



Thermal Stability of ALD-HfO₂/GaAs Pretreated with Trimethylaluminium

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The simultaneous self-cleaning and passivation of an as-received GaAs substrate using trimethylaluminium (TMA) pretreatment before the atomic layer deposition (ALD) of HfO₂ was systematically investigated. The change of the interfacial characteristics was probed as a function of the number of treatment cycles and the post-deposition annealing temperature and related with various electrical properties of the HfO₂ film. The TMA pretreatment removed the Ga- and As-oxides more effectively than the ALD-HfO₂ process, which reduced the amount of frequency dispersion. In addition, compared to the As case, it showed more predominant suppression of both Ga out-diffusion and Ga-O bond formation, which is believed to have delayed the thermal degradation of the capacitance equivalent thickness (CET). The optimal number of TMA treatment exhibited the best thermal stability without increasing the as-deposited CET.

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For the development of high-*k*/GaAs metal-oxide-semiconductor (MOS) capacitors in high performance transistors with superior electrical properties, researchers have used various deposition techniques of high-*k* dielectrics such as molecular beam epitaxy,¹ sputtering,² and atomic layer deposition (ALD).³ Among these techniques, ALD has been acknowledged as a strong candidate for industrial application due to its fine film quality, nearly perfect uniformity, and precise thickness controllability, attributed to its surface-saturation controlled, layer-by-layer deposition kinetics.⁴ The ALD processing of HfO₂ and Al₂O₃ films – the most widely studied high-*k* materials due to their outstanding dielectric properties – on GaAs substrates has recently revealed the self-cleaning effect of ALD as an additional benefit: the precursor dependent, *in situ* removal process of Ga- and As-related native oxides.^{5,6} Despite the introduction of additional *ex situ* cleaning/passivation solutions, such as NH₄OH, and (NH₄)₂S,⁸ prior to the high-*k* deposition, prompt surface contamination of GaAs substrates by ambient air exposure cannot be avoided during the sample transfer to the deposition chamber. Therefore, the development of *in situ* self-cleaning using a precursor with a strong reduction capability can be an essential choice for the high-*k*/GaAs integration process.

When used as a metal precursor for the Al₂O₃ deposition, trimethylaluminium (TMA) is known to have more effective self-cleaning capability for removing the Ga- and As-oxides than tetrakis(ethylmethylamino)hafnium (TEMAHf) used for the HfO₂ deposition.⁵ Furthermore, Al₂O₃ is known to have less Fermi level pinning and better thermal stability than HfO₂ on a GaAs substrate.⁷ However, because Al₂O₃ has a much lower *k* value than HfO₂, it has a potential issue in scaling the high-*k* gate dielectric film for sub-nanometer-sized high speed transistors. In order to overcome this problem, Yang *et al.*⁹ suggested a HfO₂/Al₂O₃ nanolaminate structure starting with Al₂O₃ and obtained better electrical properties than single HfO₂ gate dielectric on GaAs. Suh *et al.*^{10,11} recently proposed a stacked or sandwiched structure of HfO₂/Al₂O₃ and Al₂O₃/HfO₂/Al₂O₃ using an ultra-thin, Al₂O₃ film as an interface passivation layer. They claimed that the interfacial Al₂O₃ layer works as a diffusion barrier for the Ga and As atoms during the post-deposition annealing (PDA), leading to an enhancement of the thermal stability.^{10,11} However, as an adverse effect, the insertion of the lower *k*, Al₂O₃ interfacial layer into the HfO₂/GaAs interface may increase the apparent capacitance equivalent thickness (CET), thus limiting the further scaling of the high-*k* stack in the future.

In this paper, as a simultaneous cleaning and passivation method, we used TMA pretreatment without oxidant injection on a GaAs substrate before the ALD-HfO₂ process. The changes of the interfacial

chemical structure and the electrical properties were systematically probed by varying the number of TMA treatment cycles and the PDA temperature. Because the injected TMA precursor can remove the native oxide of the GaAs by forming an ultra-thin Al-oxide interfacial layer via the self-cleaning mechanism,⁶ this process will be helpful in simplifying the ALD process and preventing the CET increase by limiting the physical thickness of the Al-oxide, interfacial layer with low dielectric constant.

Experimental

As-received, p-type GaAs substrates (dopant: Zn, $\sim 1 \times 10^{19}$ cm⁻³) that had not undergone a native oxide removal step were intentionally used to focus on the cleaning effect of the TMA treatment during the ALD process. The treatment was performed by injecting the TMA precursor for various cycle numbers (10, 30, and 50), before the subsequent HfO₂ deposition in the same ALD chamber, where one cycle of TMA injection consists of 0.5 sec-TMA injection and 10 sec-N₂ purging steps without flowing oxidant. The untreated and TMA-treated GaAs substrates were then *in situ* coated with ~ 8 -nm-thick ALD-HfO₂ films at 300°C using TEMAHf and H₂O precursors. After the HfO₂ deposition, some samples underwent PDA at 600 or 700°C for 1 min in N₂ ambient (1 Torr) using a rapid thermal processor. The deposited HfO₂ thickness was measured by a spectroscopic ellipsometer and confirmed by a high-resolution transmission electron microscopy (HRTEM, JEOL JEM 2100F) which was also used to examine the microstructures of the HfO₂ film and interfacial structures. For the chemical analysis of the interfacial region, *ex situ* X-ray photoelectron spectroscopy (XPS) measurement was performed on the ~ 2 -nm-thick HfO₂ films using an AXIS-NOVA (Kratos Inc.) system with a monochromatic Al K α (1486.7 eV) X-ray source located at the Korea Basic Science Institute (KBSI), Jeonju in Korea. The measured spectra were then fitted by matching the As 3d_{5/2} peak coming from the GaAs substrate to 40.8 eV.¹² The depth distribution of the constituting elements in the HfO₂/GaAs stack was obtained by conducting a time-of-flight secondary ion mass spectroscopy (TOF-SIMS) measurement with oxygen and cesium guns for Ga (positive mode) and As/Al (negative mode), respectively. For the electrical characterization, MOS capacitors were fabricated through the sputter-deposition and a patterning of TaN gate electrode capped with Al, followed by annealing at 400°C for 30 min in 4% H₂/96% N₂ ambient. The capacitance-voltage (C-V) characteristics were measured by using an Agilent E4980A LCR meter and the leakage current density-voltage (J-V) characteristics were measured under a gate electron injection condition using Keithley 6514 electrometer and 230 programmable voltage source.

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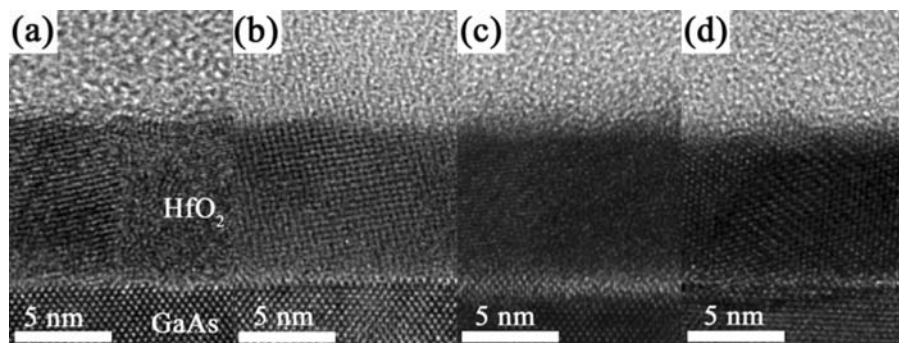
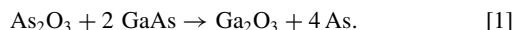


Figure 1. HRTEM images of ~ 8 -nm-thick ALD-HfO₂ films on GaAs substrates (a, b) without and (c, d) with 50 cycle TMA pretreatment; (b) and (d) samples are after PDA at 700°C.

Results and Discussion

The cross-sectional HRTEM images of the as-deposited and 700°C-annealed HfO₂ films on GaAs substrates with and without TMA pretreatment (50 cycles) are shown in Fig. 1. Moderately crystallized ~ 8 -nm-thick HfO₂ films were uniformly deposited on the untreated and TMA-treated GaAs substrates, without any notable microstructural difference of the deposited HfO₂ films. For the as-deposited, TMA-untreated sample [Fig. 1a], most of the native oxide layer was removed and no significant interfacial layer growth occurred during the ALD-HfO₂ process, implying the action of the self-cleaning process by the TEMAHf precursor, as observed in other studies.^{5,13} A similar native oxide removal also occurred for the TMA pretreated sample due to the self-cleaning action of the TMA precursor, as shown in Fig. 1c; however, it was difficult to identify any notable additional thickness increase of the interfacial region by the Al-oxide formation. When the highest annealing temperature (700°C) in our split condition was used, neither untreated nor TMA-treated sample showed any additional interfacial layer growth [Figs. 1b and 1d].

In order to confirm the occurrence of the self-cleaning process and to study the consequential change of the interfacial chemical bonds as a function of the number of TMA injection cycles and the PDA temperature, *ex situ* XPS analyses were performed on the ~ 2 -nm-thick HfO₂ films, which is comparable to the escape length of the photoelectrons. Although further self-cleaning might have occurred during the consecutive HfO₂ deposition to a thickness of ~ 8 nm, which was used for the electrical characterization, we assumed that this early stage information obtained from this model experiment would be helpful in understanding the effect of the TMA treatment process. Figure 2 shows the deconvoluted As 3d spectra of HfO₂/GaAs with different TMA treatment cycles as a function of the PDA temperature. For the as-deposited HfO₂ film on uncleaned GaAs substrate, two different As states corresponding to elemental As and As₂O₃ were observed with binding energy shifts of 0.7 and 3.4 eV, respectively, from that of the As-Ga bonding of the substrate [Fig. 2a]. As₂O₅ was not identified even in the TMA-treated sample because the self-cleaning process occurred during the ALD-HfO₂ process.⁵ When PDA was performed on this HfO₂ on untreated GaAs sample, most of the As₂O₃ was removed after 600°C-annealing and a continuous decrease in the elemental As peak was observed as the PDA temperature was increased to 700°C. This phenomenon can be understood by a possible thermal reduction of the As₂O₃ and a subsequent desorption of elemental As during PDA.¹⁴ This thermal reduction process may happen via the following chemical reaction,¹⁴



Although this reaction path can generate many As atoms as a by-product, most of them were probably desorbed from the interface during PDA, which is believed to have simultaneously induced the observed decrease of the elemental As peak intensity.

For the TMA-treated samples, as the number of treatment cycle increased [Fig. 2a], the As₂O₃ peak continuously decreased, which revealed stronger self-cleaning capability of the TMA precursor compared to that of TEMAHf. This precursor-dependent cleaning capa-

bility can be explained by the different oxidation states of Al and Hf atoms in the metal-organic precursors. Hinkle *et al.*⁵ suggested that because Al and Hf atoms have 3+ and 4+ oxidation states in TMA and TEMAHf, respectively, TMA is more favorable in replacing As³⁺ (in As₂O₃) than TEMAHf. Therefore, as a result of this strong reduction capability, more elemental As generation is expected during the TMA pretreatment. As discussed above in the HfO₂/TMA-untreated GaAs sample, the generated As atoms may have undergone thermal desorption in this system. However, in contrast to the HfO₂ on the TMA-untreated GaAs sample, no significant reduction of the elemental As peak occurred in the TMA-treated sample even after PDA at 700°C [Fig. 2c]. Because the ultra-thin Al-oxide (probably nonstoichiometric oxide⁶) layer formed at the interface of HfO₂ and GaAs can block the diffusion of elemental As, many elemental As bonding states may have remained even after PDA at high temperature such as 700°C, as observed in the spectrum [Fig. 2c]. Another possible explanation for a relatively smaller decrease in the peak intensity corresponding to the elemental As bonding state in the TMA-treated sample after high temperature PDA, compared to the untreated sample, is the formation of a new As/Al-related bonding state having a similar binding energy with elemental As, as inferred from the XPS analysis of As 2p spectrum in Al₂O₃/InAs system.¹⁵

As well as the As 3d spectrum, we also examined the Ga 2p_{3/2} spectrum as a function of the number of the TMA pretreatment cycles and the PDA temperature, as shown in Fig. 3. For all the samples,

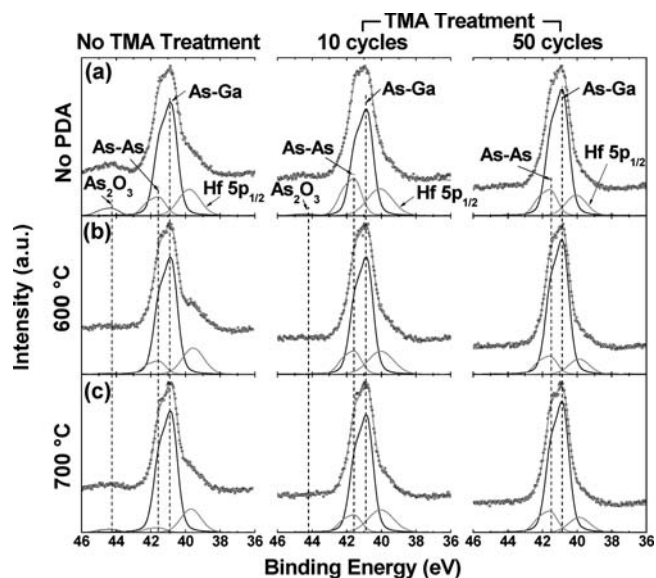


Figure 2. Measured and deconvoluted XPS spectra of As 3d peaks from ~ 2 -nm-thick ALD-HfO₂ films grown on untreated and TMA-treated GaAs substrates as a function of the PDA temperature: (a) no PDA, (b) 600°C, and (c) 700°C.

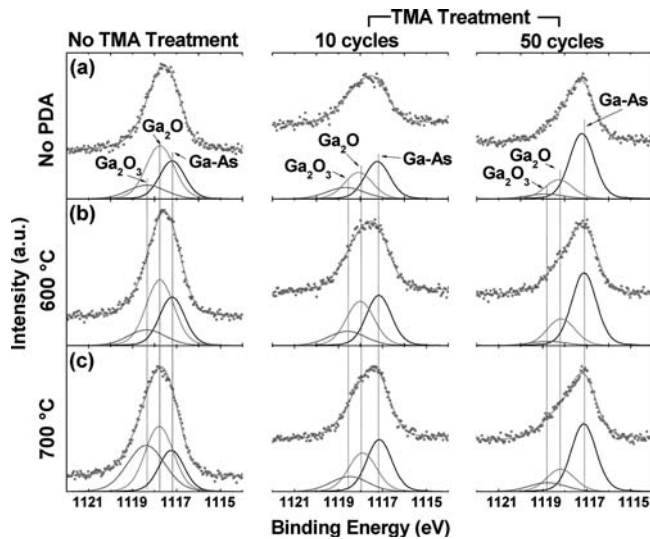


Figure 3. Measured and deconvoluted XPS spectra of Ga $2p_{3/2}$ peaks from ~ 2 -nm-thick ALD-HfO₂ films grown untreated and TMA-treated GaAs substrates as a function of the PDA temperature: (a) no PDA, (b) 600°C, and (c) 700°C.

two different kinds of Ga-oxide phase, i.e., Ga₂O and Ga₂O₃, were identified with positive binding energy shifts from that of the Ga-As bonding of the substrate. In the case of the reference sample, HfO₂ on TMA-untreated GaAs sample, the amount of the Ga-oxides increased as the PDA temperature was increased, exhibiting a different trend to the aforementioned As-oxide case. It matched well with the expected production of Ga₂O₃ phase accompanied by the thermal reduction of As₂O₃ as described in equation 1 and also with the recent Suh *et al.*'s report.¹⁰ However, after the TMA pretreatment, the amount of Ga-oxide bonds was significantly reduced by the self-cleaning mechanism, similar to the As-oxide case, thereby demonstrating the effectiveness of the TMA cleaning method. In addition, a notable suppression of the Ga-oxide bond formation was observed even after PDA at 700°C as the TMA treatment cycle was increased. One interesting observation was slight shifts of the Ga-O peak positions to a higher binding energy side as the TMA treatment cycle was increased. It may be related to a transition of the second nearest neighboring atoms⁵ or a charging effect near the interface region by the formation of the Al-oxide layer.

In addition to the chemical analysis of the interfacial region between the HfO₂ and GaAs, elemental depth profiling using TOF-SIMS measurement was performed on identical samples to those used for the HRTEM study and the results are shown in Fig. 4 for the as-deposited and 700°C-annealed HfO₂ films on GaAs substrates with and without TMA pretreatment (50 cycles). Figure 4a, showing the Al depth profile for the TMA-treated samples with and without 700°C-PDA, indicates that the Al-oxide layer was formed only at the interfacial region by the TMA treatment and that no substantial Al diffusion occurred during PDA. According to the measured As profile shown in Fig. 4b, some As already existed on the surface region of the HfO₂ film even for the as-deposited samples. This indicates a possible As incorporation into the HfO₂ film during the ALD process, which agrees well with another experiment report.¹⁶ However, even after PDA at 700°C, no notable increase of the As build-up on the surface or change of the As profile was observed, which implied an absence of more As incorporation in the HfO₂ film during the thermal annealing possibly due to the facile evaporation of As atoms. Meanwhile, the Ga profile showed a different behavior to the As case, as shown in Fig. 4c. A large amount of surface pile-up of Ga atoms that did not occur during the HfO₂ deposition only appeared after PDA. In addition, some amount of Ga diffusion into the HfO₂ layer during PDA could be inferred from the slope change at the interfacial region. The 50-cycle TMA treatment

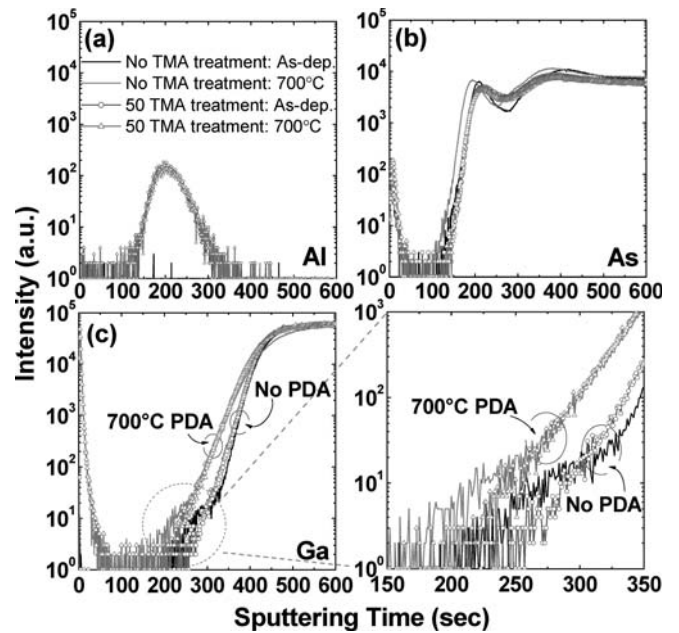


Figure 4. Elemental depth profiles of ~ 8 -nm-thick HfO₂/GaAs with and without 50 cycle-TMA pretreatment measured by TOF-SIMS: (a) Al, (b) As, and (c) Ga. The right graph of figure (c) is a magnified one of the Ga profile at the interfacial region.

suppressed some of the Ga diffusion, as indicated by the enlarged profile at the interfacial region shown in Fig. 4c.

In order to deduce various capacitor parameters, such as CET, frequency dispersion, and hysteresis, high frequency C-V curves were obtained at different frequencies (10 kHz, 100 kHz, and 1 MHz) and plotted as a function of the TMA pretreatment conditions and the PDA temperature in Fig. 5. The capacitor parameters extracted from the measured C-V curves are also plotted in Fig. 6. At this moment, CET was defined from the accumulation capacitance measured at 100 kHz without considering a quantum-mechanical correction and the amount of frequency dispersion was ascribed as the percentage ratio of the maximum accumulation capacitance change measured from 10 kHz to 1 MHz.¹⁷ For the untreated sample, the frequency dispersion was higher than that of TMA-treated sample regardless of the PDA condition, as shown in Fig. 6a. Because the high frequency dispersion in the high- k /GaAs was mainly attributed to the high interface state density generated by the Ga- and As-oxides,¹⁷⁻¹⁹ it can be concluded that the TMA pretreatment was beneficial in reducing the interface state density.

Meanwhile, for the untreated reference sample, CET drastically increased after PDA at 600°C and continuously escalated with increasing temperature, as shown in Fig. 6b. The substrate element out-diffusion (Ga and/or As) was presumed to be the main origin for the observed thermal CET instability of HfO₂ on the GaAs system.^{10,19} According to the aforementioned XPS and TOF-SIMS results (see Figs. 3 and 4), Ga diffusion followed by Ga-O bond formation was revealed to be more significant than As diffusion during PDA. This supports a conclusion that Ga may be a more dominant factor in degrading the CET characteristics than As. On the other hand, after the TMA pretreatment, the CET stability was significantly improved, irrespective of the number of the TMA pretreatment cycles, as presented in Fig. 6b. The XPS analyses of the TMA-treated sample as a function of the treatment cycles (see Fig. 2) revealed that the TMA precursor immediately formed the ultra-thin Al-oxide layer by scavenging oxygen atoms from the surface native oxide as soon as it was introduced. This suggests that the formed interfacial Al-oxide may have acted as a barrier layer for the diffusion of Ga and As atoms to HfO₂ – more probably the former than the latter according to the TOF-SIMS

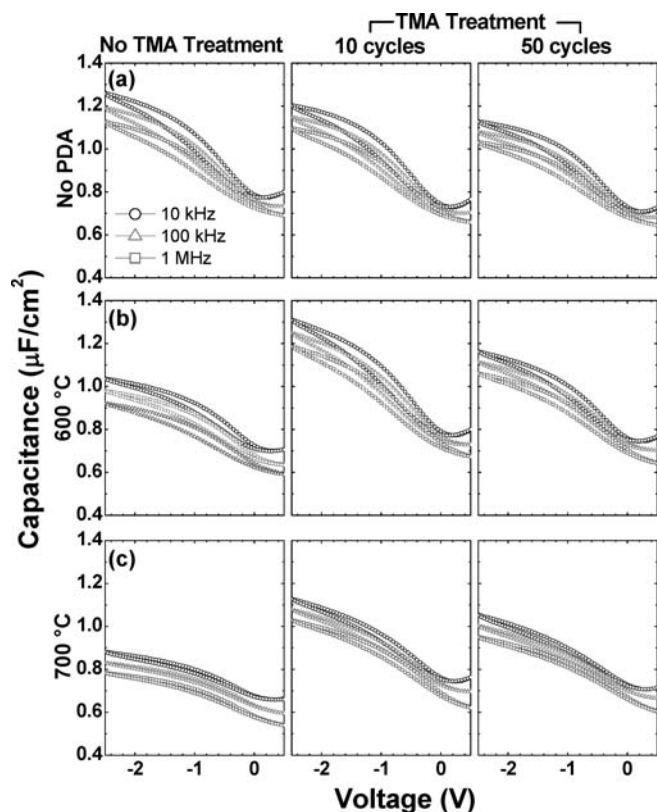


Figure 5. C-V curves measured from ~ 8 -nm-thick ALD-HfO₂ capacitor samples fabricated on untreated and TMA-treated GaAs substrates as a function of the PDA temperature: (a) no PDA, (b) 600°C, and (c) 700°C.

result – during the subsequent thermal annealing. Considering the CET of the as-deposited high- k films, the increased number of the TMA injection cycles induced a CET increase due to the thickening of the subsequently formed Al-oxide, interfacial layer with a lower dielectric constant. The CET was significantly thickened as the number of TMA injection cycles was increased above 50, indicating that the optimum number of treatment cycles was less than 30. All the samples showed a decreasing trend in the hysteresis characteristics following the PDA introduction and PDA temperature increase, as shown in Fig. 6c. PDA-induced hysteresis reduction was also observed in the high- k on the Si system and was caused by the reduction of the bulk trap density.²⁰

The leakage current characteristics were measured for all the samples and plotted in Fig. 7. For the as-deposited sample set, the TMA

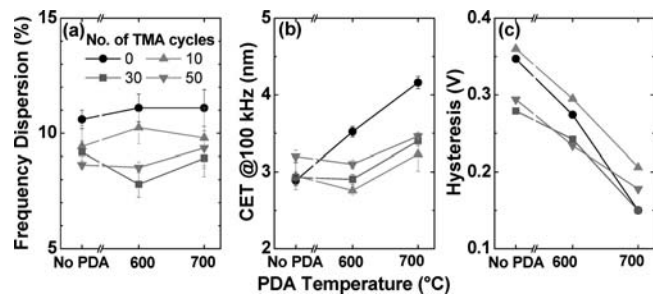


Figure 6. Various electrical properties of the ~ 8 -nm-thick ALD-HfO₂ films on GaAs substrates pretreated with TMA injections for different cycle numbers as a function of the PDA temperature: (a) frequency dispersion, (b) CET, and (c) hysteresis voltage.

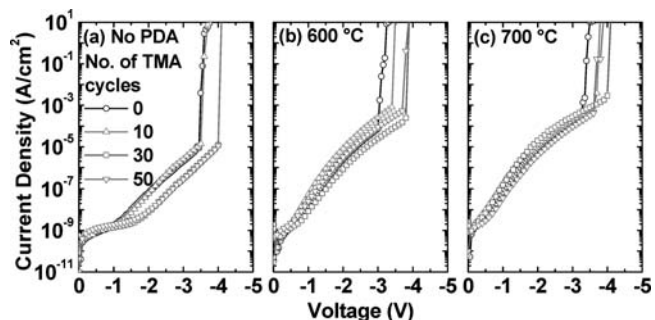


Figure 7. J-V characteristics measured from ~ 8 -nm-thick ALD-HfO₂ capacitor samples fabricated on untreated and TMA-treated GaAs substrates as a function of the PDA temperature: (a) no PDA, (b) 600°C, and (c) 700°C.

treatment with many cycles exhibited a somewhat lower leakage current behavior than that of the untreated samples, which was attributed to the growth of the Al-oxide layer that has a lower leakage current than HfO₂. With increasing PDA temperature, all the samples exhibited a similar degradation behavior of the leakage current, independent of the TMA treatment conditions. This may have been related to the crystallization-induced degradation because PDA can enhance the degree of crystallization of the HfO₂ film. These phenomena warrant further study.

Conclusions

In summary, we investigated the interfacial and electrical properties of ALD-HfO₂ films on the GaAs substrates pretreated with a range of TMA cycle numbers as a function of the PDA temperature. HRTEM and XPS analyses revealed that the TMA pretreatment effectively reduced the amount of the native Ga/As-oxides through the self-cleaning mechanism. The TMA treatment-induced, ultra-thin Al-oxide layer formation improved the frequency dispersion characteristics probably due to the more enhanced interfacial cleaning than ALD-HfO₂ process. It also delayed the thermal degradation of the CET, possibly by suppressing both the out-diffusion of rather Ga atoms than As into the HfO₂ film and the subsequent Ga-O bond formation during PDA, as evidenced by the TOF-SIMS depth-profiling and the XPS analyses, respectively. An optimal number of 30 TMA pretreatment exhibited the best thermal stability without increasing the as-deposited CET due to thickening of the Al-oxide interfacial layer.

Acknowledgments

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