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Thin Film Coated Energy-efficient Glass Windows

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À minha mãe e à mãe dela, os grandes pilares da minha vida.

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ABSTRACT

The increasingly concern about energy sustainability empowered scientist's interest in energy-efficient systems. Consequently, advanced, energy-efficient glazing systems have been widely explored. The main objective of this work was to develop a dielectric/metal/dielectric (D/M/D) multilayer thin film coated system for application in energy-efficient glazing systems.

An initial study over optical transmittance and reflectance variation with film thicknesses was performed for different metal thin films on glass substrates, namely silver, copper, aluminium, nickel and tin.

Furthermore, the three-layer systems of D/M/D on glass were produced with the metals mentioned above and system performance is optimized by changing the layers thicknesses. Layers were deposited by thermal evaporation and two dielectrics were used: V_2O_5 and WO_3. Most of the tests were performed on as-deposited samples but some of them were also annealed in air or vacuum in order to understand how post-deposition annealing influences the transmittance and reflectance properties.

D/M/D samples with high visible transmittance (>60%) along with high infrared reflectance (>80%) were obtained. Air annealing in certain samples may increase samples absorption in infrared region.

Some of the results were compared to theoretical simulation using Wolfram Mathematica software. A good agreement between the theoretical and experimental spectra was obtained.

Keywords: Energy sustainability; Energy-efficient glazing systems; D/M/D multilayer; Thermal evaporation;

Resumo

A crescente preocupação com a sustentabilidade energética impulsionou o interesse científico relacionado com sistemas energeticamente mais eficientes. Consequentemente, sistemas avançados de vidros energeticamente sustentáveis é um tema que tem recebido muita atenção. O principal objetivo deste trabalho foi o desenvolvimento de um sistema multicamada do tipo dielétrico/metal/dielétrico (D/M/D) para aplicação em sistemas de vidros energeticamente mais eficientes.

Foi feito um estudo inicial da variação de transmitâncias e refletâncias de diversos filmes metálicos (prata, cobre, alumínio, níquel e estanho) para diferentes espessuras. No geral, a transmitância aumenta e a refletância diminui para maiores espessuras.

Adicionalmente, os sistemas de multicamadas D/M/D em vidro foram produzidos os referidos metais e otimizados através da variação das espessuras dos *layers* metálicos. As deposições dos filmes foram feitas através de evaporações térmicas e foram utilizados dois dielétricos: WO_3 e V_2O_5. Algumas amostras foram submetidas a recozimentos para fins de teste.

Uma vez testados, pode concluir-se que, os sistemas D/M/D permitem obter elevadas transmitâncias no visível (>60%) e, simultaneamente, elevadas refletâncias no infravermelho (>80%). Ambos os dielétricos permitiram obter bons resultados, e os recozimentos em ar podem aumentar a absorvância dos sistemas.

Alguns dos resultados forem comparados com aproximações teóricas obtidas através do software *Wolfram Mathematica*. Os resultados teóricos e experimentais estão concordantes.

Palavras-chave: Sustentabilidade energética; sistemas avançados de vidros; sistemas multicamada do tipo dielétrico/metal/dielétrico; evaporação térmica;

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MOTIVATION AND OBJECTIVES

Motivation

In the past few years world has seen a global movement towards the attempt of achieving a perfect, sustainable, green, self-sufficient civilization. With the growing energy crises and the awareness about how some of the most important resources of today's society are getting exhausted, the urge to find new alternatives has led to a widespread interest for higher performance products, especially those that could contribute to energy savings. [1,2] The aim for lower power consumption encourage scientists to think of better ways to make good use of natural energy supplies, such as the sun. Given this, there is a glaring application in which humans greatly take advantage of sun's light and where they may not be making the most of its potential: building's windows.[2,3]

The building energy consumption in developed countries accounts for 20–40% of the total energy use. The ability to achieve energy saving and optimal solar energy utilisation in todays' architectures impacts the sustainable development of human race. Buildings represent almost 40% of all energy consumption in the United States (as the second largest consumer of world energy representing about 19% of global consumption), according to the US Department of Energy. That means buildings cost more than US$400 billion (355.72 billion euros) every year, just in USA. Buildings in China, as the largest consumer of world energy, consumed 26% of total primary energy in 2006; the figure is anticipated to rise to more than 30% by 2020. [3-6] If these buildings could improve efficiency by 20%, they could save more than US$40 billion (35.58 billion euros). Given this and the fact that windows are a key component of any building, it's only fitting that they are also an essential part of new strategies to improve energy efficiency. More specifically, glazing areas are of paramount importance for the overall heat loss and heat gain of a building. In the USA, over 3% of total energy consumption is lost through windows, in Sweden is 74% and in Britain 6% for residential buildings alone. [7] Driving forces into the evolution of this area presents one of the main motivations of the present work.

Some of the most important energy-efficiency challenges on glazing systems include control heat loss and admit daylight with minimal solar heat gain. In cold climates, the most important parameter to be considered is heat loss from the building to the environment. In hot climates, the main target is to avoid heat gain via glazed areas. [1,2]

Many technological advances in glazing systems have been made in the past years. Some of them include improved thermal insulation glazing (Low-e coatings [8] and dielectric/metal/dielectric (D/M/D) films [9]); adaptable glazing "Smart windows" including electrochromic windows (ECW) [10,11], thermochromic windows (TCW). [5] and others such as gasochromic windows [12] and liquid crystal glazing. [13]

It has been showed that initially clear glass had a thermal emittance of about 0.84, meaning that it emits 84% of its energy and also that 84% of the long-wave radiation striking the surface of the glass is absorbed and only 16% is reflected. These values have been reduced to about 0.10-0.20 by the first available coatings. With the introduction of dielectric/metal/dielectric low-emittance coatings it was possible to reduce the emittance further to as low as 0.04 which means that such glazing would emit only 4% of its energy, and thus reflect 96% of the incident long-wave radiation. This work is primarily focused on studying the potential of various dielectric/metal/dielectric systems. [14,15]

The solar reflectance of low-emittance coatings can be manipulated to include specific parts of the visible and infrared spectrum so that desirable wavelengths of energy are transmitted and others reflected. Figure 1 represents the effect of different low -E coatings. While conventional glazing systems (clear) allow almost all the radiation to pass through, coated systems allow most of the visible light through, but block portions of the solar spectrum, including ultraviolet and near-infrared radiation, as well as long-wave heat radiated from outside. [14]

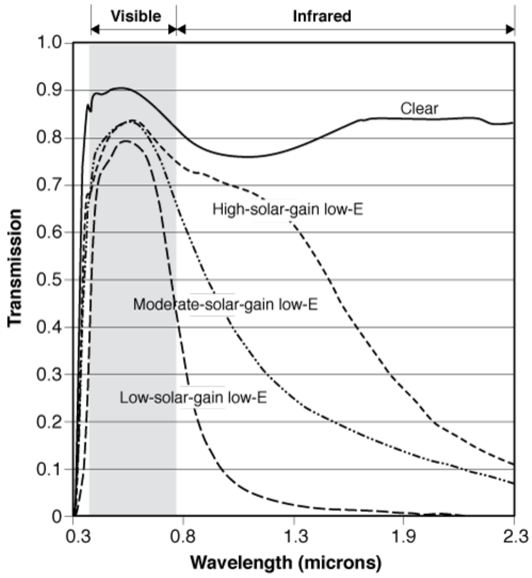

Figure 1 Spectral transmittance curves for glazing systems with low-emittance coatings [15]

In general, the use of spectrally selective glazing results in important energy performance and costs saving improvements. Duo to the spectrally selective glazing's higher visible transmittance the need for lighting energy decreases. Furthermore, cooling energy demand during summer also decreases because spectrally selective glazing will produce a reduction in solar heat gains. If spectrally selective glazing with low thermal conductance and emissivity are used the required heating energy may also decrease.[14] [16]

As well as low emittance coatings, smart glass windows, based in electrochromic and thermochromic materials, have also been receiving lots of attention. It is estimated that smart windows are about 70% more energy efficient during the summer and 45% more efficient in the winter compared to standard dual-pane glass. Some buildings in USA have already installed smart windows and after one year of installation, energy savings of US$2.4 million and cut carbon emissions of 4,000 metric tonnes have been reported. This is equivalent to planting 750 acres of pine forests. This means that the introduction of energy efficient glazing systems on windows can help reduce the overall pollution and energy spending and make a huge impact in the energy bills of today's biggest buildings. [15] [17]

With all that's been said it's only natural that markets are opening up to these concepts and giving energy efficient windows technology an opportunity for continued growth. In a report released in September 2016, *Technavio* said that the worldwide smart glass market is set to grow at a compound annual growth rate of 21.13% from 2016 to 2020. Moreover, clean energy market research firm, *Pike Research*, projects that smart glass market will reach US$700 million (636.94 million euros) per year by 2020.[18,19]

It is obvious that smart windows are expected to become an architectural mainstay and a significant part of long-term energy-saving initiatives and consequently, at a scientific research level the interest and efforts directed to the continuously development of this technological field are imperative. Glazings will become 'energy suppliers' as well as 'energy managers'.

Objectives

The main objective of the present work is the production and characterization of D/M/D multilayer systems on glass substrates in order to determine the result's controllability and trying to identify the conditions and variables that allow obtaining the best results for possible subsequent devices development.

In order to do that one can define some specific tasks and key point that should be accomplished:

- Theoretical simulation of some D/M/D systems
- Study, production and characterization of thin film metallic layers on glass substrates
- Study, production and characterization of D/M/D multilayer systems on glass substrates
- Performance of after-deposition annealing and subsequent characterization
- Complementary studies

Therefore, the present work presents a complete study over D/M/D systems.

1 INTRODUCTION

The present chapter consists of an introduction to the following chapters. The intention is to provide a theoretical comprehension of some fundaments involved with the main technological concept as well as with the materials and techniques utilized.

1.1 Spectrally Selective Glazing Systems: Fundamentals and Applications

Reflection and transmission consist in two possible forms of energy being redirected when a propagating electromagnetic wave encounters an interface with different refractive indexes. In many applications there is the aim of controlling transmittance and reflectance over some spectra regions. Based on this, one of the most important innovations made in glazing technology, for windows application, over the last few years, has been the development and widespread use of large area, low cost, multilayer thin film coatings.

When it comes to windows, without any coating almost all of the IR radiation present in sun's light is transmitted through the window. IR radiation represents about 34% of the solar photon flux. Multilayer selective glazing systems, which are used to minimize heat loss, reflect infrared (IR) radiation, while permitting most visible light from the exterior to enter. Spectral selectivity is achieved by a very thin, low-emissivity (low -E) coating on the glass or on a film applied to the glass, generally in its surface. [15,16]

After their introduction, in the early 1980s, low -E coatings have rapidly marked a position in the glass market. A strong driving force for the quick introduction of these coatings had been the fact that glass surfaces with low thermal emittance can virtually eliminate the thermal infrared radiation loss through the glazing and thus drastically improve the thermal insulation properties of a window, resulting in lower heating energy cost and higher thermal comfort. [20]

Advanced glazing systems have been widely explored in recent years aiming to achieve more energy efficient systems capable of controlling solar heat gains and limiting heat losses. In order to do that, one of the things scientists have been given special attention is the use of thin film spectrally selective coatings on glass windows. These coatings can be used for a wide variety of windows, solar-collectors, photovoltaic panels, electronic lighting, aircraft, spacecraft, and vehicle applications among others. [21]

There are some basic considerations that must be taken into consideration in order to understand the context of this concept on energy efficient windows.

The spectrum regions of interest when studying applications in which the sun light represents the incident light, such as smart windows or solar-collectors, include the visible region (300- 770 nm), the near infrared region (NIR) (770- 2000 nm) and infrared (IR) (2000- 100 000 nm). [21]

Spectra selective coatings generally exhibit medium to high transmittance over the visible region and high reflectance throughout the infrared region and there are two main situations (Figure 2) in which spectrally selective coatings may be of good use in energy efficient windows. It can help keeping a warm ambience inside buildings during the winter and preventing the outside hot from getting into the buildings during the summer preventing the excessive use of expensive climatizers used for either heating or cooling the building.

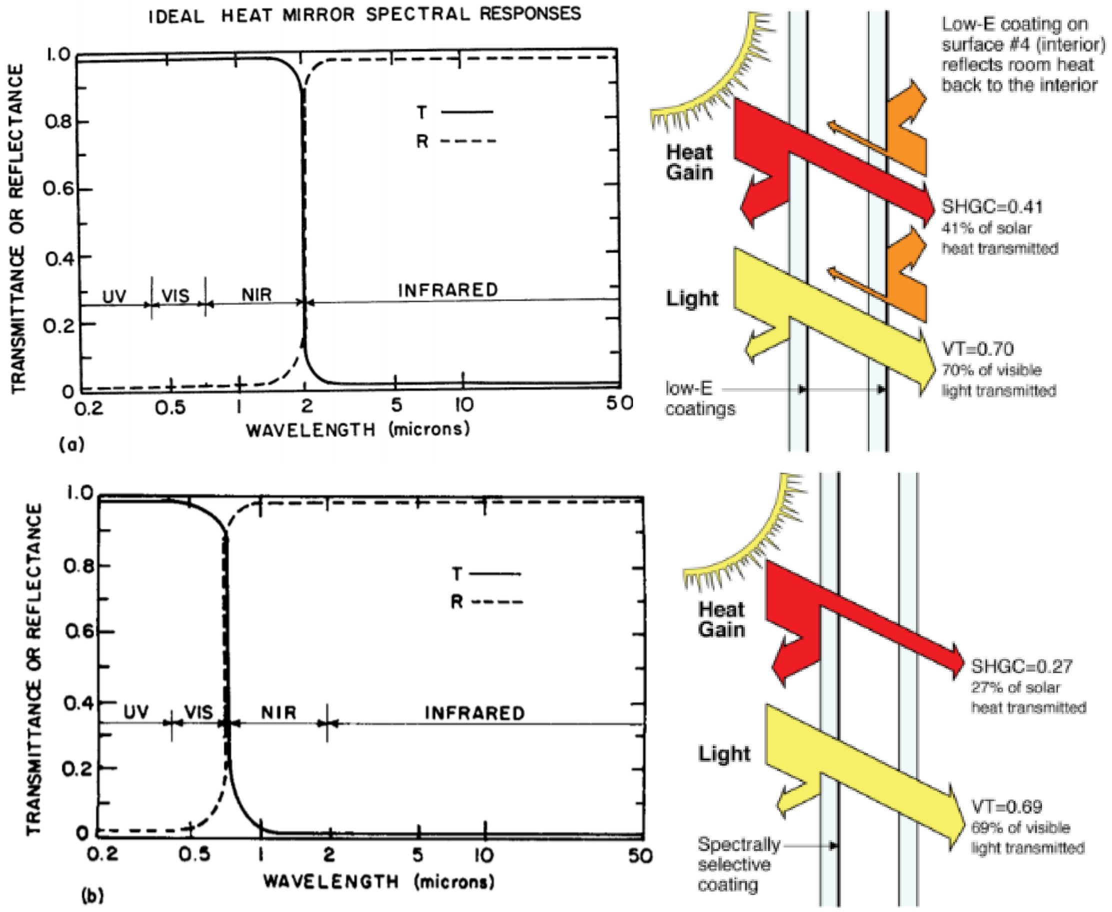

Figure 2 Spectral responses (on the left) [21] and radiation flows (on the right) [15] of ideal spectrally selective coatings. Winter control films save energy through passive cooling of a building by reflecting or absorbing heat-generating IR radiation (a). Summer control films reduced IR transmission through the glass window (b).

In the first scenario, almost every high energy solar light including visible light and NIR are transmitted trought the glaze to the inside while the ambient IR radiation is reflected back into the building. Given this, the majority of sun's energy can be utilized to iluminate and passively heat the inside. On the other hand, in the secon scenario, all IR incident light is reflected away from the builing while visible light is able to pass trought.[21]

In the present days, the state-of-the-art on commercially available solar control films is largely explored. Design, fabrication and properties of D/M/D films have been studied thoroughly by many researchers.[5] [9] [22] However, D/M/D multilayer systems are of consistent interest and the wide range of possibilities these systems may bring empowers scientists to further study and try to understand them. The present work focuses on performing a complementary study by producing different possible D/M/D systems and better understanding their properties.

1.2 Dielectric-Metal-Dielectric Multilayer Structures

When light travels from one medium into another it can be either reflected or refracted. In the particular case of thin films, since the distance between one interface and the other is really small, the light will suffer multiple reflections and refraction leading to waves of different intensities that will interfer with each other in either a constructive or destructive way. By manipulating the refractive indexes used and the film thicknesses one can manipulate those interferances and then control the final outcome for example in terms of transmittance and reflectance.

In the case of d/m/d multilayers, it consists of a very thin metallic film sandwiched between two oxide dielectric layers. By nature, the metal film is highly IR reflective, with low transmittion of visible energy. The visible transmission of the metal films is primarily limited by their reflectivity. Therefore, their effectiveness as transparent heat mirrors can be improved by reducing their visible reflectivity without affecting their infrared reflectivity. Because of the refractive index discrepancy between the dielectric layers and the thin metal layer, when sandwiched between the two dielectric layers that act as antireflective coatings, the energy transmitted in the visible region is enhanced without compromising the infrared reflectivity. The interference effects in the dielectric coatings causes the wave reflected from the anti-reflection coating top surface to be out of phase with the wave reflected from the metal surfaces. These out-of-phase reflected waves destructively interfere with one another, resulting in zero net reflected energy, as presented in Figure 3. [22][9][25,26]

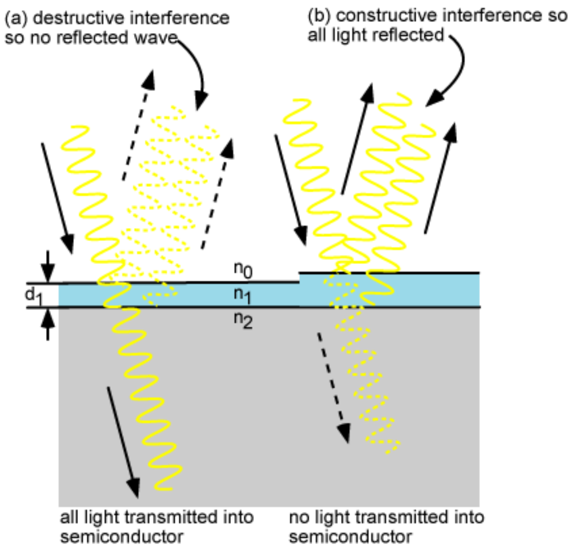

Figure 3 Light waves destructive (a) and constructive interference in the presence of an anti reflecting coating [26]

In the present work, various multilayer D/M/D systems were produced and Figure 4 represents the adopted structure, where the different constituiting layers are represented.

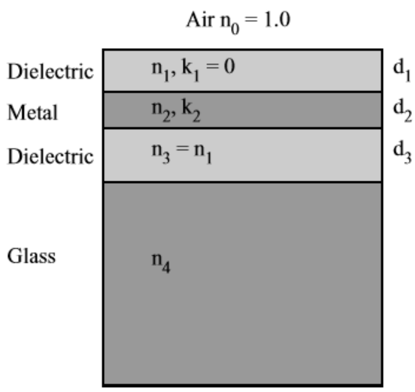

Figure 4 Three-layer thin film (D/M/D) system on glass substrate where a metal layer with optical constants n_2 and K_2 and a thickness d_2 sandwiched between two dielectric layers with optical constants n_1 and n_3 with $n_1 = n_3$ and k=0 [27]**.**

The two dielectric layers consist on the transmitting optical components and are usually characterized by having a large refractive index. Different dielectrics may be used such as TiO_2 [24], ZnS [22], and WO_3. [27] WO_3 is one of the most suitable dielectric materials for the D/M/D multilayer. It has a high refractive index (n= 2.0 at wavelength of 580 nm) and high transmittance (>90% in the wavelength range of visible light) as well as high electrical conductivity. [25] WO_3 thin films are also well known for their electrochromic phenomenon making this material the most promising and most applied electrochromic material in electrochromic windows and devices. [13] On the other hand, vanadium is another promising material, famous for its thermochromic properties and its oxidized forms, VO_2 and V_2O_5 have been proposed for application in smart energy efficient windows [5] [28] In this work, WO_3 and V_2O_5 are both tested and compared on their performance as dielectric materials on D/M/D systems. Materials with well-known good performances for this application, such as TiO_2 could have been used but it was one of the team’s purpose to study the specific mentioned materials to evaluate their behaviour.

Equally important is the metallic, reflective layer sandwiched between the two dielectric layers. Silver is one of the most popular reflecting material once it shows lower visible absorption and high infrared reflectivity. [24,25] Other used metals include Au and Cu. Cu electrical and optical properties are very close to those of silver with the advantage of having a much lower price. Al has also been used as film material for the production of reflecting coatings given its good reflectance and easy evaporation together with the additional advantage of adhering strongly to most substances. In order to improve the optical performance of D/M/D systems it is necessary to try original materials or constructions. In literature very few references report the use of Ni and Sn for optical optimization of glazing systems. In this work these material are also tested as metals for D/M/D structures. [29]

In general, by varying the material and thickness of one or more of the three layers, the optical behaviour of the multilayer D/M/D device can be tailored to suit different applications. [22][9] In general, from literature, transmittance increases with the metal thickness up to a critical value. Then, as expected, it decreases with the increase of the metal film thickness. [30]

1.3 Deposition Technique: Thermal Deposition

The electrical and optical properties of the D/M/D thin films are directly related to its chemistry and physical morphology. The degree of crystallinity, crystal structure and impurities are of great influence on both oxide and metal films. Oxide coatings are very dependent on stoichiometry, impurities and defects in the films such as metal films depend strongly upon nucleation phenomena. Consequently, D/M/D systems' performance is intimate related to the layers' deposition process. [21]

Thermal evaporation under vacuum conditions is a widely known process that permits achieving multilayer devices with reproducible properties and high purity and allows facile control of the layers' thickness. A large number of materials can be evaporated and condensed on cooled surfaces. Materials are either boiled or sublimed by resistive, inductive or electron beam methods. Vacuum pressures below 10^{-4} Torr are typically used and deposition rated can vary from as little as 1 nm/s to above 1 μm/s. [21] [30]

Dielectric materials such as WO_3 and V_2O_5 as well as metals in general can be easily deposited by this technique and therefore this deposition technique have been successively performance in D/M/D structures development and is the deposition technique used to accomplish the present work.

2 MATERIALS AND METHODS: SIMULATION, FABRICATION AND CHARACTERIZATION OF D/M/D MULTILAYERS

2.1 D/M/D Design/ Simulations

In order to come to a better understanding of the influence of the materials used and their thickness in the D/M/D and to have theoretical simulated results to compare with the experimental ones, it was first performed systematic studies by varying D/M/D design parameters. All simulations were done using Mathematica software thought an algorithm based on Fresnel equations explained elsewhere. [31]

Simulations of the spectral T and R were carried out for the glass/metal different systems. Al, Ag, Cu, Ni and Sn metal layers for different films thickness (5, 10, 15 20, 30nm) were used. Furthermore, WO_3/metal/WO_3 multilayer systems coated on glass (n=1.5) substrates were also simulated for all of the previous mentioned metals. While WO_3 films thicknesses were kept constant at 30 nm, metal film thickness were also varied from 5 to 30 nm (5, 10, 15, 20, 30nm). Simulations were performed for wavelengths ranging from 190nm to 2500 nm. The optical constants considered for the simulation are taken from different sources, from others scientists work,[32 -34] and consequently variations in the experimental results are expected. Each optical constants file used in the software contains the optical data (λ, n and k) associated with a single material.

2.2 Film Depositions

Thin films of different dielectric materials (WO_3 and V_2O_5) and metals (Ag, Al, Cu, Ni and Sn) with different thickness were deposited on Corning glass substrates by thermal evaporation technique in a vacuum chamber assisted by a resistive crucible. These materials were evaporated from tungsten crucibles and the glass substrates were cleaned with isopropanol. The dielectric materials used were WO_3 powder with 99.9% purity (Sigma Aldrich) and V_2O_5 powder with 99.999% purity (Super Conductor Materials). The metallic materials used were Ag wire with 99.999% purity (Alfa Aesar); Cu granules (CERAC) with 99.9% purity; Sn granules (Alfa Aesar) with 99,9% purity; NiO (Sigma Aldrich) with 99,9% purity and Al wire (Alfa Aesar) with 99.999% purity.

The deposition pressure in the chamber has been maintained between 5×10^{-6} and 8×10^{-7} mbar and the source-substrate distance has been kept at approximately 30 cm. During deposition films' thickness were controlled by quartz crystal thickness monitor.

2.3 D/M/D Fabrication

Three layer dielectric/metal/dielectric (D/M/D) systems were accomplished by successive thermal evaporations under the conditions described in section 2.2.

Two dielectric materials were tested using the following configuration: WO_3/Metal/WO_3 and V_2O_5/Metal/V_2O_5. For each of these configurations, various metal species were tested, such as Ag, Cu, Al, Ni and Sn. The dielectrics thickness was kept constant at around 30 nm while various metal layer thicknesses were tested (5 nm, 10 nm, 15 nm, 20 nm, 30 nm).

Some of the D/M/D multilayer systems were submitted to post-annealing in order to understand the annealing effect on the sample's optical properties. Some of the samples were annealed under atmospheric pressure conditions while others were annealed under vacuum conditions. Annealing under atmospheric pressure conditions were performed in a furnace (Nabertherm L 3/11/B180) with a ramp up of 8 °C/min for one hour at 500°C. Moreover, annealing on vacuum chamber were performed in a furnace (MIT Corporation OTF-1200X-4-RTD) with a ramp up of 8 °C/min for two hours at 250°C.

2.4 Characterization Techniques

The film thickness was measured with a KLA TENCOR D-600 Profilometer.

The optical measurements were performed in a JASCO V-770 spectrophotometer (UV-Visible/NIR) for wavelengths in the range of 190-2500 nm, with a step of 0.5 nm. The total reflectance was measured using an integrating sphere.

The structural properties of the films were ascertained by XRD using a PANalytical X'Pert PRO equipped with an X'Celerator detector using CuKα radiation at 45 kV and 40 mA, in a Bragg–Brentano configuration. XRD patterns were collected over the angular 2θ range 15°– 80°, with a scanning step of 0.03°.

The surface morphology was analysed using scanning electron microscopy (Hitachi S-2400).

Materials optical properties where determined by ellipsometry spectroscopy with a Horiba Jobin Yvon UVISE with an average spectral range between 1.5 and 6.5 eV and an incident angle of 70 º.

3 RESULTS AND DISCUSSION

A study to define the best optical properties of single metallic and dielectric films and a combination of both was attempted in this thesis envisaging selective radiation windows glass application. In the following section the obtained results of transmittance and reflectance of thin metallic layers with different thickness is shown, being compared the experimental results with the simulated ones. The metallic layers studied are silver, copper, aluminium, nickel and tin while the dielectrics are tungsten oxide and vanadium pentoxide.

3.1 Silver Layers

Silver thin film with thickness in the range of 10 to 30 nm was deposited on a corning glass by thermal evaporation, from a pure Ag source. The measured and simulated transmittance and reflectance spectra are shown in Figure 5. The experimental graphs do not include Ag thin films with a thickness of 5 nm given the difficulty on depositing such thin Ag layer. Furthermore, reflectance experimental spectra do not represent the spectral response of Ag 15 and 10 nm due to samples breaking during manipulation.

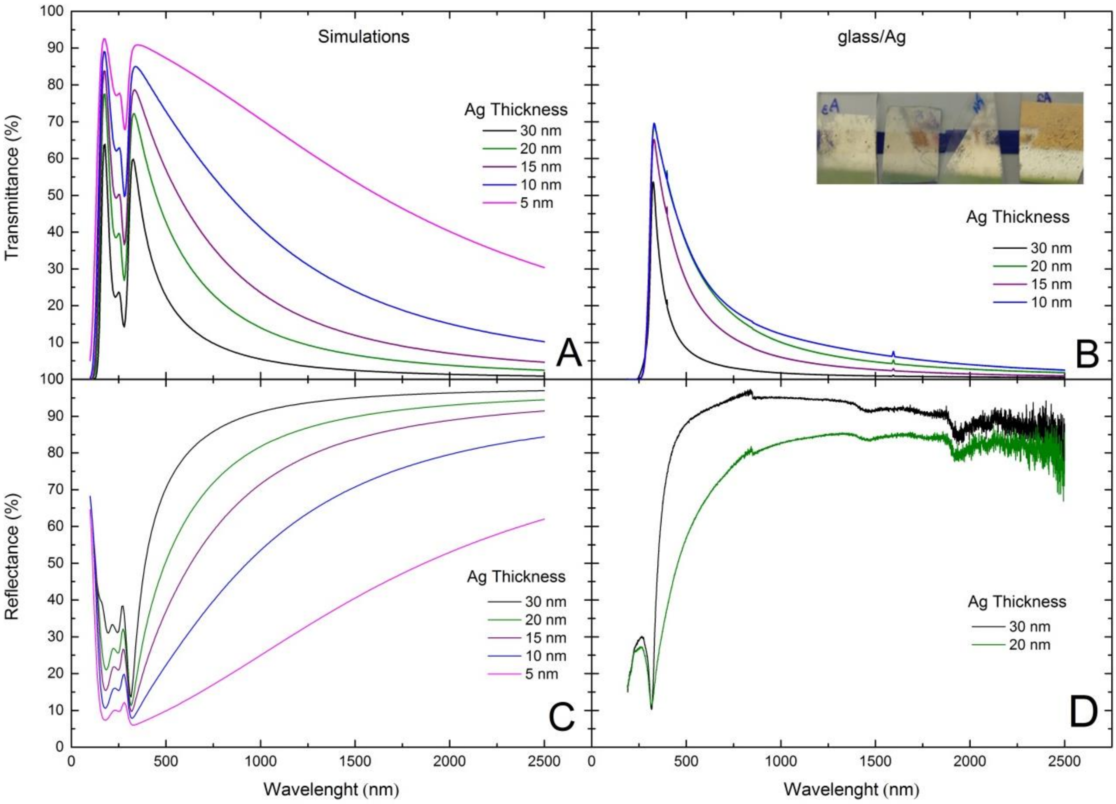

Figure 5 Transmittance and Reflectance spectra of silver thin films on glass for different films thickness A and C are the simulatel results; B and D correspond to the experimental results.

The presented spectra shows that, as expected, for a metallic layer, the increase in film thickness leads to a decrease in transmittance and an increase in reflectance. According to the experimental results at a Ag thickness of 10 nm occurs the transmittance peak (approximately 70%) in the visible region, around 260nm. The experimental results agree with the simulated ones on the influence of thickness, although the simulated values for T are higher than experimental ones. Furthermore, the T peak on simulated results occurs for the same wavelength but, again, with higher intensity (85% with 10 nm) for the simulated results. To this may contribute the refractive index used for simulation purposes taken from Rakic et al. applied optics (1998). [34]

3.2 WO3/Ag/WO3 multi-layers

Multilayers of WO_3/Ag/WO_3 whereas WO_3 has a fixed thickness (30nm) and Ag thickness varied in the range shown before. The obtained transmittance and reflectance measurements and the simulated ones are plotted in figure 6.

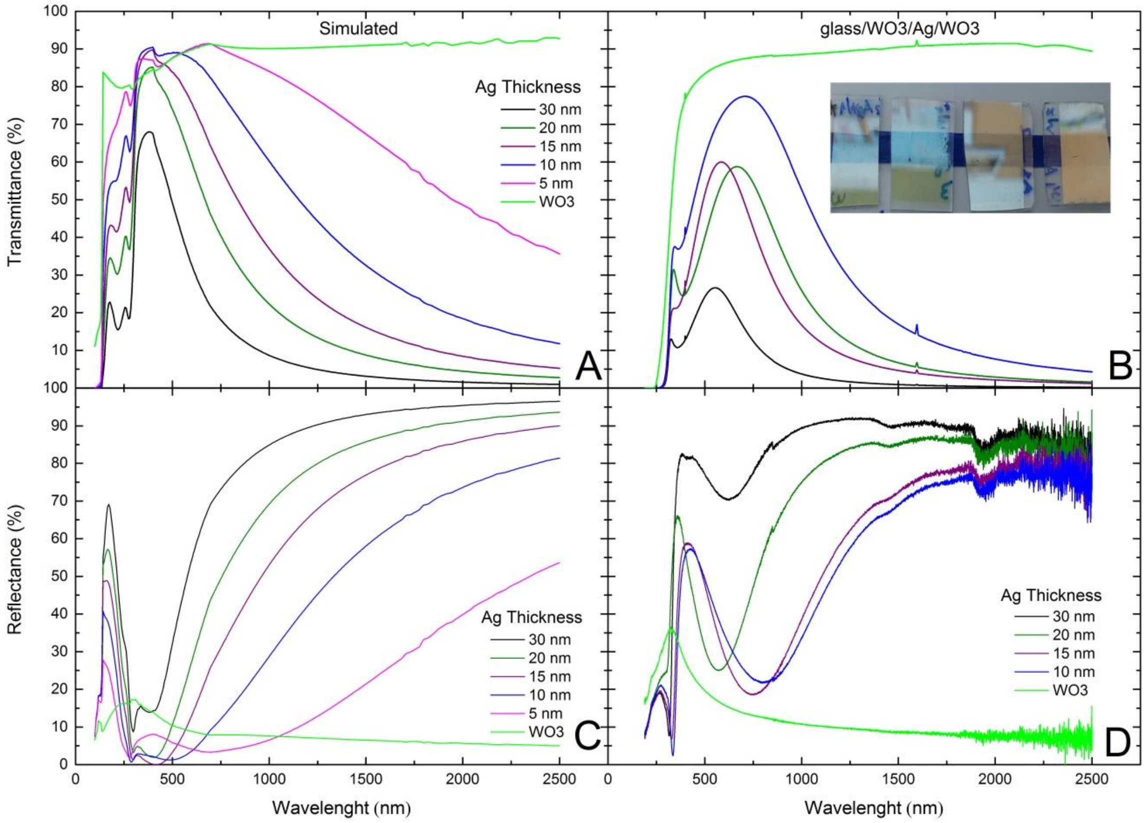

Figure 6 Optical T and R of silver thin films sandwiched between two WO_3 layers on glass for different film's thicknesses. Simulated transmittance (A) and reflectance (C) on the left and experimental transmittance (B) and reflectance (D) on the right.

Figure 6 also contains the T and R spectra of WO_3 and, as dielectric; it has very high transmittance, above 90%, while the reflectance is below 20% above 500nm.

Analysing the given results for multilayers, one can see the transmittance has a peak in the range of 500-600 nm that decreases as the metal thicknesses increases. Similar trend is observed for the simulated results, but high T values in the visible wavelength range are displayed. The refractive index of the WO_3 layers taken for the simulations can be the source of this difference or the interfaces WO_3/Ag and Ag/WO_3 are not well represented by the simulation model used. Furthermore, the reflectance is very high in the infrared region (λ>100nm), caused by the Ag layer and predicted by the Ag R spectra shown in figure 6.

Overall from results of figure 6 we conclude that the use of these WO_3/Ag/WO_3 multilayers as selective radiation for windows is possible considering application where relatively high transmittance in the visible region (around 60%) and high reflectance in the infrared region (above 70% for λ>100nm) are needed. A WO_3 (50nm)/Ag(15nm)/WO_3(50nm) structure matches this condition.

The WO_3/Ag/WO_3 multilayers shown in figure 6 were deposited by thermal evaporation without any further thermal treatment. Therefore, we wanted to analyse the influence of thermal treatment on the optical properties of these multilayers. The influence of thermal annealing are plotted for all Ag thickness in the graphs of figure 26 in annex 1. There we can observe that thermal annealing in vacuum at 250ºC has a minor influence on the R and T spectra relatively to the as-deposited samples or has tendency to decrease T and increase R. The annealing in vacuum could promote the reduction of oxide layers (WO_3) leading to a more metallic like layer. On the opposite the thermal annealing at 500ºC in air will promote the oxidation of metal layers and so an increase in T while R tends to diminish. One should note that the oxidation of the metallic layer will result in a small increment of the layer thickness which will also influence the final optical properties.

Figure 7 compares the T and R spectra of WO_3/Ag/WO_3 multilayers without and with thermal annealing at 500ºC 1h in air for the different Ag thickness studied.

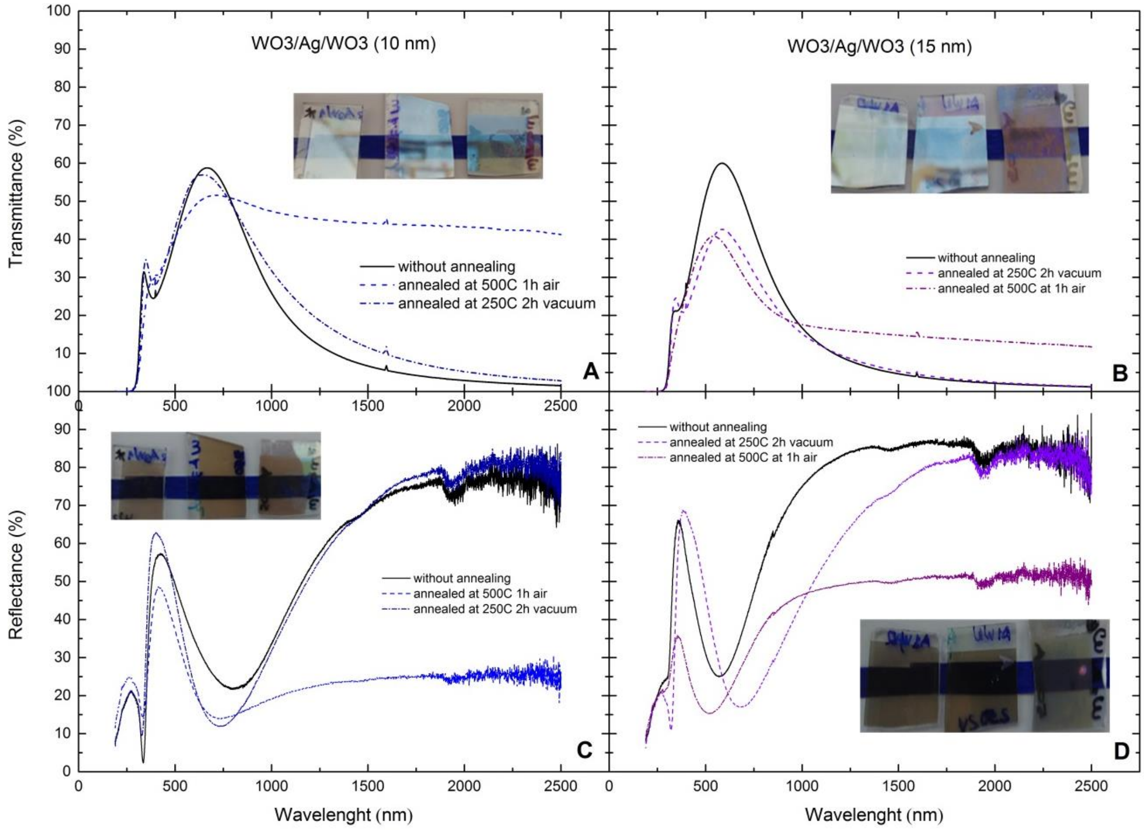

Figure 7 Annealing effect on transmittance (A and B) and reflectance (C and D) of silver thin films sandwiched between two WO_3 layers on glass for different film's thicknesses. A and C represent, respectively, the transmittance and reflectance for a 10 nm silver layer and B and D correspond to the transmittance and reflectance of a 15 nm film.

Figure 8 shows, T and R spectra of V_2O_5/Ag/V_2O_5 multilayers where can be seen the influence of annealing. One can see that T is greatly enhanced in films annealed 1h at air compared to films as-deposited for both thicknesses tested. On the contrary vacuum annealing promotes an enhancement of T and reduction of R in the IR region, that is, absorption increases to expected values of around 40%.

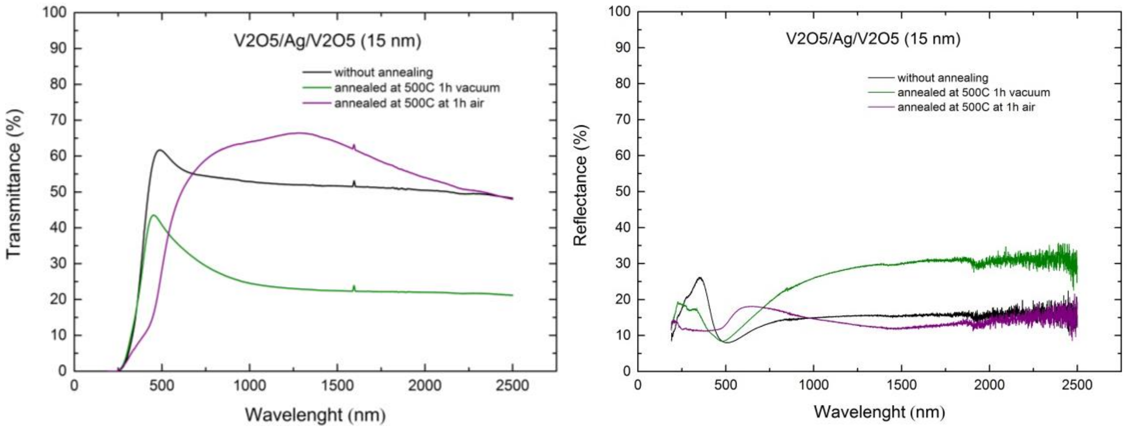

Figure 8 Annealing effect on Transmittance (A) and Reflectance (B) of silver thin films sandwiched between two V_2O_5 layers on glass for 15 nm Ag films thickness.

3.3 Copper Layers

Similar to what was processed for silver, different thickness layers of Cu were deposited and the transmittance and reflectance spectra were plotted and shown in figure 9. Accordingly, to the expected results the T decreases as the film thickness increase, in the range of 5 to 30nm, while the reflectance has the opposite behaviour. The simulated spectra are quite similar to measured values for both R and T as a function of copper film thickness.

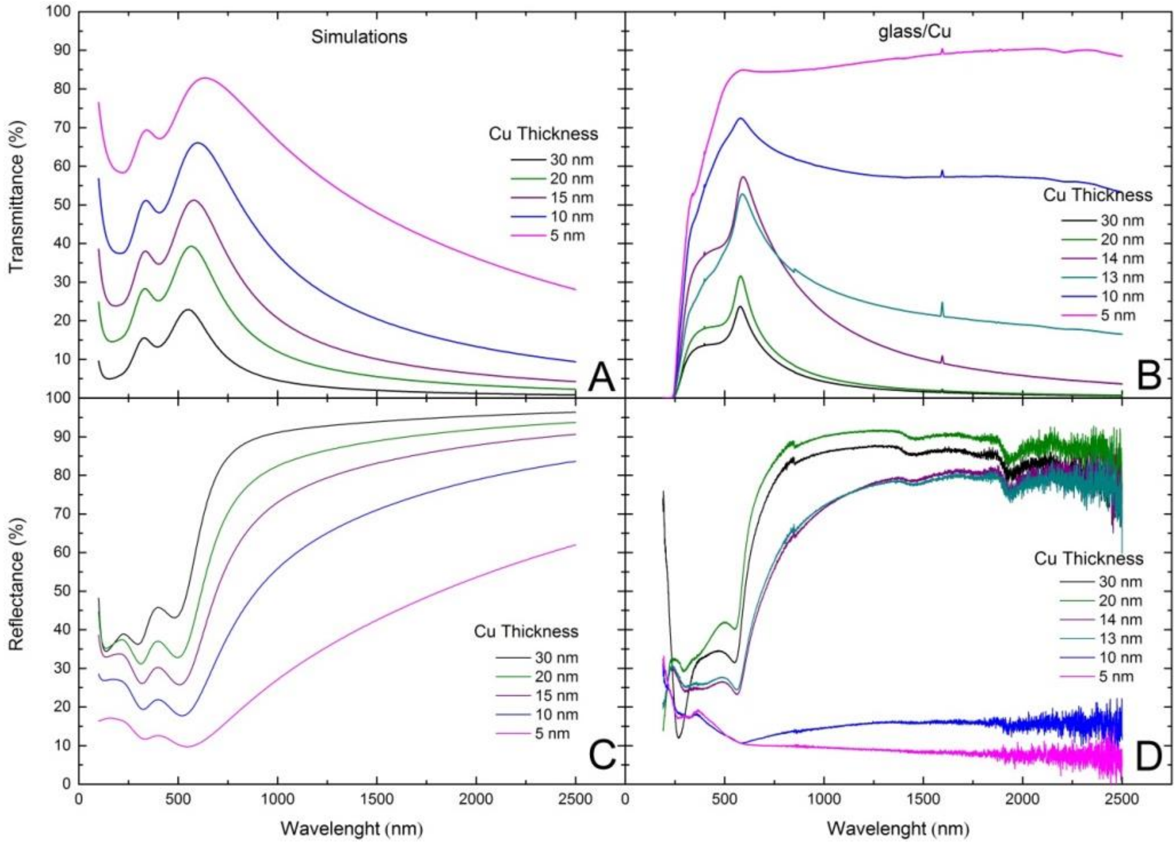

Figure 9 Simulated transmittance (A) and reflectance (C) of the Cu layers for different film thickness (5, 10, 15, 20, 30nm) and experimental transmittance (B) and Reflectance (D) of cooper thin films on glass for different film's thickness.

The T and R results for the Cu layers confirm this material as good reflector for wavelengths above 600nm when films thickness is superior to 13nm while bellow it T is above 60% in the wavelength range of 400-2500nm. The simulated spectra are quite similar to the experimental T and R despite the mismatch in the refractive index used for simulation. The difference between experimental and simulated values are higher for the lowest film thickness which may also corresponds to a more accentuated error in the film thickness measurement.

3.4 $WO_3/Cu/WO_3$ multilayers

The transmittance and reflectance spectra of the multilayers produced with a fixed WO_3 thickness (30nm) and varying the Cu thickness are shown in figure 10 together with the simulated spectra for the corresponding samples.

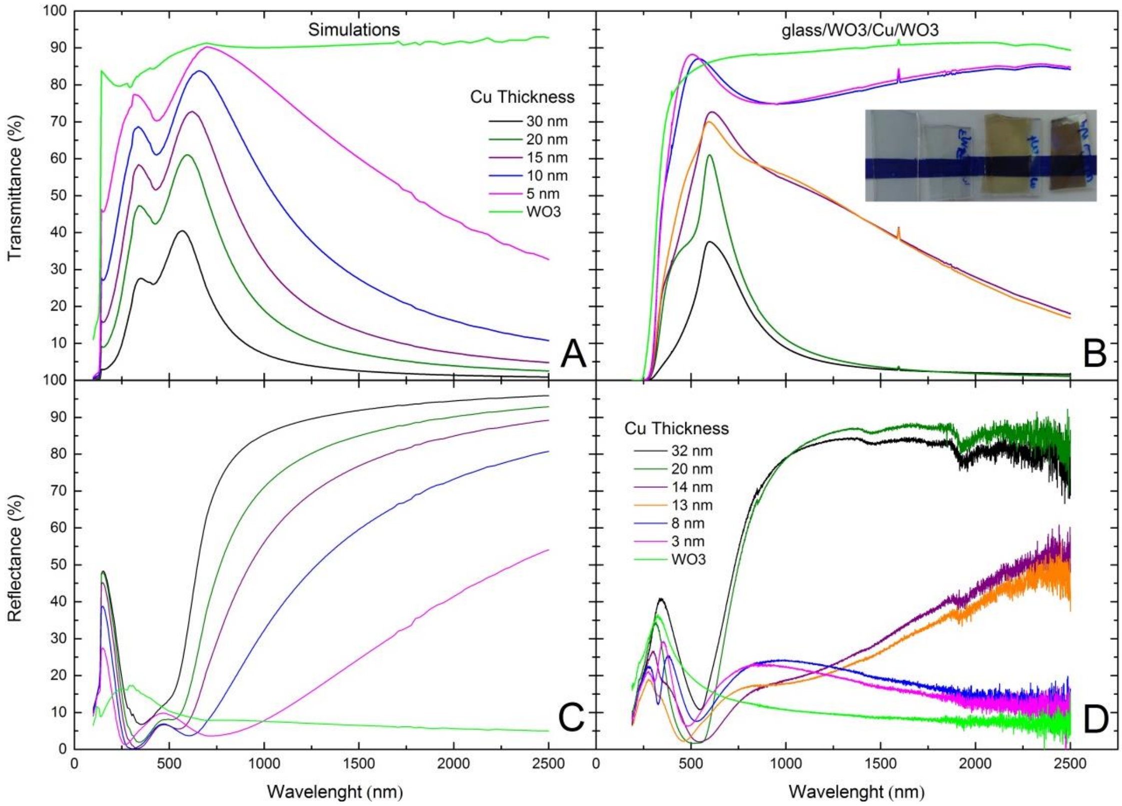

Figure 10 Simulated transmittance (A) and reflectance (C) and experimental transmittance (B) and reflectance (D) of cooper thin films sandwiched between two WO_3 layers on glass for different film's thickness.

Transmittance has its maximum value in the visible region nearly 550-600nm varying from almost 90% for the tiniest (5 nm) metal thickness to 30% for the thickest one (30 nm). In the infra-red region the multilayers with a metal layer of 3 and 6 nm have a transmittance of about 80%; for copper layers of 13 and 14 nm the transmittances in the same region are about 40 to 50% and finally, 20 and 30 nm copper multilayers have a near zero transmittance.

The reflectance presents the transmittance opposite behaviour. The most reflective samples are the thickest ones with a reflectance approaching 90% in the IR region and the tiniest ones with around 10%.

The samples with 13 and 14 nm may absorb some radiation in the infrared region between 1500 to 2500 nm once they have a transmittance between 20 to 40% and a reflectance of 30 to 50% which means that approximately 30 to 40% of the radiation should be absorbed.

Figures 11 and 12 show the plots of T and R spectra of $WO_3/Cu/WO_3$ multi-layers, when annealed at different temperature and environment conditions with the as deposited ones, for two Cu films thickness, 5 and 10nm. Vacuum annealing at 250ºC 1h or 2h has no relevant effect on the T and R spectra for 5nm Cu, while vacuum annealing at 500ºC for 1h promotes a remarkable decrease of T in the infrared region but in the visible region (around 500nm) it is reduced from 80% to 70%, so still quite transparent for windows applications. The same trend was observed on 10nm Cu samples but annealing at air conditions at 500ºC for 1h. As the R was minor variation for both samples it means that they should have a high absorption in the IR region, expected to be in the range of 40%. However, air annealing at 500ºC for 5nm Cu sample lead to almost complete oxidation of the metallic films and therefore, T is enhanced while R is below 20% in whole wavelength range. Cu layer 20nm thickness was also studied but the enhancement of absorption was not achieved, the results are shown in annex 2.

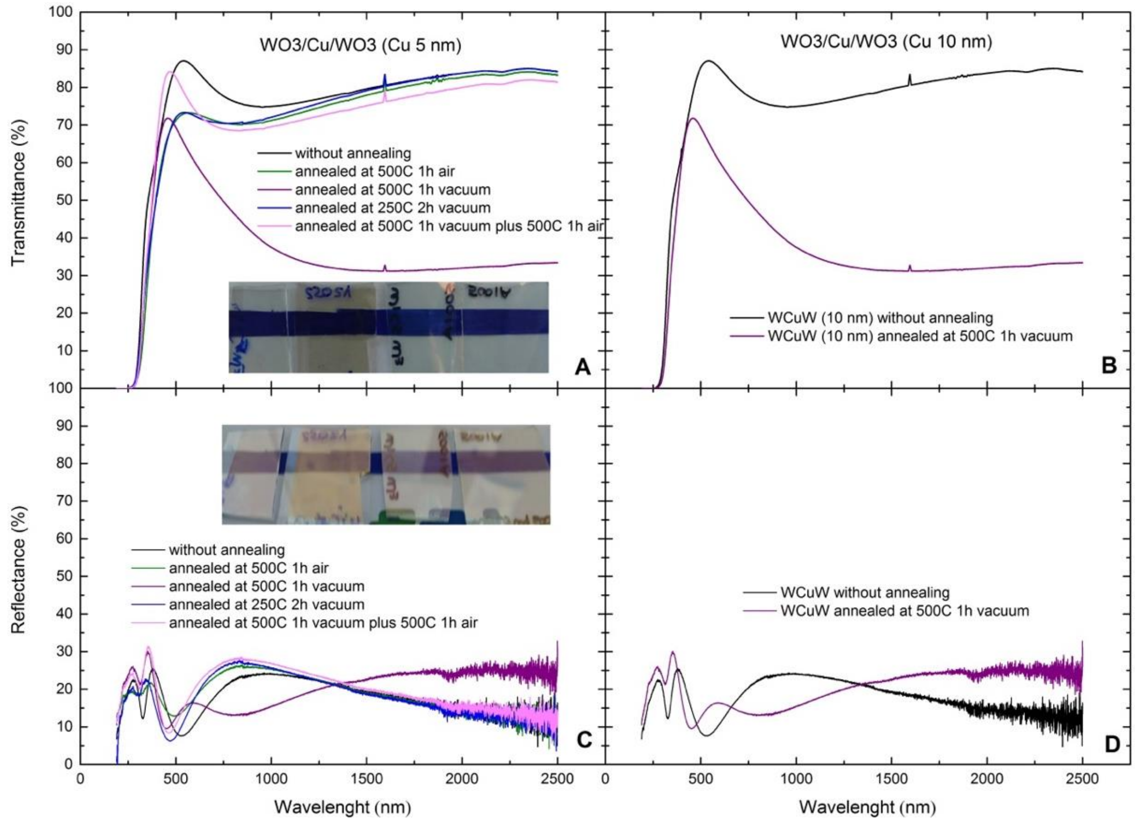

Figure 11 Annealing effect on Transmittance (A and B) and Reflectance (C and D) of cooper thin films sandwiched between two WO_3 layers on glass for different films thickness.

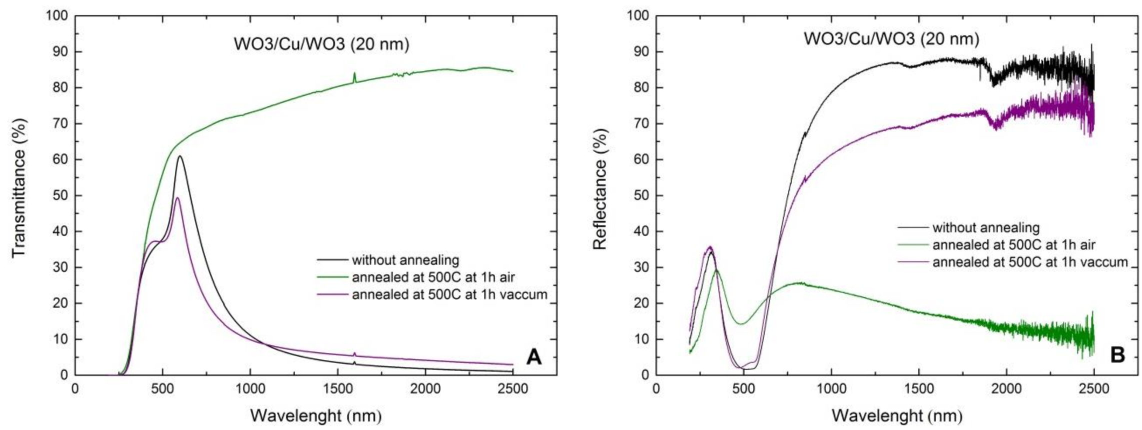

Figure 12 Annealing effect on Transmittance (A) and Reflectance (B) of copper thin films sandwiched between two WO_3 layers on glass for 20 nm Cu films thickness.

Furthermore, reflectance decreased from 20% to 10% near 900nm and increased from 10% to 25% between 1250nm to 2500nm. The annealed sample has a transmittance of 30% and a reflectance of 20% in the infrared region which means that almost half of radiation (50%) is probably being absorbed in this region.

Figure 13 shows T and R spectra of V_2O_5/Cu/V_2O_5 multilayers studied where can be seen the influence of annealing for two distinct thickness Al film layers (12 and 20nm). One can see that T is greatly enhanced in films annealed 1h at air compared to films as-deposited for both thicknesses tested. On the contrary vacuum annealing promotes a decrease of T in the visible and NIR regions and R dropped for the IR region, that is, absorption increases to expected values of around 20% for both thicknesses.

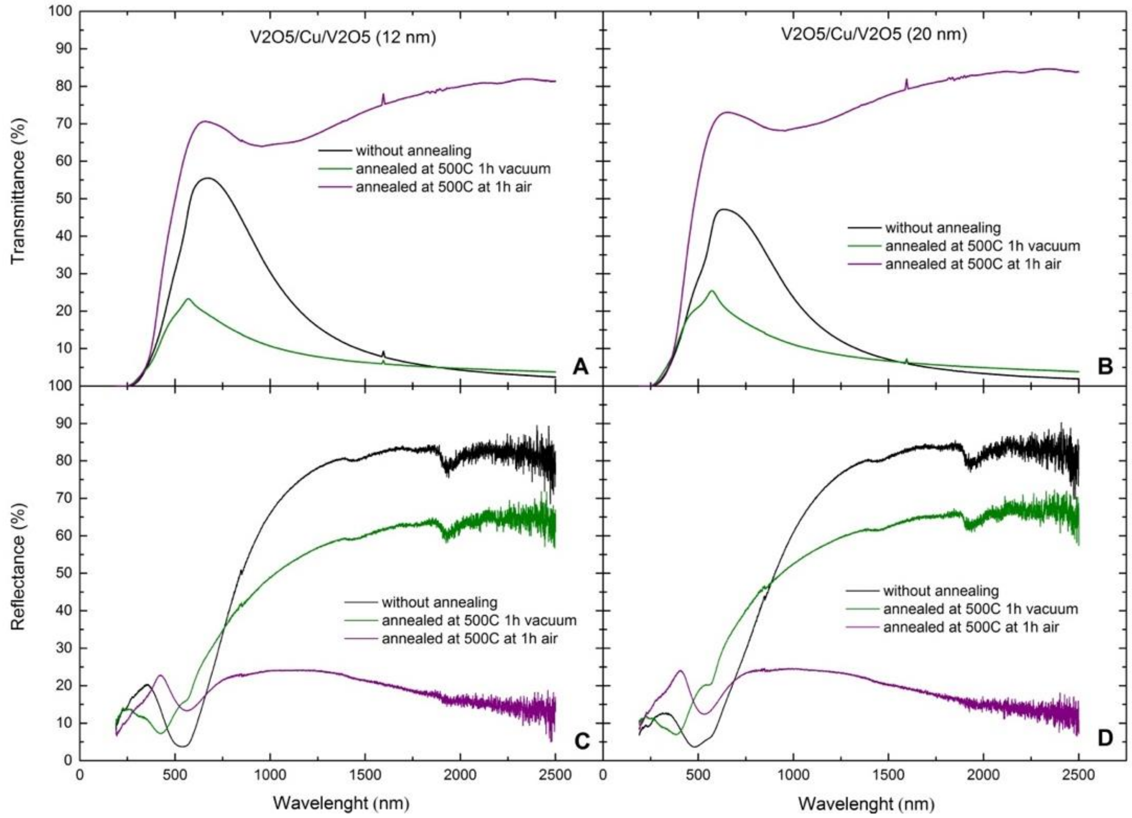

Figure 13 Annealing effect on Transmittance (A) and Reflectance (B) of copper thin films sandwiched between two V_2O_5 layers on glass for 12 (A and C) and 20 nm (B and D) Cu films thickness.

3.5 Aluminium Layers

Aluminum layers even with very low thickness are good reflectors and due to that their are used as mirrors (figure 14). Indeed the T and R spectra of Al layers with thickness in the range of 5 to 30nm show maximum tranmittance below 20% decreasing to 10% when thickness increase to 30nm while reflectance varies in the opposite way from 90% to 60%.

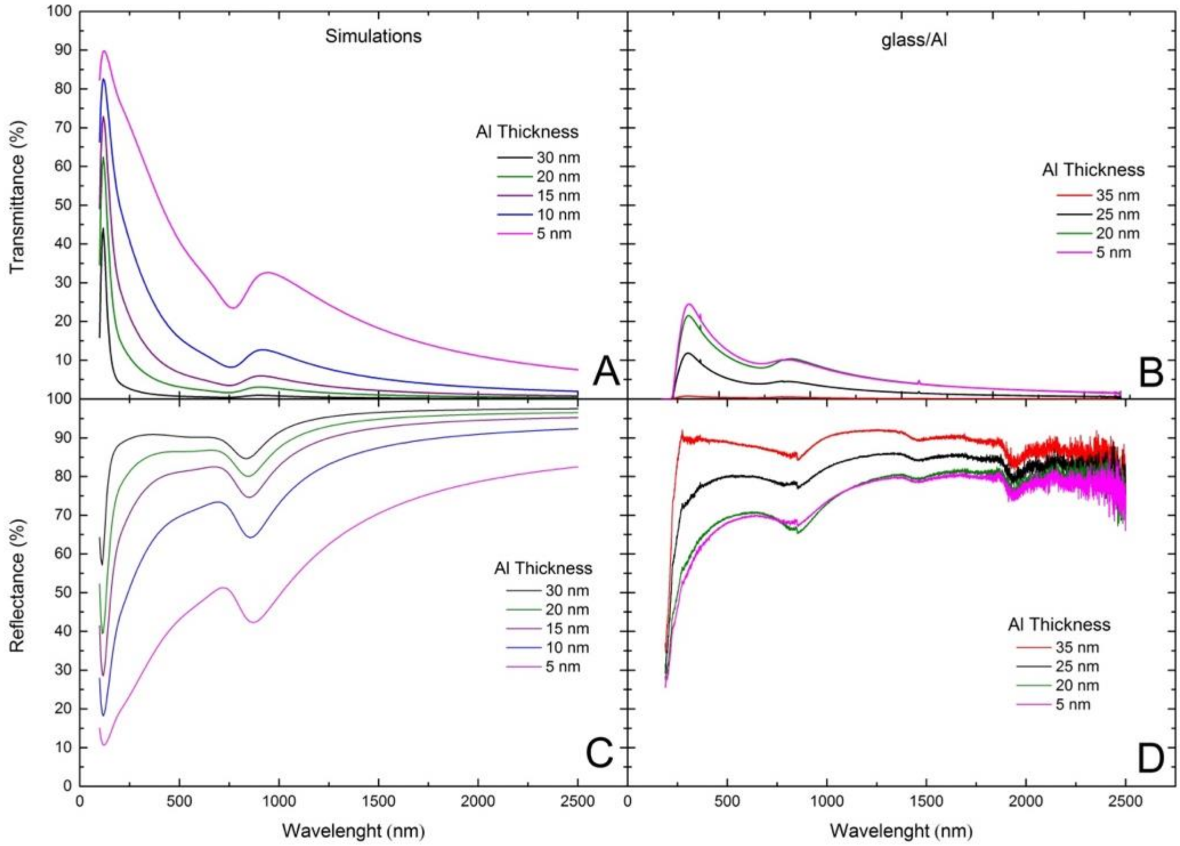

Figure 14 Simulated transmittance (A) and reflectance (C) and experimental transmittance (B) and reflectance (D) of aluminium thin films on glass for different film's thicknesses.

The T and R spectra of WO_3/Al/WO_3 show a small increment on the maximum T value from 20 to 40% and a corresponding decrease of R, but still not suitable for windows applications.

The difference in transmittance between experimental and simulated values are related to the difference between the real optical constants that characterize the experimental produced Al thin films and the optical constants used for simulation, taken from literature.

3.6 $WO_3/Al/WO_3$ multilayers

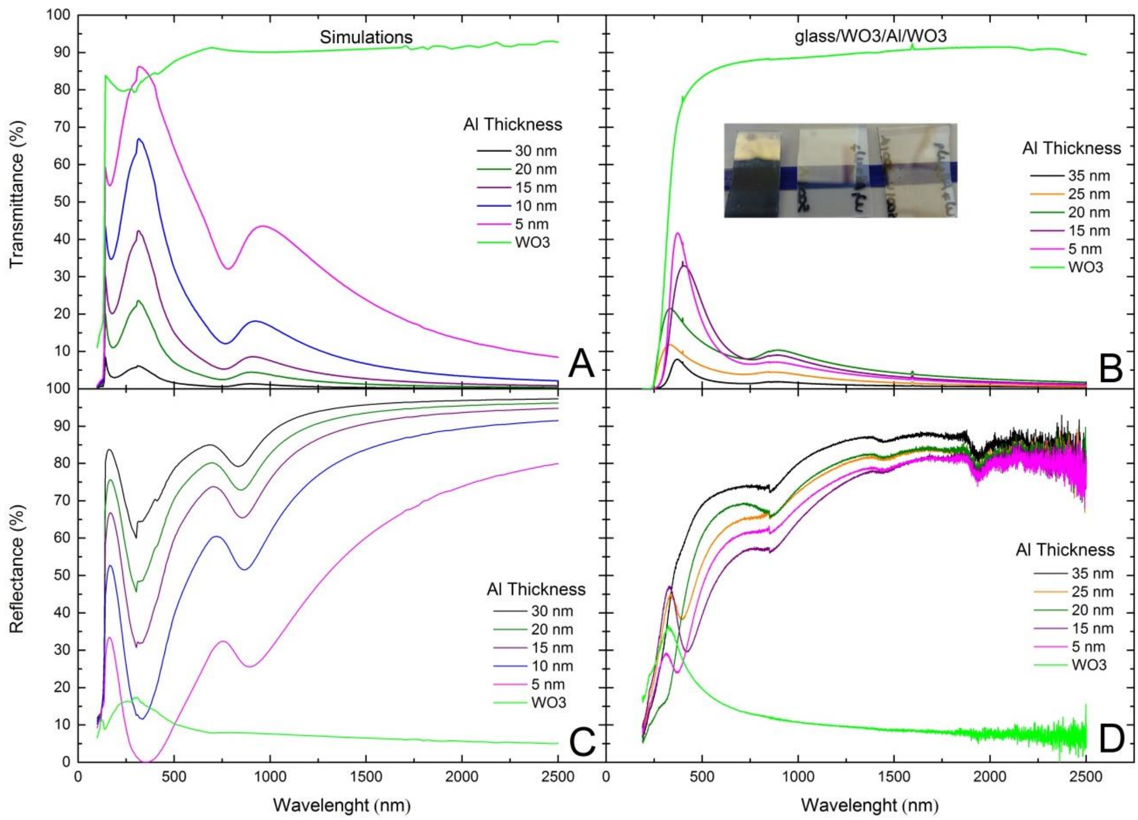

Figure 15 Simulated transmittance (A) and reflectance (C) and transmittance (B) and reflectance (D) of aluminium thin films sandwiched between two WO_3 layers on glass for different film thickness.

Figure 16 represents $WO_3/Al/WO_3$ multilayer's transmittance and reflectance variation with different annealing procedures. Annealing under air conditions (1h 500ºC) induces sample's oxidation greatly, increasing its transmittance and decreasing reflectance. The transmittance in the infrared region increased from near zero to 90% while for annealing at 500ºC for 1h in vacuum followed by 500ºC for 1h in air environment the T is enhanced for 65% and if annealed in vacuum at 500ºC T is enhanced to above 55%. Reflectance decreased from 80% (initial sample) to 10 to 20% (annealed samples) independently of the annealing treatment performed. From the above results we conclude that Al is not a good metal material to be used as selective coating in windows.

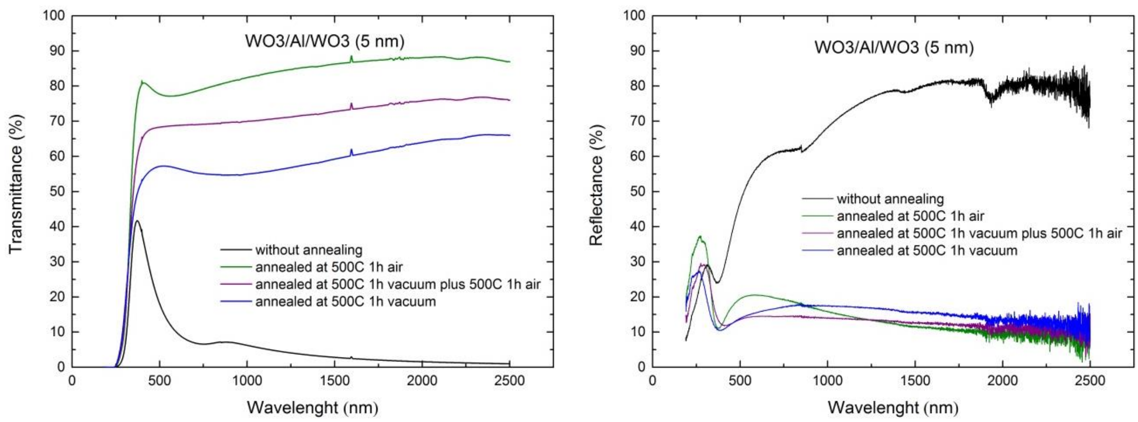

Figure 16 Annealing effect on Transmittance and Reflectance of a 5 nm aluminium thin film sandwiched between two WO_3 layers on glass.

Figure 17 shows, T and R spectra of $V_2O_5/Al/V_2O_5$ multilayers where can be seen the influence of annealing. One can see that T is greatly enhanced in films annealed 1h at air compared to films as-deposited for both thicknesses tested. On the contrary vacuum annealing promotes an enhancement of T and reduction of R in the IR region, that is, absorption increases to expected values of around 40%.

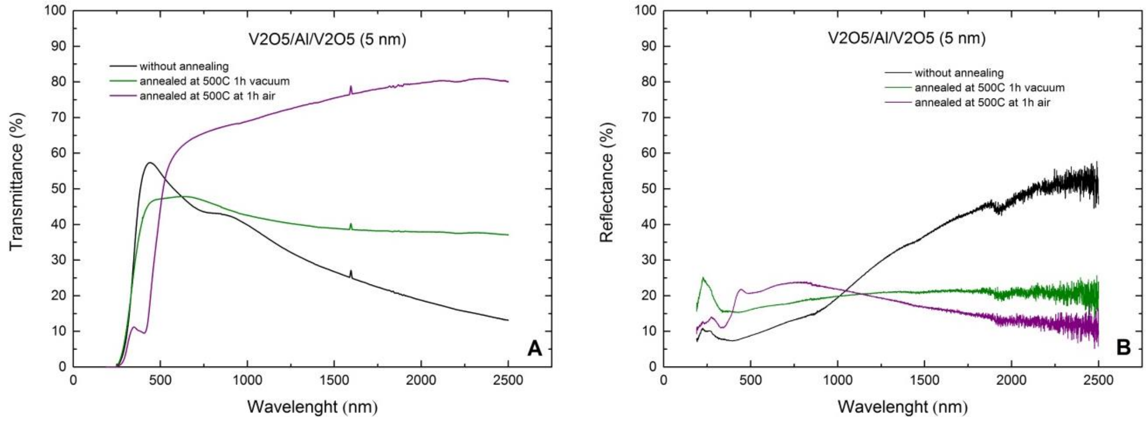

Figure 17 Annealing effect on Transmittance (A) and Reflectance (B) of aluminium thin films sandwiched between two V_2O_5 layers on glass for 5 nm Al films thickness.

3.7 Tin and Nickel Layers

Ni and Sn thin layers and the respective $WO_3/Ni/WO_3$ and $WO_3/Sn/WO_3$ structures were also studied and the results are shown in annex 3. The Ni layers studied with 20 and 40nm have both high transmittance and low reflectance in the wavelength studied 300nm-2500nm, therefore they are not suitable for light control in windows. The same happen when these layers are sandwiched between WO_3 layers. This means that after the Ni deposition the metal oxidised very quickly forming a NiO layer which has typically high transmittance and low reflectance. A control of the absorption in the IR region was possible by annealing the $WO_3/Ni/WO_3$ structures.

Figure 18 represents $WO_3/Ni/WO_3$ multilayer's (Ni thickness equals 20 nm) transmittance and reflectance variation with different annealing procedures influence.

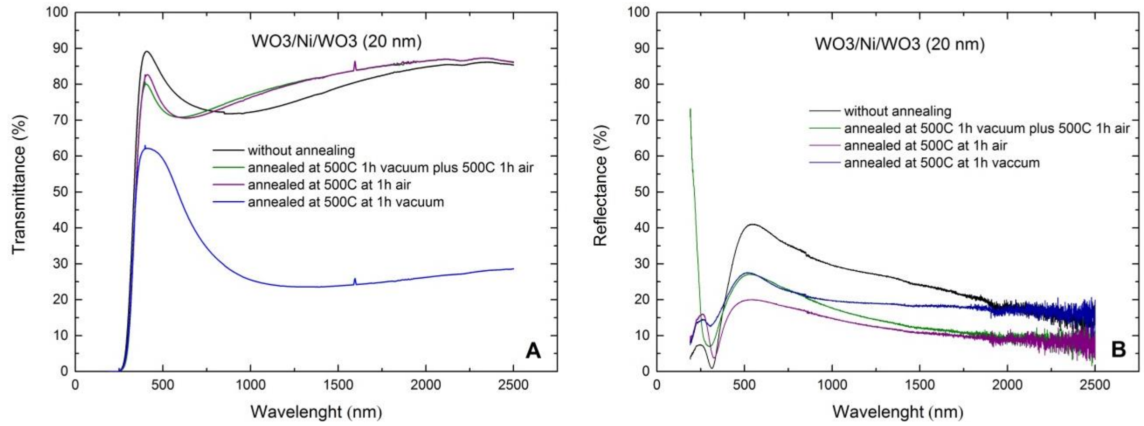

Figure 18 Annealing effect on Transmittance and Reflectance of a 20 nm nickel thin films sandwiched between two WO_3 layers on glass.

Results show that annealing procedures involving air environment do not have a significant effect on the transmittance and reflectance of samples. On the other hand, the annealing at 500ºC for 1 hour in vacuum decreases transmittance in the visible region from 90% to 60% and from 90% to 30% in the infrared region. Furthermore, reflectance decreases as well, going from 40% to 25% in the visible spectrum's range and from 30 to 20% in the near infrared region, being kept the same in the infrared region. As both transmittance and reflectance are decreased, there may be a change the samples are absorbing radiation in the visible and near infrared regions. This may happen because since the metallic film is extremely thin, it may happen that instead of a thin film one is obtaining separated aggregates of material. These phenomena may be further induced by annealing and thus promote a higher absoptance.

The Sn films and WO_3/Sn/WO_3 structure results are shown in annex 3 as well, figures 30 and 31, being the obtained results also unsuitable for windows application. The Sn layers of 5 and 15 nm show different transmission and reflectance behaviour. While for 5n Sn the T is high in the visible and IR region the 10nm shows a low transmittance in the visible region and high transmittance in the IR. The reflectance has opposite behaviour of T. When these Sn layers are between dielectric layer, WO_3, the similar trend of T with thickness of Sn is observed. However, when these structures are annealed at 500ºC for 1h a transmittance of the order of 50% for wavelengths above 500nm is obtained with a reflectance in the same range below 20%. Then an absorbance of the order of 30% is expected. The other annealing conditions are inadequate for windows' transmittance control.

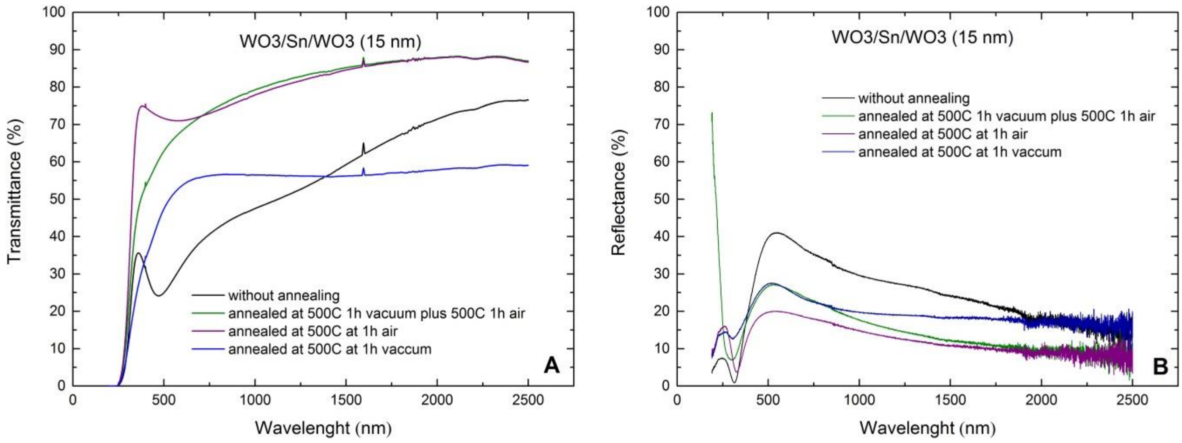

Figure 19 Annealing effect on Transmittance (A) and Reflectance (B) of tin thin films sandwiched between two WO_3 layers on glass for different film's thicknesses.

3.8 Multilayers structures

In order to define possible applications for the D/M multilayers studied, several attempts were tried. The Cu and Ag layers were deposited on glass/GZO (Ga doped ZnO). The GZO is a TCO often used as transparent electrodes and here it was used to simulate possible applications in multifunctional windows devices. As such a 12nm Ag and V_2O_5 (27nm) layers were choose to produce a glass/GZO/Ag/V_2O_5 structure. The T and R spectra are plotted in figure 20 where are also displayed the respective spectra of the individual layers and also Ag/V_2O_5 bilayers. Similarly it was performed for glass/GZO/Ag/WO_3, glass/GZO/Al/V_2O_5, glass/GZO/Cu/V_2O_5, glass/GZO/Cu/WO_3 and the results are plotted in figure 34 of annex 4 for T and R, respectively. The absorbance spectra for the glass/GZO/Ag/V_2O_5, glass/GZO/Ag/WO_3, glass/GZO/Al/V_2O_5, glass/GZO/Cu/V_2O_5, glass/GZO/Cu/WO_3 and its comparison with glass GZO are shown in figure 21.

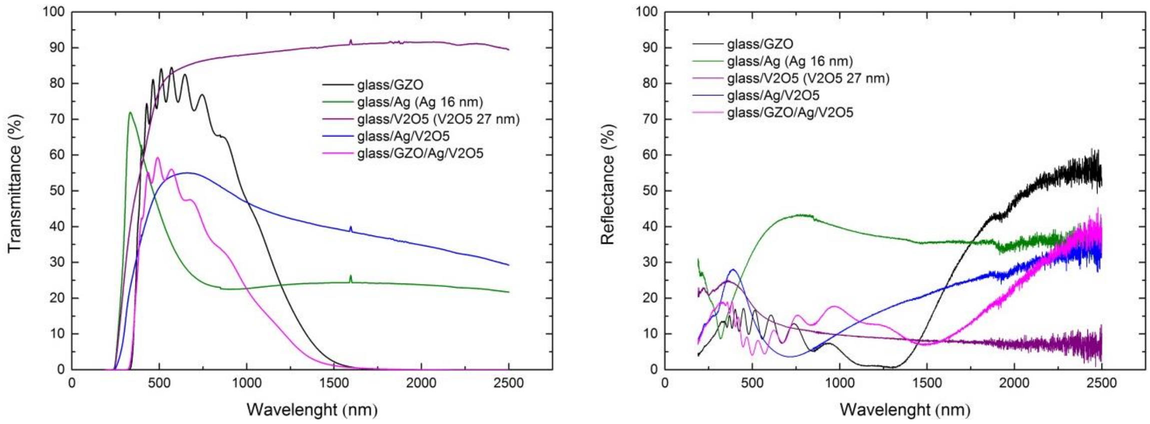

Figure 20 Transmittance and Reflectance of glass/GZO/Ag/V_2O_5 structure and respective influence of each constituting layer.

3.9 Absorptance

The absorptance of the selected multilayers was calculated from A+T+R=1, with T and R being shown in previous graphs. This gives an idea of the light percentage that is absorbed by the samples. Thus, graphs of figure 21 clearly demonstrate a strong light absorption in 1000-2000nm wavelength region of GZO, GZO/Al/V_2O_5, GZO/Ag/V_2O_5, GZO/Ag/WO_3, and a very low absorption in the visible wavelength region. Exceptionally, GZO/Cu/V_2O_5 and GZO/Cu/WO_3 structures do not present the same behaviour showing low absorption in IR region and absorbing radiation of wavelengths below 700nm.

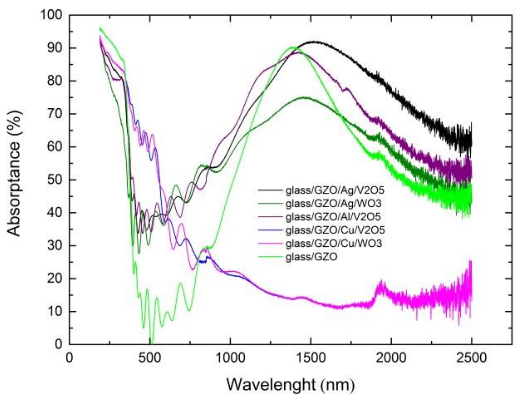

Figure 21 Absorptance spectra (in %) of different structures on glass/GZO substrate.

Similarly, absorptance was calculated for structures that were previously identified as possible absorptive samples in the IR region. These are glass/WO_3/Sn/WO_3, glass/WO_3/Ni/WO_3, glass/V_2O_5/Ag/V_2O_5, glass/V_2O_5/Al/V_2O_5, glass/WO_3/Al/WO_3. Given this, a calculated absorptance with values of 50-60%, for the range of wavelengths above 500nm, is observed for not annealed glass/V_2O_5/Ag/V_2O_5 samples. Interestingly the glass/WO_3/Ni/WO_3 annealed samples show about 20% of absorptance in the visible range and around 40% above 750nm.

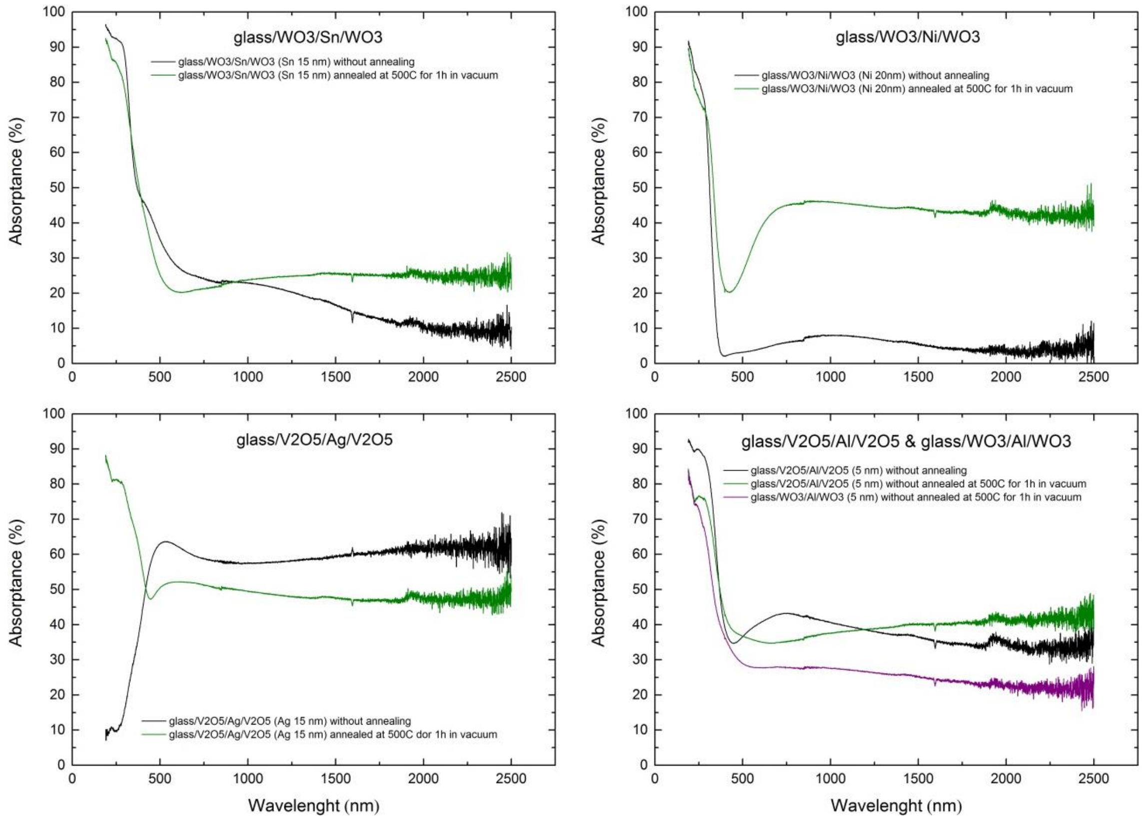

Figure 22 Absorbance spectra of different D/M/D structures, including annealed and non-annealed samples.

3.10 Samples morphology

SEM images presented on figure 23 illustrate the surface morphology of some of this study's representative samples. Figure 23 a) shows WO_3/Cu/WO_3 as deposited sample not annealed. Figure 23 b) represents WO_3/Cu/WO_3 annealed at 500°C in air. Figure 23 c) represents V_3O_5/Cu/V_3O_5 sample annealed at 500°C in air. Figure 23 d) represents V_3O_5/Al/V_3O_5 sample annealed at 500°C in vacuum and figure 23 e) represents V_3O_5/Ag/V_3O_5 sample annealed at 500°C in vacuum.

By observations of the presented images it can be concluded that not annealed samples have a surface morphology very smooth while after annealing samples got a more roughness surface whose morphology depends on the metal and dielectric layers introduced.

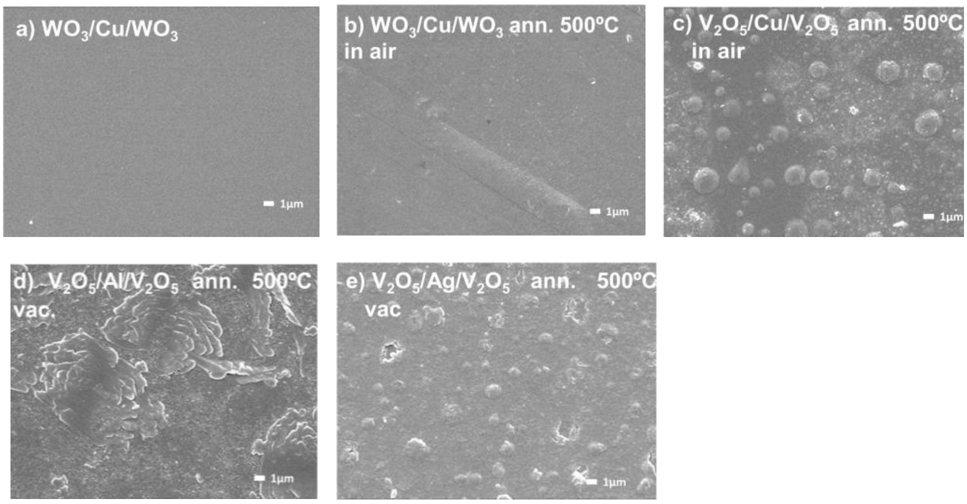

Figure 23 SEM images of WO_3/Cu/WO_3 structure (a) and WO_3/Cu/WO_3 structure annealed at 500°C in air (b); V_2O_5/Cu/V_2O_5 samples annealed at 500°C in air (c); V_2O_5/Al/V_2O_5 annealed at 500°C in vacuum and V_2O_5/Ag/V_2O_5 annealed at 500°C in vacuum. Imaging conditions: x3,700; 15.0 kV SEI; SEM; MicroLab

Additionally, XRD images are presented on figure 24 being identified the respective diffraction plans based on [35-37]. The characteristics amorphous bump of glass is observed for the analysed samples. Figures 24 C and D has a clear evidence of a Cu peak corresponding to (111) phase at 43.42° and the V_2O_5 and WO_3 seemed to be amorphous as their main diffraction peaks are indecipherable. Samples annealed in air are more likeable to have Cu oxide species, more evident for WO_3/Cu/WO_3 samples with high crystalline and intense WO_3 (200) and Cu_2O (110) peaks. In V_2O_5/Cu/V_2O_5 are also seen V_2O_5 (001). Overall the SEM images and XRD are in good agreement.

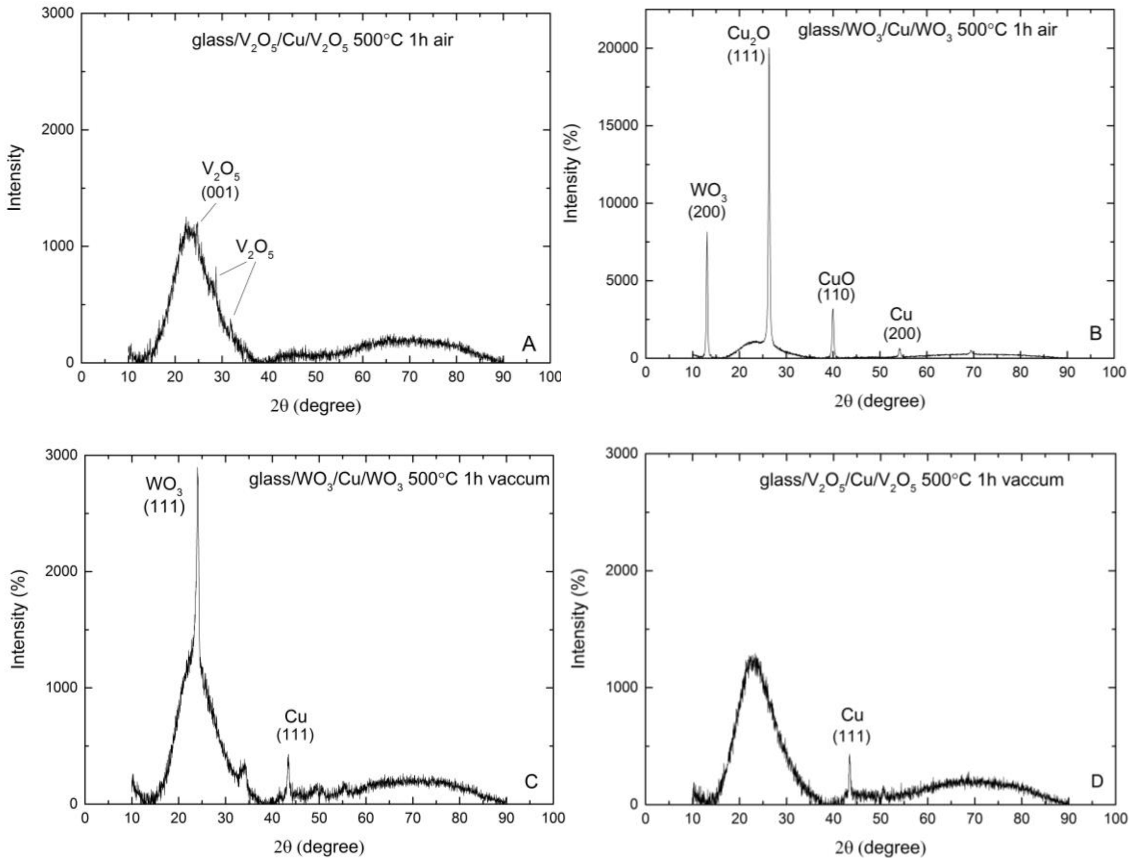

Figure 24 XRD images of annealed samples under different conditions

4 CONCLUSIONS AND FUTURE PERSPECTIVES

The present work was centred on the fabrication, characterization and improvement of D/M/D structures in order to obtain controlled optical transmittance/reflectance properties as a function of the wavelength. Al, Ag, Cu, Ni and Sn were tested as metal layers for different films thickness (5, 10, 15, 20, 30nm) while V_2O_5 and WO_3 were tested as dielectric layers with constant thicknesses equal to 30 nm.

Some difficulties have been overpassed along this work. First, all layers were deposited by thermal evaporation using a resistive crucible while the system is not adapted to produced such very thin films as the ones needed for the present study. In order to overpass this problem a previous study to understand how to properly use the shutter and its required “open time” as well as the electric power that should be admitted to the crucible in order to control the obtained film thicknesses had to be performed. Second, the system is also not prepared to perform several layers in a single run, which means each layer corresponds to a single deposition run and between layers the system was opened and the crucible filled with the material for the layer deposition. Naturally, the systems’ opening could initiate the oxidation of the metal films. Thus, the production of the samples took much more time than it should have with a more adequate system, and due to time constrains the materials thickness were not further changed which would be important to further improve the transmittance/reflectance performance of the multilayer films. Despite the mentioned difficulties the work was, in fact, successful and the final objectives, which consisted on study the optical properties of D/M/D multilayers to control the reflectance and transmittance in visible and infrared region envisaging selective glazing systems, was achieved. This final chapter is, therefore, focused on giving some final remarks about the work as well as some perspectives for possible future investigations on this specific topic.

4.1 Main Conclusions

Regarding the optical T and R properties of the present study it can be concluded that Ag’s thin film transmittance is characterized by having a sharp peak (70% for the thickest sample) at around 400nm that decreases as film thickness is increased. Similar results have been published by [38]. Its reflectance in the NIR and IR regions is equally high, starting to increase from a low value in the visible region to around 90% for wavelengths bigger than 500nm. As expected, in opposite of what happens with transmittance, thinner samples show smaller reflectance’s. However, when the Ag films are sandwiched within two WO_3 layers of 30nm the transmittance peak, in the visible range, is enhanced and enlarged. For example, the maximum value of T for a 10nm Ag layer is 70% at ≈400nm, showing a band width at T=20% of about 300nm while for a WO_3/Ag/WO_3 multilayer structure with a metal layer comprising the same thickness it reaches a 80% T at 500nm and a band width of 1000nm at T=20%. The correspondent R decrement is verified.

The same WO_3/Ag/WO_3 multilayer structure were submitted to annealing procedures, performed in air (500ºC) and under vacuum (250ºC) in the expectation of improving sample’s T. The results showed that instead of being improved, T values were reduced duo to an oxygen reduction happening in the dielectric layer, during annealing procedures, that leads to a more metallic behaviour. Annealing is, however, beneficial for V_2O_5/Ag/V_2O_5 structures greatly enhancing its transmittance and presenting a reflectance smaller than 20% in wavelength range from 500nm to 2500nm. Interestingly this structure has high absorption in the region of 300-500nm.

Cu layers also show a good T control with a T peak around 400nm but, with a more noticeable dependence with thickness than the observed with Ag layers. While for a 5nm Cu layer the T is about 80%, for a 30nm film it is only 20%. Reflectance in the IR region is strongly influenced by the film thickness as well. At a wavelength of 1500nm it varies from nearly zero with a 30nm metal layer to approximately 80% for a 5nm one. The R of thinner films is below 20%. Similarly, WO_3/Cu/WO_3 structure is remarkably influenced by film thickness. The result comprises a good combination of a high T in the visible range and a high, medium or low T in the IR region, depending on the Cu layer thickness. In these samples, annealing effect at 500ºC in vacuum results in a slightly decrease in transmittance in visible region (≈ from 90% to 70%) and a great decrement of transmittance in the IR region (≈ from 90% to 30%) together with a small change in IR region reflectance which is maintained below 20%. By comparison, annealing in air results in the increase of IR transmittance, which is not desired and may be related to the metal oxidation during the procedure.

Contrarily to Ag and Cu, aluminium shows a poor control over T and R under the variation of film thickness, presenting a highly reflective (≈90%) behaviour along with low transmittance (below 25%) in the whole spectrum region. The integration of the Al films into a WO_3/Cu/WO_3 structure does not significantly improve the results. Furthermore, annealing both under air and vacuum conditions have an impact in the increment of T, turning the samples highly transmitives (> 60%) over the whole spectra regions, which is also not intended. Surprisingly, not annealed V_2O_5/Al(5nm)/V_2O_5 structure has shown reasonable transmittance in the visible range (≈55%) with a reflectance below 20%. This indicates that V_2O_5 may be a more suitable dielectric to conjugate with Al layers for the present purposes. Further studies would have to be performed to prove this result.

Ni and Sn layers presented not to be suitable for this work purposes due to its fast oxidation. Although, by annealing the WO_3/Ni/WO_3 structures transmittance decreases, in the visible region, from 90% to 60% and from 90% to 30% in the IR while R is maintained low. This means that it is possible to control samples' absorptance in the IR region.

Throughout the work, some other studied structures samples namely glass/GZO/Ag/V_2O_5, V_2O_5/Ag/V_2O_5, V_2O_5/Al/V_2O_5 and WO_3/Al/WO_3 were found to be possible of having a controllable absorptance.

In general, the obtained optical properties of the studied thin metal layers (Al, Ag, Cu) as well as for the WO_3/metal/WO_3 structures have shown a good agreement with the simulated results despite of the non-coherency between the samples' refractive indexes and the refractive indexes used for simulation. The last ones were taken from literature (see section 2.1) and the utilized production techniques and/or conditions don't correspond to the ones utilized it this work. Given the well-known fact production method influences the morphology and porosity and hence the resultant optical parameters it is fair to assume that there may be a significant difference between the simulated materials and the produced ones. Furthermore, simulated and measured results for Sn and Ni films are significantly different and the reason underlying is the occurrence of fast oxidation of the produced, originating Sn and Ni oxides instead a pure metallic films as the ones simulated. Concerning the dielectric films WO_3 and V_2O_5, the simulated and experimental results are also in good agreement even though the refractive indexes have been obtained from literature having the same limitations, mentioned before. The overall optical performances of the D/M/D systems with different dielectrics didn't show to be significantly different except for some particular samples as is the case of V_2O_5/Al/V_2O_5 where the use of V_2O_5 showed a positive impact over the use of WO_3, as previously concluded.

Given that for an ideal energy-efficient glass window the transmittance in the visible region should be close to one (T≈1) and that it is known that an uncoated glass window has a transmittance of about 0.92, it can be concluded that, as some of the D/M/D systems optical properties showed to be easily controlled by changing layer thicknesses (allowing to obtain acceptable transmittances), it has a large potential for, under the right manipulation, being used for many different possible optical applications where high transmittances, in the visible region, and high reflectances or absorptances, in the NIR or/and IR regions, are required, such as energy-efficient glazing systems.

4.2 Future Work/Perspectives

The work presented in this dissertation is far from an exhaustive study of the optical properties of metal-dielectric multilayer structures. There are several immediately obvious directions in which this work could be expanded, ranging from further fundamental studies of the metal layer properties through further optimization and application of the same structures.

A list of directions for future work includes the proper development or understanding of a more suitable simulation method, involving either the development of a more explored algorithm concerning the present application; the use of another program found more reliable; or simply the use of the real refraction indexes (n) and absorption coefficients (k) that characterize the produced materials. Different references, in literature, use different simulation approaches. It could be interesting to reproduce some of them, applied to the present work.

An obvious improvement point that outcomes from the previous idea relates to finding a suitable approach to accurately determine the optical constants of the produced materials in order to be able to use their real n, and k for simulation purposes and also better predict the material behaviour.

The lack of information about the structural and morphological characteristics of the produced materials didn't allow a better prediction and understanding of some of the final results. A more exhaustive study over this properties would have been of good use to more accurately relate the optical properties results with the composition, morphology and structure of the materials and consequently with the utilized deposition method and conditions. The performance of further microscopies (SEM), spectroscopies (EDS) and/or x-Ray diffraction (XRD) analysis would have interesting.

Also, it is difficult to properly evaluate the obtained results in terms of optical transmittance and reflectance regarding the final objective and purpose. In order to overcome this, a figure of merit should be defined and applied to the results providing a bigger sensibility for the results and consequently a more accurate final evaluation. A simple and easily applied suggestion would be the following:

$$FM = \frac{\int T_{vis}}{\int T_{IR}}$$

It considers hypothetical transmittance results (as an example) but it can equally be applied for reflectance results, and it can give an idea over the quantity of light that is being transmitted (or reflected) in the visible light range in comparison with the infrared range. Furthermore, an interesting following approach could be to plot the different obtained figures of merit as a function of the different thicknesses, for each metallic layer.

In order to fully understand the manipulation possibilities of the materials' optical properties and trying to further optimize D/M/D systems performance some additional studies can be made. First, it would be profitable to study different metal thicknesses either than the ones that have been tested as well as repeat them to understand if results were reproducible. Additionally to vary metal thicknesses, one could also try to test D/M/D with different dielectric thicknesses or different D/M/D thickness ratios, for example, instead of testing a 30nm/ 5nm/ 30 nm system, as it's been done in this work, 30nm/5nm/15nm systems should be tried. Another parameter that would be interesting analysing its variation effect on the structures performance would be the incident angle. Samples optical properties T and R could be tested for different incident angles.

Last but not least, the measurement of some electrical characteristics of the layers and multilayers such as electrical permittivity and possible integration of the produced structures into devices prototypes and subsequent test of the same devices (such as photo sensibility tests) could be performed.

Finally, in a future work, different variations of the present multilayer structures could be tested, for example D/M/D/M structures.

5 BIBLIOGRAPHY

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6 ANNEXS

6.1 Annex 1

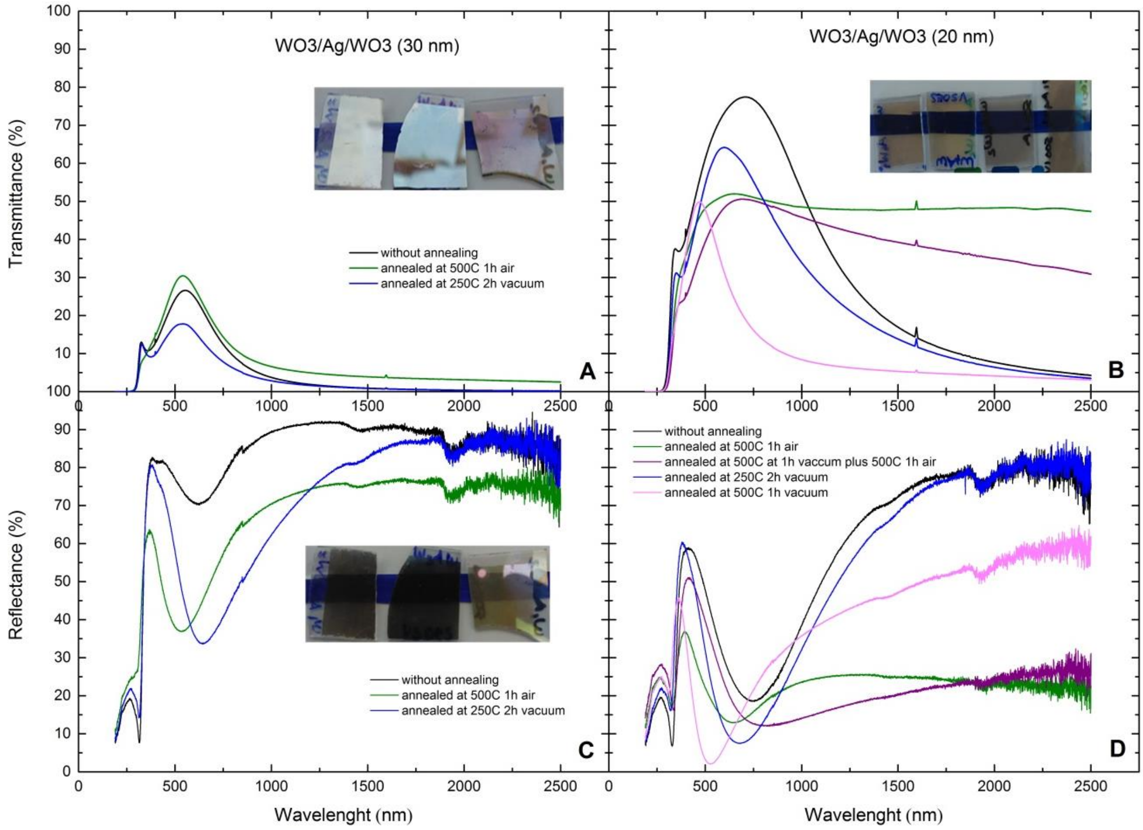


Figure 25 Annealing effect on Transmittance (left) and Reflectance (right) of silver thin films sandwiched between two WO_3 layers on glass for different film's thicknesses.

6.2 Annex 2

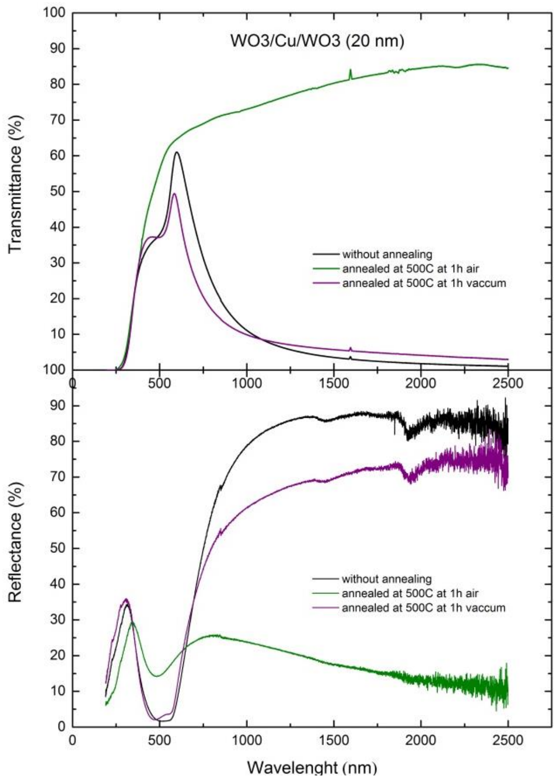


Figure 26 Annealing effect on Transmittance (left) and Reflectance (right) of cooper thin films sandwiched between two WO_3 layers on glass for a 20nm film thickness

6.3 Annex 3

6.3.1 Nickel Layers

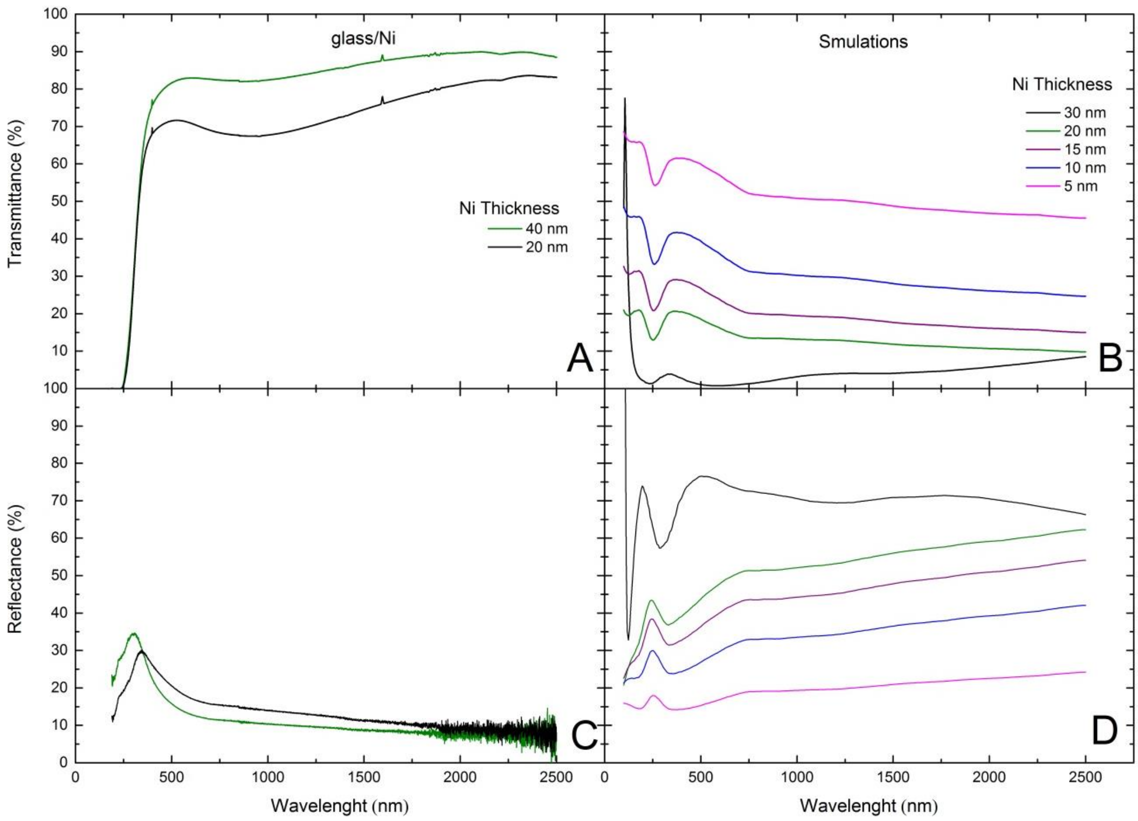


Figure 27 Transmittance (left) and Reflectance (right) of nickel thin films on glass for different film's thicknesses.

6.3.2 WO3/Ni/WO3 multi-layers

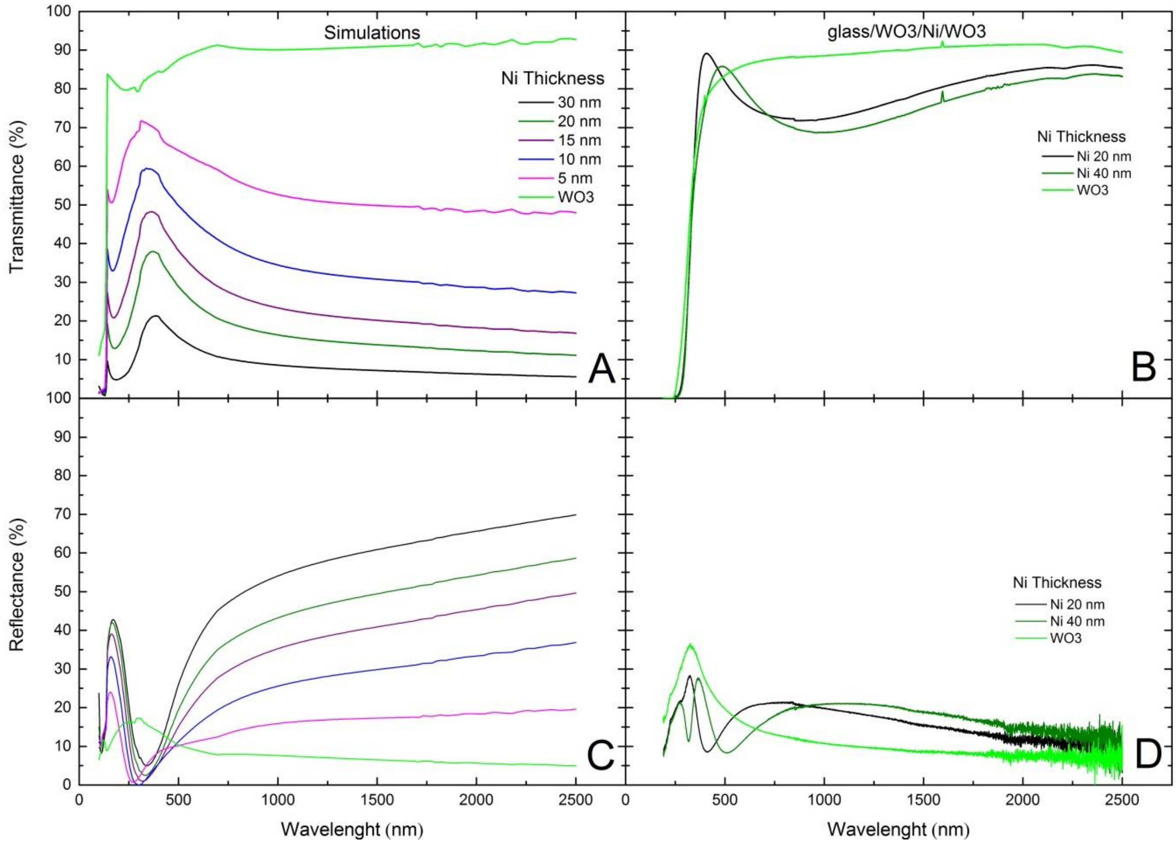


Figure 28 Transmittance (A and B) and Reflectance (C and D) of nickel thin films sandwiched between two WO_3 layers on glass for different film's thicknesses.

6.3.3 Tin Layers

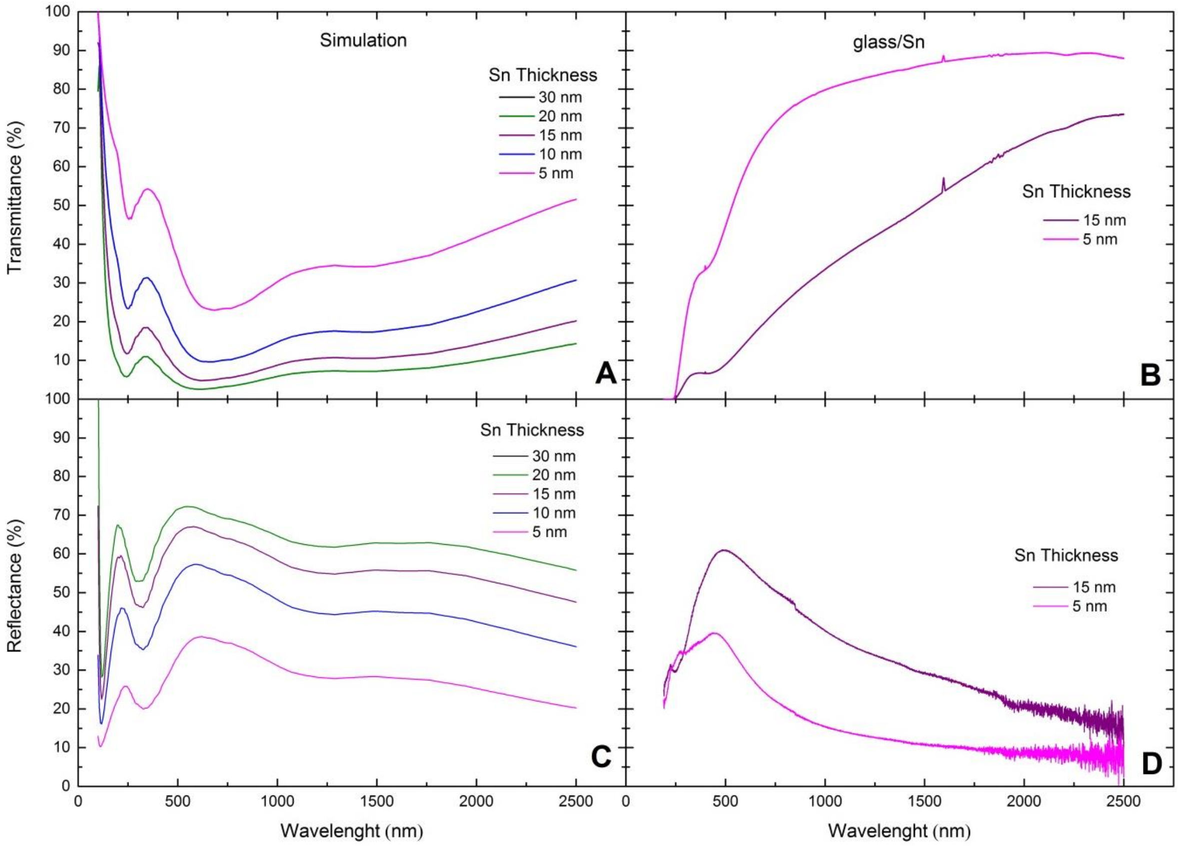


Figure 29 Transmittance (A and B) and Reflectance (C and D) of tin thin films on glass for different film's thicknesses. Experimental results on the left and simulated on the right.

6.3.4 WO3/Sn/WO3 multi-layers

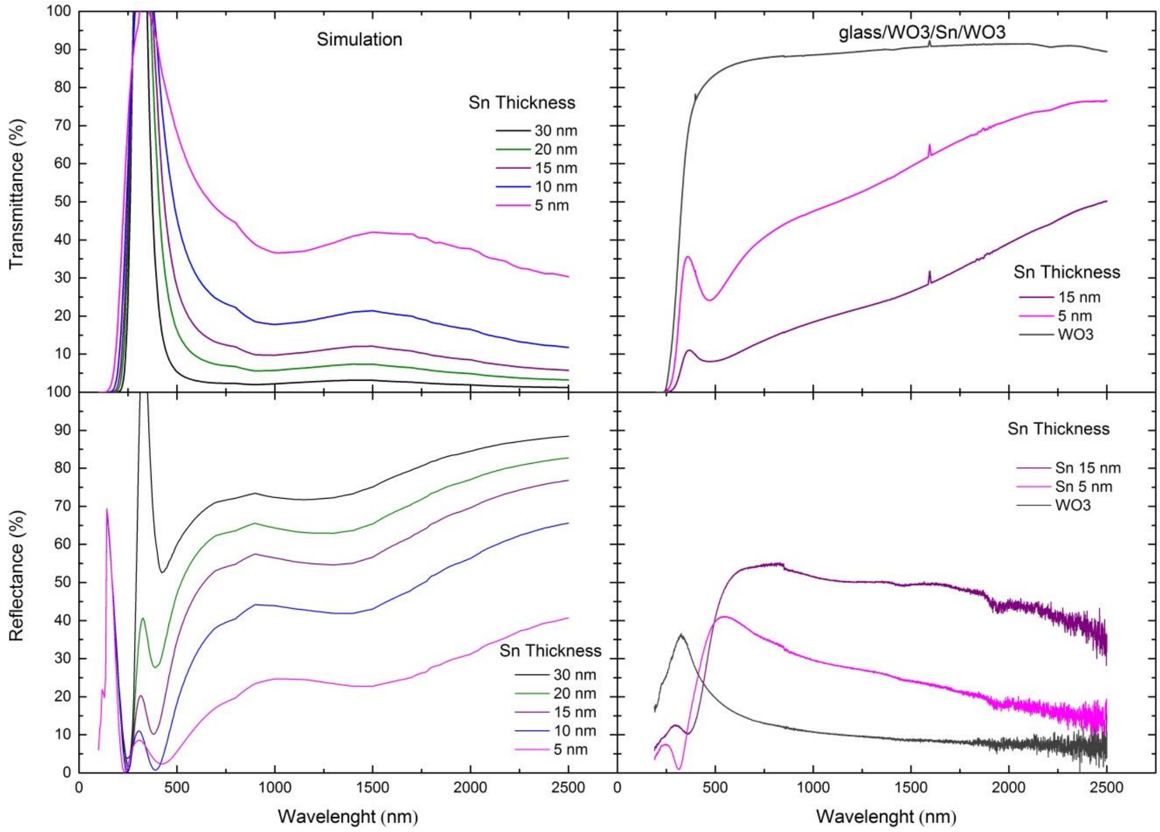
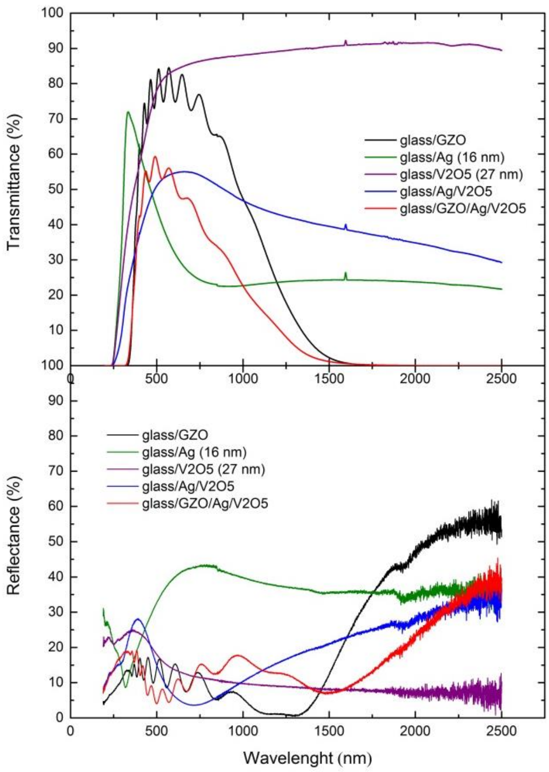
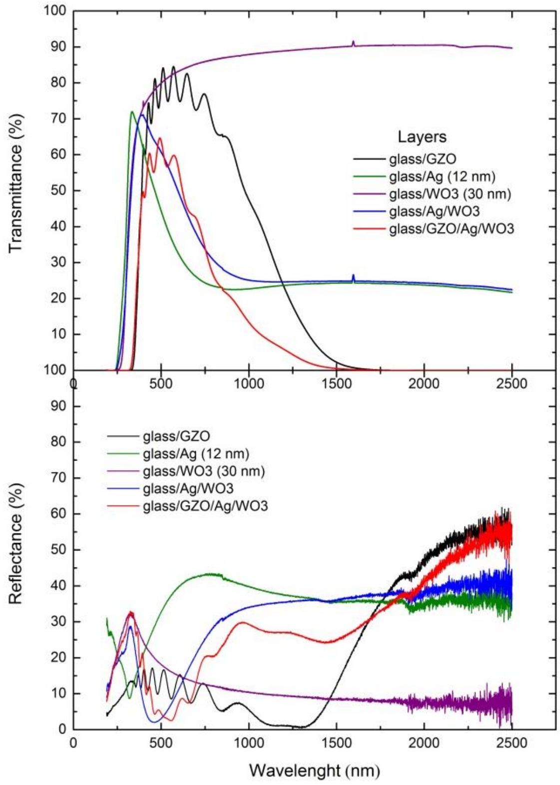


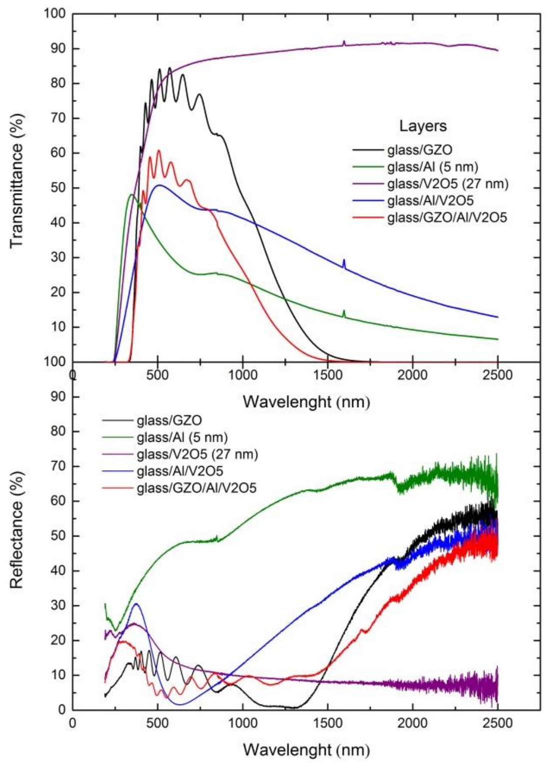
Figure 30 Transmittance and Reflectance of tin thin films sandwiched between two WO_3 layers on glass for different film's thicknesses.

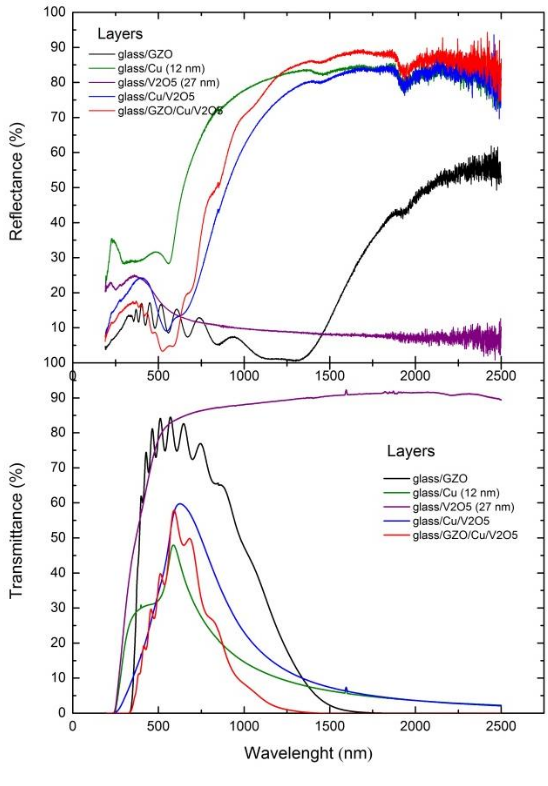
Figure 17 represents WO_3/Sn/WO_3 multilayer's transmittance and reflectance variation with the tin layer thickness.

6.4 Annex 4


Transmittance (%)
glass/GZO
glass/Ag (16 nm)
glass/V2O5 (27 nm)
glass/Ag/V2O5
glass/GZO/Ag/V2O5
Reflectance (%)
Wavelenght (nm)


Transmittance (%)
Layers
glass/GZO
glass/Ag (12 nm)
glass/WO3 (30 nm)
glass/Ag/WO3
glass/GZO/Ag/WO3
Reflectance (%)
Wavelenght (nm)


Transmittance (%)
Layers
glass/GZO
glass/Al (5 nm)
glass/V2O5 (27 nm)
glass/Al/V2O5
glass/GZO/Al/V2O5
Wavelenght (nm)
Reflectance (%)
Wavelenght (nm)


Layers
glass/GZO
glass/Cu (12 nm)
glass/V2O5 (27 nm)
glass/Cu/V2O5
glass/GZO/Cu/V2O5
Reflectance (%)
Transmittance (%)
Wavelenght (nm)

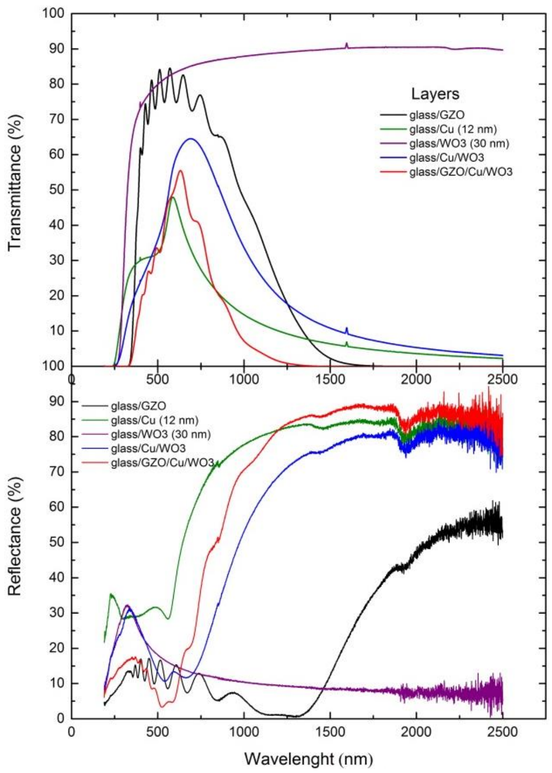


Figure 31 Different layers influence on Optical T and R sample properties