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**MULTIPURPOSE XRD HOLDER FOR THE
SIMULTANEOUSLY CHARACTERIZATION OF THE
STRUCTURAL AND ELECTRICAL PROPERTIES OF
VANADIUM OXIDES**

Dissertação para obtenção do Grau de Mestre em Engenharia
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Multipurpose XRD holder for the simultaneously characterization of the Structural and Electrical properties of vanadium oxides

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“Life is like a box of chocolates.
You never know what you're gonna get.”
Forest Gump

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Abstract

Several oxides present a severe and reversible resistance changes with the application of an external stimulus such as an electrical field, temperature, optical or magnetic properties. Among them there are two groups, those who recover for the initial stage after the stimulus is finished and those who keeps the final stage, despite the stimulus is over. In the first group, vanadium dioxide (VO_2), present a sharp and reversible metal-to-insulator transition, induced by temperature near 68 °C. Since is a low transition temperature and presents a high speed and volatile change.

In this project we optimize the crystallization of VO_2 thin film produced by e-beam evaporation and produced a versatile X-Ray Diffractometer (XRD) holder, capable to be adapted to several other characterization equipment. This holder has the capability to heat and control the temperature applied on the oxide and at the same time perform the electric characterization of the oxide in situ, during the XRD measurement. This holder will be very helpful in characterization of several material due to its ability to have a uniform heating behavior in many equipments, thus ensuring that the process is the same regardless of the equipment used.

Keyword: XRD, vanadium oxide, holder, phase change, metal-to-isolation transition.

Resumo

Vários óxidos apresentam uma mudança de resistência acentuada e reversível com a aplicação de estímulos externos, como campos elétricos ou magnéticos, temperatura ou sinais óticos. Para estas mudanças existem dois grupos, os que recuperam o estado inicial depois de o estímulo findar e aquele que mantém o estado final, mesmo depois de já não haver estímulo externo. No primeiro grupo, o dióxido de vanádio (VO_2) apresenta uma clara e reversível transição metal para isolante, induzida por temperatura perto do 68 °C. Visto que se trata de uma baixa temperatura, com uma alta velocidade e mudança volátil, faz desde oxido um excelente candidato para interruptores ultrarrápidos.

Neste projeto é produzido um suporte versátil para X-Ray Diffractometer (XRD), capaz de se adaptar a outros equipamentos de caracterização. Este suporte tem a capacidade de aquecer e controlar a temperatura aplicada no oxido e ao mesmo tempo, realizar medições elétricas do oxido *in situ*, durante a medição no XRD. Este suporte será útil na caracterização de vários materiais devido à sua habilidade de aquecimento uniforme em todos os equipamentos, assegurando assim um processo igual, independentemente do sistema utilizado.

Palavras Chave: XRD, dióxido de vanádio, suporte, mudança de fase, transição metal para isolante.

Acronyms

GND – Ground

ΔI – Increment

IC – Integrated Circuit

ICSD – Inorganic Crystal Structure Database

ITO – Indium Tin Oxide

MIT – Metal to Insulator Transition

PCB – Printed Circuit Board

PET – Polyethylene Terephthalate

PID – Proportional–Integral–Derivative

PLA – Polylactic Acid

PWM – Pulse-Width Modulation

RTA – Rapid Thermal Annealing

SCL – Serial Clock Line

SDA – Serial Data Line

SP – Set Point

T_c – Transition Temperature

TCO – Transparent Conductive Oxide

t_m – Time

XRD – X-Ray Diffraction

Symbols

R – Resistance

T – Temperature

V – Voltage

I – Current Bragg Diffraction angle

Θ – Bragg Diffraction angle

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Motivation and objectives

As an engineer, the main goal is to solve problems and to improve the world. This project will make easy to find the perfect conditions to characterize vanadium dioxide (VO₂) thin films, in particular, its reversible metal to insulator transition (MIT). The existing system is requiring an assemble of a heating chamber and it is time consuming, taking a lot of time to analyse a simple sample. So, a new system is needed in order to fit the equipment and to have a quick heating and cooling.

The VO₂ has a reversible low transition temperature point, around 68 °C, were he faces a sharp structural transition from monoclinic to tetragonal while changing its electrical properties from insulator to metal. It makes therefore a great oxide to study, being perfect to use has an ultrafast switch, due to its very significant electrical changes with the phase change.

The main goal of this project is to produce thin films of monoclinic VO₂ and to be able to perform the structural characterization simultaneous with the electrical characterization. For that to happen, a new holder is proposed that must fit the x-ray diffraction equipment, used to assess the structural transition, and must have the ability to measure, heat and control the sample temperature, while allowing the measurement of the electrical characterization of the films.

Work strategy

The present work was divided in five main stages:

1. The production and characterization of VO₂ thin films: This stage was mainly done in a clean room, for the films depositions and the Rapid Thermal Annealing processes. After that, the samples were taken to the PANalyticalX'Pert Pro X-ray diffractometer to analyze the crystallinity and structure of the vanadium oxide films. The optimized condition was electrically characterized in a probe station with a heating stage included to test the transition. For this, electrical contacts were deposited on the films to test the temperature induced electrical changes.
2. Development of the Heating element using an ITO thin film resistor: In this stage, tests were performed using Glass/ITO substrates, a thermocouple, an IC and an Arduino to allow the control of the temperature on the sample. All the electrical schemes were tested several times in a breadboard, and after the guarantee that all in correct the schemes were copied to a software in order to produce a PCB. In the stage also, the Arduino codes were also developed.
3. Multipurpose Holder design: In this stage a holder was developed, and 3D printed that would allow the heating of the samples, the usage on the XRD equipment without interfering the x-ray beam and the extraction of the electrical signal. For this the sample needs to be inserted in an *Edgecard* Connector and must possess a thin film resistor deposited on the opposite side of the VO₂ film. This was a critical stage in this project, because it will join the previous stages, guarantying that the holder does not have influence in the measurements.

4. Proof of concept: After ensuring that all previous stages were functional, the multipurpose holder is ready to perform a simultaneous test.
5. New mask design: To improve the quality of the measurements, new masks for the electrical contacts and for the VO₂ film were drawn and fabricated.

Chapter 1- Introduction

1.1 Vanadium oxide and VO₂ and its electrical, structural and optic properties

The main goal on this work is to produce a multipurpose holder capable of controlling the temperature of a sample while allowing the in-situ characterization by many other techniques. The sample proposed will have a layer of vanadium oxide VO₂. The compound vanadium dioxide (VO₂) exhibits a reversible metal to insulator transition at a temperature of 68 °C [1]. This oxide has a tetragonal structure above the phase transition temperature and presents a metallic behaviour [2]. Below the phase transition it presents a monoclinic structure [3] and an insulator behaviour. The conductivity may change between 400 Ω⁻¹cm⁻¹ for temperatures around 400 K and 1.3 Ω⁻¹cm⁻¹ for temperatures near 300 K [1]. This phase transition is reversible and , have big changes in the electrical and optical properties making this oxide thin films a great material for a few applications such as sensors and smart windows [4]. When the oxide is below the transition temperature, it is transparent to near-infrared light, but it becomes translucent when above that temperature. This is a fast transition, around 10⁻¹² s (1 ps) [4] and can occur in more than 10⁸ cycles [5].

The formation of VO₂ happens only in a small range of oxygen partial pressures [6] (showed in Figure 1) and it's been notice that this partial pressure has effects on the structural and resistivity transitions behaviours of VO₂ [7]. Vanadium generally presents synthesis difficulties due to the existence of several oxidation states [8].

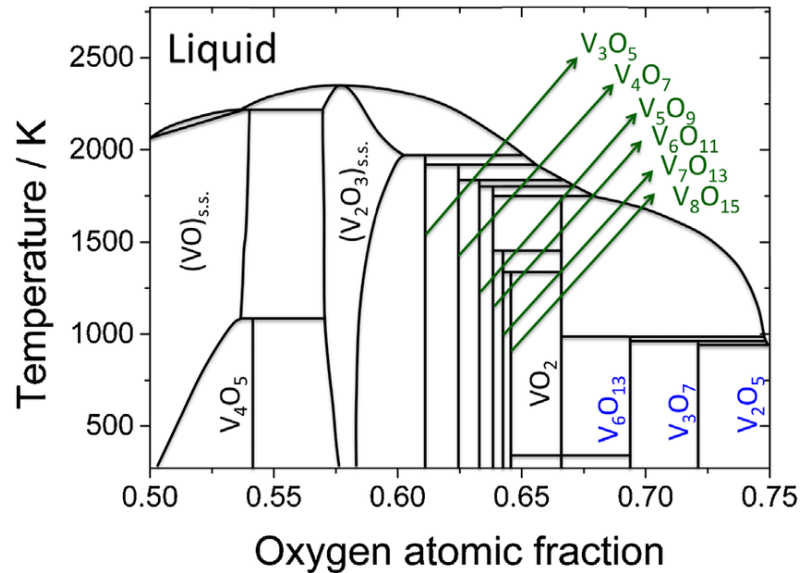


Figure 1 – Schematic V-O phase diagram with the Magnéli series (V_nO_{2n+1}) highlighted in blue and the Wadsley series (V_nO_{2n-1}) highlighted in green [9].

Table 1 shows different vanadium oxide phases and the respective transition temperature (T_c), crystalline structure and space group.

Table 1 – Vanadium oxide phases with transition temperature, crystalline phase and space group

Phase	T_c (°C)	Crystalline structure	Space group	Ref.
VO ₂ (A)	162	Tetragonal	P4 ₂ /ncm	[10]
VO ₂ (B)	-	Monoclinic	C2/m	[10]
VO ₂ (M)	68	Monoclinic	P2 ₁ /c	[10]
VO ₂ (R)	68	Tetragonal-Rutile	P4 ₂ /mnm	[10][11]
V ₆ O ₁₃	-123, -218	Monoclinic	C2/m	[12]

The VO₂ (A) phase presents a well-defined thermochromic shift at a transition temperature of 162 °C. This high temperature makes this phase less appealing (regarding energy saving) than the VO₂ (M) phase. Besides that, the VO₂ (M) phase is the only that exhibits a reversible MIT, converting to VO₂ (R) above its transition temperature [13].

To obtain the VO₂ thin film, there are some techniques available, such as sputtering[14]–[16], electron beam[17], [18] and sol-gel solution[5], [19], [20]. For the sputtering process, VO₂ can be obtained by radiofrequency reactive sputtering of pure vanadium target with a power of 300 W, a pressure of 1.5×10^{-2} Torr and a temperature of 500 °C [14]. Concerning the electron beam process using pure VO₂ powders that were formed into cylindrical shape by a press. The process begins with a fixed pressure of 1×10^{-7} Torr, after that pure oxygen was introduced inside the vacuum chamber. The substrate was heated to 250 °C and later a rapid thermal annealing procedure was made into the films [18]. About the sol-gel method, consist of a spin-coating and then an annealing process under low pressure. The coating solution can be prepared by synthesizing vanadium triisopropoxide in isopropanol [19].

To characterize the VO₂ thin film, a heat source is needed, and every equipment has its own heating system and it is not reliable the correlation of the phase change effects in the different measures of different equipment's because the heating system are not the same and to guarantee the correlation, all the heating system must be precisely calibrated. So, every sample must have a thin film resistor that will heat with a current flow. This will ensure that all measures will have the same conditions when heating and it can even be used in different equipment's like the atomic force microscope, the ellipsometer or the spectrophotometer.

To perform structural characterization, it is used the XRD equipment [17], [21] to determine the phase change through a peak shift. In the electrical characterization it is expected to observe a sudden decrease of resistance with the increase of the temperature [19]. For optical characterization, it is possible to do transmittance and reflectance test and expect a change around the predicted temperature point [5], [17], [21], [22].

As already mentioned, the main goal of this work was to develop a multipurpose holder to allow the characterization of this transition. Not just the structural but also the electrical and optical characterization performed using the same heating protocol and “stage” will allow to all properties.

In order to simplify the system, a substrate with a thin film resistor was chosen as heating element, with a help of a power supply the thin film will heat and then the substrate with the VO₂ film will heat consequently. The resistor is a transparent conductive oxide (TCO), more specifically

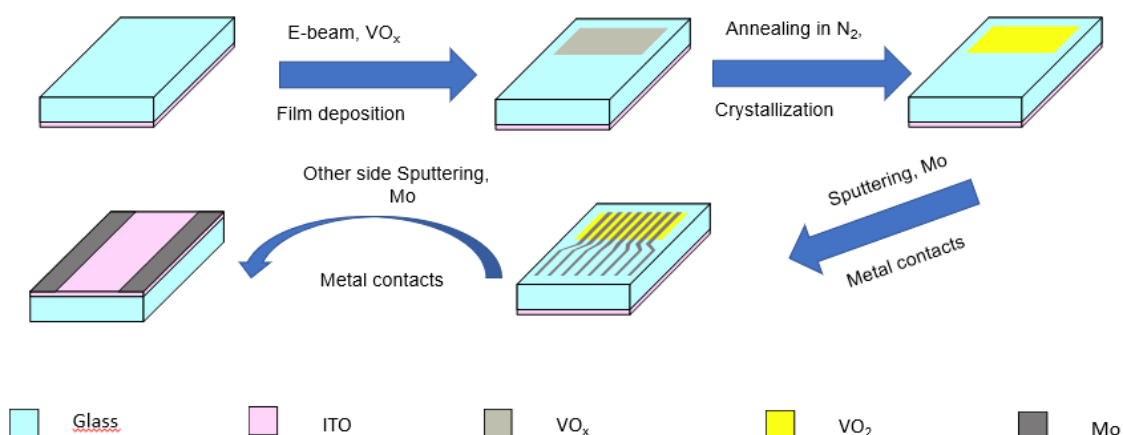
a film of indium tin oxide (ITO). To fulfil the goal of this work, an Arduino has used to control the temperature, contacts were deposited in the VO₂ thin films to do electrical characterization and a holder was designed to group all the system and to fit the X-Ray diffractometer present in CENIMAT.

Chapter 2 - Materials and Methods

2.1 Fabrication techniques

The VO₂ thin films were produced by electron-beam evaporation (e-beam) in a vacuum system existent in CEMOP. The substrate chosen was Corning Glass coated with ITO that was used as the resistive/heating elements. The VO₂ was deposited on the uncoated side. To study the formation of VO₂ in different surfaces, other substrates were also tested (Si, SiO₂ glass etc). The main substrates used were the ones with transparency properties, so Corning glass, glass and glass with ITO, being this last one, the most used due to the TCO. This TCO came already deposited in the glass from factory. After the e-beam process, the sample with VO_x, were subjected to thermal treatments in Rapid Thermal Annealing system (RTA) process in AS-One RTP System to promote the crystallization of the oxide, VO₂. Different temperatures and N₂ pressure were tested to optimize the formation of VO₂.

The optimized settings used in the final devices in this process consisted of temperature of 450 °C, in a N₂ atmosphere, during 300 s and a heating rate of 50 °C/s. After that, the samples were submitted to a sputtering process in an AJA ATC 1800 to deposit metal contacts in the top and in the bottom. Different materials were tested as electrical contacts such as Al and Cr evaporated but due to weak mechanical adhesion, sputtered Mo was the chosen metal to the contacts with a thickness of 60 nm. A schematic of the fabrication process can be seen in Figure 2.



The deposition patterns were done using shadow masks. The top contacts have the purpose to perform electrical characterization and the bottom contacts are made to allow to heat the sample. The contacts were designed to fit an *Edgecard Connector*.

2.2 Characterization techniques

To characterize the samples, different techniques were used, being the focus on XRD made in PANalyticalX'Pert Pro X-ray diffractometer in Bragg–Brentano geometry, with Cu radiation source. The measurements were performed in different 2θ ranges, but always including the region between 2θ values between 20° and 35° (where is the main peak of VO₂ can be found).

For phase identification the XRD patterns measured were compared to patterns from the Inorganic Crystal Structure Database (ICSD).

Measurements were made in profiler Ambius XP 200 in order to confirm the thickness obtained for the films in the deposition process.

To confirm the electrical change in the resistivity of VO₂ thin films below and above the transition I-V measurements were performed in Agilent 4155C semiconductor parameter analyzer connected to a Cascade Microtech M150 manual microprobe station, controlled by the software Metrics ICS and using the heating stage of the equipment, from 25 °C to 100 °C. In this characterization a voltage sweep from -1,5 V to 1,5 V, with a step size of 50 mV was performed at each temperature step ($\Delta T = 5$ °C). From the current measurements, it was possible to calculate the resistance of the VO₂ at each temperature.

2.3 Experimental Setup for MIT characterization

In this project, the experimental setup for characterizing the MIT transition was built considering three parts: the electronic control, the sample and the multipurpose holder.

In the electronic component, the goal is to have a temperature control system and to fulfill the goal an Arduino, a thermocouple and an IC (AD595) was used. The Arduino will read the information transmitted by IC and this IC will receive information from the thermocouple, that is in contact with the VO₂ thin film. With the information from the IC, the Arduino with a PID controller code, will decide if it necessary to increase or decrease the temperature of the sample, relatively to a defined Set Point. This control will be performed, with the PWM function of the Arduino, connected to a transistor, that will act like a switch, controlling the current flow in a thin film resistor deposited on the backside of the sample and insuring the temperature control. The IC used is circuit from Analog Devices, that has a supply voltage between 5 V and 30 V and has an output voltage of 10 mV/°C [23].

The VO₂ thin film is going to be deposit in a transparent TCO coated glass substrate. The TCO is going to be on the opposite side of the VO₂. The TCO will act as a heating element controlled when current is flowing between contacts. The VO₂ thin film will be deposited on the opposite side of the substrate. Electrical contacts will be deposited on this film. The top side of the sample, to do the electrical characterization of the sample.

Regarding the holder configuration, it must be able to support both the sample and the PCB with the IC and Arduino and should also be able to fit in the PANalyticalX'Pert Pro X-ray diffractometer. By using a flat design this holder can be used in several different equipment to allow the characterization while the sample temperature is controlled

To power up the whole setup, the applied voltage should be between 5 V and 30 V where the recommended voltage it ~ 10 V, because it is enough to power the circuit and it gives enough current to heat the sample. To achieve this, an external power supply was used at 10 V.

The system was projected to have square samples of 2.5 cm by 2.5 cm dimensions.

Chapter 3 - Results and Discussion

3.1 Structural Characterization of VO₂ films

3.1.1 Production of VO₂

To produce the monoclinic phase of VO₂ thin films of amorphous VO_x were e-beam evaporated using VO₂ pellets. Preliminary studies were performed to assess the specific conditions that allows the formation of VO₂ monoclinic phase using annealing process at different temperatures and with a pressure of 250 mbar in a N₂ atmosphere in a Rapid Thermal Annealing system (RTA) AS-One RTP System. From this study it was possible to conclude that 450 °C was the temperature that allowed to produce VO₂ monoclinic phase. The XRD scans performed on quartz substrates and at different annealing temperatures are presented in Figure 3.

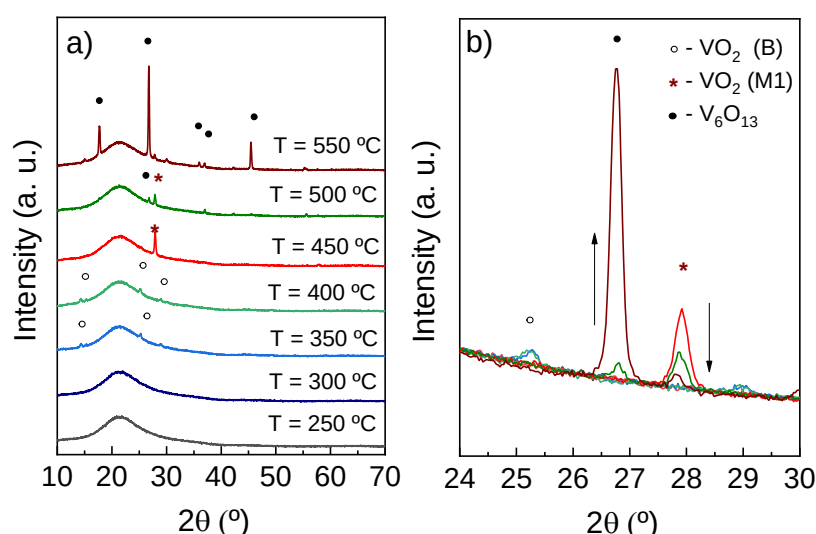


Figure 3 - XRD scans of VO_x films deposited on quartz samples annealed at different RTA temperatures in a N₂ atmosphere a) wide range scans showing the formation of VO₂(B) at 300 °C, VO₂(M) at 450 °C and V₆O₁₃ at 500 °C b) zoomed region to highlight the changes.

As it can be seen, the as deposited sample is amorphous and with increasing temperature the crystallization is promoted. Due to lack of oxygen, during the thermal treatment the films tend to keep the VO₂ stoichiometry of the evaporation pellets. For RTA treatments at 350 °C and 400 °C, the appearance of peaks at 2θ values of 14.4 °, 25.3 ° and 29.1 ° that can attributed to the (001), (110) and (002) planes of a monoclinic phase with the space group C2/m (ICSD #01–081–2392), which does not present the reversible temperature induced transition. This phase is usually found and is commonly referred as VO₂(B).

At 450 °C a sharp peak located at 27.8° (indicated by an asterisk) is attributed corresponding to the (011) plane of monocline phase VO₂(M) with space group P2₁/C (ICSD #01-072-0514), being this the desired phase that presents the metal-to-insulator transition. Annealing at higher temperatures induces the formation of another phase V₆O₁₃ that is a monoclinic structure (space group C2/m, ICSD #01-075-1140) is known and usually used in batteries as a cathode material [24]. The increase of temperature led to the conversion of VO₂(M) to V₆O₁₃ as can be

seen by the decrease of (011) main peak of VO_2 and by the increase of the (110) peak plane. The as can be seen in Figure 8b). At 600 °C, the film is decomposed.

These results show how vanadium oxides can present very similar structures, and that the optimal condition must be very well tuned in order to form the specific $\text{VO}_2(\text{M})$ phase. In this work, an optimal temperature of 450 °C was attained in a N_2 atmosphere.

The optimization of the pressure in the annealing process at 450 °C in a N_2 atmosphere during 300 s with a heat ramp of 50 °C/s was also performed. For this test 4 different pressure conditions during the thermal treatments were made, 100 mbar, 250 mbar, 500 mbar and 750 mbar and XRD scans can found on the following Figure 4.

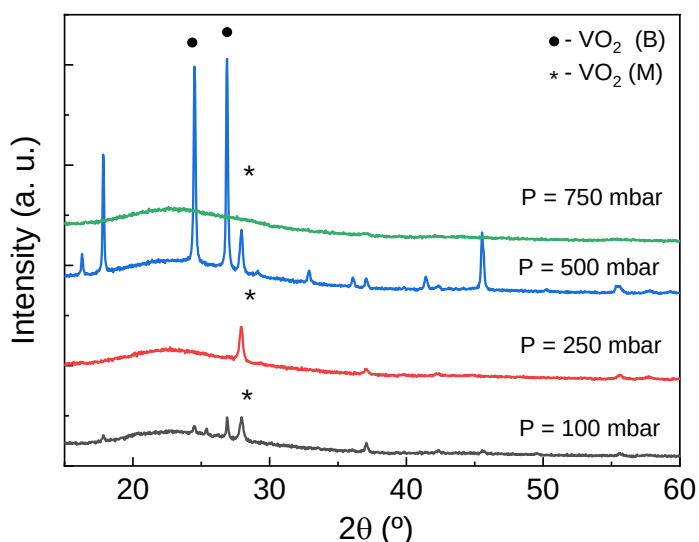


Figure 4 – RTA test with different pressure conditions on Corning glass

This test (Figure 4) was made with a Corning substrate and it is possible to conclude that the pressure of N_2 in the chamber have effect in the crystallization of the VO_2 thin film. For high pressures, there are several peaks other than the expected one from the VO_2 and a mixture of different phases are present.

The same test was made with a substrate with the VO_2 thin film in the top and a TCO (in the case ITO) in the bottom and the same conclusion were obtained (Figure 5). The best condition of pressure is 250 mbar of N_2 in the chamber.

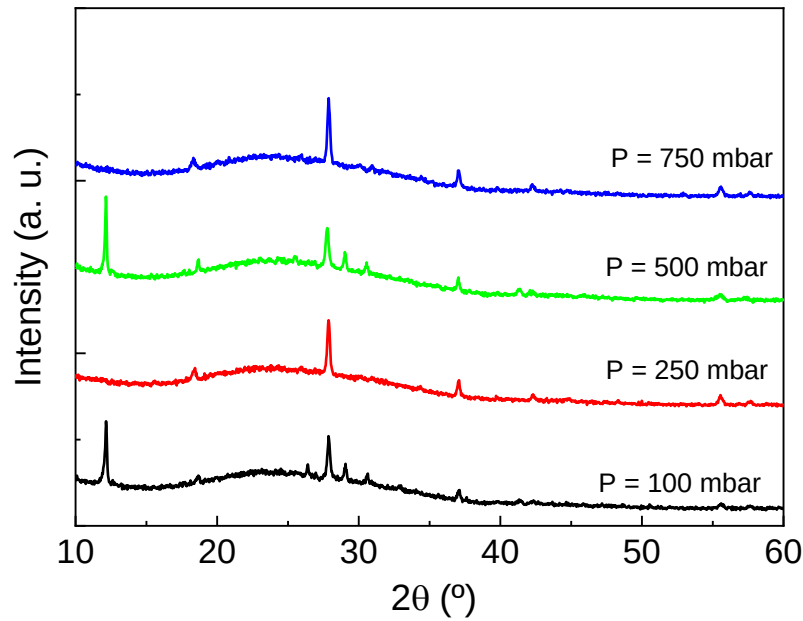


Figure 5 – XRD scans of ITO coated samples under different RTA pressure conditions.

It is possible to observe that for the pressure of 100 mbar and 500 mbar there are some peaks at 12° of 2θ , that do not correspond to the VO_2 but that indicate the formation of a different phase. In these samples a C contamination was detected possibly due to the evaporation process where the misalignment of the electron beam lead to evaporation of the graphite crucible along with VO_2 .

Comparing all the substrates used in the work, it is possible to conclude that glass substrate with ITO is the best option to use in the final sample, due to have a good crystallization of the VO_2 , it is transparent and already have the TCO build in from factory, that gives at least one less step in the fabrication process.

Due to the presence of some peaks not attributed to VO_2 phases, an essay in different substrates was also tested (Figure 6) due to the fact that as already been reported that the crystallization of VO_2 is sensitive to the substrate used [25].

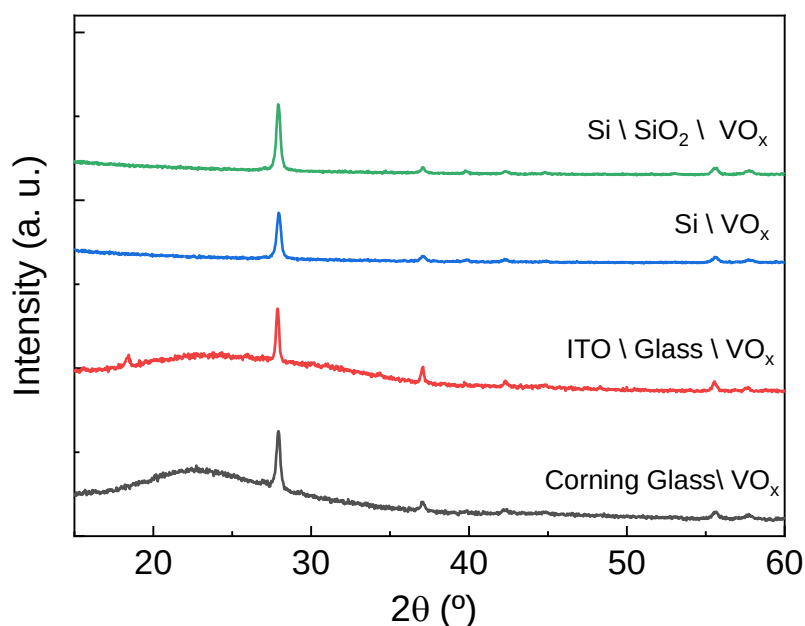


Figure 6 – XRD scans on VO_2 deposited in different substrates at a 250 mbar N_2 pressure in the RTA system.

Comparing different substrates, a pressure of 250 mbar there is no significant difference as can be seen in Figure 6, so the best choice is still the option with ITO underneath the glass, for the its transparency and for having already the TCO from factory.

3.1.2 Phase change Transition

In order to confirm the reversibility of the phase change of VO_2 the sample produced with the same RTA specifications at 250 mbar, was tested inside the heating chamber of PANalyticalX'Pert Pro X-ray diffractometer, where it was heated from 50 °C to 100 °C in 5 °C steps and then cooled from 100 °C to 30 °C, also with 5 °C steps. For each temperature 5 measurements were performed around the VO_2 main peak position, between 25.5 ° and 28.5 ° of 2θ , using a step size of 0.0334 ° of 2θ .

The performed scans are presented in the following Figure.

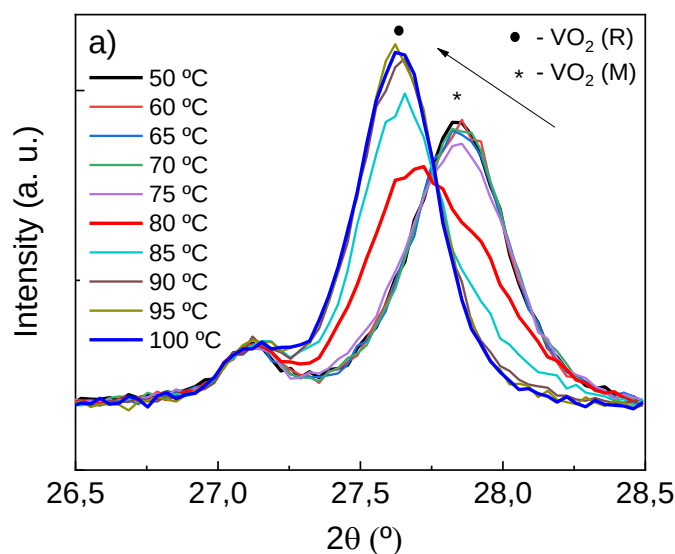


Figure 7 – XRD in-situ scans: Heating of the VO₂ thin film on a Si Substrate

It is notorious in the Figure 7 a change in the XRD measurement to the different temperatures when heating the VO₂ thin film, this shows that there is a phase change when changing the temperature and that the annealing process conditions were correct to obtain a VO₂ thin film. The conditions were 450 °C during 300 s with a heat ramp of 50 °C/s and with a 250 mbar N₂ pressure.

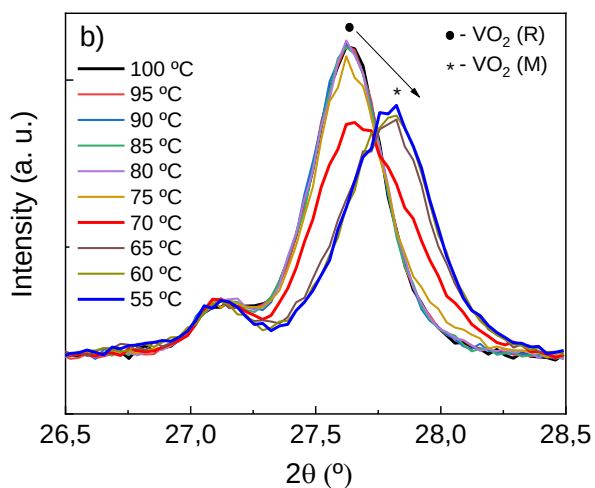


Figure 8 – Colling of the VO₂ thin film on a Si Substrate

During the same process, but this time, cooling the sample from 100 °C to 50 °C presented on Figure 8, it is possible to conclude that there a phase change, but this time, to the initial structure, this means that the produced VO₂ presents a reversible phase change.

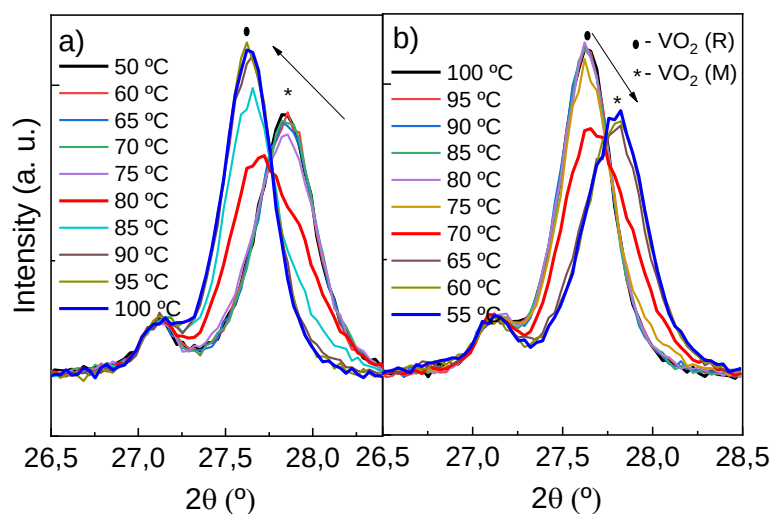


Figure 9 – a) Heating of the VO_2 thin film on a Si Substrate b) Colling of the VO_2 thin film on a Si Substrate

In Figure 9 it is possible to conclude that there is a phase change with a temperature stimulus applied and this phase change is reversible.

3.1.3 Structural characterization using the Multipurpose Holder

Knowing the processing conditions required to produce VO_2 thin films, the same protocol was used in glass coated with ITO substrates. The idea was to test the temperature control system (explained in more detail in section 3.3) and the 3D printed holder, in order to characterize in-situ the MIT transition in the XRD system and using the Arduino to control the temperature. The first testes showed a gradient heating effect possible due to the connector, as can be seen in Figure 10.

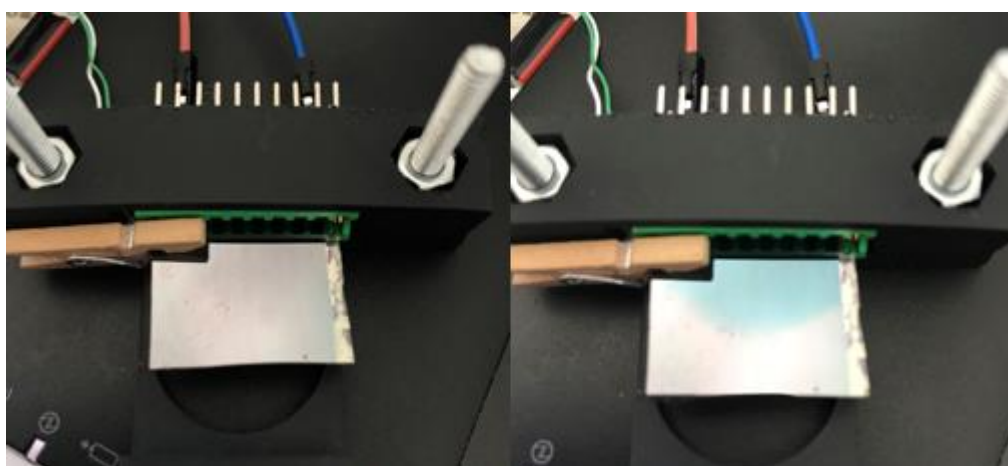


Figure 10 – Pictures of the holder and sample controlled Gradient effect on the sample

This gradient effect means that the temperature is not uniform along the sample surface. To confirm that the sample had different temperatures in different spots, the thermocouple was putted in several places confirming different temperatures.

Nevertheless, it was possible to test the holder inside the X-ray diffractometer, by placing the thermocouple near the spot measured by the equipment. The resulted scans at different temperatures are presented in Figure 11.

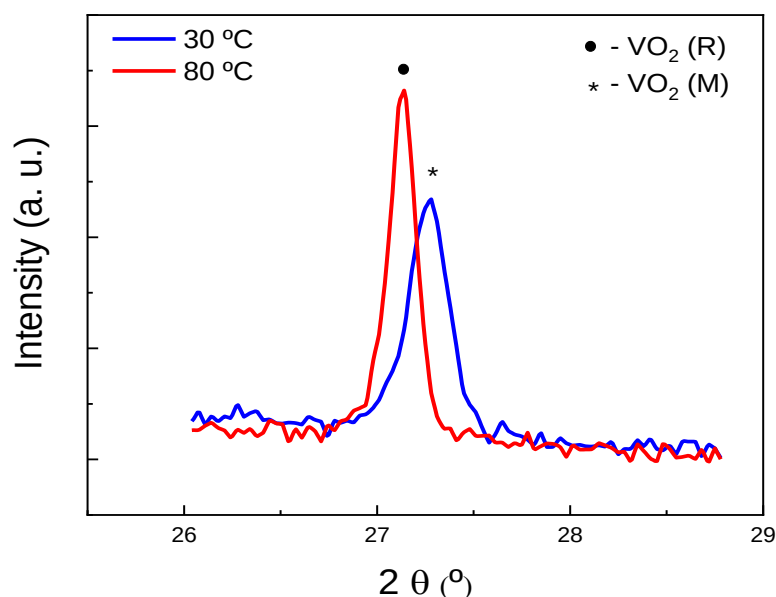


Figure 11 – XRD scans of VO_2 films where the temperature was controlled using the Arduino setup and the ITO resistor and the sample was mounted on the multipurpose holder.

In Figure 11, it is possible to observe the phase change in the VO_2 thin film, with two measures, one at 30 °C and the other at 80 °C, so it proves that the holder used and the system develop to heat and control the sample temperature works and it does not interfere in the measurement. By controlling the temperature using the Arduino it was possible to testify the reversibility of the transition although a uniform heating cannot be insured.

To minimize the temperature gradient shown, the ITO film can be etched and patterned.

3.2 Electrical characterization of VO_2 films

To characterize the transition, the samples were tested in a semiconductor parameter analyser to obtain the electrical resistance of the films. As a first step, this characterization was performed using the in-built heating stage of Agilent and electrical contacts were deposited in VO_2 thin films to allow the extraction of I-V curves.

3.2.1 Electrode Mask design

To perform the electrical characterization, two different electrical contacts designs were used, one in a “T” shape and another having vertical stripes. The first design was used because

shadow masks were already available, and the second design was developed during this work to optimized in the implementation in the multipurpose holder using the *Edgecard* Connector assembly.



Figure 12 – Design of the Vertical stripes design mask produced

This second design, (shown in Figure 12) was drawn in *Adobe Illustrator* and it was cut in PET substrates to produce shadow masks using the CO₂ infrared cutting system (Universal Laser System) with 10 W of power and 0.254 m/s of speed

3.2.2 Electrical Test

The tests were performed in Agilent 4155C semiconductor parameter analyzer connected to a Cascade Microtech M150 manual microprobe station, controlled by the software Metrics ICS, using the heat plate of the equipment, from 25 °C to 100 °C in 5 °C steps. In each measurement a potential sweep from -1.5 V to 1.5 V with 61 point, measuring the current and extracting the resistance at each temperature. In the vertical stripes design two measurements were performed at two different pairs of electrodes to test the different distance between electrical contacts as shown in Figure 13. In the “T” shape design two measurements were also performed to observe the reproducibility of the electrical changes in the VO₂ thin film.

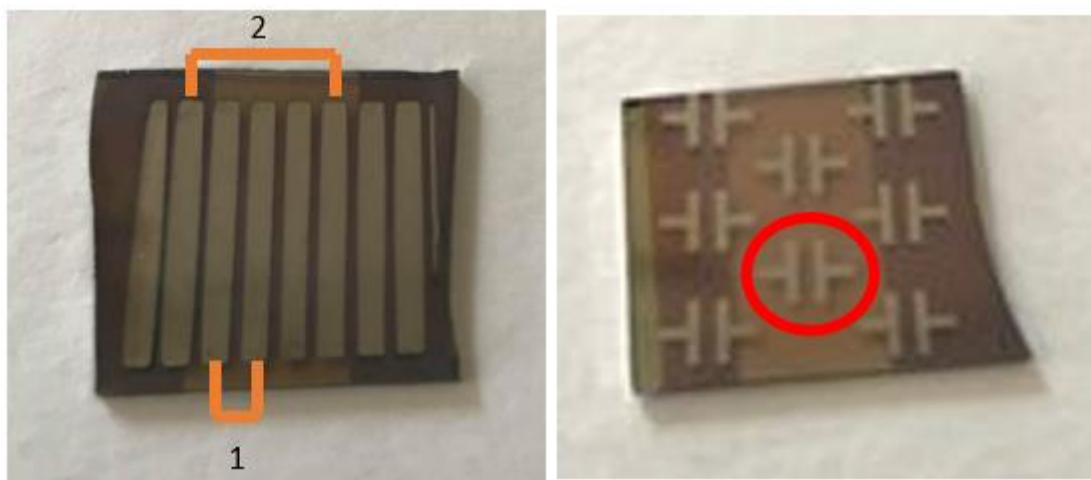


Figure 13 - On the left side vertical stripes design with two distance marked corresponding to the electrodes used during the electrical characterization. On the right side “T” shape design with a mark

In the design of Figure 13, the distance marked as “1” has 0.6 mm of separation between electrodes and the distance marked as “2” is 9.1 mm. The two measures in the “T” shape design were made in the marked spot at the Figure 13. The two measures were made to observe if the contacts between the two measure contacts have any influence in the measure.

The Figures 14 and 15 shows the values measured at the distance of 0.6 mm, being evident that there are straight lines, an ohmic behavior in the range of -1.5 V and 1.5 V.

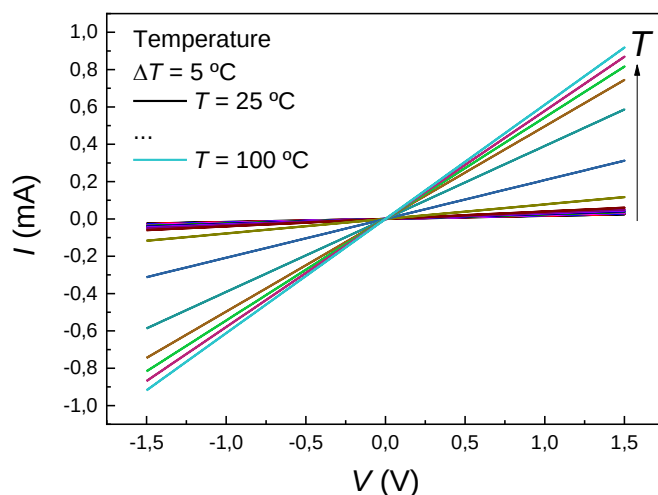


Figure 14 – I-V measurements performed at different in increasing Temperatures using contacts 0.6 mm spacing

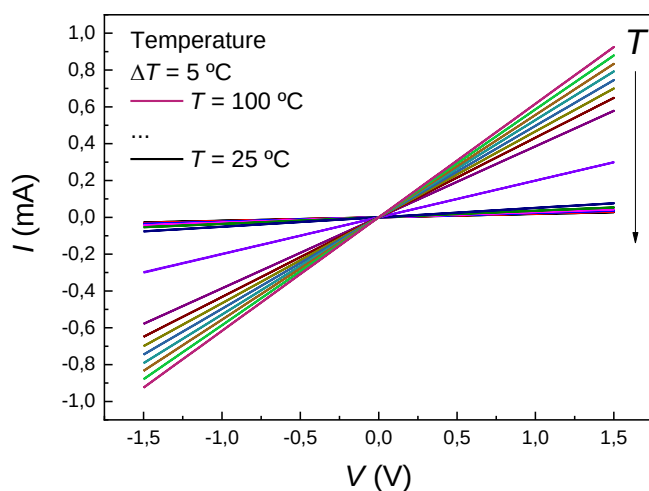


Figure 15 - I-V measurements performed at different in decreasing temperatures using contacts 0.6 mm spacing

The measurements performed using the Agilent heating stage allowed to confirm the quality of the MIT transition as can be seen in Figure 16.

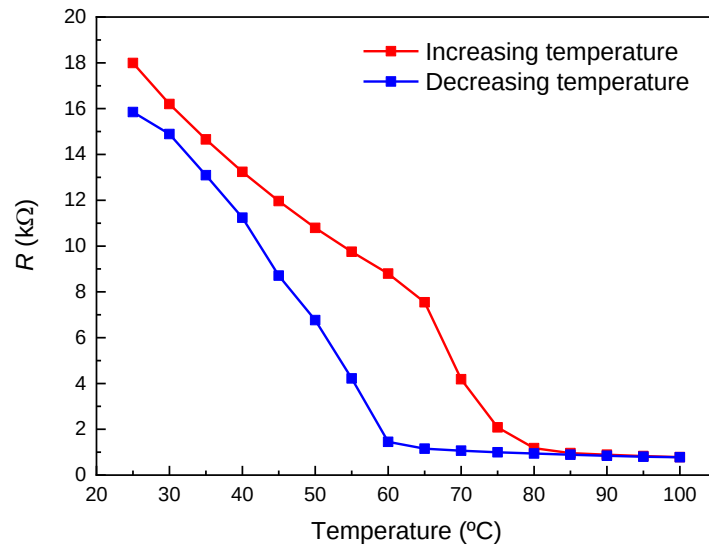


Figure 16 – Resistance evolution of VO₂ thin films for different heating temperatures using the Vertical stripes design, with a contact spacing of 0.6 mm

In the first test (Figure 16) it is possible to observe a decrease resistance with the increasing of the temperature. The resistance changes a little more than 1 order of magnitude, from near 20 kΩ in the low temperature regime (monoclinic phase and “insulator” behavior) to a resistance of near 800 Ω in the high temperature regime. The transition also presents a hysteresis. For all measurements performed, it was observed the same ohmic behavior showed on Figures 14 and 15.

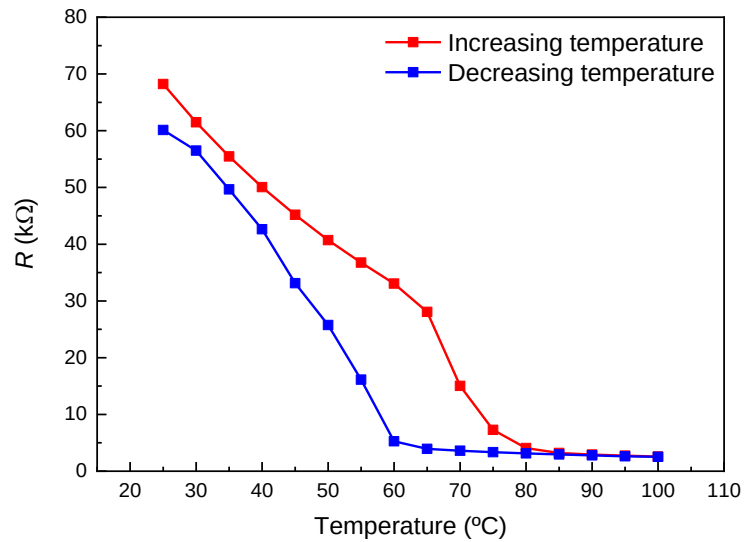


Figure 17 – Resistance evolution of VO₂ thin films for different heating temperatures using the Vertical stripes design, with a contact spacing of 9.1 mm. For this second distance, the resistance drop is more significant due to the increasing distance between contacts.

The same test was performed using another pair of electrodes with different spacing as can be seen in Figure 17.

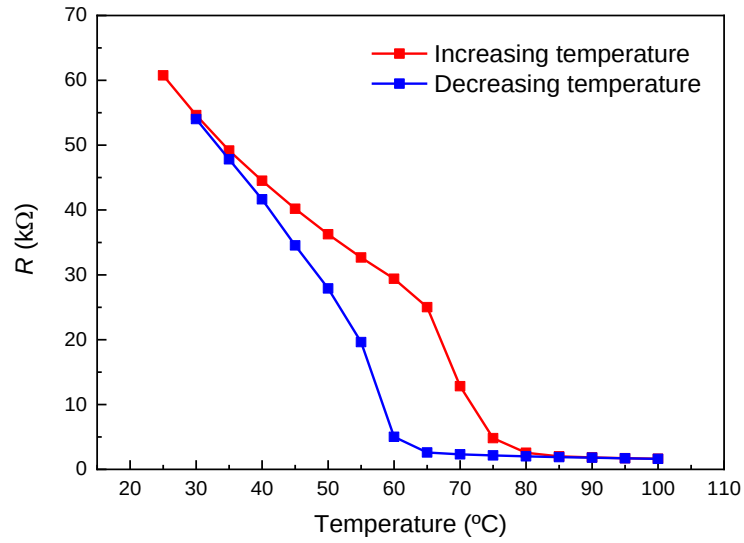


Figure 18 – Resistance evolution of VO₂ thin films for different heating temperatures using the “T” shape electrode design.

The Figure 18 shows the test performed on the “T” shape and as expect, it is notorious the electrical change with the temperature difference.

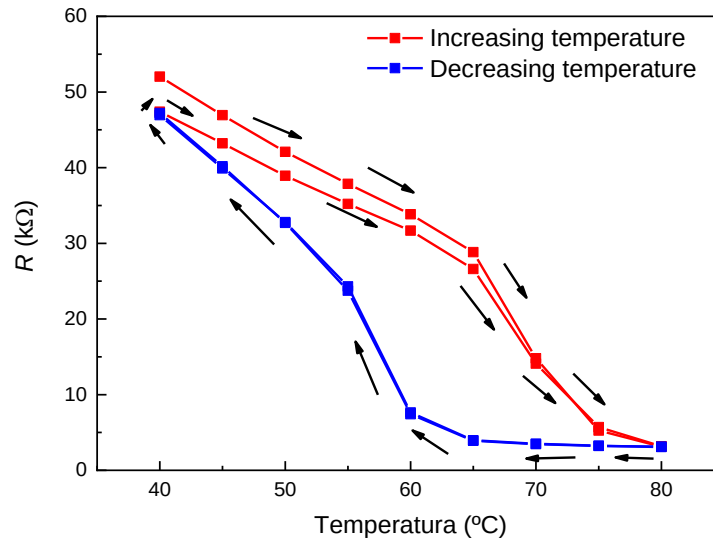


Figure 19 - Cycle test in "T" shape design

It is possible to conclude that in all shapes a decrease of the resistance with the increasing of temperature and it possible to observe that for a temperature around 65 °C there is two distinguish states, making this a great solution for switch, for instance a “on state” and a “off state”.

The cycle test (Figure 19) shows that the VO₂ thin film resistance change is reproducible.

3.3 Temperature Controller development

3.3.1 Circuit development

In order to measure and control the temperature of VO₂ thin film, an electrical circuit was designed. The brain for this circuit was an Arduino Uno which receive the temperature information from the circuit and with a PID function, the Arduino will decide if is necessary to increase or decrease the temperature and the amount needed to reach and maintain the temperature around the wanted Set Point.

The circuit has an IC (AD595) that will get the temperature information from a type K thermocouple and this reading will be send to the Arduino as a voltage value, that for this IC specific case o is 10 mV/°C. To protect the IC, a short circuit with a 10 kΩ resistor from pin 1 of the IC and the ground was introduced. In this pin is also connected the positive side of the thermocouple and the negative side is connected do pin 14. To power the IC, we can use a voltage between 5 V and 30 V, connected to the pin 11. The pins 4, 7 and 13 are connected to ground. The pins 8 and 9 have a short circuit between them and the voltage in there is the temperature information for the Arduino, the rest of the pins were unconnected. The schematic of these connections made in *Eagle®* Software is shown in Figure 20.

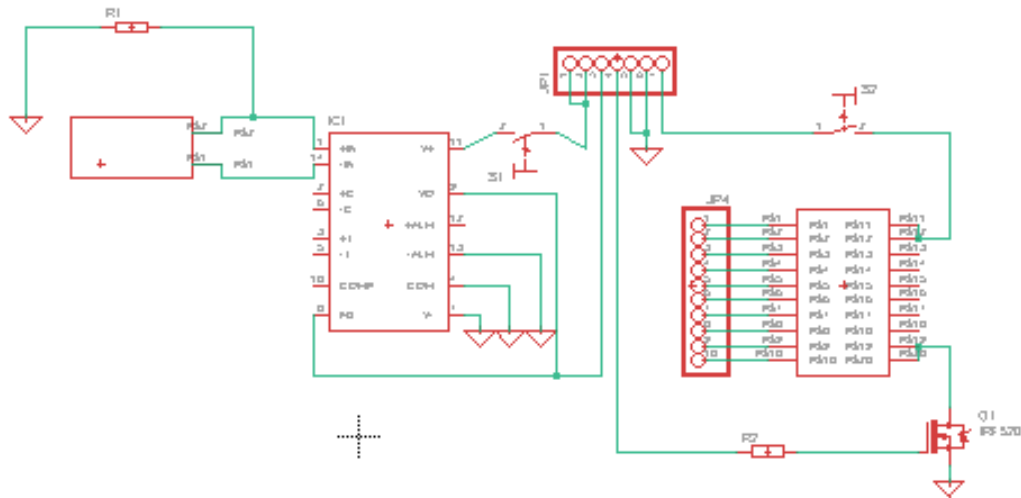


Figure 20 - Schematic of the Temperature controller setup

After processing that information through the PID function, the Arduino will control the amount of current in the thin film resistor with the PWM function, with a square wave output that gives 5 V in the maximum peak and 0 V at the lower peak. This PWM, function connected to a transistor (N-channel enhancement mode power MOS – IRF520) can act like a switch, controlling the amount of current in the thin film resistor under the substrate. The drain is connected to one side of the thin film resistor of the substrate (while the other contact is connected to the power

supply), the source is connected to ground and the gate is connected to a $330\ \Omega$ resistor that is connected to the PWM of Arduino (schematic in Figure 21). This purpose of this resistor is to protect the Arduino from unwanted and unexpected current that may damage the equipment.

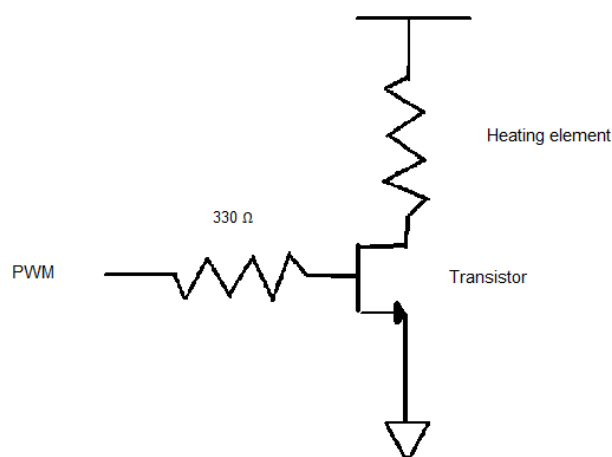


Figure 21 - Schematic of the transistor with the sample

The thermocouple is connected to the circuit through a thermocouple plug and all the connections with the sample are made with an *Edgcard* Connector with 20 pins, 10 for each side of the substrate. To connect the power supply in the system and to extract the electrical data from the sample out of the PCB, there are pin headers. In order to have the capability to turn off the circuit, it has two switches.

To design the circuit the software *Eagle* was used.

3.3.2 PCB development

Regarding the PCB specifications, there are no limitations on the size of the board, but there are a few details to consider such as the location of the components and the width of the traces. The *Edgcard* Connector should be on one of the edges of the board (so that the sample doesn't have anything under), the Pin Headers must be placed in a way, so that it is possible to connect wires, the thermocouple plug needs to be the closest possible to the IC and the switches must have some room to be operable. The traces width chosen for the PCB is 6 mil (mil is a unit used in PCB software and industry, being 1 mil equal to 1/1000 of the inch or $25.4\ \mu\text{m}$), that is enough to hold almost 1 A, more than the system reach. The thickness of the PCB is 1 mm, the manufacturer offers several sizes of PCB, but this parameter does not have effect on the outcome of the system, so it has chosen a size not too big and not too small to fit well in the holder. The PCB, shown in Figure 22 is 77.47 mm by 54.61 mm.

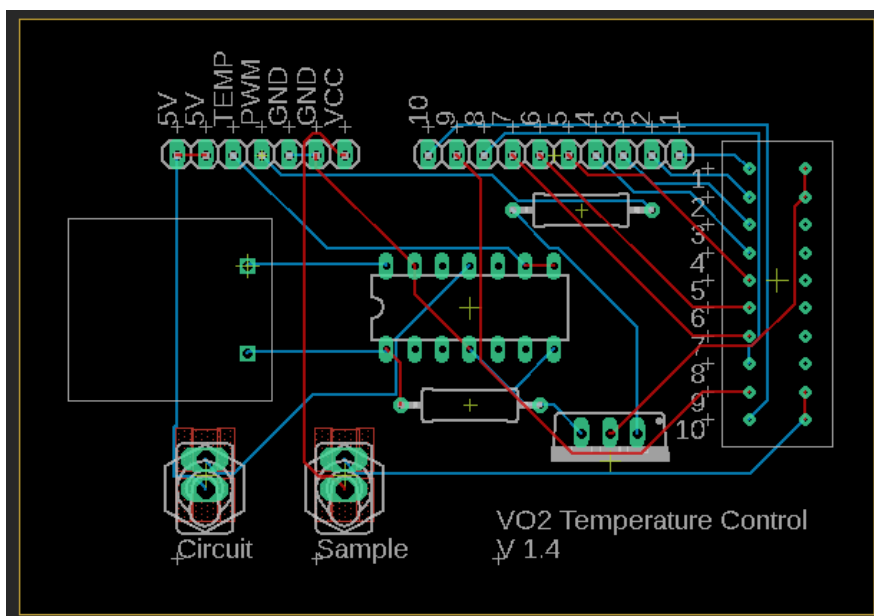


Figure 22 - PCB Layout without the ground planes and the vias.

Ground plane in both sides of the PCB and several vias along the board to connect both ground planes were projected. The vias will ensure a proper grounding of the circuit.

To design the PCB, the software *Eagle*. Pictures of the Pin Headers, the EdgeCard Connector and the PCB are available in Appendix A.

The ordered PCB was successfully build with all components soldered.

3.3.3 Arduino

The Arduino is the main part of the electrical system, being responsible to read the temperature and control the temperature of the sample. For this, a code was developed, that will work in all the Arduino types. The one used was the Arduino Uno, from a third-party supplier, but this condition will not affect the outcome of the project.

The signal from the AD595 will enter the Arduino in an analog port, after that, it is converted to a temperature value and a smoothing function to give a constant and accurate temperature reading. With this reliable value it is applied a Proportional-Derivative-Integral (PID) function, this is the function that decides if the system needs to be heated or cooled through a Pulsed-Width Modulation (PWM) function that have and exit in certain digital port (the ones with the “~” sign). The system has a changing Set Point function that can be turned on or off by the user, when turned on, the Arduino will change the Set Point of the system with the increment intended by the user after a desired time, also chosen by the user. The code is provided in Appendix B.

The Arduino software is called *IDE* and can shows the actual temperature of the sample and the Set Point in two form, numerical and graphical (Appendix C).

The code is prepared to have an LCD display with sixteen characters by two lines, with an I2C module. This module will reduce the sixteen connections to four, being these four

connections, a 5 V, a ground (GND), a serial clock line (SCL) and serial data line (SDA) ports. The SCL will connect to the analog port 5 and the SDA will connect to the analog port 4. The display is programmed to show the actual temperature read, the Set Point, the increment and the time per Set Point chosen by the user.

In Figure 23 a reading on the LCD is displayed as an example of the information retrieved by the Arduino code.



Figure 23 - LCD display with temperature, Set Point, increment and time information

It is available in Appendix D, a brief explanation of the IC used and a brief explication about the Arduino and the functions used in the code developed.

3.4 Multipurpose Holder development

The holder was developed in a “T” shape where the narrow part is the one that fits in the x-ray diffractometer. The holder is fixed to the XRD prefix, and the sample is fixed to the holder using the *Edgcard* connectors. The central part of the holder has a hole, to allow in the future to perform optical characterizations in the VO₂ sample. In the larger part of holder, there is a small salience to fix the Egdecard Connector. With the same width of the larger part of the holder, there is a loose piece with the same salience of the holder to be able to fit in the top part of the Egdecard Connector and to fix it (this connector is symmetrical, and this feature makes possible to have the same salience size in booth pieces).

The design of the holder is presented in Figure 24 and the printer holder is presented in Figure 25.

The two pieces will fit in each other with the help of two screw and two nuts, one on each side, making the Edge Connector fixed during all measurements. The nuts will fit in the loose piece and the screws will go through the holder and will be hidden so the bottom part can be flat in order to be balanced in flat surfaces of several equipment.

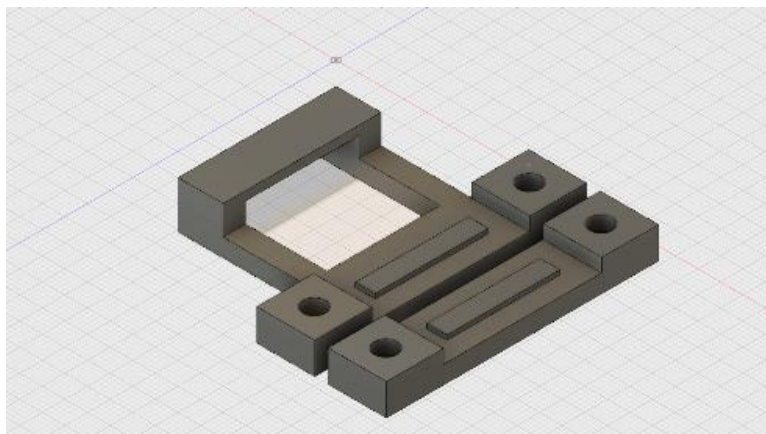


Figure 24 - Multipurpose Holder Design

The holder showed on Figure 24, has a length of 60.2 mm and a width of 42.9 mm. The segment that fits the XRD is 35.0 mm and a height of 10.4 mm. The loose piece has the same length of the holder but have a width of 12.9 mm and a height of 7.0 mm. A picture of the holder with the *Edgecard* Connector is showed on Figure 25.

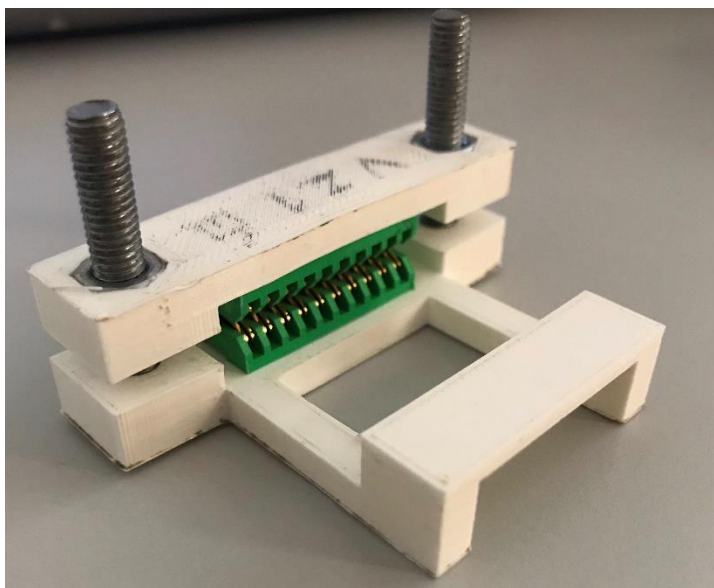


Figure 25 - Holder with the Edgecard Connector

The holder was designed and projected in *Fusion 360* and it was printed in the 3D printing Ultimaker 2 +, using a PLA compound, with an infill of 18%, a nozzle of 0.4 mm, a resolution of 0.15 mm, without the need of support. Several versions of the holder were designed, in order to correct the dimensions and the alignment of the samples. The versions evolution is in Appendix E by chronologic order. Pictures of the holder fitted on the XRD is in Appendix F.

A photograph of the developed multipurpose holder is shown (figure 26), with the produced PCB mounted on the back of the holder and set on the XRD system.

The PCB, the sample, a power source and the Arduino are kept inside the XRD fixture, having connections to a PC externally in order to allow the control of the heating element. As a reference two different temperatures ($T_1 = 30\text{ }^{\circ}\text{C}$ and $T_2 = 100\text{ }^{\circ}\text{C}$) are highlighted corresponding to a heating command from T_1 to T_2 with the Arduino code while the sample was continually scanned with x-rays.

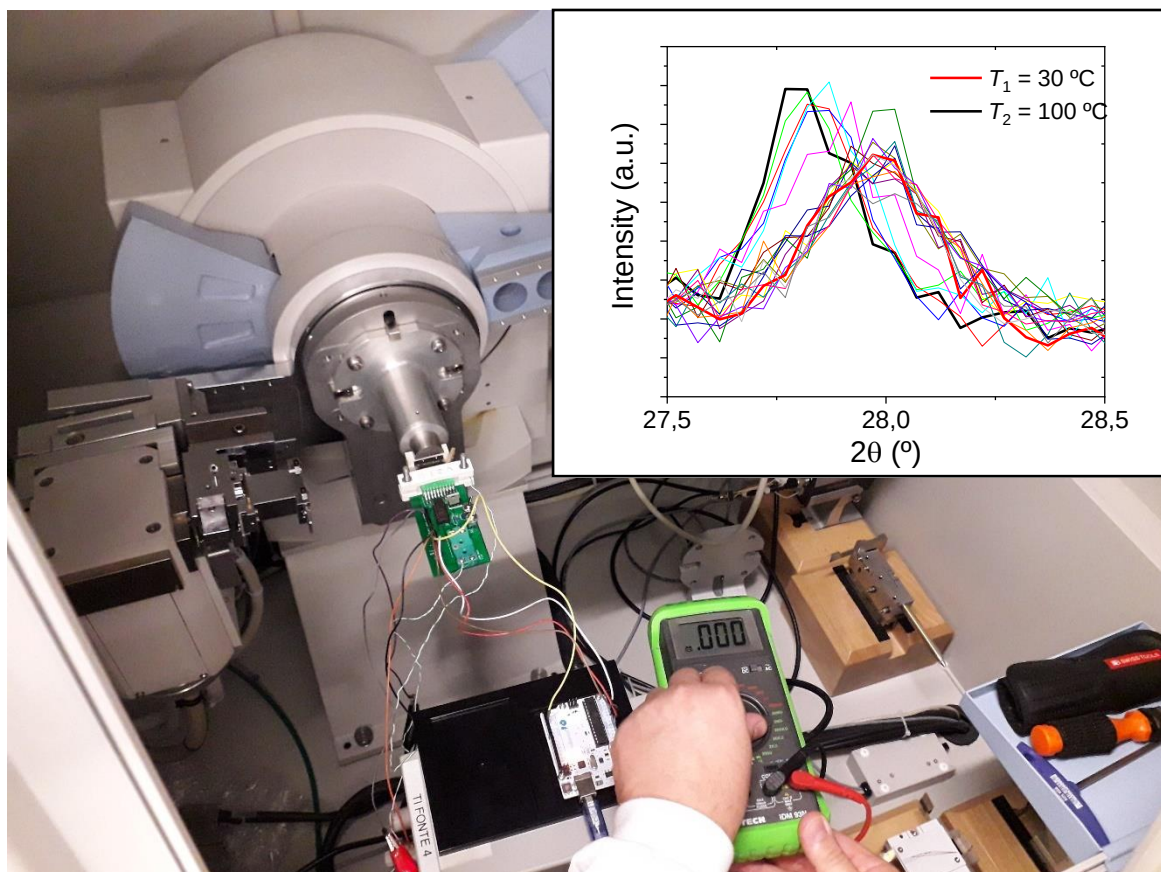


Figure 26– Final holder with the produced PCB. Diffractograms are also visible to show the structural properties of the films while the sample temperature is increased from 30 to 100 °C using the controller and the Arduino board.

It is possible to see the shift in the peak position while heating the sample, from 30 °C to 100 °C (corresponding to the scan more shifted to lower 2θ angles).

The PCB have included connections to perform in the future the extraction of the electrical characteristics of the samples, having contacts deposited on top. These measurements can be performed using a precision multimeter.

3.5 Electrical contacts optimization

After confirming that the system worked, a sample optimization was needed in order to do simultaneous characterization and correct some problems, like the gradient effect when heating. In order to perform the simultaneous characterization, a new mask (Figure 27) was

designed with eight stripes with 20 mm in length, being the lower part always the same size, 0.7 mm width and separated apart for each other 1.95 mm, so each stripe can connect to the Edge Connector individually. In the top part of the design, each stripe has 1 mm width and they have three different distance from each other, being this distance 0.5 mm, 1 mm and 1.5 mm, being this distance the same for each mask.

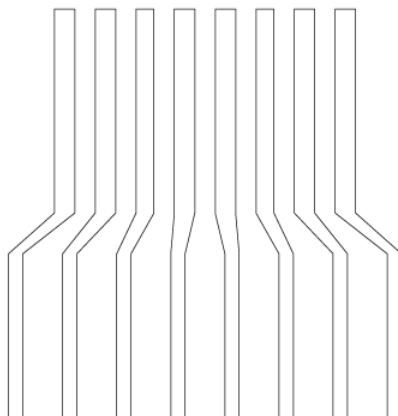


Figure 27 - Mask distance of 1 mm for electrical characterization

To prevent a short circuit between the stripes in the bottom part of the design and the Edgecard Connector, assuring that one contact stays connected with only one stripe for a better measure and to guarantee that there is no short circuit between the upper part and the bottom part of the sample through the sides, a simple mask were made, a rectangle with 20 mm by 10 mm. This mask is for the VO₂ thin film depositing process and it is placed in the upper part of the electrical design ensuring that the thin film do not reach the borders of the sample and the bottom part of the electrical design.

To have a better deposition of the metal contacts on the bottom part of the sample, a mask was made with two vertical stripes, with 20 mm in length and 5 mm in width, distance from each other 10mm. All the masks were made in Al.

In order to avoid the gradient effect observed, an etching process was made in the ITO, using the CO₂ infrared cutting system (Universal Laser System) with 25 W of power and 0.254 m/s of speed. This process was performed before every other process and it was made in the lower part of the sample, in the part that connects to the *Edgecard* Connector to ensure that the current will only flow in the top part of the sample, that will assure that if the gradient effect persist to exist, it will be minimized and the temperature reading will be more accurate.

Chapter 4: Conclusions and future perspectives

Besides the goal of this project is not the optimization of the VO₂ thin films, a condition was determined, that does gives a VO₂ with some impurities, but it is VO₂ and it was possible to observe the phase change at 68 °C. The conditions of RTA are 450 °C, with a heat ramp of 50 °C, after achieving the temperature, it stays during 300 s with 250 mbar N₂ atmosphere. Further studies may conclude better conditions to the fabrication of the VO₂.

The electrical tests proved what were expected, two different states, a metal state and an insulator state and at around 65 °C, depending if the thin film is being heated or cooled, produce two different levels, that can be transformed into to switch states, an on state and an off state.

A holder was developed, fitted well in the equipment, especially in the X-Ray Diffraction system present in the CENIMAT laboratories. Besides that, a PCB was developed at the end and tested in the XRD. Although it was not possible to perform a simultaneous test due to contact problems as the Mo contacts were oxidized at the latest tests. New samples are required.

In the future, to prevent the gradient effect situation, some new procedures must be taken, for example, have the same size of TCO as the VO₂ and they are being aligned through the substrate. This process can be done by a better etching process or a by doing a deposition of the TCO using the mask used to deposit de VO₂ thin film.

It now can start to be tested in others equipment's, for instance, the Atomic Force Microscope or the ellipsometer, to get the most information possible, always with the same conditions

A new temperature measuring system can be done, replacing the one created. The new system can have an infrared temperature measuring system, this will promote less contact with the sample (less change of contamination) and a more precise read if the gradient effect persists to exist.

To improve the user experience, a program in some sort of programing language can be made, with the possibility to change the temperature Set Point, the increment, the cycle time, change the PID constants. Can also have the actual read of the temperature. This is helpful if the user is not comfortable programing or does not know how to program the Arduino.

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Appendix A – Components used for the PCB development

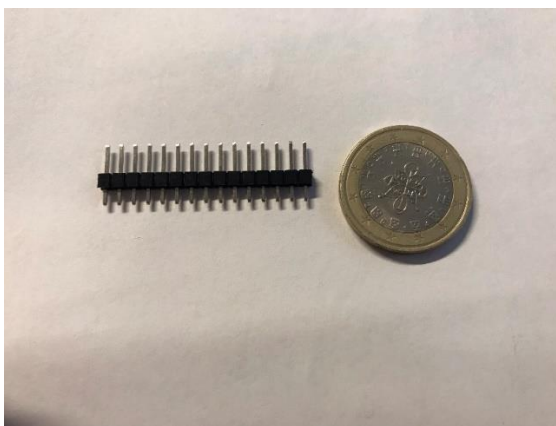


Figure 28 - 15 male Pin Header used in the PCB with an one euro coin for size comparison

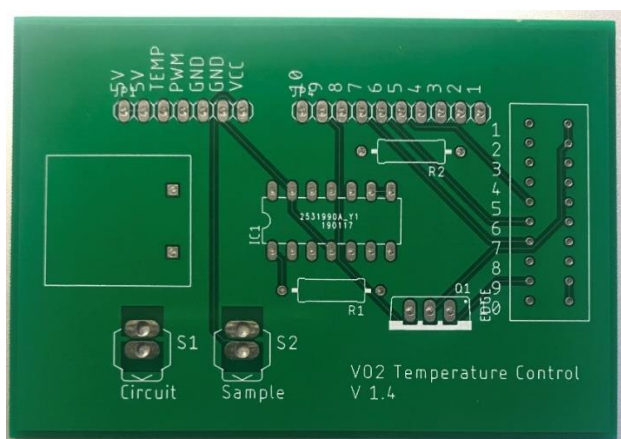


Figure 29 - PCB version 1.4



Appendix B – Arduino code developed for temperature control

```
#include <Wire.h>

#include <LiquidCrystal_I2C.h>

#define pSensor A0
#define resistor A1
#define pControlo 3

const int numReadings = 100;

float readings[numReadings]; // the
readings from the analog input

int readIndex = 0;           // the index of the
current reading

float total = 0;              // the running total

float average = 0;           // the average

float setPoint = 70;

int ControloPwm = 127;

double error = 0;

double P=0, I=0, D=0;

double kp=2, ki=4, kd=4;

double PID;

long lastProcess;

float Derror = 0;

float errorAnterior = 0;

float time_reset = 0;

float tempo = 0;

float tt = 0;

int i = 0;

float increment = 5;

float interval = 0;

float timeM = 10;

float margem = 1.5;

float tempoR = 0;

float somatempo = 0;

int raw= 0;

int Vin= 5;

float Vout= 0;

float R1= 10000;

float R2= 0;

float buffer= 0;

LiquidCrystal_I2C lcd(0x27, 2, 1, 0, 4, 5, 6,
7, 3, POSITIVE);

void setup() {
  Serial.begin(9600);
  lcd.begin (16, 2);
  lcd.setBacklight(HIGH);
  interval = timeM * 60;
  /*
  Serial.println("Qual o Set Point desejado?");
  while (Serial.available()==0){}
  setPoint = Serial.parseInt();
  */

  pinMode(pSensor,INPUT);
  pinMode(pControlo, OUTPUT);

  for (int thisReading = 0; thisReading <
numReadings; thisReading++) {
    readings[thisReading] = 0;
  }
}
```

```

}

void loop() {
  int ValorSensor = analogRead(pSensor);
  float voltage = ValorSensor * (5.0 / 1023.0);
  float Celsius = voltage*100;
  total = total - readings[readIndex];
  readings[readIndex] = Celsius;
  total = total + readings[readIndex];
  readIndex = readIndex + 1;
  if (readIndex >= numReadings) {
    readIndex = 0;
  }
  average = total / numReadings;

  /*
  //Serial Reader
  if (Serial.available() > 1)

    setPoint = Serial.parseInt();

  */

  //PID
  error = setPoint - average;
  float deltaTime = (millis() - lastProcess) /
  1000.0;
  lastProcess = millis();
  Derror = error - errorAnterior;
  errorAnterior = error;

  //P
  P = error*kp;

  //I
  I = I + (error * ki) * deltaTime;
  I = constrain (I, -255, 255);
  //D
  D = Derror* kd / deltaTime;
  //PID
  PID = P + I + D;
  // conversor de saída
  ControloPwm = constrain (PID, 0, 255);

  //timer

  if ((average > setPoint - margem) &&
  (average < setPoint + margem))
  {
    tt = (interval / deltaTime);
    i= i + 1;
    Serial.print("timer activo");
    Serial.print("\t");
    somatempo = somatempo + deltaTime;
    tempoR = interval - somatempo;

  }

  if (i > tt)
  {
    setPoint = setPoint + increment;
    Serial.print("SetPoint mudou");
    Serial.print("\t");
    i = 0;
    somatempo = 0;
  }

  else

```

```
{
}
```

```

analogWrite(pControlo, ControloPwm);
Serial.print(average);
Serial.print("\t");
Serial.println(setPoint);
/*Serial.print("\t");
Serial.println(ControloPwm/5);
Serial.print("\t");
Serial.print(millis());
Serial.print("\t");
Serial.print(tt);
Serial.print("\t");
Serial.print(i);
Serial.println("\t"); */

lcd.setCursor(0, 0);
lcd.print("T=");
lcd.print(average);
lcd.setCursor(8, 0);
lcd.print("SP=");
lcd.print(setPoint);
lcd.setCursor(0, 1);
lcd.print("I=");
lcd.print(increment);
lcd.setCursor(7, 1);
lcd.print("Tm=");
lcd.print(tempoR);
delay(10);
}
```

Appendix C – Monitor Series and Plotter Series from Arduino Software

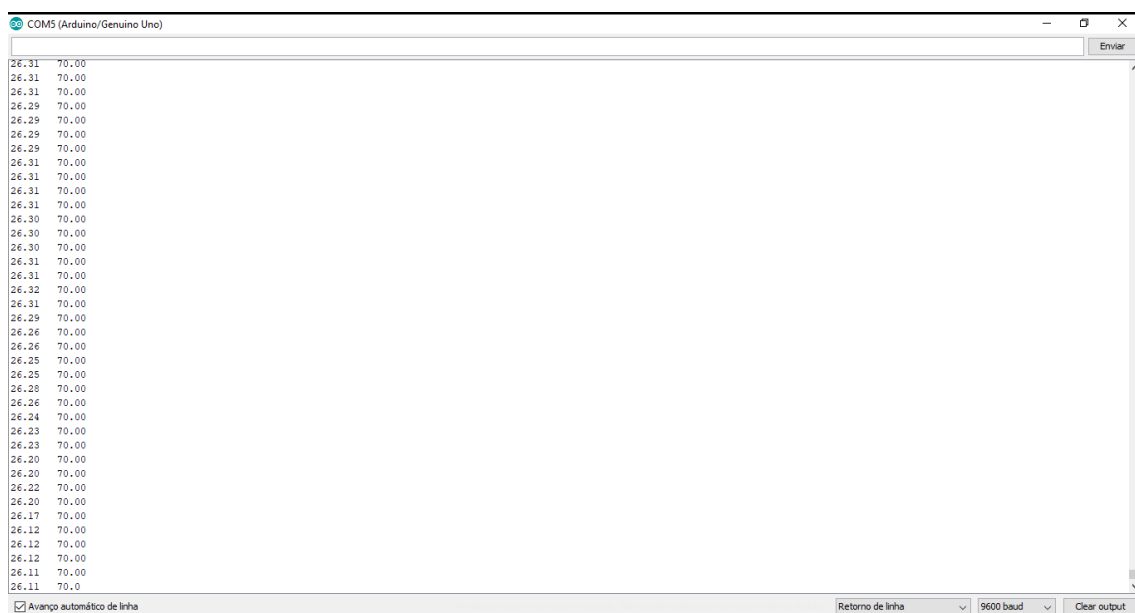


Figure 31 - Monitor Series from the Arduino software with two columns, the one from the left is the actual temperature and the right one, the Set Point

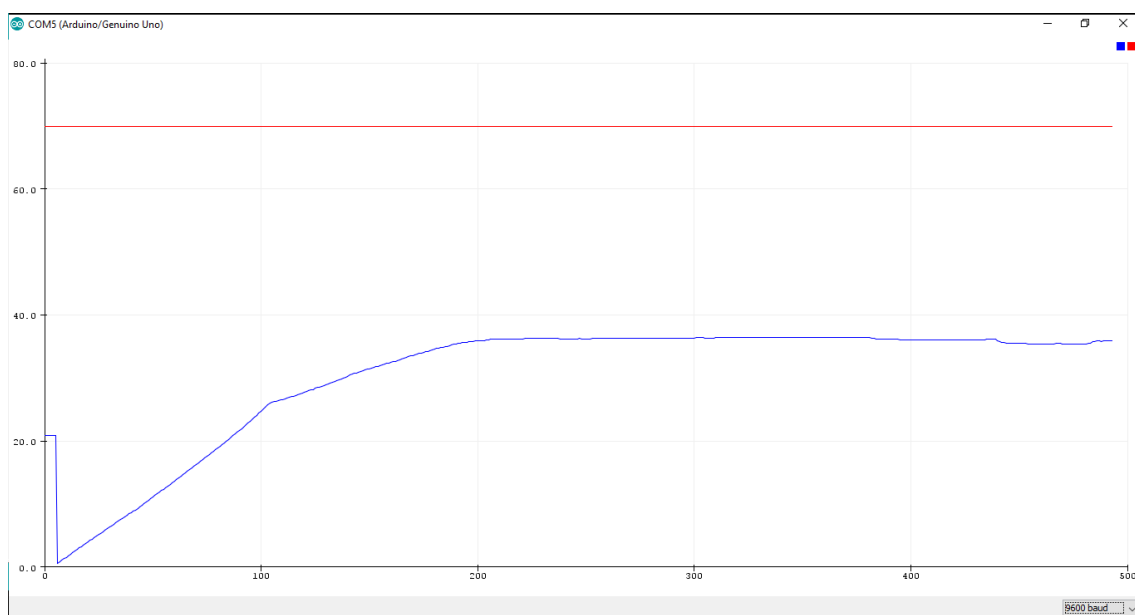


Figure 32 - Plotter Series from the Arduino software with two lines, the blue one is the actual temperature and the red one is the Set Point

Appendix D - Arduino and AD595

An Arduino is used to control the temperature of the system. An Arduino is a microcontroller, single board, with an open software and open hardware that makes possible the exploitation of new projects and ideas. It comes in several sizes, shapes and purposes. Because it is an open source hardware, several producers sell this microcontroller in the several models available, making this equipment a good choice due to his low price and high potential. The open source software makes possible to the user to program the microcontroller with several types of functions. The two key functions used in this project were the Proportional–Integral–Derivative (PID) and the Pulse-Width Modulation (PWM). The PID is the function that decides if the sample need to heat or to cool. The function has a proportional component, that has to do with the actual error value, an integral component, that relates with the previous error values and a derivative component that connects to a possible error value, based in the actual error value. These components can be moduled with constants present in the code and can be changed to achieve a better fit. The PWM is an output pulsed square wave function of the Arduino and can be assigned with values between 0 and 255. At 0 the Arduino will give 0 V to the system and at 255 it will give 5 V. At the middle point (127) the Arduino will provide a square wave with a peak to peak voltage of 5V, having the same time at 0 V and at 5V. When the value of the PWM is closest to 255, the square wave will spend more time at 5 V and when the values are closest to 0 then the wave will have more time at 0 V.

The Arduino used in this project (Figure 30) as a R3 configuration and it is known as Arduino Uno.

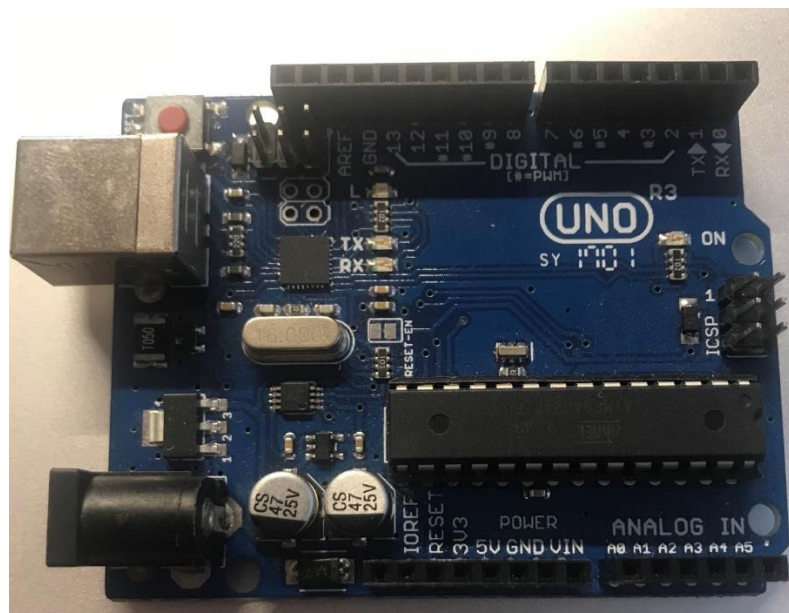


Figure 33 - Arduino used in the system

The Arduino has analog inputs that can convert a voltage range between 0 V and 5 V to a digital value between 0 and 1023. With this conversion it is possible to know the voltage applied on an Arduino analog port. The microcontrollers have also digital ports that can give and High

(5 V or 3.3 V depends of the board) and a Low (0 V). The PWM is a digital port that gives the user the capability to control the amount of Highs and the amount of Lows.

The temperature value is going to be read by a thermocouple type K and the information is going to be processed into an Integrated Circuit (IC), AD595, that gives a voltage that will be read by the Arduino through an analog port.

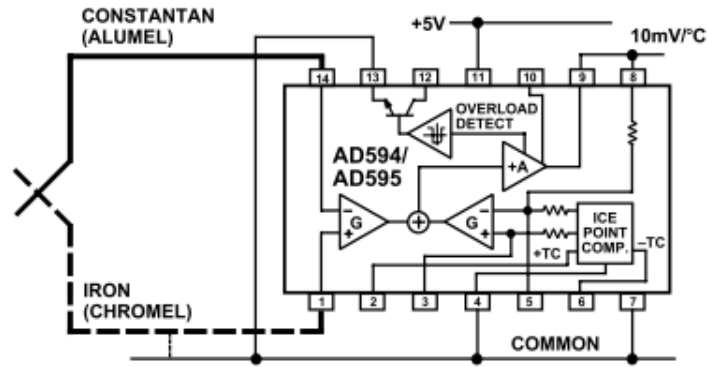


Figure 34 - AD595 configuration, pin layout and connections [23].

The AD595 is an IC, made by Analog Devices (pins layout and configuration on Figure 31) that provides a cold junction compensation amplification. This IC can be powered with a minimum of 5 V and a maximum of 30 V. The AD595 is specifically made to work with type K thermocouple, in comparison with the AD594 made to work with type J thermocouple, with the same operational specifications. The pin 1 is connect to the positive of the thermocouple and to the ground. The negative side of the thermocouple is connected to the pin 14. The power supply will connect in pin 11 and the pins 4, 7 and 13 connect to ground. The pins 8 and 9 have a short circuit between then and the voltage of that short circuit is the signal going to the Arduino with an information of 10 mv/°C, the remaining of the pins stays unconnected [23]. This device has a thermocouple failure alarm, but it not going to be used in this project.

Appendix E – 3D drawings of the multipurpose holder and its evolution

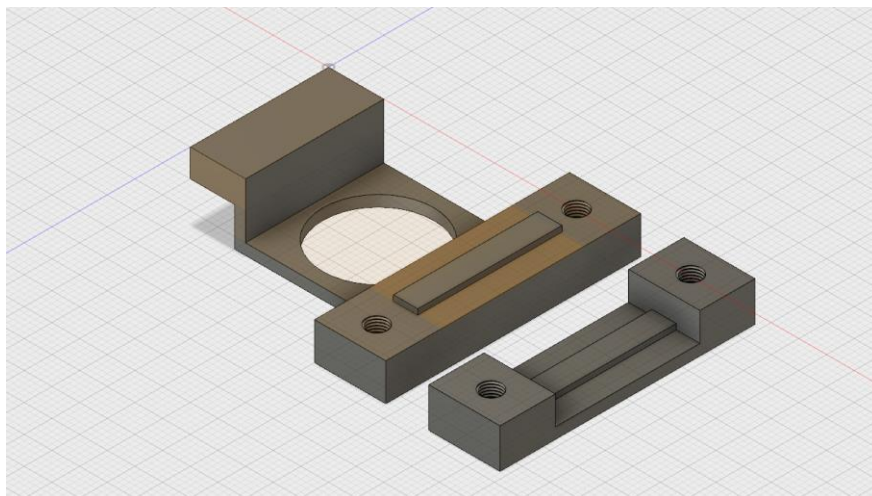


Figure 35 - Multipurpose Holder Design version 1.1

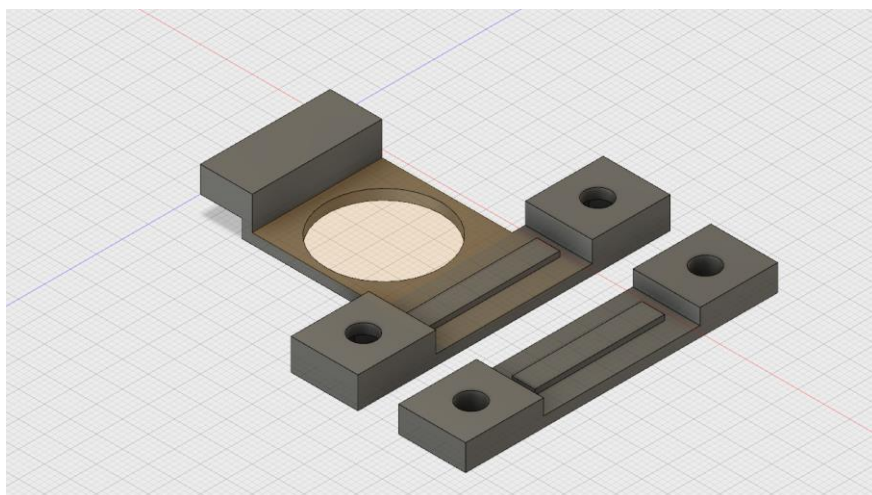


Figure 36 - Multipurpose Holder Design version 1.2

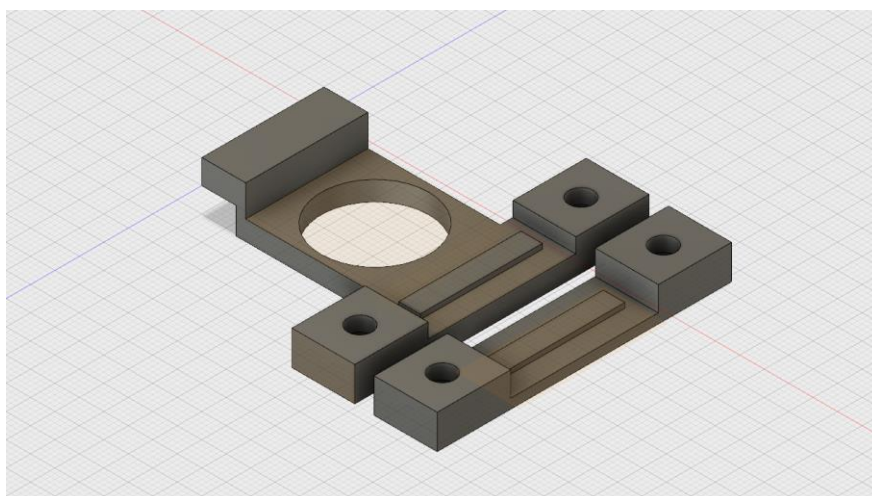


Figure 37 - Multipurpose Holder Design version 1.3

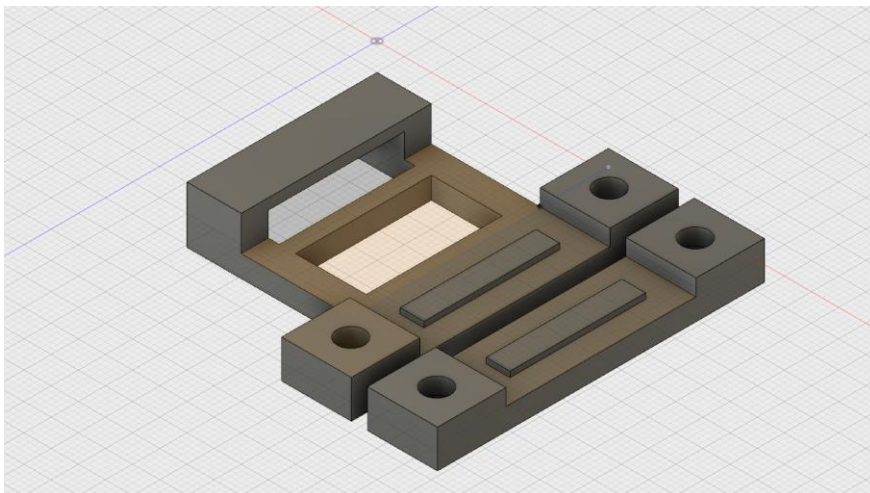


Figure 38 - Multipurpose Holder Design version 2.1

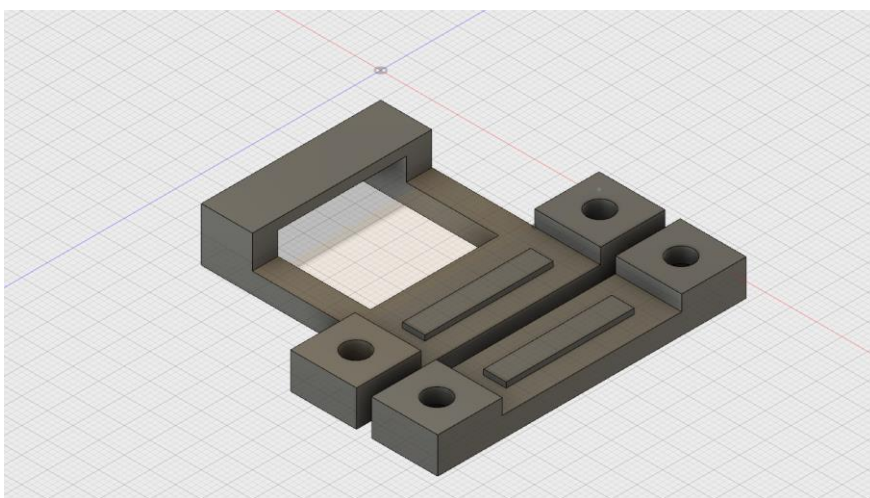


Figure 39 - Multipurpose Holder Design version 2.2

Appendix F – Holder fitted inside the XRD equipment

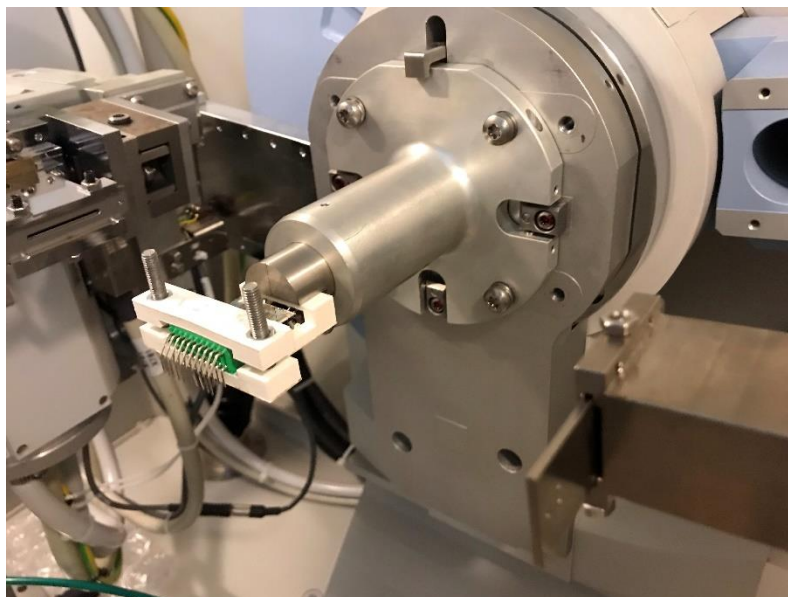


Figure 40 - Holder fitted in XRD equipment (side view)

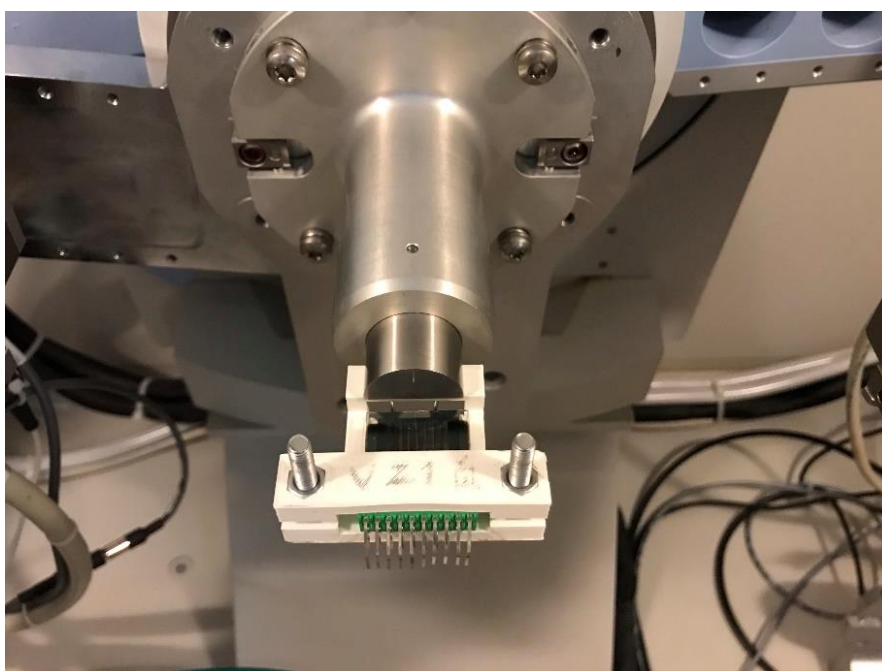


Figure 41 - Holder fitted in XRD equipment (upper view)