# OPTICAL PROPERTIES OF $ZrO_2$ AND $Ta_2O_5$

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*Abstract*

*The measurement of thin films' optical constants and their thickness involve, in general, the optical path, nd. The result obtained is a product of these two parameters, the thickness d and the refractive index n, making the independent evaluation of the each parameter complex. This work presents the results of four different techniques, Channel Spectra, Ellipsometry and Small Angle Diffractometry, to measure the thickness and the optical constants of thin films of $Ta_2O_5$ and $ZrO_2$, besides the "in situ" quartz crystal oscillator used to control the deposition process. A good agreement was found among these results. The thin films were deposited by e-beam gun and the films' thickness were around 350 nm for BK-7 and quartz substrates, and 70 nm for Si substrates.*

## 1. Introduction

The thin film optical constants and its thickness are essential data to design optical interference filters. The optical properties of thin films, from the same starting material, can be quite different, depending on the evaporation process and deposition parameters. There are many reasons for that, for example the columnar structure, substrate temperature or nature, deposition rate, stoichiometry, among others. Therefore, it is very important to control the deposition process parameters in order to have reproducible optical constants and thickness.

One of the most common processes of thin film thickness control during deposition is the quartz oscillator. However two main problems can affect the results on this kind of measurement: the packaging density[1] and the stress (or strain). The packaging density is directly connected to the specific mass of the material, and it is used as part of the data necessary to transform frequency into thickness. If the film has voids, then the adjusted (correct) specific mass should be used in order to have the correct thickness, but normally data of bulk samples are used. The stress can also cause a small bending on the quartz crystal, affecting the presented result.

In general, optical characterization techniques assume that the film is uniform at any direction, which is true just for some specific deposition processes like MBE. Also, depending on the initial assumptions adopted for the theoretical model, some optical techniques will not work if the thin film has high absorption. Or, the thin film columnar structure can absorb moisture, changing the optical parameters of the film.[2]

The low angle X-ray diffractometry depends on the substrate's flatness and roughness to allow a good agreement between experimental data and fitting procedures, used to obtain the film thickness.

This work presents results of four different techniques, low angle X-ray diffractometry, quartz crystal, ellipsometry and envelop method, to characterize the thickness of ZrO2 and Ta2O5 thin films. The optical techniques were also used to obtain the dispersion and the absorption coefficients in the visible part of the spectrum.

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envelop method, to characterize the thickness of $ZrO_2$ and $Ta_2O_5$ thin films. The optical techniques were also used to obtain the dispersion and the absorption coefficients in the visible part of the spectrum.

## 2. Thin film deposition process

The thin films were deposited by electron beam, at deposition rates of 0.4 nm/s, in a Leybold L-560 deposition system. The Si, quartz and/or BK-7 glass substrates were kept at 135°C. The system was pumped down to $10^{-6}$ mBar, then, oxygen was admitted in the chamber and a pressure of $10^{-4}$ mBar was maintained. The distance between evaporation source and the rotating substrate holder was 400 mm. The film thickness was around 350 nm, and at least two substrates were deposited at a time. After each deposition, the chamber was opened using $N_2$ gas, when the substrates were near room temperature. The thin films were examined by optical microscope (1000x), and deposition spits or other defects were not found.

The optical characterization happened in two steps. After the first characterization, the substrates received a heat treatment for 24 hours at 300 °C, in a homemade furnace. The temperature was increased at a rate of 3 °C/minute, and cooled slowly for 24 hours. The samples were then characterized again. This heat treatment was done to observe if there was a lack of oxygen in the film stoichiometry.

Hereby, the letter **z** represents $ZrO_2$, **t** represents $Ta_2O_5$ and an **a** after the **z** or **t**, represents a sample of these materials after heat treatment.

## 3. Equipment

As part of the evaporation system there is a quartz oscillator IC-6000, from Leybold, whose tooling factor has been refined for more than 10 years. This system also allows controlling the deposition rate. Even having a scanning system for the e-beam gun that scans the evaporating material surface during the deposition, some quick changes in the deposition rate happened, affecting the results as shown ahead.

A Philips High Resolution X-ray Diffractometer (MSD X'pert) was used to obtain the 2θ diffractogram; a Pelkin-Elmer Lambda 20 spectrophotometer for the transmitted spectra; and a modified (automated) Gaertner L-117 ellipsometer for the ellipsometric data. To compare results, two different softwares analyzed the transmission spectra. One is a commercially available product[5] and the other one is homemade. The latter was written taken into consideration films with very low absorption, and it did not run for some samples.

## 4. Thickness Measurement

The first step of this study was to measure and compare the thickness of the films by means of the techniques described above, as certainly they should present almost the same result, independent of the measurement's physical principle. The quartz oscillator controlled the deposition rate and the final thickness, being the first thickness result.

To analyze the X-ray data, the film must have a thickness ≈ 70 nm, which is not compatible with the thickness needed for the Envelop Method that is ≈ 350 nm, depending on the refractive index of the material. Therefore, the thickness comparison was done in two steps: 1) quartz crystal, X-ray and ellipsometry for 70 nm films; and 2) quartz crystal, ellipsometry and Envelop Method for 350 nm films.

Thin films of Ta2O5 were deposited on a polished Si substrate in order to be measured by low angle X-ray scattering and ellipsometry, because glass substrates were not flat enough to allow a resulting curve that had the expected interference aspect. The results obtained were 69.5 nm for quartz crystal, 69.5 nm for ellipsometry and 70.6 nm for low angle X-ray scattering. Figure 1 shows the graph (intensity x 2θ) obtained by low angle scattering for this film. A natural layer of 1.2 nm of SiO2 was considered. The agreement between these results is good, showing that one can expect the same behavior for thicker films, as the ones prepared for Envelop Method analysis.

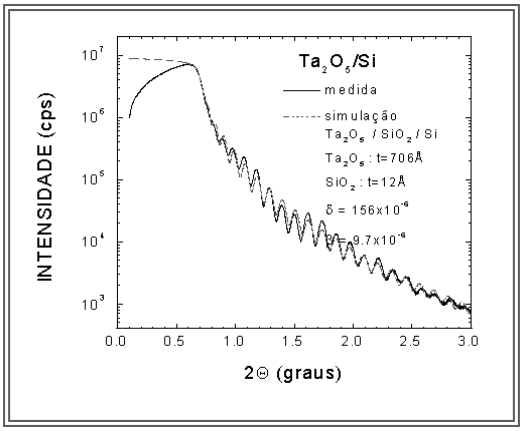


**Figure 1 -Low angle scattering data for a thin film of Ta2O5 over Si.**

## 5. Optical Characterization

Ellipsometry is a useful technique to measure the optical constants and thickness of thin film3. It is sensitive even to small changes on the surface, as reported by Netterfield[6], showing thickness measurements having an uncertainty of ± 0.1 nm, with a confidence level of 90%. The ellipsometric data were taken for periods of 24 hours, more than 100 pairs of Δ and Ψ ellipsometric parameters per sample, to check the data acquisition system stability.

Envelop Method is a traditional technique to obtain the optical constants of a thin film, starting from the minimum and maximum points of the transmission or absorption spectra[7]. It can show small differences even for samples produced in the same batch, as shown in Figure 2. The two samples of $Ta_2O_5$ were deposited at the same time, in positions diametrically opposite on the evaporation chamber rotating substrate holder. The evaporation conditions were

kept as fixed as possible, but even then the samples presented different results. The first idea was that the substrate could be misaligned during the measurement, i.e., it was not at the normal incidence. The measurements were done once again, showing the same results. Even incidence angles as high as 10° did not show that difference.

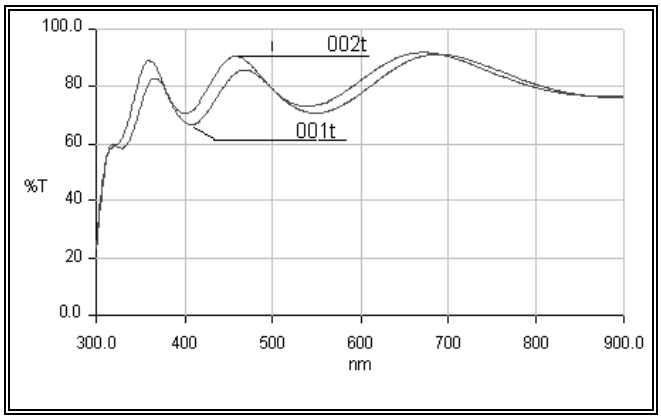


**Figure 2 - Transmission x wavelength of two samples of tantalum pentoxide, deposited in the same batch.**

After heat treatment, the sample presented an increase in the transmitted spectra, as can be observed in Figure 3, where the curve of sample 001-ta is above of 001-t. The curve difference is quite similar as the one in figure 1. Since the transmission is higher in both cases, 001-ta and 002-t, an absorption lower than the calculated one for sample 001-t can be expected.

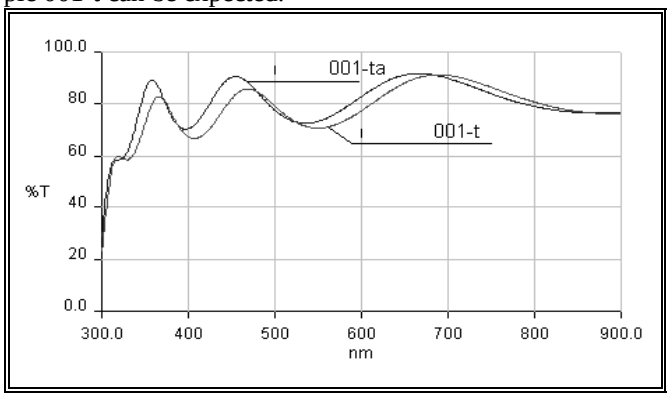


**Figure 3 - Transmission spectra of the tantalum pentoxide sample before and after heat treatment.**

To calculate the optical parameters and the thickness, two different softwares were used. One is a home made software, developed to calculate the optical parameters of thin films deposited at our facility[8], hereby called Program 1. The other one is part of a commercial product for thin film design, the Essential Macleod™, hereby called Program 2. The first software did not calculate the optical parameters for all the samples presented in this work, mainly for samples that showed an appreciable change in absorption values when calculated by the other software or ellipsometry.

The idea behind this comparison was to check the limits of the theoretical model assumed for the homemade software. It was observed then that this software just works for very low absorption changes against wavelength. As no fitting is done on the envelope functions before analysis, the program did not present results when there is a major change in absorption as function of wavelength, because there would not be a good agreement between the envelope curves and the maximum and minimum points.

The results obtained by Envelop Method are shown on table 1. There is no calculated value of n and k for the first pair of data (329.13 nm and 58.39%). These values were ignored because there is an absorption region for the substrate under 350 nm. If taken into account, the values obtained would not satisfy the normal behavior of a Cauchy curve for the dispersion. The maximum or minimum points in the substrate absorption region were ignored for all samples presented in this work. Also, as shown in Table 1, the Program 1 presents the optical parameters before and after Cauchy's adjustment.

Figure 4 presents the refractive index and absorption coefficient against wavelength, for samples 001-t and 001-ta, $Ta_2O_5$, before and after heat treatment. It shows a big change in the absorption, as expected. An appreciable change in behavior also happens for the refractive index. The two softwares showed a good agreement on thickness and optical parameters. The ellipsometric data for this sample, for 633 nm, gave the values presented on table 2. Martin and Netterfield[9] reported refractive index values for $Ta_2O_5$ between 1.9 and 2.16, for 633 nm, depending on the $O^{+2}$ current density of the ion assisted deposition process.

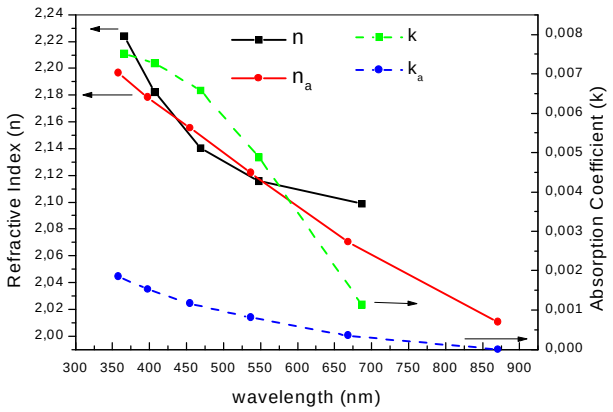


**Figure 4 -Refractive index and absorption coefficient for $Ta_2O_5$ samples 001-t and 001 –ta, before and after heat treatment.**

The thickness and the optical parameters obtained by all techniques showed a good agreement. The difference was lower than 5% for the thickness and a lower absorption after the heat treatment indicates a possible oxygen incorporation to reestablish the correct stoichiometry.

Figure 5 presents the results for sample 002-t and 002-ta. The two samples, 001-t and 002-t, were produced in the same batch, and received the same heat treatment, at the same time, becoming samples 001-ta and 002-ta. Therefore,

they should present the same results, but that happened only after the heat treatment.

| Sample 001-t | | Program 1 | | | Program 2 | |
|---|---|---|---|---|---|---|
| Wavelength | Transmission (%) | n | n (Cauchy) | k | n | k |
| 329.13 | 58.3900 | | | | | |
| 365.52 | 82.8600 | 2.2373 | 2.2340 | 0.0089 | 2.2241 | 0.0075 |
| 407.17 | 66.7700 | 2.1807 | 2.1905 | 0.0073 | 2.1821 | 0.0073 |
| 469.03 | 85.8570 | 2.1531 | 2.1423 | 0.0049 | 2.1404 | 0.0066 |
| 547.88 | 70.8480 | 2.0959 | 2.1001 | 0.0056 | 2.1157 | 0.0049 |
| 686.91 | 91.2850 | | | | 2.0988 | 0.0011 |
| Thickness (nm) | Quartz crystal 346 | 327 | | | 327 | |

**Table 1 - Data obtained by the two software used to calculate the optical parameters and the thickness for sample 001-t, Tantalum pentoxide, before heat treatment**.

| Parameter | 001-t | 001-ta |
|---|---|---|
| Refractive index | 2.0037 | 2.0505 |
| Absorption coefficient | 0.0223 | 0.0 |
| Thickness (nm) | 346 | 332.5 |

**Table 2 – Optical parameters and the thickness for sample 001-t, Tantalum pentoxide, before heat treatment, obtained by ellipsometry.**

| | Quartz Crystal | Program 1 | Program 2 | Ellipsometry |
|---|---|---|---|---|
| 001-t | 346 | 327 | 327 | 346 |
| 001-ta | | | 321 | 332.5 |
| 002-t | 346 | | 325 | 328.5 |
| 002-ta | | | 315 | 332.5 |

**Table 3 – Thickness measurement for $Ta_2O_5$ deposited in the same batch, before and after heat treatment.**

Table 3 presents the thickness data for a direct comparison. The results for samples measured before and after heat treatment should be the same, but small differences can be observed. This is probably due to non-uniformity caused by fluctuations during the deposition process. As the material is evaporated, even using a e-beam screening process over the crucible, small walls left by the e-beam collapse over the beam application point, causing a subtle change in the deposition rate. This can explain small deviations found between samples evaporated in the same batch and non-uniformity in the refractive index along the film thickness.

The dispersion and the absorption coefficient for samples of Ta2O5 and ZrO2 of some samples are presented in the next figures, numbered from 6 to 13. It is important to notice that the curves have the same behavior for all samples, but they are not exactly the same. Small fluctuations on the deposition rate during the film growing are supposed to be the main cause for these fluctuations.

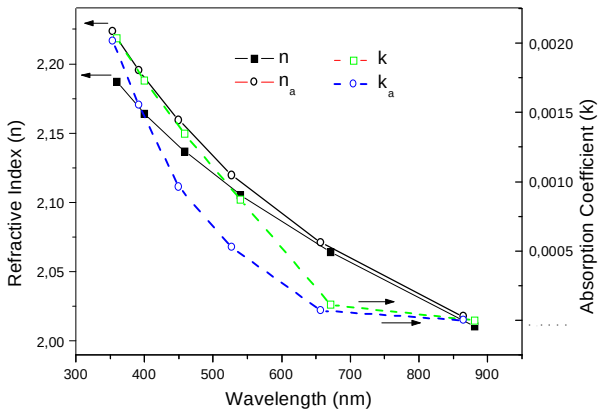


**Figure 5 - Refractive index and absorption coefficient against wavelength for samples 002-t and 002-ta, $Ta_2O_5$, before and after heat treatment.**

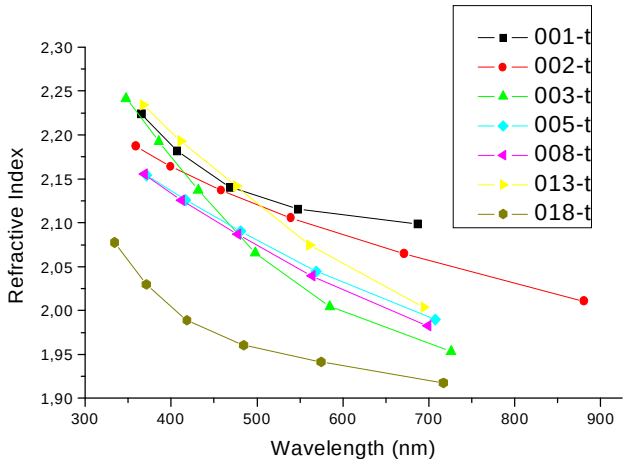


**Figure 6 - Dispersion for 7 different samples of tantalum pentoxide, before heat treatment.**

It should be noticed that samples 018-t and 024-z were deposited over quartz instead of BK-7 glass. This was taken into account when running the software but even then the results for these samples are quite different from the others as can be observed in figures 6 and 9.

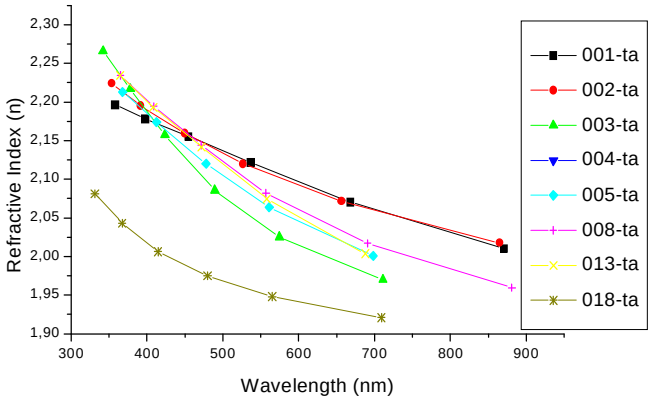


**Figure 7 - Dispersion for 7 different samples of $Ta_2O_5$, after heat treatment.**

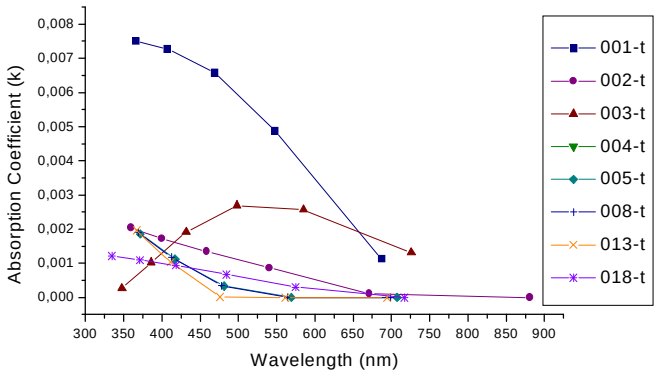


**Figure 8 - Absorption coefficient against wavelength for7 samples of $Ta_2O_5$, before heat treatment.**

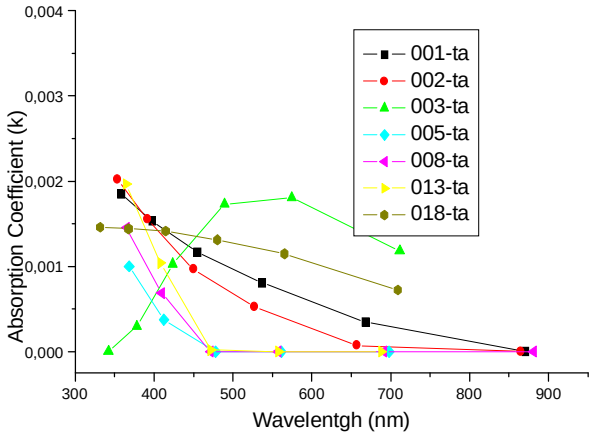


**Figure 9 - Absorption coefficient against wavelength for7 samples of $Ta_2O_5$, after heat treatment.**

After the heat treatment, the thin films of zirconium oxide presented an unexpected behavior: an increase in the absorption coefficient. It seems that there were no lack of oxygen for these films as it happened for $Ta_2O_5$.

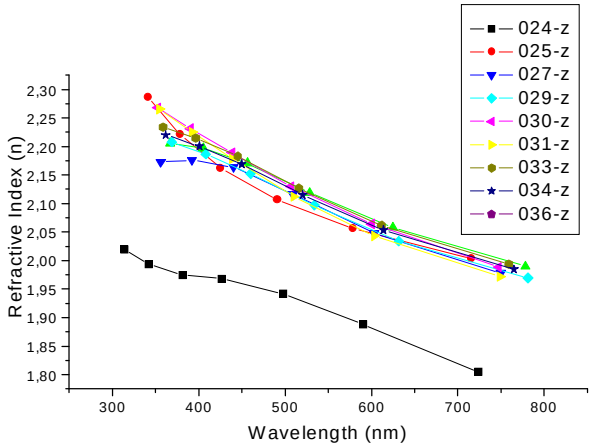


**Figure 10 - Dispersion for 9 different samples of $ZrO_2$, before heat treatment.**

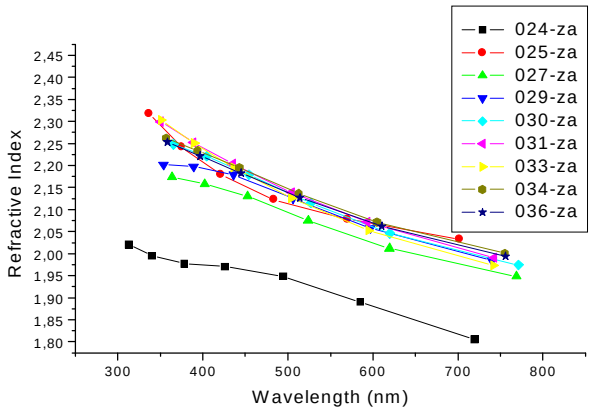


**Figure 11 - Dispersion for 9 different samples of $ZrO_2$, after heat treatment.**

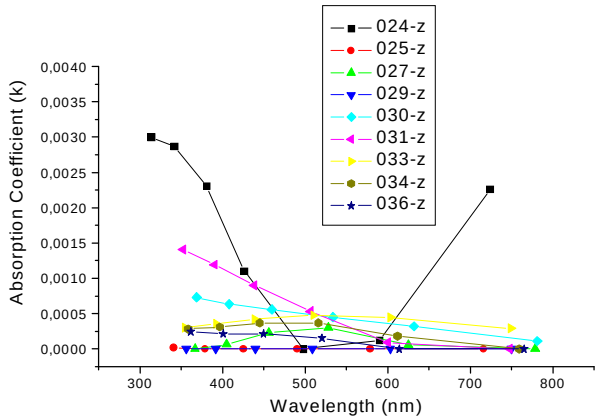


**Figure 12 - Absorption coefficient against wavelength for 9 samples of $ZrO_2$, before heat treatment.**

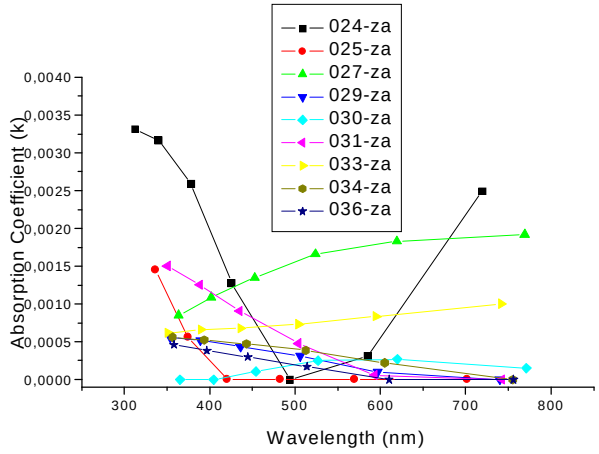


**Figure 13 - Absorption coefficient against wavelength for 7 samples of $ZrO_2$, after heat treatment.**

## Conclusion

Four different techniques, Channel Spectra, Ellipsometry and Low Angle Diffractometry, were applied to measure the thickness and the optical constants of $Ta_2O_5$ and $ZrO_2$ thin films. Good agreement was found among these results. The heat treatment after the initial measurement showed a lower absorption for $Ta_2O_5$, what was expected. The results of different samples that were presented showed minimum deviation from a unique behavior, this is probably due to the film deposition process, even when the contour conditions were kept as fixed as possible.

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