Engineering Maxwell-Wagner relaxation and interface carrier confinement in Al_2O_3/TiO_2 subnanometric laminates for high-density energy storage applications

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Supplementary materials:

RESULTS AND DISCUSSION

To verify the artificial periodic structure in the as grown $Al_2O_3/TiO_2/Al_2O_3$ nanolaminates (ATA NLs), XRR measurements of a representative [1A-1T-1A] NL, [1A-0.6T-1A] NL and [0.6A-0.6T-0.6A] NL with ~ 30 bilayers and deposited on TiN coated Si substrates, are carried out and the XRR profiles are depicted in fig. S1(a) with Y-offsets. The loss in Bragg peak intensity with decrease in sublayer thickness (t_s) down to 0.6 nm, indicates the loss in distinct layer feature of the NL with $t_s<0.6$ *nm,* plausibly owing to the increased interface roughness and enhanced interface interdiffusion in NLs. However, the appearance of Bragg peak for [0.6A-0.6T-0.6A] NL, although with diminished intensity, signifies the retention of periodic structure even down to this subnanometric regime (i.e. t_s=0.6 nm). The measured XRR profile of one of the representative NL with t_s= 1 nm (1A-1T-1A NL) is simulated by implementing a (Si-SiO_2-TiN-(Al_2O_3-TiO_2)n-Al_2O_3) based multilayer model, mimicking the NL structure, with small aperiodicity in t_s values. An excellent match between the measured and calculated XRR profiles for NL grown on TiN coated Si is depicted in Fig S1 (b). The alternate alumina and titania sublayer growth in the NL structure can be confirmed from the electron density profiles (EDP), as shown in the inset of fig. S1 (b).

The measured XRR profiles from 0.8A-0.8T NL grown on TiN coated substrate is simulated using aforementioned model and the best fit results regarding the calculated layer thickness, densities and interface width, are summarized in Table S1. From Table S1, the calculated TiO_2-on-Al_2O_3 and Al_2O_3-on-TiO_2 interface roughness values for 0.8A-0.8T NL grown on Si substrate are found to be ~ 0.38 and 0.45 nm, whereas for 0.8A-0.8T NL grown on TiN coated Si substrate are found to be ~ 0.52 and 0.64 nm, respectively. Furthermore, from the TEM image analysis of 0.8A-0.8T NL grown on Si substrate, as shown in fig. S1 (c), the calculated physical and visible interface roughness values are found to be ~ 0.25 and 0.3 nm for TiO_2 -on- Al_2O_3 and Al_2O_3-on-TiO_2 interfaces, respectively. In spite of this interface roughness, the distinct layer feature in these NLs, as observed from both XRR and TEM measurements, indicate the controlled deposition of subnanometric layers (< 1 nm) using the optimized PLD technique. From the intensity distribution profiles of a representative [0.8A-0.8T-0.8T] NL deposited on Si substrate, as depicted in fig. S1 (d), the measured t_s values for Al_2O_3 and TiO_2 sublayers 0.79 ± 0.01 and 0.82 ± 0.01 nm, respectively, are found pretty close to the intended and XRR calculated values.

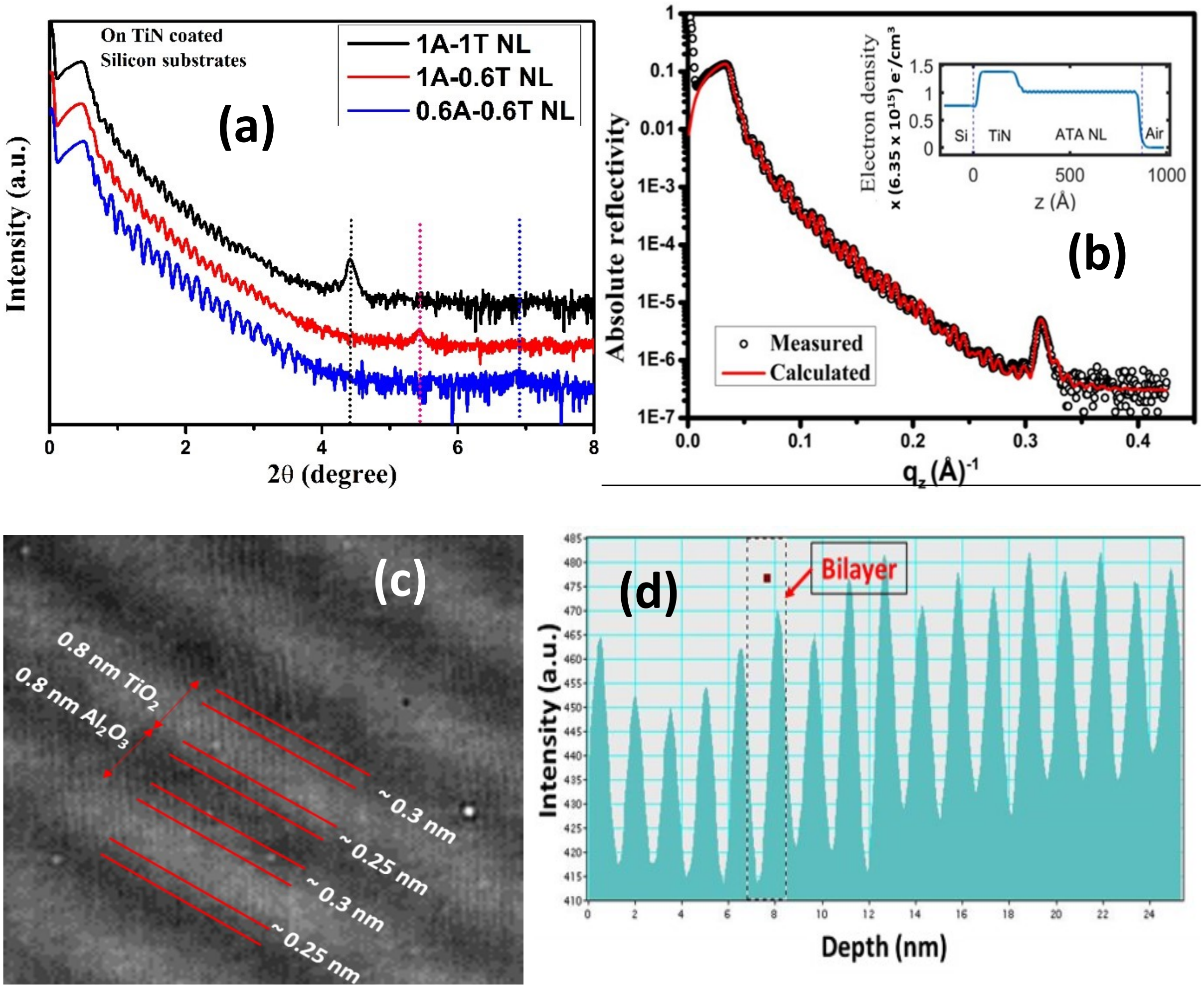

Fig. S1. (a) Measured XRR curves for three representative ATA NLs [1A-1T-1A] NL, [1A-0.6T-1A] NL, and [0.6A-0.6T-0.6A] NL deposited on TiN coated Si substrate with Y-offsets. (b) Measured and simulated XRR profile of [1A-1T-1A] NL and the depth variation of electron density profile is displayed in the inset. (c) High-resolution transmission electron microscopy image showing interface roughness of a representative [0.8A-0.8T-0.8T] NL. (d) The intensity variation profile extracted from the TEM image.

Table S1: Structural parameters of [0.8A-0.8T-0.8T] NL deposited on Si and TiN coated Si substrates extracted by simulating the XRR data.

[0.8A-0.8T-0.8T] NL	T_{BL} (nm)	M_{BL} (nm) (±0.02)	Layer thickness (nm) (±0.02)		% of sublayer Thickness aperiodicity (±1)		Individual Interface Roughness (nm) (± 0.02)		Density (g/cm³) (±0.02)	
			Al_2O_3	TiO_2	Al_2O_3	TiO_2	Al_2O_3	TiO_2	Al_2O_3	TiO_2
On Si	1.6	1.71	0.87	0.84	10	16	0.38	0.45	3.32	4.10
On TiN coated Si	1.6	1.68	0.83	0.85	3	6	0.52	0.64	3.08	3.78

* Abbreviations of T_{BL} and M_{BL} denote targeted and measured bilayer thicknesses, respectively.

Comparing device performance parameters

In order to evaluate the usefulness of the TiN/ATA-NL/TiN based MIMCAPs, it is essential to compare the dielectric performance parameters of our best performed ATA NL based dielectric (in this work) with other NL based dielectric materials in literature. Table S2, presents a quantitative comparison of few important fundamental and derived dielectric performance parameters, such as dielectric constant (ε_r), dielectric loss (*tanδ*), cut-off frequency (f_c), equivalent oxide thickness (EOT), Breakdown electric field (E_{break}), capacitance density *(C/A)* and leakage current density (J_{leak}) etc. Although the series capacitances of low dielectric constant Al_2O_3 barrier layers impose an adverse effect on the overall high dielectric constant, it is highly beneficial for reduction in carrier loss and leakage current in these NLs. Hence it needs an optimization of barrier layer thickness before integrating into final circuits to circumvent the degradation in dielectric constant values and hence the capacitance density.

Although, the *tan δ* and J_{leak} is minimum for 5A/(0.6A-1T-0.6A)/5A NL, the overall capacitance and hence the dielectric constant is reduced owing to low dielectric constant alumina layers in series with the NL. In order to preserve a sizeable Maxwell-Wagner effect, along with a reduced dielectric loss and leakage currents, an optimized Al_2O_3 interfacial barrier layer is inevitable. Considering the requirements set by international technology roadmap of semiconductors (ITRS)-2023 for the high-density energy storage applications, the MIM capacitor should have high k, high cut-off frequency, low loss and low leakage current density etc. [1] From Table S1, we found that 3A/(0.6A-1T-0.6A)/3A NL is closely satisfying these ITRS requirements. Among previous reports, [2-4] the ATA stack based MIM devices fabricated in this work, with a comparatively larger device area of 3.1 x 10^4 µm^2, seem to be superior in terms of exhibited parameters. Further improvements in the ε_r up to a higher f_c is possible by employing a large number of interfaces and simultaneous reduction in sublayer thickness.

Table S2: Comparison of the performance parameters of our PLD grown TiN/ATA NL/TiN capacitors with previously reported NLs in literature.

Dielectric stack- (sublayer thickness in nm) (Total stack thickness in nm) [Reference]	**Growth technique, processing temperature (^{0}C), top/Bottom electrode**	**Dielectric Constant, Loss tangent, Cut-off frequency**	**EOT (nm), Capacitance density (fF/µm^2),** @100Hz	**Leakage current density (A/cm^2), Breakdown voltage (volt)**
Requirement set by ITRS 2023 [1]	**____, < 400 for BEOL, ____**	**>> 3.9, <0.04, 1MHz**	**< 2 nm, >13fF/µm^2 @ 1KHz-1MHz**	**< 1 X 10^{-8} @1V, >3V**
(0.6A-1T-0.6A) NL - (60) [Our work]	PLD, 300, TiN/ TiN	733, 0.18, 100 KHz	0.32, 108.16	1.18 x 10^{-5} @1V, 1.59

1A/(0.6A-1T-0.6A) NL/1A - (60) [Our work]	PLD, 300, TiN/ TiN	484, 0.078, 250 KHz	0.5, 69.11	3.2 x 10^{-6} @1V, 2.91
3A/(0.6A-1T-0.6A) NL/3A - (60) [Our work]	PLD, 300, TiN/ TiN	247, 0.032, 500 KHz	1.04, 33.13	3.08 x 10^{-7} @1V, 4.26
5A/(0.6A-1T-0.6A) NL/5A - (60) [Our work]	PLD, 300, TiN/ TiN	100, 0.013, 1 MHz	2.73, 12.64	2.1 x10^{-9} @1V, 7.007
ATA NL-5A/{0.5A/0.5T}/2A-(5/80/2) - [2]	PLD, 100, TiN/TiN	90, 0.07, 10 KHz	3.77, 9.15	1X 10^{-6}@ 0.87V, ____
(0.5A-0.5T-0.5A) NL-(150) - [3]	ALD, 300, Pt/Pt	810, 6 10 KHz	0.722, 47.81	3 X10^{-1} @1V, ______
5A/{0.3A/0.7T} NL-(5/150) - [4]	ALD, 300, Pt/Pt	550, 0.02 1 MHz	1.009, 31.4	3X 10^{-8} @1V, ___

[Specimen designation are as follows: A-Al_2O_3, T-TiO_2, Z-ZrO_2, S-SiO_2, H-HfO_2, L-La_2O_3 ALD-Atomic layer deposition, 3A/20T/3A signifies the 3nm thick Al_2O_3 encapsulation of 20 nm TiO_2 film.]

References

1. P.S. Padhi, R.S. Ajimsha, S. K. Rai, A. Bose, and P. Misra, Effect of Al_2O_3 layer thickness on leakage current and dielectric properties of atomic layer deposited $Al_2O_3/TiO_2/Al_2O_3$ nano-stack. J Mater Sci: Mater Electron, 34(14) (2023), p.1160.
2. M. Ben Elbahri, A. Kahouli, B. Mercey, O. Lebedev, W. Donner, U. Lüders, Study on the dielectric properties of Al_2O_3/TiO_2 sub-nanometric laminates: effect of the bottom electrode and the total thickness. J. Phys. D: Applied Physics, 51(6) (2018), 065101
3. W. Li, O. Auciello, R. N. Premnath, and B. Kabius, Giant dielectric constant dominated by Maxwell–Wagner relaxation in Al_2O_3/TiO_2 nanolaminates synthesized by atomic layer deposition. Appl. Phys. Lett. 96 (2010), 162907.
4. G. Lee, B.-K. Lai, C. Pathak, R. S. Katiyar, and O. Auciello, “Tailoring dielectric relaxation in ultra-thin high-dielectric constant nanolaminates for nanoelectronics,” Appl. Phys. Lett. 102 (2013), 142901.