Joana M. Ribeiro
Departamento de Física
Universidade do Minho
Campus de Azurém
4800-058 Guimarães
Joanaribeiro93@hotmail.com

Report for PhD project

"TRANSPARENT THERMOELECTRIC TITANIUM DIOXIDE-BASED THIN FILMS FOR THERMAL ENERGY HARVESTING"

Physics Doctoral Program: Minho, Aveiro and Porto (MAP-Fis)

Supervised by:

Professor Carlos José Macedo Tavares[1]

Doctor Torben Boll[2]

1 Centre of Physics, University of Minho, 4804-533 Guimarães, Portugal

2 Institute for Applied Materials (IAM), and Karlsruhe Nano Micro Facility (KNMF), Karlsruhe Institute of Technology (KIT), D-76344 Eggenstein-Leopoldshafen, Germany

The focus of this project is the preparation, characterization, optimization and application of doped TiO_2 thin films that are electrically conductive, transparent in the visible region and show thermoelectric properties.

Energy is key part of our everyday life and the demand for reliable, affordable, sustainable and cleaner energy is ever growing due to global warming and increasing cost of the conventionally used fossil fuel sources. Hence, the design of a transparent thermoelectric material is a promising technology for touch–screen displays and solar cell applications, rendering a more sustainable powering of the device. In order to enhance the thermoelectric performance, the material must have a high Seebeck coefficient, high electrical conductivity but low thermal conductivity.

The first objective of this work is to develop an optically transparent electrically conductive, thermoelectric thin film of TiO_2 doped with Nb that is inexpensive to produce, non-toxic, durable and applicable in a variety of thermoelectric devices.

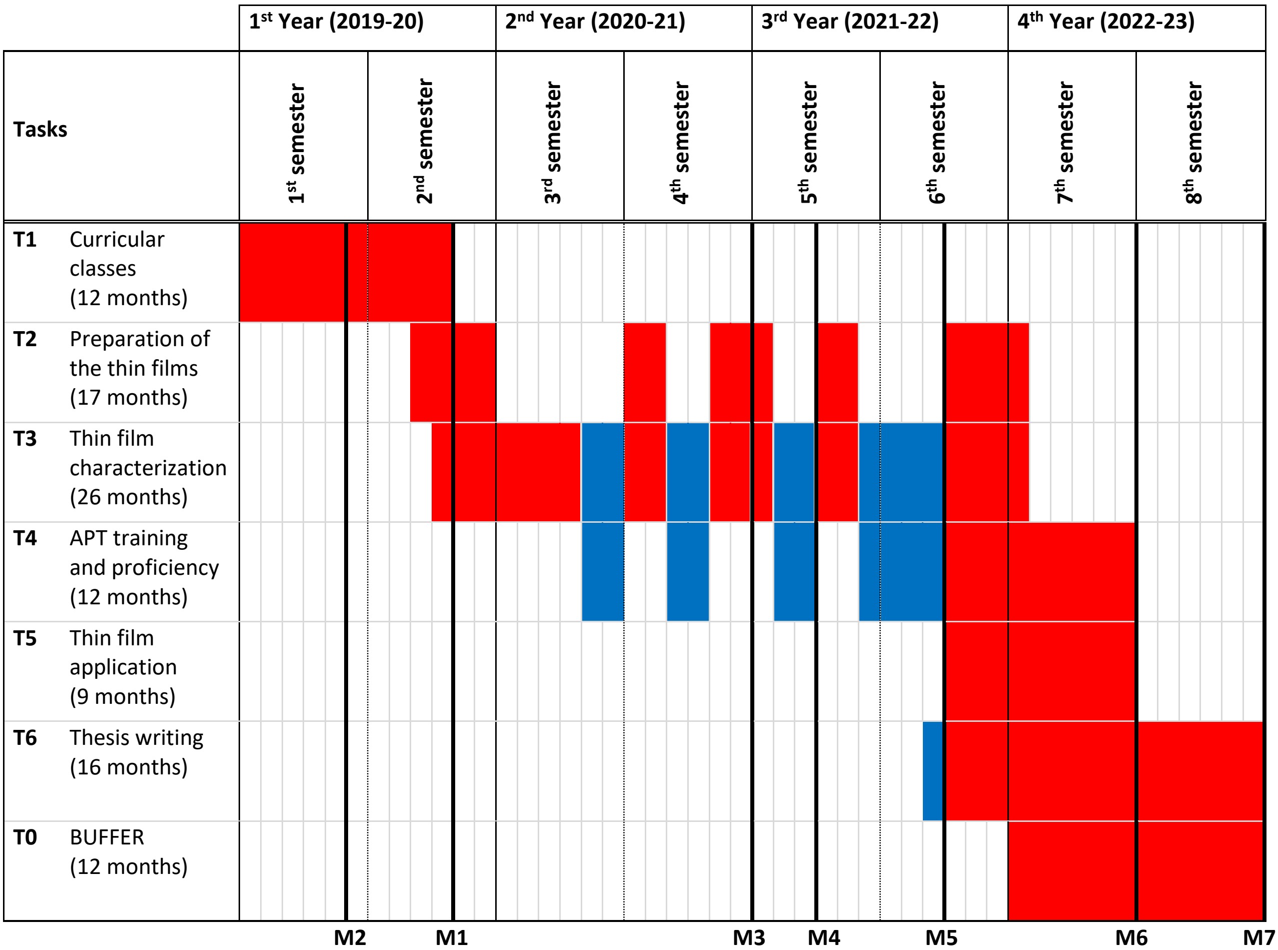
The second objective is to understand what is happening in the grain boundaries of the thin films through the technique of Atom Probe Tomography (APT), which will be done at the Karlsruhe Institute of Technology (KIT), in Germany. This understanding involves monitoring of segregation of host and dopant ions, oxide phases development, electron and phonon scattering mechanisms, and will enable the fine tuning of the production method of the thin films and further the relation between the production parameters and the properties of the thin films. This method does not yet exist in Portugal, but its part in understanding the role of doping in the properties of these materials is undeniable.

Finally, the third and final objective is to envisage a working thermoelectric device prototype in which to apply the developed transparent thermoelectric thin films.

This project will follow seven milestones:

M1. Finalization of the curricular year and up to date state of the art (to be updated all along the project).
M2. First insight on the effect of doping on TiO2 with 1-5 at.% of Nb.
M3. Optimized film production parameters through the reactive magnetron sputtering and annealing of the thin films.
M4. Satisfactory thermoelectric Power Factor (350 $\mu W \cdot K^{-2} \cdot m^{-1}$) and figure of merit (0.1) for energy harvesting applications.
M5. Get proficiency in the technique of APT, aptitude with the hardware and software, be able to prepare and analyse a variety of samples and efficiently interpret the resulting data.
M6. Design of a working prototype using the developed films as a thermoelectric or TCO layer.
M7. Finalization of the PhD (48th month).

The project has work spanning in two primary locations. The majority of the work is done at University of Minho, Guimarães, Portugal. Originally, a total of 12 months at the KIT, in Karlsruhe, Germany, was predicted for the objectives to be achieved. However, due to the current situation regarding the global pandemic, this period is being reorganized, divided into four periods, of 1-4 months each. Additionally, a small period at the ICMAB, in Barcelona, Spain, for the thermal characterization of the films is predicted with some flexibility, so it will not be included in the calendarization.



Work done at KIT (Germany).

Work done at UMinho (Portugal).

According to the proposed work plan, thus follows a detailed job description developed in the first two years (from 1st January 2020 to 31st December 2021).

Task 1: Curricular classes - The first year was dedicated to curricular classes, elaborating an up-to-date state of the art and getting acquainted with the experimental and theoretical scientific tools of the trade. The curricular Units consisted in 47421 Entrepreneurship, 49873 Essay and 40289 Advanced Physics Topics I. The Curricular unit in *Advanced Physics Topics I*, encompassed in the first year of the MAP Doctoral Program in Physics, included six modules chosen based on the best provided tools to best assist the development of the student and this work. *Communicating Science* provided powerful tools to support the development of public speaking skills and oral presentations. *Clean Room and Micro-fabrication* provided a good hands-on approach on the main microfabrication and deposition techniques used to produce functional devices in a Clean Room environment. *Energy Harvesting* provided a good background on energy harvesters and thermoelectric materials and devices for the motivation and application of this work. *Advanced Materials Preparation and Characterization*, *Spectroscopic techniques for the characterization of materials* and *Scanning Microscopy Techniques and Electronic Microscopy* provided insight about some of the production and characterization techniques to be used in this work. The end of this task reflected on the first Milestone on the calendarization.

Task 2: Preparation of the thin films – Thin films of titanium dioxide doped with niobium were deposited by DC reactive magnetron sputtering in vacuum. Several process parameters, which affect the transparency, morphology and crystalline structure of the thin films, were studied and adjusted, such as reactive gas (oxygen) flow, deposition time and temperature. After deposition, the films were subjected to an annealing process in vacuum, in the range of 400-500 °C.

As an alternative to the conventionally used ITO, TiO_2 has been extensively investigated due to its interesting optical and electronic properties and good stability in the adverse environment. Modifying the atomic structures of TiO_2 by deliberately introducing defects can enhance its properties to a great extent, while a cationic doping of TiO_2 has been documented to improve its electrical conductivity.

Due to reproducible surface morphology, good film adhesion and long-term stability, magnetron sputtering has become a preferred method for the deposition of thin films. The thin films are deposited on glass, Si and kapton by reactive d.c. magnetron sputtering in high vacuum at the center of Physics of the University of Minho. Several process parameters, which affect the morphology and crystalline structure of the thin films, are adjusted, such as reactive gas (oxygen) partial pressure, deposition time and temperature. After deposition, the films are subjected to an annealing process in vacuum or ambient pressure.

Task 3: Thin film characterization - The morphological, optical, electrical, thermal and thermoelectrical properties of the thin films are characterized by using a complete array of techniques: **UV-Vis-NIR spectrophotometry** – measurement of the film optical transmittance and reflectance as a function of wavelength; **Seebeck coefficient** – measurement of the electric current generated in the film after applying a thermal gradient; **Hall effect** – measurement of the electrical properties of the thin films, concerning resistivity, carrier mobility, and carrier concentration; **Scanning electron microscopy** - investigate the morphology and cross-section of the thin films, besides providing the thickness; **X-ray diffraction** - investigate the crystallographic structure of the thin films and determine the diffraction patterns to distinguish between TiO_2 phases; **X-ray reflectivity** - determination of thin film thickness and surface roughness; **X-ray photoelectron spectroscopy** - evaluate the film composition, along with the valent state and binding energy of dopant ions, as well as of the Ti and O ions; **Frequency Domain**

thermoreflectance, done at the *Institut de Ciència de Materials de Barcelona-CSIC* (ICMAB), in Spain – measurement of the thermal conductivity; **Time-of-flight secondary ion mass spectrometry** (TOF-SIMS) – in-depth chemical identification of the aforementioned ions, in order to determine the bulk homogeneity of the film, surface layers composition, as well as the composition of the atomic layers at the interface with the substrate; **Atom probe tomography** (APT) – quantify the cation segregation, as well as to study the morphology of the grain boundaries. APT and TOF-SIMS, done at the (Karlsruhe Institute of Technology) KIT, in Germany, are powerful tools to understand the role of doping in the properties of the thin films, enabling a deeper understanding of the local structure of the thin films and a further fine tuning of the production method. It is also necessary to learn and properly apply these techniques to the comprehensive study of thin films in a complementary way. Hence, these was a strong need for collaboration between research centres, including on-site training and instruction.

Task 4: APT Training: To acquire proficiency in the technique of APT and sample preparation, this task was enabled by the first and second mobility to the (Karlsruhe Institute of Technology) KIT, Germany, from April to June and September to October of 2021. The same mobilities also enabled to get some experience with ToF-SIMS. A sample was prepared for APT and TOF-SIMS and analysed in order to understand the best analysis conditions. Another two mobilities are being planned.

The first results associated with this work were published in *"**J. M. Ribeiro**, et, al., **Journal of Alloys and Compounds. 838 (2020)** 155561, **doi:**10.1016/j.jallcom.2020.155561."* and *"**J. M. Ribeiro,** et, al., **Surface & Coatings Technology. 425 (2021)** 127724, **doi:**10.1016/j.surfcoat.2021.127724.".*

By using XPS and extended X-ray absorption fine structures (EXAFS), 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, confirming the Nb substitutes Ti in the TiO_2 matrix.

The optimization of the production parameters results in thin films with thickness of 120-300 nm, maximum average optical transmittance in the visible range of 73 %, n-type electrical resistivity of 0.05 W·cm, thermal conductivity below 1.7 $W{\cdot}m^{-1}{\cdot}K^{-1}$ and a maximum absolute Seebeck coefficient of 223 $mV{\cdot}K^{-1}$. The resulting maximum thermoelectric power factor is 60 $mW{\cdot}K^{-2}{\cdot}m^{-1}$ and the maximum thermoelectric figure of merit is 0.014. These optimized thin films also resulted in a **National patent** published by the INPI – *Instituto Português de Propriedade Intelectual* on 08-09-2021 (PT 110639 B).

Communications

Oral presentations in International conferences:

J. M. Ribeiro, F. C. Correia, C. J. Tavares, *"Transparent TiO2:Nb thin films for thermal energy harvesting"*, VCT2020 - Virtual Conference on Thermoelectrics 2020 (Online Event, Zoom), 21 - 23 Jully (2020).

J. M. Ribeiro, F. C. Correia, C. J. Tavares, *"Transparent Niobium-doped Titanium Dioxide Thin Films with high Seebeck coefficient for thermoelectric applications"*, Society of Vacuum Coaters Technical Conference 2021 (Online Event, Zoom), 3 - 7 May (2021).

J. M. Ribeiro, F. C. Correia, F. J. Rodrigues, J. S. Reparaz, A. R. Goñi, C. J. Tavares, *"Transparent Niobium-doped Titanium Dioxide Thin Films with high Seebeck coefficient for thermoelectric applications"*, RIVA Online 2021 – Iberian Vacuum Online Meeting (Online Event, Zoom), 4 – 6 October (2021).

Poster presentations in International conferences:

J. M. Ribeiro, F. C. Correia, C. J. Tavares, *"Transparent Niobium-doped Titanium Dioxide Thin Films with high Seebeck coefficient for thermoelectric applications"*, Jornadas of CF-UM-UP - Centro de Física das Universidades do Minho e do Porto (Braga, Portugal), 13 December (2019).

J. M. Ribeiro, F. C. Correia, T. Boll, C. J. Tavares, *"Study of Transparent Thermoelectric ZnO-based Thin Films for Energy Harvesting through Atom Probe Tomography"*, 1st Workshop of LaPMET (Online Event, Twitter), 23 - 24 September (2021).

J. M. Ribeiro, F. C. Correia, T. Boll, C. J. Tavares, *"Transparent Thermoelectric ZnO-Thin Films for Energy Harvesting applications"*, Atom Probe Tomography & Microscopy Virtual Conference 2021 (Online Event, Zoom), 27 - 30 September (2021).

J. M. Ribeiro, F. C. Correia, F. J. Rodrigues, J. S. Reparaz, A. R. Goñi, C. J. Tavares, *"Transparent Niobium-doped Titanium Dioxide Thin Films with high Seebeck coefficient for thermoelectric applications"*, EVC-16 – 16th European Vacuum Conference (Marseille, France), 21 - 26 November (2021).

Articles Published in Scientific Journals:

L. Dias, F. C. Correia, **J. M. Ribeiro**, C. J. Tavares, *"Photocatalytic Bi_2O_3/TiO_2:N thin films with enhanced surface area and visible light activity"*, Coatings. 10 (2020) 445. https://doi.org/10.3390/coatings10050445

J. M. Ribeiro, F. C. Correia, A. Kuzmin, I. Jonane, M. Konge, A. R. Goñie, J. S. Reparaz, A. Kalinko, E. Welter, C. J. Tavares, *"Influence of Nb-doping on the local structure and thermoelectric properties of transparent TiO_2:Nb thin films"*, Journal of Alloys and Compounds. 838 (2020) 155561. https://doi.org/10.1016/j.jallcom.2020.155561

F. C. Correia, **J. M. Ribeiro**, A. Kuzmin, I. Pudza, A. Kalinko, E. Welter, A. Mendes, Joana Rodrigues, Nabiha Ben Sedrine, Teresa Monteiro, Maria Rosário Correia, C. J. Tavares, *"The role of Ga and Bi doping on the local structure of transparent zinc oxide thin films"*, Journal of Alloys and Compounds. 870 (2021) 159489. https://doi.org/10.1016/j.jallcom.2021.159489

J. M. Ribeiro, F. C. Correia, F. J. Rodrigues, J. S. Reparaz, A. R. Goñi, C. J. Tavares, *"Transparent niobium-doped titanium dioxide thin films with high Seebeck coefficient for thermoelectric applications"*, Surface & Coatings Technology. 425 (2021) 127724. https://doi.org/10.1016/j.surfcoat.2021.127724

Patents:

Carlos José Tavares, Filipe Correia Costa, **Joana Margarida Ribeiro,** *"Filme Termoelétrico transparente e respetivo método de obtenção",* PT 110639 B, Universidade do Minho, Portugal. National patent published by the INPI – Instituto Português de Propriedade Intelectual on 08-09-2021.
http://servicosonline.inpi.pt/pesquisas/GetFasciculo?bole_ano=2019&bole_nume=182&proc_moda=01&proc_nume=110639

Awards:

IUVSTA Elsevier award at EVC-16 – 16th European Vacuum Conference (21-26 Nov. 2021) in Marseille, France, for a Poster presentation in "Transparent niobium-doped titanium dioxide thin films with high Seebeck coefficient for thermoelectric applications", https://www.evc16.org/IUVSTA-Elsevier-Awards.

Guimarães, January 27th 2022,

The student,

(Joana Margarida Fernandes da Silva Ribeiro)