The Effect of NH₃ on the Interface of HfO₂ and Al₂O₃ Films on GaAs(100) Surfaces

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We investigate the effects of heat-treatment under NH₃ ambient on the formation of Ga–O at the interface between GaAs and high-*k* dielectric materials deposited by atomic layer deposition. Compared with the heat-treatment under N₂ ambient, the monochromatic X-ray photoelectron spectroscopy analysis reveal that the formation of Ga–O is greatly suppressed under NH₃ ambient for HfO₂ on GaAs. However, the same experiments for Al₂O₃ on GaAs show that the effect is negligible. We examine the different reaction mechanisms of the NH₃ nitridation processes for two different high-*k* dielectric materials on GaAs.
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Recent advances in atomic layer deposition (ALD) high-*k* dielectric materials have attracted such materials for future-scaled metal–insulator–semiconductor (MIS) devices on high mobility channel materials, including III-V materials.[1,2] However, the performance of an inversion-type III-V MIS capacitor is strongly dependent on the amount of native oxides at the interface between the substrate and the high-*k* material, which could potentially lead to the Fermi level pinning.[3-7] For instance, it has been reported that the removal of native oxides from the surfaces of GaAs substrates minimizes frequency dispersion of accumulation capacitances in GaAs MIS capacitors due to the Fermi level pinning.[8]

Previous studies on ALD of Al₂O₃ or HfO₂ on III-V substrates report that self-cleaning reaction processes occur, which reduce the native oxide films. During the ALD processes, ligand exchange reactions occur between the native oxide films and the precursors of ALD that result in a complete removal of native films between ALD high-*k* dielectric films and InGaAs[9,10] or GaAs.[11] However, the self-cleaning reaction process is strongly dependent on the type of precursor used for ALD. For instance, remnant oxide films are clearly seen at the interface between GaAs and HfO₂[12] or Al₂O₃,[13] which have been deposited using different types of ALD precursors.

Efforts have been made to reduce the native oxides at the interface. For instance, Gao et al. successfully demonstrated a reduction of Ga(As)O at the interface between HfO₂ and GaAs by forming GaN on the surface of GaAs via thermal nitridation before the ALD process.[14]

In this article, the effects of heat-treatment under NH₃ ambient on the formation of Ga–O at the interface between GaAs and the high-*k* dielectric materials deposited by ALD were investigated and compared with those under N₂ ambient. Experimental results show that the nitridation processes exhibit different reaction mechanisms for the two different high-*k* dielectric materials, HfO₂ and Al₂O₃, on GaAs.

The substrates used in this work were 400 μm thick n-type GaAs(100) wafers doped with Si [(2.2–3.3) × 10¹⁸ atom/cm³]. First, the GaAs samples were cleaned with buffered oxide etch (BOE) and then rinsed in deionized (DI) water. Then HfO₂ and Al₂O₃ films were deposited by an in-house ALD system. The ALD system had a vertical warm wall reactor with a showerhead and a heat susceptor. The HfO₂ and Al₂O₃ films that were approximately 4 nm thick were deposited at a temperature of 320°C using tetrakis-(ethylmethylamino)hafnium, trimethylaluminum, and DI water as reactant sources for hafnium (Hf), aluminum (Al), and oxygen (O); N₂ was supplied as a purge and a carrier gas. For postdeposition annealing after the ALD deposition, rapid thermal annealing (RTA)

was performed at 500 and 700°C under NH₃ (99.999% purity) ambient for 1 min. For comparison, RTA was also performed at the same temperatures under N₂ (99.999% purity) ambient for 1 min for the other sets of GaAs samples with the high-*k* dielectric materials. Analysis of the deposited films was done using a monochromatic X-ray photoelectron spectroscopy (XPS) [AXIS-Nova (Kratos)] using an Al Kα (1486.6 eV) X-ray source.

Figure 1a shows the XPS analysis results for the Ga 2p₃/₂ spectra at the interface between HfO₂ and GaAs after the heat-treatments. Also shown are the XPS analysis results without any postdeposition annealing. The spectra of Ga 2p can be deconvoluted into three peaks. The peak at 1117.56 eV, which is the lowest binding energy level among the three, represents the Ga–As binding. The other two peaks at higher binding energy levels represent the interfacial oxides, the Ga–O bindings. Two peaks are seen for Ga–O due to the multiple oxidation states of Ga₂O₃ and Ga₂O.[15] Although not shown here, the other type of possible interfacial oxide, the As–O binding, is not seen in any of the experiments performed in this work.

The absence of the As–O binding is due to the decomposition of As₂O₃ in the vicinity of GaAs that can be explained by the following chemical reaction
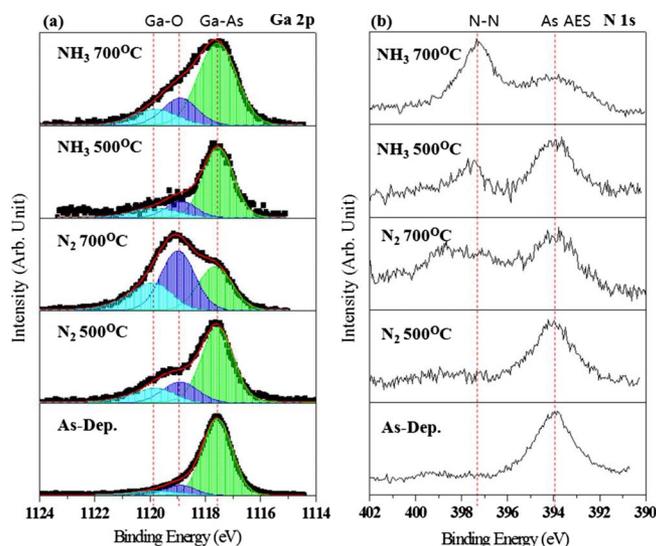

Figure 1. (Color online) XPS spectra of (a) Ga 2p₃/₂ and (b) N 1s for HfO₂ on GaAs.

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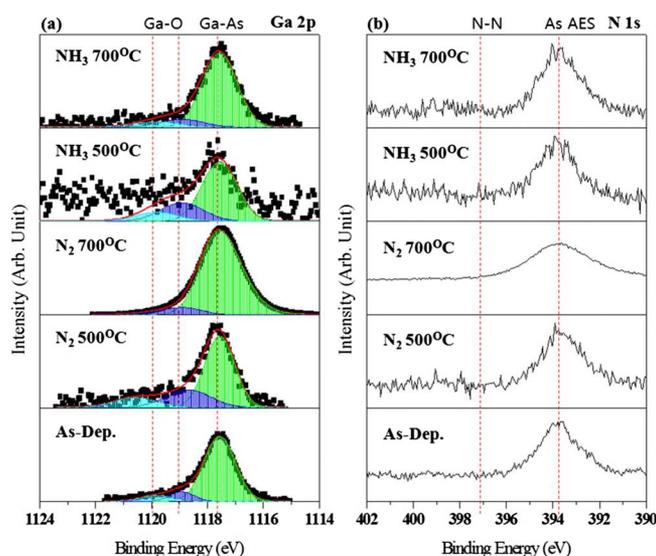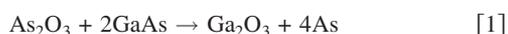z E-mail: yongshik.lee@yonsei.ac.kr; dhko@yonsei.ac.kr

Figure 2. (Color online) XPS spectra of (a) Ga $2p_{3/2}$ and (b) N 1s for Al_2O_3 on GaAs.

$$As_2O_3 + 2GaAs \rightarrow Ga_2O_3 + 4As \qquad [1]$$

As can be seen in Fig. 1a, the increase in the amount of Ga–O after the heat-treatment is substantially larger when annealed under N_2 ambient than under NH_3 ambient. Moreover, the difference in the increased amount of Ga–O after annealing under the two ambient gases is prominent at higher temperatures.

Under an inactive N_2 ambient, GaAs reacts with oxygen, mostly those diffused from HfO_2 but also in part from the impurities in N_2 ambient, thus forming Ga–O products. Such a reaction is accelerated as the process temperature increases, resulting in an enhanced formation of Ga–O products. Under NH_3 ambient, ligand exchange reactions occur between the oxygen of Ga–O products, and the nitrogen atoms form reactive NH_3. This can be explained with the XPS spectra of N 1s in the HfO_2 films shown in Fig. 1b. When the postannealing is performed under NH_3 ambient, the nitrogen atoms are incorporated at the interface between GaAs and HfO_2. Yet no nitrogen is seen when the postannealing is performed under N_2 ambient. Because these incorporated nitrogen atoms act as obstacles to Ga–O formations, the heat-treatment under NH_3 ambient is very effective in suppressing those formations. Such effects are not observed when the heat-treatment is performed under the inactive N_2 ambient.

Figure 2a shows the XPS analysis results for the Ga $2p_{3/2}$ spectra at the interface between Al_2O_3 and GaAs after being postannealed under N_2 and NH_3 ambient. Compared with the XPS analysis results for HfO_2 in Fig. 1, it can be seen that the effects of ambient gas during postannealing are different for Al_2O_3 films. That is, the difference in the amount of Ga–O bonding is negligible for Al_2O_3 on GaAs before and after postdeposition annealing under any gas type.

The standard heats of formation are -1676.81 kJ/mol for Al_2O_3, -1118.29 kJ/mol for HfO_2, -1089 kJ/mol for Ga_2O_3, and -355.9 kJ/mol for Ga_2O.[15] The standard heats of formation per O atom are -558.9 kJ/mol for Al_2O_3, -559.1 kJ/mol for HfO_2, -363.0 kJ/mol for Ga_2O_3, and -355.9 kJ/mol for Ga_2O.[16] Thus, the difference in the effects of heat-treatment on Al_2O_3 and HfO_2 cannot be explained with the heats of formation for the two materials.

In contrast to the HfO_2 case, however, the XPS analysis results for the N 1s spectra in Fig. 2b show that no nitrogen atoms from the reactive NH_3 gas are incorporated in Al_2O_3. Because the deposition conditions for the HfO_2 and Al_2O_3 films in our experiments are similar, the Al_2O_3 film is considered to be denser than the HfO_2 film based upon the data on the densities of the two materials in bulk states.[17] Thus, the diffusivity of nitrogen atoms is presumed to be much smaller in Al_2O_3 than in HfO_2.

Therefore, nitrogen atoms are hardly incorporated in Al_2O_3, making the effects of heat-treatment under the reactive NH_3 ambient negligible on suppressing the formation of Ga–O bindings.

In summary, heat-treatments under NH_3 ambient have been found to be an effective method in suppressing the formation of interfacial oxides between HfO_2 and GaAs. HfO_2 and Al_2O_3 thin films were grown by ALD on GaAs substrates that was cleaned by BOE. Then 1 min postannealing processes were performed under NH_3 or N_2 ambient. The effects of NH_3 nitridation on the properties of the HfO_2/GaAs and Al_2O_3/GaAs interfaces were investigated through XPS. At the HfO_2 and GaAs interface, the amount of Ga–O binding increases due to the postannealing processes under NH_3 ambient as well as under N_2 ambient. However, the amount of increase is considerably less under NH_3, especially at a higher temperature. This is mainly due to the nitrogen atoms from the reactive NH_3 gas incorporated in HfO_2 that suppress the formation of Ga–O bindings. The effects of heat-treatment under NH_3 ambient on the interfacial oxides are negligible for Al_2O_3 on GaAs. This is due to the significantly low diffusivity of nitrogen atoms in the denser Al_2O_3 that makes them hardly effective in suppressing the formation of Ga–O bindings.

References

1. R. W. Keyes, *Science*, **195**, 1230 (1977).
2. S. Suthram, Y. Sun, P. Majhi, I. Ok, H. Kim, H. R. Harris, N. Goel, S. Parthasarathy, T. Koehler, T. Acosta, et al., *Dig. Tech. Pap. - Symp. VLSI Technol.*, **2008**, 182.
3. C. D. Thurmond, G. P. Schwartz, G. W. Kammlotot, and B. Schwartz, *J. Electrochem. Soc.*, **127**, 1366 (1980).
4. W. E. Spicer, P. W. Chye, P. R. Skeath, C. Y. Su, and I. Lindau, *J. Vac. Sci. Technol. B*, **16**, 1422 (1979).
5. J. G. Ping and H. E. Ruda, *J. Appl. Phys.*, **83**, 5880 (1998).
6. E. R. Weber, H. Ennen, V. Kaufmann, J. Windscheif, J. Schneider, and T. Wosinski, *J. Appl. Phys.*, **53**, 6140 (1982); E. R. Weber and J. Schneider, *Physica B & C*, **116**, 398 (1983).
7. S. I. Yi, P. Kruse, M. Hale, and A. C. Kummel, *J. Chem. Phys.*, **114**, 3215 (2001).
8. C. L. Hinkle, A. M. Sonnet, E. M. Vogel, S. McDonnell, G. J. Hughes, M. Milojevic, B. Lee, F. S. Aguirre-Tostado, K. J. Choi, J. Kim, et al., *Appl. Phys. Lett.*, **91**, 163512 (2007).
9. M. L. Huang, Y. C. Chang, C. H. Chang, Y. J. Lee, P. Chang, J. Kwo, T. B. Wu, and M. Hong, *Appl. Phys. Lett.*, **87**, 252104 (2005).
10. C. H. Chang, Y. K. Chiou, Y. C. Chang, K. Y. Lee, T. D. Lin, T. B. Wu, M. Hong, and J. Kwo, *Appl. Phys. Lett.*, **89**, 242911 (2006).
11. M. M. Frank, G. D. Wilk, D. Starodub, T. Gustafsson, E. Garfunkel, Y. J. Chabal, J. Grazul, and D. A. Muller, *Appl. Phys. Lett.*, **86**, 152904 (2005).
12. D. Shahrjerdi, D. I. Garcia-Gutierrez, T. Akyol, S. R. Bank, E. Tutuc, J. C. Lee, and S. K. Banerjee, *Appl. Phys. Lett.*, **91**, 193503 (2007).
13. G. K. Dalapati, Y. Tong, W.-Y. Loh, H. K. Mun, and B. J. Cho, *IEEE Trans. Electron Devices*, **54**, 1831 (2007).
14. F. Gao, S. J. Lee, D. Z. Chi, S. Balakumar, and D.-L. Kwong, *Appl. Phys. Lett.*, **90**, 252904 (2007).
15. C. C. Surdu-Bob, S. O. Saied, and J. L. Sullivan, *Appl. Surf. Sci.*, **183**, 126 (2001).
16. K. J. Hubbard and D. G. Schlom, *J. Mater. Res.*, **11**, 2757 (1996).
17. G. V. Samsonov, *The Oxide Handbook*, 2nd ed., IFI/Plenum Data Co., New York (1982).