ALD and pulsed-CVD of Ru, RuO_2, and $SrRuO_3$[#]

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As technology road map for DRAM capacitor with a design rule below 20 nm requires t_{ox} of less than 0.4 nm, noble metals, such as Ru, and higher-k dielectrics, TiO_2 and $SrTiO_3$, have gained a lot of interest as innovative materials for future DRAM. Among various electrode candidates, Ru, RuO_2, and $SrRuO_3$ have been spotlighted due to their low resistivity (Ru~7 μΩ·cm, RuO_2~30 μΩ·cm, $SrRuO_3$~300 μΩ·cm), high chemical stability, and high work function (Ru~4.7 eV, RuO_2~5.1 eV, $SrRuO_3$~5.1 eV). Atomic layer deposition (ALD) and chemical vapor deposition (CVD) are techniques of choice for fabricating nano-scale Ru based films because of their excellent thickness controllability and conformal growth characteristic over the three-dimensional substrate.

In this presentation, the authors will report on the growth behaviors and characteristics of Ru film by ALD and pulsed-CVD using MO precursor, Ru(DMPD)(EtCp), and inorganic RuO_4 precursor, respectively. Pulse-CVD Ru film showed enhanced mass-production compatibility, where a higher growth rate of 0.18 nm/cycle was obtained than that of ALD Ru. Additionally, growth of RuO_2 and $SrRuO_3$ electrodes were explored by pulsed-CVD and combined ALD/CVD process using RuO_4 and $Sr(iPr_3Cp)_2$ as Ru and Sr precursor, respectively. Pulsed-CVD RuO_2 film showed growth rate of 0.24 nm/cycle and excellent conformality over a hole structured substrate with a opening diameter of 100 nm and aspect ratio of 10 as shown in Fig. 1 (a). [1] Study on the initial growth behavior of pulsed-CVD RuO_2 revealed that highly oxidative and electronegative properties of RuO_4 precursor results in rather different nucleation behavior from that of ALD Ru(RuO_2) using MO precursor. Electrical properties of (Al-doped) TiO_2 films grown on Ru and RuO_2 are compared. Figure 1 (b) shows that Al-doped TiO_2 film has lower leakage current density of on RuO_2 bottom electrode compared to that on Ru electrode even with slightly lower t_{ox} value. [2]

Stoichiometric $SrRuO_3$ film was deposited by alternating ALD SrO and pulsed-CVD RuO_2 at 230 °C. The cation ratio of Sr/Ru was controlled by modulating the SrO/RuO_2 sub-cycle ratio. To obtain crystallized $SrRuO_3$ film, post deposition annealing at 600-700 °C was performed. Figure 2 (a) and (b) shows GAXRD patterns and HRTEM images of Pt/$SrTiO_3$/$SrRuO_3$ capacitor, respectively. In-situ crystallization of ALD $SrTiO_3$ was achieved on crystallized $SrRuO_3$ film, indicating crystallized $SrRuO_3$ electrode plays a role as a seed layer for perovskite $SrTiO_3$ growth. [3]

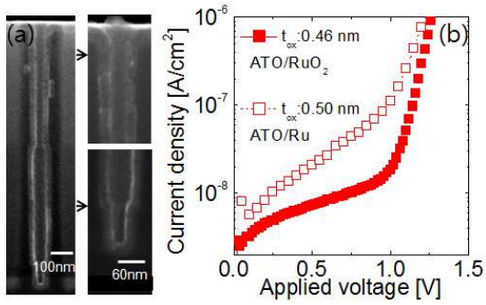

Figure 1 (a) The SEM images showing film conformality of pulsed-CVD RuO_2 over a hole structured substrate with an opening diameter of 100 nm and aspect ratio of 10. (Data reproduced from Ref. 1) (b) Leakage current density of ATO on Ru and RuO_2 bottom electrodes. (Data reproduced from Ref. 2)

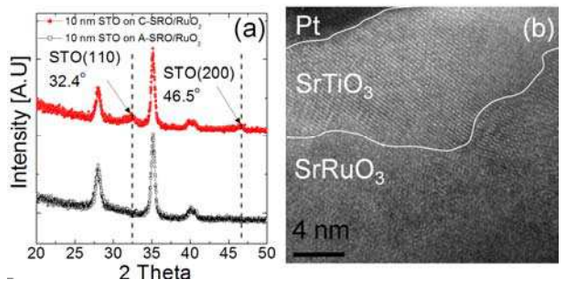

Figure 2 (a) GAXRD of 10-nm-thick ALD $SrTiO_3$ films grown on crystallized $SrRuO_3$ and amorphous $SrRuO_3$ electrodes. (b) HRTEM images of Pt/$SrTiO_3$/$SrRuO_3$ capacitor, showing the STO is in-situ crystallized. (Data reproduced from Ref. 3)

References

[1] J. H. Han et al., *Chem. Mater.*, 22, 5700, (2010)
[2] J. H. Han et al., *Appl. Phys Lett..*, 99, 022901, (2011)
[3] J. H. Han et al., *Chem. Mater.*, 24, 4686, (2012)

[#]Invited presentation

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