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# Impacts of Annealing Conditions on the Flat Band Voltage of Alternate $La_2O_3/Al_2O_3$ 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 $La_2O_3/Al_2O_3$ 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 $Al_2O_3$ 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 $Al_2O_3$/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, $La_2O_3/Al_2O_3$ 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 ($Y_2O_3$), zirconium oxides ($ZrO_2$), lanthanum oxide ($La_2O_3$), aluminum oxide ($Al_2O_3$), and other transition-metal oxides. Among them, $La_2O_3$ 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 $La_2O_3$ and $Al_2O_3$ 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 $Hf_xLa_{1-x}O_y$ 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 $La_2O_3/Al_2O_3$ 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.

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## 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 $La_2O_3/Al_2O_3$ 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. $La(^{i}PrCp)_3$ and trinethylu-minium (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 $La_2O_3/Al_2O_3$ 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]:

$$V_{\mathrm{FB}} = \frac{\varphi_{\mathrm{ms}}}{q} - \mathrm{EOT}\left(\frac{Q_0}{\varepsilon_0 \varepsilon_{\mathrm{ox}}}\right) + \left(\Delta_{\mathrm{metal/SiO_2}} + \Delta_{\mathrm{SiO_2/Si}}\right), \tag{1}$$

where $\varphi_{ms}$ is the work function difference between metal and Si substrate and $Q_0$ represents the fixed charges located in oxide layer. Δmetal/$SiO_2$ and Δ$SiO_2$/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 $Al_2O_3$ and $La_2O_3$, so the $V_{FB}$ of samples with alternate high-*k* dielectric gate stacks can be expressed as:

$$V_{\mathrm{FB}} = \frac{\varphi_{\mathrm{ms}}}{q} - d_0\left(\frac{Q_0}{\varepsilon_0 \varepsilon_{\mathrm{Al_2O_3}}}\right) - d_1\left(\frac{Q_1}{\varepsilon_0 \varepsilon_{\mathrm{La_2O_3}}}\right) + \left(\Delta_{\text{metal/high-}k} + \Delta_{\text{high-}k\text{/Si}} + \Delta_{\mathrm{La_2O_3/Al_2O_3}}\right). \tag{2}$$

In this equation, $Q_0$ and $Q_1$ represent the fixed charges in $Al_2O_3$ and $La_2O_3$ 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/$La_2O_3$, and dipoles at interfaces of $Al_2O_3$/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 $La_2O_3$ inserted layer) and 1.47 V (with $La_2O_3$ 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 $Al_2O_3$/Si need to be examined on the next step.

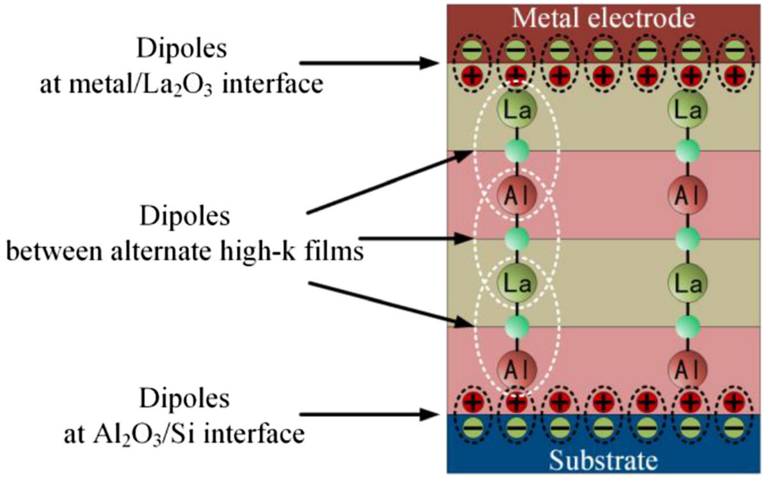

**Fig. 1** The schematic of three kinds of dipoles in $La_2O_3/Al_2O_3$ high-*k* dielectric stacks

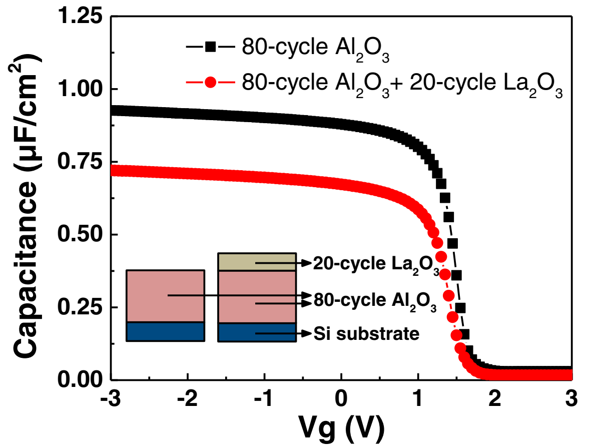

**Fig. 2** The simplified schematic structures and C-V curves of $La_2O_3$/Si and $Al_2O_3$/$La_2O_3$/Si

Samples S1~S5 were deposited for different structures in an identical annealing condition (annealed at 600 °C for 60 s in $N_2$ atmosphere). The schematic of alternate high-*k* films S1~S5 is shown in Fig. 3. For each of the samples S1~S4, 40-cycle $La_2O_3$ and 40-cycle $Al_2O_3$ 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 $Al_2O_3$ and 80-cycle pure $La_2O_3$ 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 $Al_2O_3$ film to the pure $La_2O_3$ 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 $La_2O_3$ inserted layer at $HfO_2$/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 $Al_2O_3$ and $La_2O_3$ films have few fixed charges. Therefore, the fixed charge $Q_0$ and $Q_1$ 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 $Al_2O_3$/Si interface.

**Table 1** The structures and thicknesses of annealed samples S1~S5

| Sample | Film structures | Thickness (nm) |
|---|---|---|
| S1 | 1 × (40-cycle $Al_2O_3$ + 40-cycle $La_2O_3$) | 7.06 |
| S2 | 2 × (20-cycle $Al_2O_3$ + 20-cycle $La_2O_3$) | 7.02 |
| S3 | 4 × (10-cycle $Al_2O_3$ + 10-cycle $La_2O_3$) | 6.99 |
| S4 | 40 × (1-cycle $Al_2O_3$ + 1-cycle $La_2O_3$) | 7.57 |
| S5 | 4 × (20-cycle $Al_2O_3$ + 20-cycle $La_2O_3$) | 13.4 |

The samples were annealed at 600 °C for 60 s

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 $N_2$ 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 $HfO_2$ and $Al_2O_3$ 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 $La_2O_3$/$Al_2O_3$ 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 $Al_2O_3$ and $La_2O_3$ diffuse into each other and form $LaAlO_3$ at $Al_2O_3$/$La_2O_3$ 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.

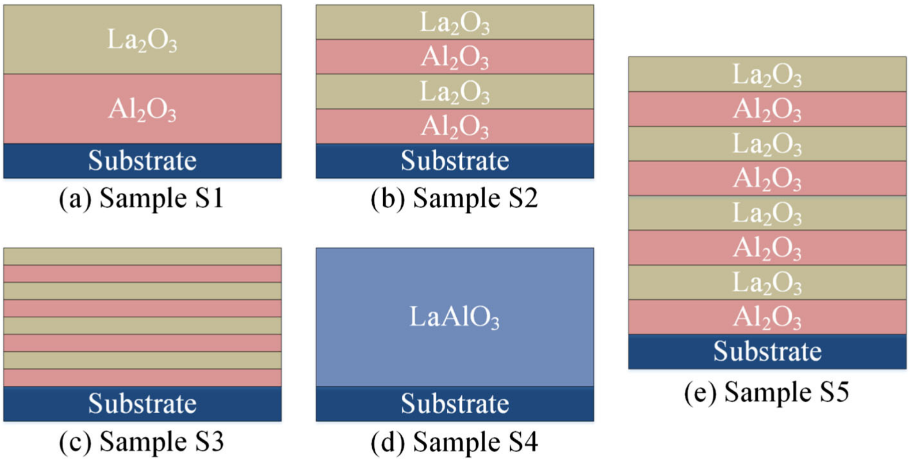

**Fig. 3** The schematic structures of samples S1~S5

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 $Al_2O_3$ layer, which leads to more $La_2O_3$ diffusing into $Al_2O_3$/Si interface and replacing the Si–O–Al with Si–O–La bonds. Based on the theory of diffusion, more $La_2O_3$ can diffuse through the bottom $Al_2O_3$ layer forming Si–O–La bonds at higher annealing temperature. Similarly, increasing annealing duration can also cause more $La_2O_3$ diffusing into $Al_2O_3$/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 $HfO_2$ and $Al_2O_3$ stacks diffusing into each other and into the metal/high-*k* and high-*k*/Si interfaces 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 $Al_2O_3$/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 $Al_2O_3$/Si interface the closer to blue dotted line, the $V_{FB}$ will be. Moreover, the $V_{FB}$ shift in

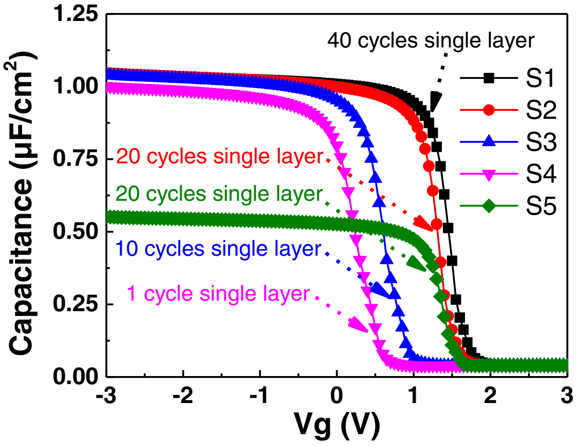

**Fig. 4** C-V curves of samples S1~S5 which contain 40, 20, 10, 1, and 20 single-layer cycles, respectively

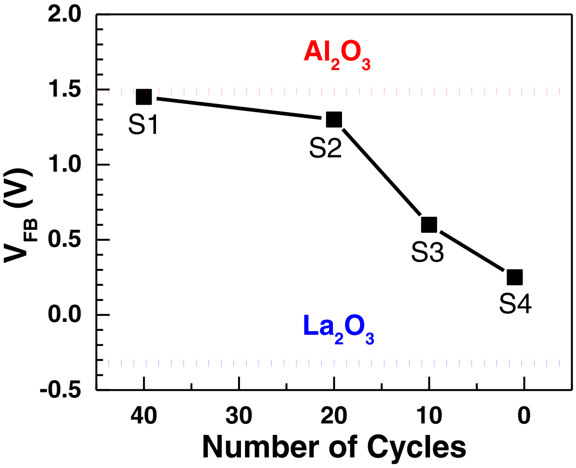

**Fig. 5** $V_{FB}$ of samples S1~S5. The *red* and *blue dotted lines* represent the $V_{FB}$ of 80-cycle $Al_2O_3$ and $La_2O_3$ films, respectively

**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 × (20-cycle $Al_2O_3$ + 20-cycle $La_2O_3$)

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 $Al_2O_3$ should also diffuse into the metal/$La_2O_3$ 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, 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.

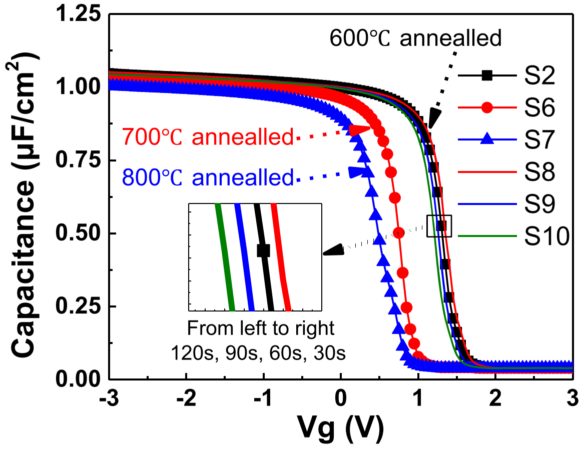

**Fig. 6** C-V curves of samples S2 and S6~S10. Samples S2, S6, and S7 were annealed at different temperatures for 60 s, while samples S2 and S8~S10 were annealed at 600 °C for different duration

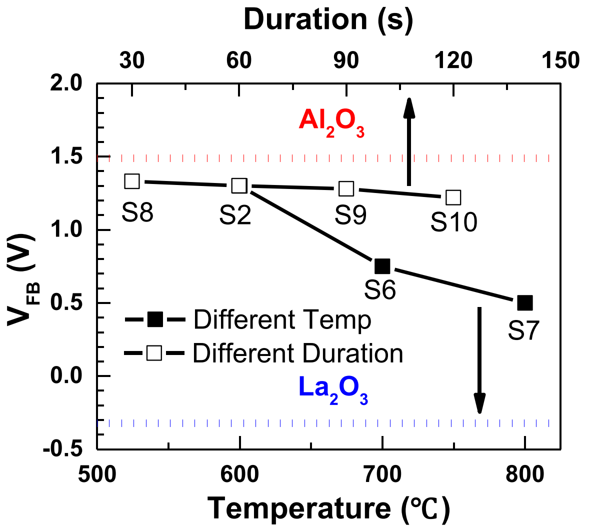

**Fig. 7** $V_{FB}$ of samples S2 and S6~S10. S2 is a shared point for different annealing temperature and duration. The *red* and *blue dotted lines* represent the $V_{FB}$ of 80-cycle $Al_2O_3$ and $La_2O_3$ films, respectively

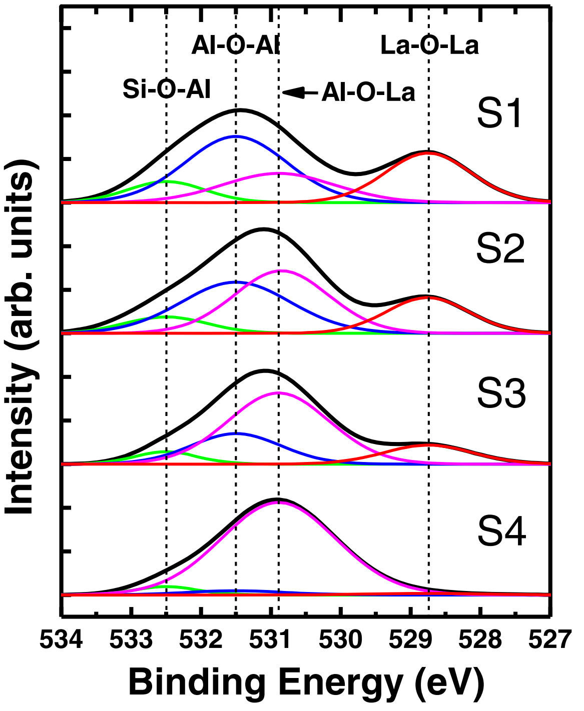

**Fig. 8** O1s XPS spectra of samples S1~S4. The O1s spectra were fitted with four peaks (Si–O–Al, Al–O–Al, Al–O–La and La–O–La)

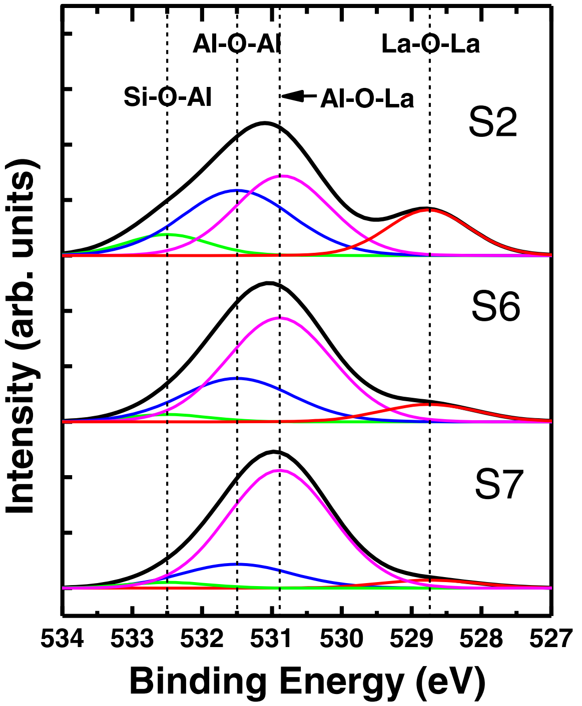

**Fig. 9** O1s XPS spectra of samples S2, S6, and S7. The O1s spectra was fitted with four peaks (Si–O–Al, Al–O–Al, Al–O–La and La–O–La)

## Conclusions

The C-V curves and XPS results of alternate $La_2O_3$/$Al_2O_3$ 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 $Al_2O_3$ to the pure $La_2O_3$ direction for thinner bottom $Al_2O_3$ layer, increasing annealing temperature or longer annealing duration. In such a condition, more $La_2O_3$ can diffuse into the $Al_2O_3$/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.

### Abbreviations

ALD: Atomic layer deposition; C-V: Capacitance-voltage; EOT: Equivalent gate oxide thickness; MOS: Metal oxide semiconductor; RTA: Rapid thermal annealing; SE: Spectroscopic ellipsometry; TMA: Trinethyluminium; $V_{FB}$: Flat band voltage; XPS: X-ray photoelectron spectroscopy

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### Authors' contributions

XyF generated the research idea, analyzed the data, and wrote the paper. XyF and XW carried out the experiments and the measurements. XW, LZ, CxF, and HlL participated in the discussions. HxL has given the final approval of the version to be published. All authors read and approved the final manuscript.

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XyF and HlL are Master students in the Xidian University. HxL is a professor in the Xidian University. XW, LZ, and CxF are PhD students in the Xidian University.

### Competing interests

The authors declare that they have no competing interests.

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