Supporting Information

Layered Si-Ti Oxide Thin Films with Tailored Electrical and Optical Properties by Catalytic Tandem MLD-ALD

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1. Deposition parameters for Si-Ti LO films using various Tri-, and Tetra-alkoxy silane precursors:

Table S1. M/ALD Optimization. Optimized parameters of tandem M/ALD process at 153 ^{0}C using DM-APTMS, APTMS, DE-AMTMS and TMOS. Precursor oven set to 80 ^{0}C for DM-APTMS, APTMS and TMOS. Precursor oven set to 95 ^{0}C for DE-AMTMS.

M/ALD Process step open time (exposure) and close time (purge) (sec)	**Silane precursor**			
	DM-APTMS	**DE-AMTMS**	**APTMS**	**TMOS**
Silane exposure time	0.4	0.7	1.2	0.4
Ar purge time	11	11	20	20
H_2O exposure time	1	1.2	1	1
Ar purge time	25	25	17	20
$TiCl_4$ exposure time	0.15	0.2	0.2	0.2
Ar purge time	9	12	7	7
H_2O exposure time	0.5	0.65	0.5	0.5
Ar purge time	21	25	9	7

2. Si-Ti LO film deposition omitting water exposure steps:

The tandem M/ALD process was studied by repeating the tandem M/ALD process without H_2O exposure step after: (i) silane step in the MLD cycle (denoted by m*), and (ii) after TiCl4 step in the ALD cycle steps (denoted by n*). This knock-out experiment allows exploring suggested etching mechanism, involving hydrolysis of the Si-O-Ti, and Ti-O-Ti bonds possibly involved for the acidic deposition conditions of the TiO2 phase (**Fig. S1**).

Analysis of the GPC for the various ratios and water knock-out processes conditions reveal different behavior for incrementing ALD cycles (n) compared to the MLD cycles (m) in the tandem M/ALD process GPC increment linearly with ALD cycles for each MLD and ALD steps without H_2O exposure, represented by 1*:n and 1:n*, respectively (**Fig. S2**). TiO_2 growth without H_2O exposure after silane step at the MLD cycle is understandable as the hydrolysis and condensation required for the growth occur at the water step after $TiCl_4$. However, the growth of TiO_2 without exposing H_2O after $TiCl_4$ is not straightforward. Similar increment in GPC was obtained for both MLD and ALD increments without H_2O exposure (1*:n and 1:n*) presented in **Fig. S2**. This result suggest that water molecules may be adsorbed at the deposited film by forming hydrogen bonds with the amine functionality, assisting in the hydrolysis even when no direct water exposure is performed following that step. Repeating the same procedure of omitting the water vapor exposure step with MLD step increment (m*) yielded qualitatively different results (**Fig. S2b**). The GPC increment of ~ 0.6 Å/cycle is obtained per MLD (SiOx) increment without H_2O exposure in ALD step (n*) while only ~0.15A/cycle obtained for MLD step without H_2O exposure (m*) (**Fig. S2d**). In addition, higher increment of SiO_x obtained for ALD step without H_2O exposure (n*) compared to the full M/ALD process with H_2O exposure in both MLD and ALD steps (**Fig. S2c**). These results point at the possibility of film etch when exposed to the HCl vapor evolving in the ALD step, cleaving part of the film which then released to the vacuum chamber, and possibly reducing surface adsorption of reactants over protonated surface, overall leading to lower GPC values, in agreement with literature. In addition, density functional theory (DFT) calculations performed in our group recently show facile cleavage of the Si-O-Si bond under acidic conditions in the presence of water. Therefore, the excess protons released at ALD step result in film etching by siloxane bond cleavage which result in overall lower GPC values.

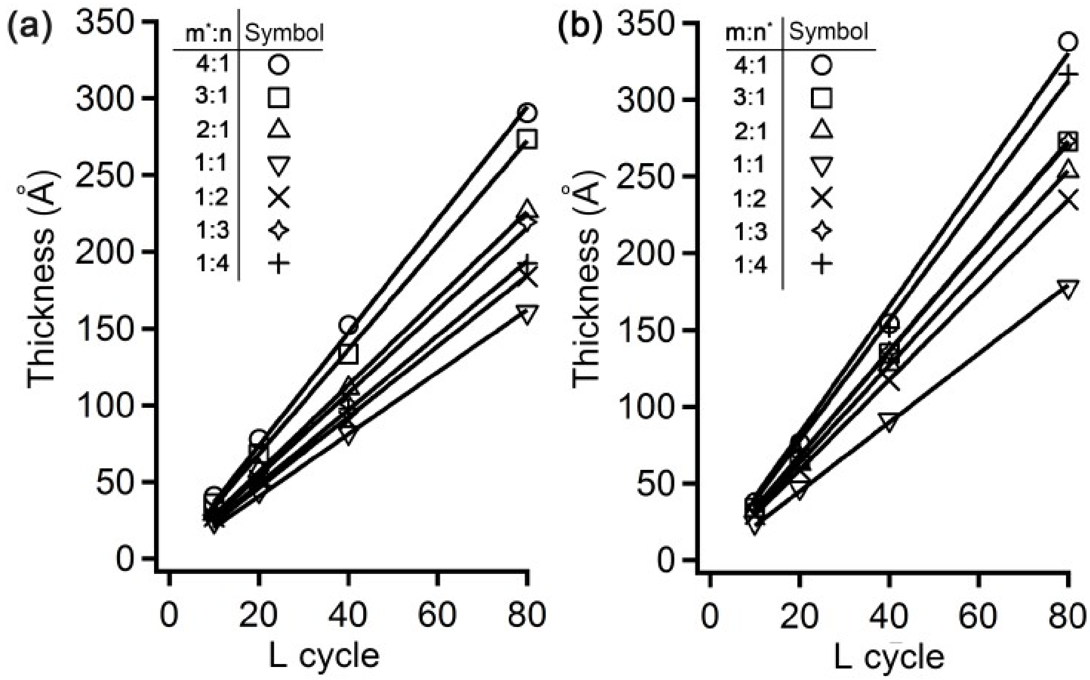

Fig. S1. Film thickness vs. number of super-cycle repetition (L) for M/ALD films omitting water exposure steps. (a) Omitting H_2O exposure for ALD cycle (denoted by n^*) and (b) omitting H_2O exposure for MLD cycle (denoted m^*). Marker size represent experimental error limit.

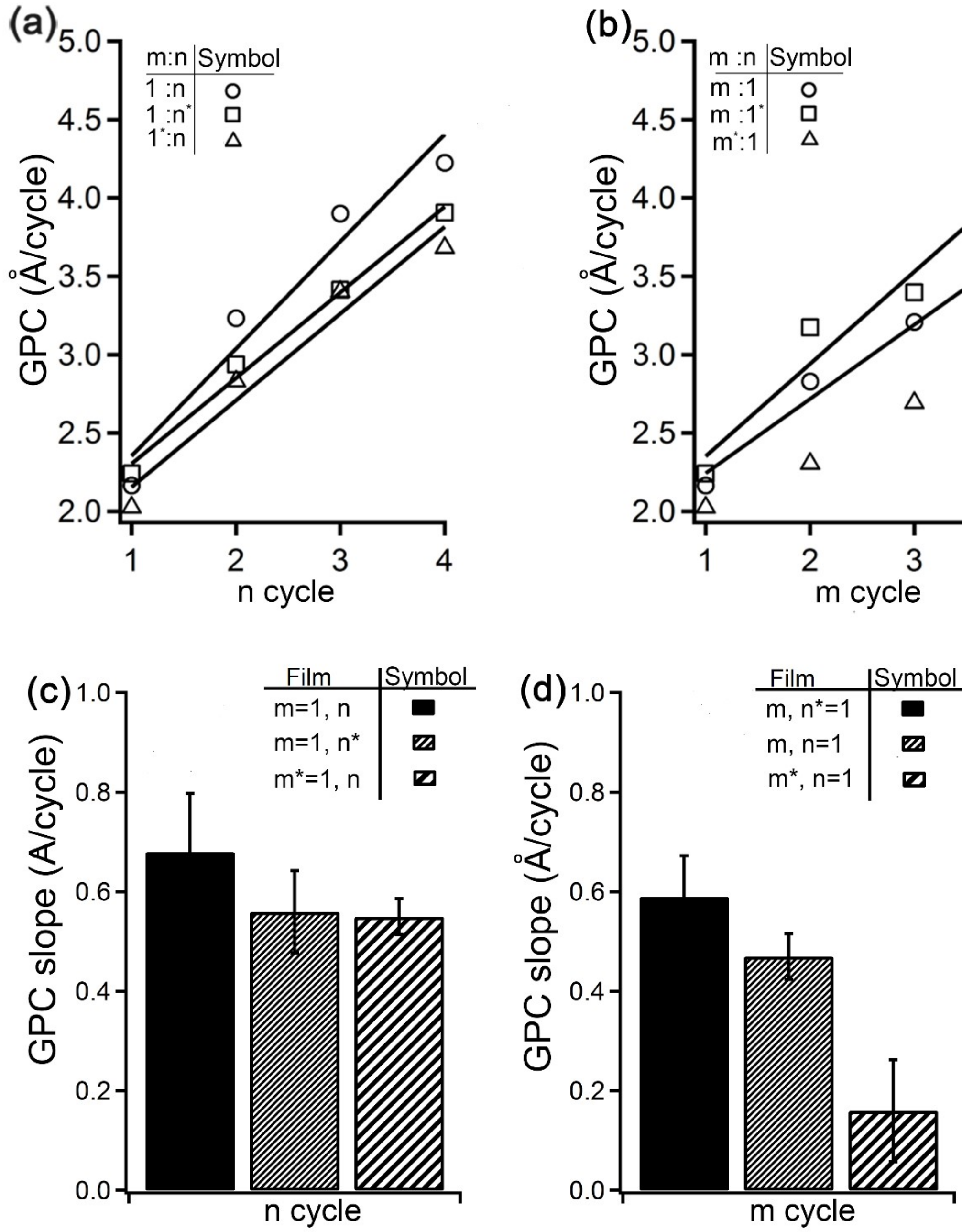

Fig. S2. Growth per cycle analysis for Si-Ti LO films with and without H_2O exposure (denoted by m*, n*, respectively). Growth per cycle with increasing (a) ALD cycles (n), and, (b) MLD cycles (m). Marker size represent experimental error limit. (c), (d) GPC slope obtained from (a), (b), respectively, measuring the incremental deposition yield of subsequent ALD and MLD repetitions in the CT-M/ALD super cycle.

3. Characterization of Si-Ti LO films Composition:

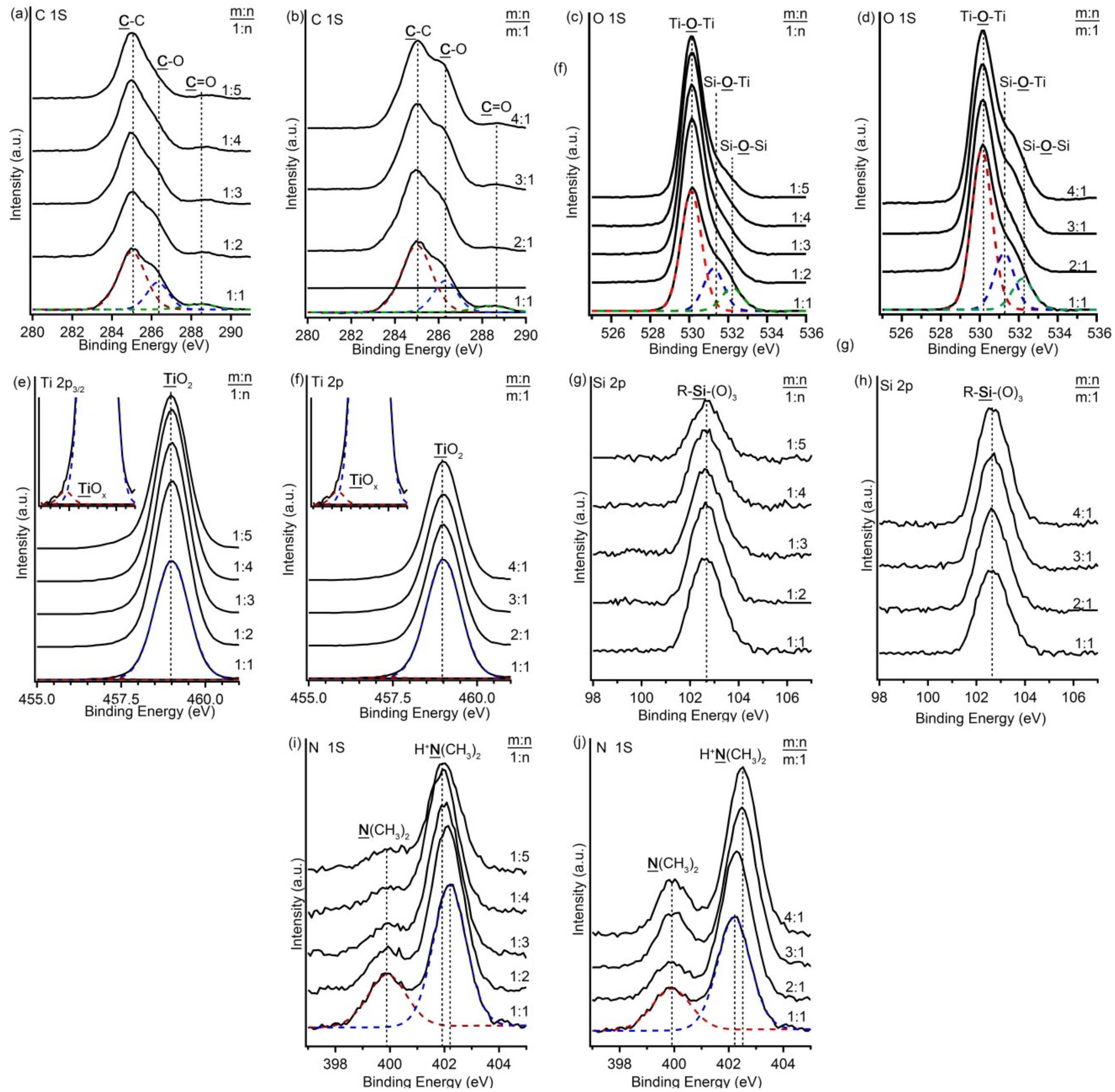

Fig. S3. XPS spectra for Si-Ti LO films with various ratios of 4:1 – 1:5 (MLD:ALD). High resolution spectra: $C1_s$ (a,b), $O1_s$ (c,d). Ti 2_p (e,f), $Si2_p$ (g,h), and $N1_s$ (I,j).

Table S2. XPS analysis for Si-Ti LO films with various MLD:ALD process ratios of 4:1 – 1:5. Binding energies of N 1_s, C 1_s, Ti $2_{p3/2}$,O1S and Si 2_p presented for as-deposited films (without calcination) and the corresponding atomic ratios for the species.

Binding Energy (eV)											
N 1S		C 1S			O 1S			Ti $2p_{3/2}$		Si 2p	
$\underline{N}(CH_3)_2$	$(CH_3)_2\underline{N}H^+$	$O\text{-}\underline{C}\text{=}O$	$\underline{C}\text{-}O$	$\underline{C}\text{-}C$	$Ti\underline{O}_2$	$Si\text{-}\underline{O}\text{-}Ti$	$Si\underline{O}_2$	$\underline{Ti}O_2$	$\underline{Ti}O_x$	$R\text{-}\underline{Si}\text{-}(O)_3$	
399.9	401.9-402.5	288.4-288.8	286.3	285.0	530.3	531.2-531.5	532.2	459.0	457.4	102.7	Si-Ti as prepared films
31	69	4	21	75	78	26	6	97.4	2.6	100	% From total element

References

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2 W.L. Huang, K.M Liang and S.R Gu, *Journal of non-crystalline solids.*, 1999, ***258***, 234-238.