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2017

Yong, Z., Linghu, J., Xi, S., Tan, H. R., Shen, L., Yang, P., . . . Pan, J. (2018). Ti_{1-x}Sn_xO₂ nanofilms : layer-by-layer deposition with extended Sn solubility and characterization. *Applied Surface Science*, 428, 710-717. doi:10.1016/j.apsusc.2017.09.135

<https://hdl.handle.net/10356/80273>

<https://doi.org/10.1016/j.apsusc.2017.09.135>

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Ti_{1-x}Sn_xO₂ Nanofilms : Layer-by-layer Deposition with extended Sn solubility and Characterization

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Keywords: thin film, titanium dioxide, pulsed laser deposition, X-ray absorption spectroscopy, X-ray-photoemission spectroscopy, density functional theory

Abstract

High quality rutile $\text{Ti}_{1-x}\text{Sn}_x\text{O}_2$ nanofilms were successfully grown in a layer-by-layer mode at a moderately low temperature of 400°C using pulsed laser deposition (PLD). High solid solubility of up to $x = 0.216$ has been achieved in the $\text{Ti}_{1-x}\text{Sn}_x\text{O}_2$ films despite theoretical prediction by Density functional theory (DFT) of large formation energy (~ 5.64 eV) required for the substitutional alloy to exist at such high Sn concentration. The resultant films have smooth interfaces and step-terraced surfaces with well controlled stoichiometry and are optically transparent. Sn L_3 -edge Extended X-ray absorption fine structure (EXAFS) reveals the substitution of Sn^{4+} in the Ti^{4+} lattice sites of TiO_2 . The lattice spacing along $[110]$ increases linearly with increment in x due to substitution of Sn^{4+} ions in the Ti lattice sites of the $\text{Ti}_{1-x}\text{Sn}_x\text{O}_2$ films. X-ray photoelectron spectroscopy (XPS) and Rutherford backscattering (RBS) show that Sn is uniformly distributed on the surface and in the bulk of the films. These results are crucial when considering $\text{Ti}_{1-x}\text{Sn}_x\text{O}_2$ with suitable composition for making TiO_2 based quantum structures in advanced optoelectronic devices and solar energy materials, where high-quality crystalline thin film-substrates are important.

1. Introduction

TiO₂ holds an important role in many research fields due to its desirable properties such as highly efficient photocatalytic activity in water and air [1], high refractive index, resistance to photo-corrosion, strong ultraviolet resistance and environmentally benign nature [2-4]. TiO₂ also holds great potential in making optoelectronic devices such as blue and ultraviolet light emitters/absorbers and photo-detectors operable at room temperature. Most of these applications depend on the value of the bandgap (E_g). Band gap engineering of TiO₂ by doping and alloying is a key technology towards design and fabrication of efficient TiO₂-based superlattices and quantum structures which requires the oxide to be in the form of a thin film or coating. Doping or combining TiO₂ with metal or non-metal ions could also be an effective method to induce dramatic changes in the structural, electrical and optical properties [5-9]. The incorporation of Sn into the TiO₂ lattice could be effective because 1) Sn⁴⁺ and Ti⁴⁺ have the similar ionic radii and 2) SnO₂ and TiO₂ oxides have the similar crystal structure [10, 11]. However, the nanoscale mixing of TiO₂/SnO₂ composites also inherits the disadvantage of each component due to the ease of phase separation, and doping of metal ions into oxide matrix at the atomic level is also a challenging task.

Several techniques have been used to grow Sn-doped TiO₂ films which include hydrothermal process[12, 13], spray pyrolysis[4], sputtering [14], electron beam evaporation deposition [15], chemical vapor deposition [7] and sol-gel [16, 17]. These efforts to produce high-quality films at lower substrate temperature often result in amorphous or polycrystalline films with rough surfaces. Moreover, these techniques require a post-deposition annealing of the films at high temperature (> 450°C) which generally damage surfaces of both the substrate and the film. In

this paper, PLD is utilized to grow high-quality $\text{Ti}_{1-x}\text{Sn}_x\text{O}_2$ films. PLD provides several advantages compared to other techniques. The composition of the films grown by PLD is relatively close to that of the target, which allows precise control of the film stoichiometry and is extremely critical in the growth of doped or alloyed films. The deposition rate of PLD is typically higher than techniques (e.g. MBE) with competing control over stoichiometry. Another advantage of PLD for the growth of TiO_2 films is that it results in a much smoother film surface as compared to many other growth techniques. To date, no report exists for the PLD of $\text{Ti}_{1-x}\text{Sn}_x\text{O}_2$ single crystalline films, especially at high dopant concentration.

Here, epitaxial growth of the single-crystalline $\text{Ti}_{1-x}\text{Sn}_x\text{O}_2$ (110) nanofilms with ($0 \leq x \leq 0.216$) and low defect content are successfully prepared at a moderately low temperature of 400°C . The resultant films possessed smooth interfaces and step-terraced surfaces, with well controlled stoichiometry. Sn, Ti and O elements are also found to be homogenously distributed on the surface and in the bulk of the $\text{Ti}_{1-x}\text{Sn}_x\text{O}_2$ films. Sn^{4+} is also found to substitute Ti^{4+} in Ti lattice site in the films.

2. Experimental Methods

2.1. Sample Preparation

SnO_2 and TiO_2 powders with high-purity (bought from Sigma Aldrich Co.) were grind for a few hours before sintering in a furnace at high temperatures of more than 1000°C and these processes are repeated twice to form the $\text{Ti}_{1-x}\text{Sn}_x\text{O}_2$ ($x = 0, 0.01, 0.02, 0.05, 0.10$ and 0.20) target pellets. Rutile $\text{Ti}_{1-x}\text{Sn}_x\text{O}_2$ nanofilms were deposited on surface-treated rutile TiO_2 (110) single crystal substrates at 400°C by PLD, using a 248 nm Lambda Physik excimer laser with laser

energy density of about 2 J/cm^2 . Target to substrate distance was kept at $\sim 7 \text{ cm}$ inside the vacuum chamber. The oxygen partial pressure during deposition was maintained at 0.4 mTorr throughout the deposition. In each deposition, $\sim 15 \text{ nm}$ of pure TiO_2 film was first deposited as a buffer layer on the substrate, followed by approximately 3.5 nm of $\text{Ti}_{1-x}\text{Sn}_x\text{O}_2$ film. The growth of the $\text{Ti}_{1-x}\text{Sn}_x\text{O}_2$ films was monitored by in situ reflection high-energy electron diffraction (RHEED). Post-deposition annealing is not needed.

2.2. Characterization

Atomic force microscopy (AFM) was used to examine the surface topography of the $\text{Ti}_{1-x}\text{Sn}_x\text{O}_2$ films. The crystallographic phases, orientations and strain states of the films were investigated by performing high resolution X-ray diffractometry (HR-XRD) and reciprocal space mapping (RSM) on the films, using the diffractometer Huber 4-circle system 90000-0216/0 at the X-ray diffractometry and development beamline (XDD) [18] of Singapore Synchrotron Light Source (SSLS). The Rutherford backscattering (RBS) – ion channeling was performed using 2 MeV He^+ ion beam at 20 nA from a 4 MV ion electrostatic accelerator, with a Au-Si surface barrier detector at an angle of 15° (165° backscattering geometry) with respect to the beam axis. The impinging He^+ ions strike the sample surface at normal incidence. The standard reference samples used for surface energy calibration are Si, Pd and Pt. Sn L_3 -edge EXAFS spectra were measured in a 45° incident alignment ($\theta = 45^\circ$), on both reference samples and the $\text{Ti}_{1-x}\text{Sn}_x\text{O}_2$ films at the X-ray absorption fine-structure (XAFS) spectroscopy for fundamental and applied catalysis research beamline (XAFCA) of SSLS [19]. Sn L_3 -edge EXAFS spectra were collected using fluorescence mode using silicon drift detector. The Sn absorption curves were first

subjected to pre-edge subtraction and then normalized to the edge jump at 3930 eV, the difference in absorption coefficient just below and at a flat region above the edge. High resolution transmission electron microscopy (HR-TEM) was performed using FEI TITAN 80 – 300 kV TEM / STEM microscope, at an operating voltage of 200 kV, to study the interfacial structure and verify the crystalline properties of the films. TEM samples were first prepared using a focused ion beam (FIB), prior to viewing under TEM. The samples were protected by a 5 nm SiO₂ and 40 nm Au sputtered-on layers prior to FIB. The FIB-prepared sample was less than 100 nm thick. RBS is used for the quantification and depth profiling of Sn in the films. The X-ray photoelectron spectroscopy (XPS) spectra were obtained using a VG ESCALAB 220i-XL instrument with Al-K α monochromatic X-ray source (1486.6 eV). A low-energy electron flood gun was utilized for compensation of sample charging. The pass energy of the analyzer was set to 20 eV to achieve high energy resolution. C 1s peak from adventitious carbon at 285.0 eV was used as a reference for charge correction.

3. Theoretical Calculations

First-principles calculations based on DFT were performed on the Vienna Ab-initio Simulation Package (VASP). The projector-augmented wave (PAW) [20] basis set was used for wave function. The generalized gradient approximation (GGA) [21] with Perdew-Burke-Ernzerhof (PBE) functional [22] was applied for the exchange-correlation interaction of electrons. To mimic the thin film construction, 5 layers of TiO₂ orientated along the z-direction (110) with Oxygen termination on both sides were utilized. To avoid the interaction of mirror image caused by periodical boundary condition, a vacuum layer larger than 15 Å was added on the direction perpendicular to the plane of thin film. A $3 \times 1 \times 1$ supercell with 90 atoms was

built for the defect-related calculations, together with a $4 \times 5 \times 1$ Monkhorst-Pack k-mesh setting. The doping concentration was controlled to be 3.3 %, 6.7 %, 10 % and 20 % through one, two, three and six Sn atoms substitution, respectively. Formation energy of defect Y is calculated by the formula as follows:

$$E_f(Y) = E_{tot}(Y) - E_{tot}(bulk) - \sum_i n_i \mu_i$$

where $E_{tot}(Y)$ is the total energy of the thin film model with a defect Y, $E_{tot}(bulk)$ is the total energy of pristine TiO₂ thin film. n_i is the number of atoms of type i (host atoms or dopant) that have been added to ($n_i > 0$) or removed from ($n_i < 0$) the thin film model to construct the defect, and μ_i are the corresponding chemical potentials.

4. Results and discussions

To explore the solid solubility limit and formation energy of Sn dopant in TiO₂, first-principles calculations based on DFT were performed on VASP. The calculated formation energies per supercell of the 3.3 %, 6.7 %, 10 %, and 20 % Sn-substitution defect which are uniformly distributed in TiO₂ thin film models are 0.90 eV, 1.92 eV, 2.60 eV and 5.64 eV, respectively. The increase in formation energies indicates that it is increasingly more difficult to dope at higher Sn concentration. In particular, the formation energy of 5.64 eV for 20 % Sn-substitution defect is high, revealing that it is very hard to realize doping at such high concentration. Based on the DFT calculation results and no known report, to the author's knowledge, on Sn-TiO₂ substitutional alloy at high Sn concentrations (≥ 20 %), we conclude that it is difficult for Sn⁴⁺ ion to substitute Ti⁴⁺ ion in the Ti lattice site at such high concentration.

Furthermore, the synthesis of Sn-TiO₂ substitutional alloy with high Sn concentration is difficult as Sn tends to agglomerate at high concentration [23, 24] due to its low melting temperature [25]. However, we have proven experimentally that it is physically viable to achieve high Sn concentration substitutional alloying in TiO₂ by using PLD. With non-equilibrium processes such as PLD, the alloying of TiO₂ and SnO₂ can be achieved with a large solid solubility that is well beyond the thermodynamic limit [26]. During the PLD process, the laser ablated species gained sufficient kinetic energy and can thus nucleate and grow into film at a relatively low temperature. This is different from the equilibrium growth where only thermal energy is supplied by high temperature heating [27].

Fig. 1. (a) In-situ RHEED oscillations of Ti_{0.913}Sn_{0.087}O₂ film deposited on TiO₂ (110) substrate. The arrow indicates the start of deposition. Insets (top) include the streaky RHEED pattern before and after growth of the film. (4μm x 4μm) Topography image of ~3.5 nm of (b) 2.3% Sn-doped TiO₂ film (Inset: annealed TiO₂ (110) substrate), (c) 4.8% Sn-doped TiO₂ film, (d) 9.3% Sn-doped TiO₂ film and (e) 21.6%

Sn-alloyed TiO₂ film, all deposited on annealed TiO₂ (110) substrates. Sn concentration in atomic % (X) is quantified by XPS analysis.

Fig. 1a shows the typical in-situ reflection high-energy electron diffraction (RHEED) intensity oscillations during the Ti_{0.83}Sn_{0.17}O₂ film growth. Both the periodical RHEED oscillations and streaky RHEED pattern reveal the good layer-by-layer growth for the deposition of Sn-doped TiO₂ film. The growth rate could be determined as ~80 laser pulses per monolayer (3.268Å), consistent with the result obtained from HR-XRD Θ –2 Θ measurement. The clean terrace patterns of the ex-situ AFM images of various Ti_{1-x}Sn_xO₂ films (Fig. 1b – d) are similar to that of the annealed TiO₂ substrate displayed in the inset of Fig. 1b. This observation attests to the high quality of epitaxial layer-by-layer growth of the fully covered Sn-doped TiO₂ overlayers. Analysis of AFM images revealed that the root mean squared (RMS) roughness of the film surfaces generally increases (up to 5Å) with the increment in Sn doping content in the films.

Fig. 2. (a) Specular HR-XRD Θ - 2Θ scans displaying (220) peaks of all $\text{Ti}_{1-x}\text{Sn}_x\text{O}_2$ films / TiO_2 film / TiO_2 (110) substrates, of which the $\text{Ti}_{1-x}\text{Sn}_x\text{O}_2$ layer thickness is ~ 3.5 nm and TiO_2 film layer thickness is ~ 15 nm. Off-specular RSMs around (b) (130) and (c) (332) of $\text{Ti}_{0.784}\text{Sn}_{0.216}\text{O}_2$ / TiO_2 film / TiO_2 substrate. (d) 2.0 MeV He^+ RBS random spectrum for $\text{Ti}_{0.946}\text{Sn}_{0.054}\text{O}_2$ deposited on annealed TiO_2 (110) substrate. The elemental positions are indicated on the spectrum.

To understand the epitaxy, coherency, and strain state of the ~ 3.5 nm $\text{Ti}_{1-x}\text{Sn}_x\text{O}_2$ nanofilms/ ~ 15 nm of TiO_2 film deposited on top of TiO_2 (110) substrate, RSM and Θ - 2Θ scans were performed. Specular Θ - 2Θ scans around (220) were also measured as shown in the Fig. 2a. The smaller 2Θ value of (220) film peaks, as compared to the TiO_2 substrate, indicates that the films have slightly larger lattice spacing than bulk TiO_2 . This shift to lower 2Θ with respect to the TiO_2 substrate signifies an out-of-plane expansion of the $\text{Ti}_{1-x}\text{Sn}_x\text{O}_2$ unit cell, indicative of in-plane compressive strain of the thin film on the substrate due to the substitution of Sn^{4+} ion which has a larger ionic radius ($\text{Sn}^{4+} = 0.69\text{\AA}$, $\text{Ti}^{4+} = 0.605\text{\AA}$) [11, 28] at the Ti lattice site. Moreover, the well-defined Laue oscillations (thickness fringes) observed in all our $\text{Ti}_{1-x}\text{Sn}_x\text{O}_2$ films verify the sharp interface and high quality of the crystal growth. The observation of only (l 0) types of diffraction further confirms the epitaxial growth of the $\text{Ti}_{1-x}\text{Sn}_x\text{O}_2$ films. Fig. 2b and 2c display the typical off-specular RSMs of the $\text{Ti}_{0.784}\text{Sn}_{0.216}\text{O}_2$ film (highest x) around (130) and (332), respectively. Clearly, both the film and substrate share the same projection along the in-plane $[\bar{1}10]$ and $[001]$ axes but at displaced positions in the out-of-plane (L : $[110]$) direction, indicating the coherent growth (along $[001]$ and $[\bar{1}10]$) of the $\text{Ti}_{1-x}\text{Sn}_x\text{O}_2$ films on TiO_2 substrate. This can be attributed to the in-plane epitaxial constraint of the rutile substrate.

Due to depth resolution limitations of RBS, it is performed on slightly thicker film. Fig. 2d shows a typical RBS random spectrum for the thicker ($\sim 38\text{nm}$) 5.4% Sn incorporated TiO_2 thin film grown on TiO_2 substrate. The homogeneous distribution of Sn element in the bulk of the $\text{Ti}_{0.946}\text{Sn}_{0.054}\text{O}_2$ film is verified by RBS, implying that the distribution of Sn should be homogeneous in the nanofilms as well.

Fig. 3. (a) Sn L_3 -edge EXAFS spectra of the $\text{Ti}_{1-x}\text{Sn}_x\text{O}_2$ films along with the Sn, SnO and SnO₂ reference samples, measured in fluorescence mode. Pre-edge peaks **M** and **N** arise from $2p_{3/2} \rightarrow 5s$ while peak **P** arises from $2p_{3/2} \rightarrow 5d_{5/2}$ excitations. Inset shows the expanded **N** feature, indicating the slight shift to lower energy with increase in x as a result of an increase in the average Sn–O bond distance. (b) Sn L_3 -edge EXAFS scattering intensity functions 21.6% and 9.3% Sn-doped TiO₂ films. (c) Sn L_3 -edge Fourier transformed EXAFS spectra (i.e., the radial structure function, RSF) for 21.6% and 9.3% Sn-doped TiO₂ films, together with SnO₂. Phase shift was not corrected.

The normalized Sn L_3 -edge EXAFS spectra from the $\text{Ti}_{1-x}\text{Sn}_x\text{O}_2$ films are presented in Fig. 3a. The spectra of reference samples: Sn metallic foil, SnO₂ and SnO nano-powder are displayed for comparison. Because of poor data statistics, only two $\text{Ti}_{1-x}\text{Sn}_x\text{O}_2$ films with high Sn concentration were shown. The Sn L_3 spectra mainly result from $2p_{3/2} \rightarrow 5s$ (pre-edge peaks **M**

and **N**) and $2p_{3/2} \rightarrow 5d_{5/2}$ (peak **P**) excitations, respectively [29]. For the metallic Sn foil, Sn L_3 -spectra is almost featureless except for the edge step at the absorption edge, indicating a transition to the free electron like conduction band above the Fermi level (E_F). In SnO and SnO₂, the Sn ion has electron configuration of [Kr]4d¹⁰5s²5p⁰ and [Kr]4d¹⁰5s⁰5p⁰, respectively. The 5s atomic orbitals are completely filled in SnO but are empty in SnO₂. In an octahedral environment of SnO₂, the d orbitals are split into two groups, e_g (d_z^2 and $d_{x^2-y^2}$ orbitals) and t_{2g} (d_{xy} , d_{xz} and d_{yz} orbitals). The t_{2g} anti-bonding orbitals have energy lower than the degenerated atomic orbitals. Some bound excited d -type states exist in the conduction band, which can serve as the final states for the photoelectron. Thus, feature **P** is present at the Sn L_3 -edge spectra in SnO and SnO₂ [29].

From Fig. 3a, we can tell that the surface sensitive fluorescence spectra of Ti_{1-x}Sn_xO₂ are more similar to that of SnO₂ nano-powder rather than the Sn foil and SnO. No significant shift in absorption energy or change in intensity of the pre-edge peak **M** was observed with varying x . As the position of feature **M** of Ti_{1-x}Sn_xO₂ are very close to that of SnO₂, this implies that the valence state of Sn in the samples is 4+. The sharp peaks **M**, **N** and **P** seen in the spectra of Ti_{1-x}Sn_xO₂ and SnO₂ indicate localized electronic states [30]. The fourier transform of EXAFS scattering intensity calculations (Fig. 3b) give the atomic locations in real space and is known as Radial structure function (RSF). The phase-uncorrected RSF of Ti_{1-x}Sn_xO₂ films are compared with those of SnO₂ nano-powder in Fig. 3c. The peaks are attributed to the nearest neighboring shells which surrounds the absorbing Sn Atom in 7.5Å distance. The peak distances are associated with the atomic distances between the source Sn atom and the neighboring Sn or O atoms. Each peak provides information about the spherical localization of atoms in the crystal [31]. Due to weak signal detected from the nanofilms, we will only analyze the first radial peak

($\sim 1.5 \text{ \AA}$) which is contributed by the Sn–O bond pairs in the first coordination shell of $\text{Ti}_{1-x}\text{Sn}_x\text{O}_2$ films and SnO_2 . Accordingly, the local symmetry and coordination number (CN) of Sn sites in $\text{Ti}_{1-x}\text{Sn}_x\text{O}_2$ are similar to that in SnO_2 , implying that the Sn ion is bonded to six Oxygen ions in $\text{Ti}_{1-x}\text{Sn}_x\text{O}_2$. In comparison with the position of Sn–O in SnO_2 , the downshifts of the first radial peak by $0.03 \text{ \AA}$ and $0.09 \text{ \AA}$ indicate the slight contraction of the Sn–O bond length in 21.6% and 9.3% Sn-doped TiO_2 , respectively. This is most likely due to the substitution of Sn^{4+} in Ti^{4+} lattice site. The reported bond length of SnO_2 and TiO_2 are $2.05 \text{ \AA}$ and $1.95 \text{ \AA}$, respectively [32]. Since the ionic Ti–O has shorter bond length than Sn–O, the overall Sn–O bond length of the substituted Sn^{4+} will need to contract so as to fit into the TiO_2 lattice. Furthermore, the intensity of the first radial peak of $\text{Ti}_{1-x}\text{Sn}_x\text{O}_2$ is observed to be much higher than that of nano-powder SnO_2 , indicating the orderly arrangement of Sn^{4+} ions in the $\text{Ti}_{1-x}\text{Sn}_x\text{O}_2$ crystal lattice, relative to the disorderly arrangement of Sn^{4+} ions in the amorphous SnO_2 nano-powder. All these results indicate successful substitution of Sn^{4+} in the Ti^{4+} lattice site of TiO_2 .

Fig. 4.(a) HAADF-STEM image of the $\text{Ti}_{0.784}\text{Sn}_{0.216}\text{O}_2$ film / TiO_2 film / TiO_2 substrate, of which the $\text{Ti}_{0.784}\text{Sn}_{0.216}\text{O}_2$ layer thickness is $\sim 3.5 \text{ nm}$ and TiO_2 film layer thickness is $\sim 15 \text{ nm}$. (b) HR-TEM image of the $\text{Ti}_{0.784}\text{Sn}_{0.216}\text{O}_2$ film. FFT images are extracted from the regions of the HR-TEM image marked with squares. (c) Graph of Lattice spacing along [110] (extracted from FFT) vs. Sn concentration in atomic % (X) for $\text{Ti}_{1-x}\text{Sn}_x\text{O}_2$ films.

Cross-sectional transmission electron microscopy (TEM) is performed to study the interfacial structure and verify the crystalline properties of the films. The high angle annular dark field scanning transmission electron microscopy (HAADF-STEM) image in Fig. 4a depicts clearly that the $\text{Ti}_{0.784}\text{Sn}_{0.216}\text{O}_2$ film of ~ 3.5 nm thickness is deposited on top of ~ 15 nm TiO_2 film. HR-TEM image in Fig. 4b shows the high quality single crystalline nature of the $\text{Ti}_{0.784}\text{Sn}_{0.216}\text{O}_2$ film. Fast Fourier transform (FFT) images are extracted from regions of the HR-TEM image marked with squares. The lattice spacing, c , along $[110]$ for the $\text{Ti}_{1-x}\text{Sn}_x\text{O}_2$ nanofilms is calculated from FFT. From Fig. 4c, c is shown to increase almost linearly with increment in Sn concentration in atomic % (**X**), which is in accordance with the Vegard's law. The phenomenon can be explained by the substitution of Sn^{4+} ions into the Ti lattice sites of the TiO_2 host matrix. Since Sn^{4+} has a larger ionic radius than Ti^{4+} , c will naturally increase with larger number of substituted Sn^{4+} ions replacing Ti^{4+} ions in the TiO_2 lattice sites.

Fig. 5. (a) $\text{Ti}^{4+} 2p$, (b) $\text{Sn}^{4+} 3d_{5/2}$ (inset: $\text{Sn } 3d$ spectra of 4.8 %, 9.3 % and 21.6 % Sn-doped/alloyed TiO_2 films) and (c) $\text{O}^{2-} 1s$ XPS core level de-convoluted spectra of $\text{Ti}_{1-x}\text{Sn}_x\text{O}_2$ films deposited on TiO_2 (110) substrates. x in $\text{Ti}_{1-x}\text{Sn}_x\text{O}_2$ films is quantified by XPS composition analysis. Error bar of XPS core level spectra is within ± 0.05 eV.

Table 1. Surface Analysis by XPS for $\text{Ti}_{1-x}\text{Sn}_x\text{O}_2$ films and TiO_2 substrate.

$\text{Ti}_y\text{Sn}_z\text{O}_n$			$\text{Ti}_{1-x}\text{Sn}_x\text{O}_2$	Binding Energy [eV]						
y (10^{-2})	z (10^{-2})	$n^{\text{a)}$ (10^{-2})	x (10^{-2})	Sn $3d_{5/2}$	FWHM (Sn $3d_{5/2}$)	Ti $2p_{3/2}$	FWHM (Ti $2p_{3/2}$)	O $1s$ (O_L)	FWHM (O $1s$ (O_L))	O $1s$ (O_H)
33.95	0	66.05	0 (Substrate)	0	---	458.86	1.01	530.10	1.17	531.87
33.95	0	66.05	0 (Film)	0	---	458.76	1.01	530.00	1.17	531.77
32.18	0.35	67.47	1.1	486.52	1.66	458.63	1.02	529.92	1.23	531.67
31.76	0.74	67.51	2.3	486.50	1.46	458.65	1.00	529.89	1.2	531.72
28.55	1.43	70.01	4.8	486.57	1.49	458.76	0.98	529.92	1.26	531.85
27.14	2.77	70.09	9.3	486.65	1.39	458.72	1.10	529.9	1.25	531.88
26.01	7.14	66.85	21.6	486.57	1.49	458.62	1.05	529.99	1.39	531.86

^{a)} refers to the atomic concentration of O_L species. Error bar of XPS core level spectra is within ± 0.05 eV.

XPS was performed on the films and the annealed TiO_2 (110) substrate to further study the surface composition and the chemical states of the $\text{Ti}_{1-x}\text{Sn}_x\text{O}_2$ films. Fig. 5a – c show the XPS spectra of Ti $2p$, Sn $3d_{5/2}$ and O $1s$ of the samples, respectively. The Ti $2p$ doublet and O $1s$ spectra were fitted using Gaussian–Lorentzian mix functions after an iterated Shirley-type background subtraction. The Sn $3d_{5/2}$ spectra were fitted using a single Gaussian–Lorentzian mix function after an offset linear background subtraction.

From Table 1, it was observed that the FWHM of the Ti $2p$, Sn $3d_{5/2}$ and O $1s$ peaks remained generally consistent across samples with different x . In Fig. 5a, the XPS peak positions of Ti $2p_{3/2}$ and Ti $2p_{1/2}$ for all samples are located at about 458.7 eV and 464.4 eV, which indicates that the valence state of the majority of Ti in the films is 4+ [17, 33]. Furthermore, the energy difference ($\Delta = 5.8\text{eV}$) due to spin-orbit splitting of Ti $2p$ is about the same as that of Ti $2p$ spin-orbit splitting in pure TiO_2 [34] which further corroborates the fact that the oxidation state of Ti is 4+. The transparency of the films and the lack of Ti^{3+} as observed by XPS, imply that a comparable quantity of oxygen vacancies is not present in the films [35]. As

seen in Fig. 5b and its inset, the peak position corresponding to Sn $3d_{5/2}$ is about 486.6 eV and the energy difference ($\Delta = 8.4$ eV) due to spin-orbit splitting of Sn $3d$ is approximately equal to that of pure SnO₂ [34]. Thus, the valence state of Sn in the films can be assigned as 4+. No additional Sn $3d$ peak of other valence state has been observed in the spectra, indicating the absence of other secondary Sn phases in the near-surface region. Fig. 5c shows that O $1s$ XPS spectra are asymmetrical in shape, indicating at least two kinds of chemical forms. After curve fitting, the O $1s$ spectrum can be de-convoluted into two peaks: a well formed peak at 529.9 eV and a shoulder at 531.8 eV. The peak at 529.9 eV can be ascribed to the O²⁻ ion under fully oxidized stoichiometric conditions - oxygen (O_L) in TiO₂ lattice [36]. The shoulder peak at higher BE of 531.8 eV is attributed to the bridging hydroxyls (O_H) [33, 37].

Table 1 shows the fitted values of the binding energy (BE) and full-width half maximum (FWHM) of Ti $2p$, Sn $3d_{5/2}$ and O $1s$ peaks. In general, the stoichiometry of Ti to O_L is (or close to) 1 : 2 for an ideal TiO₂ crystal. Thus, it can be deduced from the evaluated atomic number ratio of Ti and Sn ($y + z$) to O_L (n) in Table 1 that there are very few oxygen vacancies on the film surfaces. The quantification of Sn by XPS analysis is also displayed in Table 1, as well as the surface stoichiometry of Ti, Sn and O_L . The Sn concentration on the film surfaces is found to be close to the stoichiometry of the respective targets used in PLD, implying that Sn is uniformly distributed on the surface of the Ti_{1-x}Sn_xO₂ nanofilms. These results verified the precise control of the film stoichiometry during PLD.

5. Conclusions

We have demonstrated a moderately low temperature (400 °C) PLD process for the growth of high-quality epitaxial nanofilms of $\text{Ti}_{1-x}\text{Sn}_x\text{O}_2$ ($0 \leq x \leq 0.216$) where no post-deposition annealing is needed. The resultant films possessed smooth interfaces and step-terraced surfaces and are optically transparent with well controlled stoichiometry. Because Sn^{4+} ion has a larger ionic radius than Ti^{4+} ion, the out-of-plane [110] lattice spacing of $\text{Ti}_{1-x}\text{Sn}_x\text{O}_2$ films increases almost linearly with x due to the substitution of Sn^{4+} ion at the Ti lattice site. Sn, Ti and O elements are found to be homogeneously distributed on the surface and in the bulk of the $\text{Ti}_{1-x}\text{Sn}_x\text{O}_2$ films. DFT calculations predicted large formation energy of 5.64 eV for the substitutional Sn-TiO₂ alloy with 20 % Sn. However, the extended Sn solid solubility (up to 0.216) achieved in this work implies that PLD is an efficient way to incorporate Sn into TiO₂ beyond the thermodynamic limit.

ACKNOWLEDGMENT

The authors would like to thank Dr. M. Yang, Dr Z. Huang and X. Chi for their invaluable discussion, as well as Dr. Y.H. Du who commissioned and calibrated the XAFCA beamline in SSLS.. The authors would also like to thank Nanocore under National University of Singapore (NUS) for providing resources and the pulsed laser facility for the deposition of films. The authors would also like to acknowledge the Singapore Synchrotron Light Source (SSLS) for providing the facility necessary for conducting the research. The Laboratory is a National Research Infrastructure under the National Research Foundation Singapore. This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

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Comments from the Editors and Reviewers: Reviewer #1:

This paper is based on the study of high quality rutile Ti_{1-x}Sn_xO₂ nanofilms grown by PLD at a moderately low temperature. It is a detailed study with numerous investigation techniques. The paper is well written, but the English must be improved. The Highlights are clear. I recommend to be accepted after the language improvement.