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Characterization of Novel HfTiO Gate Dielectrics Post-treated by NH_3 Plasma and Ultra-violet Rays

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1. Introduction

To solve the leakage and reliability problems of ultra-thin (<1nm) SiO_2 films, hafnium-based high-k dielectrics like HfO_2 and its aluminates, silicate and oxy-nitride are attracting much more attention in recent years [1-2]. Nevertheless, thermal stability, mobility degradation and charge trapping induced reliability issues are still challenge for the application into CMOS technology. Some new HfTiO and HfTaO gate dielectrics are developed and exhibited superior properties such as high interface quality, low bulk traps, high mobility and high electrical stability as compared with the conventional Hf-based dielectric films [3-4]. In this work, we investigate the properties improvement of HfTiO gate dielectrics post-treated by NH_3 plasma and ultra-violet (U.V.) rays. A current jump under constant voltage stress (CVS) is observed only at the NH_3 plasma treated films and disappeared after the following U.V. rays irradiation. By extracting the activation energy, we propose that the current jump is owing to the hydrogen release effect catalyzed by TiO_2 in NH_3 plasma treated HfTiO gate dielectrics.

2. Experimental

Typical process flows of HfTiO and HfO_2 capacitors fabrication are shown in Fig. 1. First, HfTiO films (5nm) were deposited by electron beam evaporation with the target consisted of HfO_2 (99.9%) and TiO_2 (0.1%). For comparison, pure HfO_2 films were deposited by ALD with the precursors of $HfCl_4$ and H_2O. Then, the films were treated by NH_3 plasma, U.V. rays (λ=350nm), and rapid thermal annealed at 600°C for 1min. A TaN film of 25nm was deposited by sputter and the gate was defined lithographically and etched. Finally, EOT ranged from 1.23 to 1.7nm was obtained from the high frequency (0.1 MHz) C-V curves. The secondary ion mass spectrometer (SIMS) was performed to investigate the HfTiO film composition (Fig. 2), and significant TiO_2 was observed in our HfTiO films. Besides, electrical properties were measured by using an HP4156B semiconductor parameter analyzer and an HP4284A precision LCR meter.

3. Results and Discussion

Fig. 3 shows the J-V characteristics of the HfTiO gate dielectrics. Significant properties improvement of the NH_3 plasma treated samples was observed and further enhanced after the U.V. rays irradiation. This must be owing to the charge trapping elimination after these treatments as shown in the flat-band voltage shift of the high frequency C-V curves in inset of Fig. 3. On the other hand, we did not observe any improvement of HfO_2 films after the U.V. rays irradiation (Fig. 4). Moreover, the increase in TDDB lifetime projection of HfTiO gate dielectrics treated by NH_3 plasma and U.V. rays was displayed in Fig. 5. As shown in Fig. 6, a current jump under CVS was observed at the NH_3 plasma treated HfTiO films, and disappeared after the following U.V. rays irradiation. Nevertheless, we did not observe the jump at HfO_2 films. Fig. 7 shows measured gate current density under CVS of HfTiO films. Current jump was disappeared after RTA. In addition, jump occurs at a local stress current density for some gate area. This was verified by measuring the generation probability with different gate area, as shown in Fig. 8. Fig. 9 shows the Weibull distribution of time-to-failure (T_f) for current jump and SBD. The Weibull slope β of jump was about 1.02, which was quite different from that of SBD for β=1.45. Fig. 10 shows the Arrhenius plots of time-to-failure ($t_{63\%}$) at different stress voltage. To compare the temperature acceleration behavior of current jump and SBD, the activation energies (Ea) were extracted and shown in Fig. 11. By the thermochemical E-model, we have obtained that Ea of 0.94eV for current jump corresponding to the bond strength of 362.52 kJ/mol, which was between the H-O and N-H bonds strength [5]. We can rationally speculate that the breakage of H-O and N-H bonds brings about the jump. The possible chemical reactions of the NH_3 plasma treated HfTiO films irradiated by U.V. rays were illustrated in Fig. 12.

4. Conclusions

For the first time, characteristics improvement of HfTiO gate dielectrics with NH_3 plasma treatment and U.V. rays irradiation have been developed. A current jump under CVS is observed from the NH_3 plasma treated HfTiO films and disappeared after U.V. rays irradiation. We concluded that the current jump were caused by hydrogen release effect catalyzed by TiO_2 in the NH_3 treated HfTiO gate dielectrics.

References

[1] M. Koyama, et al., *IEDM Tech. Dig.*, (2002) p. 849
[2] J.-H. Lee, et al., *VLSI Tech. Symp. Dig.*, (2002) p. 84
[3] J. C. Lee, et al., *VLSI-TSA Tech. Symp. Dig.*, (2005) p. 122
[4] X.-F. Yu, et al., *VLSI Tech. Symp. Dig.*, (2004) p. 110
[5] D. R. Lide, *CRC Handbook of Chemistry and Physics*, (2000)

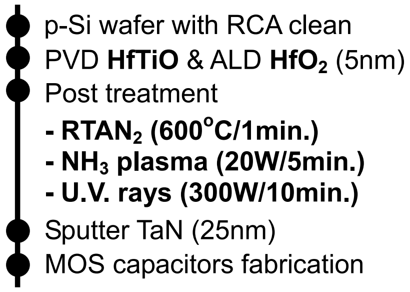

Fig. 1 Typical process flows of HfTiO and HfO_2 capacitors fabrication with various post treatment techniques.

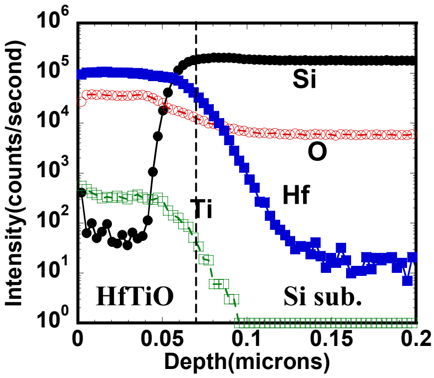

Fig. 2 Secondary ion mass spectrometer (SIMS) analysis of HfTiO films. Significant titanium intensity is observed in the dielectric film.

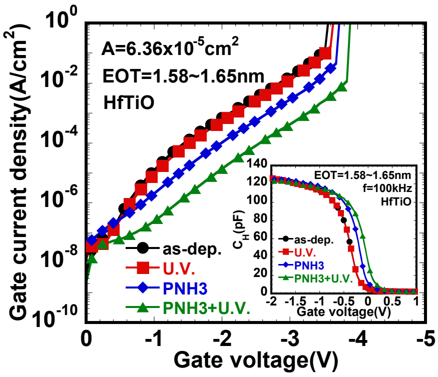

Fig. 3 J-V characteristics of HfTiO gate dielectrics post-treated by NH_3 plasma and U.V. rays. The inset shows the high-frequency (100kHz) C-V characteristics of these samples.

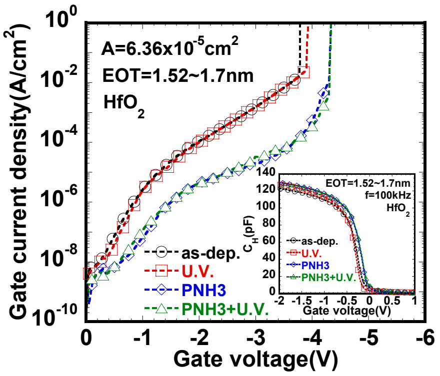

Fig. 4 J-V characteristics of HfO_2 gate dielectrics post-treated by NH_3 plasma and U.V. rays. The inset shows the high-frequency (100kHz) C-V characteristics of these samples.

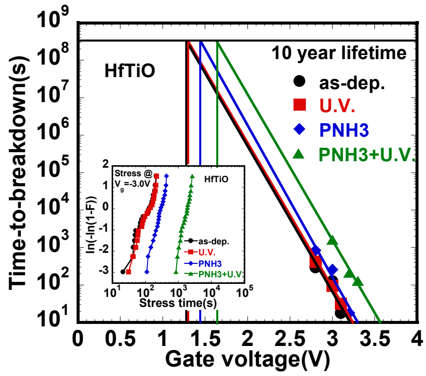

Fig. 5 TDDB lifetime projection of HfTiO gate dielectrics post-treated by NH_3 plasma and U.V. rays. The inset shows the Weibull distribution of these samples stressed at Vg = -3.0 V.

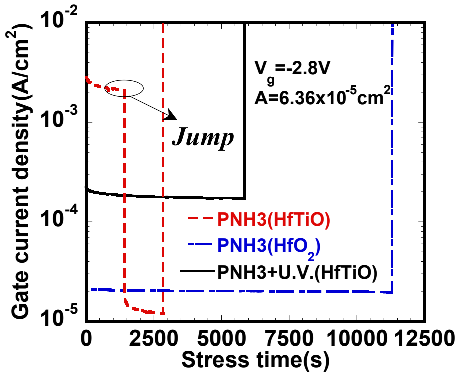

Fig. 6 Charge trapping curves of HfTiO and HfO_2 films post-treated by NH_3 plasma and U.V. rays. The jump was observed only at the NH_3 plasma treated HfTiO films.

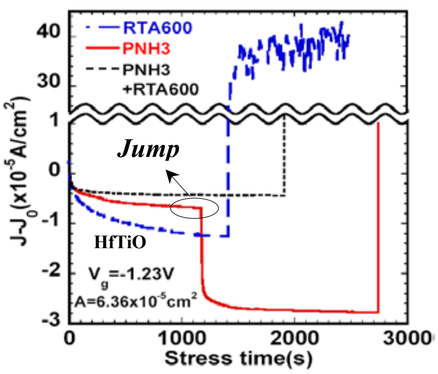

Fig. 7 Measured gate current density of HfTiO films with treatments. The jump was observed only at the PNH3 sample.

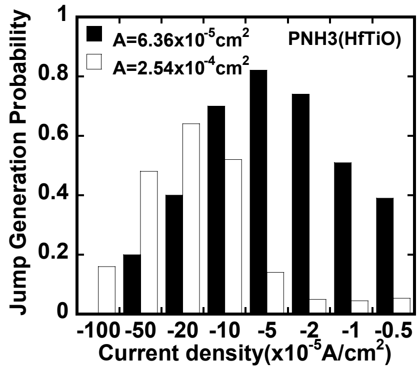

Fig. 8 Generation probability of jump effect under constant current stress (CCS) with two different gate area.

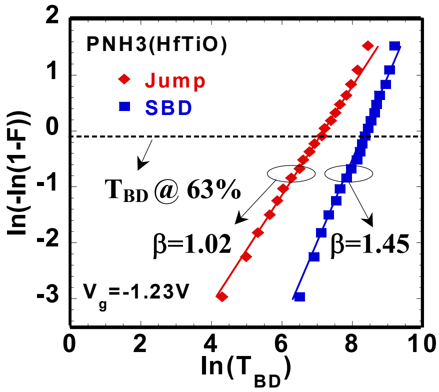

Fig. 9 Weibull plots of time-to-failure (T_f) stressed at V_g=-1.23V for jump and SBD.

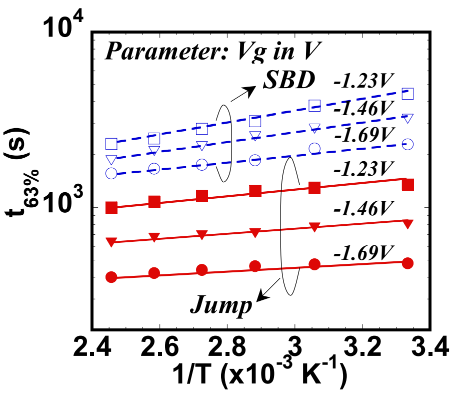

Fig. 10 Arrhenius plots of time-to-failure at different stress voltages for jump and SBD in the temperature range from 300 to 380 K.

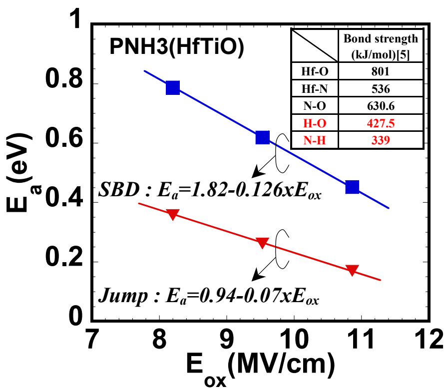

Fig. 11 Linear fit of the activation energy (E_a) for SBD and jump vs. the electric oxide field (E_{ox}) for HfTiO films. The inset shows lists of the bond strength for Hf-O, Hf-N, N-O, H-O, and N-H bonds.

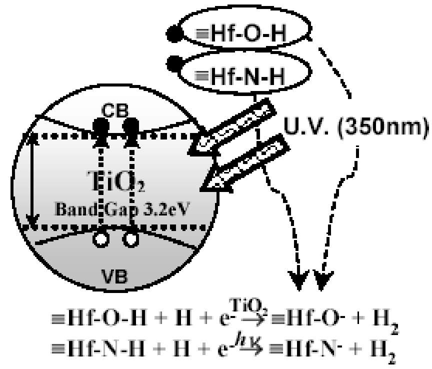

Fig. 12 Possible chemical reaction mechanism of HfTiO films post-treated by NH_3 plasma and U.V. rays.