

Influence of Nb-doping on the local structure and thermoelectric properties of transparent TiO₂:Nb thin films

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Abstract

Transparent n-type niobium-doped titanium dioxide thin films (TiO₂:1.5 at.%Nb) with pronounced thermoelectric properties were produced from a composite Ti:Nb target by reactive magnetron sputtering. The thin films were comprehensively characterized by X-ray diffraction, X-ray photoelectron spectroscopy, optical spectroscopy, electrical conductivity, and thermoelectric measurement techniques. The local structure of the thin films was investigated in detail by X-ray absorption spectroscopy at the Ti and Nb K-edges. A set of radial distribution functions were extracted from the simultaneous analysis of EXAFS data at two absorption edges using the reverse Monte Carlo method. It was found that Nb dopant atoms modify the local environment of the films, but their average structure remains close to that of the anatase phase. This conclusion is also supported by the ab initio simulations of XANES. A very high absolute Seebeck coefficient ($S=155 \mu\text{V/K}$) for n-type TiO₂ was achieved with Nb doping, yielding a maximum power factor and thermoelectric figure of merit of $0.5 \text{ mW}\cdot\text{m}^{-1}\cdot\text{K}^{-2}$ and 0.18 at a temperature of 300 K, respectively, for a 150 nm thick film. From frequency-domain thermoreflectance experiments, a thermal conductivity value of $1.3 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ was obtained for the optimized TiO₂:Nb film.

Keywords: Thin films; TiO₂:Nb; Seebeck; Thermoelectric; EXAFS; Sputtering

1. Introduction

Transparent conducting oxides (TCOs) are electrically conductive materials with high transparency in the visible range. TCOs have wide-ranging applications in optoelectrical devices including photovoltaics, displays, optoelectrical interfaces and window glass technologies [1]. Touch-screen and solar cell applications require TCO coatings with high transparency (transmissivity >85% when averaged from 400 nm to 1100 nm and weighted by the solar spectrum), combined with useful electrical conductivity (typical resistivity around 10^{-4} Ωcm). In general, to achieve simultaneously the required transmittance and conductivity, the film thickness must be ~150 nm. The most utilized TCO is tin-doped indium oxide (ITO) [2]. Although it is easy to fabricate and possesses good conductive properties, because of its scarcity, poor chemical stability in hydrogen atmosphere and toxicity, there is a huge interest to develop alternative TCOs. Many potential candidates include doped ZnO and SnO₂, amongst other oxide materials, but it is necessary to explore new materials, in particular, thin film-based [3–6].

Recently, thin films have been also widely studied for thermoelectric applications [7]. Thermoelectric materials can convert thermal differences into electrical energy and vice-versa, where the Seebeck coefficient of a material is a measure of the magnitude of an induced thermoelectric voltage in response to a temperature gradient across it. The design of a TCO material with thermoelectric properties is the desired technology for touch-screen displays and solar cell applications, making it possible to produce electrical energy through the harvesting of heat from the environment [8].

Among different materials, titanium dioxide (TiO₂) thin films have interesting structural, optical, electronic and photocatalytic properties, which have been extensively documented in the literature [9]. To further this interest, cationic doping of TiO₂ and SrTiO₃ has been documented to improve its electrical conductivity properties [10,11]. In particular, in the present study, Nb-doped TiO₂ thin films were produced and investigated bearing in mind the material potential as a thermoelectric device. Most likely, niobium ions will be present in oxidation states 4+ and 5+ with ionic radii equal to 0.68 Å and 0.64 Å, respectively. It is expected that heavier pentavalent ions added through doping, such as Nb⁵⁺ in TiO₂, will inhibit the propagation of phonon vibration modes, thus reducing the phononic component of the thermal conductivity below $4 \text{ W m}^{-1} \text{ K}^{-1}$, and increasing the thermoelectric power and figure of merit of the film [12–14]. The choice of Nb for a pentavalent dopant is two-fold. First, the ionic radius of Nb⁵⁺ (0.64 Å) is slightly higher than that of Ti⁴⁺ (0.61 Å). Thus, it is suitable to create more phonon scattering and lower the thermal conductivity of the resulting microstructure, without introducing too much stress when the doping is below 5 at.%. Second, when Nb⁵⁺ substitutes Ti⁴⁺ in the TiO₂ lattice below the level of solubility, a charge unbalancing occurs, increasing the charge carrier concentration and, thus, also in electrical conductivity [10]. Other pentavalent ions such as vanadium and tantalum have a larger ionic mismatch and are prone to produce other oxides that will compete and inhibit the formation of a stable TiO₂ doped thin film.

2. Experimental details

Nb-doped titanium dioxide thin films with a thickness of 150 nm and 750 nm were deposited in an Ar/O₂ atmosphere at room temperature on Kapton® film (15 mm × 15 mm and 50 μm thick), glass slides (75 mm × 26 mm and 1 mm thick) and silicon substrates (15 mm × 15 mm and 0.5 mm thick) by reactive magnetron sputtering, from a pure Ti:Nb alloy target with 4 wt.% of Nb (FHR, 99.99% purity). Before the depositions, a turbo molecular pump was used to achieve a base pressure of ~10⁻⁴ Pa. The argon (working gas) and oxygen (reactive gas) flow rates were fixed at 40 sccm and 7.5 sccm, respectively, to attain optimised plasma conditions at a working pressure of 0.35 Pa. During the deposition of these films, the target-to-substrate distance was fixed at 100 mm, the cathode current density was set to 12.7 mA/cm², a substrate bias of -60V was applied to the substrate holder, with a temperature of 175 °C for substrate heating. These deposition conditions enable an effective ~2 at.% of Nb substitutional doping in the TiO₂ cell [10]. Subsequently to deposition, the as-deposited TiO₂:Nb films were annealed in the air for 1 h at 400 °C.

The thin film samples were comprehensively characterized by X-ray diffraction, X-ray photoelectron spectroscopy, optical spectroscopy, electrical conductivity and thermoelectric measurements.

A Bruker AXS D8 Discover system equipped with the copper anode X-ray tube (CuKα radiation) was used for X-ray diffraction experiments (XRD). The diffraction patterns were collected in the range of 2θ = 22-42° for as-prepared and annealed thin film samples to distinguish between anatase and rutile TiO₂ phases. The X-ray photoelectron spectroscopy measurements were carried out using monochromatic Al-Kα radiation (1486.6 eV) from a Kratos Axis-Supra instrument, from 3Bs Group, University of Minho. Photoelectrons were collected from a take-off angle of 90° relative to the sample surface. The measurement was done in a Constant Analyser Energy mode (CAE) with a 160 eV pass energy and 15 mA of emission current for survey spectra and 40 eV pass energy for high-resolution spectra, using an emission current of 15 mA. Charge referencing was done by setting the lower binding energy of the C1s hydrocarbon peak at 284.8 eV; an electron flood gun was used to minimize surface charging. Spectral transmittance and reflectance responses were measured with a Shimadzu UV-2501PC spectrophotometer, and the band-gap energy was calculated by plotting the squared absorbance versus the photon energy and extrapolating the linear fit of the plot to the photon energy axis [15].

The electrical properties were measured with an Ecopia AMP55T Hall Effect equipment equipped with a four-point probe in van der Pauw method. The Seebeck coefficient was evaluated in custom-made equipment operated in a vacuum (1 Pa) using two Peltier devices (Quick-Ohm Küpper & Co. GmbH) for heating and cooling the edges of 26 mm × 75 mm sample area. The heating and cooling stability was controlled by custom-developed software and hardware. The thermal conductivity of the TiO₂:Nb films was determined using frequency-domain thermoreflectance (FDTR) [16]. This technique is a non-destructive contactless optical method that uses two lasers, pump (405 nm) and probe (532 nm), to locally heat and probe the local temperature, respectively. In order to

1 enhance the thermal sensitivity of the method, a 60 nm thick Au transducer was
2 evaporated onto the surface of the specimens. Both lasers were focused using an
3 achromatic 30 mm focal distance lens to a spot size of $\approx 10 \mu\text{m}$ in diameter. The output
4 power of the pump laser was modulated to a harmonic waveform in the frequency range
5 between 30 kHz and 5 MHz, which generates thermally induced harmonic oscillations
6 of the reflectivity of the sample; thus, leading to a modulation of the reflected power of
7 the continuous wave probe laser. The key quantity that is addressed through this method
8 is the phase lag between the pump heat wave generated by the pump laser, and the
9 harmonic response of the sample as sensed by the probe laser using a lock-in amplifier.
10 The frequency dependent phase lag is modelled numerically solving the parabolic heat
11 equation for the described geometry. The thermal model used to fit the phase lag
12 response curve describes the behaviour of a stack of layers composed by the Au
13 transducer, the studied film, the substrate, and an effective thermal boundary
14 conductance that accounts for the two interfaces defined between the layers. The cross-
15 plane thermal conductivity (κ) and the specific heat capacity (C_p) of the thin films, as
16 well as the substrate-dependant effective thermal boundary conductance of the system
17 were fitted using a least-squares routine. It is important to note that the values of κ and
18 C_p for the Au transducer and the substrates were independently measured, and are used
19 as input parameters in the fitting procedure of the thermal properties of the thin films. In
20 addition, no difference between the in-plane and the out-of-plane components of the
21 thermal conductivity is expected since the typical crystallite size ($< 20 \text{ nm}$) is smaller
22 than the thickness of the thin films.
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29 Temperature-dependent X-ray absorption spectroscopy study of TiO₂:Nb thin films was
30 performed to determine the coordination environment of the dopant ions (Nb) and their
31 influence on titanium oxide matrix. Experiments were done in transmission and
32 fluorescence modes at P65 Applied XAFS beamline [17] of the PETRA III storage ring.
33 A set of powder samples (TiO₂, Nb₂O₅) was used for reference. The harmonic rejection
34 was achieved by uncoated and Rh-coated silicon plane mirrors. Fixed exit Si(111) and
35 Si(311) monochromators were used for the Ti and Nb K-edges, respectively. X-ray
36 absorption spectra were collected using two ionization chambers in transmission mode,
37 whereas passivated implanted planar silicon (PIPS) detector was used in fluorescence
38 mode. The Oxford Instruments liquid helium flow cryostat was used to maintain the
39 required sample temperature in the range of 10-300 K. For transmission measurements
40 at the Ti K-edge, a stack of thin films deposited on Kapton was produced, with the
41 number of layers giving the value of the absorption edge jump $\Delta\mu \approx 1$.
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49 **3. Data analysis**

50 **3.1. Reverse Monte Carlo calculations**

51 X-ray absorption spectra of Nb-doped TiO₂ thin film recorded at the Ti and Nb K-edges
52 were analyzed using the reverse Monte Carlo (RMC) method based on the evolutionary
53 algorithm (EA), implemented in the EvAX code [18]. First, the extended X-ray
54 absorption fine structures (EXAFS) $\chi(k)k^2$ were extracted using a conventional
55 procedure [19]. Strong overlap of the outer coordination shells coupled with the
56 presence of multiple-scattering contributions requires the use of the RMC approach.
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Further, simulation boxes (supercells) having different size ($4a \times 4b \times 2c$ for pure TiO₂, $5a \times 5b \times 2c$ for TiO₂:Nb) with periodic boundary conditions (PBC) were constructed based on anatase TiO₂ (I4₁/amd) crystallographic structure [20]. The size of the box was determined by the concentration of the dopant (Nb) element. RMC/EA calculations were simultaneously performed for 32 atomic configurations. At each iteration, the new atomic configuration was generated by randomly displacing all atoms in the simulation box with the maximally allowed shift of 0.4 Å to get the best possible agreement between the Morlet wavelet transforms (WTs) of the experimental and calculated EXAFS spectra at the Ti and Nb K-edges simultaneously. Note that for pure anatase TiO₂ only data for the Ti-K edge was used. The calculations were performed in the k -space range from 2.5 to 13 Å⁻¹ and in the R -space range from 0.8 to 4.5 Å. No significant improvement in the residual was observed after 5000 iterations. The configuration-averaged EXAFS spectra were calculated by ab initio real-space multiple-scattering (MS) FEFF8.50L code [21,22], including the MS effects up to 4th order. The scattering potential and partial phase shifts were calculated only once within the muffin-tin (MT) approximation [21,22] for the cluster with the radius of 5.5 Å, centred at the absorbing Ti (Nb) atom and constructed based on crystallographic anatase TiO₂ structure [20]. Small variations of the cluster potential due to atom displacements during the RMC/EA simulations were neglected. The photoelectron inelastic losses were accounted for within the one-plasmon approximation using the complex exchange-correlation Hedin-Lundqvist potential [23]. The amplitude reduction factor S_0^2 is included in the scattering amplitude [21,22], calculated by the FEFF code, and no additional correction of the EXAFS amplitude was performed.

3.2. XANES calculations

X-ray absorption near edge structure (XANES) calculations were performed using ab initio real-space FDMNES code [24,25] implementing the finite difference method (FDM). The dipole and quadrupole transitions were taken into account, and the energy-dependent real Hedin-Lundqvist exchange-correlation potential was used [24,25]. The relativistic FDM calculations were performed with self-consistent potential. The calculated XANES spectra were broadened to account for the core-hole level widths ($\Gamma(K\text{-Ti})=0.94$ eV and $\Gamma(K\text{-Nb})=4.14$ eV) [26] and other multielectronic phenomena. The energy origin was set at the Fermi level E_F . The clusters of different size (radius) were constructed from the crystallographic anatase structure [20] centred at the absorbing Ti atom, which was substituted by Nb to simulated doping.

4. Results and discussion

X-ray diffraction patterns of the as-deposited and thermally annealed TiO₂:Nb thin films deposited on Kapton substrates are shown in Figure 1. A single diffraction peak corresponding to a reflection from the (101) planes of anatase TiO₂ (I4₁/amd) is discerned at 25.4°, whereas for the thermally annealed film an additional diffraction peak is present at 27.3°, associated with a reflection from the (110) planes of rutile TiO₂ (P4₂/mnm). The broad background extended to lower diffraction angles is assigned to

the Kapton substrate. The average crystallite size for anatase and rutile phases are 19 and 9 nm, respectively. It should be noted that, experimentally, EXAFS averages over all atoms located both in crystalline and amorphous structures, while XRD amplifies the crystalline domains.

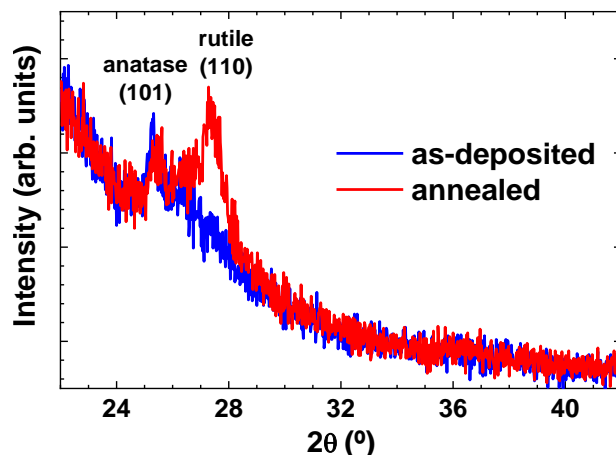


Figure 1. X-ray diffraction patterns of the as-deposited and annealed TiO₂:Nb thin films deposited on Kapton substrates.

To determine the chemical bonding state and film composition, XPS experiments were performed on a TiO₂:Nb thin film, as seen in Figure 2. The main peaks associated with binding energies of 458.9 eV, 530.3 eV and 207.5 eV are ascribed to Ti 2p, O 1s and Nb orbitals [27–29], as listed in Table I.

Peak	Position (eV)	FWHM (eV)	L-S (eV)	L-G	Area ratio	Concentration (at.%)
Ti 2p C1	458.9	1.2	5.7	0.3	2:1	28.7
Ti 2p C1	459.3	1.8	5.7	0.3	2:1	
O 1s C1	530.3	1.3	-	0.2	-	69.8
O 1s C2	532.1	1.3	-	0.2	-	
Nb 3d	207.5	1.1	2.8	0.2	3:2	1.5

Table I. XPS fitting parameters for as-deposited TiO₂:Nb thin film.

The spin-orbital (L-S) splitting is observed for both Ti 2p and Nb 3d core levels, being this splitting 5.7 eV and 2.8 eV, respectively; which is in agreement with the literature. It is also clear that the TiO₂ thin films have been efficiently doped with niobium, since peaks ascribed to binding energies of 207.5 eV are indexed to Nb 3d orbitals, while the L-S doublet separation (16 eV) registered in the survey spectra between 364 eV and 380 eV is attributed to Nb 3p orbitals of pentavalent Nb ions. From this analysis, it was obtained a level of Nb doping of 1.5 at.%. The Ti 2p core-level was fit with two components (C1 and C2) due to the asymmetry of the Ti 2p_{3/2} and 2p_{1/2} doublet peaks, which is not evident for undoped TiO₂ (not shown). C1 is attributed to Ti-O bonding, as in undoped anatase TiO₂. This asymmetry, registered for the C2 component (6.6% relative contribution), is attributed to the local order around the Ti⁴⁺ ions, resulting from

Ti-O and Nb-O bonds. As for the O 1s core level, the fit includes two components, C1 and C2, with respective weights of 48.5% and 51.5%, being associated with Ti-O bonds and adsorbed oxygen species at the film surface, respectively. Silicon traces were found in the survey spectra due to the incidence of the beam spot on the sample border, where the Si substrate is exposed. Specific constraints were considered for all XPS fits [28], namely relative area ratio, full width at half maximum (FWHM) and Lorentzian-Gaussian relative profile in doublet peaks.

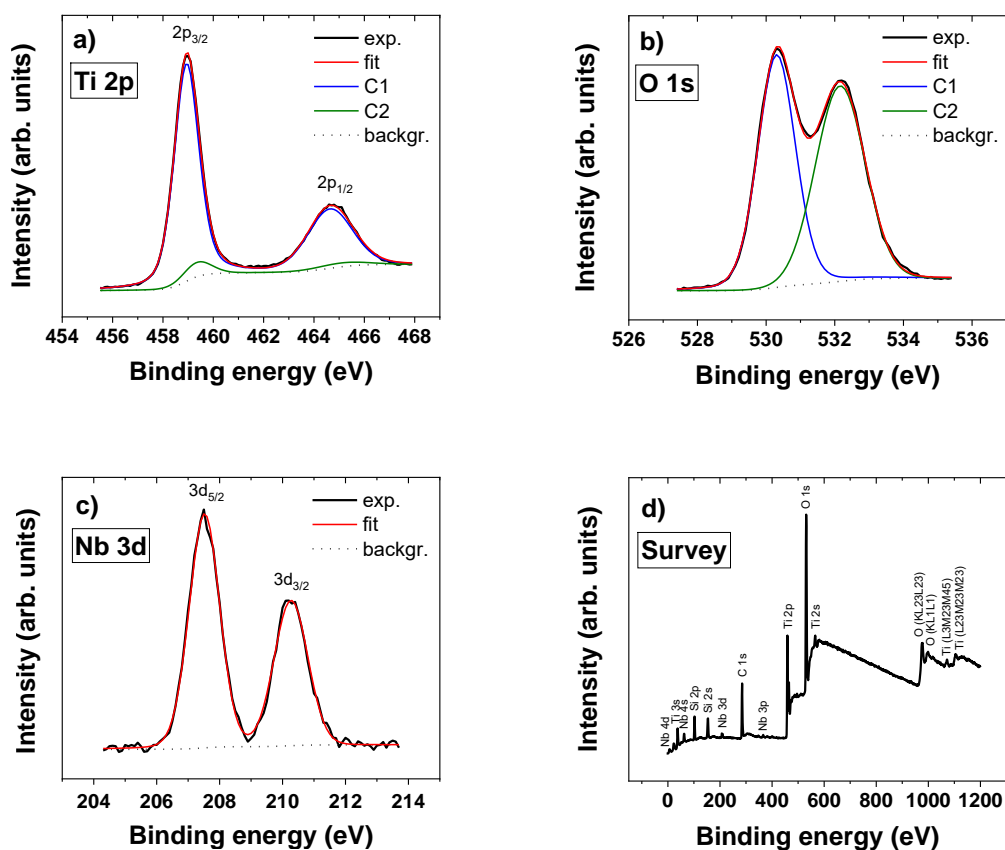


Figure 2. XPS experimental (exp.) spectra and respective fits for a TiO₂:Nb thin film where a) Ti 2p (fitted with 2 components, C1 and C2), b) O 1s (fitted with 2 components, C1 and C2) and c) Nb 3d core levels; in these plots the background (backgr.) is also shown. d) survey spectrum.

The local structure of as-prepared TiO₂:Nb thin film was studied by X-ray absorption spectroscopy. The experimental EXAFS spectra and their Fourier transforms (FTs) at the Ti and Nb K-edges for as-prepared TiO₂:Nb thin film and reference powders (TiO₂ and Nb₂O₅) are shown in Figure 3. A comparison of the EXAFS Ti K-edges in the film and two TiO₂ phases (rutile and anatase) unambiguously indicates the dominant anatase phase in the film. Subsequently, by comparing signals at the Nb K-edge in the film and Nb₂O₅ powder with the signal at the Ti K-edge in anatase TiO₂ powder, one can conclude that the local environment of Nb atoms in the film is close to that of Ti atoms in the anatase phase, but differ significantly from that in Nb₂O₅ powder. This suggests

that the substitution of Ti by Nb ions occurs in the film without a strong influence on the TiO₂ matrix.

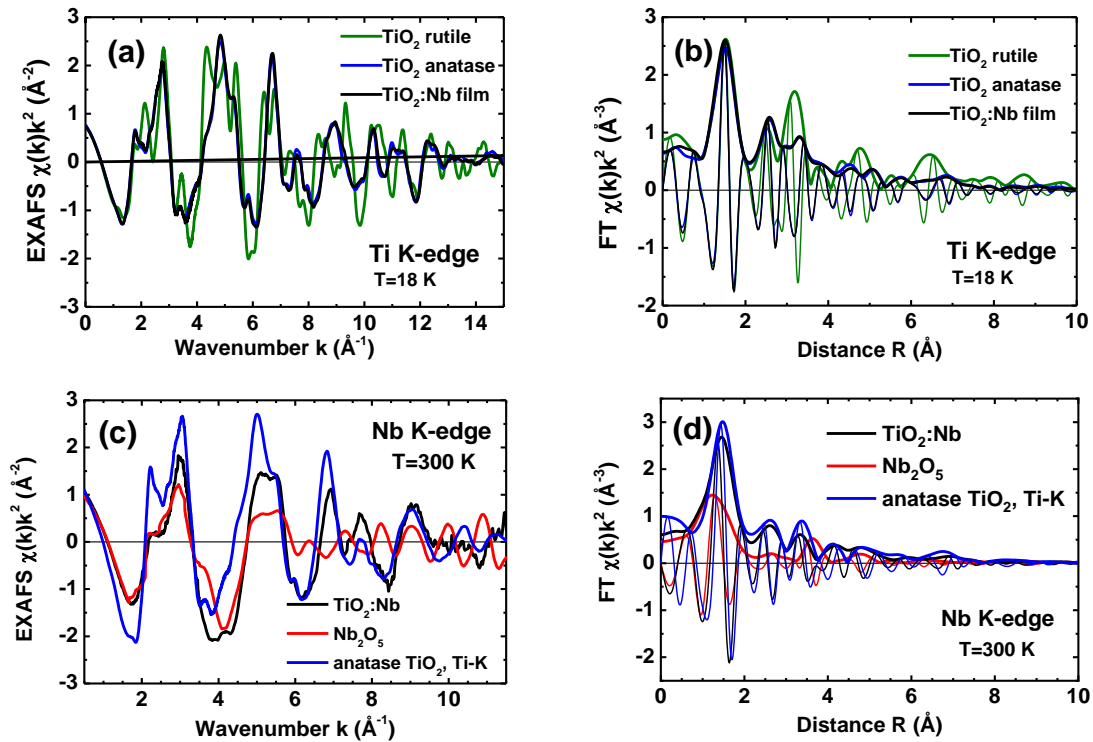


Figure 3. (a) Ti K-edges EXAFS $\chi(k)k^2$ spectra and (b) their Fourier transforms (FTs) at 18 K for rutile and anatase reference powders, and for as-prepared TiO₂:Nb thin film. (c) Ti and Nb K-edges EXAFS $\chi(k)k^2$ spectra and (d) their Fourier transforms (FT) at 300 K for as-prepared TiO₂:Nb thin film (Nb-K edge) and two reference powders – anatase TiO₂ (Ti K-edge) and Nb₂O₅ (Nb K-edge).

Before performing the RMC analysis of EXAFS for the Nb-doped TiO₂ film, an approach was tested using reference anatase TiO₂ powder. Figure 4 shows the experimental and calculated by RMC method Ti K-edge EXAFS spectra $\chi(k)k^2$ and their Fourier and Morlet wavelet transforms for anatase TiO₂ at two different temperatures (18 K and 300 K). The strong interatomic bonding in the anatase phase is responsible for a rather weak temperature dependence of the Ti K-edge EXAFS. However, some EXAFS oscillation damping at high- k values occurs upon temperature increase from 18 K to 300 K (Figure 4(a,b)) leading to the peak broadening in FTs (Figure 4(c,d)). The wavelet transforms (WTs) of EXAFS reflect the same thermal disorder effect simultaneously in k and R space. The WTs are dominated by the first shell contribution of six oxygen atoms (bright spots at $R=1.5$ \AA), whereas titanium atoms of the outer shells are main responsible for the WT complex pattern at longer distances (Figure 4(e,f)). The RMC simulation box was a $4a \times 4b \times 2c$ supercell with anatase TiO₂ structure and PBC, including 128 Ti and 256 O atoms. Hence, the RMC fits reproduce well the temperature-dependence of the Ti K-edge EXAFS spectra and respective WT patterns for anatase TiO₂, so that the EXAFS analysis including the contributions from the coordination shells located as far as up to 4-5 \AA can be reliably performed.

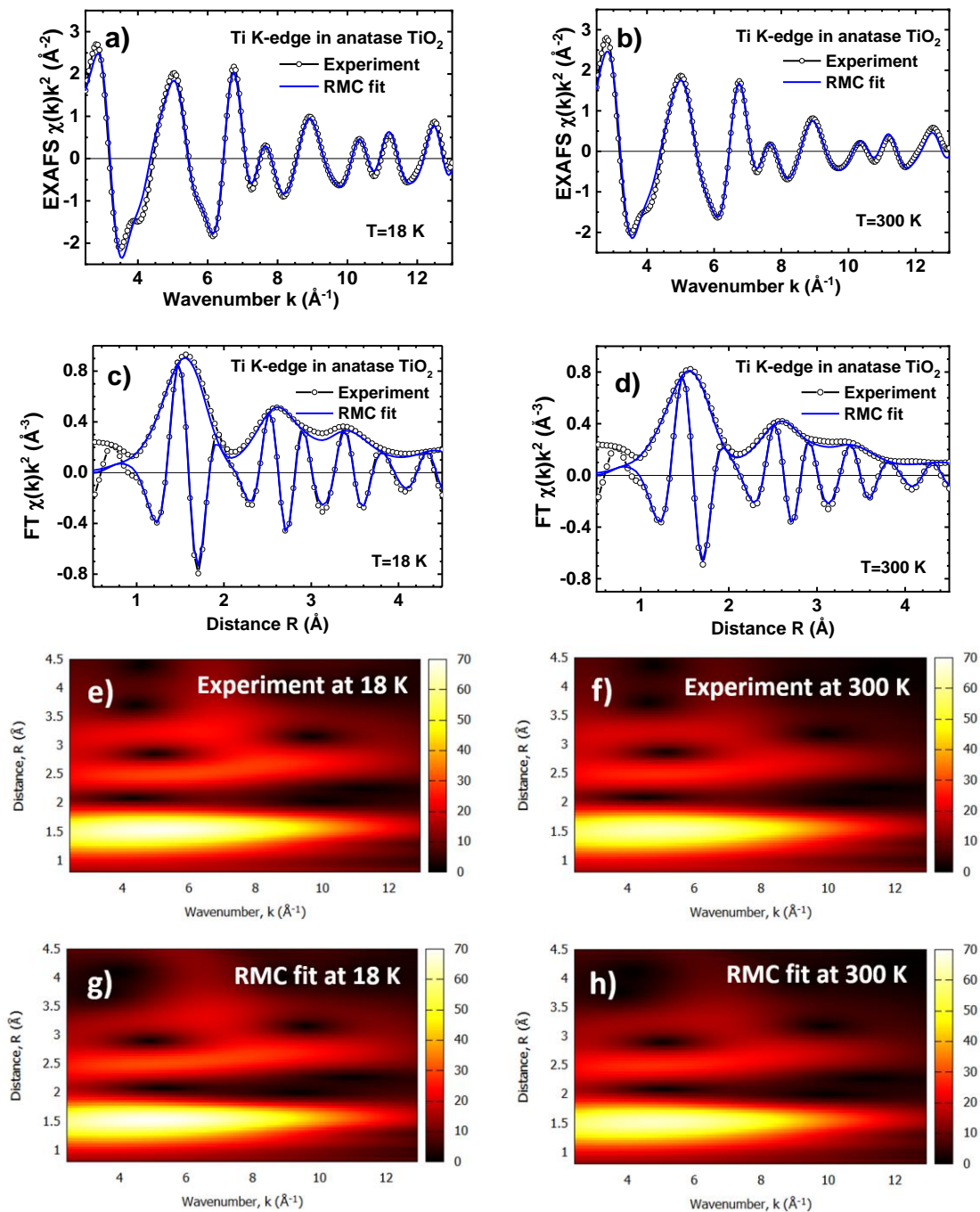


Figure 4. Experimental and calculated by RMC Ti K-edge EXAFS spectra $\chi(k)k^2$ (a, b) and their Fourier (c, d) and Morlet wavelet (e, f, g, h) transforms for anatase TiO₂ reference powder at 18 K and 300 K.

On a subsequent step, the RMC simulations were applied to the simultaneous analysis of the Ti and Nb K-edges EXAFS spectra of TiO₂:Nb thin film at 300 K. The obtained results are shown in Figure 5. The RMC simulation box was a larger 5a×5b×2c supercell with anatase TiO₂ structure comprising 10% of Ti atoms substituted randomly by Nb atoms, resulting in a total of 180 Ti, 20 Nb and 400 O atoms in the supercell. As in the case of anatase TiO₂, the RMC simulation fits very well the experimental data of TiO₂:Nb thin film at both edges simultaneously and over a large (more than 4 Å)

distance range in *R*-space. Note that in this case, the single structural model can describe well the environment around both Ti and Nb atoms taking into account the structure relaxation due to a difference in the Ti-O and Nb-O bonding. The similarity of the local atomic structure around Ti and Nb atoms in the TiO₂:Nb thin film is well reflected by close WT patterns (Figure 5(e,f)), which are well reproduced in the RMC simulations (Figure 5(g,h)). Similar RMC simulations (not shown), with 5% of substituting Nb atoms and including 190 Ti, 10 Nb and 400 O atoms in the supercell, gave close agreement with the experimental data.

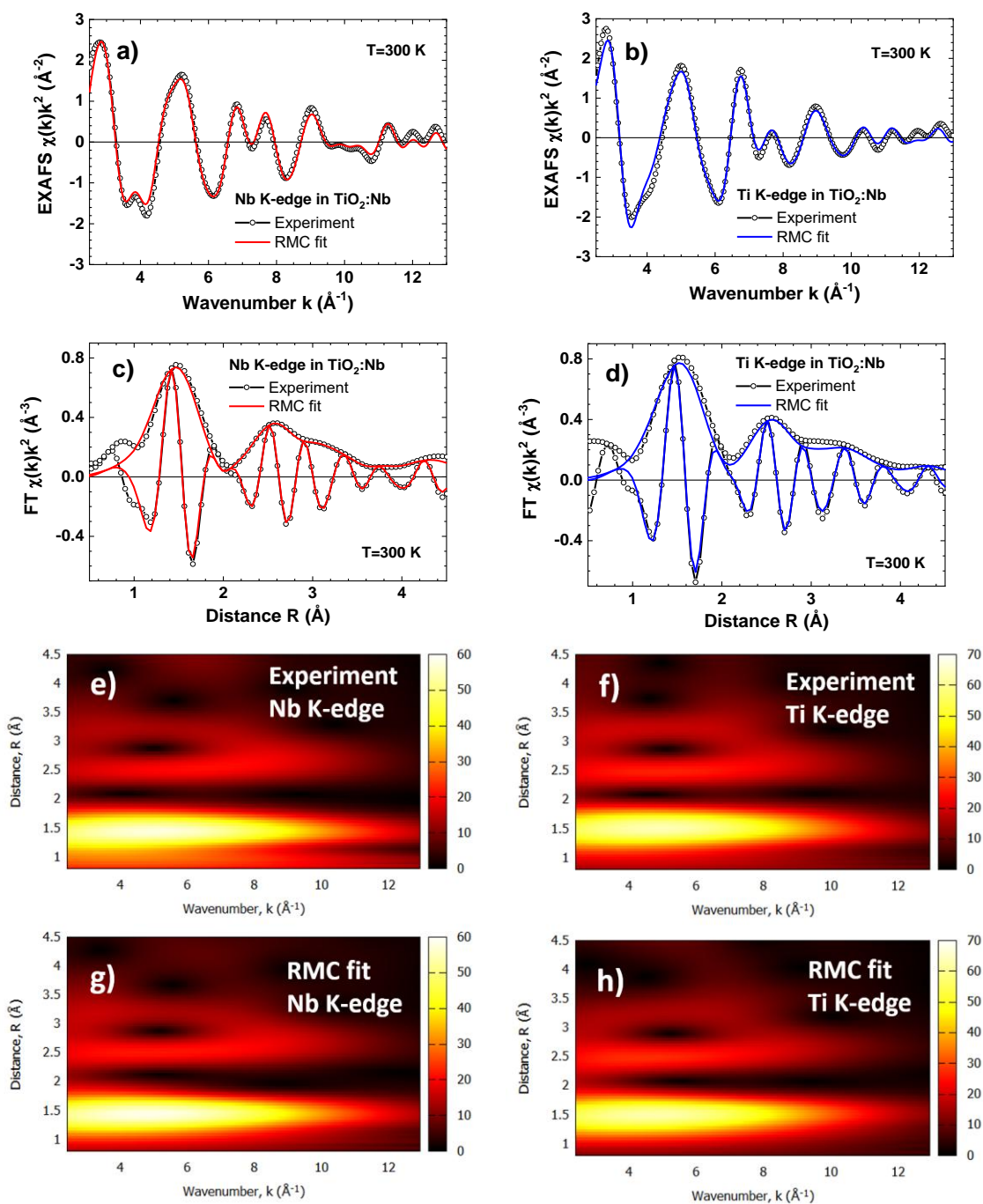


Figure 5. Experimental and calculated by RMC Ti and Nb K-edge EXAFS spectra $\chi(k)k^2$ (a, b) and their Fourier (c, d) and Morlet wavelet (e, f, g, h) transforms for TiO₂:Nb thin film at 300 K.

The atomic coordinates obtained in the RMC simulations of the TiO₂:Nb thin film with 5% and 10% of dopant Nb atoms at 300 K were used to calculate the radial distribution functions (RDFs) $G(R)$ for Nb-O, Nb-Ti, Ti-O and Ti-Ti atom pairs. They are shown in Figure 6(a, b) in comparison with the RDFs $G(\text{Ti-O})$ and $G(\text{Ti-Ti})$ for anatase TiO₂. To improve statistics, the RDFs were evaluated as an average over six independent RMC calculations. The two models with different percentage of Nb doping give close RDFs. Also, the RDFs $G(\text{Ti-O})$ and $G(\text{Ti-Ti})$ are rather close in the thin film and anatase suggesting that doping by niobium does not change significantly the local environment of Ti atoms.

A comparison of the RDFs $G(\text{Nb-O})$ and $G(\text{Ti-O})$ in the thin film indicates that both Nb and Ti atoms are octahedrally coordinated by oxygen atoms. However, Nb environment relaxes leading to a larger splitting of the first coordination shell than that in the anatase structure. The first shell of Ti atoms in anatase is split into two groups (3+3) of oxygen atoms located at 1.93 Å and 1.98 Å [20]. In our RMC calculations, the first shell of Ti atoms in both film and anatase does not split and is represented by a broad peak centered at ~1.95 Å. At the same time, the larger distortion of Nb environment leads to its first shell splitting into two groups (3+3) of oxygen atoms at ~1.88 Å and ~2.01 Å. Note that the second coordination shell of Nb (peak at 3 Å in Figure 6(a,b)) is also displaced slightly compared to that of Ti but to longer distances. The average values of the Nb-Ti and Ti-Ti distances are 3.11 Å and 3.04 Å, respectively. Thus, doping by Nb atoms modifies the local environment in the film; however, its average structure still resembles that of anatase (Figure 6(c, d)).

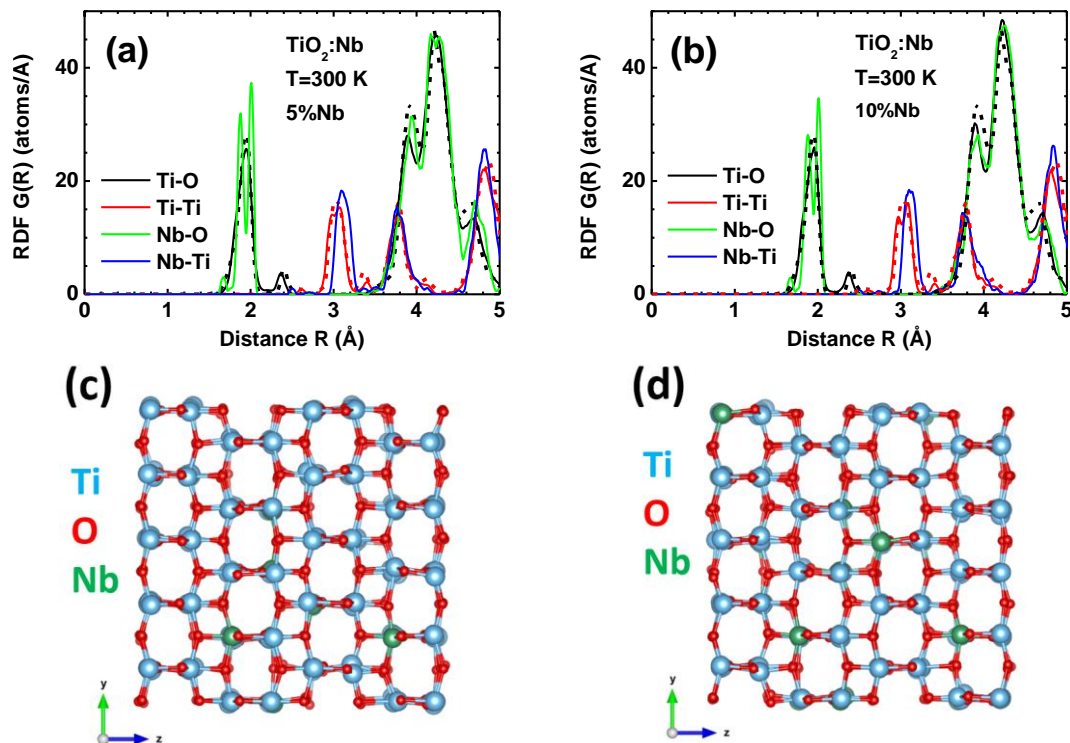


Figure 6. (a, b) Radial distribution functions (RDFs) $G(R)$ calculated from the coordinates of atoms in a TiO₂ 5×5×2 supercell at 300K, for 5% and 10% of dopant Nb atoms. Dashed (black and red) curves are for RDFs $G(\text{Ti-O})$ and $G(\text{Ti-Ti})$ in anatase TiO₂ at T=300 K. (c, d) Fragments of the RMC 5a×5b×2c supercells for c) 5% of Nb and d) 10% of Nb atoms.

The X-ray absorption near edge structure (XANES) spectra of TiO₂:Nb thin film measured at the Ti and Nb K-edges are presented in Figure 7. XANES spectra are better resolved at the Ti K-edge due to the smaller value of the core-level width ($\Gamma(K\text{-Ti})=0.94$ eV vs $\Gamma(K\text{-Nb})=4.14$ eV) [26]. This makes a difference mainly in the pre-edge region at 0-10 eV above the Fermi level. The main variance around 20 eV comes from the difference in the Ti(Nb) p-orbitals density of states (p-DOS, as seen later on). Note also that there is a slight difference in the fine structure above the two edges due to some modification of the local environment around Ti and Nb atoms caused by a difference in the Ti-O and Nb-O bonding. The Ti K-edge XANES spectra of the thin film and reference anatase TiO₂ powder are very similar, suggesting resemblances of their local environment in agreement with the results of our EXAFS analysis.

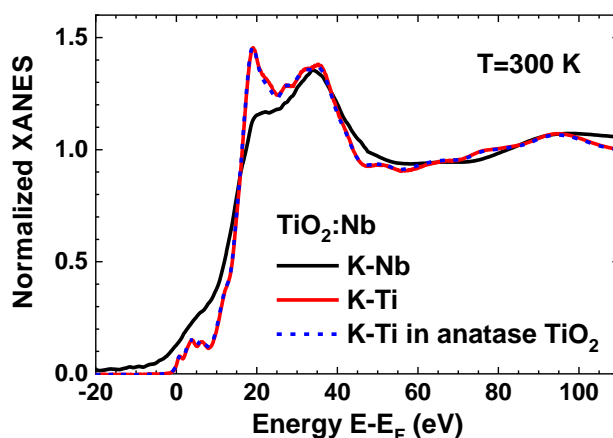
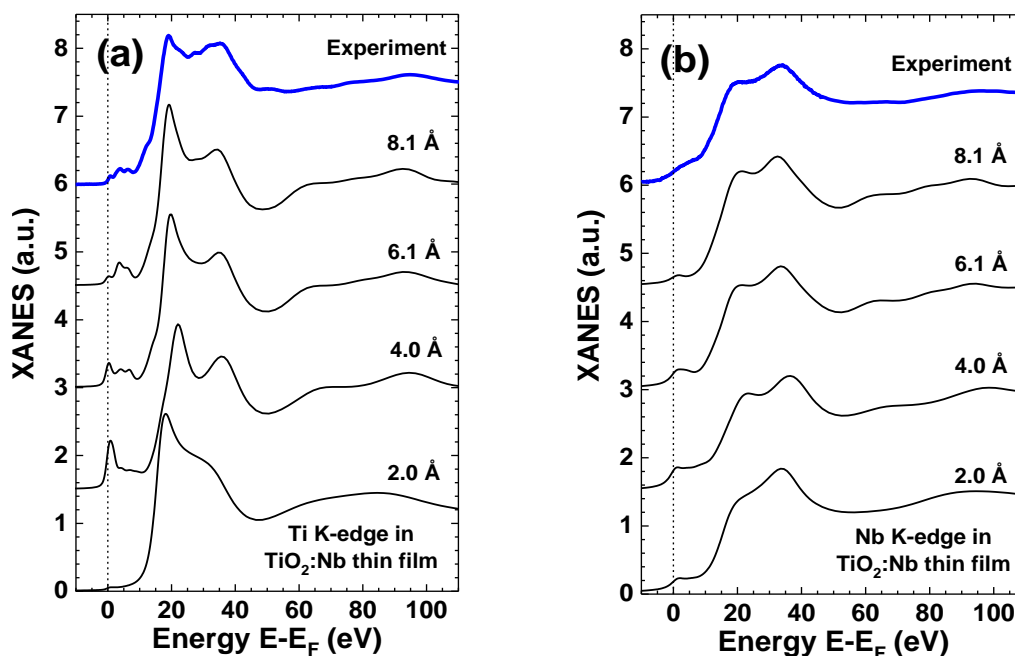


Figure 7. Experimental XANES spectra of TiO₂:Nb thin film at the Ti and Nb K-edges measured at 300K. The Ti K-edge XANES spectrum (dashed line) of reference anatase TiO₂ powder is shown for comparison.

To understand the origin of the XANES features, theoretical simulation using *ab initio* FDMNES code [24,25] were performed using the finite difference method. This approach, while being more computationally time-consuming, gives better results in the case of the distorted environment, as in the case of both pure and Nb-doped TiO₂, than the Green function formalism with spherical muffin-tin potentials. Note also that the origin of XANES features above the absorption edge is due to the dipole-allowed transitions from 1s(Ti/Nb) core state to unoccupied p-states, whereas three pre-edge peaks have mixed quadrupole-dipolar origin, involving d-metal states in the conduction band [30].

Experimental XANES spectra of TiO₂:Nb thin film at 300 K measured at the Ti and Nb K-edges are compared with those calculated by *ab initio* FDMNES code in Figure 8. A good agreement is observed for both Ti and Nb K-edges XANES for the cluster radius of 8.1 Å. However, main XANES features are reproduced already for the small cluster (4.0 Å) containing four coordination shells. It is interesting to note that, despite of similarities of the local structure around Nb and Ti atoms, their XANES spectra differ appreciably in the range of 15-40 eV above the edge, where the two main peaks have opposite amplitude. At the Ti K-edge, the peak at ~20 eV is more intense than the peak

1 at ~35 eV, whereas, at the Nb K-edge, the situation is the opposite, i.e. the peak at ~20
2 eV has a smaller amplitude than that at ~35 eV. To understand the origin of this
3 difference, a more detailed analysis was performed. First, it was studied the influence of
4 the core-level width on the shape of XANES. The results of the Nb K-edge XANES
5 simulations with the two core-level widths $\Gamma=0.94$ eV and 4.14 eV [26] corresponding
6 to the Ti and Nb K-edges, respectively, are shown in Figure 9(a). The small pre-edge
7 peak located just above the Fermi level is related to mixed Ti d-states and O p-states in
8 the conduction band. As one can see, the reduction of the natural broadening influences
9 the sharpness of all features but does not change their relative amplitudes. At the same
10 time, the observed differences in the XANES at two absorption edges correlate well
11 with the partial unoccupied DOS probed by 1s electron, i.e. p(Ti/Nb)-DOS, shown in
12 Figure 9(b). Also, in Figure 9(b) the opposite amplitude effect that is registered for the
13 two main peaks at the Ti and Nb K-edges is more evident (highlighted by the blue oval
14 shapes).
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44 Figure 8. Experimental and calculated XANES spectra of TiO₂:Nb thin film measured at the Ti
45 (a) and Nb (b) K-edges at 300K. The calculations were performed for varying atomic cluster
46 sizes. The spectra are vertically shifted for clarity.
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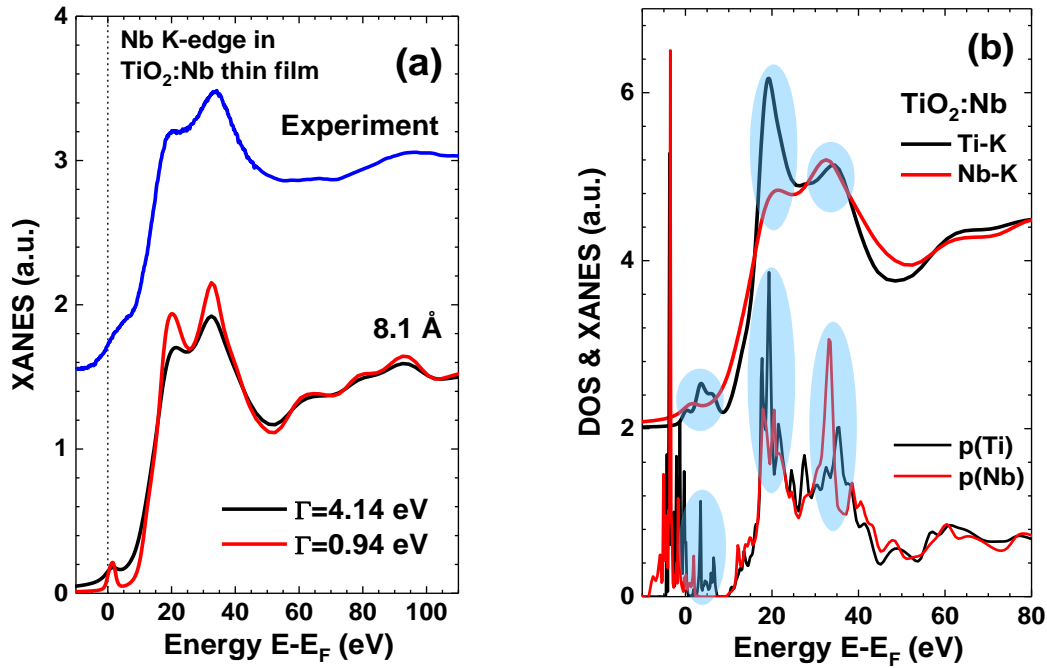


Figure 9. (a) Experimental and calculated Nb K-edge XANES spectra of TiO₂:Nb thin film. The calculations were performed for the cluster radius of 8.1 Å and two different core-level widths $\Gamma=0.94$ eV and 4.14 eV. (b) A comparison of the calculated XANES spectra at the Ti and Nb K-edges (top) with p-DOS for Ti and Nb (bottom).

The measured thermal, thermoelectric, electrical and optical properties of the TiO₂:Nb film deposited on glass and Si substrates are presented in Table II, and were experimentally determined as described in Section 2. A very high absolute Seebeck coefficient, $S=155$ $\mu\text{V}/\text{K}$, for n-type TiO₂ was achieved with Nb doping for the thinner film (150 nm). For the thicker film (750 nm), a 65% lower value, $S=101$ $\mu\text{V}/\text{K}$, was obtained. These Seebeck coefficients were determined from, the slope of the ΔV vs. ΔT and the respective experimental errors are listed in Table II. In Figure 10, the Seebeck coefficient values were measured for both of these films at 5 K step values with a stabilization of 60 min. per step, integration time of 40 min. at that step, in order to thermally stabilize both ends of the sample. These S step values are a bit lower for the thicker film when compared to that obtained for the whole temperature gradient range (from the aforementioned slopes) due to a small potential offset originated at the start of the experiment. This variation in S for both films is further elucidated later in the manuscript when discussing the electrical properties. It is noteworthy to mention that this magnitude of the Seebeck effect was registered within a relatively small thermal gradient of 50 K across the film surface (75 mm \times 26 mm), for a 750 nm thick film. This thermal gradient is more than the authors expect for applications of these films as thermal energy harvesters in touch displays or photovoltaic cells. The resulting power factor (PF) and figure of merit (ZT) were calculated using the following expressions $S^2\sigma$ and $S^2\sigma T/\kappa$, respectively, where σ is the electrical conductivity, T is temperature and κ is the thermal conductivity of the TiO₂:Nb film. PF and ZT values at 300K of 0.5 $\text{mW}\cdot\text{m}^{-1}\cdot\text{K}^{-2}$ and 0.18, respectively, were obtained for optimized (150 nm) TiO₂:Nb films; which for transparent thin films excels what is commonly found in the literature.

1 The data in Table II were recorded from a large collection of similar samples; hence, the
2 registered uncertainty in some properties, such as thermal and electrical conductivities.
3 The value of the thermal conductivity measured by FDTR at 300 K is 1.3 W·m⁻¹·K⁻¹ and
4 2.3 W·m⁻¹·K⁻¹, for 150 nm and 750 nm thick TiO₂:Nb films, respectively. The values of
5 κ are quite low compared to what is known for undoped TiO₂ (5-10 W·m⁻¹·K⁻¹) [31].
6 From the fit of the phase lag data in Figure 11, for both a) 150 nm and b) 750 nm
7 TiO₂:Nb thick films, it was possible to calculate κ , with a maximum uncertainty of ± 0.3
8 W·m⁻¹·K⁻¹. Also, from these fits, values for C_p of 1200 J·kg⁻¹·K⁻¹ and 1050 J·kg⁻¹·K⁻¹
9 were obtained for 150 nm and 750 nm thick TiO₂:Nb films, respectively, which is in
10 agreement with the variation in κ .
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14 As comparison with the present results, Min-Hee Hong [32] and co-workers published
15 ZT Values lower than 0.01 for mesoporous TiO₂ sol-gel films, without disclosing
16 thickness. In a similar deposition process, Ling Xu and co-workers [33] prepared 320
17 nm thick TiO₂:Al films, with Al varying from 0 - 5 at.%, also presenting ZT values
18 lower than 0.01. Kurita et al. [34] reported thermoelectric power factors in the range of
19 0.25 mW·m⁻¹·K⁻² at 900K for heavily Nb-doped TiO₂ epitaxial films deposited at 800K
20 by pulse-laser deposition (PLD) with similar thickness, about 50% of the value obtained
21 in this work, albeit with similar S values, 145 μ V/K. Moreover, the latter PF value was
22 assessed at the triple of the temperature measured for the present TiO₂:Nb thin films,
23 which are polycrystalline and were deposited below 450K, in order to meet industrial
24 applications. On the other hand, Ohta et al. [35] obtained a much higher PF and ZT
25 values at 1000 K, ~ 1.5 mW·m⁻¹·K⁻² and ~ 0.3 , respectively, for ~ 100 nm thick SrTiO₃
26 films deposited by PLD at ~ 1000 K, nonetheless with a much higher Nb content (40
27 at.%). No information in transmittance levels of the films is given for both literature
28 references.
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34 The average values at 300 K for electrical conductivity, n-type carrier concentration and
35 mobility for TiO₂:Nb films are also displayed in Table II. The thicker film has a higher
36 electrical conductivity, 992 (Ω ·cm)⁻¹, when compared to the thinner one, 219 (Ω ·cm)⁻¹,
37 as it would be expected. This explains why the Seebeck coefficient and thermal
38 conductivity is higher in the thinner film, as mentioned in the last paragraph, since the
39 number of impurities and defects (Nb⁵⁺ dopant ions, ionized oxygen vacancies) is lower,
40 owing to the lower carrier concentration ($\sim 10^{20}$ cm⁻³) and higher mobility (26 cm²·V⁻¹·s⁻¹)
41 when compared to the thicker film, in Table II. Moreover, for the thinner film,
42 electron and phonon scattering is increased, due to decrease both in σ and κ , hence
43 resulting a larger separation of charges between the hot and cold sides, and thus the
44 increase in S. For the thicker film, the net result of cationic pentavalent doping of Nb in
45 TiO₂ results in a substantial enhancement of transport properties due to charge
46 unbalancing and oxygen vacancies creation [36], which concomitantly impacts on the
47 increase in PF. Also, with the increase in impurities in TiO₂ for the thicker film, the
48 mobility is reduced [37].
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Table II. Thermoelectric, thermal, electrical and optical properties of TiO₂:Nb film for different thickness: Seebeck coefficient (S); thermoelectric power factor (PF) and figure of merit (ZT); thermal conductivity (κ); electrical conductivity (σ), carrier concentration (n) and mobility (μ); optical band-gap (E_g).

Thick (nm)	S ($\mu\text{V}\cdot\text{K}^{-1}$)	PF ($\text{mW}\cdot\text{m}^{-1}\cdot\text{K}^{-2}$)	ZT	κ ($\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$)	σ ($\Omega\cdot\text{cm}$) ⁻¹	n (cm^{-3})	μ ($\text{cm}^2\cdot\text{V}^{-1}\cdot\text{s}^{-1}$)	E_g (eV)
150	-155±2	0.5±0.1	0.18±0.05	1.3±0.2	(2.19±0.02)×10 ²	(8±2)×10 ¹⁹	26±10	3.27±0.01
750	-101±2	1.0±0.1	0.13±0.02	2.3±0.3	(9.92±0.01)×10 ²	(4±2)×10 ²¹	2±1	3.24±0.01

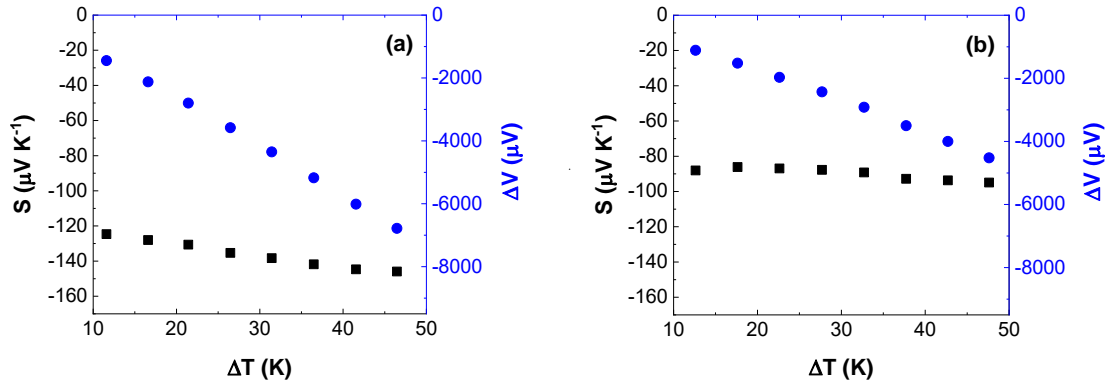


Figure 10. Evolution of the Seebeck coefficient (squares) and potential difference (dots) with a thermal gradient across the surface of a 75 mm × 26 mm, for a) 150 nm and b) 750 nm thick, TiO₂:Nb film on a glass substrate.

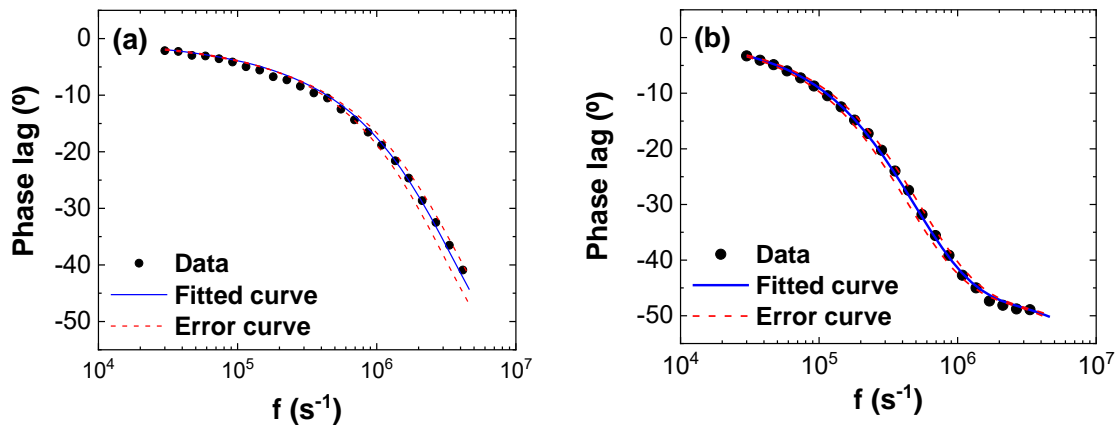


Figure 11. Frequency-dependent phase lag between the pump (405 nm) and probe (532 nm) lasers for a) 150 nm and b) 750 nm thick TiO₂:Nb thin film. The results from the fits are listed in Table II. Error curves represents ±0.2 and ±0.3 uncertainty in κ for a) and b), respectively.

The TiO₂:Nb semiconductor band-gap (E_g) was derived from the measurement of optical transmittance and reflectance and subsequent calculation of the absorption

coefficient (α), as presented in the Tauc plot in Figure 12. From the intercept of the linear decay of α with the photon energy axis, a value of $E_g=3.24$ eV was determined a 750 nm thick TiO₂:Nb film, which is slightly higher than that known for undoped TiO₂ (3.20 eV) [38]. The slight increase in E_g is attributed to the Burstein-Moss effect [39] and can be explained through the Pauli Exclusion Principle, where a broadening of the band-gap is observed with increasing doping. This shift arises because the Fermi energy lies in the conduction band for heavy n-type doping (as is the case for TiO₂:Nb). The filled states, therefore, block thermal or optical excitation. Consequently, the measured band gap determined from the onset of interband absorption moves to higher energy (i.e. blue shift).

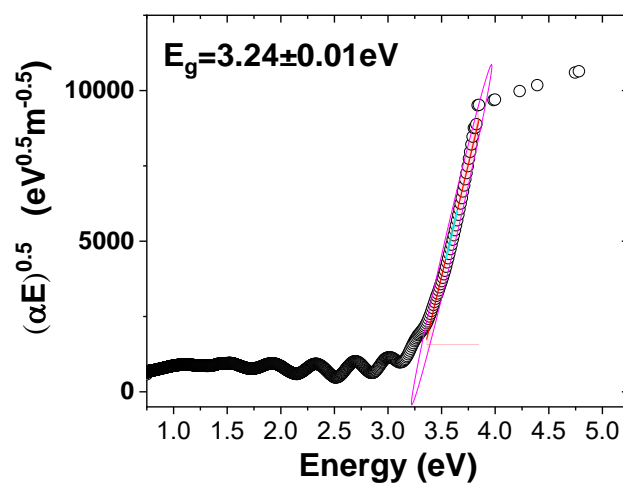


Figure 12. Determination of the optical band-gap of the TiO₂:Nb thin film deposited on glass, 750 nm thick. The ellipse shows a region within 95% confidence for the linear regression.

5. Conclusions

Transparent n-type niobium-doped titanium dioxide thin films (TiO₂:Nb), with an optical band-gap of 3.21-3.24 eV, were successfully produced by reactive magnetron sputtering from a composite Ti:Nb target in an oxygen atmosphere. An amount of 1.5 at.% Nb doping was estimated from X-ray photoelectron spectroscopy experiments. Optimized Nb-doped films exhibit pronounced thermoelectric properties with a very high absolute Seebeck coefficient of 155 $\mu\text{V/K}$ for a 150 nm thickness. The maximum power factor (PF) and figure of merit (ZT) values of 0.5 $\text{mW}\cdot\text{m}^{-1}\cdot\text{K}^{-2}$ and 0.18, respectively, were obtained for TiO₂:Nb films with a thermal conductivity of 1.3 $\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$, which excels what is commonly found in the literature for transparent thin films.

Structural investigations by X-ray diffraction and X-ray absorption spectroscopy at the Ti and Nb K-edges were performed to elucidate the role of Nb dopant on the film structure and properties. The as-deposited films possess anatase TiO₂ phase evidenced by XRD, however, the rutile phase is additionally formed upon film thermal annealing at 400 °C. Detailed information on the local structure of the thin films was obtained in terms of the radial distribution functions determined from the simultaneous analysis of

EXAFS data at two absorption edges using the reverse Monte Carlo method. It was concluded that the local environment of the thin films is affected by Nb doping, however, their average local structure remains close to that of the anatase TiO₂ phase. This result is also supported by the analysis of XANES using ab initio simulations.

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