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Surface and Optical Properties of Zinc Oxide Doped With Fluor Synthesized By Magnetron Sputtering: Applications in Transparent Conductive Oxides (TCO)

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Abstract: Transparent conductive oxides, commonly known under « TCO » are widely used in many modern applications (Flat screens, Windows antifreeze, Solar cells…), this is essentially due to the good compromise between transparency in visible light and good electrical conductivity. This kind of oxides includes many materials like: In_2O_3, SnO_2, Cd_2SnO_4, $CdSnO_2$. Non-toxicity and abundance in the Land of zinc make it a best candidate for study, when oxygen is added as a reactive gas in the plasma and fluor as a doping agent, the zinc oxide is more stable in this kind of plasma compared to other examples. Thin films of zinc oxide are synthesized by the magnetron sputtering; this technique deposit thin layers of metal, semiconductor or dielectric. It is based on the interaction of plasma with the electric field E and magnetic field B, in the magnetron cathode, E and B are perpendicular. A complete study is done, beginning with the deposition of thin layers of zinc oxide doped with fluor and the analysis by X-ray photoelectron spectroscopy (XPS) which allows us to know the concentration of chemical elements present on the surface layers, and terminated by the Fourier Transformer Infrared (FTIR) Spectroscopy which gives us the optical properties [1], the results were interesting to reach our aim: transparent conductive oxide of zinc, but some issues concerning the electric conductivity have been reported and solutions suggested.

Keywords: TCO, Magnetron Sputtering, Thin Films, X-ray photoelectron spectroscopy, FTIR.

1 Introduction

The discovery of TCO back to the early twentieth century, when Bädeker [2] found that thin films of cadmium oxide (CdO) placed inside a room glow discharge were both conductive and transparent. This initial observation has given rise to a new research topic that remains after a century a hot topic. Many materials TCO appeared then include in particular: In_2O_3, SnO_2, Cd_2SnO_4, $CdSnO_2$, In_2O_3: Sn (ITO), ZnO: F, SnO_2: Sb, SnO_2: Cd, SnO_2: F, ZnO: Al, $CdInO_x$, In_2O_3:F…etc. The production of such materials, with a good compromise between transparency in visible light and good electrical conductivity, is an important industrial issue. However, there is a family of oxides that, in addition to being transparent, can become conductors (n-type) if they have an excess of electrons in their network. This excess of electrons can be created by structural defects inducing an imbalance in the stoichiometry of the oxide, or by appropriate doping. These kinds of oxides are called “transparent conductive oxides (TCO)”. They have a higher gap and present degenerate semiconductors, in other meaning, their Fermi level is close to the conduction band (CB), and even within the band in the case of heavily doped TCO. This means that BC is already well filled with electrons at room temperature, making the TCO conductor. In addition, the high gap of TCO (~ 3-4 eV) prevents them to absorb photons with energies below this gap, and thus makes them transparent to visible light [3].

These TCO materials are widely used because many applications need that combination of optical transparency with electrical conductivity. Some of these applications are listed below:

- Flat screens
- Windows antifreeze
- Heat-reflecting windows (buildings, ovens, ...)
- Electrochromic mirrors and windows

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- Screens Touch Control
- Protection electromagnetic
- Dissipation of electrostatic charges
- Solar cells: as before contact through which light must pass to enter the solar cell…

For each of these applications, a special TCO is chosen, depending on manufacturing requirements and other properties (stability against certain items...) required by the application [4]. Many reports concerning the research on TCO are regularly published since 1950 [5,6,7,8,9,10,11]. These reports relate the progress of works on TCO, with the conductivity values, preparation techniques developed, the new synthesized TCO...

The synthesis of a TCO can be summarized in general as a compromise between transparency and conductivity of the TCO layer. Therefore, tests of quantitative assessment of the quality of TCO have been proposed in the form of "figures of merit" [12], an example is described by equation (1) [9]:

$$\sigma/\alpha = -\left(\frac{1}{R_{sq}\ln(T+R)}\right) \quad (1)$$

$\sigma\left[\Omega^{-1}cm^{-1}\right]$: Conductivity

$\alpha\left[cm^{-1}\right]$: Absorption coefficient

$R_{sq}\left[\Omega_{sq}\right]$: Resistance square

$T[\%]$: Total Transmission

$R[\%]$: Total reflection

Thus, if the absorption (α) of the TCO is too high, or if its conductivity (σ) is too low, this figure of merit will have a low value. This allows comparing several TCO.

Using equation (1), Gordon evaluated the merits of several figures of TCO [4,13]. The values he obtained are between 0 and 7. Some studies on the different figures of merit has concluded that a good TCO electrons with high mobility and low effective mass [8]. The quality factor Q of a TCO thin film can be defined as the ratio of electrical conductivity σ / optical absorbance in the visible A.

The table gives some quality factors for TCO obtained by CVD and cited in the literature [13]. We note that zinc oxide doped with fluor (ZnO: F) and Cd2SnO4 have the best quality factors.

Table 1: Quality factors σ / A for some TCO [13].

Material	Resistance square (Ω/□)	Absorbance in the visible : *A*	Quality factor Q (Ω^{-1})
ZnO:F	5	0.03	7
Cd_2SnO_4	7.2	0.2	7
ZnO:Al	3.8	0.05	5
In_2O_3:Sn	6	0.04	4
SnO_2:F	8	0.04	3
ZnO:Ga	3	0.12	3
ZnO:B	8	0.06	2
SnO_2:Sb	20	0.12	0.4
ZnO:In	20	0.2	0.2

The diversity of TCO and their applications corresponds to the fact that the criteria for choosing a TCO does not depend only on the quality factor, Other parameters such as thermal stability, chemical and mechanical, or toxicity, the low cost of preparation, implementation constraints, and also the work function (fundamental to respect the injection of carriers) play a main role in the choice of TCO. ZnO has a hexagonal crystal structure of compact type. Its density is 5.72 gcm^{-3}, which corresponds to a molecular density of 4.21x1022 molecules per cm^3. The stoichiometric ZnO is an intrinsic semiconductor with a minimum gap of 3.1 eV. But in general, we get ZnO with n conductivity, by using the usual techniques of manufacture. The n-type conductivity is produced by an excess of zinc in the ZnO layers. For more improvement of the conductivity of the ZnO layers, it is possible to dope these layers.

Doping mechanisms are either substitutional or interstitial. The type of dopant used may belong to groups III and IV of the Mendeleïev table (B, Al, Ga, In, Ge,). To do this, the dopant atoms will, in the case of substitutional doping, replace the zinc atoms of the atomic lattice of ZnO [14,15]. Two electrons of the external orbital will be used for the ionic bond with the oxygen atoms, and the rest will be transferred into the conduction band. But you can also use dopant from the group VII of the periodic table of elements, such as fluor. In this case, the dopant atoms will replace the oxygen atoms of the atomic lattice of ZnO [16].

Among the many methods of surface treatment, the synthesis of thin films by sputtering is widely used for the past several decades. This technique involves depositing a thin film with a thickness between a few manometers and several micrometers on the surface. So how it works? By applying an electrical potential difference between two electrodes immersed in a gas at low pressure (of the order of a few millitorr), a plasma is created.

Cations from the plasma bombard the cathode on which a metallic target is generally placed. As consequence, neutral atoms on the surface of the target are ejected into the plasma. The metallic vapor is condensing on the substrate and producing a thin film, by analogy to water vapor film formed on the surface of a mirror (Figure 1). The chemical nature of the films is not limited to pure metals. For example, the addition of oxygen or nitrogen to argon paves the way for the synthesis of oxidized or nitride compounds.

For this work, we chose to study the magnetron sputtering of zinc oxide doped with fluor in order to have a transparent layer in the visible and also conductive.

This process is based on the application of an electrical discharge; the injection of a reactive gas (oxygen) controlled by an emission spectrometer via a piezo valve and also controls the flows of argon and fluor. The diagnosis is an essential step for better understanding of the mechanisms and conditions for the production of ionized metallic vapor. It allows to study the behaviour of the plasma depending on working conditions (pressure, electrical power delivered to the plasma,). Plasma is analyzed by emission spectroscopy method provides information on the behaviour of atomic populations in electrical discharge.

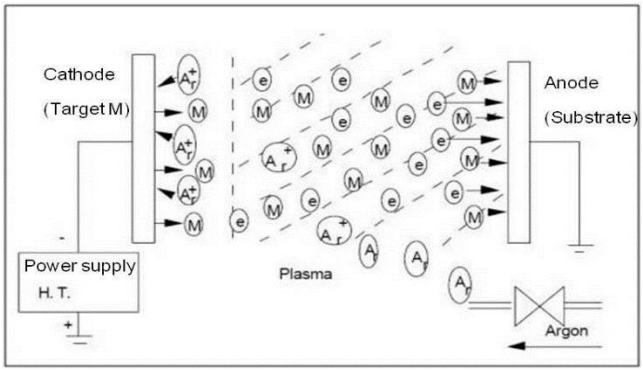

Fig. 1: Diagram of sputtering deposition [17].

2 Experimental Details

The chamber used for thin film deposition by magnetron sputtering is a stainless steel cylinder. The walls of the enclosure are grounded and present the anode of the system.

To minimize pollution in both: plasma and films synthesized, the gases inside the chamber is pumped continuously by a turbomolecular pump PFEIFFER VACUUM (pumping speed 440 l/s). The second pump stage is provided by a rotary vane pump (vacuum to 10^{-1} Torr). The system achieves an ultimate pressure of 10^{-6} Torr. The deposition chamber is connected by various orifices for pressure control systems. MKS 627A Baratron gauge measure the pressure in the discharge. The pressure range explored extends generally from a few millitorr to a few tens of millitorr. Lower pressures are measured by an ion gauge Alcatel 74009. The pressure reading is done on a controller PFEIFFER VACUUM.

The controller controls the opening of the butterfly valve MKS 253A located between the turbo pump and the enclosure. The pressure is maintained at the value recorded by the valve that regulates the pumping speed depending on its degree of openness. The introduction of discharge gas is performed using three flowmeters (Brooks Mass Area Fc and DC-7700). A controller can set the percentage opening of each flowmeter. It is necessary to calibrate the flowmeter depending on the gas used. The flow rates are given in standard cubic centimetre per minute (sccm). One is used to regulate the flow of argon, the other to regulate the flow of reactive gas (nitrogen or possibly oxygen). In the case of reactive discharge, the gas is mixed before being introduced into the chamber. The reactor is schematically shown in Figure 2

The surface chemistry of the allylamine and cyclopropylamine PPF has been investigated by X-ray photoelectron spectroscopy (XPS). In XPS, we are concerned with the emission of core-level electrons from the atoms of the sample being examined when irradiated with photons in the X-ray energy range. The photoelectrons are separated in turn according to their kinetic energy and counted. Through the kinetic energy analysis, one can come across the energy levels from which the photoelectrons originate and hence, determine the elemental composition of the sample.

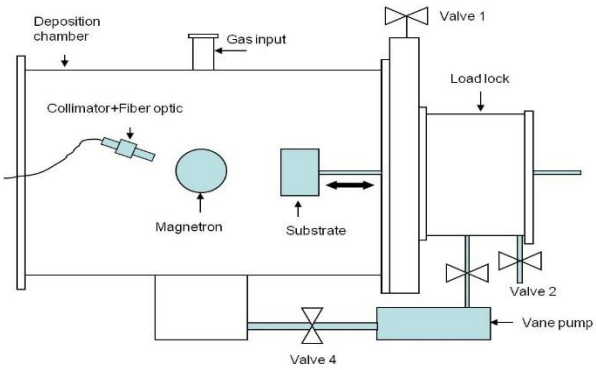

Fig. 2: Deposition chamber.

3 Results and Discussion

Using the mechanical profilometer (Dektak), we managed to measure the thickness of thin films deposited on glass.

Table 2: Table summarizes the discharge conditions.

Time(min)	Pressure (mTorr)	Discharge (mA)	Gas (sccm)		Thickness (Å)
			Ar	O_2	
60	10	125	17	03	759
90	10	125	17	03	1128

Under the same conditions (pressure, discharge and gas) we can calculate the deposition rate for films deposited.

Table 3: Deposition rate.

Time (min)	Thickness (Å)	Deposition rate (Å/min)
60	759	12.65
90	1128	12.53

According to the results, especially the deposition rate, we can say that layer obtained is not dense, the distance between the cathode and the substrate may be the cause, surely we will have a more dense layer if the distance is shorter than before.

With emission spectroscopy, the excitation mechanisms of neutral and ionized zinc have been studied and the apparent ionization rate of vapor is estimated. The term apparent is used because in this case, this estimate assumes that all the neutral zinc disappears, after amplification, is found as a zinc ion.

The optical emission spectrum was recorded with the spectrometer, about 5 cm above the cathode. The pressure is 10 mTorr in this case. We fix the opening of the butterfly valve to 46.7% to maintain stable pressure and current to 125 mA. From the spectrum, we notice that the line of ionized zinc is 308.6 nm and the former increases with pressure [18].

The samples studied were doped with fluor. Figure 4 show us the total elements contain the surface of thin films, the scanning of all the chemical components given as function to kinetic energy.

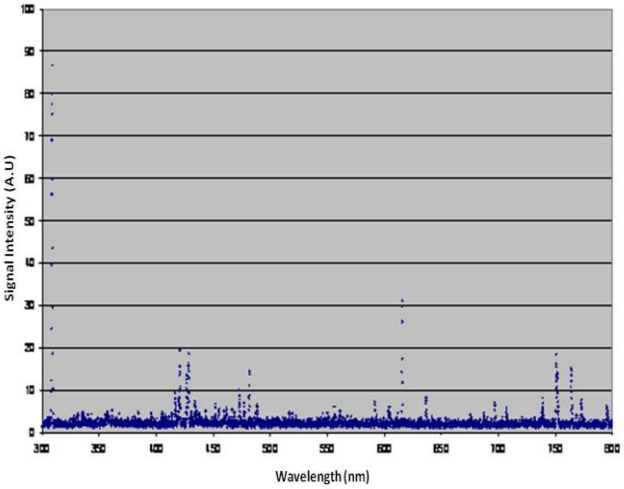

Fig. 3: Diagnostic by emission spectroscopy.

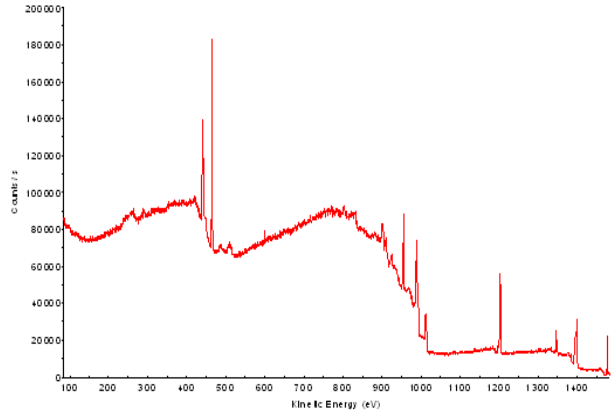

Fig. 4: The kinetic energy of ZnO:F on glass.

The following figure shows the presence of carbon in the layer.

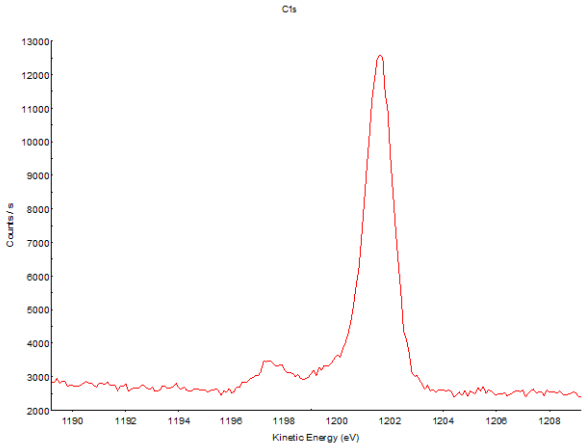

Fig. 5: Rate of carbon in ZnO:F / glass (kinetic energy).

The presence of oxygen is the purpose of the following Figure 6.

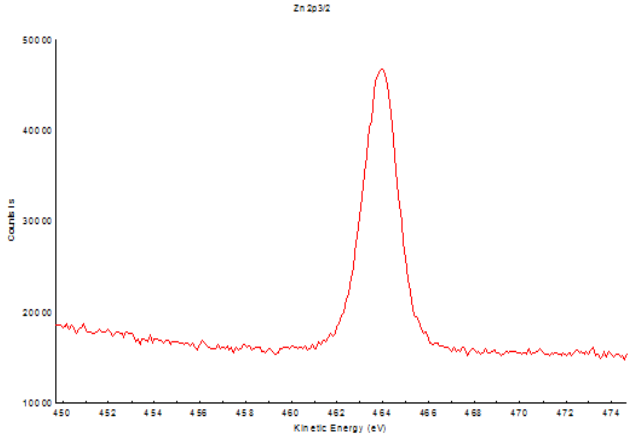

Fig. 6: Rate of oxygen in ZnO:F / glass (kinetic energy).

The rate of zinc in the ZnO layer doped with fluor on the glass is observed in Figure 7.

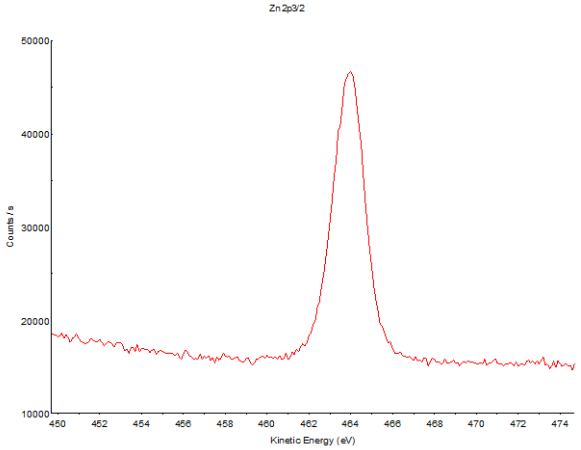

Fig. 7: Rate of zinc in ZnO:F / glass (kinetic energy).

The rate of fluor in the layer analyzed is the most important component in this part. This importance takes place because the film that has been analyzed is doped with fluor. Figure 8 show the absence of fluor in the layer, maybe it

happened due to do quick oxidation of the fluor.

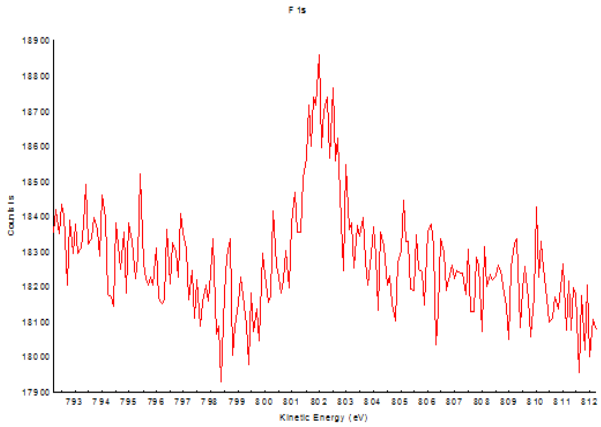

Fig. 8: Rate of fluor in ZnO:F / glass (kinetic energy).

In this study, we will do a comparison of two types of samples deposited on glass, the only difference between these samples is the amount of oxygen and argon injected into the deposition chamber.

Both samples were deposited under the following conditions:

Sample (a)	**Sample (b)**
Oxygen : 02 sccm	Oxygen : 03 sccm
Argon : 18 sccm	Argon : 17 sccm
Pressure : 10 mtorr	Pressure : 10 mtorr
Current : 125 mA	Current : 125 mA

In this part we will do an analysis by Spectroscopy Fourier Transform Infrared (FTIR) for the two samples (a) and (b). An analysis of each sample face in the visible and infrared is given below:

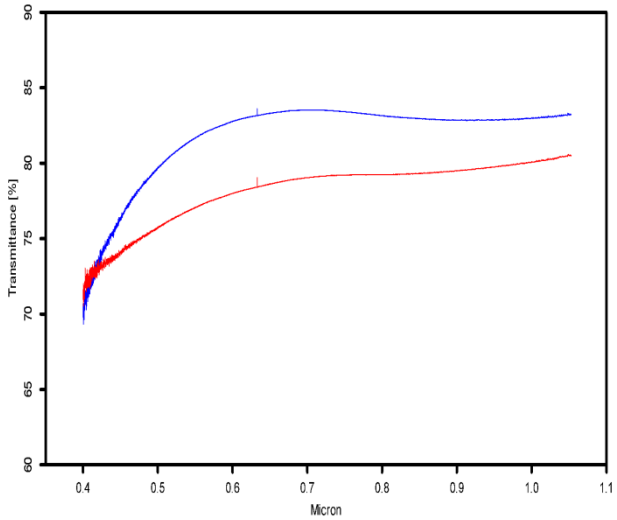

Fig. 9: Faces of the samples (a) and (b) in the visible.

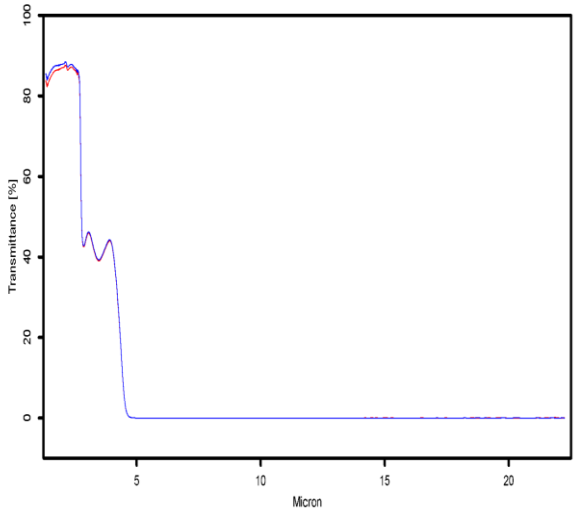

Fig. 10: Faces of the samples (a) and (b) in infrared.

___ (a) ___ (b)

The two samples (a) and (b) are identical in chemical composition, they differ only by the deposition conditions, which are the rate of argon and oxygen injected into the chamber.

For transmittance (Figures 9 and 10), the spectra obtained for the two samples have the same shape, even though the sample (a) has a transmittance greater than that the (b) one in the visible, after the limit of the visible-infrared (0.7 microns) we see that the two curves begin to be so close to cross at the end of near-infrared, and keep been superimposed in the rest of this range of study. From a quantitative point of view, the two samples transmits a lot in the visible with percentages reaching 80% and keep that until the limit of the near infrared (2.5 µm) where there is a sudden drop which reduce the transmittance by half in the mid-infrared [18].

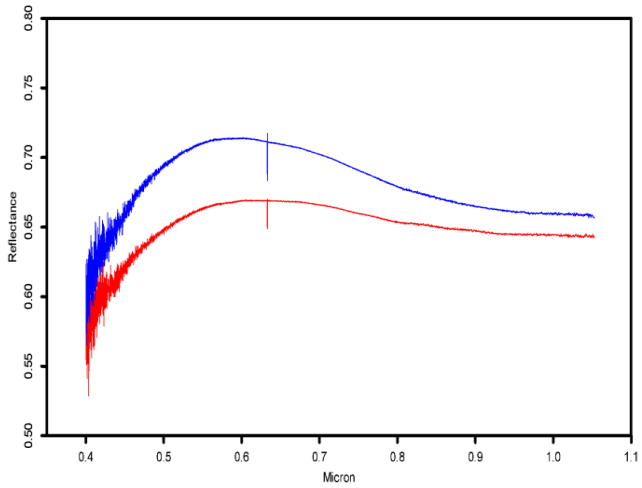

Fig. 11: Reflection of the two samples in the visible.

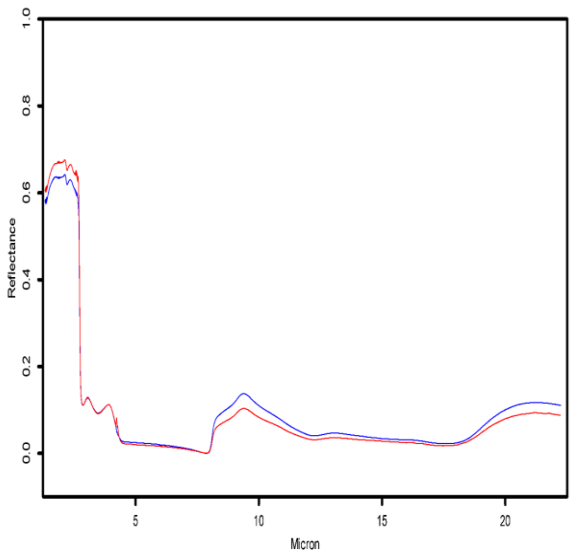

Fig. 12: Reflection of the two samples in the infrared.

___ (a) ___ (b)

Figures 11 and 12 have the same shape by analogy to what has just seen in the transmittance, and therefore it is clear that the spectra have an average reflectance in the visible range, and begin to be close when we cross the infrared interface, we note also a strong drop when we pass into the mid-infrared [20]. They present a constant curve with two small jumps in 10 µm and 20 µm.

4 Conclusions

In this work, we were interested in the development and characterization of thin films of zinc oxide doped with fluor, obtained by magnetron sputtering.

The chemical synthesis of the layers is analyzed by X-ray photoelectron spectroscopy (XPS). Based on this analysis, we can study the chemical compositions existing in the film.

The study of optical properties of films obtained by Fourier Transform Infrared (FTIR) spectroscopy, tells us about the conditions that must be followed during the deposition to have a transparent layer, but unfortunately we could not reach a conductive layer, this is due to several factors.

The conductivity of ZnO can be changed by adjusting:

- The ratio Zn/O (in other meaning the stoichiometry of the material). In this case, it's the excess zinc atoms that act as electron donor impurities.
- Temperature is a deposition parameter that influences significantly the intrinsic conductivity of the material.
- The use of another gas for doping, such as the addition of diborane in the gas phase, allows the doping with boron layers of ZnO.

This doping is done by interstitially way, meaning that the three electrons in the external orbital of the boron atoms are transferred into the conduction band, or substitutional, in this case, the boron atoms replace the zinc ones, so two electrons are used for the ionic bond with the oxygen atoms and the third is given to the conduction band.

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