Process Temperature dependent Interface Quality and Maxwell-Wagner Interfacial Polarization in Atomic Layer Deposited Al₂O₃/TiO₂ Nanolaminates for Energy Storage Application

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Supplementary information of S1:

Surface microstructures of alumina and Titania films deposited at various T_d ranging between 100 to 300 °C are analysed using AFM topographic images as shown in Fig. S1, which demonstrates the typical AFM 2D and 3D images of as grown Al₂O₃ and TiO₂ single layer thin

films are scanned over a ~ $5 \times 5 \,\mu\text{m}^2$ area in tapping mode, where the brighter colours indicate taller surface features. From AFM micrographs of films grown at 100 °C, the whitish precipitation in TiO₂ thin film and as flake/flower-shaped depositions in Al₂O₃ film indicates precursor condensation plausibly owing to insufficient thermal energy for complete chemisorption reaction. This precursor condensation has resulted in much higher surface R.M.S roughness (R_q) values of TiO₂ and Al₂O₃ film and can be inferred from Table 1.

Table.1: Best fit XRR results of Al_2O_3 and TiO_2 thin films grown at different substrate temperatures between 100 to 300 °C at an interval of 50 °C.

Sub. Temp (±2 °C)	Al ₂ O ₃ (200 cycles (TMA +	TiO ₂ (500 cycles (TiCl ₄	
	H ₂ O))	+ H ₂ O))	
	Roug. (AFM) (nm) (±0.05)	Roug. (AFM) (nm)	
		(±0.05)	
100	57.3	0.93	
150	0.54	0.74	
200	0.6	0.70	
250	0.75	1.01	
300	0.68	2.75	

Additionally, the appearance of a few grain-like features at 150 °C and a minor increase in their number at 200 °C indicates that the TiO_2 films are partially crystallising into the anatase phase. Further confirmation of this anatase phase is provided by GIXRD and SEM studies in a 60 nm film grown at 200 °C. (figure not shown here). With further increase in temperature beyond 200 °C, the as-deposited TiO₂ surfaces exhibits dot-shaped and columnar polycrystalline morphology of various size, which clearly demonstrates an improved crystallinity with defined grain structure within or on an underlying amorphous background. On the other hand, the AFM images of Al₂O₃ films produced at T_d beyond 150 °C, clearly demonstrated a smooth, crack free and flat surface morphology with no discernible crystalline structures, which signifies that the alumina films have maintained their amorphous structure throughout the studied temperature range and is verified using GIXRD measurements. The R_q values for TiO₂ and Al₂O₃ film deposited at 150 and 200 °C is found close to that of the Si substrate (~ 0.5 nm) and above this temperature the roughness values of titania films are significantly increased owing to improvement in crystallinity. From this overall AFM study, we confirm that deposition temperature had a marked effect on the grain size and hence the surface roughness of the films plausibly due to grain refinement and emergence of faceting on the film surface.









Fig. S1 AFM topographic images of Al_2O_3 and TiO_2 thin films deposited at different temperatures ranging between 100 to 300 °C in a step of 50 °C. These 2D and (insets) 3D scans are taken at an area of 5 x 5 μ m².

Supplementary information of S2:

Fig. S2 demonstrates the high-resolution scans and its detailed deconvoluted XPS spectra of O 1s and Al 2p core levels in Al₂O₃ thin films prepared at 200, and 300 °C deposition temperature, where the presence of Al-O bond is confirmed from the O 1s and Al 2p main peaks (denoted as O_L and Al-O-Al) at ~ 530.96 and ~73.97 eV, indicating lattice oxygen and the bonded Al in alumina thin films.¹ Besides these main peaks, we can also observe shoulder peaks around ~ 75.23 ± 0.1 eV and at ~ 532.3 ± 0.1 eV binding energy (B.E) values in both Al 2p and O 1s core level scans, which corresponds to surface adsorbed oxygen and/or chemisorbed oxygen from C-O & O-H bonds (labelled as Al-OH and O_{OH}), respectively originating either from surface contamination or from H₂O, used as the oxygen precursor in this deposition.¹ At lower T_d of 200 °C, the OH-defect like peak in Al₂O₃ films is more pronounced, plausibly owing to insufficient thermal energy of dissociation for water precursor and impurity species like CH₄, and this contribution is decreasing with increase in T_d from 200

to 300 °C as depicted in Fig. S2.^{1,2} In addition, both the Al 2p and O 1s major peaks are showing a slight shift of ~ 0.3 ± 0.1 eV towards the low B.E side with a rise in T_d from 200 to 300 °C, which can be attributed to a drop in the concentration of OH- ions or the coordination number of Al³⁺ ions in Al₂O₃ film.³ This decrement in concentration of H- related defect/impurities (such as -OH or CH₄) with increase in T_d is in line with the results from SIMS measurements and is actually contributing to improve the insulating nature of Al₂O₃ sublayers.



Fig. S2 The deconvoluted XPS spectra of O 1s and Al 2p core levels in Al₂O₃ films prepared at 200, and 300 °C deposition temperature.

Supplementary information of S3:

To support the XPS findings and to further delineate the role of deposition temperature on chemical composition and OVs concentration in Titania films, the RBS measurements are carried out on as grown TiO₂ single layer films deposited between 150 to 300 °C. To simulate the measured RBS spectra, we employed a tri-layer model, similar to those used for SE and XRR measurements, and the simulated curves closely matches with the measured curves. The film thicknesses extracted from RBS measurements are found to be in close agreement with the SE and XRR results. The simulated RBS spectra for two representative TiO₂ films fabricated at 150, and 300 °C deposition temperature are depicted in Fig. S3a & b respectively, where the presence of different elements like silicon, titanium, oxygen, and some trace chlorine are indicated by arrow marks. From simulation, the concentrations of Ti, O, and Cl atoms in the respective films are computed and the ratio between elemental oxygen to titanium (O/Ti) and chlorine to Titanium (Cl/Ti) is depicted in Fig. S3 c. With increase in T_d from 150 to 300 °C, the O/Ti and Cl/Ti ratio are found to be decreasing from 1.81 to 1.63 and 0.13 to 0.02 respectively, which demonstrate that the stoichiometry and impurity content of the TiO₂ film produced from (TiCl₄ + H₂O) precursors are strongly correlated with the deposition temperature.⁴ From the calculated O/Ti ratio, it can also be concluded that the TiO₂ film is having a considerable amount of oxygen deficiency at higher deposition temperatures, which further supports our XPS results. Since the oxygen deficiency in TiO₂ films are well known in contributing to its n-type semiconducting behaviour, the TiO₂ sublayers are highly semiconducting in ATA-300 as compared to ATA-150 NL and is further supporting the improvement in conductivity contrast driven enhanced MW interfacial polarization effect in ATA NLs with increasing T_d.^{5,6}

The signature of decreasing Cl content with increasing T_d can be clearly observed from the insets of Fig. S3a & b, which confirms a decrement in impurity concentration in titania sublayers towards higher deposition temperatures and is in line with the ATA NL SIMS measurement results. We have further utilized Synchrotron radiation-based GIXRF technique to verify the impurity level i.e. Chlorine, if any embedded during the growth process of TiO₂ thin films of similar thickness grown at 200, 250 and 300 °C deposition temperature. From the XRF plot as shown in Fig. S3d, we can observe both Ti and Si fluorescence peaks as well as a small chlorine contribution in the form of Cl K α and K $_{\beta}$ fluorescent signals around 2.5 to 2.9 keV, as highlighted in the inset of Fig. S3d. Few additional peaks observed in Fig. S3d, are plausibly originating from ambient air environment and surrounding instrument hardware. The measured chlorine profile, as depicted in the inset of Fig. S3d, clearly displayed a similar decreasing trend of Cl contamination with increase in T_d as concluded from RBS measurement of TiO₂ films and SIMS measurements of ATA NLs. Owing to insufficient thermal energy and incomplete chemisorption reactions towards low temperature regime i.e. < 200 °C, the high amount of trace chlorine incorporated in the film is plausibly coming from the incorporation of TiCl₄ precursor fragments and reaction by-product i.e. HCl generated during the ALD growth process.⁷ The re-adsorption of these impurities onto active surface sites can generate chlorine terminated surfaces, which severely affects the number of active surface adsorption sites and subsequent growth kinetics of TiO₂ film.⁸ Further at low deposition temperatures, the incorporation of these corrosive HCl content include the risk of surface etching of as grown thin films and hence is unwanted and detrimental towards growth of high-quality sublayers and distinct interfaces in ATA NLs.



(b)



Fig. S3 Experimental and simulated RBS spectra of TiO_2 thin films grown at (a) 150 °C (b) 300 °C deposition temperatures. The inset shows the enlarged view of the corresponding chlorine peak position and the positions of constituent elements are indicated by arrow marks. (c) O/Ti and Cl/Ti ratio in TiO₂ films as a function of deposition temperature (d) GIXRF of single layer TiO₂ films deposited at various temperatures ranging between 200 to 300 °C, where the inset shows the enlarged view of the corresponding trend in chlorine content.

Supplementary information of S4:

Fig. S4 (a) and (b) indicates the measured and fitted XRR curves for *ATA NL-250*, and *ATA NL-300*, respectively, along with the associated depth variation of electron density profiles as shown

in the respective insets. During simulation of these XRR curves, a small aperiodicity in bilayer thickness values is considered to accommodate the observed Bragg peak broadening. The calculated reflectivity profiles are found to produce excellent match with the Bragg peak intensity and Kiessig oscillations, as displayed in Fig. S4 (a), (b). The details of these fitting parameters, including individual layer thickness, densities, and interface width obtained from best-fit results, are summarized in Table 2 of main manuscript.



Fig. S4 shows the measured and fitted XRR curves along with the depth variation of associated electron density profiles (shown in respective insets) for (a) *ATA NL-250*, (b) *ATA NL-300*

Supplementary information of S5:

GIXRD and AFM measurements of ATA NLs. No evidence of crystalline peak is observed in GIXRD measurements of two representative NLs i.e. *ATA NL-150 and ATA NL-300 as shown in* Fig. S5 (a), which confirms the amorphous structure of the NLs regardless of the growth temperature. The absence of no discernible phase is expected at this nanometric layer thickness regime and is supported from literature.⁶ Further owing to this amorphous phase, the smooth surface morphology of NL fabricated even at higher deposition temperatures

is verified using AFM measurements as shown in Fig. S5 (b), where R.M.S roughness value for *ATA NL-300* is found close to substrate roughness values i.e. ~ 0.6 nm.



Fig. S5 shows the (a) Measured GIXRD profiles for *ATA NL -150* and *ATA NL -300* with Y-offsets. (b) 2D AFM micrograph image of *ATA NL-300*.

Supplementary information of S6:

Comparison of dielectric and electrical performance parameters of ATA NLs of our work and with previous literature.

Since, in literature, the ALD grown ATA NLs are fabricated with different combinations of sublayer thickness and electrode materials, for performance comparison, few standard parameters, which are independent of device dimension and completely explains the electrical properties are introduced. First parameter is quality factor (Q), which is defined as the ratio between dielectric constant and dielectric loss values, and it describes the energy stored to energy dissipation ratio. The second parameter is equivalent oxide thicknesses (EOT), which is defined by relation $\{3.9/(\epsilon_r \text{ of oxide dielectric})^*(\text{oxide dielectric thickness})\}$, and it signifies the equivalent thickness of SiO₂ thin film that will provide the same electrical performance as that of the high- κ oxide material is providing. Third and fourth important parameters are

capacitance density (capacitance/area) and leakage current density (leakage current/ area), which describes the energy storage performance and variation of conductivity of dielectric with applied dc bias. The best results related to the aforementioned performance parameters of ATA NLs from our work and from literature results are listed below in table-2.

Table-2: A comparison table for energy storage performance and electrical properties of our ALD grown ATA NLs based devices fabricated at various processing temperatures with the works reported in literature.

Sample,	NL Stack	Dielectric	EOT (nm),	Leakage current
Temperature (ºC),	thickness (nm),	Constant,	Capacitance density	density (A/cm ²)
sublayer thickness	Number of	Loss tangent,	(fF/μm²)	
(nm)	interfaces	Q factor		
[Reference]				
ATA NL, 300, 1.2	72, 60	190, 0.2, 950	1.48, 23.36	5.26 x 10 ⁻⁵
[Our work]		[@ 1Hz]	[@ 1Hz]	[@ 0.56 MV/cm]
ATA NL, 250, 1.2	72,60	165, 0.26, 635	1.7, 20.3	8.7 x 10 ⁻⁵
[Our work]		[@ 1Hz]	[@ 1Hz]	[@ 0.56 MV/cm]
ATA NL, 300, 1	150, 150	260, 1.2, 217	2.25, 15.35	IV measurements
[9]		[@ 100Hz]	[@ 100Hz]	were not done
ATA NL, 250, 0.8	40, 54	95, 0.25, 380	1.64, 21.02	1 x 10 ⁻⁴
[10]		[@ 11Hz]	[@ 11Hz]	[@ 0.56 MV/cm]
AZA NL, 200, 1	100, 100	8.3,	45.5,	1.57 X 10 ⁻⁴
[11]		[@ 100 kHz]	[@100 kHz]	[@ 0.5 MV/cm]
AZA NL,150, 1	170, 126	24, 0.05	27.6, 1.2	IV measurements
[12]		[@ 100Hz]	[@ 100Hz]	were not done
HZH NL, 175, 1.7	90, 53	100, 0.12, 833	3.51, 9.84	IV measurements
[13]		[@ 100Hz]	[@ 100Hz]	were not done

[ATA NL- Al₂O₃/TiO₂/Al₂O₃ Nanolaminate, AZA NL- Al₂O₃/ZnO/Al₂O₃ Nanolaminate, HZH NL- HfO₂/ZnO/ HfO₂ Nanolaminate.]

By comparing the aforementioned device parameters for our best performed ATA NL with sublayer thickness of ~ 1.2 nm, and 60 interfaces fabricated at 300 0 C and 250 0 C, our results

for ALD grown ATA NLs seems to be favourably comparable with the work reported by W. Li et. al. [9] and A. Kahouli et. al. [10]. Additionally, the device performance parameters of our ATA NLs are found to be slightly superior to its ALD grown counterparts such as $Al_2O_3/ZnO/Al_2O_3$ (AZA) [11,12] and HfO₂/ZnO/HfO₂ (HZH) NLs. [13]

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