High-bias-stability Al₂O₃ films formed by high-temperature annealing after atomic layer deposition

K Horikawa¹, A. Hiraiwa^{2,4}, S. Okubo¹, T. Kageura¹ and H. Kawarada¹⁻³

Fac. Sci. Eng., Waseda Univ.¹, RONL, Waseda Univ.², KMRIMST, Waseda Univ.³, IMaSS, Nagoya Univ.⁴

3-4-1 Okubo Shinjuku-ku, Tokyo 169-8555, Japan

Phone : +81-3-5286-3391 E-mail : kiyotaka92@akane.waseda.jp

Abstract

We intensively investigated a high-temperature annealing effect on the bias instability of atomic-layer-deposited (ALD) Al₂O₃ films, which, as an alternative to the well-established thermal SiO₂ on Si, are a promising candidate for gate insulators of wide-bandgap semiconductor (WBGS) devices. The flat-band voltage shift of stressed Al₂O₃ metal-insulator-semiconductor (MIS) capacitors is approximately a Kohlrausch-type complementary extended exponential function of stress time, thereby enabling to estimate the maximum flat-band voltage shift based on a finite-time data set. The maximum flat-band voltage shift thus obtained for the samples annealed at 750°C after ALD is found to be smaller than 0.2 eV even at 200°C under an expected rating voltage, i.e., an equivalent SiO₂ field of 4 MV/cm, exhibiting excellent bias stability. Hence, the technology developed here will enhance the performance and reliability of WBGS MIS field-effect transistors.

1. Introduction

Wide-bandgap semiconductors, such as GaN and diamond, have recently been attracting attention from power device engineers as a substitute for the traditional Si. Since the well-established thermal SiO₂ is difficult to form as a gate insulator on these materials, various insulators have been investigated using atomic layer deposition (ALD), which forms films with unparalleled uniformity and reproducibility. Among those films, ALD-Al₂O₃ is an attractive candidate, having a wide bandgap of 7eV [1], a high dielectric constant of 9 [2], etc. A major challenge for the Al₂O₃ in practical applications is the suppression of threshold voltage shift of Al₂O₃-insulated metal-insulator-semiconductor field-effect transistors (MISFETs) during long-term operation. The purpose of this study is to achieve this by performing high-temperature annealing after ALD.

2. Experimental methods

For ease of experiments, instead of the threshold voltage of MISFETs, this study investigates the flat-band voltage of Al / 29-32-nm-thick Al₂O₃ / 1.2-nm-thick SiO₂ / *n*-Si MIS capacitors fabricated as follows. After cleaning (001) *n*-type 2–4 Ω cm Si substrates in an NH₄OH/H₂O₂ mixture, which formed a SiO₂ film, an Al₂O₃ film was deposited by ALD at 450°C with trimethylauminum and H₂O as precursors. The samples were subsequently annealed for 30 minutes at 600–1000°C in a 4% H₂/Ar atmosphere. Finally, gate electrodes were formed by thermally evaporating Al through a shadow mask with openings.

The thicknesses of the SiO₂ and Al₂O₃ films were measured immediately after their formation, using a spectroscopic ellipsometer. The flat-band voltage shift was estimated by alternately repeating capacitance-voltage (C-V) measurement and constant-voltage stressing of the MIS capacitors. The results from different samples in this study were compared for the same equivalent SiO2 field (EOF), Feo, defined by $F_{eo} = V_{ins}/EOT$, where EOT is the equivalent SiO₂ thickness of the Al_2O_3/SiO_2 stack and V_{ins} is the voltage applied to the stack, being given by $V_{ins} = V_G - (W_G - \chi_s)/q$ with V_G as the gate voltage, W_G as the gate work function, χ_s as the substrate electron affinity, and q as the electronic charge. EOT was estimated by fitting theoretical C-V curves [3] to experimental ones. Under the same EOF, the results from different samples can be compared for the same MISFET performance [4].

3. Results and Discussion

The flat-band voltage shift, ΔV_{fb} , of the Al₂O₃-MIS capacitors for $F_{eo} = 4$ MV/cm, a Si device guideline, is shown in Fig. 1 (symbols) as a function of stress time. It is remarkably reduced by the post-deposition annealing (PDA) at 750°C or lower. To estimate the value after 10–20 years, a reliability target, the flat-band voltage shift, ΔV_{fb} , is approximated by a Kohlrausch-type [5] complementary extended exponential function, given by



Fig. 1. Flat-band voltage shifts of Al_2O_3 MIS capacitors under $F_{eo} = 4$ MV/cm vs. stress time. The symbols and lines represent experimental and simulated results, respectively. (The open plots represent negative values.)

$$\Delta V_{fb} = \Delta V_{fb,max} \left\{ 1 - \exp\left[-\left(\gamma_0 t_{stress}\right)^{\beta} \right] \right\}, \tag{1}$$

where $\Delta V_{fb,max}$ is the maximum of ΔV_{fb} , γ_0 is the effective value of trap creation/charge capture rate γ , t_{stress} is the stress time, and β is a constant that determines the spread of γ distribution. The optimized simulations using Eq. (1) (lines in Fig. 1) excellently fit the experimental results (symbols), validating the approximation using Eq. (1). As shown in Fig. 2, the maximum flat-band voltage shift thus obtained is reduced by PDA at temperatures up to 750°C, but abruptly increases by PDA at 780°C or higher.

This sudden increase is possibly caused by Al₂O₃ crystallization, as revealed by the γ -phase crystalline Al₂O₃ peaks observed in grazing incidence X-ray diffraction patterns of the samples for PDA at 800°C or higher (Fig. 3). Due to the inevitable power consumption by devices themselves, package heat resistance, and a high temperature environment required of power devices, the device temperature mostly increases to 100°C or higher. To assess the bias instability at these temperatures, Fig. 4 shows the maximum flat-band voltage shift of 750°C-PDA samples, measured at room temperature (RT) to 200°C, as a function of equivalent SiO₂ field.



Fig. 2. Maximum flat-band voltage shifts of Al_2O_3 MIS capacitors under $F_{eo} = 4$ MV/cm vs. PDA temperature. (The open plot represents a negative value.)



Fig. 3. X-ray diffraction patterns of annealed ALD-Al₂O₃.



Fig. 4. Maximum flat-band voltage shifts of Al_2O_3 MIS capacitors prepared using 750°C PDA vs. equivalent SiO₂ field. For comparison, the inset shows the results from unannealed samples.

Interestingly and conveniently, the maximum flat-band voltage shift of the PDA samples remains unchanged, smaller than 0.2 V for $F_{eo} = 4$ MV/cm, even in higher-temperature environments, in stark contrast to the results for non-PDA samples (inset of Fig. 4), which exhibited a remarkable increase in the maximum flat-band voltage shift above 100°C. In this manner, we confirmed a high bias-stability of Al₂O₃ films annealed at 750°C or lower after ALD.

4. Conclusion

The flat-band voltage shift of stressed Al_2O_3 MIS capacitors is approximated by a Kohlrausch-type complementary extended exponential function of stress time, thereby enabling to estimate the maximum flat-band voltage shift based on a finite-time data set. The maximum flat-band voltage shift thus obtained for the samples annealed at 750°C is smaller than 0.2 eV even at 200°C under an equivalent SiO₂ field of 4 MV/cm, exhibiting an excellent bias stability. Hence, the technology developed here will enhance the performance and reliability of wide-bandgap semiconductor MISFETs.

Acknowledgements

This research is supported by the "Project of Creation of Life Innovation Materials for Interdisciplinary and International Researcher Development" of the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan.

References

- [1] S. Canulescu, et al., Appl. Phys. Lett. 109, 091902 (2016).
- [2] A. Hiraiwa, et al., J. Appl. Phys. 117, 215304 (2015).
- [3] A. Hiraiwa, et al., J. Appl. Phys. 91, 6571 (2002).
- [4] A. Hiraiwa, et al., J. Appl. Phys. 119, 064505 (2016).
- [5] R. Kohlrausch, Annal. Phys. 167, 179 (1854).