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PhD THESIS SUMMARY

TCO-based multifunctional structures prepared by physical and chemical methods for optoelectronic applications

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Keywords: transparent conducting oxides, opto-electrical applications, sensors, ITO, TiO_2, ZnO.

1. Introduction

Transparent conducting oxides (TCOs) are a vast class of materials that are used for solar cells, displays, electrochromic devices, LEDs, transistors, etc. [1, 2]. As the name implies, TCO materials consist of semiconducting oxides with special electronic structures that allow the facile transport of electrical charge, while maintaining a high transmission value. A competitive TCO will exhibit a transmission in the visible range of 85 – 90% [3, 4], while resistivity may be as low as 10^{-4}–10^{-5} Ωcm [4, 5].Transmission depends on the refractive index, the extinction coefficient, the band gap and morphology, the chemical composition and the solid structure of the material. Resistivity depends on carrier concentration and mobility within the material. The carrier concentration is limited by the requirement of high transmission, as indicated by the Burnstein-Moss effect which states that absorption in VIS-NIR range increases with the increase in carrier concentration and thus transmission decreases [6, 7]. In theory, the carrier concentration in any material can reach 10^{22} cm^{-3} but this would affect its transmission.

While extensive research has already been conducted over the last decade in the area of multifunctional TCOs, three directions have remained unresolved: lowering the production cost of classic n-type TCOs (e.g. ITO), obtaining new n-type TCO thin films as an alternative to ITO, development of new p-type TCO thin films with stable conduction type.

a) Improving classic n-type TCOs to create a more appealing cost-efficiency balance

Among the classic TCO materials, the most widely used is indium tin oxide (ITO), due to its high transmission, high conductivity, n-type degenerate semiconductor behaviour and wide band gap energy (~3.6 eV). However, due to the scarcity of indium and the lack of primary ores, the price of this material is likely to increase in the future. Therefore it is necessary to identify ways of reducing costs for the manufactured products based on ITO, even from the laboratory stage. When discussing thin film deposition the following act as cost variables: the precursors, the substrates, the deposition method, the temperature regime used which affects the energy consumption, the additives (which can be expensive or toxic). For this thesis, only the *deposition method* and the *substrate* have been considered. ITO thin films deposited by the sol-gel method have been compared to those obtained by r.f. sputtering, studying their resistivity and transmission as well as the parameters that influence these characteristics. The sol-gel films were deposited on low-cost microscopic glass (covered with a sol-gel SiO_2 buffer layer), whereas the sputtered films were deposited on the more expensive fused silica substrate.

May et al. looked at the difference between direct current and mid frequency sputtered ITO films as this method seemed to be the most promising in obtaining low-resistivity films [8]. Kim et al. compared the films obtained through e-beam evaporation or radio frequency sputtering and concluded that the latter exhibit a larger average grain size which make them better for LED applications [9]. *No comparison between sputtered and sol-gel deposited ITO thin films was reported in literature, so the work included in this thesis is original and new: the complex characterization and the step-by-step investigation of how the structural and* *morphological differences between the chemically- and physically-deposited films directly affect their opto-electrical properties.*

b) Replacing classic n-type TCOs altogether with new, alternative materials

As a long-term option, ITO should be replaced with a new material with competitive opto-electrical properties, but with higher availability and lower cost. One option could be TiO_2 doped with transitional donor ions such as Nb or V, due to non-toxicity, easy doping and low resistivity (10^{-4} Ωcm) [10]. However, conflicting results about the electrical properties of TiO_2:Nb [10-12] and insufficient data regarding TiO_2:V [13-15] thin films justify the need for further investigation of these systems. In order to successfully obtain a high-working TCO material, it is necessary to understand the conduction mechanism of the film, to determine the carrier concentration and mobility and their influence factors in order to control and improve them. In this thesis, we have obtained Nb- and V-doped TiO_2 thin films using the sol-gel method, on glass and Si substrates. Using I-V and C-V measurements, the role of deep levels related to point defects has been identified and correlated to the structural, morphological, chemical and optical properties. The results can be linked to previous findings reported in literature and can lead to a better understanding of the barriers which may arise in obtaining a “transparent metal”. Since the films obtained in this thesis displayed inadequate electrical properties for TCO-type applications (although optical transparency was promising), an alternative application has been investigated, namely CO gas sensing. *As far as we know, V-doped TiO_2 films have never been reported as CO sensors making this investigation an original and novel point. The comparison to Nb-doped films adds interest and novelty. In this thesis, the influence of the film thickness of sol-gel deposited Nb or V-doped TiO_2 thin films on CO sensing abilities was studied and for the first time reported. A correlation was done between the thin film structure and morphology and the gas sensing properties of the doped TiO_2 thin films.*

c) Obtaining new oxide semiconductors with stable p-type conduction

At present, the development of semiconductors with stable p-type conduction is a requirement for multiple applications based on junctions, such as solar cells, lasers and light emitting diodes [5]. Zinc oxide is a candidate in this field especially due to the possibility of obtaining high-functioning homojunctions. However, the material poses some problems due to localized charges, the auto-compensating effect and low solubility of acceptor ions. In order to improve this last point, co-doping with a donor-acceptor pair has been attempted. Reports show that using co-doping increases the solubility of acceptor ions in the ZnO matrix, by creating strong acceptor-donor attractive interactions which overcome the repulsive interactions between acceptors [16, 17]. Moreover, due to the versatility of ZnO, by choosing the right deposition method, different morphologies can be obtained. The hydrothermal method can lead to nanorods, nanowires or nanotubes which can be used in opto-electrical applications. For this reason and also due to the promising results reported in co-doped systems, we have also attempted to obtain p-type conduction in ZnO thin films while doping with In and N. Most reports of p-ZnO obtained through In, N co-doping involve physical methods [17-20], but a great advantage could be drawn from employing a chemical route which implies low temperature budget and feasibility for large-scale production. *The novelty of the work included in this thesis consists in obtaining ZnO thin films on different substrates with stable p-type conduction which was achieved by In and N co-doping through a two step chemical method involving sol-gel and hydrothermal methods. The p-type conduction was confirmed through two different electrical analyses and its stability was maintained in excess of 6 months.*

The **main aim** of this thesis was the *development, characterization and optimization of the properties of TCO thin films obtained through physical or chemical methods for opto-electronic applications.* Three main objectives have been set, which proceed from the three research directions described above and refer to a different thin film oxide.

Objective 1: Performing a systematic comparative analysis of physically- and chemically-deposited ITO thin films linking their opto-electrical properties to structure and morphology.

Objective 2: Performing a complex electrical characterization of Nb and V-doped TiO_2 thin films with a view towards opto-electronic and gas sensing applications.

Objective 3: Development, characterization and optimization of ZnO thin films with stable p-type conduction.

The present thesis is structured 7 Chapters which follow and verify the fulfilment of the proposed objectives.

Chapter 1 contains a review of the recent progress in the field of multifunctional TCO materials. Three major trends regarding future research have been identified and investigated. A review regarding the most important aspects of n and p-type TCOs has been made, focusing on pure and doped ITO, TiO_2 and ZnO identifying the as yet unresolved issues in each case. Based on this critical analysis, the aim and objectives of the PhD programme have been formulated.

In **Chapter 2** the physical and chemical methods used have been succinctly described.

In **Chapter 3** the characterization methods used to analyze the structure, morphology, chemical composition and opto-electrical properties of the samples have been described.

In **Chapter 4** a systematic comparison of two series of ITO films prepared by r.f. sputtering and by sol-gel was presented, focusing on how different deposition parameters affect structure and morphology which in turn influence their opto-electrical properties. The substitution of the more expensive sputtered films with the sol-gel ones was considered.

In **Chapter 5** a detailed comparison between sol-gel deposited Nb- and V-doped TiO_2 films is put forward. The influence of structure, morphology and chemical composition on their opto-electrical and gas sensing properties is investigated and discussed.

In **Chapter 6** the In and N co-doped ZnO system obtained by a two-step chemical method is investigated from a structural, morphological, chemical, optical and electrical point of view. The conduction type of the films is studied as well as the factors responsible for it.

The synthesis of the most significant contributions brought by the present work and the results dissemination are presented in **Chapter 7**.

2. Experimental results and discussion

ITO thin films obtained through physical and chemical deposition methods

Two sets of ITO thin films have been obtained for this thesis: one was obtained through a physical method (r.f. sputtering) and one through a chemical method (the sol-gel technique). For each of these sets of samples, a series of deposition parameters have been varied in an effort to obtain the most promising optical and electrical properties. The r.f. sputtered ITO thin films were obtained using two different *atmospheres* (25% Ar – 75% N_2 or 100% N_2) and applying rapid thermal *annealing temperatures* of 400, 500 or 600^oC for 1 minute as post-deposition treatment. The sol-gel films were obtained by varying the *deposition number* between 1-10 layers, the *substrate type* (glass, SiO_2/glass or Si) and the *sol concentration* (0.1 M and 0.25 M). The aim of this research was to establish whether the chemical deposition method could lead to thin films with competitive opto-electrical properties with those obtained through the physical method, while also maintaining the advantages of low-cost, possibility for large area coverage, doping control and accessibility. Therefore the control parameters for the ITO films were their opto-electrical parameters, in particular transmission (T) and resistivity (ρ). The indirect influence of the deposition parameters on T and ρ, through morphology and structure, was investigated. In both cases, morphology had the largest influence on the electrical behaviour of the films, through roughness and porosity which imply scattering and recombination of charges.

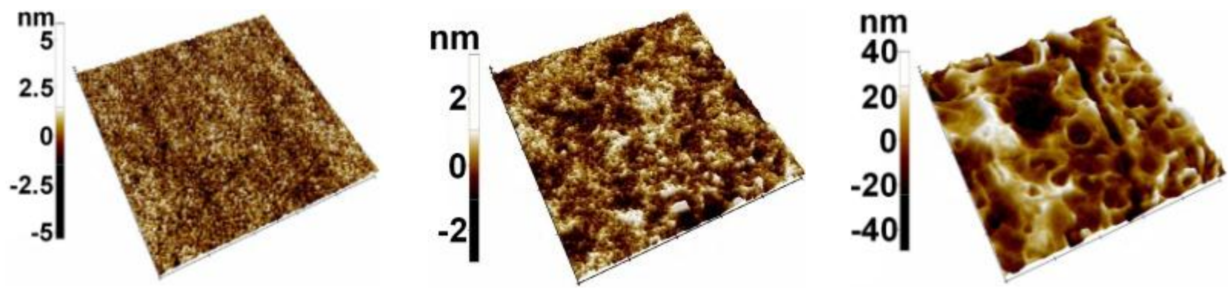


Fig. 1. 3D AFM images of the sputtered and sol-gel ITO films: 100% N_2, RTA 500^oC on fused silica (left), 0.1M – 10 layers on glass (middle) and 0.25 M – 5 layers on glass (right).

For the sputtered films, morphology is largely influenced by the RTA temperature and less so by the deposition atmosphere; therefore at RTA 600^oC, micro-cracks are formed which affect carrier mobility. For the sol-gel films, morphology is mostly affected by the solution concentration as 0.1 M leads to dense films with small roughness and porosity values comparable to those obtained in the sputtered films (Fig. 1).The substrate type is also an important parameter as it can influence roughness through its reactivity (SiO_2/glass) while the deposition number can be linked to film thickness.

The most promising sputtered sample was obtained in 75% N_2 and annealed at 500^oC, while for the sol-gel films, the optimal deposition parameters are 0.1 M sol concentration, 10 layers on SiO_2/glass. Both these samples exhibit comparable transmission (>80% - Fig. 2) and carrier concentration (10^{20}-10^{21} cm^{-3} – Fig. 3), confirming their degenerate semiconductor behaviour. Thus the sol-gel ITO films prove competitive to sputtered ones.

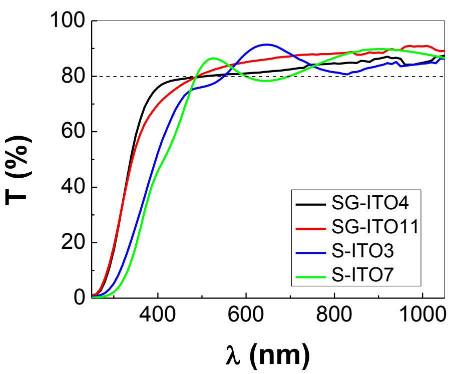


Fig. 2. Transmission of sputtered ITO films (75% and 100% N_2, RTA 500^{o}C – S-ITO 3 and 7) in comparison with sol-gel films (0.1M – 10 layers on Glass and SiO_2/glass – SG-ITO4 and 11)

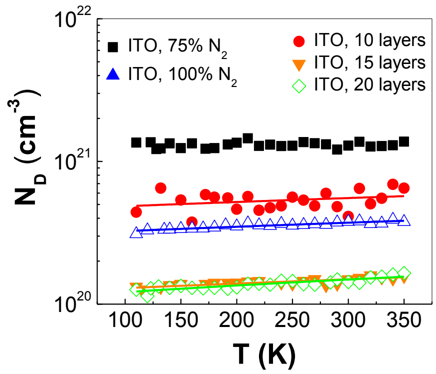


Fig.3. Carrier concentration variation with ΔT=110-350 K for sputtered (S-ITO3 and S-ITO7) in comparison with sol-gel films (0.1 M – 10, 15 and 20 layers on SiO_2/glass)

<u>Doped TiO_2 thin films obtained by the sol-gel method</u>

Multilayered Nb and V-doped TiO_2 thin films were obtained by the sol-gel method on glass and Si substrates. The doping percentage was fixed at 1.2 at %, while the parameters varied were the *doping species* (Nb or V) and the *number of layers* (1-10 depositions). Although their optical properties were promising (>80% transmission), the high resistivity made them insufficiently attractive as TCO materials (Table 1).

Table 1. Doping concentration, N_D, specific resistivity, ρ, and the effective electron mobility, μ_{ef}, of the 5 and 10-layered Nb- and V-doped TiO_2: films on Si substrate

Electrical parameters	**5TiO$_2$:Nb**	**10TiO$_2$:Nb**	**5TiO$_2$:V**	**10TiO$_2$:V**
ρ (Ωcm)	3.0x10^5	6.3x10^4	4.8 x10^4	5.2x10^5
μ_{ef} (cm^{2}V-^{1}s^{-1})	9.1x10^{-4}	1.7x10^{-3}	3.3x10^{-3}	4.6x10^{-4}
N_D (cm^{-3})	>2.2x10^{16}	>5.7x10^{16}	> 3.9x10^{16}	>2.6x10^{16}

This was due to the low mobility of e^- which are trapped at some deep level acceptor sites. Therefore our goal of replacing ITO thin films by doped TiO_2 ones could not be achieved.

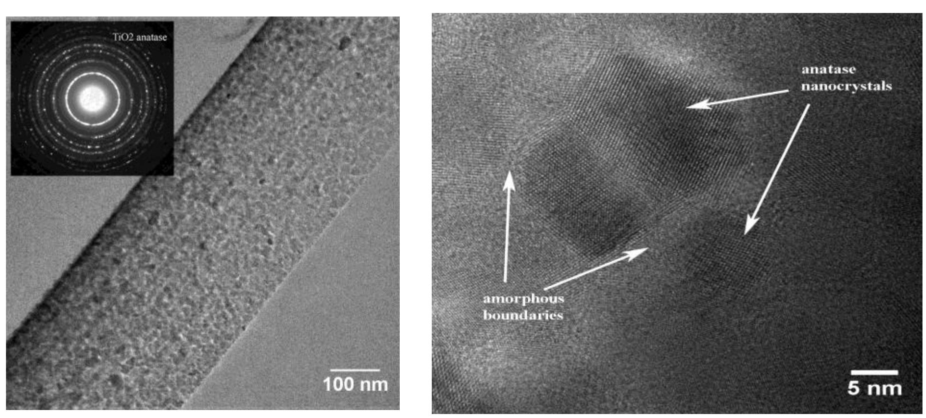


Fig. 4 XTEM image and the corresponding SAED pattern (left) and high resolution TEM image (right) for the $10TiO_2$:Nb film deposited on Si

Structural and morphological analyses showed that the films contain anatase grains with amorphous boundaries (Fig. 4). This could either be some amorphous TiO_2 phase that still remains non-crystallized or some amorphous Nb containing compound. Continuous, adherent multilayeres were obtained both on Si (Fig. 4) and glass substrates.

High porosity and lack of rutile phase crystallization identified through SEM and XRD&SAED analyses make the obtained films good candidates for gas sensing applications. We have studied the influence of the number of depositions and dopant type on the structure, morphology, opto-electrical properties and chemical composition in order to establish how each of these affect sensitivity to CO. The most promising results in terms of sensitivity and response and recovery were obtained for the V-doped thin films with 10 layers, at 400^{o}C (Fig. 5).

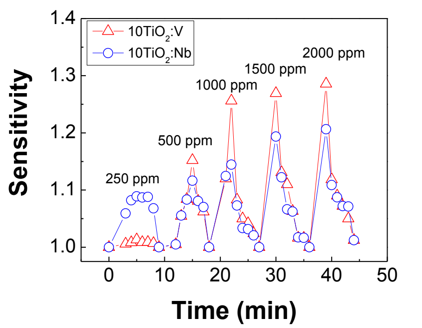


Fig. 5. Response and recovery of 10TiO$_2$:Nb and 10TiO$_2$:V at an operating temperature of 400^{o}C

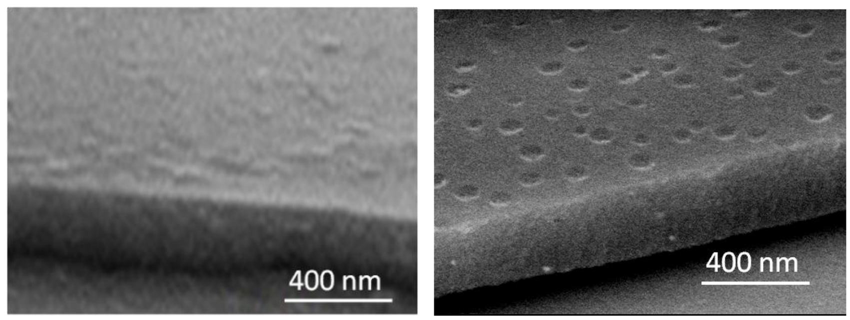


Fig. 6. SEM images of the 5TiO$_2$:Nb (left) and 5TiO$_2$:V (right) films deposited on glass

The following correlations have been established:

- CO sensing is strongly influenced by morphology through porosity which affects surface area and by electrical properties due to defect concentration and distribution in the film;
- Porosity and roughness are primarily dependent on the dopant type, with V-doped films exhibiting higher values of both (Fig. 6);
- Electrical properties can be tailored both by dopant type and the number of layers and are dependent on structure and morphology which can affect scattering and trapping of charged carriers;
- Structure is affected by the number of depositions and afferent thermal treatment cycles.

<u>ZnO thin films with p-type conduction obtained through a two-step chemical method</u>

The In, N co-doped ZnO films were deposited on insulating (glass and Al_2O_3) and conducting (Si (100)) substrates, by a chemical method consisting of two steps: first a ZnO sol-gel seed layer was deposited to increase adherence and promote the growth of the co-doped films; secondly, in the hydrothermal step, the substrates covered with the seed layer were introduced in the Teflon autoclave for 2 hours at 90^{o}C. The films thus obtained, were annealed at 100^{o}C-12 hours, 300^{o}C-1 hour or 500^{o}C-1 hour. Therefore the deposition parameters varied have been the *substrate type* and the *annealing conditions*. The purpose of this research was to establish the influence of each of these parameters on the structure, morphology and chemical composition which in turn may affect the opto-electrical properties of the films and especially their conduction type.

The films deposited on insulating substrates were tested by Hall Effect measurements, while the ones deposited on Si were integrated in Metal-Insulator-Semiconductor (MIS) structures and tested under I-V, C-V and admittance set-ups. The positive sign of the Hall coefficient as well as the shape of the I-V and C-V graphs (Figs. 7 and 8) indicate the p-type conduction of the films. We have repeated our tests 6 months later and again obtained p-type conduction thus confirming *stability* of the property of interest.

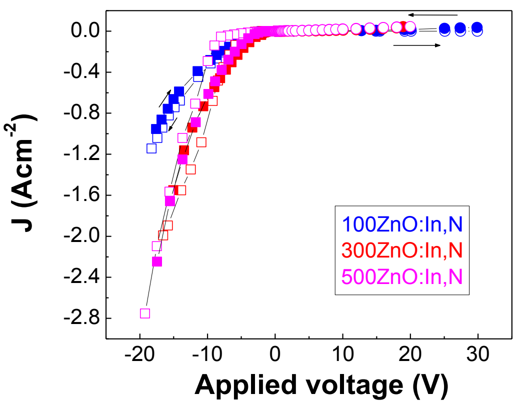


Fig. 7.Current density versus applied voltage of MIS structure with ZnO:In,N films annealed at different temperatures.

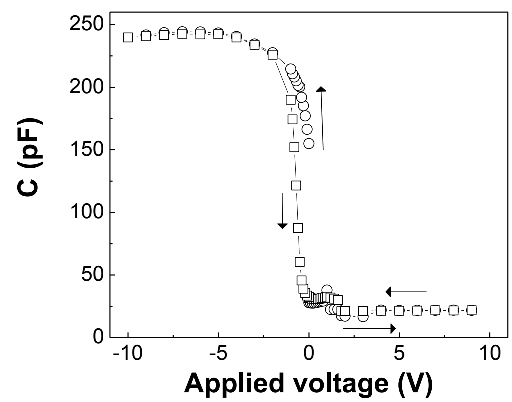
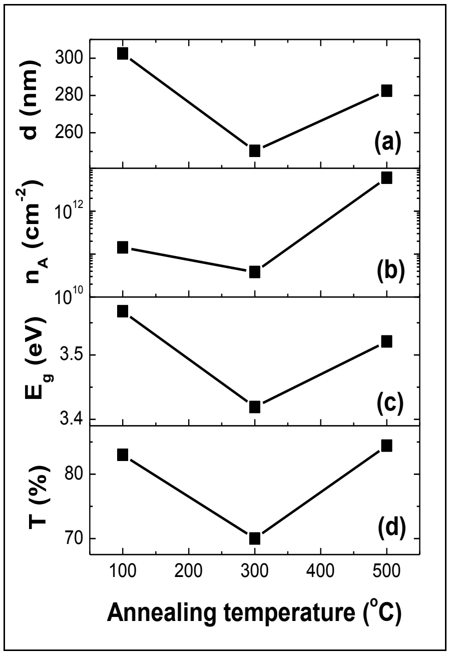


Fig. 8. Capacitance-voltage characteristics of MIS structure with co-doped ZnO films annealed at 500^{o}C.

Their opto-electrical properties were investigated and prove attractive, as transmission above 80% and carrier concentration of the order 10^{17} cm^{-3} could be obtained. The influence of substrate type (glass, alumina and Si) and annealing temperature (100^{o}C, 300^{o}C and 500^{o}C) on the structure, morphology and chemical composition of the films was investigated in order to obtain the optimum recipe for high-quality opto-electrical properties in ZnO:In,N films. The most attractive sample in the series was ZnO:In,N deposited on glass and annealed at 500^{o}C. The following correlations have been established:

- Opto-electrical properties (Fig. 9) are most influenced by chemical composition (by the nitrogen gradient in the depth of the film determined by XPS depth profiling - Fig. 10) followed by morphology (film uniformity, continuity) and structure (the level of stress in the matrix - Fig. 11);
- Chemical composition is most influenced by annealing temperature (the presence of a dip in elemental composition at annealing temperature of 300^{o}C - Fig. 10);
- The nanorod morphology of all films is most influenced by substrate type (non-uniform film on Al_2O_3 but homogenous films on glass and Si) and deposition method (Fig. 12);
- Structure is influenced by both annealing temperature (annealing at 500^{o}C promotes the highest level of crystallinity and reduces stress in the matrix - Fig. 11) and substrate type.



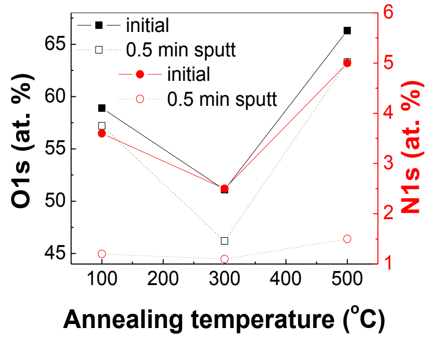


Fig. 8. The evolution with the annealing temperature of the relative elemental concentration for N1s, O1s.

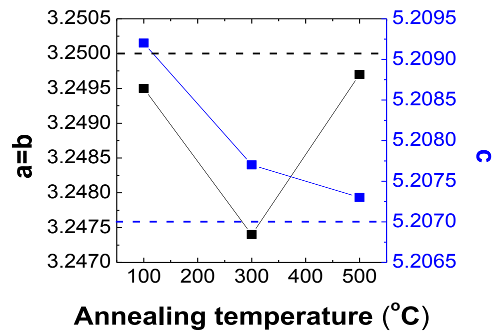


Fig. 9. Crystallite cell parameters variation with annealing temperature (dotted lines represent DB values of bulk ZnO).

Fig. 7. (a) Film thickness, d, (b) sheet carrier concentration, n_A, (c) band gap energy, E_g and (d) transmittance, T, values registered at λ=700 nm variation with annealing temperature.

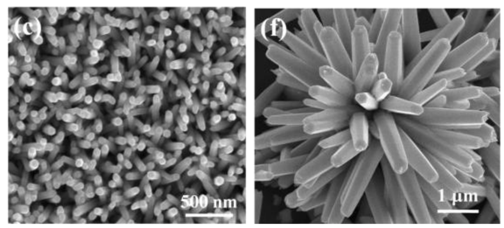


Fig. 10. SEM images of the 500ZnO:In,N film on Si with (left) and without a seed layer (right).

3. General conclusions

1. Transparent conducting oxides are a class of multifunctional materials that incorporate both high transmission and high conductivity.
2. The opto-electrical properties of TCO materials are dependent on their structure, morphology and chemical composition which, in turn, can be tailored through carefully considered deposition parameters.
3. There are three major research directions open at the moment: (a) lowering the production cost of classic n-type TCO materials; (b) development of alternative, low-cost, competitive n-type TCO materials (c) obtaining new TCO materials with stable p-type conduction.
4. Based on the critical analysis of the state of the art in TCO materials and their properties, the aim of the thesis was defined: development, characterization and optimization of the properties of TCO thin films obtained through physical or chemical methods for opto-electronic applications;
5. The main objectives have been fulfilled:

a. A systematic comparative analysis of physically and chemically deposited ITO thin films was performed in order to determine that:

- R.f. sputtered ITO films deposited on fused silica can be replaced by the more low-cost sol-gel ones obtained on SiO_2/glass;

- Comparable transmission (>80%) and carrier concentration (~10^{21} cm^{-3}) were obtained for both series of films;
- The most promising sputtered ITO films was obtained in 75% N_2 deposition atmosphere, after being subjected to 500^{o}C RTA treatment;
- The most promising sol-gel ITO films was obtained from 0.1 M solution, on SiO_2/glass, after 10 depositions;
- Opto-electrical properties of both series have been more strongly influenced by the morphology (roughness and porosity) than the structure (level of crystallinity);
- For the sputtered films, the RTA temperature affects the morphology as micro-cracks appear at 600^{o}C regardless of the deposition atmosphere employed;
- For the sol-gel films, the solution concentration and substrate type affect porosity, roughness, thickness, while the deposition number affects the level of crystallinity.

b. *A complex electrical characterization of Nb and V-doped TiO_2 thin films was achieved, considering opto-electrical and gas sensing applications:*

- High transmission (>80%) and high resistivity (10^4-10^5 Ωcm) were obtained for sol-gel Nb and V-doped TiO_2 films;
- None of the films could be used to replace ITO as an n-type TCO material due to poor electrical properties, but they are promising CO sensors due to their large surface area;
- The most promising sample for gas sensing applications is the 10-layered V-doped TiO_2;
- The dopant type affects both porosity and the electrical properties of the films;
- The number of layers can be used to tailor film thickness, E_g and increase crystallinity.

c. *A co-doped stable p-type ZnO system was developed, characterized and optimized:*

- p-type conduction was obtained in In and N co-doped ZnO films as confirmed by Hall Effect, I-V and C-V measurements. The conduction was stable up to 6 months;
- High transmission (>80%) and carrier concentration (~10^{17} cm^{-3}) were obtained;
- The most promising sample in the series was the film deposited on glass and annealed at 500^{o}C for 1 hour;
- The opto-electrical properties could be tailored through structure (stress in the matrix), morphology (uniformity/homogeneity) and chemical composition (nitrogen distribution);
- The annealing temperature can be used to tailor the structure and chemical composition of the films, while the substrate type can affect the film growth mechanism.

In conclusion, it can be seen that the PhD program has reached its aim through the fulfillment of all the objectives set.

4. Original contributions

Considering the results obtained in the frame of this doctoral thesis and comparing them with the state of art in the field of TCO materials, the original contributions can be identified as:

- Sol-gel ITO films with optimized tailored properties were obtained that can successfully compete with r.f. sputtered ones;

- A new material with optimized properties for CO sensing was obtained by doping TiO_2 with Vanadium;
- Stable p-type conduction was obtained in In and N co-doped ZnO thin films with nanorod morphology.

5. Future research directions

The present research allows the future development of the current TCO films to the final stage of opto-electronic applications. To this end, the following research directions are noted:

- Integration of optimized TCO materials (sol-gel deposited ITO and hydrothermally obtained ZnO:In,N) into hetero- and homojunctions for solar cells, lasers, etc; characterization and optimization of the junctions need to be considered;
- Further investigation of the detection limit, selectivity, stability and reproducibility of V-doped TiO_2 films as CO sensors;
- Integration of the V-doped TiO_2 films in CO sensors with standardized circuitry and substrates followed by their characterization and optimization;
- Testing of ITO or co-doped ZnO films as gas sensors; characterization and optimization can be considered if results prove promising;
- Improvement of the electrical properties of Nb and V-doped TiO_2 films through microwave treatment, annealing in reducing atmosphere or deposition in forming gas.

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