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Unravelling uniaxial strain effects on electronic correlations, hybridization and bonding in transition metal oxides

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Abstract

The interplay among spin, lattice, charge and orbit is of central importance for several rich and fascinating properties of oxides, and is the subject of intense research at present. Here, we present an approach to manipulate this interplay by Sn doping to effectively apply uniaxial strain on the TiO_2 lattice. The evolution of this interplay in pseudo-homoepitaxial $\text{Ti}_{1-x}\text{Sn}_x\text{O}_2$ films is measured using a combination of X-ray absorption near edge spectroscopy at the O K and Ti $L_{3,2}$ -edges. Supported by various theoretical calculations, we find that the multiplet-type electronic correlations, long-range bonding and hybridization in the system can be controlled by independently modifying uniaxial strain, thereby allowing us to establish the correlations among these effects, doping concentration, and strain. This significantly widens the phase space for experimental exploration of predictive models and leads to new possibilities for manipulation over materials' functional properties. The methodology presented here can be applied in general to study the nature of the multiplet-type electronic correlations and bonding properties in octahedral-coordinated $3d^N$ transition metal oxides.

Keywords: Extended X-ray absorption fine structure (EXAFS, XANES); DFT; Thin film; Lattice strains; Semiconductors.

1. Introduction

Octahedral-coordinated transition metal oxides (TMO) span over a huge class of important functional oxide materials including perovskite oxides, manganites, ferrites and cuprates. In these oxides, the centrally coordinated octahedron bond flexibility allows for a multitude of distortions. This distortion from the ideal octahedron paves the way for a variety of technologically promising phenomena related to superconductivity, multiferroicity, magnetoresistivity, piezoelectricity, ferroelectricity, pyroelectricity, and nonlinear optical phenomena [1,2]. Most of these functional properties arise from the interplay among spin, lattice, charge, and orbital degrees of freedom of the material[3, 4]. As a result of this interplay, strain doping, which causes lattice distortion, has

emerged as a powerful technique to control the electrical, optical, and magnetic properties of TMO [1, 4-6]. However, the relationship between this interplay and strain doping presents formidable challenges to experimental manipulation and theoretical understanding of the underlying physics due to its complexity. Identification of the effects caused by strain doping and elucidation of its influence on electronic and bonding properties are important topics in fundamental material research, as well as for applications of oxide materials in electronic devices [2].

In strain engineering, the lattice constant, and hence the electronic structure, usually vary in all three directions, obscuring the cause-effect relations between single degrees of freedom and order parameters [1, 5]. In the present work, we use $\text{Ti}_{1-x}\text{Sn}_x\text{O}_2$ films grown layer-by-layer on TiO_2 (110) substrates as a model system to investigate how strain doping plays a role in influencing the electronic properties in octahedral-coordinated TMO. Due to the in-plane epitaxial constraint of the rutile substrate [7], the internal stress introduced by Sn will therefore be relieved only by an increment of the out-of-plane lattice constant or a change in metal-oxygen bond angle. This allows us to efficaciously bypass the Poisson limitations [1,5], and tailor the strain independently along a single axis. We established a linear relationship between the Sn atomic concentration in % (**X**) and the lattice spacing along [110] in $\text{Ti}_{1-x}\text{Sn}_x\text{O}_2$, as observed from the high resolution transmission electron microscopy (HR-TEM) results, which we reported in reference [7]. The linear gain in the lattice constant along [110] with linear increment in **X** thereby translates to linear increase in strain in $\text{Ti}_{1-x}\text{Sn}_x\text{O}_2$ along the same direction. Thus, strain can be independently and continuously controlled in a linear manner along the film-growth axis using Sn substitution.

Here, we designed the experiments to reveal comprehensively how strain affects hybridization, multiplet-type electronic correlations, ligand field strength and long-range bonding in pseudo-homoepitaxial $\text{Ti}_{1-x}\text{Sn}_x\text{O}_2$ films, using X-ray absorption near edge spectroscopy (XANES) at the O K and Ti $L_{3,2}$ -edges. Our detailed analysis is further supported by three types of theoretical calculations based on Density Functional Theory (DFT) using Vienna Ab-initio Simulation Package (VASP), SIESTA and FDMNES codes, and CTM4XAS program, respectively.

2. Experimental method

2.1 Sample Fabrication and characterization

Single-crystalline $\text{Ti}_{1-x}\text{Sn}_x\text{O}_2$ (110) nanofilms with $0 \leq x \leq 0.093$ and low defect content are successfully prepared by pulsed laser deposition on TiO_2 (110) substrates at a moderately low temperature of 400°C [7]. The films are found to have smooth interfaces and step-terraced surfaces using atomic force microscopy (AFM) and possess well controlled stoichiometry based on X-ray photoemission spectroscopy (XPS) results [7]. The lattice spacing, c , along [110] for the $\text{Ti}_{1-x}\text{Sn}_x\text{O}_2$ nanofilms is calculated from the Fast Fourier transform (FFT) images that are extracted from regions of the HR-TEM images. c is deduced to be linear to x , which is in accordance with the Vegard's law [7]. Since Sn^{4+} has a bigger ionic radius than Ti^{4+} , this phenomenon can be explained by the substitution of Sn^{4+} ions into the Ti lattice sites of the TiO_2 host matrix. 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. More details of the film growth and characterization are provided in the Supplementary Information and reference [7].

2.2 XANES measurement details

Ti $L_{3,2}$ -edge and O K -edge XANES spectra were obtained using linearly polarized X-ray Absorption spectroscopy at room temperature from the SINS beamline [8] of Singapore Synchrotron Light Source in a normal-incident alignment ($\theta = 0^\circ$). For X-ray linear dichroism (XLD) measurements, XANES spectra with an additional grazing angle incidence ($\theta = 20^\circ$) alignment were also collected. The spectra were collected in total electron yield mode to minimize signal from the underlying rutile substrate. The XANES data were normalized to the incident photon flux. After background correction, the spectra at the Ti $L_{3,2}$ -edge and O K -edge were normalized to the edge jump (457.3 eV and 528.7 eV for Ti and O, respectively).

3. Theoretical Calculations

First-principles calculations based on DFT were performed on VASP to calculate the PDOS of $\text{Ti}_{1-x}\text{Sn}_x\text{O}_2$. Detailed information can be found in reference [7]. Furthermore, ligand field and charge transfer atomic multiplet calculations were performed in D_{4h} symmetry using CTM4XAS program 5.5 to generate the Ti $L_{3,2}$ -edge XANES spectra [9]. Initial values for these parameters were obtained from XLD results and then subsequently modified to improve the simulation. The

Lorentzian and Gaussian broadening factors are as follows: 0.17 and 0.15 (Ti $L_{3,2}$ -edge t_{2g} peaks), 0.15 and 0.35 (L_3 -edge e_g peak), and 0.05 and 0.58 (L_2 -edge e_g peak). Additional calculations were performed using SIESTA [See Supplementary Information] and FDMNES codes. Ti $L_{3,2}$ -edge XANES spectra for rutile $Ti_{1-x}Sn_xO_2$ films were calculated using full-potential finite difference method by solving the Schrödinger equation with the Hedin–Lundqvist exchange-correlation potential in the FDMNES code on 7 Å radius clusters [10, 11]. All simulated Ti $L_{3,2}$ -edge XANES spectra were convoluted with Lorentzian to account for finite core-hole lifetime and with a Gaussian FWHM of 0.2 eV and 0.3 eV for L_3 -edge and L_2 -edge respectively, to simulate experimental broadening.

4. Results and Discussions

In-depth analysis of the band structure changes in $Ti_{1-x}Sn_xO_2$ will be explained via O K -edge XANES and Ti $L_{2,3}$ -edge XANES studies in section 4.1 and section 4.2, respectively. The electronic transitions that correspond to the various peaks in the spectra are identified; the intensity ratios and the energy separation of the peaks of interest are plotted and studied in great detail to reveal conclusions on hybridization, electronic correlations, ligand field strength and long range bonding. Theoretical calculations are used to provide further insight into the results. Section 4.1 also covers the investigation of the effects of X /strain on hybridization in sub-section 4.1.1. Section 4.2 is further divided into three sub-sections: the evolution of multiplet-type electronic correlations (sub-section 4.2.1), ligand field strength (sub-section 4.2.2) and long-range bonding (sub-section 4.2.3) with variations in X /strain in $Ti_{1-x}Sn_xO_2$ films.

4.1 O K-edge XANES

FIG 1. (a) O K-edge XANES experimental spectra of $\text{Ti}_{1-x}\text{Sn}_x\text{O}_2$ films. (b) Spectra in (a) are stacked together to clearly demonstrate the evolution of the intensity for features H – N as X varies. The changes of absorption spectra $\Delta\mu(\text{X})$, defined as $\mu(\text{X}) - \mu(0\%)$, are presented below the XANES spectra, where $\mu(\text{X})$ is the absorption spectrum at Sn doping concentration X%. Inset shows the least-squares fit of Gaussian and Lorentzian functions and an arctan function for the O K-edge XANES spectrum of the 9.3% Sn-substituted TiO_2 film.

(c) Integrated spectral weight (ISW) (Left) defined as $\frac{SW(\text{X})}{SW(0\%)} = \frac{\int_{\omega_1}^{\omega_2} \mu(\omega, \text{X}) d\omega}{\int_{\omega_1}^{\omega_2} \mu(\omega, \text{X}=0\%) d\omega}$ for peaks H and I after arctan background removal in O K-edge spectra; ratio of the spectral weight (SW) (right) between peaks H and I. Dashed lines serve as visual guide. The error bars in X and the very small error bars on y-axes are marked in purple and green, respectively. The error bar in X is $\pm 5\%$ of the actual values. More details on error analysis can be found in Supplementary Information. (d) PDOS of Sn 5s and 5p orbitals and O 2p orbitals in $\text{Ti}_{1-x}\text{Sn}_x\text{O}_2$ thin films (X = 3.3%, 6.7% and 10%), as calculated by DFT-VASP.

The spectra in **Fig. 1a – b** were characterized by two relatively sharp features (526 – 535 eV)

near the absorption edge, followed by three broad resonances (535 – 572 eV) at higher energies; they are acquired with polarization parallel to the film surface. The transitions of O1s electron to all four molecular orbitals of TiO₂ are dipole allowed due to presence of *p*-character in these hybridized orbitals. Generally, the first four O *K*-edge features (526 – 548 eV) can be assigned to the one electron transition from the O1s orbital to the 2*t*_{2g}, 3*e*_g, 3*a*_{1g} and 4*t*_{1u} orbitals of TiO₂, respectively [12]. The changes of absorption spectra $\Delta\mu(\mathbf{X})$, defined as $\mu(\mathbf{X}) - \mu(0\%)$, are presented below the spectra in **Fig. 1b**. The prominent fine structures in the O *K*-edge spectra from 525 – 550 eV in **Fig. 1b** indicate low concentration of oxygen vacancies in the Ti_{1-x}Sn_xO₂ films [13].

4.1.1 Effects of X/strain on hybridization

The edge onset region of the O *K*-edge XANES spectrum is generally very sensitive to transition metal 3*d* and O2*p* hybridization whereas the higher energy features are more susceptible to *sp* hybridization [14]. The first two peaks (**H** and **I**) in each spectra constitute electron transitions from O1s states to the O2*p*–Ti3*d* hybridized states (2*t*_{2g} and 3*e*_g), which are split into *t*_{2g} and *e*_g orbitals because of ligand-field splitting. Since the O *K*-edge XANES reveals transitions from O1s to unoccupied states related to O2*p* states hybridized with metal states, it is directly related to the corresponding hybridization strength. The relative hybridization strength of O2*p*–Ti3*d* *t*_{2g} and *e*_g orbitals in Ti_{1-x}Sn_xO₂ and their ratio as functions of **X**/strain are summarized in **Fig. 1c**. The trends of the O2*p*–Ti3*d* hybridization strength vs. **X**/strain are found to be opposite for *t*_{2g} (**H**) and *e*_g (**I**) orbitals, which follow positive and negative quadratic-like trends respectively. At low **X** (~2.3%),

Ti3d e_g –O2p hybridization of feature **I** is the strongest, while the Ti3d t_{2g} –O2p hybridization of peak **H** is the weakest.

The second broad resonance (535 – 548 eV) exhibits larger dispersion effects and is more sensitive to long-range order [15]. Feature **J** is attributed to the transition from O1s to the O2p antibonding state [13, 16] whereas features **K** and **L** are primarily ascribed to O2p character hybridized with Ti4s and 4p states ($3a_{1g}$ and $4t_{1u}$) [17]. This broad resonance is related to the O_h symmetry set up by the nearest oxygen neighbors which surround the Ti atoms octahedrally [17]. The pronounced differences among the $Ti_{1-x}Sn_xO_2$ films and pure TiO_2 observed in this spectral region thus evince different stacking of the MO_6 (M : Ti/Sn) octahedron across different **X**/strain values [18]. The hybridization of O2p–Sn5sp orbitals in the CB has also been confirmed in the calculated partial density of states (PDOS) of $Ti_{1-x}Sn_xO_2$ (overlapping region: 2 – 4.5eV), as shown in **Fig. 1d**. At low **X** (~1.1 – 4.8%) /strain, peaks **J** and **K** became much more enhanced due to additional contributions of electron transfer from O1s states to the strongly hybridized O2p–Sn5sp unoccupied states [19, 20]. However, at high **X** (~9.3%) /strain, the intensities of peaks **J** and **K** decrease. This phenomenon can be accounted by the corresponding changes in the Sn5sp PDOS calculated by DFT-VASP, as shown in **Fig. 1d**. The changes in the integral area of the Sn5s and 5p PDOS (number of Sn5s and 5p orbitals) with respect to **X** displayed similar trend as the variation in intensities of peaks **J** and **K** relative to **X**. This implies that the larger number of Sn5s and 5p orbitals will lead to more hybridization of the O2p–Sn5sp states.

The higher energy resonance peak **M** corresponds to the transition to higher-lying t_{1u} type orbitals [21]; its existence signifies the presence of long-range order in the band structure and crystalline nature of the samples [22]. As X /strain increases, the spatial distribution of the Sn ions in the TiO_2 lattice tends to be more uniform, giving rise to long-range order in the crystal. This explains the presence of feature **M** in the O K -edge spectra of 9.3% Sn-substituted TiO_2 .

4.2 Ti $L_{3,2}$ -edge XANES

FIG. 2. (a) Ti $L_{3,2}$ -edge XANES experimental spectra of $\text{Ti}_{1-x}\text{Sn}_x\text{O}_2$ films. The dashed lines represent the best fit lines for estimation of the onset values of the Ti L_3 -edge XANES spectra. For each spectrum, this onset was estimated using the intercept on the abscissa obtained by extrapolating the low energy edge to the baseline using a best fit. The black dotted line provides a rough guide to the shift in peak **A** with respect to pure TiO_2 . (b) Spectra in (a) are stacked together to clearly demonstrate the evolution of the intensities for features **A** – **E** as X

varies. The changes of absorption spectra $\Delta\mu(\mathbf{X})$ are presented below the XANES spectra. Inset shows the least-squares fit of Gaussian, Voigt, Lorentzian functions and an arctan function for the Ti $L_{3,2}$ -edge XANES spectrum of the 9.3% Sn-substituted TiO_2 film. (c) Simulated Ti $L_{3,2}$ -edge XANES spectra using CTM4XAS program. (d) Simulated Ti $L_{3,2}$ -edge XANES spectra using FDMNES code.

The spectra of $\text{Ti}_{1-x}\text{Sn}_x\text{O}_2$ films are acquired with polarization parallel to the film surface in **Fig. 2a**. Since $L_{3,2}$ -edge XANES is more surface sensitive than K -edge, it is more suitable for the analysis of the ~ 3.5 nm $\text{Ti}_{1-x}\text{Sn}_x\text{O}_2$ films. The spectra arise from excitations of a core electron from ground state $2p^6 3d^n$ to excited electronic configuration $2p^5 3d^{n+1}$ with different multiplet excitations [23]. SO splitting of the $2p$ orbitals into $2p_{3/2}$ (L_3) and $2p_{1/2}$ (L_2), and ligand field splitting of the $3d$ orbitals into e_g (d_z^2 and $d_{x^2-y^2}$ orbitals) and t_{2g} (d_{xy} , d_{xz} and d_{yz} orbitals), results in a manifold of four absorption peaks for the Ti $L_{3,2}$ -edge XANES of TiO_2 [24].

From **Fig. 2a**, there are two weak pre-edge shoulder peaks (**F** and **G**), followed by two series of sharp resonances denoted by **A**, **B** and **C** (L_3 band: 456 – 462 eV) and **D** and **E** (L_2 band: 462 – 468 eV) respectively [22]. The pre-edge region of the Ti $L_{3,2}$ -edge XANES spectra reflects the electronic structure near Fermi level (E_F). The two weak pre-peaks **F** and **G** correspond to transitions towards low lying virtual orbitals of t_{2g} -like symmetry, and are an effect of the mixing of particle-hole configurations [25]. They possess triplet character and are mixed into the L_3 -edge by spin-orbit coupling and Coulomb repulsion [26]. They are associated with forbidden transitions in the SO coupling but become allowed as a result of the pd multipolar interactions [27]. The pre-peaks originated from $2p^6 d^0 \rightarrow 2p^5 d^1$ transition for Ti^{4+} in O_h symmetry [16, 28].

Peaks **A** and **D** can be ascribed to transitions to unoccupied t_{2g} levels whereas peaks **B**, **C**, and **E** are attributed to transitions to unoccupied e_g levels [28]. The intensity of peak **C** (I_c) is higher than peak **B** (I_b) for all samples. This substantiates that the $Ti_{1-x}Sn_xO_2$ films are rutile [21, 22]. Since the e_g orbitals point to the ligands, the line shape of the e_g band is more sensitive to the symmetry of the Ti cation [28]. This implies that the variation in the Ti–O bond lengths due to the Ti displacement has a direct effect on peaks **B**, **C** and **E**. In contrast, the t_{2g} orbitals point in directions between the O^{2-} ions, so peaks **A** and **D** are less affected by the displacement of a Ti atom [27]. Thus, peaks **B**, **C** and **E** ($L_{3,2}-e_g$ states) show pronounced changes in intensities with variation in X /strain. Due to second-order Jahn–Teller distortion [29] where both the e_g orbitals are asymmetrically filled, the TiO_6 octahedron becomes distorted and is elongated along the [110] direction with different axial and equatorial Ti–O bond lengths ($Ti-O_{ax} = 1.984 \text{ \AA}$ and $Ti-O_{eq} = 1.944 \text{ \AA}$) [22, 24, 30]. As a result, the local D_{4h} symmetry at the Ti^{4+} site is reduced and this effect is made prominent by substitution of Sn^{4+} cation at the Ti^{4+} lattice site. Both multiplet-type electron correlation effects and the long-range bonding properties on a length scale of 1 nm in rutile TiO_2 influence the spectra shape significantly [13, 31]. The splitting of the e_g states denotes differences in the long-range band structure and the existence of the two pre-edge peaks signifies multiplet-type electron correlation effects. The two split $L_{2-}e_g$ peaks (**D** and **E**) in Figure 1a are unresolvable in the XANES spectra due to extra broadening of peak **E** ($L_{2-}e_g$). This happens as a result of shorter lifetime of the $p_{1/2}$ states and final-state vibrational broadening [26].

The changes of absorption spectra $\Delta\mu(X)$ are presented below the Ti $L_{3,2}$ -edge XANES spectra in

Fig. 2b. To deconvolute the numerous peaks for further analysis, Ti $L_{3,2}$ -edge XANES spectra are fitted with a series of Gaussian, Voigt, Lorentzian functions to correspond to the spectral features and an arctan function was used to model the ionization edge of the samples. The inset in **Fig. 2b** shows a typical example of the least-squares fit for the 9.3 % Sn-substituted TiO_2 film.

To gain deeper understanding of the multiplet-type electronic correlations within the $\text{Ti}_{1-x}\text{Sn}_x\text{O}_2$ system, ligand field and charge transfer atomic multiplet calculations are performed using the CTM4XAS program. The Ti $L_{3,2}$ -edge XANES spectra in **Fig. 2c** are generated from CTM4XAS calculations to match the parameters of the experimental spectra and the FDMNES-simulated spectra. However, screening effects in solid state are not included during the calculations [32], leading to some discrepancies of the CTM4XAS-simulated results at the pre-edge region, as compared to the experimental ones. To further support the qualitative deductions, simulations of the Ti $L_{3,2}$ -edge XANES spectra for rutile $\text{Ti}_{1-x}\text{Sn}_x\text{O}_2$ ($x = 0, 2.3, 4.8$ and 9.3 %) films were also performed using FDMNES codes and the resultant simulated spectra are plotted in **Fig. 2d**. The simulated spectra shows evident splitting of the e_g states (peaks **B'** and **C'**) and presence of the two pre-edge peaks **F'** and **G'**. The analysis of the CTM4XAS and FDMNES-simulated spectra will be further discussed in **Fig. 3** and **4**.

4.2.1 Effects of X/strain on multiplet-type electronic correlations

FIG. 3. (a) Experimental (left) and FDMNES-simulated (right) onset of Ti L_3 -edge XANES spectra as functions of $\mathbf{X}$ /strain. Inset: onset of Ti3d PDOS from DFT-VASP calculations. (b) Experiment [from **Fig. 2a**]: peak A position (left) and its separation from pre-edge peak F (right) as functions of $\mathbf{X}$ /strain. (c) FDMNES-simulations [from **Fig. 2d**]: Position of peak A' (left) and its relative position to pre-edge peak F' (right) are given as functions of $\mathbf{X}$. Inset displays the graph of the total integral area of Ti3d PDOS in CB vs. $\mathbf{X}$, as calculated by DFT-VASP. (d) Experimental Ti L_3/L_2 Branching Ratio (left) and CTM4XAS-calculated G_{pd}^1 and G_{pd}^3 terms (right) as functions of $\mathbf{X}$ /strain. (e) Experimental values of apparent Ti2p SO splitting are presented as a function

of $\mathbf{X}$ /strain. Dashed lines serve as visual guide to the trends in (a) and (b) whereas dotted lines through the experimental points in (d) and (e) are the best fit lines. The error bars in $\mathbf{X}$ in (a), (b), (d) and (e) are $\pm 5\%$ of the actual values. More details on error analysis can be found in Supplementary Information.

Here, we present the first experimental investigation of the evolution of the following parameters with respect to $\mathbf{X}$ /strain: 1) onset of Ti L_3 -edge XANES, 2) position of peak **A** and its separation from the first pre-edge peak **F** (S_{AF}), 3) Ti L_3/L_2 branching ratio (B_R), 4) apparent Ti2*p* SO splitting [33, 34], 5) ligand field splitting and 6) e_g splitting of the $Ti_{1-x}Sn_xO_2$ films.

The experimental onset of Ti L_3 -edge XANES spectra was estimated using the intercept on the abscissa obtained by extrapolating the low energy edge to the baseline using a best fit line which is plotted in the form of a dashed line in **Fig. 2a**. The experimental and simulated onset of Ti L_3 -edge XANES spectra as functions of $\mathbf{X}$ /strain are plotted in **Fig. 3a**. From the DFT-VASP results plotted in the inset of **Fig. 3a**, the energy onset of the Ti3*d* PDOS in the CB was shown to increase with increment in $\mathbf{X}$. This indicates upshift of the Ti3*d* band with addition of Sn, which supports the experimental and simulated FDMNES results.

The experimental and FDMNES-simulated energy of peak **A** (Ti $L_3 t_{2g}$) and S_{AF} as functions of $\mathbf{X}$ are displayed in **Fig. 3b** and **3c**, respectively. The trend of peak **A** position vs. $\mathbf{X}$ resembles that of S_{AF} vs. $\mathbf{X}$. These experimental results are consistent with the FDMNES-simulated results, thereby verifying that Sn^{4+} ions have indeed substituted Ti^{4+} in the host lattice sites which formed the initial start-off point in the simulations. The exact positions of the small leading pre-edge peaks are related to the covalent screening of intra-atomic ($p-d$) Coulomb repulsion term $g(i, j)$ [See

Supplementary Information]. When the pre-peaks are closer to the rest of the spectra, it is a mark of decreased $g(i, j)$ [26]. The inset in **Fig. 3c** displays the total integral area of Ti3d PDOS in the conduction band (CB) vs. **X**, as calculated by DFT-VASP. It shows a similar trend to the curve of S_{AF} ($S_{AF'}$) in **Fig. 3b**, verifying that Sn substitution has led to Ti3d orbital reconstruction. During XAS, Ti2p electrons are promoted to the unoccupied Ti3d states in the CB. Thus, the amount of intra-Coulomb repulsion experienced by the electrons within the same orbital is proportional to the number of unoccupied Ti3d (antibonding) orbitals in the CB of $Ti_{1-x}Sn_xO_2$, which eventually determines S_{AF} in a proportional manner.

B_R is deduced from the ratio between the area of Ti L_3 and Ti L_2 features which are obtained from peak fitting the spectra in **Fig. 2b** and is plotted as function of **X**/strain in **Fig. 3d**. B_R for rutile TiO_2 is found to be ~ 0.72 . Within one-electron approximation, B_R should follow the ideal statistical value 2:1 according to the numbers of electrons in the $2p_{3/2}$ and $2p_{1/2}$ subshells [25]. This observed deviation is caused by the interplay of configuration mixing and SO relativistic coupling [25]. From the CTM4XAS results, the exchange multi-pole interaction terms G_{pd}^1 and G_{pd}^3 are found to be the dominant factors in determining B_R . They are also plotted as functions of **X**/strain in **Fig. 3d**. B_R , G_{pd}^1 and G_{pd}^3 values [See Supplementary Information] all decrease almost linearly with **X**/strain, indicating that B_R is proportional to G_{pd}^1 and G_{pd}^3 . The results reinforce the importance of multiplet effects in determining the changes in B_R .

The SO coupling splits the Ti2p initial levels into $2p_{3/2}$ and $2p_{1/2}$ states. From **Fig. 2a**, the

apparent SO splitting of Ti $L_{3,2}$ -edge XANES is measured as the peak-to-peak distance from peak **A** ($L_3 t_{2g}$) to **D** ($L_2 t_{2g}$) and plotted as a function of X /strain in **Fig. 3e**. The apparent Ti2*p* SO splitting of rutile TiO₂ is ~5.53 eV, in excellent agreement with the 5.5 eV experimental value reported in reference [35]. Ti2*p* SO splitting is found to decrease linearly with X due to increase in compressive strain, which is in agreement with the results of the CTM4XAS-calculated Ti2*p* SO coupling. The increase in strain leads to inversion symmetry breaking at the interface of the Ti_{1-x}Sn_xO₂ films, thereby creating and drastically affecting the strain-induced Dresselhaus term [36] in the effective Hamiltonian H_{SO} [See Supplementary Information], and hence results in the decrease of the Ti2*p* SO splitting.

4.2.2 Effects of X /strain on ligand field strength

FIG. 4. (a) ISW (Left) defined as $\frac{SW(X)}{SW(0\%)} = \frac{\int_{\omega_1}^{\omega_2} \mu(\omega, X) d\omega}{\int_{\omega_1}^{\omega_2} \mu(\omega, X=0\%) d\omega}$ for peaks **D** and **E** after arctangent background removal in Ti L_2 -edge spectra; ratio of SW (right) between peaks **D** and **E**. The error bars in **X** in (a) and (b) are $\pm 5\%$ of the actual values. More details on error analysis can be found in Supplementary Information. Peak separation (left) and relative intensity ratios (right) vs. **X** are plotted for the following: (b) Ti L_2 band: Peaks **D** and **E** [from **Fig. 2a**]; Dashed lines serve as visual guide and (c) Ti L_2 band: Peaks **D'** and **E'** [from **Fig. 2d**]. (d) CTM4XAS-calculated ligand field strength as a function of **X**.

Since the Ti $L_{3,2}$ -edges reflect $Ti2p_j \rightarrow Ti3d$ transitions, they are directly related to the occupancy of $Ti3d$ orbitals. The integrated spectral weight (ISW) shows an increase in the $Ti3d$ orbitals occupancy in both t_{2g} and e_g orbitals with increment in **X**/strain, as shown in **Fig. 4a**. The splitting of the t_{2g} and e_g features in L_3 and L_2 -edge XANES is related, though not equal and both of them are related to the ligand field strength (Δ). Generally, increase in Δ will lead to a greater separation between t_{2g} and e_g states, as well as an increase in the intensity of the t_{2g} peak relative to the e_g peak [22]. To account for the changes in Δ with respect to **X**/strain, the trends of the experimental energy separation (E_R) and relative intensity ratio (I_R) of the Ti L_2 -edge features (**D** and **E**) are deduced from the experimental data obtained in peak fitting the experimental spectra (**Fig. 2b**); they are presented in **Fig. 4b**. These trends are found to be similar to those of the Ti L_3 -edge. The experimental E_R between peaks **D** and **E** for pure TiO_2 is 2.34 eV, close to the computational value reported in reference [25]. Similarly, the E_R and I_R of peaks **D'** and **E'** are extracted from the FDMNES-simulated spectra (**Fig. 2d**) and their variation tendencies as functions of **X** are plotted in **Fig. 4c**; they share similar trends as the experimental results in **Fig. 4b**. CTM4XAS-calculated ligand field strength (Δ_c) is plotted as a function of **X**/strain in **Fig. 4d** and surprisingly, this trend is found to be proportional to the trends in the variation of I_R of peaks **D(D')** and **E(E')** vs.

$\mathbf{X}$ /strain. Interestingly, the change in Δ_c is not proportional to $\mathbf{X}$ /strain. In addition, the trend in the variation of Δ_c vs. $\mathbf{X}$ /strain is similar to the trend in the ratio between relative hybridization strength of $O2p$ - $Ti3d_{t_2g}$ and e_g orbitals vs. $\mathbf{X}$ /strain (**Fig. 1d**), as well as the trend in the ratio between $Ti3d_{t_2g}$ and e_g orbitals occupancy vs. $\mathbf{X}$ /strain (**Fig. 4a**). This implies that both $O2p$ - $Ti3d$ hybridization and occupancy of $Ti3d$ antibonding orbitals contribute to Δ . Furthermore, the variation tendency of E_R seems to be opposite to that of its respective I_R , as observed in **Fig. 4b-c**. This trend of E_R between $Ti3d_{t_2g}$ and e_g states of $L_{3,2}$ -edges vs. $\mathbf{X}$ /strain is found to be opposite to the trends of the energy of peak **A** and S_{AF} vs. $\mathbf{X}$ /strain in **Fig. 3b**. These observations are in accord with ligand field theory, suggesting that Δ is tunable by $\mathbf{X}$ and hence strain.

4.2.3 Effects of $\mathbf{X}$ /strain on long range bonding

FIG. 5. (a) The Ti $L_{3,2}$ -edge XANES spectrum ($E \parallel z'$ and $E \perp z'$) and the resultant Ti $L_{3,2}$ -edge XLD spectra of the 4.8 % Sn-doped TiO_2 film. (b) Experimental peak separation (left) and ratio of SW (right) between peaks **C** ($Ti3d_z^2$) and **B** ($Ti3d_{x^2-y^2}$) [from **Fig. 2a**] (right) vs. $\mathbf{X}$. Dashed lines serve as visual guide. The error bar in $\mathbf{X}$ is ± 5 % of the actual values. More details on error analysis can be found in Supplementary Information. Inset: Ratio S of the integral area of $Ti3d_z^2 : 3d_{x^2-y^2} (e_g)$ PDOS in the CB as a function of $\mathbf{X}$, as calculated by DFT-VASP.

X-ray linear dichroism (XLD) is particularly sensitive to any distortion of the TiO_6 octahedron, thus useful information on the eventual presence of orbital reconstructions can be obtained. **Fig. 5a** shows the Ti $L_{3,2}$ -edge XLD spectrum for the 4.8 % Sn-substituted TiO_2 film. The XLD spectra of all other $\text{Ti}_{1-x}\text{Sn}_x\text{O}_2$ films possess similar shape. XLD is obtained by taking the difference between Ti $L_{3,2}$ -edge XANES spectra acquired with a parallel polarization and a perpendicular polarization to the film surface. The XLD results shows that the $\text{Ti}3d_{xy}$ orbital has lower energy than the d_{xz} and d_{yz} orbitals whereas the $\text{Ti}3d_{x^2-y^2}$ orbital is lying at a lower energy than d_z^2 orbital in the CB. These results implied an elongation of the TiO_6 octahedron [37] along the surface normal [110] and is consistent with atomic theory [See Supplementary Information], our X-ray diffraction (HR-XRD) and HR-TEM results reported in reference [7].

The E_R (S_{BC}) and ratio of the spectral weight (SW) between the L_3 - e_g features **B** ($d_{x^2-y^2}$) and **C** (d_z^2) vs. X/strain are presented in **Fig. 5b**. S_{BC} for pure TiO_2 is 1.16 eV, close to the experimental value reported by reference [35]. Non-local long-range interactions [30] between states originating from the donor-acceptor orbitals located on different Ti centers are responsible for the characteristic e_g orbital splitting; these interactions are essentially determined by the long-range band structure [28, 31] that changes with X/strain . This is ascribed primarily to the structural differences beyond the first nearest-neighbor shell - the different stacking of the MO_6 octahedron, rather than the distortion of the individual octahedron [31]. Firstly, the Sn–O bond length and bond angle differ from those of Ti–O, this causes the stacking of the MO_6 octahedron to vary with

X /strain. Secondly, the larger size of the substituted Sn^{4+} ions will cause the cell volume of the MO_6 octahedron to expand. All these changes influence the overall connectivity of the MO_6 octahedrons, thus leading to changes in the long-range bonding. The inset in **Fig. 5b** shows the plot of ratio S between the integral area of $\text{Ti}3d_{z^2} : 3d_{x^2-y^2}$ PDOS in the CB as a function of X , as calculated by DFT-VASP; the results are consistent with the XLD results and implies that $\text{Ti}3d_{z^2}$ orbital is lying at a higher energy than $d_{x^2-y^2}$ orbital in the CB. When $1.1\% \leq X \leq 4.8\%$, S_{BC} is relatively smaller than those of pure TiO_2 and 9.3% Sn-substituted TiO_2 , implying the distinct difference in the long-range bonding in the samples. These results are also in parallel with existence of long range order (feature **M** in **Fig. 1b**) in TiO_2 and 9.3% Sn-substituted TiO_2 which is absent in the low X films. This indicates that the spatial distribution of Sn ions in low X films is similar but different from that of 9.3% Sn-substituted TiO_2 .

Furthermore, charge transfer effects involving ligand electron transferred to metal site and metal-metal charge transfer are found to play an important role in the characteristic e_g orbital splitting in the CTM4XAS calculations, which include the correlation energies of two or more configurations on top of the transition of the core electron to the valence state. The two initial states and two final states are coupled by hybridization between $\text{O}2p$ and $\text{Ti}3d$ orbitals. Charge-transfer effects are amplified as X /strain changes, which vary the ratio among e_g and t_{2g} mixing, thereby drastically affecting the e_g orbital split.

5. Conclusions

In summary, we have established the correlations between the changes in hybridization, multiplet-type electronic correlations, and bonding properties with strain doping along a single axis in rutile pseudo-homoepitaxial $\text{Ti}_{1-x}\text{Sn}_x\text{O}_2$ (110) films. The trends of the $\text{O}2p\text{--Ti}3d$ hybridization strength as functions of $\mathbf{X}$ /strain are found to be opposite for t_{2g} and e_g orbitals, which follow positive and negative quadratic-like trends, respectively, with $\mathbf{X} \approx 2.3\%$ as the turning point in the curves. As $\mathbf{X}$ increases from 0% to 4.8%, the corresponding increase in the number of $\text{Sn}5s$ and $5p$ orbitals leads to more hybridization of the $\text{O}2p\text{--Sn}5sp$ states while the corresponding decrease in the number of $\text{Sn}5s$ and $5p$ orbitals leads to less hybridization of the $\text{O}2p\text{--Sn}5sp$ states when $\mathbf{X}$ further increases from 4.8% to 9.3%. Ligand field strength varies with $\mathbf{X}$ /strain in the form of a positive quadratic-like curve, with $\mathbf{X} \approx 2.3\%$ as the turning point. Both $\text{O}2p\text{--Ti}3d$ hybridization and occupancy of $\text{Ti}3d$ antibonding orbitals are found to contribute to the ligand field strength. In terms of electronic correlations, the increment in $\mathbf{X}$ /strain also results in the linear decrease of the following terms: 1) exchange multi-pole interaction terms G_{pd}^1 and G_{pd}^3 , 2) $\text{Ti } L_{3,2}$ branching ratio and 3) apparent $\text{Ti}2p$ SO splitting. Increasing $\mathbf{X}$ /strain leads to the upshift of the $\text{Ti}3d$ band and also results in the continuous elongation of the MO_6 octahedron along [110], causing the energies of the $\text{Ti}3d$ orbitals to further split in the ascending order: $d_{xy} < d_{xz}, d_{yz} < d_x^2 - y^2 < d_z^2$. The changes in e_g splitting relative to $\mathbf{X}$ /strain reveal that the long-range bonding, charge transfer, and spatial distribution of Sn^{4+} ions in TiO_2 films with low $\mathbf{X}$ (1.1% - 4.8%) are similar but different from those of pure TiO_2 and 9.3% Sn-substituted TiO_2 . We find that the multiplet-type electronic correlations, long-range bonding and hybridization in the system can be controlled

by independently changing uniaxial strain, thus significantly broadening the phase space for experimental exploration of predictive models and thereby leading to new possibilities for manipulation over materials' functional properties. The methodology presented here can be applied in general to study the nature of the electronic correlations and bonding properties in octahedral-coordinated $3d^N$ transition metal oxides.

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Editor's/Reviewer's comments:

Reviewer #1: The submitted manuscript is focusing on XANES and DFT calculation of strain induced by Sn doping in TiO₂ rutile substrate.

The presented work is unique, and the analysis approach is well worth for the publication. The reported work is based on recently reported work (Ref .7, *Applied Surface Science* 428 (2018) 710-717).

However, since the author mostly focusing on the XANES and DFT calculation, the manuscript lacks in detail of sample preparation and some of essential characterization of samples. It could fail to convince the reader or at least very difficult to follow. For example, Fig 3. a), b) and Fig 4. a), b) are plotted based on "lattice spacing along (110)". The lattice spacing was characterized by HR-TEM in the ref. 7, but no description was given in the manuscript. Also, the stoichiometry of samples were calculated by XPS in ref. 7, but I could not find any description in the manuscript.

In my opinion, this would be a much better paper if author combined this manuscript with the

published paper. To improve the manuscript, I would recommend the author to provide more material; at least how the samples's structure and stoichiometry were characterized.

Supplementary characterization approach like surface diffraction or GIWAXS would be very helpful to strengthen the quality of manuscript.

Minor suggestions and corrections

1. Fig 2. It would be much easy to compare with identical x-scale for both experiment and simulation.
2. almost all the figures do not have error bars in the plot
3. Fig 4 a) lattice spacing along (110) is not correct.