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Supplementary Information

Dielectric properties and reliability enhancement of atomic layer deposited thin films by in situ atomic layer substrate biasing

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Section 1. The ALSB treatment with different processing conditions

The substrate bias with different time-averaged voltage (V_{bias}) and bias time has been tested. Figure S1 shows the *C-V* and *I-V* curves of the MOS capacitors, in which the ZrO_2 layers were prepared at V_{bias}=8, 10, and 15 V, respectively, for 10 sec. It can be seen that the increase of V_{bias} leads to significant suppression of the leakage current but degradation of the capacitance. The increase of the IL thickness with V_{bias} may be responsible for this result. A higher V_{bias} provides a higher energy for plasma bombardment, which facilitates oxygen diffusion toward the interface and results in an increase in the IL thickness. Since the substrate bias can control the plasma energy precisely, a small change in V_{bias} contributes to a direct impact on the energy of the incident ions.

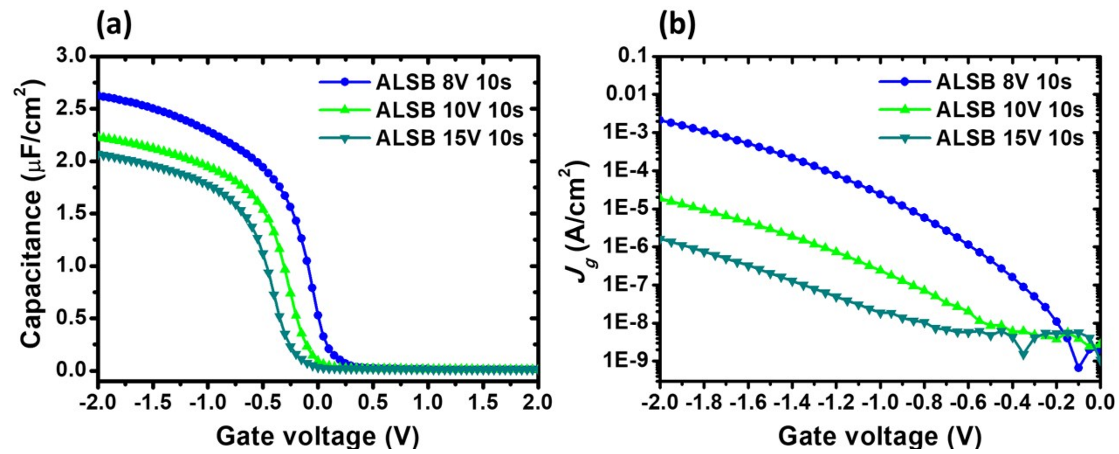

Figure S1. (a) *C-V* and (b) *I-V* characteristics of the MOS devices, in which the ZrO_2 layers were deposited by the ALSB process at V_{bias}=8, 10, and 15 V, respectively, for 10 sec. The leakage current is greatly reduced and the capacitance is degraded by the increase of V_{bias}.

In order to investigate the effect of bias time, the ALSB process was conducted at V_{bias}=8 V for the bias time of 10, 20, and 30 sec, respectively, and the corresponding *C-V* and *I-V* curves are revealed in Figure S2. Although the leakage current is dramatically suppressed (Figure S2(b)), the increase of the bias time deteriorates the capacitance (Figure S2(a)). The outcome might result from the surplus growth of IL due to the increase in the bias time.

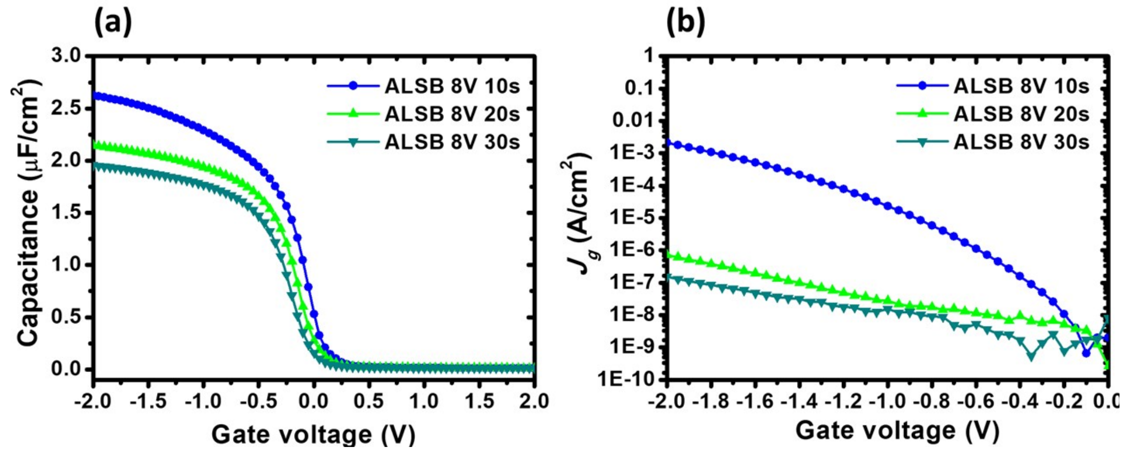

Figure S2. (a) *C-V* and (b) *I-V* characteristics of the MOS devices, in which the ZrO_2 layers were deposited by the ALSB process at V_{bias}=8 V for 10, 20, and 30 sec, respectively. The leakage current is significantly suppressed and the capacitance is decreased by the increase of the bias time.

Figure S1 and S2 reveal that the increase of V_{bias} and the bias time in the ALSB treatment leads to significant suppression of the leakage current but degradation in the capacitance of the MOS capacitors. Therefore, in order to avoid the deterioration of the capactitance, the ALSB process with V_{bias}=8 V for 10 sec was selected to investigate the dielectric properties and the reliability of nanoscale thin films in this study.

Section 2. Statistical data of the reference and ALSB MOS/MIM capacitors

Figure S3 shows the statistical data of the capacitance equivalent thickness (CET) and effective dielectric constant (K_{eff}) of the reference and ALSB MOS capacitors. The average (AVG) CET of the reference and ALSB samples is 1.26 and 1.32 nm, respectively, along with the standard deviation (STDEV) of 0.0095 nm. The AVG K_{eff} and the corresponding STDEV of the reference sample are 16.08 and 0.12, and those of the ALSB sample are 15.0 and 0.11, respectively.

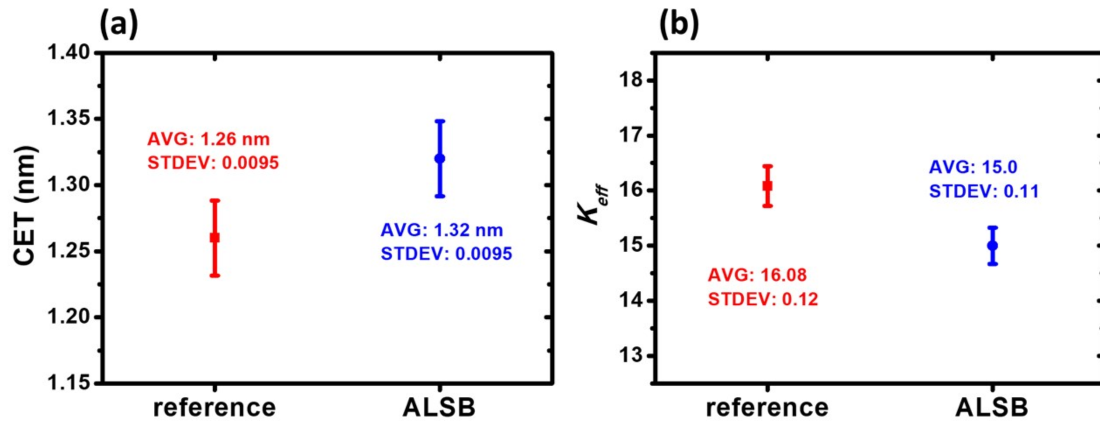

Figure S3. The statistical analysis of (a) CET and (b) K_{eff} of the reference and ALSB MOS capacitors. Each error bar represents three times the STDEV, indicating the confidence interval of 99.7%.

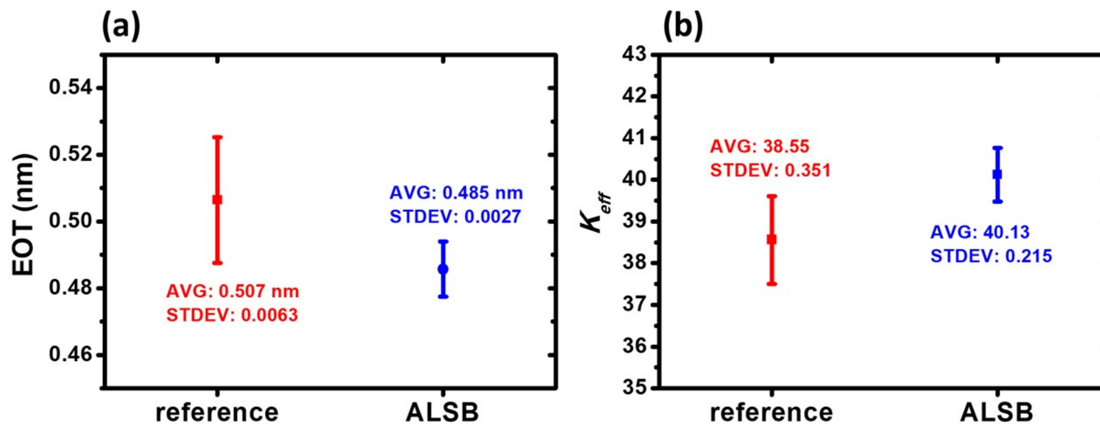

Figure S4. The statistical analysis of (a) EOT and (b) K_{eff} of the reference and ALSB MIM capacitors. Each error bar represents three times the STDEV, indicating the confidence interval of 99.7%.

Similarly, the statistical data of the effective oxide thickness (EOT) and K_{eff} of the reference and ALSB MIM capacitors are shown in Figure S4. The AVG EOT of the reference and ALSB samples is 0.507 and 0.485 nm, respectively. The STDEVs are 0.0063 and 0.0027 nm, respectively, for the reference and ALSB samples. The AVG K_{eff} and the corresponding STDEV of the reference sample are 38.55 and 0.351, and

those of the ALSB sample are 40.13 and 0.215, respectively.

The trend of statistical data is in good agreement with the results presented in the manuscript. The AVG EOT of the ALSB samples is smaller than that of the reference samples, which can be attributed to the film densification caused by the ALSB treatment.