SUPPORTING INFORMATION

Tailoring phase and composition at the nanoscale: atomic layer deposition of Zn-Ti-O thin films

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S1 Experimental

ALD and annealing

Optimal conditions for depositing ZnO and TiO_2 at 90°C were obtained by our previous studies (*see* references 8 and 9 and references therein). Experimental deposition temperature and pressure were 90°C and 0.5 Torr, respectively. All the thin films were grown by ALD in a continuous-flow mode onto natively oxidized 100 boron doped Si wafer (Siltronic AG, Germany) in a Savannah-100 ALD flow reactor (Cambridge Nanotech Inc., MA). Before deposition the substrates were throroughly cleaned with acetone (Aldrich) and placed for 5 minutes at 50°C in a UV cleaner (PSD-UVT Novascan Technologies, Inc., USA). Metal precursors for ALD were tetrakis(dimethylamido)titanium(IV) (TDMAT - 99.999%; Sigma–Aldrich, Germany), as titanium source and diethylzinc (DEZ; 99.999%; Sigma–Aldrich, Germany) as zinc source. Oxygen source is ultrapure water (H_2O - Conductivity 0.054 mS/cm) produced directly from tap water with a Direct-Q system (Millipore, Italy). All the reagents effused from stainless-steel reservoirs held respectively at 90°C (TDMAT) and at room temperature, 25°C, (DEZ and H_2O which have higher vapor pressure). All the reagents are fed into the reactor through solenoid valves by a carrier gas, Nitrogen (99.9999% Praxair Inc., USA), used also as purging gas.

The processing cycle for the deposition of TiO_2 consists in 0.1 s pulse of TDMAT, 10 s purging time with N_2, 0.015 s pulse of H_2O, and 10 s purging time with N_2. The processing cycle for the

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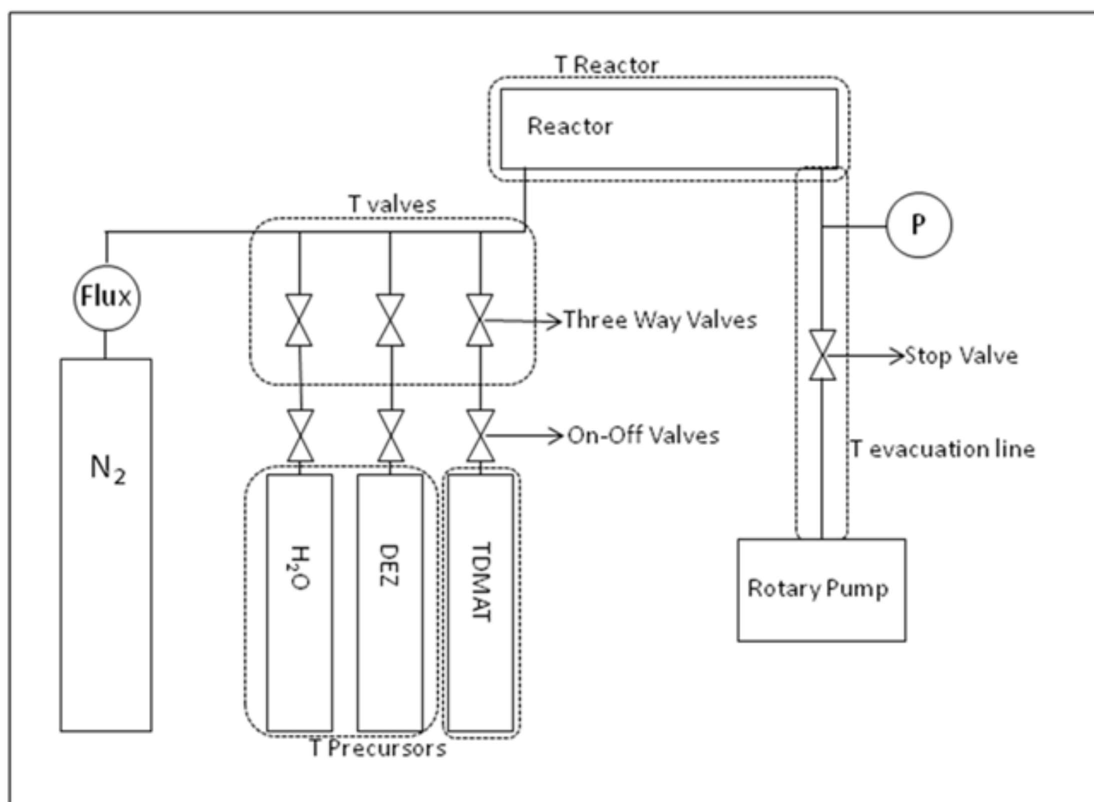
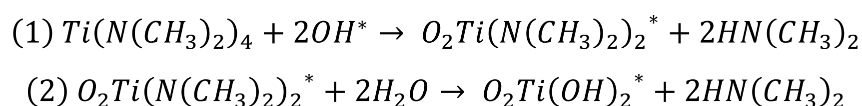
deposition of ZnO consists in 0.1s pulse of DEZ, 10s purging time with N_2, 0.015 s pulse of H_2O, and 10 s purging time with N_2.

The scheme of the ALD reactor and the reactions occurring in ALD process are reported below:

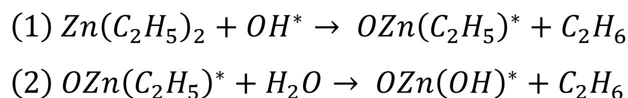


TiO_2-layer:



$$(1)\ Ti(N(CH_3)_2)_4 + 2OH^* \rightarrow O_2Ti(N(CH_3)_2)_2^* + 2HN(CH_3)_2$$
$$(2)\ O_2Ti(N(CH_3)_2)_2^* + 2H_2O \rightarrow O_2Ti(OH)_2^* + 2HN(CH_3)_2$$

ZnO-layer:



$$(1)\ Zn(C_2H_5)_2 + OH^* \rightarrow OZn(C_2H_5)^* + C_2H_6$$
$$(2)\ OZn(C_2H_5)^* + H_2O \rightarrow OZn(OH)^* + C_2H_6$$

The as-deposited samples were annealed in air for 6 and 12 hours at 600°C in a Carbolite furnace. A preliminary *in situ* XRD study of thin film crystallization as a function of the annealing temperature was performed at the MCX beamline (ELETTRA Synchrotron, Trieste).

XRR

X-ray reflectivity (XRR) measurements are performed in a ‘D8 Advance’ diffractometer (Bruker GmBH, Germany) equipped with a Göbel mirror and a CuKα radiation tube (λ = 0,154 nm). The beam is collimated by slits; the cross section of the X-ray beam behind the slit is 600 µm high and 1.5 cm wide. All XRR spectra are analyzed with the REFSIM software (Bruker GmBH, Germany) to extract thickness and density of the deposited films.

TXRF

Thin films composition is analyzed by a S2 Picofox total reflection x-ray fluorescence (TXRF) spectrometer (Bruker GmBH, Germany), equipped with well-focussing polycapillary lens and X-ray beam dimension about 8 x 0.1 mm^2. Excitation settings are 50 kV and 750 mA. 600-s measurements are performed.

XRD

Micro X-ray diffraction (µXRD) images for phase identification are collected by a D/max-RAPID micro-diffractometer (Rigaku, Japan) with Cu K_a radiation. This system is equipped with a cylindrical imaging plate (IP) detector, which can record 2 dimensions X-ray diffraction data in angular diffraction ranges from -45° to 160° (2θ) horizontally and ± 45° (2θ) vertically with respect to the direct beam position (0°). The irradiated area can be chosen by using collimators of diameters ranging from 800 down to 10 microns. In the experiments, the diameter of the collimator is 300 microns.

AFM

Morphological analysis is performed by means of atomic force microscopy (AFM). The measurements are carried out by means of a JSPM 4210 (Jeol, Japan) scanning probe microscope (SPM) equipped with a wide-area scanner (maximum xy-movement = 50 µm; maximum z-movement = 8 µm) and a four-segment photodetector for cantilever deflection monitoring. The

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images are recorded in a 10x10 μm^2 area and roughness average (Ra) is calculated on the same area.

HRTEM

High Resolution Transmission Electron microscopy (HRTEM) was performed with a JEM 2010 microscope (Jeol, Japan).

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S2 Compositional Analysis (TXRF)

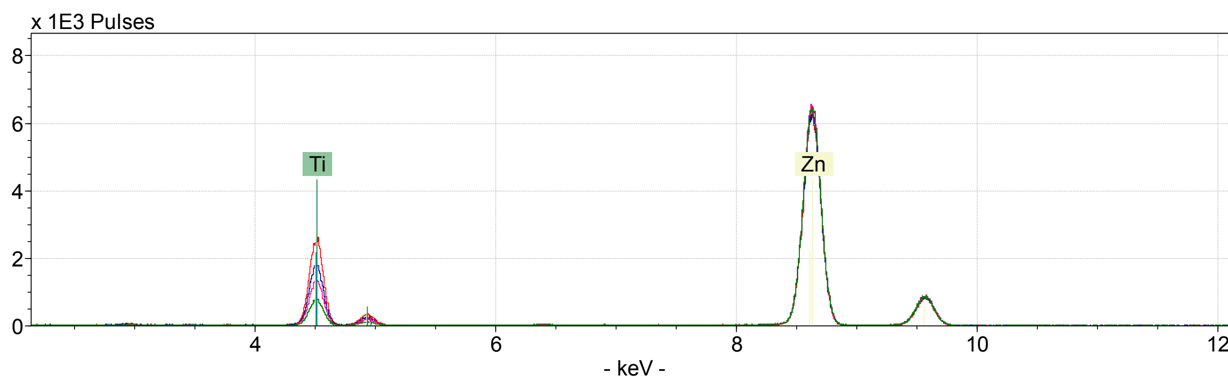


Figure S1. TXRF spectra of samples 1Ti:1Zn (green), 2Ti:1Zn (pink), 3Ti:1Zn (blue) and 4Ti:1Zn (red) normalized on the Zn content.
Samples composition and relative errors were calculated as the average of four values for each sample.

A comparison between experimental and expected thin films composition is reported in **Figure S2**. The expected composition is calculated on the basis of experimental growth-per-cycle (GPC) of pure TiO_2 and ZnO, oxides bulk densities, metals and metal oxides masses. The data lay on a line whose slope is very near to one, demonstrating a very good agreement between the two data sets.

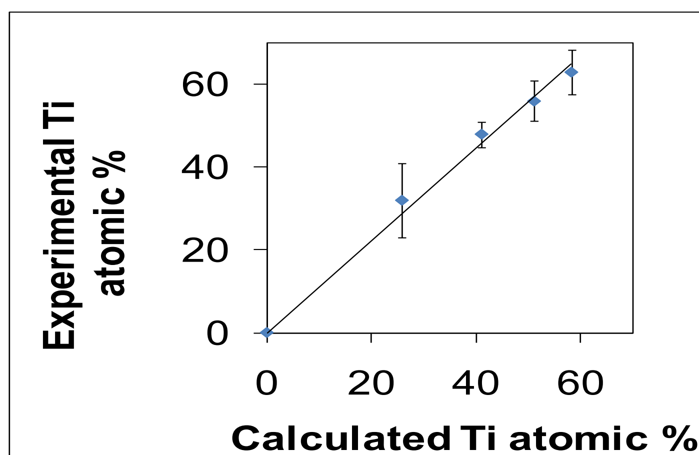
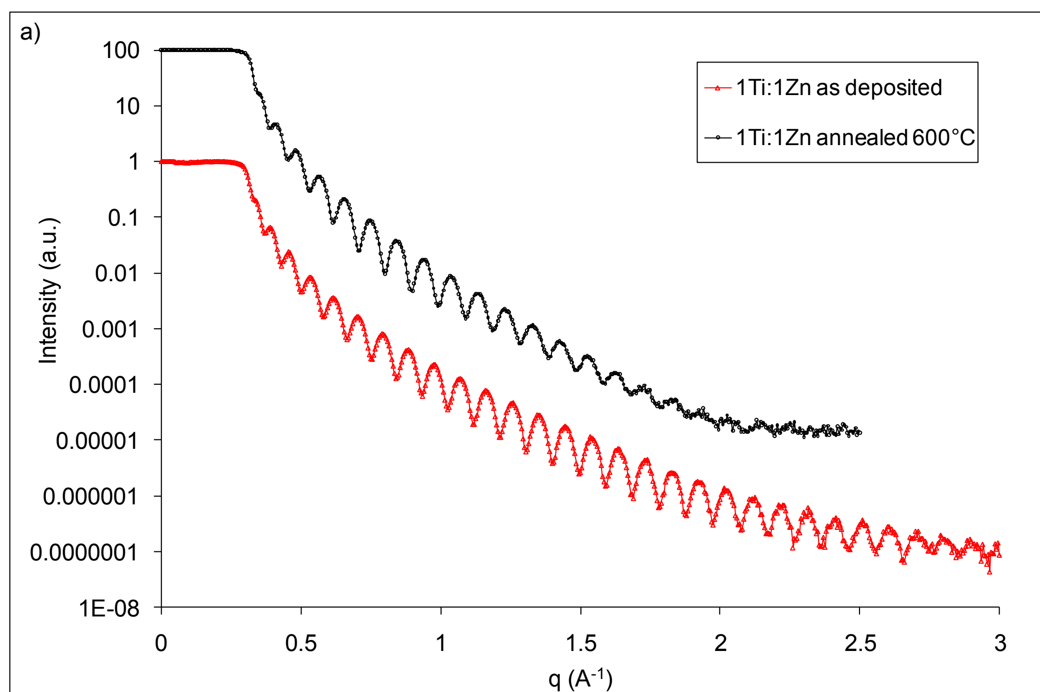


Figure S2. Experimental composition, measured by TXRF, as a function of composition calculated by GPC of pure oxides, metals and oxides masses and densities.

S3. XRR



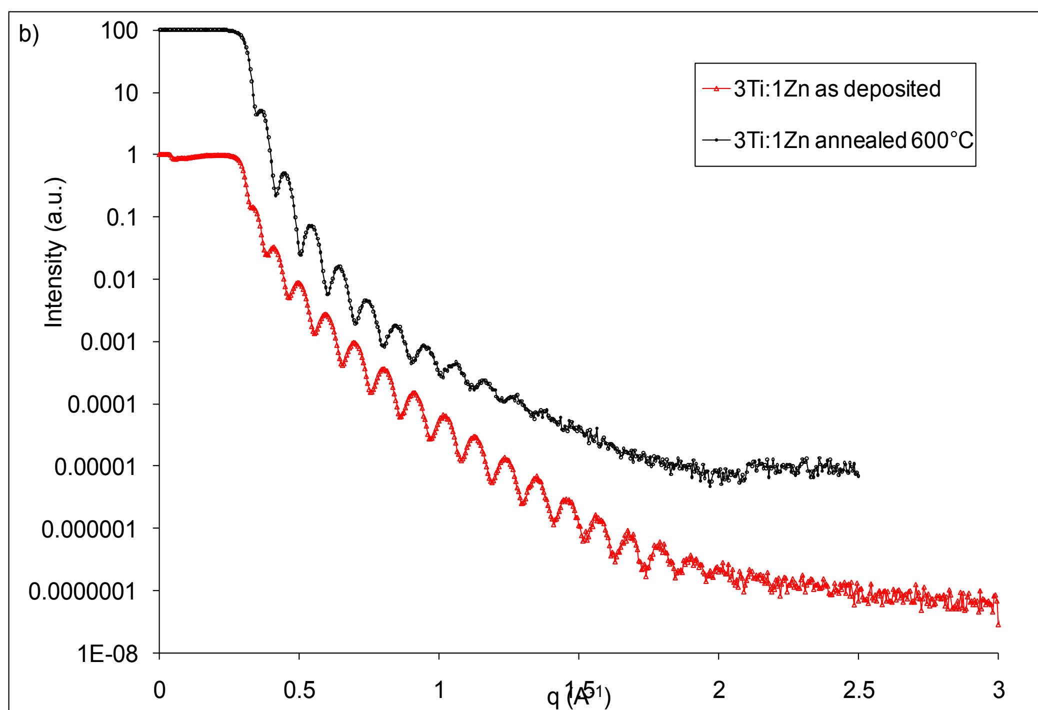


Figure S3.a XRR spectra measured on a) sample 1Ti:1Zn and b) sample 3Ti:1Zn, both as deposited (red) and annealed (black).

The ALD characteristics linearity of as deposited thin films thickness versus the number of cycles is verified by all zinc titanate series (see **Figure S3.b**)

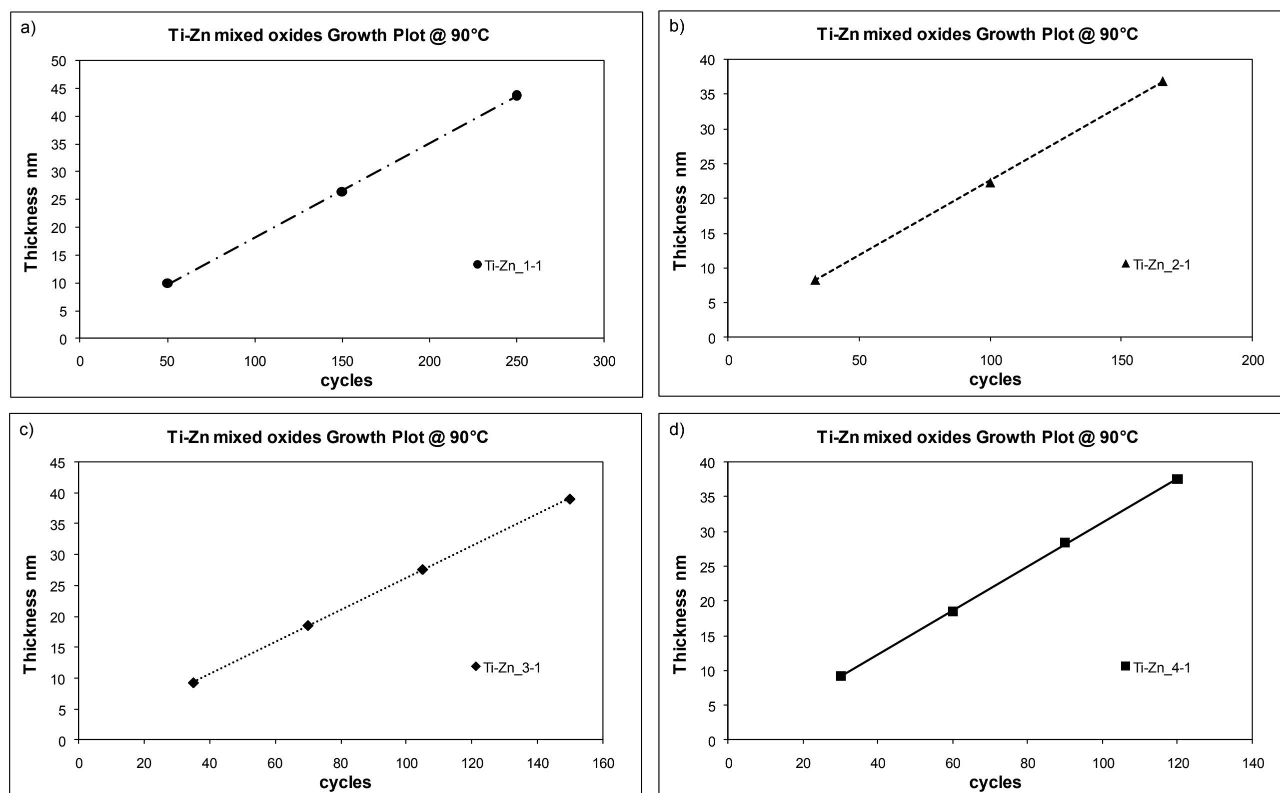


Figure S3.b Thickness measured by XRR as a function of ALD cycles for all the sample compositions: a) 1Ti:1Zn; b) 2Ti:1Zn; c) 3Ti:1Zn; d) 4Ti:1Zn

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S4 Moiré fringes in 1Ti:1Zn samples

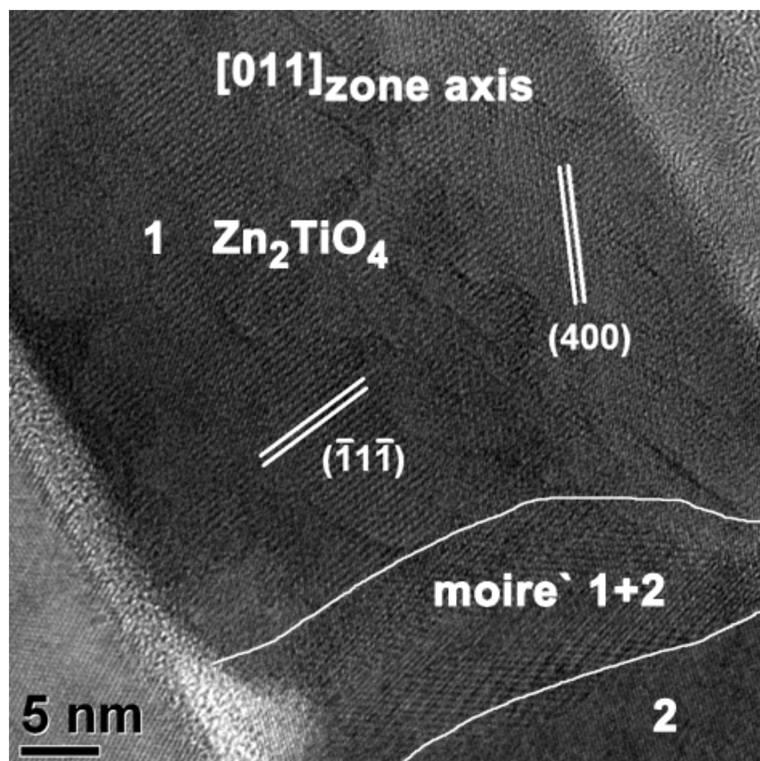

Figure S4. HRTEM images of sample 1Ti:1Zn viewed close to a [011] zone-axis, showing the (400) and (-1 1-1) lattice planes. Moiré fringes can be observed at the superposition between crystal domains 1 and 2. (*See* the text for details).

S5. Compositional Analysis (EDS-HAADF-STEM)

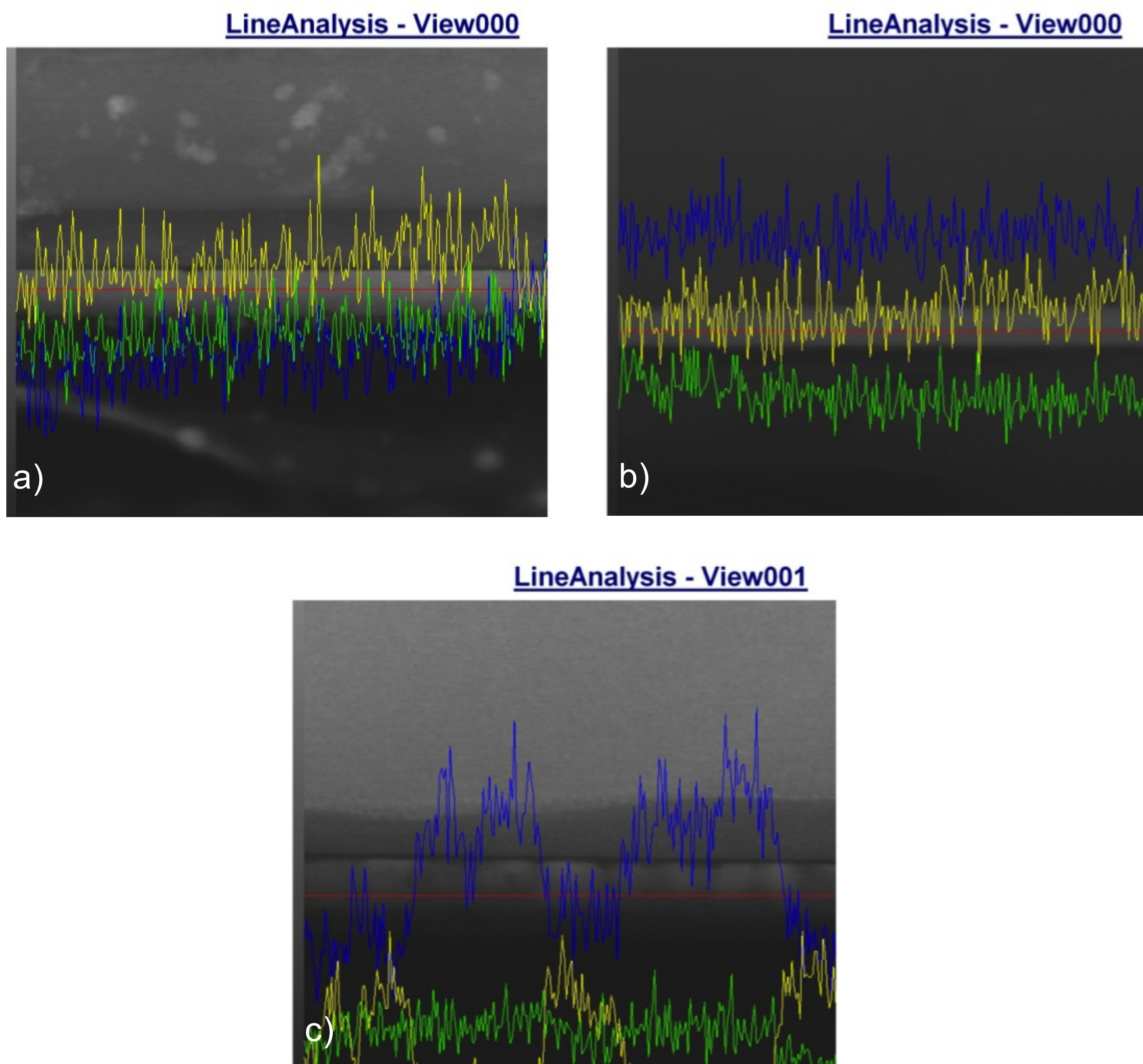

Figure S5. Compositional analysis (EDS) obtained with STEM/HAADF for sample a) 1Ti:1Zn; b) 2Ti:1Zn; c) 4Ti:1Zn. Colored lines represent the spatial distribution of each element (Kα lines): green-oxygen, yellow-zinc and blue-titanium. *See* the text for further details.