Supporting Information

Effect of Al_2O_3 Seed-Layer on the Dielectric and Electrical Properties of Ultrathin MgO Films Fabricated using *In Situ* Atomic Layer Deposition

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Regarding the thickness of the ALD-Al_2O_3 seed layers (SLs), we actually have tried different thickness (or ALD cycles in the range of 0.22-0.55 nm (or 2-5 cycles) using both in vacuo STS study and transport measurement on the M/I/M devices. The seed layer plays significant role on initial nucleation and dense hydroxylation for subsequent ALD-MgO. When there is no seed layer, deprotonated releasing hydrogen from water may leave oxygen on the Al surface, resulting in formation of native oxides and incomplete coverage of the hydroxyl groups on the sample surface. We observe that with decrease in thickness of seed layer dielectric properties of MgO film decreases possibly due to non-uniform nucleation for MgO as discussed in Figure S1. For example, MgO with 5C- Al_2O_3 SL show ε_r close to bulk value with barrier height ~1.50 eV and almost 100% coverage. However, with further decrease in SL thickness ε_r decreases and reduced to ~22-30 % for 3C-Al_2O_3 SL with reduction in ALD coverage. Unfortunately, the dielectric study for SL thickness below 0.33 nm (or 3 cycles) is unreliable with high leakage due to non-uniform nucleation resulting defects and pinholes. This agrees well with the *in vacuo* STS result of incomplete coverage of MgO dielectric with 0.22 nm (or 2 cycles) seed layer or MgO directly on Al. Based on these studies, the 0.55 nm (or 5 cycle) ALD-Al_2O_3 SL leads the best dielectric properties of the ALD-MgO.

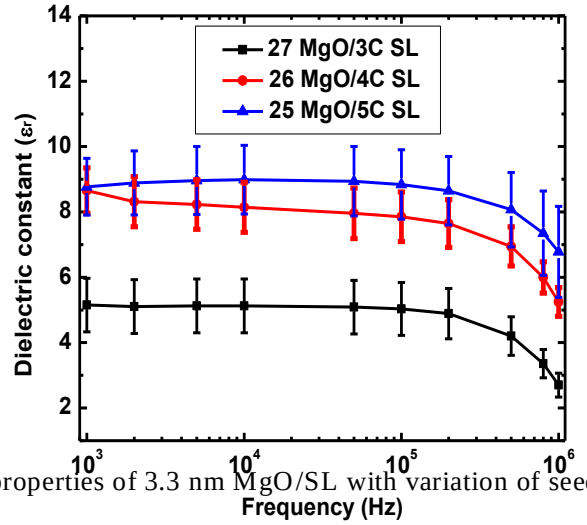

Figure S1: Dielectric properties of 3.3 nm MgO/SL with variation of seed layer thickness

In order to give insight into different growth mechanism responsible for MgO and Al_2O_3 dielectric film, the detailed comparison between leakage current characteristic for different dielectric thickness MIM capacitors is shown in S1. Figure S2 (a) show the non-linear I-V for 25C ALD-MgO/SL and 30C ALD-Al_2O_3 confirming high quality dielectric film above this critical thickness with dielectric constant (ε_r) comparable to bulk dielectric as in Figure 3 (b). But after reducing thickness to 20C ALD-MgO/SL and 20C ALD-Al_2O_3 MIM capacitors both show linear I-V as a consequence of quantum tunneling as in Figure S2 (b). This confirms that decrease in ε_r is due to increase in leakage after a certain dielectric thickness rather than interfacial layer formation, which is confirmed with observed barrier height ~1.5 eV for 10 cycles (Al_2O_3 (10 C) and Al_2O_3 (5 C) + MgO (5 C)) samples with STS. However, ALD-MgO/WoSL show reduced dielectric constant and increase in leakage current along with *in vacuo* STS suggesting non-uniform nucleation with significant portion of the Al surface remaining conductive confirming IL formation along with the presence of defects, vacnancies and pinholes inherent to MgO dielectric [1-2].

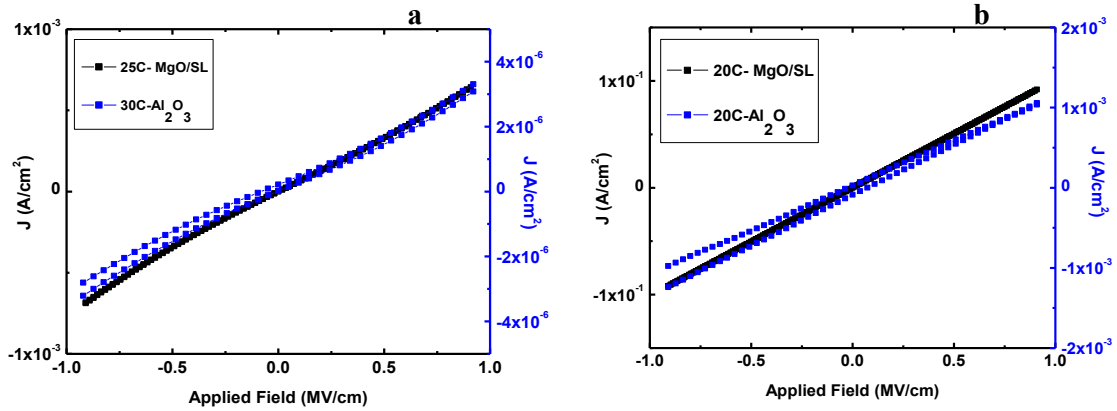

Figure S2: Characteristic of leakage current with same applied field with a) 25C-MgO/SL and 30C-Al_2O_3 and b) 20C-MgO/SL and 20C-Al_2O_3

Reactive molecular dynamics simulations were carried out to validate the proposed growth mechanism for ALD-MgO with and without SL, we extended the approach by studying two cases: a) OH^- are distributed as a regular pattern on top of Al (111) surface (referred to as ALD-MgO/SL) and b) OH^- are placed randomly on the same Al (111) wetting layer (referred to as ALD-MgO/WoSL). Figure S3 and S4 represents atomic trajectories and videos for two different cases ALD-MgO/SL and ALD-MgO/WoSL at 0, 2500, 5000, 7500, 10,000, 20,000 and 25,000 respectively. Our simulation results point out two important finding, first, in the case of regularly placed OH deposition, which would represent the case ALD-MgO/SL, we barely see any occurrence of water vapor release. This implies that the retention of OH molecules through the OH^- - OH^- lateral bonding formation on the surface, presumably creating a denser oxide film. The surface reaction also involves the formation of Al(center)-OH clusters which further maintain the OH^- content on the surface. We also note that there is a more limited extent of O^{2-} ions released inside the Al layer. This is because there is a better connectivity of adsorbed OH^- maintained on the surface and the polarity of H^+ prevents the OH^- molecules from diffusing inward. In contrast, for ALD-MgO/WoSL we see the continuous formation of water molecules as a result of the reaction between the adsorbed OH- molecules, some are deprotonated, releasing hydrogen on the surface. This leads to the release of water molecules. The release of water vapor also implies that the surface density and coverage of the remaining adsorbed OH on the Al surface will be *much less*, possibly leading to more defective MgO produced with the subsequent ALD process. Second, as a result of the deprotonation itself, a few of the oxygen ions start to penetrate into the Al layer. The supplementary information provides videos of the reaction dynamics from these MD simulations. We here point out advantage of using SL for ALD-MgO deposition, the introduction of Al wetting layer is still mandatory to generate relatively high quality of oxide layers. Without

the Al wetting layer, there is a likelihood of the formation Nb-based oxides or interfacial layer, neither of which is desirable. An XPS and AES experimental work on exposed Nb in the past has shown that the layer initially would be comprised of *inhomogeneous* Nb_2O-NbO [3]. The use of SL in MgO allows for a more regularly distributed Al and OH ligands so that a denser and high quality of MgO layer can be produced.

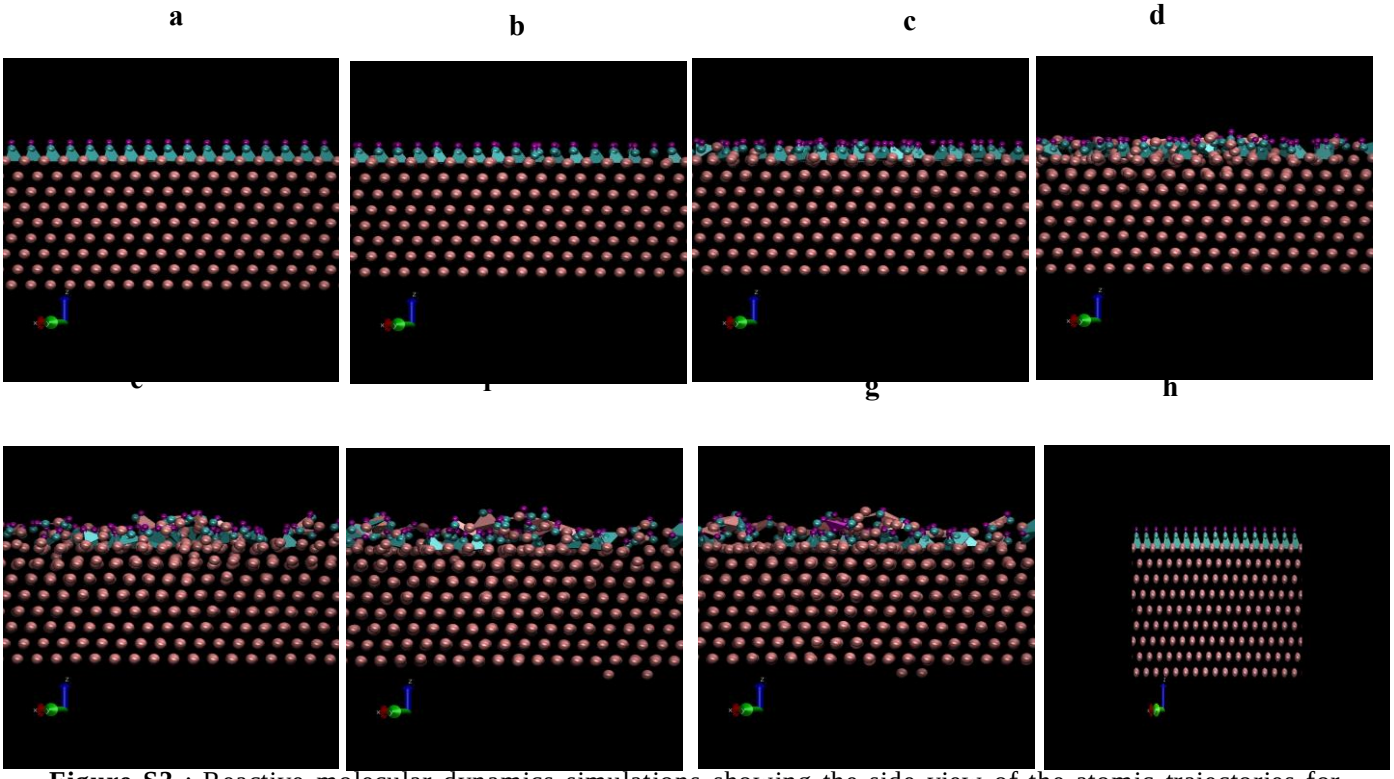

Figure S3 : Reactive molecular dynamics simulations showing the side view of the atomic trajectories for ALD-MgO/SL after a)0 fs, b) 2500 fs, c)5000 fs, d)7500 fs, e) 10,000 fs, f)20,000 fs and g)25,000 fs; and h) MD simulation video respectively

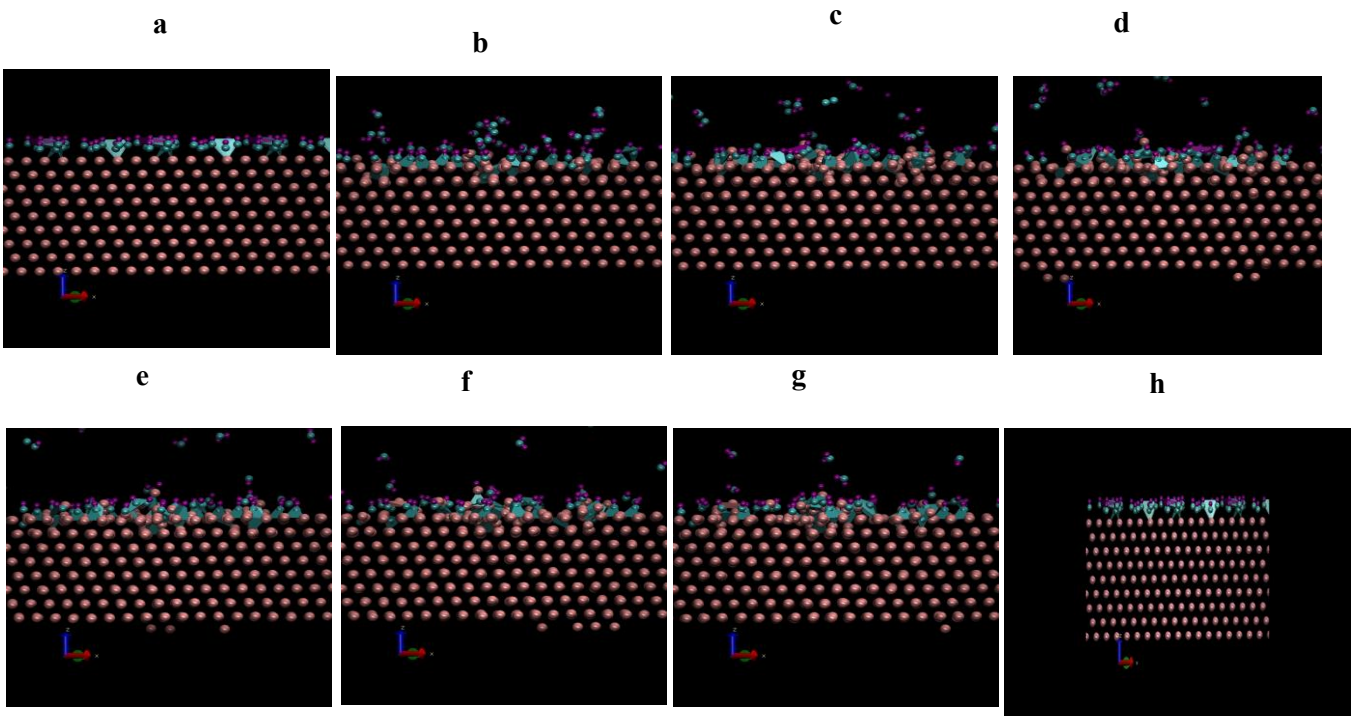

Figure S4 : Reactive molecular dynamics simulations showing the side view of the atomic trajectories for ALD-MgO/WoSL after a) 0 fs, b) 2500 fs, c)5000 fs, d)7500 fs, e) 10,000 fs, f)20,000 fs and g)25,000 fs; and h) MD simulation video respectively

REFREENCES

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