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PH.D. THESIS ABSTRACT

Study of thin films and multilayered structures with possible applications in transparent electronics and spintronics

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Introduction

Technologies that lead to the apparition of the domain named *Transparent electronics or invisible electronics* are those of obtaining transparent oxides and conductors (TCO) and transistors based on thin films (TFT) [1].

In the last years, the domain of thin films transparent and conductors based on different transparent metallic oxides has raised a special interest due their characteristic physical properties as large bandgap and, in consequence, a high optical transparency associated with lower resistivity ($\rho < 10^{-2}\,\Omega \cdot m$), properties for which the TCO thin films are suitable for applications in transparent electronics [2, 3].

In function of the nature of the impurities (donor or acceptor), TCO materials are classified in two categories, type n and type p [4]. Both types of TCO materials present interest for realization of active devices for transparent electronics [2]. It has been proved that the process of co-doping with acceptor and donor elements determines the increasing of element solubility in the oxide matrix, respectively, allows the control of the majority charge carriers (obtaining of n or p semiconductors) [5].

In the last time, the domain of spin transport or spintronics had an accentuated development, new materials of which properties have been improved in order to can be used in such applications were obtained [6, 7]. The use of conventional ferromagnetic and ferromagnetic system has been proven a good choice.

Recent studies has shown that thin films of $Fe_{3-x}Zn_xO_4$ (cu $0<x<0.9$) present spin polarizable electrical conductivity at 300K, confirming the potential of these materials for spintronics applications at the room temperature [8].

This thesis is focused on two important aspects: study of deposing conditions of undoped and doped oxide thin films in order to control their properties for applications in transparent electronics and spintronics and investigation of correlations between microstructure, electrical, optical and magnetic properties.

This thesis is focused on obtaining of TCO materials that presents both p and n conductivity for application in transparent electronics and respectively on obtaining of transparent magnetic semiconductor materials with applications in transparent electronics and spintronics, using different obtaining methods. The obtained thin films and multilayered structures were characterized from the point of view of structure, morphology and composition with modern study methods, respectively, were characterized from the point of view of optical, electrical and magnetic properties.

The thesis approaches an actual thematic and is structured on four chapters, preceded by an introduction and followed by conclusions.

CHAPTER 1. STATE OF THE ART IN THE DOMAIN OF THIN FILMS AND MULTILAYERED STRUCTURES FOR APPLICATIONS IN TRANSPARENT ELECTRONICS AND SPINTRONICS

In this chapter are presents the principally results, from the literature, connected to the oxide semiconductor materials with applications in transparent electronics and spintronics.

CHAPTER II. METHODS FOR PROCESSING AND CHARACTERIZATION OF THIN FILMS AND MULTILAYERED STRUCTURES

In this chapter, a description of deposing methods used in growing of oxide semiconductor thin films and multilayered structures with possible applications in transparent electronics and spintronics is made, respectively, the investigation methods used for characterization of obtained thin films and multilayered structures being presented.

CHAPTER III. OBTAINING AND STRUCTURAL CHARACTERIZATION OF SOME THIN FILMS AND MULTILAYERED STRUCTURES WITH APPLICATIONS IN TRANSPARENT ELECTRONICS AND SPINTRONICS

In this chapter are presented the experimental results connected to the obtaining and structural, morphological and compositional characterization of the thin films and multilayered structures, searching the way in which the structural properties are influenced by the deposition conditions, nature and temperature of the substrate, post deposing thermal treatment, nature and concentration of the doping element.

3.1. Structural analysis of thin films and multilayered structures in function of the temperature and nature of the substrate

In order to obtain ZnO thin films doped with Ga, GZO, RF cathodic spraying in magnetron regime (VUP-5M) has been chosen as deposition method.

The diffractograms corresponding to thin films of Ga:ZnO deposited on glass have emphasized the increase of crystallinity of thin films once with the increasing of substrate temperature [20]. It can be observed the decrease of the c parameter value with the increase of the temperature, respectively the increase of crystallites dimensions

The diffractograms obtained for the thin films deposited on glass and thermal treated emphasize an improvement of crystalline structure. It is observed a reduction of dislocation density due to the thermal treatment in N_2 + 5%H_2 atmosphere, respectively in N_2 and then in N_2 + 5%H_2 [18].

From the diffractograms obtained for the thin films of Ga:ZnO/SiO_2/Si and Ga:ZnO/p-Si, the correlation between the crystalline structure and the substrate temperature is sustained. For all substrate types, the dimensions of the crystallites increase with the increase of the substrate temperature. Comparing the values obtained for the substrate p-Si and SiO_2/Si with those obtained for the glass substrate, it can be observed that these favorite the increase of samples crystallinity and reduction of the stress in the substrate.

3.1.3. Investigations of surface roughness morphology of thin films and multilayered structures based on Ga:ZnO using AFM and SEM

The AFM studies have emphasized the increase of surface roughness, respectively the increase of average crystallites dimensions, once with the increase of substrate temperature [20].

3.1.4. XPS investigations of the composition of thin films and multilayered structures basez on Ga:ZnO

The XPS studied confirm the insertion by substitution of Ga^{3+} in the crystalline lattice of ZnO. The chemical composition of the surface has emphasized a content of 1,6 Ga at%, fact that reflects the chemical composition of the target.

In the case of multilayered structures, the XPS spectrums of Zn2p and Ga2p keep their aspects confirming the Zn^{2+} state in a oxygen deficient matrix, respectively of insertion by substitution of Ga^{3+} ions in crystalline lattice of ZnO.

3.2. Obtaining and structural characterization of thin films and multilayered structures p and n type in the system $In_{2-(x+y)}Sn_xZnyO_{3-\delta}$

Studies had emphasized the maintaining of the bixbyit type structure and the absence of other possible phases. A dependency of crystallites dimensions and parameter of the elementary cells by the content in Zn, the nature of the substrate on which the thin film has been deposited, respectively by the thermal treatment applied has been observed [19].

3.2.3. Investigations of surface morphology of thin films and multilayered structures based on $In_{2-(x+y)}Sn_xZn_yO_{3-\delta}$ using SEM method

SEM images have emphasized modification of layers morphology in function of composition and the methods of thermal treatment. EDX spectrum have emphasized the elements In, Zn and Sn and allow the determination of chemical formulas. From SEM images of multilayered structures can be observed that the ZITO layers are homogeneous, with crystallite without dimensional variations, the uniform character being kept once the increase of Zn content [19].

3.2.4. XPS investigations of the composition of thin films and multilayered structures based on ZITO

The registration of XPS spectrum on the elements emphasize a single bond energy for In, Sn and Zn, typically for oxide vicinity of them.

3.3. Obtaining and structural characterization of thin films in the system $Ni_{1-x}Zn_xFe_2O_4$

The diffractograms obtained by GAXRD for the thin films deposited on glass have emphasized a nanocrystalline structure, with preferentially orientation of crystallites with the plane (311). The influence of Zn content over the crystalline lattice is observed.

3.3.3. Investigations of surface morphology of thin films and multilayered structures of $Ni_{1-x}Zn_xFe_2O_4$ using SEM methods

The SEM imanges emphasize the fact that all thin films obtained are nanostructured. The elementally chemical composition determined by EDX spectrum indicates the fact that the elements have been entered into the film composition.

3.3.4. XPS investigations of $Ni_{1-x}Zn_xFe_2O_4$ thin films compositions

The XPS spectrum of Fe2p and Ni2p emphasize the clearly presence of Fe^{3+} and Fe^{2+} species, respectively Ni^{2+} and Ni^{3+}. The different content in elements is sustained also by the different intensity of the XPS peaks, respectively by the small displacing towards high values of the bond energy.

CHAPTER IV. STUDY OF OPTICAL AND ELECTRICAL PROPERTIES OF THIN FILMS AND MULTILAYERED STRUCTURES WITH POSSIBLE APPLICATIONS IN TRANSPARENT ELECTRONICS AND SPINTRONICS

In this chapter are presented original results about optical, electrical and magnetic properties of thin films and multilayered structures obtained during the Ph.D.stage, these results being correlated with the deposition conditions, respectively with structural, morphological and compositional properties. The optical properties of thin films and multilayered structures based on ZITO and GZO, respectively of thin films of ferrite are analyzed, the results being completed by the data obtained from absorption spectrum. The optical properties were correlated with the structure and morphology of thin films and multilayered structures following the way in which these are influenced by the substrate temperature, thermal treatments applied post-deposition, the nature and concentration of the dopant element, nature and characteristics of the substrate. Also, using absorption spectrum[9, 10, 14], a series of characteristic parameters has been determined.

4.1.1 Study of transparency of thin films and multilayered structures based on Ga:ZnO/glass untreated and treated

The effect of substrate temperature over ZnO:Ga thin films transmittance and of applied thermal treatment was followed. All the thin films presents transmittance higher than 80% [11,17]. The modification of atmosphere in which the thermal treatment is done, the duration of the thermal treatment influence the structure of studied thin films, this being observed also in the shape of the graphics that give the dependency of transmittance by the wavelength.

4.1.2. Study of transparency of thin films and multilayered structures in the system In_2O_3-SnO_2-ZnO

From the transmission spectrum it can be observed that the analyzed thin films and multilayered structures present a very good transmittance, over 70%, the thin films type p present lower transmittance than the n types. Applying thermal treatments at high temperature during 2h, determines modifications of the transmission spectrum aspects.

4.1.3. Study of transparency of thin films and multilayered structures in the system $Ni_{1-x}Zn_xFe_2O_4$

The effect of Zn content over transmittance of $Ni_{1-x}Zn_xFe_2O_4$.thin films has been followed. All the $Ni_{1-x}Zn_xFe_2O_4$ thin films have transmittance higher than 90% and lower reflectance in the visible domain.

4.2. Study of electrical properties of thin films and multilayered structures

The increase of electrical conductivity with the increase of support temperature [11] is observed both in the case of untreated thin films as well as in the case of treated ones. It can be observed that the thermal treated thin films in different controlled atmospheres present electrical conductivity better than the untreated films. This is due to the improvement of their crystalline structure. Significant differences can be observed for the thin films obtained in the same range of deposition but having different substrate. The values of electrical conductivity are influenced by the substrate temperature and the nature and characteristic of the substrate.

A series of models has been taken into consideration in order to explain the electrical conductivity of the thin films [12, 13] and of analyzed multilayered structures. On the basis of these models, a series of characteristic parameters was calculated, following the way in which the transport properties are influenced by the substrate temperature , the nature and characteristics of the substrate, the thermal treatments applied post-deposition, the nature and concentration of dopant element [13].

4.2.2. Study of electrical properties of thin films and multilayered structures in the system $In_{2-(x+y)}Sn_xZn_yO_{3-\delta}$

It can be observed that thin films, p type present electrical conductivity smaller than the one of n type, both being smaller that the thin films in which Zn=Sn.

The electrical conductivity of thin films deposited on ITO/glass is higher than the one of thin films deposited on glass, increasing in the same time the difference between the electrical conductivities if thin films n and p type. The measurements of Hall effect have emphasized concentrations of the charge carriers in the range of a $2x10^{22}$ cm^{-3} for n type thin films and $5x10^{21}$ cm^{-3} for p type. Significant differences have been observed also in the case of films with the same chemical composition, respective the same thermal treatment but having different substrates.

4.2.3. Study of electrical properties of thin films in the system $Ni_{1-x}Zn_xFe_2O_4$

In the case of $Ni_{1-x}Zn_xFe_2O_4$, thin films, the electrical conductivity measured at the room temperature, before the application of thermal treatment, increase with the increasing of Zn content [15].

The conduction mechanism in the Ni-Zn ferrite is due to the presence of Ni and Fe ions in octahedral positions, favoring the conduction mechanism $Ni^{2+}+Fe^{3+}\leftrightarrow Ni^{3+}+Fe^{2}$. These mechanisms depend by the Zn atoms content.

4.3. Study of magnetic properties of thin films of $Ni_xZn_{1-x}Fe_2O_4$

The study of magnetic properties emphasizes that once with the increasing of Zn content, the saturation magnetization increase , reaching the maximum value for x=0.6, after that starting to decrease. The increase of saturation magnetization once with the increase of Zn content might be attributed to no compensation of magnetic moments of Fe^{3+} and Ni^{2+} ions from the tetrahedral, respective octahedral positions. The increase of Zn content leads to diminishing of magnetic ions interactions from the tetrahedral and octahedral positions. The decrease of coercive field, respective of remnant magnetization is noticed once with the increase of Zn content. This decrease can be attributed to the entrance by substitution of Zn^{2+} ions in the spinel type structure of the Ni ferrite, in A positions [16].

These hypotheses are sustained by the RES studies effectuated in function of the angle made by the surface of the sample with the direction of the magnetic field (Fig. 4.45).

Comparing the results of RES with those of the magnetic measurements we can say that the samples with 0.6 Zn content have the best magnetic properties. The structural investigations have shown that in these samples, Ni^{3+} and Ni^{2+} are in almost the same proportion, fact that leads to the idea that these species enter in the spinel type structure so that the exchange between positions A and B shall be dominant.

Conclusions:

In my thesis are presented the principal original results obtained at the structural, morphological and compositional characterization of thin films and multilayers structures, respectively are presented the original results obtained at the analysis of the optical, electrical and magnetic properties in order to use them in different applications in transparent electronics and spintronics. Thus, in the frame of Ph.D.thesis, three types of systems have been studied, namely thin films and multilayered structures based on Ga:ZnO obtained by rf cathodic spraying; thin films and multilayered structures based on In_2O_3-SnO_2-ZnO obtained by thermal evaporation in vacuum, thin films of $Ni_{1-x}Zn_xFe_2O_4$ obtained by spin coating method.

- The influence of substrate temperature over the structural, optical and electrical properties of the analyzed thin films have been studied. It has been observed that the Zn films, doped with 2wt.% Ga_2O_3 obtained at 373 K and 473 K presents these properties better that those obtained for heated substrate.
- In the case of thin films deposited on Si/SiO_2 and Si-p, the XRD images sustain the correlation between the substrate temperature and their crystalline structure. It can be observed that the structural properties depend by the nature and the characteristics of the substrate on which the thin film is deposited and by temperature of the substrate.
- By optimization of deposition parameters, the obtaining of thin films of ZnO:Ga and ZITO with very good values of electrical resistance and optical transmittance in the visible domain has been succeeded, films that can be used at realization of transparent electrodes, transparent heaters, as channel layers in field effect transistors, with different applications as sensors, etc.
- XPS spectrum corresponding to thin films and multilayered structures of GZO emphasize the fact that these have and high content of flaws.
- It can be observed significant differences for the thin films obtained in the same deposition stage but having different substrate. Analyzing the electrical properties f the thin films obtained in the same stage of deposition but having different

substrate we reach to conclusion that the use of SiO_2/Si and p-Si support influences in positive way the structure, less stressed, leading to the increase of samples crystallinity, respective to the increasing of charge carrier mobility.

- From the study of electrical properties it can be observed that, after the application of thermal treatments, the electrical conductivity of thin films increases significantly.
- It has been observed that the thin films and multilayered structures based on $In_{2-(x+y)}Sn_xZn_yO_{3-\delta}$ with x>y presents n type conductivity meanwhile for x<y these present p type conductivity
- The compositional analysis from EDX spectrum, respective XPS studies have allowed the establishing of the chemical formulas corresponding to the thin films and multilayered structures obtained.
- All the obtained thin films and multilayered structures are conductive, a part presenting a metallic behavior un the domain of high temperature. Also, the values obtained for the electrical conductivity are influenced by the Zn content, the applied thermal treatment, the thickness of the layer , respectivelym the nature of the substrate.
- In the case of thin films of Ni ferrite doped with Zn, it has been observed a dependence of electrical conductivity by the chemical composition. In this case, the activation energy is associated with the variation of the charge carriers mobility and less by the increasing of charge carriers concentration, the conduction

mechanism being due to the jump of the electrons between divalent and trivalent ions.

- All the analyzed thin films presents magnetic properties. The results obtained with VSM method show that the sample with 0.6 Zn content presents high saturation magnetization compared with the other compositions.
- RES studies effectuated at the room temperature function on the orientation of sample in magnetic field confirm the results obtained by other methods, emphasizing the fact that the magnetic moments presents preferentially orientations, especially for the samples with high Zn content.
- All these results, obtained during these studies confirm the potential of the ferrites as magnetic semiconductor materials, semitransparent with magnetic properties at the room temperature
- Improving magnetic, optical and electrical properties we can use these materials at realization of different devices, in transparent electronics, spintronics, respectively in applications as sensor.

KEYWORDS: thin films, TCO materials, transparent electronics, semitransparent magnetic materials, sprintronics, multilayered structures

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