

Supporting Information

Synergic Impacts of CF₄ Plasma Treatment and Post-Thermal Annealing on Nonvolatile Memory Performance of Charge-Trap-Assisted Memory Thin-Film Transistors Using Al-HfO₂ Charge Trap and In-Ga-Zn-O Active Channel Layers

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1. Effects of CF₄ plasma power condition on the memory characteristics of the CTM-TFTs

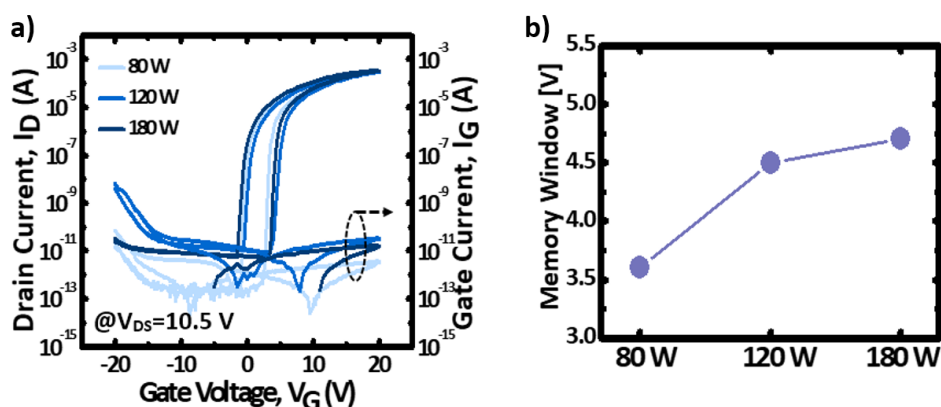


Figure S1. (a) I_{DS} - V_{GS} transfer curves and (b) estimated MW values for the fabricated CTM-TFTs using Al:HfO₂ CTLs treated with CF₄ plasma, in which plasma power was varied to 80, 120, and 180 W to investigate the effect of plasma power on the NVM operations of the CTM-TFTs. It was found that the charge-trap-assisted MWs increased from 3.6 to 4.7 V increasing the CF₄ plasma power from 80 to 120 W. It means that the qualities of Al₂O₃ TL/Al:HfO₂ CTL interfaces were improved by CF₄ plasma treatment, which can be explained by the neutralization of oxygen vacancies. However, the increase in MW value was found to be saturated owing to the negatively charged F ions accumulated at the TL/CTL interfaces. Alternatively, when the CF₄ plasma power was adjusted to 200 W, the CTM-TFT showed negatively shifted threshold-voltage owing to plausible damage induced by severe plasma power condition. Thus, these results suggest that the CF₄ plasma power condition could be optimally determined to be 180 W without any degradation of device characteristics.

2. Effects of Al doping concentration within the Al:HfO₂ CTL on the device characteristics

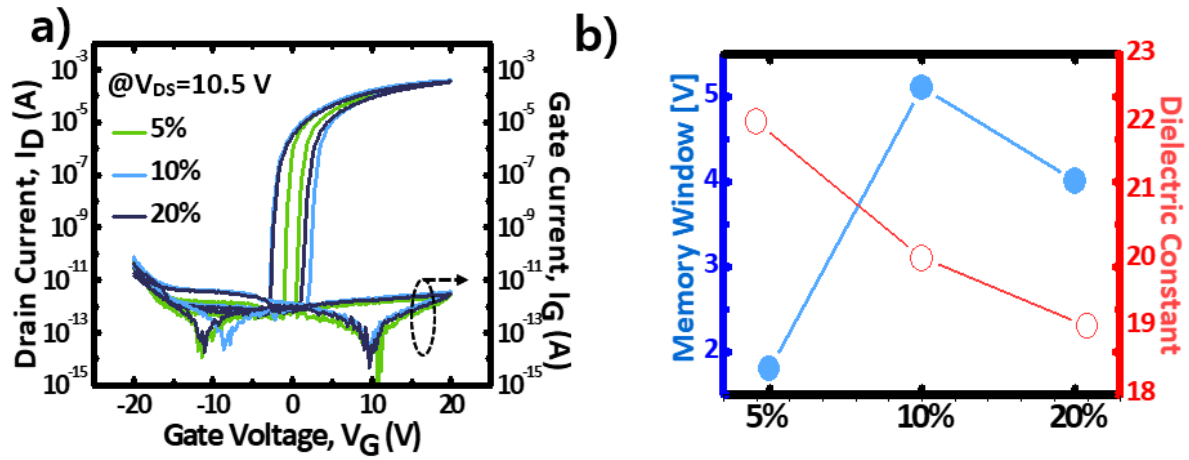


Figure S2. (a) I_{DS} - V_{GS} characteristics of the CTM-TFTs using the Al:HfO₂ CTLs with various Al incorporation amounts of 5, 10, and 20%. (b) MW values obtained from the CTM-TFTs and estimated values of dielectric constants of the Al:HfO₂ with Al dopant amounts of 5, 10, and 20%. When the Al doping concentration increased from 5 to 10%, the MW increased from 1.8 to 5.1 V owing to the increase in charge-trap sites within the Al:HfO₂ bulk. However, the MW value inversely decreased to 4.0 V with an Al doping concentration of 20%, which was suggested to result from the decrease in trap density of the Al:HfO₂ CTL owing to the formation of Al-Hf second phases by excessive incorporation of Al dopants. Furthermore, the monotonous decrease in dielectric constant of the Al:HfO₂ as the increase in the Al doping concentration degraded the charge-trapping efficiency due to the reduction of applied electric field across the CTL. Therefore, excessive doping of the Al atoms could be concluded to be inappropriate for improving the NVM performance of the proposed CTM-TFTs.

3. Retention characteristics evaluated for the A3 CTM-TFTs

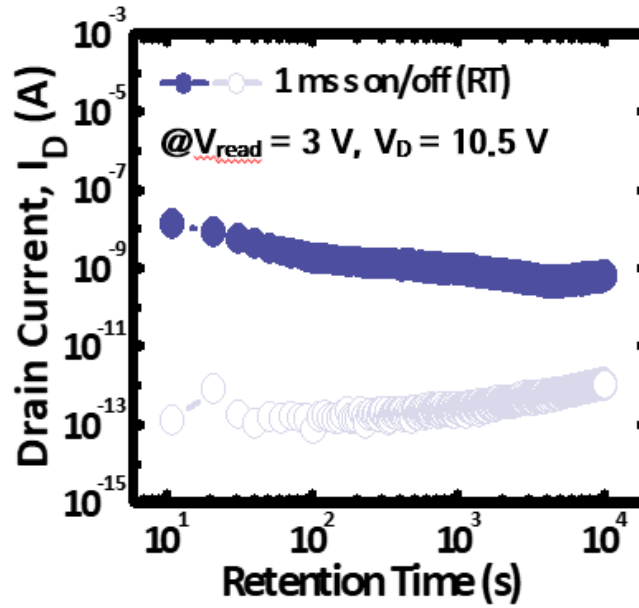


Figure S3. Variations in programmed I_{DS} with a lapse of retention time for 10^4 s for the A3 device at RT, which were evaluated at V_{read} of 3 V and V_D of 10.5 V. The pulse amplitude and duration were fixed as ± 20 V and 1 ms, respectively. The initial on/off ratio of 9.5×10^4 decreased to 6.3×10^2 after a retention time of 10^4 s. For the A3, the charges could be captured at shallow trap sites, which were generated by the formation of grain boundaries within the Al:HfO₂ CTL. However, since the grain boundaries were expected to behave as undesirable leakage current paths, the stored charges might be readily detrapped, resulting in significant charge loss. As results, for the A3 employing the Al:HfO₂ treated by only thermal annealing, it was difficult to ensure the stable long-term retention characteristics. To overcome these limitations, the Al:HfO₂ CTL was simultaneously treated with CF₄ plasma, and hence, the retention time could be enhanced thanks to the additional formation of deep traps even when the P/E pulse duration was reduced as short as 100 μ s.

4. Comparisons in the GIXRD patterns between the A and T samples

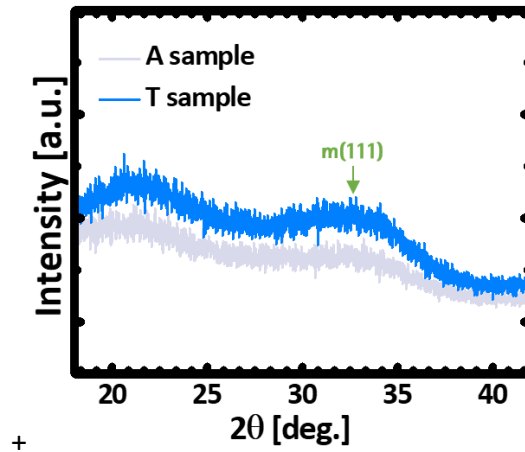


Figure S4. GIXRD patterns for the as-deposited (A) and the 500-°C-annealed (T) Al:HfO₂ thin films which were analyzed in the 2θ range from 18° to 43°. Broad and weak diffraction peaks assigned to (111) plane of monoclinic phase were detected for the T sample. It has generally been reported that the HfO₂ thin films could be completely crystallized by annealing treatment at temperatures above at least 600°C. Thus, the obtained weak peak can be suggested to originate from the partial crystallization of Al:HfO₂ thin film at 500°C. Since the peak intensity obtained from the XRD patterns were unavoidably weak for clearly discriminating the crystalline phase within the annealed Al:HfO₂ thin films, the degree of crystallinity should be checked by TEM analysis as future works. Additionally, as mentioned in the manuscript, the excessive amount of grain boundaries formed in the Al:HfO₂ thin films may attribute to the increase in trap sites as well as the increase in leakage current components. Thus, the partially crystallized Al:HfO₂ thin films can be rather considered to provide advantages to operate the memory devices in terms of suppression of the leakage currents.

5. Comparisons in the XPS depth profiles between the P and P+T samples

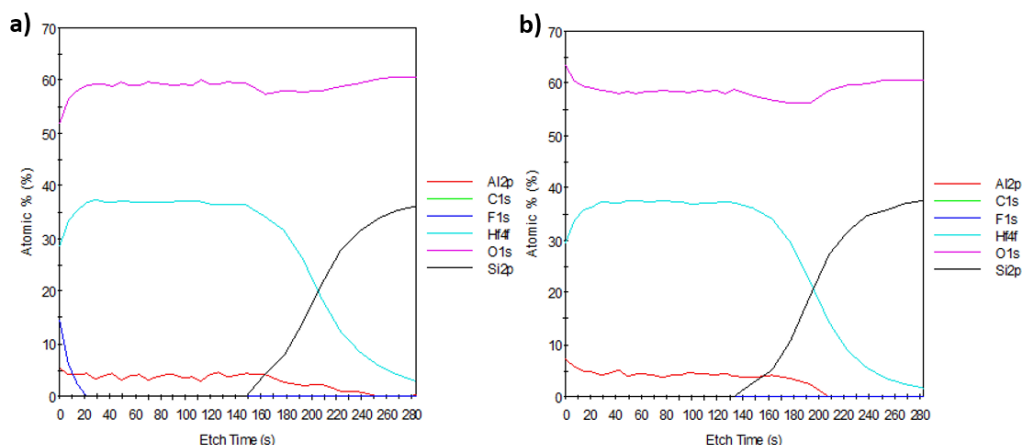


Figure S5. XPS depth profiles with the atomic percent of the component elements as function of the sputtering time for the (a) P and (b) P+T samples to investigate the spatial distributions in depth for chemical species. For the P sample, the F species less than approximately 15 at% was detected at surface regions in the sputtering time range from 0 to 20 s. On the contrary, it was noteworthy that the presence of F species was not detected within the Al:HfO₂ layer for the P+T sample. Considering that the small amount of F species were initially introduced by CF₄ plasma treatment, it was so difficult to exactly extract the redistributed F species within the Al:HfO₂ bulks with XPS depth profile technique. Here, the possibility of sublimation of the F-compound located at Al:HfO₂ surfaces cannot be completely excluded. However, in this work, it could be demonstrated that the CTM-TFT using Al:HfO₂ CTL treated with plasma and thermal annealing (P+T) definitely exhibited far superior nonvolatile memory device characteristics and operational reliabilities among the fabricated devices, which correspond to an indirect evidence for the F diffusions during the thermal annealing process at 500°C, as previously suggested in some publications.

6. XPS analysis on the Al:HfO₂ surfaces treated by CF₄ plasma and/or thermal annealing

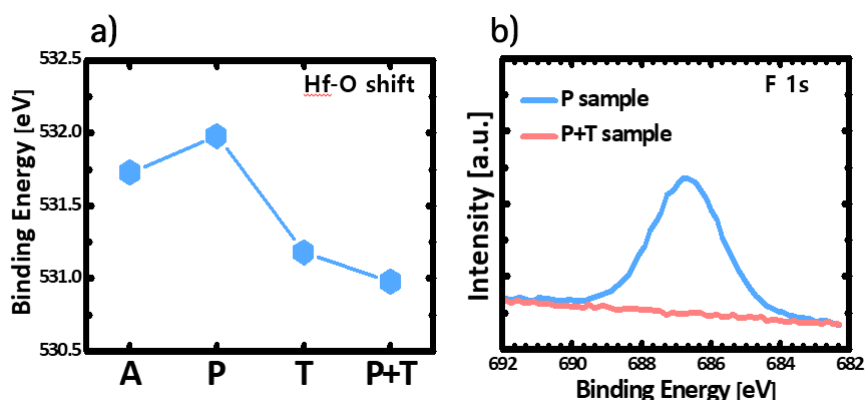


Figure S6. (a) Variations in the Hf-O peak positions extracted from O 1s spectra for the A, P, T, and P+T samples. The binding energies of Hf-O peaks were determined to be 531.73, 531.98, 531.18, and 530.98 eV for the A, P, T, and P+T samples, respectively. The Hf-O peaks were shifted to a lower energy side for the T and P+T samples, indicating the increase in the total number of Hf-O bonds by annealing process. In other words, these results suggest that the undesirable trapping event at interfaces could be effectively reduced for the T and P+T samples, compared to the A and P samples. (b) Comparison of F 1s spectra for the P and P+T samples. While the peak resulted from the presence of F ions was clearly verified for the surface of P sample, the F 1s peak was not detected for the P+T sample. Thus, it was suggested that the F ions located at the surface of P sample were diffused into the bulk regions during high-temperature post-annealing process, and hence, the peak in F 1s spectra disappeared at the surface of P+T sample.

7. AFM images of the Al:HfO₂ surfaces for the A, P, T, and P+T samples

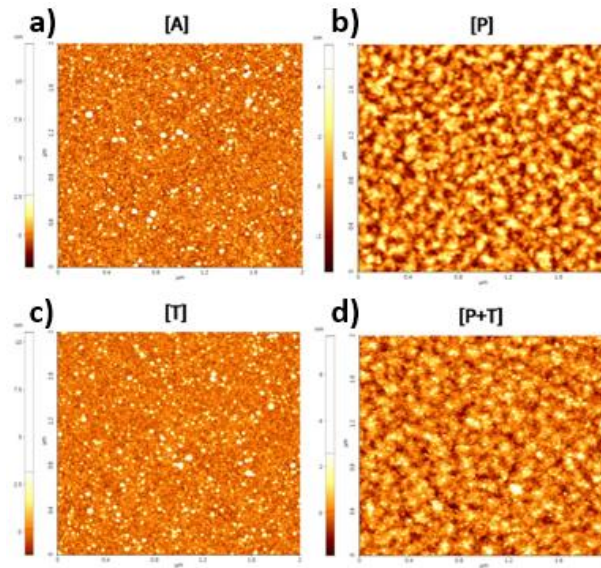


Figure S7. AFM images of the Al:HfO₂ surfaces for the (a) A, (b) P, (c) T, and (d) P+T samples. The root-mean-square (RMS) values were estimated to be 0.81, 1.24, 0.75, and 0.64 nm for the A, P, T, and P+T samples, respectively. It can be noted that the RMS value (1.24 nm) increased after the CF₄ plasma treatment (P sample), compared to the as-deposited sample A (0.81 nm). The deterioration of the RMS value was supposed to result from the presence of F ions at the surfaces of the P sample owing to the CF₄ plasma treatment. On the other hand, a lower RMS value obtained (0.64 nm) for the P+T sample can be explained by the spatial incorporation of F ions from surface to bulk regions during high-temperature annealing process.