Research plan for doctoral Thesis

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

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Supervised by:

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Introduction

This work plan is related to the PhD project entitled "Transparent thermoelectric titanium dioxide-based thin films for thermal energy harvesting" with reference FCT scholarship SFRH/BD/147221/2019, to be developed by the student Joana Margarida Fernandes da Silva Ribeiro under the supervision of Professor Carlos José Macedo Tavares and Doctor Torben Boll. The activities will be carried out for a period of 24 months, beginning in January 1st, 2022 and ending on December 31th, 2024, at the Center of Physics of the University of Minho and Institute for Applied Materials at the Karlsruhe Institute of Technology.

Objectives

This research is a continuation of the work developed in the first two years by the PhD student Joana Ribeiro (1st January 2020 to 31st December 2021).

The main aim of this work is to develop an optically transparent electrically conductive, thermoelectric thin film that is inexpensive to produce, non-toxic, durable and applicable in a variety of thermoelectric devices.

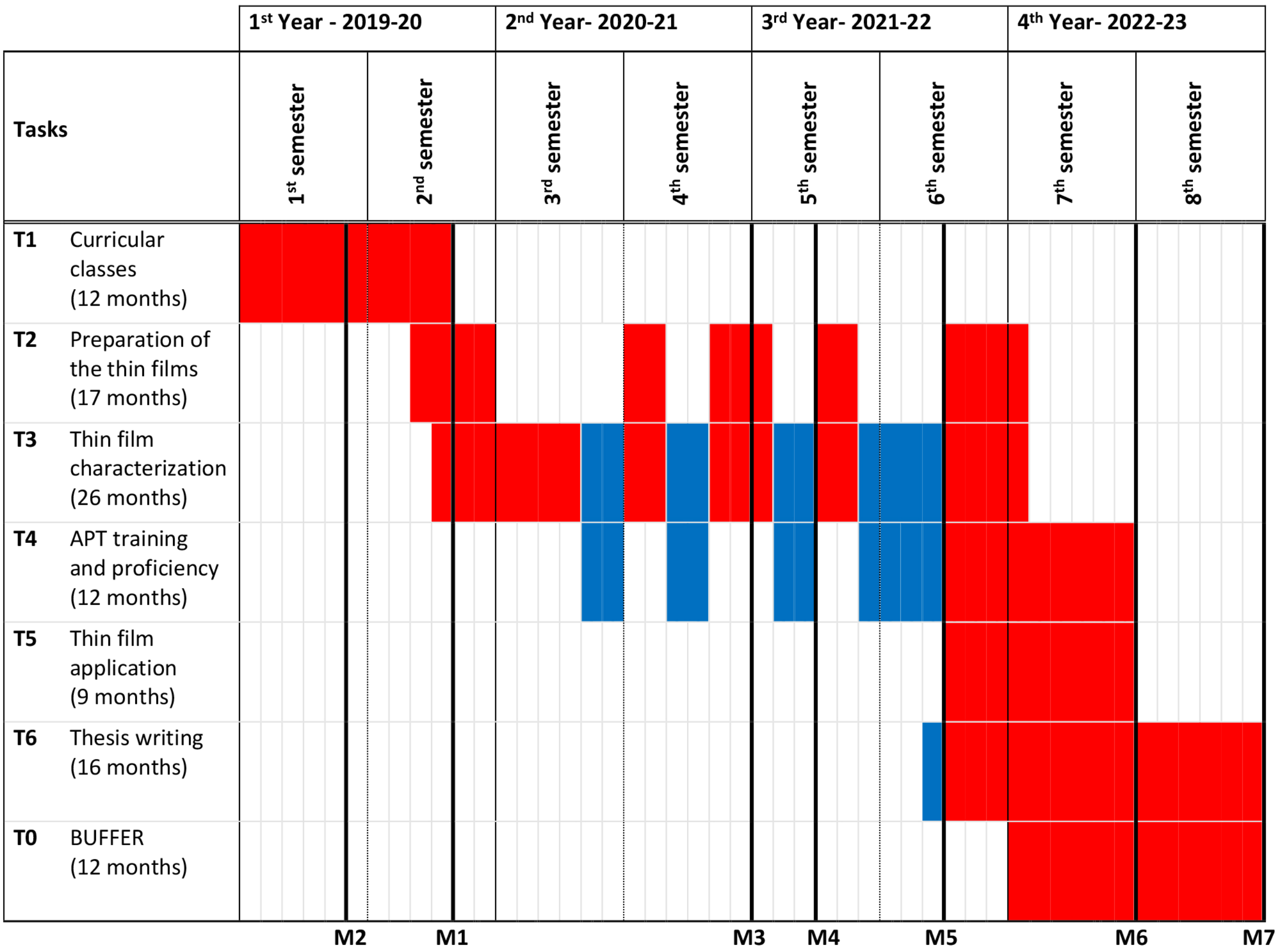
This project envisages the production, development, characterization, study and application of TiO_2–based thin films that are electrically conductive, transparent in the visible region and show thermoelectric properties. It has been documented that a cationic doping of TiO_2 improves its electrical conductivity, which will increase the thermoelectric figure of merit of the film. These films have the potential to efficiently harvest thermal energy from the environment and convert it to electricity. In this project, TiO_2 (titanium dioxide) films (~50-500 nm thick) doped with Nb have been deposited on glass, Si and Kapton substrates by reactive magnetron sputtering in high vacuum at the center of Physics of the University of Minho. The films were thoroughly characterized so that several process parameters could be optimized.

To understand the role of doping in the properties of the thin films, Atom Probe Tomography (APT) will be used, measured 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.

This project will follow seven milestones, some of which have already been reached:
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).

The proposed work plan for the remaining two years of this project, predicts a continuation of **Tasks 2: Preparation of the thin films, 3: Thin film characterization and 4: APT Training**.

According to the optimization of the production parameters previously obtained, thin films of TiO_2:Nb deposited with the best conditions will be further characterized and studied. 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. The mechanical properties of the thin films, namely **Scratch-testing and Nano indentation** – mechanical suitability, adhesion strength and hardness – will also be studied.

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. To acquire proficiency in the technique of APT and sample preparation, two more mobilities are planned to work at the KIT.

The ultimate objective of the produced thin films is to be functional in thermoelectric applications, such as thermoelectric or TCO layers in photodetectors, solar cells, light-emitting diodes or touch displays, to render them more energetically sustainable. As such, after the samples are tested as individual films, they will be implemented in modules to suit the desired application, reflected in **Task 5: Application of the thin films**. The device will be tested to quantify the efficiency gain obtained, in order to be able to carry out a cost/benefit assessment and comparison with similar devices.

The first idea is to implement the thermoelectric thin film is a perovskite solar cell. Due to the transparent nature of the transparent layer, it could be implemented on the top side of the cell, taking advantage of the thermal gradient inherently generated by the cell while enabling the solar light to still pass through. None the less, because this process generates a thermal gradient perpendicular to the surface of the film and due to the thinness of the film, the thermal gradient between the top and bottom of the thin film would be quite low, losing effectiveness as a thermoelectric. Hence, there is a need to develop an approach in order to successfully implement this thin film in a useful way to generate thermoelectric power.

The second idea is to implement the thin film as a thermoelectric sensor por transparent surfaces i.e. touch screens, by designing a module capable of sensing a thermal gradient between two in-plane positions of the film. This way, it would be possible to detect the position of a human finger by touch and its inherent temperature difference to the device. Of course, in theory, one could also make use of this thermal gradient to further boost the powering of the device.

The PhD dissertation will be written mainly in the last three semesters of the working programme. The end of this task will reflect on **Task 6: Thesis Writing** and the final Milestone – Finalization of the PhD.

Guimarães, 27th January 2022,

The student,

(Joana Margarida Fernandes da Silva Ribeiro)

Assinado por: **CARLOS JOSÉ DE MACEDO TAVARES**
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The supervisors,

Hier Text eingeben

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