Electronic Supplementary Information for

Enhancing the crystallinity and dielectric performance of ALD-grown $SrTiO_3$ films by introducing a sub-nm-thick Pt layer

Hong Keun Chung[1,2], Jihoon Jeon[1,3], Seungwan Ye[1,3], Sung-Chul Kim[4], Sung Ok Won[4], Tae Joo Park[2], Seong Keun Kim[1,3,*]

[1]Electronic Materials Research Center, Korea Institute of Science and Technology, Seoul 02792, Republic of Korea

[2]Department of Materials Science and Chemical Engineering, Hanyang University, Ansan 15588, Republic of Korea

[3]KU-KIST Graduate School of Converging Science and Technology, Korea University, Seoul 02841, Republic of Korea

[4]Advanced Analysis and Data Center, Korea Institute of Science and Technology, Seoul 02792, Republic of Korea

*Corresponding author: s.k.kim@kist.re.kr

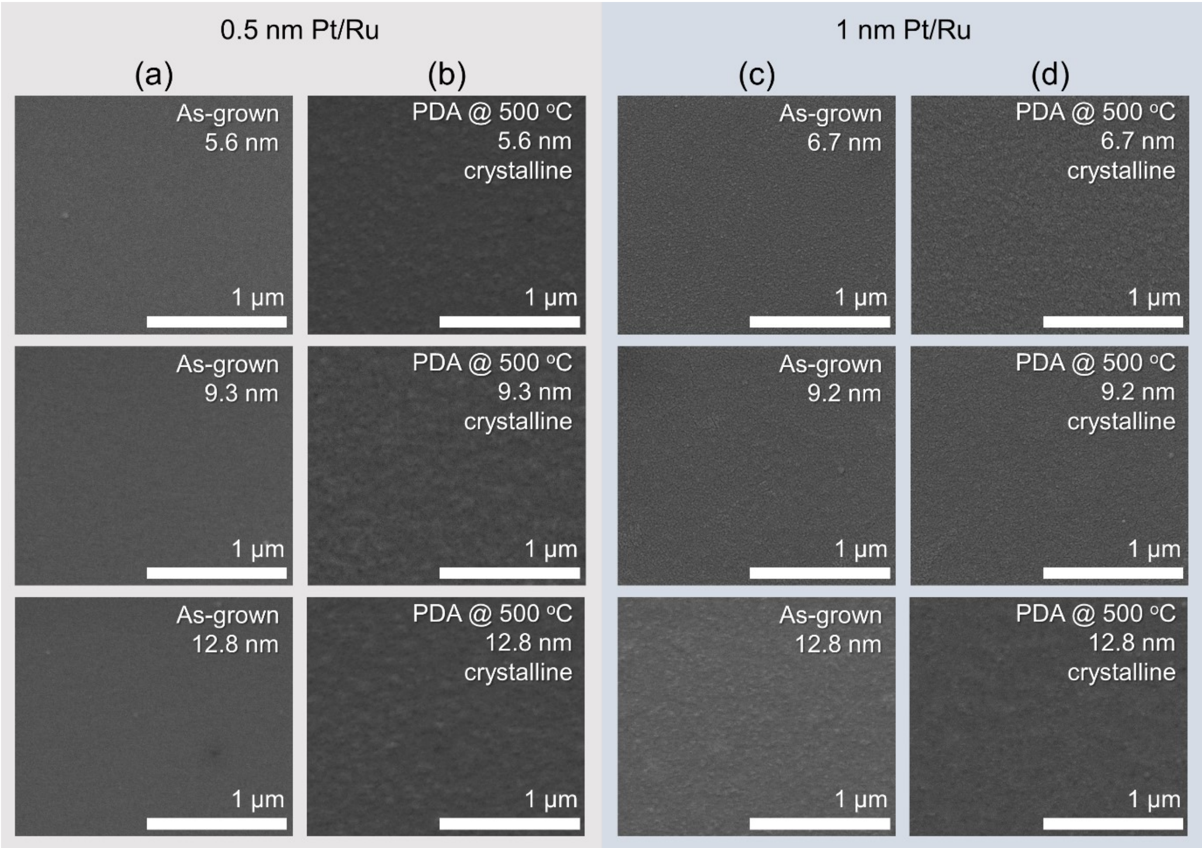

Figure S1. SEM images of the (a) as-grown and (b) PDA at 500 °C STO films grown on 0.5 nm-thick Pt/Ru and the (c) as-grown and (d) PDA at 500 °C STO films grown on 1 nm-thick Pt/Ru.

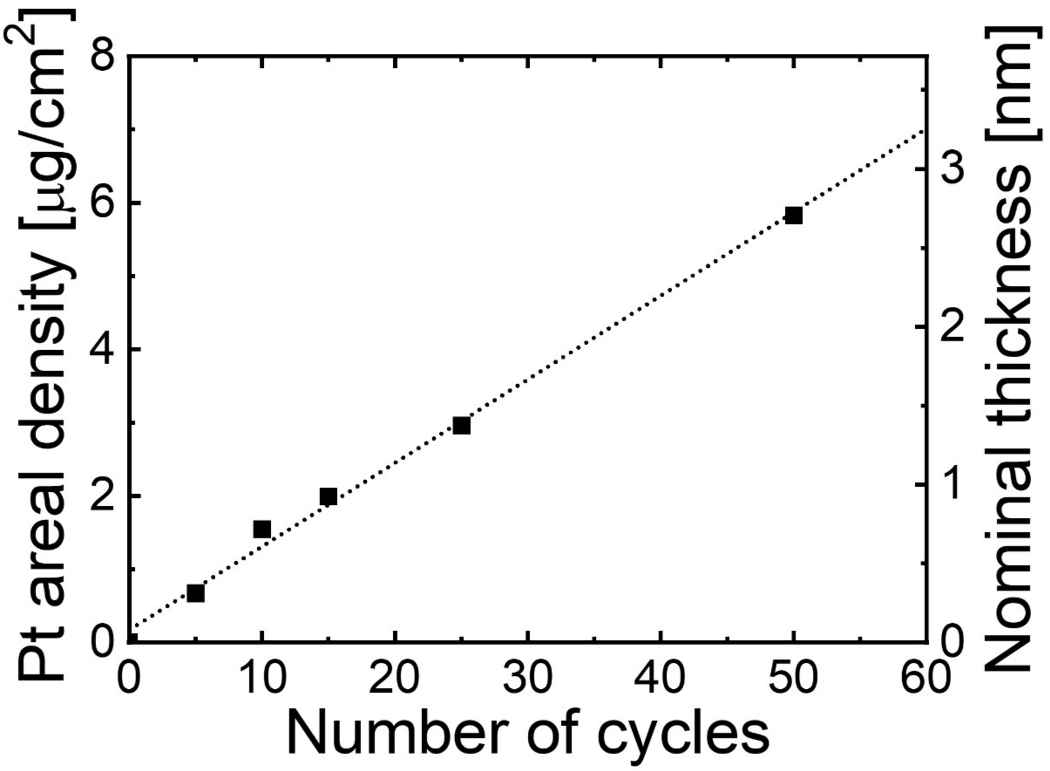

Figure S2. Variation in the Pt areal density and the thickness estimated from the areal density of the Pt films grown on Ru.

Note S3.

To quantitatively determine the thickness and coverage of an ultrathin Pt layer deposited on Ru using the ARXPS technique, the Straight-Line Approximation (SLA) method was employed. The SLA approach assumes that photoelectron elastic scattering events are negligible in the XPS measurements, significantly simplifying the analytical expression for the photoelectron transport mechanism.[1] Based on these assumptions, the photoelectron signal intensity as a function of the angle for a sufficiently thick (bulk, typically 10 nm or more) substrate (I_S) can be expressed as follows:

$$I_S = I_{S,0} \cos\theta \qquad (1)$$

When a thin overlayer is deposited on the substrate, the photoelectrons emitted from the substrate undergo additional scattering. In this case, the equations for the photoelectron signal intensity from the substrate (I_S) and the overlayer (I_O) as a function of the overlayer thickness (d_O) can be expressed as follows:

$$I_S = I_{S,0} \times \cos\theta \times \exp(-d_O/(\lambda_S \cos\theta)) \qquad (2)$$

$$I_O = I_{O,0} \times \cos\theta \times [1 - \exp(-d_O/(\lambda_O \cos\theta))] \qquad (3)$$

where $I_{S,0}$ and $I_{O,0}$ represent the photoelectron signal intensity values for the substrate and the overlayer bulk material, respectively, measured along the surface normal. λ_S and λ_O represent the inelastic scattering mean free path (IMFP) values for the substrate and overlayer materials, respectively, and were treated as fixed values within the measurement range of 20–60°,[2] where elastic scattering is negligible. This approach is commonly used in the quantification of thin film thicknesses through ARXPS.[3-6]

We used eqs.(2) and (3) to model the photoelectron signal intensity of Pt film overlayer and

Ru bulk substrate as follows:

$$I_{Pt}^{Film} = I_{Pt,0} \times \cos\theta \times [1 - \exp\left(\frac{-d_{Pt}}{\lambda_{Pt} cos\theta}\right)] \quad (4)$$

$$I_{Ru}^{Bulk} = I_{Ru,0} \times \cos\theta \times \exp\left(\frac{-d_{Pt}}{\lambda_{Ru} cos\theta}\right) \quad (5)$$

From NIST Electron Inelastic-Mean-Free-Path Database,[7] the IMFP values for Pt 4f and Ru 3d electrons were determined to λ_{Pt}=1.14 nm and λ_{Ru}=1.74 nm, respectively.

Using eq. (1), eq. (4) can be normalized by the expression for the Pt bulk intensity to derive the following expression:

$$I_{Pt}^{Film}/I_{Pt}^{Bulk} = 1 - \exp\left(\frac{-d_{Pt}}{\lambda_{Pt} cos\theta}\right) \quad (6)$$

The Pt 4f ratio calculated from the Pt film and Pt bulk is shown in Fig. 2(b). The thickness of the Pt overlayer calculated using eq. (6) was 0.58 nm, which is in excellent agreement with the thickness of 0.5 nm determined via WDXRF measurements.

Additional modeling was performed to calculate the coverage of an ultrathin 0.58 nm Pt film on a Ru bulk substrate. Although the same amount of Pt is deposited on the Ru bulk, the extent to which photoelectrons emitted from Ru are scattered by the Pt film varies depending on the coverage of the Pt film.[3,4] Consequently, the photoelectron signal intensity from the Ru bulk as a function of coverage can be divided into two components: Ru covered by Pt (Ru covered) and Ru not covered by Pt (Ru uncovered). Based on this theoretical framework, the equations for the Pt film and Ru bulk as functions of fractional coverage (f) are expressed as follows:

$$I_{Pt}^{Film} = f \times I_{Pt,0} \times \cos\theta \times [1 - \exp\left(\frac{-d_{Pt}}{\lambda_{Pt} cos\theta}\right)] \quad (7)$$

$$I_{Ru\,covered}^{Bulk} = f \times I_{Ru,0} \times \cos\theta \times [1 - \exp\left(\frac{-d_{Pt}}{\lambda_{Ru} cos\theta}\right)] \quad (8)$$

$$I_{Ru\,uncovered}^{Bulk} = (1 - f) \times I_{Ru,0} \times \cos\theta \quad (9)$$

Accordingly, the equation considering the coverage of the Pt film deposited on the Ru bulk is summarized as follows.

$$\frac{I_{Pt}^{Film}}{I_{Ru}^{Bulk}} = \frac{I_{Pt}^{Film}}{I_{Ru\,covered}^{Bulk} + I_{Ru\,uncovered}^{Bulk}} = \frac{I_{Pt,0}}{I_{Ru,0}} \frac{f \times [1 - \exp\left(\frac{-d_{Pt}}{\lambda_{Pt} cos\theta}\right)]}{1 - [f \times \exp\left(\frac{-d_{Pt}}{\lambda_{Ru} cos\theta}\right)]}$$

(10)

The value of $\frac{I_{Pt,0}}{I_{Ru,0}}$ was observed to be 1.36, and the coverage results for a Pt film thickness (d_{Pt}) of 0.58 nm were calculated and presented in Fig. 2(c).

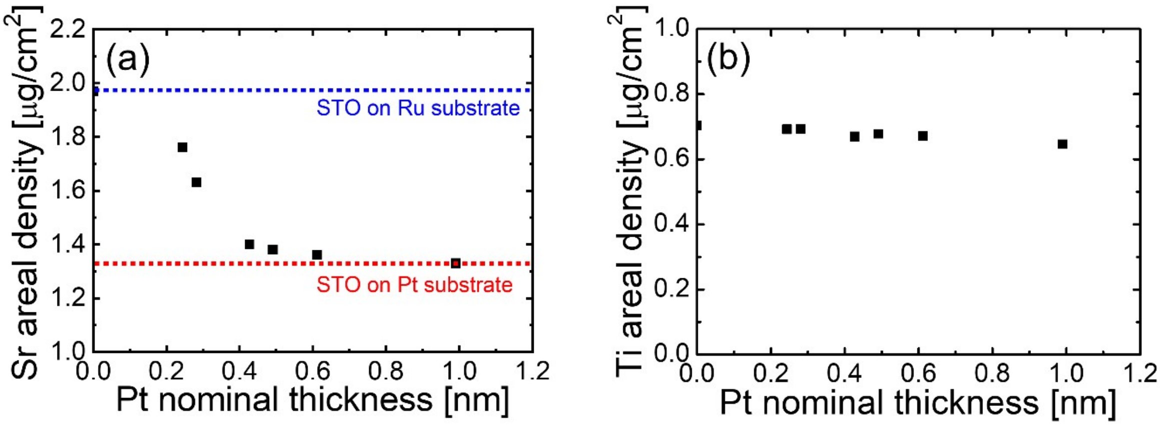

Figure S4. Variations in the areal densities of (a) Sr and (b) Ti ions in the STO films as a function of the thickness of the Pt reaction barrier layer.

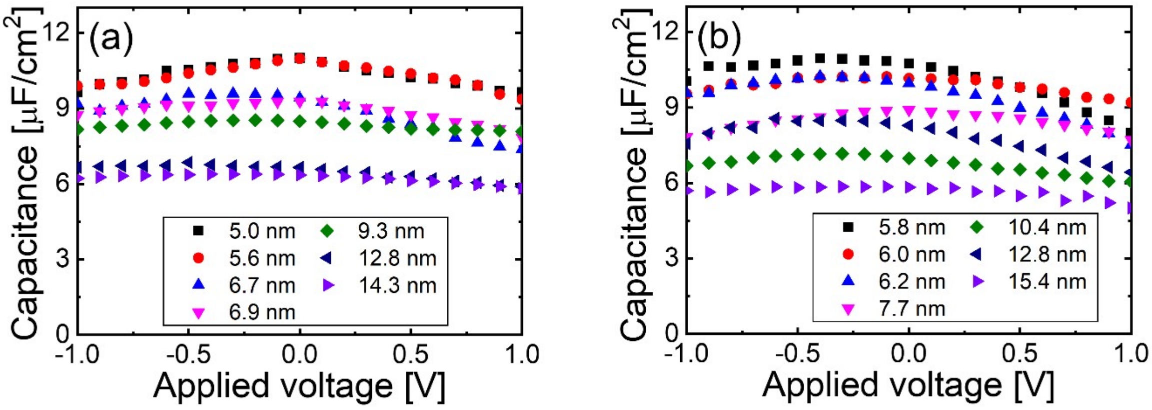

Figure S5. Capacitance – applied voltage curves of the STO films grown on (a) 0.5 nm- and (b) 1 nm-thick Pt/Ru after PDA at 500 °C

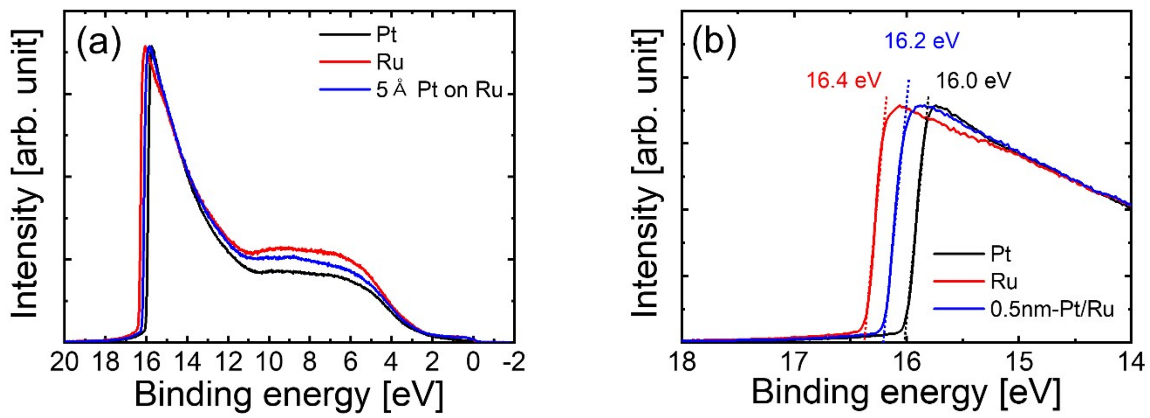

Figure S6. (a) Ultraviolet photoelectron spectra and (b) their magnified spectra of Pt, Ru, and 0.5 nm-thick Pt/Ru. The work function was calculated by subtracting a He I radiation energy of 21.2 eV from the binding energy cutoff: 5.2 eV for Pt, 4.8 eV for Ru, and 5.0 eV for 0.5 nm-thick Pt/Ru.

References

[1] A. Jablonski, Evaluation of procedures for overlayer thickness determination from XPS intensities, *Surf. Sci.*, **688** (2019) 14-24.

[2] C.J. Powell, Practical guide for inelastic mean free paths, effective attenuation lengths, mean escape depths, and information depths in x-ray photoelectron spectroscopy, *J. Vac. Sci. Technol. A*, **38** (2020) 023209.

[3] P. Mack, R. White, J. Wolstenholme, T. Conard, The use of angle resolved XPS to measure the fractional coverage of high-k dielectric materials on silicon and silicon dioxide surfaces, *Appl. Surf. Sci.*, **252** (2006) 8270-8276.

[4] K.V. Egorov, Y.Y. Lebedinskii, A.A. Soloviev, A.A. Chouprik, A.Y. Azarov, A.M. Markeev, Initial and steady-state Ru growth by atomic layer deposition studied by in situ Angle Resolved X-ray Photoelectron Spectroscopy, *Appl. Surf. Sci.*, **419** (2017) 107-113.

[5] T. Bure, O. Renault, E. Nolot, T. Lardin, C. Robert-Goumet, N. Pauly, Assessing advanced

methods in XPS and HAXPES for determining the thicknesses of high-k oxide materials: From ultra-thin layers to deeply buried interfaces, *Appl. Surf. Sci.*, **609** (2023) 155317.

[6] M. Jang, J. Jeon, W. C. Lim, K. H. Chae, S.-H. Baek, S. K. Kim, Interfacial layer suppression in ZrO_2/TiN stack structured capacitors via atomic layer deposition, *Ceram. Int.,* **50** (2024) 47910-47915.

[7] NIST Electron Inelastic-Mean-Free-Path Database, Prepared by C.J. Powell, A. Jablonski, NIST Standard Reference Database 71