7.0. Raleigh, USA: Department of Electrical and Computer Engineering, North Carolina State University
18. Pantisano L, Schram T, Ossullivan B et al (2006) Effective work function modulation by controlled dielectric monolayer deposition. Appl Phys Lett 99:113505
19. Narayanan V, Paruchuri V, Bojaruct N et al (2006) Band-edge high-performance high-k/metal gate n-MOSFETs using cap layers containing group IA and IB elements with gate-first processing for 45 nm and beyond. In: VLSI Technology, pp 178–179