



Revista EIA, ISSN 1794-1237 /
e-ISSN 2463-0950
Año XVII/ Volumen 17/ Edición N.34
Julio-Diciembre de 2020
Reia34014 pág 1-6

Publicación científica semestral
Universidad EIA, Envigado, Colombia

**PARA CITAR ESTE ARTÍCULO /
TO REFERENCE THIS ARTICLE /**

Quiroz, H.P.; Bohórquez, A.J.;
Dussan, A. (2020). Effects of Co
Addition on the Microstructure and
Morphological Properties of TiO₂:
Multicomponent Oxide of Transition
Metals. Revista EIA, 17(34), Julio-
Diciembre, Reia34014. [https://doi.
org/10.24050/reia.v17i34.1344](https://doi.org/10.24050/reia.v17i34.1344)

✉ *Autor de correspondencia:*

Quiroz, H. (Heiddy): Universidad
Nacional de Colombia - Bogotá,
Dpto. de Física, Grupo de
Materiales Nanoestructurados
y sus Aplicaciones, Cra. 30 No.
45-03 Edificio 404 Lab. 121C
Ciudad Universitaria – Bogotá,
Postal Cod. 11001, Colombia.
Teléfono: +57 1 3165000 Ext.
13088, Fax: +57 1 3165000
Ext. 13089. Correo electrónico:
hpquirozg@unal.edu.co

Recibido: 19-07-2019
Aceptado: 18-06-2020
Disponibile online: 21-10-2020

Effects of Co Addition on the Microstructure and Morphological Properties of TiO₂: Multicomponent Oxide of Transition Metals

HEIDDY PAOLA QUIROZ GAITÁN¹
ANDRÉS JHOVANNY BOHÓRQUEZ¹
ANDERSON DUSSAN CUENCA¹

1. Universidad Nacional de Colombia - Bogotá, Dpto. de Física, Grupo de Materiales Nanoestructurados y sus Aplicaciones

Abstract

This work presents the process of fabrication and characterization of cobalt-doped titanium dioxide thin films on soda-lime glass substrates useful in spintronic applications. The samples were fabricated via the DC Sputtering technique, under the magnetron configuration. The samples were submitted of annealing at atmospheric pressure, after deposit process. Annealing process affect the structural properties of thin films, evidencing the formation of the Co₃O₄ with spinel structure. XPS measurements corroborated the presence of cobalt oxide species with a spinel-like arrangement. Morphological characterization showed an overall granular nature of the fabricated samples, which varied depending on the deposition time and annealing process. PPMS measurements revealed a ferromagnetic behavior of the thin films at room temperature.

Keywords: Alloys, titania, ferromagnetic, room temperature.

Efecto de la adición de Co sobre las propiedades de la microestructura y la morfología de TiO₂: óxido multicom- ponente de metales de transición

Resumen

Este trabajo presenta el proceso de fabricación y caracterización de películas delgadas de dióxido de titanio dopado con cobalto depositado sobre vidrio tipo Soda-lime, y usado para aplicaciones Espintrónicas. Las muestras fueron fabricadas por la técnica de DC "Sputtering"

en configuración "magnetron". Después del proceso de depósito, las muestras fueron sometidas a recocidos en a presione atmosférica. Los procesos de recocido afectaron las propiedades estructurales, evidenciad en la formación de Co₃O₄ con una estructura espinela. Las medidas de XPS corroboraron la presencia de especies de cobalt con un arreglo de espinela. La caracterización morfológica mostro una naturaleza granular de las muestras, que variaron con el tiempo de depósito y los procesos de recocido. Medidas de PPMS revelaron un comportamiento ferromagnético a temperatura ambiente de las películas delgadas.

Palabras clave: Aleaciones, titania, ferromagnético, temperatura ambiente.

1. Introduction

Titanium dioxide thin films have been the subject of numerous investigations due to its numerous potential applications and ability to form alloys with metallic compounds such as copper (G. Charlton, et al. 2000), iron (U. Diebold, et al. 1994) or cobalt (Y. Shao, et al. 1994, C. Huang, et al. 2006). The use of different additives inside a semiconductor matrix bears a significant change in its properties, affecting aspects such as its original crystalline structure, morphology and magnetic properties. Internal oxidation of compounds during the synthesis process give insight regarding the stabilization of the mix and it is the key process for alloys to occur. The fabrication and analysis of different multicomponent oxides is therefore crucial in the enforcement of materials science and engineering.

In the several studies of the system and stability Co-Ti-O, it was established the important factor of the oxidation state in the transition metals and effect in the permeability of oxygen in the structure (Y. Xue, et al. 2005, J. Megusar, et al. 1976). However, the formation of the ternary system changes for fabrication method, synthesis parameters, and formation of the binary oxides (A. Yankin, et al. 1999, Bohuslav Brezny, et al. 1969). The study of stability in the binary oxides, cobalt titanates and oxides compounds (Co-Ti-O system) are interesting due to correlate the thermodynamic and magnetic properties of these compound (Bohuslav Brezny, et al. 1969).

This work presents the synthesis and characterization of TiO₂ thin films mixed with cobalt atoms, which have been proved to useful in applications such as information storage and energy conversion from sunlight (S. Rout, et al. 2013, A. Earnshaw, et al. 1997). TiO₂:Co thin films were prepared using DC Magnetron Sputtering technique and were subsequently characterized morphological, compositional and magnetically in order to fully understand the process of growth, formation of alloy compounds and magnetic behavior of the resultant samples. XPS measurements revealed the presence of a spinel-like structure for Cobalt, which was obtained after annealing processes were performed on the thin films. Said post-annealings also pertained a significant change in morphology, exhibiting larger grains distributed over the surface of the substrate. Finally, a mainly ferromagnetic behavior was found for as-deposited thin films.

2. Materials and Methods

Intermetallic alloys of cobalt mixed with TiO₂ were fabricated under an argon inert atmosphere (99.999% purity) using the sputtering technique, under the DC Magnetron configuration. The work pressure inside the vacuum chamber was fixed at 2.5×10^{-2} torr, substrate temperature was established at 523 K, magnetron powers were 120 W for the TiO₂ target (99.99% pure) and 75 W for the cobalt target (99.99% pure). All the thin films were deposited over soda-lime glass substrates (2.5 cm x 3 cm), which were previously cleaned in an ultrasonic bath using deionized water; the samples were then annealed in-situ at 450 °C for 2 hours. Different fabrications were

carried out using different deposition times (t_d): 15, 30 and 45 minutes. Samples were subject to annealing processes after deposition in an oven exposed to ambient conditions at different temperatures: 723 K, 823 K and 873 K for a period of 5 h.

The thin films were structural, morphological and magnetically characterized using XPS, SEM and PPMS measurements. The structural data was acquired using a surface characterization platform XPS/ISS/UPS-ACenteno provided by SPECS (Germany), said platform is provided with a PHOIBOS 150 2D-DLD energy analyzer, monochromatic Al-K α X-Ray radiation was used to irradiate the sample with a power of 200W, the software used to analyze the data was the CASAXPS (by Casa Software Ltd.).

Scanning electron microscopy measurements were carried out using the VEGA 3SB electron microscope equipped with a tungsten filament, data collection was made under high vacuum conditions (10^{-6} mbar) using an Xflash 410 m detector. Morphological characterization was complemented with Atomic Force Microscopy measurements (AFM) in tapping mode employing a (AFM ANDES).

Finally, the magnetic behavior of one of the samples was evaluated through a Physical Properties Measurement System (PPMS) using the Vibrating Sample Module (VSM) under the Zero Field Cooled (ZFC) configuration; the sample had to undergo a preliminary de-magnetization to later be brought to the measurement temperature. An additional study regarding the dependence of the magnetic moment with increasing temperature was also performed.

3. Results and Analysis

Figure 1 shows the obtained XPS spectrum for the sample fabricated with a 30 min deposition time and post-deposition annealing at 873K for 5 h. As it can be observed, titanium, oxygen and cobalt species are evident in the surface of the sample. Annealing in ambient conditions enforces the oxidation of the thin film, causing the formation of the cobalt oxide species: Co_3O_4 . This particular compound is commonly known as a mixed-valence compound, wherein the transition element can exhibit 2 separate oxidation states simultaneously, in this case, +2 and +3.

In addition to said property, the discrepancy between valences of cobalt originates a change in the crystalline structure of the compound, where consistently, two different structures are formed: A tetrahedral and an octahedral coordination. The first contains the cobalt with a +2 oxidation state among its interstices, whilst the latter bears the Co^{+3} ions in between its interstices; additionally, the satellite peak around 697 eV and 638 eV are associated to the formation of Co_3O_4 such as spinel structure (Jeong-Min Lee, et al. 2007, Dagoberto Cabrera-German, et al. 2016). The inset of **Figure 1** shows a spinel structure of Co_2O_3 . In the case of titanium, the XPS analysis allowed the determination of the oxidation state +4 for titanium, which can be associated to the formation of TiO_2 .

Figure 2 and **Figure 3** shows SEM and AFM micrographs of the TiO_2 :Co thin films with annealing process *in situ* and in a reactive oxygen atmosphere. An overall granular nature of the samples was evident, which was a condition present both before and after annealing at elevated temperatures (873 K). **Figure 2a** presents the morphological study of the sample fabricated with a 30 min deposition time and annealing *in situ*, in which AFM measurements allowed the determination of a root mean square roughness (RMS) of 16.73 nm, which would change to 15.68 nm after annealing at 873 K for 5 h in a reactive oxygen atmosphere (**Figure 2b**). This is possible to associate at increasing of grain size by nucleation due al increased annealing temperature.

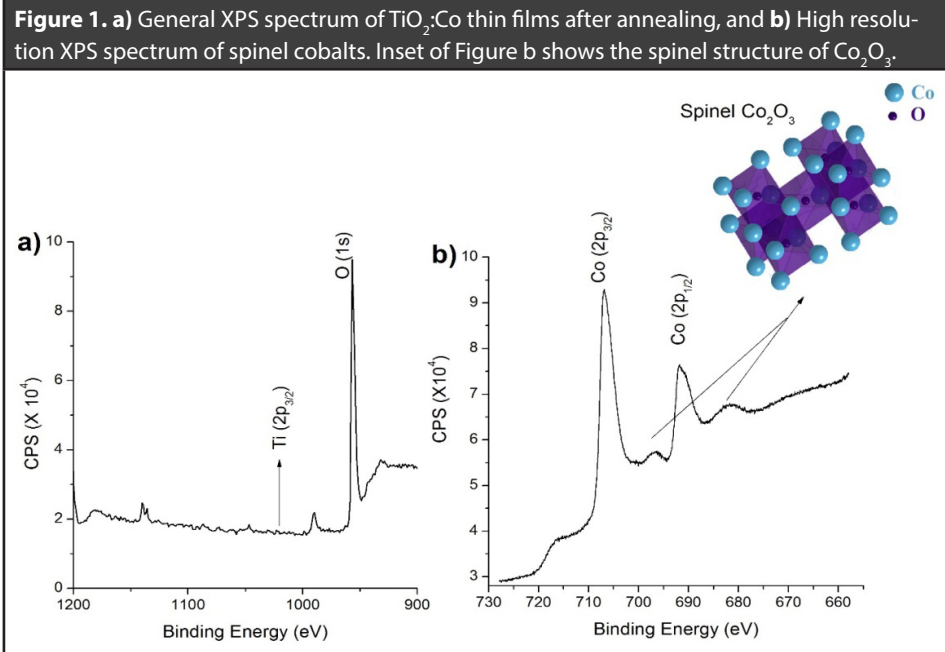


Figure 2. AFM micrographs a) TiO_2 :Co thin film with $t_d = 30$ min with annealing process in situ, **b)** TiO_2 :Co thin film after annealing at 873 K for 5 h in ambient conditions, and **c)** SEM micrograph.

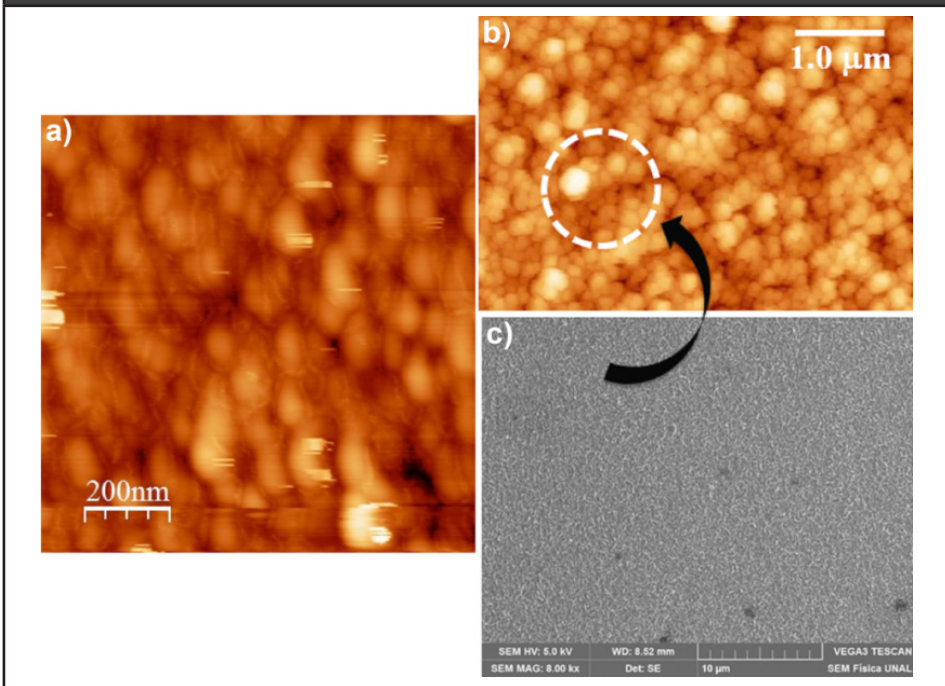


Figure 3 shows the comparative morphological study of the samples varying the deposition time between 15 and 45 min without post-deposition annealing in a reactive oxygen atmosphere. The granular nature spread throughout the surface is more prominent for longer deposition times, bearing an increase in grain size greater than 30% associated to the nucleation and formation of the thin films (model MD for sputtering method) (Randima P. Galhenage, 2013, J. M. Albella, 2003).

Figure 3. SEM micrographs of $\text{TiO}_2:\text{Co}$ thin films varying the deposition time: a) 15 min, b) 30 min, and c) 45 min.

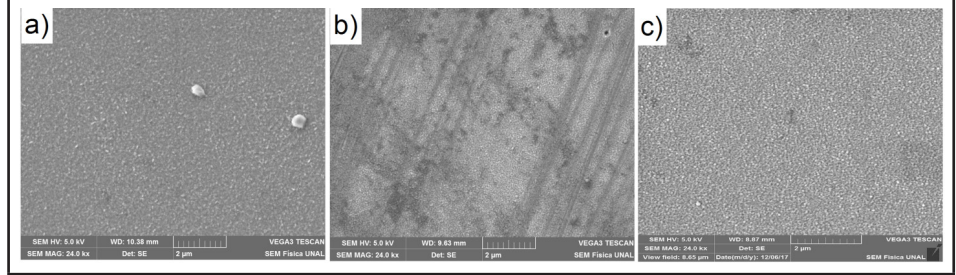


Figure 4 shows the magnetic characterization of the intermetallic alloy deposited for 30 min. **Figure 4a)** presents the variation of the magnetic moment as a function of the applied magnetic field, measured at two separate temperatures: 150 K and 300 K. The result is a hysteresis loops for the sample analyzed at 150 K and room temperature (300 K), reaching a saturation magnetization of $11.21 \times 10^{-2} \text{ emu/cm}^3$ and exhibiting a limited coercive field (H_c) of -129.5 Oe and -137.7 Oe for the 150 K and 300 K, respectively. The contrast observed with the sample studied at 300K, where the magnetization has a decreasing tendency with increasing magnetic field, points towards a diamagnetic behavior of the substrate of thin films. These behavior are associated to the weak ferromagnetic behavior (A. Tomou, et al, 2006) due to the competition between antiferromagnetic phase (Co_3O_4) and ferromagnetic phase (Co clusters) in the thin films.

Figure 4. a) Magnetization as a function of the applied magnetic field, **b)** Magnetization as a function of temperature for the $\text{TiO}_2:\text{Co}$ thin film with $t_d = 30$ min. Inset shows the hysteresis loop.

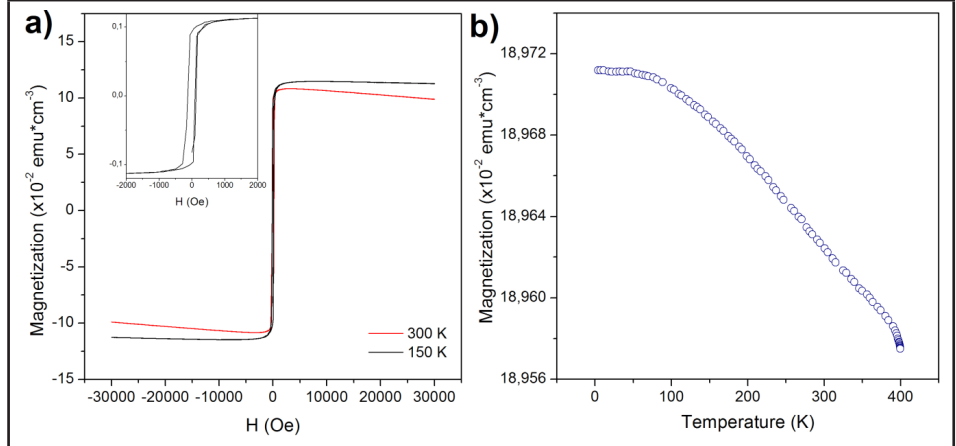


Figure 4b) shows the magnetization as a function of temperature of $\text{TiO}_2:\text{Co}$ thin film with $t_d = 30$ min and annealing in situ for a field of 0.087 Oe. It is possible to observe the saturation magnetization at low temperature (< 50 K), and the typical ferromagnetic behavior when temperature increases with T_c around 400 K.

4. Conclusion

$\text{TiO}_2:\text{Co}$ alloy thin films were fabricated using the DC Magnetron Co-Sputtering technique and were subsequently submitted to annealing processes in a reactive atmosphere. Structural characterization revealed a spinel-like crystalline structure for the cobalt oxide species present on the samples after annealing, bearing a mixed-

valence compound Co₃O₄, along with a possible intermetallic alloy based on cobalt titanate formation. Morphological characterization revealed a preponderant granular nature of the thin films which was enforced after annealing at elevated temperatures, causing an increase in grain size, product of the formation of Co₃O₄ crystals. Magnetic characterization at different study temperatures showed a ferromagnetic behavior at room temperature.

Acknowledgements

This work was supported by Universidad Nacional de Colombia - COLCIENCIAS Code: 201010026991. Heiddy Paola Quiroz has a PhD scholarship from of Doctorados COLCIENCIAS Conv. 727 - 2015.

References

- Albella, J. M. Láminas Delgadas y Recubrimientos: Preparación, Propiedades y Aplicaciones. Madrid. Consejo Superior de Investigaciones Científicas, (2003), pp. 120.
- Brezny, Bohuslav; Muan, Arnulf. Phase Relations and Stabilities Of Compounds In The System CoO-TiO₂. *Journal of Inorganic and Nuclear Chemistry*, 3 (1969), pp. 649-655.
- Cabrera-German, Dagoberto; Gomez-Sosa, Gustavo; Herrera-Gomez, Alberto. Accurate peak fitting and subsequent quantitative composition analysis of the spectrum of Co 2p obtained with Al K α radiation: I: cobalt spinel. *Surface and Interface Analysis*, 48 (2016), pp. 252-256.
- Charlton, G.; Howes, P.; Murny, C.; Raza, H.; Jones, N.; Taylor, J.; Norris, C.; McGrath, R.; Norman, D.; Turner, T.; Thornton, G.. Copper interface induced relaxation of TiO₂ (110)-1 \times 1. *Physical Review B*, 61 (2000), pp. 16117.
- Diebold, U.; Tao, H. S.; Shinn, N. D.; Madey, T. E. Electronic structure of ultrathin Fe films on TiO₂(110) studied with soft-x-ray photoelectron spectroscopy and resonant photoemission. *Physical Review B: Condensed Matter*, 50 (1994), pp. 14474.
- Earnshaw, A.; Greenwood, N. *Chemistry of the Elements*. Oxford Butterworth-Heinemann, (1997), pp. 961.
- Galhenage, Randima P.; Yan, Hui; Tenney, Samuel A.; Park, Nayoung; Henkelman, Graeme; Albrecht, Peter; Mullins, David R.; Chen, Donna A. Understanding the Nucleation and Growth of Metals on TiO₂: Co Compared to Au, Ni, and Pt. *Journal of Physical Chemistry C*, 117 (34) (2013), pp. 7191-7201.
- Huang, C.; Guo, Y.; Liu, X.; Wang, Y. Structural and optical properties of Ti_{1-x}Co_xO₂ films prepared by sol-gel spin coating. *Thin Solid Films*, 505 (1-2) (2006), pp. 141-144. [5] Xue, Y.; Wang, H. M. Microstructure and wear properties of laser clad TiCo/Ti₂Co intermetallic coatings on titanium alloy. *Applied Surface Science*, 243 (1-4) (2005), 278-286.
- Lee, Jeong-Min; Kim, Ju Wan; Lim, Ji Sun; Kim, Tae Jin; Kim, Shin Dong; Park, Soo-Jin; Lee, Young-Seak. X-ray Photoelectron Spectroscopy Study of Cobalt Supported Multi-walled Carbon Nanotubes Prepared by Different Precursors. *Carbon Science* 8 (2) (2007), pp. 120-126.
- Megusar, J.; Meier, G. H.; Internal Oxidation of Dilute Co-Ti Alloys. *Metallurgical Transactions A*, 7 (1976), pp. 1133-1140.
- Rout, S.; Popovici, N.; Dalui, S.; Paramês, M.; da Silva, R. Phase growth control in low temperature PLD Co:TiO₂ films by pressure. *Current Applied Physics*, 13 (2013), pp. 670-676.
- Shao, Y.; Chen, W.; Wold, E.; Pau, J. Dispersion and electronic structure of titania-supported cobalt and cobalt oxide, *Langmuir*, 10 (1994), pp. 178-187.
- Tomou, A.; Gournis, D.; Panagiotopoulos, I.; Huang, Y.; Hadjipanayis, G. C.; Kooi, B. J. Weak ferromagnetism and exchange biasing in cobalt oxide nanoparticle systems. *Journal of Applied Physics*, 9 (2006), pp. 123915.
- Yankin, A.; Vikhrev, O.; Balakirev, V. P-T-x diagram of the Co-Ti-O system. *Journal of Physics and Chemistry of Solids*, 60 (1) (1999), pp. 139-143.