Supplementary material

Effect of *in situ* stress on grain growth and texture evolution in sputtered YSZ/Si films

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S-1. Stress determination from Stoney's equation

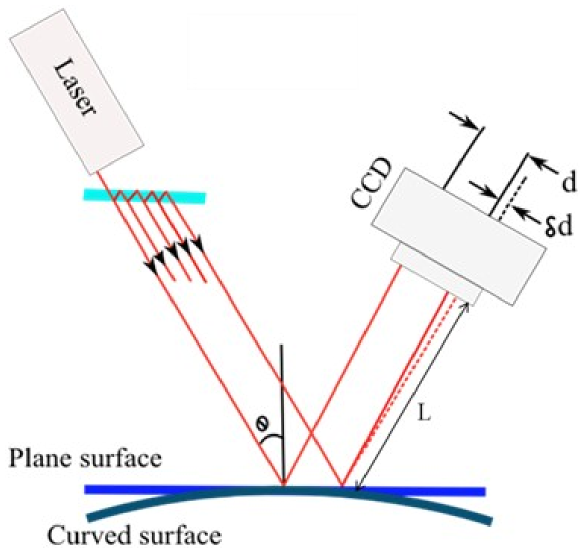

Figure S1 Schematic of in-situ curvature measurement during thin film growth by a multiple beam optical stress sensor (MOSS) and determination of stress from the change in curvature by Stoney's equation.

Stress thickness can be determined after Stoney as follows [1]

$$\sigma h_f = \left[\frac{\delta d}{d}\right] M_s h_s cos\theta / 12L$$

Where σ, h_f, δd, d, M_s, h_s, θ and L are stress in a film, film thickness, difference in spot positions, spot position, biaxial modulus of substrate, substrate thickness, incident angle of laser and distance from substrate to CCD respectively.

S-2. Compressive-tensile-compressive (ctc) behaviour of volmer-weber films:

Films growing by Volmer-Weber mode exhibits CTC behaviour[2] as shown in schematic Fig. 14.

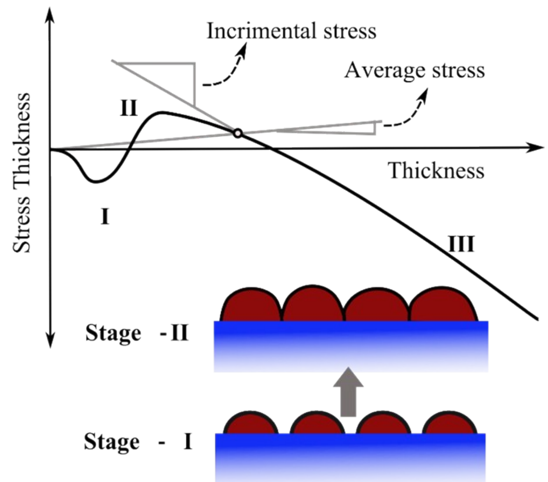

Figure S2 Stress thickness plot representing stages in the CTC behaviour of films by Volmer-Weber growth mode.

S-3. Thermal stresses in a film:

Thermal stresses are generated in a film, during heating or cooling, due to differences between the coefficients of thermal expansion (CTE) for the film and substrate. The thermal mismatch stress can be calculated from the following equation

$$\sigma_f = \varepsilon_f M_f = M_f \int_{T_g}^{T} (\alpha_s - \alpha_f) dT$$

Where T_g is growth temperature, ε_f is strain in the film due to thermal mismatch and M_f (405.2 GPa) is biaxial modulus of the film material. α_s and α_f are CTE of Si and YSZ respectively which the following expressions[3,4]

$a = 3.084 + 0.00196T$ ppm/°C (Temperature range 20-1000°C)

$a = 7 + 0.01T - 2.15 * 10^{-5}T^2 + 4.70 * 10^{-8}T^3 - 3.77 * 10^{-11}T^4$

ppm/°C (Temperature range -150-1000°C)

CTE of YSZ is higher than that of Si, which results in compressive stress (-0.5 GPa) in films during heating from growth temperature (700°C) to annealing temperature (1000°C).

S-4. Following are the θ-2θ scans of as-deposited, 1st annealed (annealed at 1000°C for one hour) and 2nd annealed (annealed at 1000°C for one more hour) YSZ films.

Grain sizes for all the as-deposited, 1st annealed (annealed at 1000°C for one hour) and 2nd annealed (annealed at 1000°C for one more hour) YSZ films were calculated from the X-ray diffraction peak broadening. All these θ-2θ scans of as-deposited, 1st annealed and 2nd annealed YSZ films are given below.

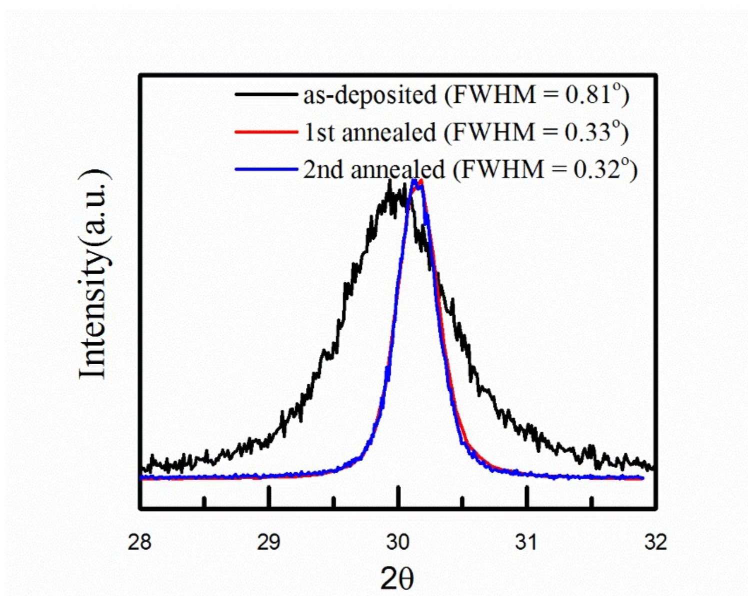

Figure S3 θ-2θ scan for the YSZ film with a growth stress of -0.8 GPa. Grain sizes calculated from the FWHM is 10, 24 and 25 for as-deposited, 1st annealed and 2nd annealed YSZ films respectively.

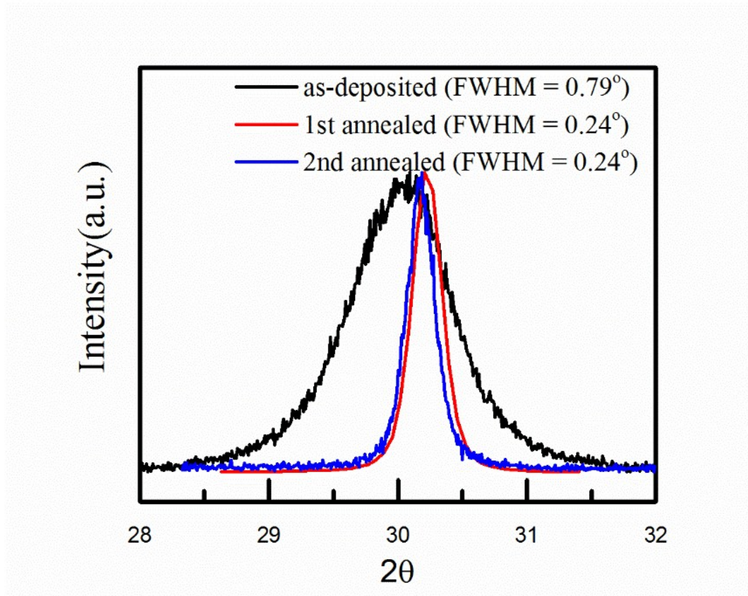

Figure S4 θ-2θ scan for the YSZ film with a growth stress of -1.2 GPa. Grain sizes calculated from the FWHM is 10, 34 and 34 for as-deposited, 1st annealed and 2nd annealed YSZ films respectively.

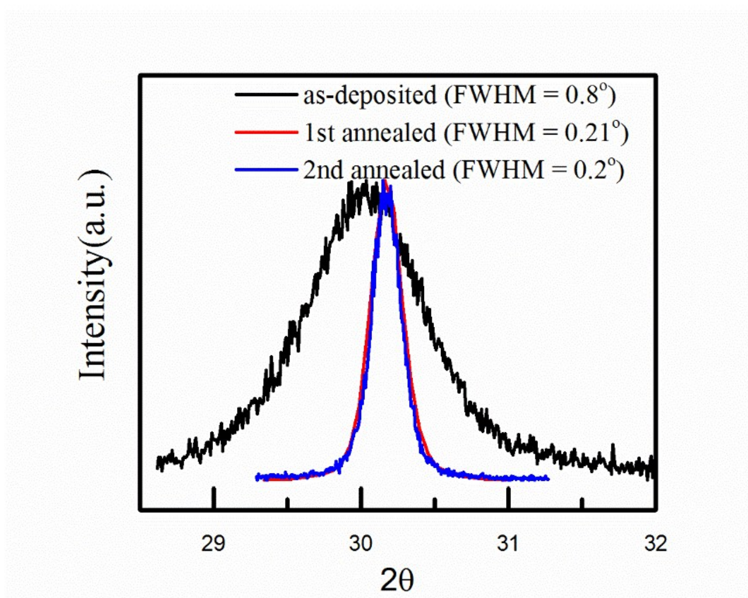

Figure S5 θ-2θ scan for the YSZ film with a growth stress of -1.4 GPa. Grain sizes calculated from the FWHM is 10, 38 and 39 for as-deposited, 1st annealed and 2nd annealed YSZ films respectively.

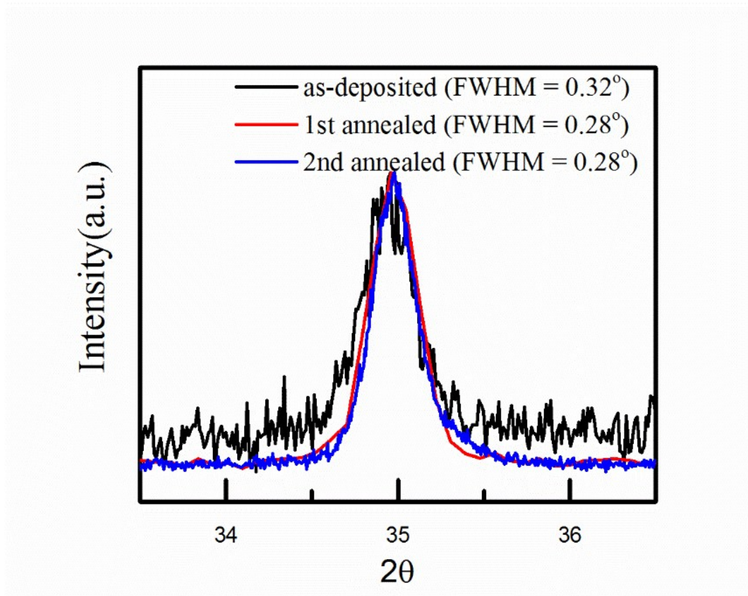

***Figure S6** θ-2θ scan for the YSZ film with a growth stress of 0.2 GPa. Grain sizes calculated from the FWHM is 24, 28 and 29 for as-deposited, 1st annealed and 2nd annealed YSZ films respectively.*

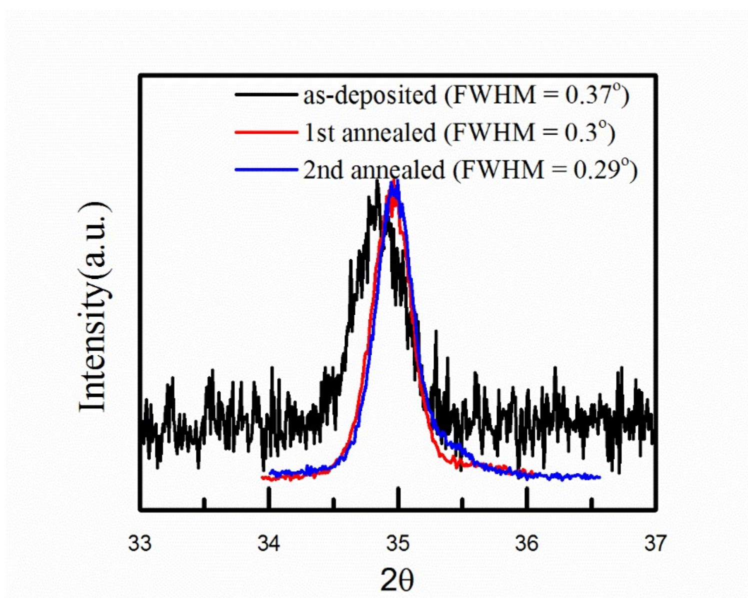

***Figure S7** θ-2θ scan for the two layered YSZ film with a growth stress of 0.05 GPa (bottom) and -1.7 GPa (top). Grain sizes calculated from the FWHM is 21, 26 and 27 for as-deposited, 1st annealed and 2nd annealed YSZ films respectively.*

S-5. Stress evolution and grain size:

The grain size that is responsive to in-plane stress, as measured, is actually the lateral grain size. It is not the vertical grain size as measured by x-ray diffraction. The use of vertical coherence length makes the assumption that grain size and grain growth are equi-axed. This translates to assuming that when the vertical coherence length increases, during annealing, so does the lateral coherence length. While not strictly correlated, such a trend in often seen in thin films. In the absence of more accurate data on crystal domain size as a function of thickness, we have chosen to use the “XRD grain size” for want of a better way to do it.

References

[1] S.Suresh, L. B. Freund, Thin Film Materials: Stress , Defect Formation and Surface Evolution, Cambidge, 2003.

[2] J.A. Floro, E. Chason, R.C. Cammarata, D.J. Srolovitz, Physical Origins of Intrinsic Stresses in Volmer–Weber Thin Films, MRS Bull. 27 (2002) 19–25. doi:10.1557/mrs2002.15.

[3] J.W. Reiner, A.M. Kolpak, Y. Segal, K.F. Garrity, S. Ismail-Beigi, C.H. Ahn, et al., Crystalline Oxides on Silicon, Adv. Mater. 22 (2010) 2919–2938. doi:10.1002/adma.200904306.

[4] K.J. Hubbard, D.G. Schlom, Thermodynamic stability of binary oxides in contact with silicon, J. Mater. Res. 11 (1996) 2757–2776.