UNIUNEA EUROPEANĂ

GUVERNUL ROMÂNIEI MINISTERUL MUNCII, FAMILIEI ŞI PROTECŢIEI SOCIALE AMPOSDRU

Fondul Social European POS DRU 2007-2013

Instrumente Structurale 2007-2013

MINISTERUL EDUCAŢIEI CERCETĂRII TINERETULUI ŞI SPORTULUI OIPOSDRU

UNIVERSITATEA „ALEXANDRU IOAN CUZA" IAŞI

UNIVERSITY "AL. I. CUZA"
FACULTY OF PHYSICS

Summary

RESEARCH CONCERNING MAGNETIC NANOCOMPOSITE MATERIALS OF Co-TiO_2 SYSTEM

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~2012~

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This doctoral thesis has been carried out with financial support from* "POSDRU/88/1.5/S/47646 PROJECT *co-financed by the European Social Fund through the Sectoral Operational Programme for Human Resources Development 2007 - 2013".

Introduction

After the discovery of room-temperature ferromagnetism in cobalt-doped titanium dioxide semiconductor, more attention has been focused on the study of Co doped TiO_2 films, for potential applications in spintronics. We chose to study this composite for the semiconductor properties of the TiO_2 with applications in photocatalysis and fotoelectrocatalysis as well for the ferromagnetic properties of cobalt, but especially because such characteristics have not yet been studied for the Co-TiO_2 nanocomposite coatings in Co metal matrix.

The aim of this study was focused on the preparation of magnetic nanocomposite thin films based on Co-TiO_2 system by electrodeposition and to study the morphological, structural, magnetic, transport and photocatalytic properties occurring from these structures in order to find opportunities for technological applications.

To study the magnetic characteristics, hysteresis cycles and torque curves were drawn in order to determine the following characteristic: the saturation magnetization M_s, remanent magnetization M_r, coercive field H_c ratio M_r / M_s called rectangularity factor of the hysteresis cycle, anisotropy field H_K, effective anisotropy constant K_{ef}. The type of anisotropy of Co and Co-TiO_2 films was determined from the torque curves. In order to find possibilities for technological applications, transport properties of the films were studied, from which the resistance R and magnetoresistance MR of samples were determined.

In Chapter 2, **Experimental research concerning the electrochemical preparation of nanocomposite thin films from the Co-TiO_2 system,** basic notions on the electrolytic preparation mechanism and the experimental results obtained from cyclic voltammetry and cronoamperometrie studies, concerning the type of nucleation and growth of Co and Co-TiO_2 films are presented. Electrodeposition and experiments to characterize magnetic samples of Co and Co-TiO_2 nanocomposite films were performed at room temperature. The electrodeposition was done in potentiostatic and galvanostatic regime, by using an electrolytic cell and a three electrode system consisting of a platinum (Pt) foil anode, a textured cfc (100) copper foil cathode in the form of discs with a diameter of 23.0 mm and a quasi-reference electrode made of platinum wire embedded in glass, having the contact surface with the electrolytic solution of 0.06 mm^2. The electrolytic solution contains: cobalt sulfate ($CoSO_4 \cdot 7H_2O$), boric acid (H_3BO_3), nanoparticles of titanium dioxide TiO_2 nanoparticles, Degussa (mixture of rutile and anatase) with an average diameter around 28 nm were dispersed in the electrolyte and several additional substances (NaCl, $Na_2SO_4 \cdot 10H_2O$, $C_6H_{15}NO_3$) selected by preliminary experiments of electrodeposition, to obtain good quality deposited films. The TiO_2 particles were kept suspended in electrolyte by stirring the solution with a magnetic stirrer.

Eight series of samples were obtained by electrodeposition by modifying the following parameters: the TiO_2 nanoparticles concentration from electrolytic solution c_{TiO2} (series A and B); the deposition voltage applied source U_{bias} (series C and D); the deposited films thickness d (series E and F); the stirring speed of the electrolytic solution v (G series); applied current density during electrodeposition *J* (H series). In each case the other working parameters were maintained at constant values.

In Chapter 3, **Structural and morphological characterization of Co-TiO_2 nanocomposite thin films,** own experimental results concerning the structure, composition and morphology of the Co and Co-TiO_2 films are presented. XRD analyzes indicated that both in Co thin films as well as in Co-TiO_2 nanocomposite films the cobalt is deposited with a *hcp* structure. The average size (D) of Co crystallites determined by means of Scherrer relation [2, 3] depends on the studied working parameter for each series of samples, as follows:

- D increase (from 13 nm to 16 nm) with increasing TiO_2 concentration in solution (from 0.0 g/L to 3.5 g/L) for the A series samples and with increasing electrodeposition voltage from 3.5 V to 4.0 V for series D;

- the increasing in deposited film thickness (from 0.07 μm to 0.63 μm) for films of F series and in applied current density during electrodeposition (H series) have determined an increase of the average crystallites size of Co from 9 nm to 10 nm and from 10 nm to 12 nm, respectively;

- the increase in stirring speed of electrolytic solution from 300 rot/min to 750 rot/min for samples G1, G2 and G3 lead to the lowering of D values from 24 nm to 20 nm.

In the following, we present for exemplification the XRD difractograms for the samples A1, A2 and A3. The diffractograms were obtained in the 2θ range of 20 to 100 degrees, but here we presented only the region specific to Co lines.

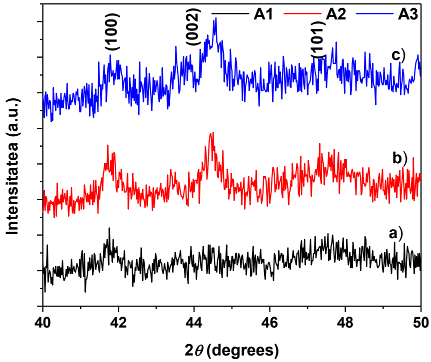

Figure 3.1: XRD patterns (enlargement for the region of Co lines) for the films: a) A1, b) A2 şi c) A3 [1]

By identifying the peaks in the diffractogram it can be seen that both the Co film (A1 sample) and the Co–TiO_2 nanocomposite films (A2 and A3 samples) contain mainly hcp Co phase. Average crystallite size of nanocrystalline Co calculated from the diffractogram using Scherrer relation [2, 3] is 13 nm for A1 sample and 16 nm for A2 A3 samples [1].

Experimental results on the chemical composition of the Co and Co-TiO_2 films performed by scanning electron microscopy (SEM/EDAX) showed that the amount of Ti (respectively TiO_2) in the film increased (from 0.0 % to 1.2 at %) with increasing the c_{TiO2} parameter (from 0.0 g/L to 3.5 g/L) and with increasing U_{bias} from 3.5 V to 4 V. In the case of H series samples largest amount of Ti (9.8 at %) in the film was obtained for the highest current density (3.2 A/dm^2).

The experimental results concerning surface morphology of films showed that the Co grains grew starting from different nucleation sites on the substrate through a mechanism of nucleation and progressive growth Volmer-

Weber type and they tend to form conglomerates, especially for the samples with high content of TiO_2.

For exemplification, we present in Figure 3.2 (a and b) SEM images obtained for the H1 and H4 nanocomposite films deposited of electrolytic solutions with c_{TiO2} = 2.8 g/L at different values of J (1.1 A/dm^2 and 3.2 A/dm^2).

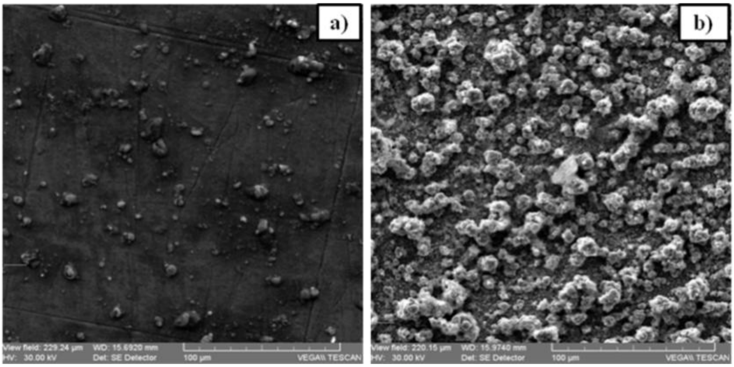

Figure 3.2: SEM micrographs for the films: a) H1 (1.1 A·dm^{-2}) and b) H2 (3.2 A·dm^{-2}) [4]

By TiO_2 incorporation in the films, the surface morphology of the nanocomposite samples is gradually changed. By increasing the working parameters c_{TiO2}, J şi d, the morphology of the films is completely changed appearing crystallites as „cauliflower” with pyramid crystallites shapes in around. Because the cathode surface is covered partially by TiO_2 nonconductive nanoparticles, the current density is increased locally leading to the increase of the cobalt nucleation on preferred sites. Thus, the cobalt crystals are nucleated and grown in the shape of cauliflower and wide pyramid in the coatings [4]. This behavior can be understood in terms of the two-step adsorption model of Guglielmi [5].

XPS spectra (obtained using X-ray Photoelectron Spectroscopy) of Co and Co-TiO_2 samples revealed the presence of $Co2p_{3/2}$ and $Co2p_{1/2}$ peaks for cobalt, $Ti2p_{3/2}$ and $Ti2p_{1/2}$ peaks for titanium and O1s peak for the oxygen incorporated into nanocomposite film.

XPS spectra deconvolution of Co2p, O1s and Ti2p lines showed the following:

- the cobalt exists in the films as Co^{2+} similar to [6], and as cobalt metal particles.
- the film surface is partially covered with the OH group [7].
- the presence of TiO_2 at the surface film [6, 8-10].

In Chapter 4, **Research concerning the magnetic characteristics of Co-TiO_2 nanocomposite thin films,** experimental results concerning the influence of electrodeposition parameters on the magnetic characteristics of the Co and Co-TiO_2 samples are presented. From the comparison of hysteresis loops corresponding to each series of samples it was found that by increasing the working parameters c_{TiO2}, U_{bias} and J the values Ms, Mr, and χc are influenced in a descending mode. For samples deposited at different stirring speeds of the electrolytic solution (series G) magnetic characteristics M_s, M_r, and χ_c decrease with increasing speed. This magnetic behavior of the samples in each series can be attributed to the different chemical composition of the films, as seen from the data concerning the concentration of chemical elements in the film obtained by SEM/EDAX, (data presented in & 3.2). Thus, the inclusion of the non-ferromagnetic components TiO_2 and $Co(OH)_2$ in nanocomposite film decreases the saturation magnetization of the samples [1].

The increase in cauliflower grain size with increasing *J* is thought to be a possible cause of the reduction in coercivity, implying that the energy barriers to domain wall motion are easier to overcome.

For exemplification, in Figure 4.1 (a and b) we presented the $M = f(H)$ and $\chi = f(H)$ curves for H series samples obtained by electrodeposition at different values of current density (1.1 $A\cdot dm^{-2}$; 2.2 Adm^{-2}, 2.6 $A\cdot dm^{-2}$ and 3.2 $A\cdot dm^{-2}$).

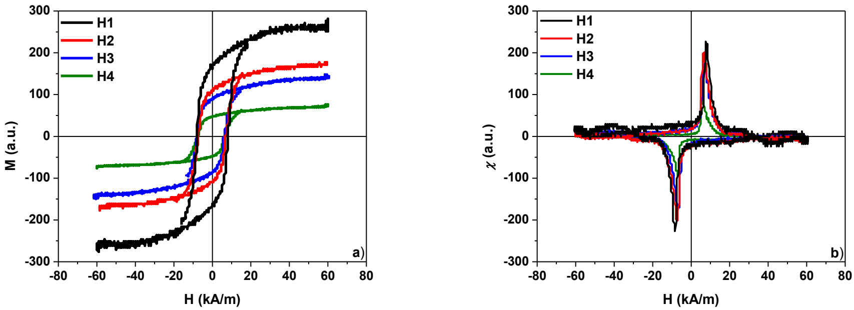

Figure 4.1: The curves M = f (H) (a) and χ = f (H) (b) for H1, H2, H3 and H4 samples [4]

The torque curves $L = f(\theta)$ presented in & 4.2 show that the magnetic anisotropy of Co and Co-TiO_2 samples is influenced by working parameters. Thus, according to the obtained experimental results, the samples with very low or even 0 at % concentration of TiO_2 nanaoparticule present uniaxial magnetic anisotropy with an easy axis of magnetization closer to the sample plane. Samples with high content of TiO_2 have an easy magnetization axis almost normal to the film plane.

Figure 10 (a and b) presents the $L = f(\theta)$ curves for samples A1 and A3, obtained for clockwise rotation from 0◦ to 360◦ (F) and anticlockwise rotation from 360◦ to 0◦ (B); the applied magnetic field values are 17.0 kA/m, 20.0 kA/m and 40.0 kA/m .

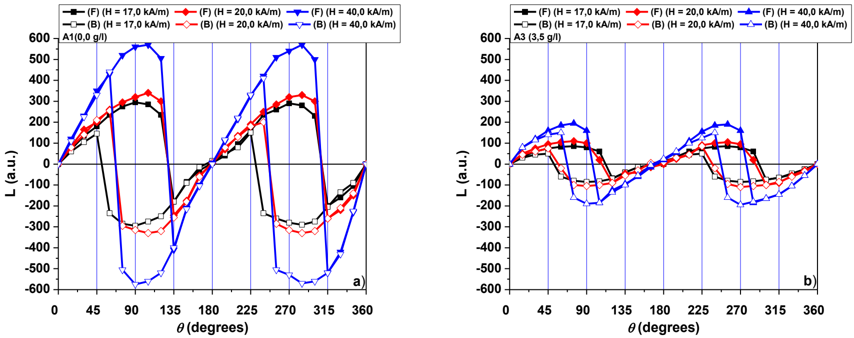

Figure 4.2: $L = f(\theta)$ curves for samples: a)A1 and c) A3 (**c**) [1]

According to Figure 4.2, with increasing the applied magnetic field (from 17.0 kA/m to 40.0 kA/m) the area between the curves F and B is increasing due to the increased in the energy loss by rotational hysteresis. This is a specific effect to the samples where magnetostatic antiferromagnetic type interactions between the magnetic moments located in the interface between crystalline grains are present[11, 12]. The shape of the curves from Figure 4.2 indicates an easy magnetization axis closer to the film plane for the A1 sample and an easy magnetization axis almost normal to the film plane for the A3 sample. Thus, we can say that the introduction of TiO_2 nanoparticles into the thin nanocomposite thin film changes the direction of the easy magnetization axis in relation to the film plane as an effect of the morphology modification of the nanocomposite films [1].

Chapter Five, **Researches concerning functional characteristics of the nanocomposite thin films of Co-TiO$_2$**, of the thesis is dedicated to research on the functional characteristics of of Co-TiO_2 nanocomposite thin films.

The measurements of the magnetoresistance were carried in the configuration CIP (current in plane sample, by using two-terminal gold pressure contacts applied on the film surface). In this configuration the magnetic field is applied in the sample plane perpendicular to the current (called CIP transversal configuration) or parallel to the current (CIP longitudinal configuration). We used the following formula to calculate the magnetoresistance for different values of applied magnetic field (H):

$$MR = \frac{R(H) - R(H_S)}{R(H_S)} \times 100\%$$

where H_{s+} represents the positive saturation magnetic field, *R(H)* denotes the film resistance measured in the field *H* and *R(Hs)* denotes the resistance in the maximum positive applied magnetic field.

By comparing the curves *R = f(H)* and *MR = f(H)* obtained for samples from each series, it was observed that R and MR depend on the working parameters to each series and implicitly on the chemical content of the samples. The experimental results showed high values for R and MR in each series for the samples that contain a larger amount of non-magnetic material (nanoparticles TiO_2).

In Figure 5.1 (a) are presented *R = f (H)* curves for samples of series A. Figure 5.1 (b) shows $R = f(c_{TiO2})$ and $MR = f(c_{TiO2})$ curves. Due to the limited number of the points, the lines should be considered only as guides to the eyes.

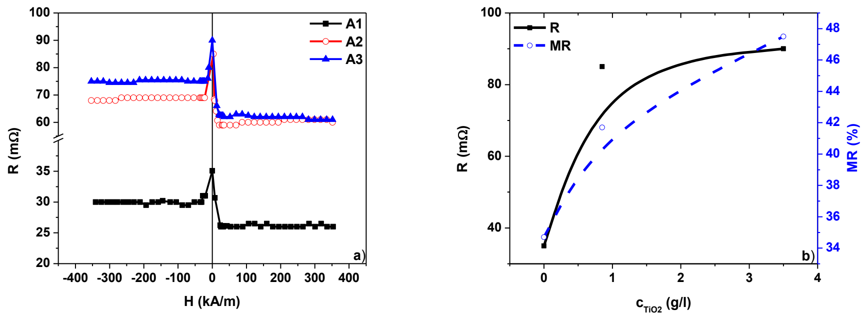

Figure 5.1: $R = f(H)$ curve (a) and (b) $R = f(c_{TiO2})$ and $MR = f(c_{TiO2})$ curves for A1, A2 and A3 films [1]

From Figure 5.1 (a) it can be noted that high values of MR is obtained at fields lower than 30 kA/m and this low field magnetoresistance is caused through spin disorder, by the tunneling process at the grain boundaries and at the interface between embedded TiO_2 nanoparticles and Co matrix. When a magnetic field is applied, the spin disorder is suppressed, resulting in the high *MR*, especially at low field ~ ± 30 kA/m. An analysis of Fig. 5.1(a and b) shows that, the value of *R* and *MR* for high TiO_2 content in film is larger than for Co film. So, the change in MR is greater in the Co-TiO_2 nanocomposite films as compared to Co film, which indicates that the enhancement in *MR* basically comes through the formation of nanocomposites (figure 5.1 b).

In section 5.3. the influence of UV radiation on the magnetic and transport properties of Co and Co-TiO_2 thin films is studied. To achieve these experiments the samples were kept under UV radiation for 4 hours. During the illumination of samples, an external magnetic field has not been applied. Analysing the hysteresis loops obtained after samples irradiation with UV radiation we observed that the magnetic characteristics M_s, M_r, H_c and χ_c

decreased. The decrease of H_c shows that the process of magnetization reversal occurs at lower magnetic fields compared to the value field reversal of magnetizations registered before the illumination with UV radiation. The reduction of the coercive force to UV light is associated with carrier-induced magnetism. We propose the interpretation of this behavior in accordance with articles [13, 14], which refers to the magnetization reversal by phototunability.

For exemplification, we show the $M = f(H)$ and $\chi = f(H)$ curves for H3 sample before and after illumination with UV radiation.

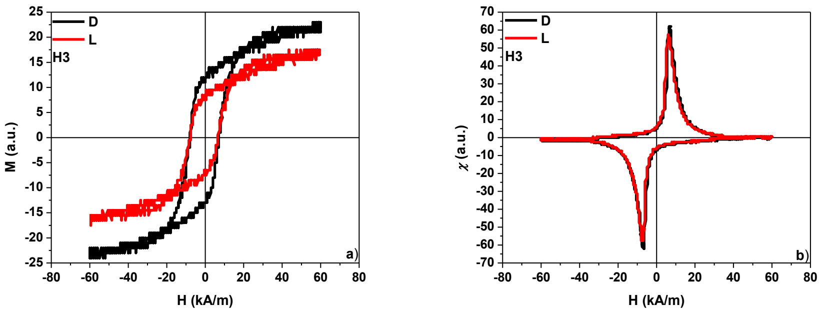

Figure 5.3: $M = f(H)$ (a) and $\chi = f(H)$ (b) curves for H3 sample

Electrochemical experiments (presented in & 5.4.) achieved in NaOH solution (0.1 M) to pH 11 have shown by comparing curves $J = f(Uref)$ plotted for A1 and A3 films in the dark (D) and under irradiation UV (L), that at darkness the O_2 reduction potential is lowered in the A3 film than in A1, and hence the dark Co-TiO_2 nanocomposite film is a more active photocatalyst than the Co films. At light, A1 and A3 films have equal potential to reduce O_2, so they have the same photocatalytic activity. Experimental results were interpreted by the paper [15].

Figure 5.4 (a and b) are shown to zoomed $J = f(U_{ref})$ curves registered for A1 and A3 samples to highlight the discharge potential of O_2.

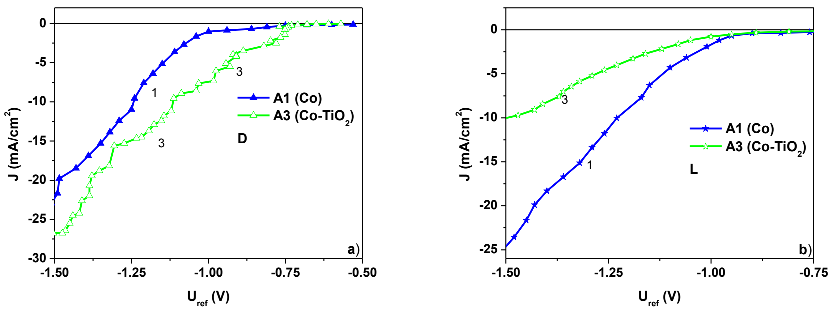

Figure 5.4: The $J = f\,(Uref)$ curves drawn in the dark (a) and under UV radiation (b) for A1 and A3 samples

Comparing the courves of Co film (A1) and of Co-TiO_2 nanocomposite film (A3) at dark and under UV irradiation we found that at dark, the O_2 reduction potential is lower in the A3 film than in A1, and hence the dark Co- TiO_2 nanocomposite film is more active photocatalyst than the Co films. At light, A1 and A3 films have equal potential to reduce O_2, so they have the same photocatalytic activity.

The main **Conclusions** which can be drawn from Chapters 2 - 5 are synthesized at the end of the thesis there :

- ***In the doctoral thesis I realized nanocomposite films of Co-TiO_2 system in the Co metal matrix by electrodeposition and I studied their magnetic and magnetotransport characteristics (for the first time in literature).***
- To determine the ***optimal conditions*** of preparation, eight series of samples, containing at least three samples, were obtained by

electrodeposition on copper support modifying the following parameters: the TiO_2 concentration from electrolytic solution c_{TiO2}; the deposition voltage applied source U_{bias}; the deposited films thickness *d*; the stirring speed of the electrolytic solution *v*; applied current density during electrodeposition *J*.

- The performed studies by voltammetry (curves $J = f(Uref)$) and cronoamperometry have allowed us to determine optimal parameters for electrodeposition of films and showed that the nucleation type of the films is progressive (as Volmer-Weber mechanism).
- Following the analysis of ***microstructure, morphology and composition*** made by X-ray diffraction (XRD), scanning electron microscopy (SEM-EDAX) and X-ray photoelectron spectroscopy (XPS), we found that Co-TiO_2 nanocomposite films containing between 0 and 31.3 at % TiO_2 nanoparticles embedded in a Co (*hcp*) metal matrix were obtained .
- Experiments carried out for magnetic characterization of nanocomposite films showed the following:
  - Saturation magnetization, remanent magnetization and magnetic susceptibility χc depends on the content of TiO_2 nanoparticles deposited in the film, namely decreasing with increasing it. This behavior may be due to the inclusion in the deposited magnetic film with greater quantities of non-magnetic material (TiO_2 + $Co(OH)_2$).
  - Increasing the content of TiO_2 nanoparticles in the film lead to a lower anisotropy constant and changed the direction of the easy magnetization axis in relation to the film plane, determineing the formation of nanocomposite structures with the easy magnetization axis

perpendicular to the film plane, especially in films with small thickness (0.07 μm and 0.21 μm);

- From the research concerning the influence of the deposition parameters on the transport properties of Co and Co-TiO_2 thin films we found the following:
  - Electrical resistance and magnetoresistance increases with increasing content of non-magnetic material (TiO_2 + Co $(OH)_2$) in nanocomposite film;
  - ***The highest values for MR*** (up to 207.7%) is obtained for samples deposited under the following conditions: a) the electrodeposition voltage of 4.0 V, b) deposited thickness below 0.2 μm and c) stirring speed the electrolyte solution of 300 r/min, of samples belonging to B, F or G series. Such Co-TiO_2 nanocomposite samples could ***be suitable for obtaining technological applications.***
- From the study concerning the influence of thermal treatment (performed at 400°C for 30 min) on the structural, morphology, magnetic and magnetotransport properties of Co and Co-TiO_2 thin films we concluded that:
  - After thermal treatment, the average size of Co crystallite increases and the surface of deposited film is covered with a film of cobalt oxide due to the formation of CoO on the Co grains surface;
  - The thermal treatment determined a decrease in saturation magnetization, magnetic susceptibility, magnetic anisotropy constant K_{ef} and changed the angle between the easy axis of magnetization and

the film plane, perpendicular anisotropy formation being disfavored for samples containing TiO_2.

- Resistance and magnetoresistance of samples increased after the thermal treatment;

➢ Experimental results concerning the influence of UV radiation on the magnetic properties and transport of Co and Co-TiO_2 films showed the following:

- The magnetic properties of the studied samples (M_s, M_r, H_c, χ_c) changes after UVirradiation, result which we can interpret as due to the process of magnetization reversal by phototunable;
- Because the same processes, electrical resistance and magnetoresistance values of analyzed films are smaller at light from the values registered in the dark ($R_L < R_D$).

➢ From the experiments mare to ***study the photoelectrochemical processes it can be deduced that nanocomposite films deposited from the electrolytic solution with TiO_2 nanoparticles concentration of 3.5 g/L can be considered more active as fotocatalist in the dark***, which could be an advantage in terms of view of technological applications (effect of depollution and self-cleaning surfaces with a low energy consumption). At the same time these nanocomposite films (containing 1.2 at % Ti, thickness 3.0 μm) presents significant magnetoresistive effects (27 % at dark and 10% at light), while the film's easy magnetization axis is perpendicular to the film plane.

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List of published or submitted papers

1. Papers published in ISI journals

1. **M. Poiană**, L. Vlad, P. Pascariu, A. V. Sandu, V. Nica, V. Georgescu, ***Effects of current density on morphology and magnetic properties of Co-TiO$_2$ electrodeposited nanocomposite films***, Optoelectronics and Advanced Materials – Rapid Communications 6, (2012) p. 434–440;

2. **M. Poiana**, M. Dobromir, A. V. Sandu and V. Georgescu, ***Investigation of Structural, Magnetic and Magnetotransport Properties of Electrodeposited Co-TiO_2 Nanocomposite Films,*** Journal of Superconductivity and Novel Magnetism, 25, (2012) p. 2377-2387.

3. **M. Poiana**, M. Dobromir, V. Nica, I. Sandu and V. Georgescu, ***Microstructure, magnetic and electronic transport properties of Co-TiO_2 nanocomposite films in metal matrix,*** Journal of Physics D: Applied Physics (submitted)

II. Papers presented at national and international conferences: 7 (poster presentation)