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Spectroscopic Ellipsometry Study of Co_3O_4 Thin Films Deposited on Several Metal Substrates

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Abstract: Spectroscopic ellipsometry and atomic force microscope techniques were employed to analyze optical properties, microstructure and thickness of cobalt oxide thin films deposited on metal substrates by the sol-gel dipping method. The ellipsometric data were conveniently fitted, assuming a stratified structure for the deposited film, which consists of a sublayer native oxide that was coated with a bi-layered Co_3O_4 film. The dispersion curves (refractive indices and extinction coefficients) were reported in the 1.5–4.5 eV photon energy range. Excluding the Fe substrate, in which nucleation failed to grow Co_3O_4, all deposited films have the Co_3O_4 cobalt oxide phase as the predominant one. Additional data concerning solar parameters such as absorptance, emittance and selectivity of Co_3O_4/metal structures were also reported.

Keywords: Spectroscopic ellipsometry, optical properties, cobalt oxide, metal substrates.

1. INTRODUCTION

Because of its electronic and magnetic properties, cobalt oxide is a promising material for various technological applications such as protective corrosion coatings [1], electrochromic [2] and solar photothermal converters [3].

The optical properties of cobalt oxide thin films have been studied by several workers. Ruzakowki *et al.* [4] determined the optical constant (refraction indices and extinction coefficients) and microstructure of spray pyrolyzed Co_3O_4 deposited on glass substrates. Draseovan and others [5] and Barrera and others [6] determined the energy gap value of the same material but deposited on micro slide substrates by sol-gel method.

Cobalt oxide thin films have been prepared by a number of techniques, including sol-gel [3, 5, 6], spray pyrolisis [7], electrodeposition [8] and chemical vapor deposition [9]. In this work, cobalt oxide thin films were deposited on metal substrates using the sol-gel dipping method and were studied in order to know their optical and microstructural characterization, using spectroscopic ellipsometry and atomic force microscopy (AFM). Spectroscopic ellipsometry is an optical non-destructive technique suitable to study optical properties and microstructure of thin films deposited on opaque substrates such as the metal ones.

Due to the importance of Co_3O_4 as a selective coating for photo-thermal applications, the photo-thermal parameters (emittance, absorptance and selectivity) of cobalt oxide/ metal tandems are also reported.

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2. EXPERIMENTAL DETAILS

Aluminum, copper, 304 stainless steel and iron sheets were used as substrates to deposit cobalt oxide thin films, using the dipping sol–gel method. Prior to the deposition process, the substrates were mechanically polished with a commercial buff paste, then rinsed in hot carbon tetrachloride and finally ultrasonically rinsed in ethylic alcohol.

In the deposition process, a cobalt propionate complex based solution was used as sol and was prepared as described elsewhere [3]. The films were prepared in a closed chamber under controlled humidity (55%) using only one dipping-drying-heating cycle in which the substrate was immersed in the sol for 3 minutes, withdrawn at a speed of 1 mm/s, dried at room temperature and finally annealed for 2 hours at 400 ºC.

The surface morphology of bare and Co_3O_4–coated substrates was inspected by AFM using a 250 Quesant instrument, and the film thickness was determined with a DekTak II Talystep profilometer.

The ellipsometric characterization was carried out in the 1.56-4.5 eV energy range using a Phase Modulated Ellipsometer Jobin Yvon Uvisel DH10 system, at an incidence angle of 70°. All the experimental data was acquired and analyzed by means of the version 2.1 of Delta Psi software.

3. RESULTS AND DISCUSSION

3.1. AFM Analysis

In a previous paper [3], it was reported that the aforementioned deposition procedure led to Co_3O_4 thin films when it was applied to glass substrates. In that work, the

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phase composition of the films, which were consisted of cobaltite Co_3O_4, was corroborated by X–ray diffraction, X-ray photoelectron spectroscopy and transmittance measurements. In the present work, the phase composition of deposited film was indirectly verified from ellipsometric data analysis.

The AFM images of uncoated and Co_3O_4–coated substrates are shown in Fig. (**1a**, **b**), respectively. The root-mean-square (RMS) roughnesses of uncoated and Co_3O_4–coated substrates, as measured by AFM, are listed in Table **1**.

From Table **1**, it is essentially seen that the same roughness (about 12 nm) is obtained for all the substrates after the polishing process. Nevertheless, this trend does not preserve after the film deposition; the Co_3O_4–coated surfaces display a roughness higher than the uncoated ones: ~ 40 nm for SS and Fe substrates and ~ 100 nm for Al and Cu substrates.

Regarding the substrate surface morphology (Fig. **1b**), cone–shaped structures are observed. We believe that during the polishing process, the metal is heated locally and is eventually melted, developing such structures from genuine crystal growth phenomena. On the other hand, the surface morphology of Co_3O_4–coated substrates seems to be consisted of irregular 3D structures surrounded by coarse–grained regions. The shape of the 3D structures is described in Table **1** along with the grain size.

3.2. Spectroscopic Ellipsometry Characterization

Ellipsometry does not directly measure the optical constants or the film thickness, but two ellipsometric angles, Δ and Ψ. These angles describe the change in the polarization state of light which was caused by the sample. From the software of ellipsometry, we can get Δ and Ψ, as well as the ellipsometric parameters $I_s=\sin2\Psi\sin\Delta$ and $I_c=\sin2\Psi\cos\Delta$, as output. In order to find the optical constants and other film characteristics, an optical model for the bare and Co_3O_4–coated substrate must separately be proposed. The optical model includes a model for the film layer structure and one based on the Optical Physics. The optical constants (n and k) are then obtained by a fitting procedure where the data, which are generated from the optical model, are compared with the experimental ones.

3.2.1. Uncoated Substrates

Because the metals oxidize easily, it is obvious that the film layer structure for Co_3O_4–free substrates should be consisted of substrate and a native oxide overlayer [10]. In this case, a good fitting was obtained by using an amorphous dispersion model [11] and a classical dispersion model [12] to model the native oxide layer and the substrate, respectively.

As an example, Fig. (**2**) displays the Is and Ic *vs* photon energy plots corresponding to the copper substrate; the dotted line and continuous line represent the experimental data and the data generated from the fitting procedure, respectively.

From the fitted data, the ellipsometer software calculates and graphs the n and k values as a function of the photon energy for the native oxide layer and the substrate. Figs. (**3**, **4**) show the dispersion spectra (n and k *vs* photon energy plots) of the native oxide layer of all substrates that underwent the ellipsometric characterization. It is known that some insight on the phase composition of a material may be gained from its k–spectrum by determining the energy value in which a given absorption band attains the maximum.

In the present case, it is hard to assess the actual nature of native oxide coating of the metal substrates, because of broadness or absence of absorption bands in the k–spectra. However, in the case of the Fe substrate, the native oxide layer mainly seems to be consisted of $CoFe_2O_4$; its k–spectrum (Fig. **4c**) displays two relatively wide absorption bands centred at 2 and 3.2 eV, which have been observed in the spinel phase of $CoFe_2O_4$ [13, 14]. Similarly, the native oxide on the copper substrate can be identified as corresponding to CuO because the n and k dispersion spectra resemble to those observed by Derlin and Kantarli [10], for the CuO phase developed at the copper-sheet surface, after a thermal process at 125 °C in air. The k and n dispersion spectra of Al native oxide resemble to those published by Arakawa and Williams for Al_2O_3 thin films [15].

3.2.2. Co_3O_4/Substrate Tandem

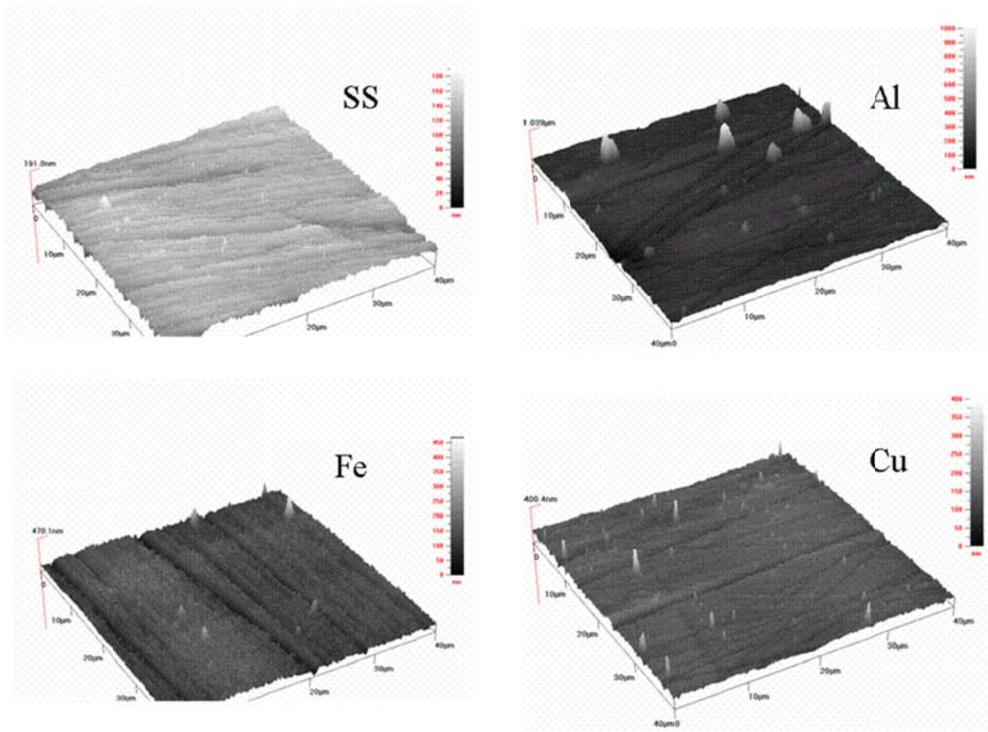
As previously mentioned, the ellipsometric characterization requires the proposal of an optical model; which should include the layer structure of the film, as well as a dispersion model for the optical constants. The starting film layer structure, which is employed to model the ellipsometric data, is shown in Fig. (**5**); it consists of a native oxide film of thickness ft_1, a Co_3O_4 bilayered film that is consisted of an underlying dense film of thickness ft_2 and an outer rough film of thickness ft_3. The outer film roughness was modeled as consisting of a solid film fraction, x (%), and a void fraction, y (%).

The optical constants of a material can be represented by a variety of dispersion models derived from Optical Physics [12, 13]. In the present work, various dispersion models were tested, but the best fit was obtained by using the Tauc Lorentz dispersion model with two oscillators to model the Co_3O_4 layer. Furthermore, it was also assumed that the native oxide remained unaltered after depositing the Co_3O_4 film. Besides the optical constants, the unknown ft_1, ft_2, ft_3 (thin film thicknesses, see Fig. **5**) and void fractions, y, were obtained from the fitting procedure.

In Fig. (**2**), the experimental (dotted lines) and fitted (continuous lines) ellipsometric parameters Ic and Is of the Co_3O_4/Cu structure are shown as an example. Figs. (**6**, **7**) display the n and k dispersion spectrum of the Co_3O_4 layer deposited on different substrates. Table **2** summarizes the native oxide thickness, the Co_3O_4 whole thickness (ft_2+ft_3) and the void percentage, obtained from ellipsometric analysis.

From Table **2** it is noted that, even though similar dipping conditions were used, the whole thickness and microstructure of the deposited film are different for each substrate, indicating that the surface density of active sites for the nucleation and growth mechanisms are different for each substrate. This feature is reflected on the n and k spectra of Co_3O_4, which significantly differ from a substrate

(**a**)



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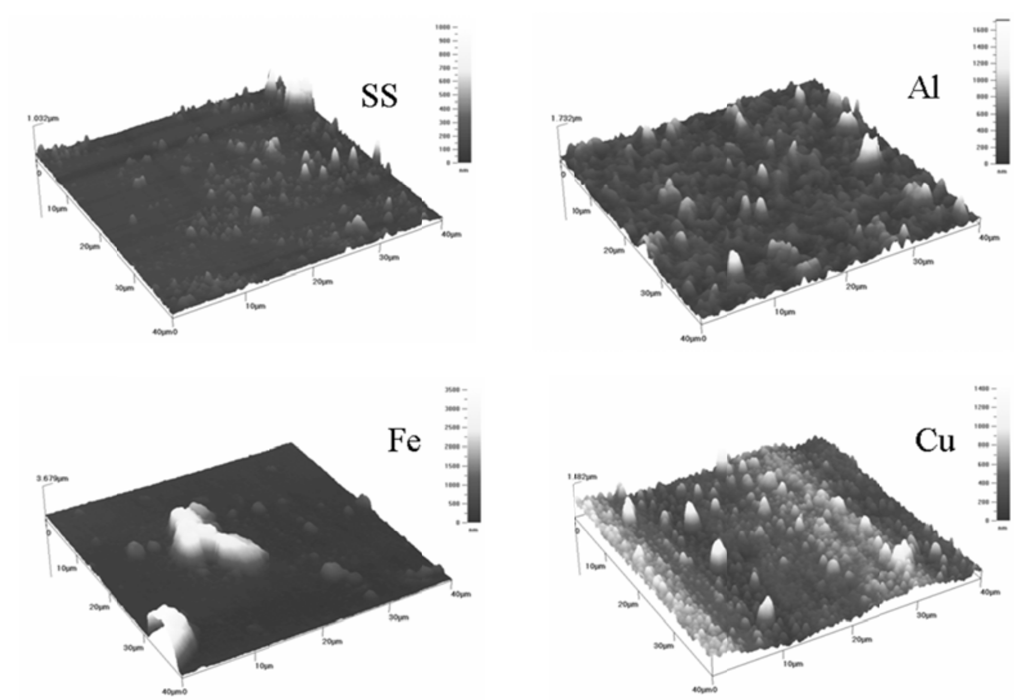

Fig. (1). AFM images of **a**) uncoated metal substrates (Fe = iron, SS = stainless steel, Al =aluminum, Cu = copper) and **b**) Co_3O_4- coated substrates.

Table 1. RMS Roughness (nm) of Co_3O_4 - Free and - Coated Metal Substrates

Substrate	RMS Roughness of Bare Substrate (nm)	RMS Roughness of Co_3O_4 (nm)
Cu	12	96
Fe	10	42
SS	11	43
Al	16	102

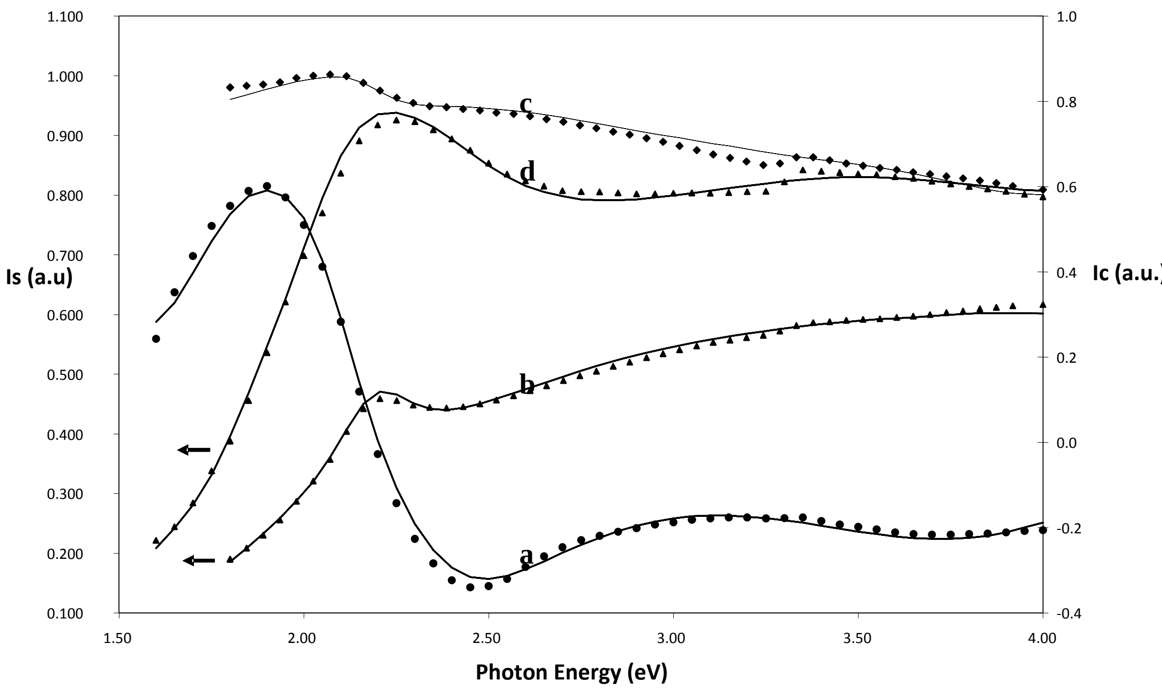

Fig. (2). Experimental (dotted line) and fitted (continuous line) ellipsometric parameters Is and Ic *vs* photon energy plots of the uncoated cooper substrate (a and b), and Co_3O_4 – coated copper substrate (c and d).

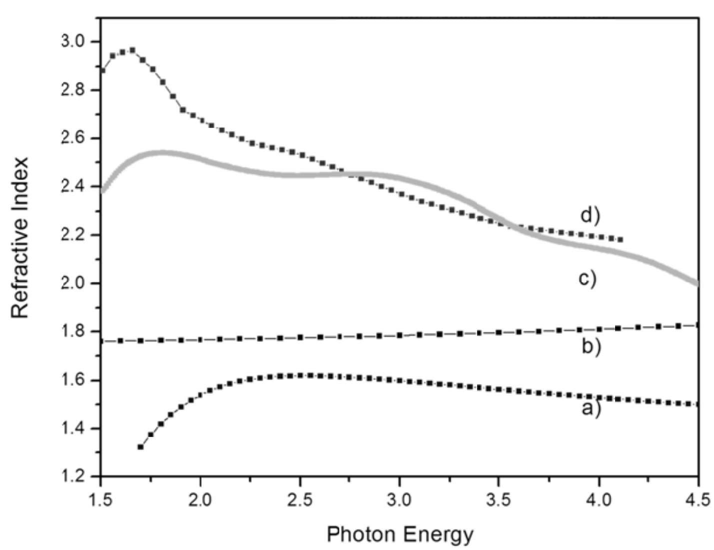

Fig. (3). Refractive index of native oxides of the metal substrates: a) SS, b) Al, c) Fe and d) Cu.

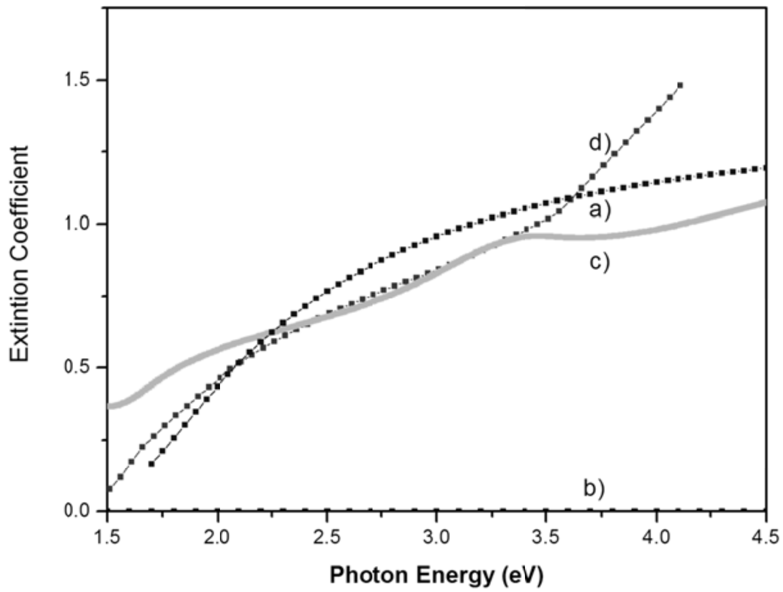

Fig. (4). Extinction coefficient of native oxides of the metal substrates: a) SS, b) Al, c) Fe and d) Cu.

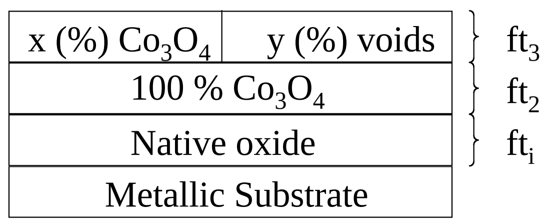

Fig. (5). Film layer structure that was employed to model the ellipsometric data. The ft_1, ft_2 and ft_3, stand for the thickness of the native oxide, the Co_3O_4 solid film, and the mixed void–solid Co_3O_4 film, respectively.

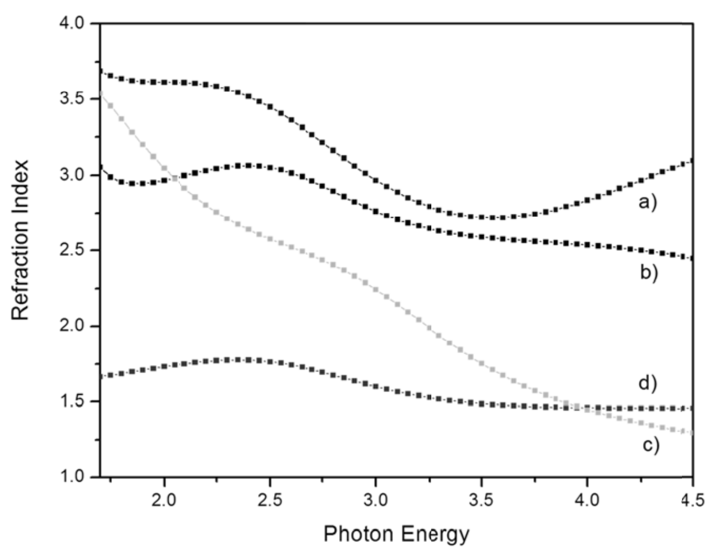

Fig. (6). Refraction index as a function of the photon energy (1.75–4.5 eV) of sol-gel deposited film on a) SS, b) Al, c) Fe and d) Cu. As indicated in the text, the film deposited on Fe is CoFe2O4, better than Co3O4.

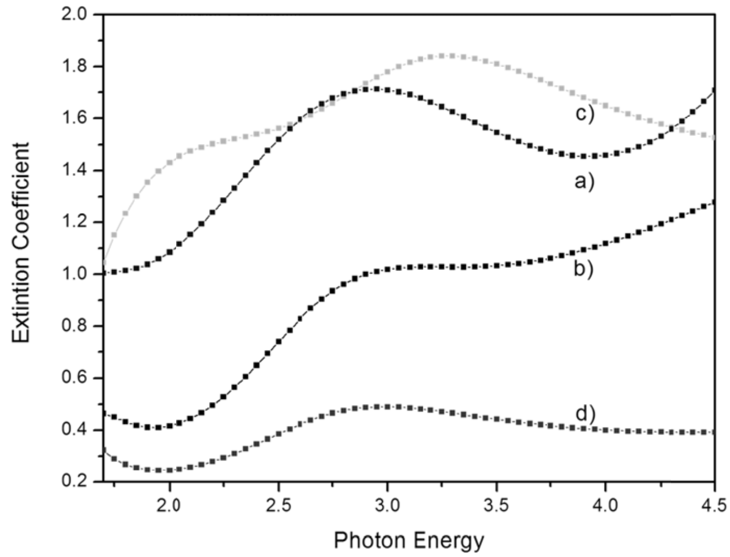

Fig. (7). Extinction coefficient as a function of the photon energy (1.75 – 4.5 eV) of sol-gel deposited film on a) SS, b) Al, c) Fe and d) Cu.

Table 2. The Film Layer Structure Parameters as Determined by Ellipsometric Analysis According to Fig. (5)

Substrate	ft_1, Native Oxide Thin Film, (Ǎ)	ft_2, Co_3O_4 Thin Film, (Ǎ)	ft_3, Co_3O_4 Coating Plus a Void Fraction, (Ǎ)	x+y (%)
Cu	10	1999	223	71+29
Fe	103	1416	963	52+48
SS	164	513	951	34+66
Al	310	-	480	64+36

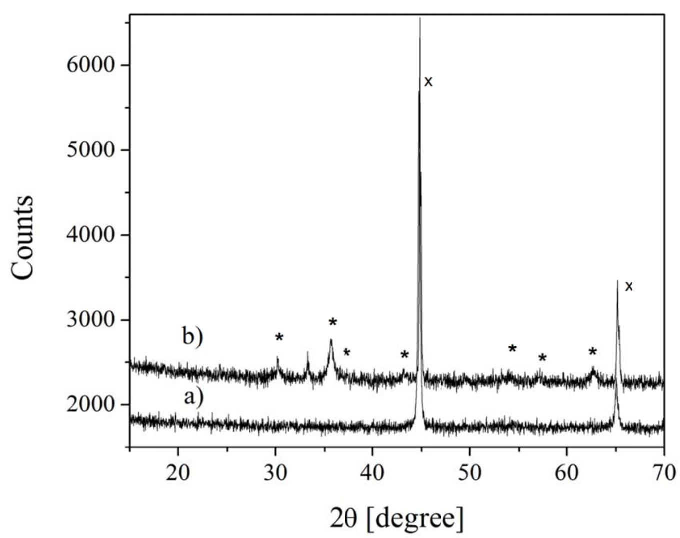

Fig. (8). X-ray diffractograms of the Iron substrate a) and the Iron substrate coated with Co_3O_4 after heat treatment b). The peaks marked with an (x) correspond to iron (PDF 04-007-9753), and those identified with a (*) correspond to $CoFe_2O_4$ phase (PDF 04-016-3954).

to another. Surprisingly, in the case of the Fe substrate, the deposited film seems to be consisted of $CoFe_2O_4$ rather than Co_3O_4; its k spectrum (Fig. **7c**) resembles that reported by Martens and Peters for the $CoFe_2O_4$ single crystal [14]. In Fig. (**8**) are shown the X-ray diffractograms before (Fig. **8a**) and after (Fig. **8b**) deposition and heat treatment of Co_3O_4 coating. As it is noticed, before deposition and heat treatment, only diffraction maxima, corresponding to iron (x), are observed (PDF 04-007-9753). On the other hand, in Fig (**8b**), the diffraction maxima at (*) in 2θ are in agreement with (PDF 04-016-3954) which corresponds to the $CoFe_2O_4$ phase. Thus, this fact supports the ellipsometric model assumption, concerning the $CoFe_2O_4$ phase formation on iron substrate.

For substrates other than Fe, the deposited films seem mostly to be consisted of Co_3O_4 because the n and k spectra are in well accordance with those reported by other authors for Co_3O_4 deposited on glass substrates [4]. In particular, the presence of the absorption bands, at 1.7 and 2.8 eV, in the k–spectra confirms that the deposited films are mostly cobalt oxide Co_3O_4 [4, 6].

Regarding the film thickness, it was found that the measured values, which were determined by spectroscopic ellipsometry (Table **2**), are good in accordance with the film thickness measured directly by means of a Talystep dek Tak II device. The Fig. (**9**) shows a Talystep thin film thickness profile evaluation for a representative sample, Co_3O_4/SS. It shows a clear thin film thickness correlation in accordance with the ellipsometric estimation (Table **2**).

3.2.3. Solar Optical Properties

The optical properties of a selective absorber are characterized by the solar parameters such as the overall absorptance (α) and the infrared emittance (ε); the former measures the capability to absorb electromagnetic radiation in the whole spectral range, and the latter measures the capability to avoid the heat re-radiation from the absorber/ substrate. Here, emittance and absorptance were evaluated according to the Duffie and Beckman methodology [16]. A good selective absorber displays both high absorptance and low emittance and its performance is better measured by the absorptance to emittance ratio, which defines the so called selectivity.

Fig. (**10**) shows the ultraviolet-visible-infrared reflectance spectra of the cobalt oxide films deposited on different substrates, and Table **3** lists the corresponding absorptance, emittance and selectivity values.

Table 3. Solar Parameters of Co_3O_4/Metal Tandem. The Absorptance and Emittance were Determined from the Reflectance Spectra as Shown in Fig. (10) Following the Duffie and Beckmann Procedure

Substrate	α	ε	S
Cu	0.755	0.134	5.63
Fe	0.832	0.081	10.27
SS1	0.754	0.062	12.61
Al	0.783	0.01	78.3

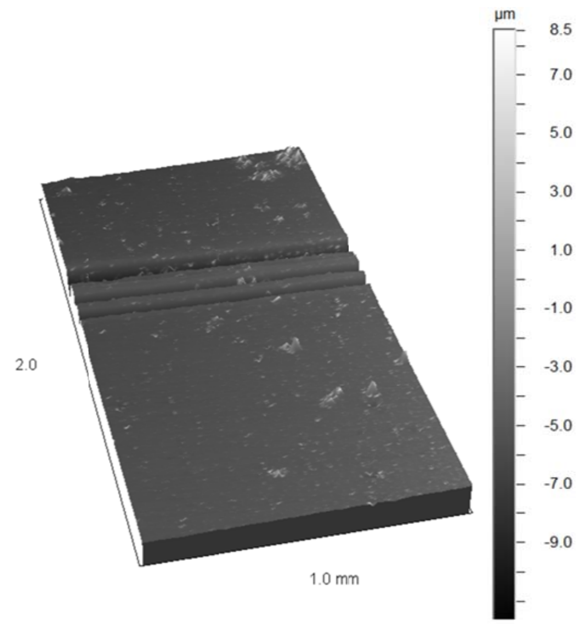

Fig. (9). Talystep 3D thin film thickness profile evaluation, 1x2 mm, corresponding to a representative sample, Co_3O_4/SS.

The reflectance spectrum, Fig. (**10**) displays the usual behavior of selective absorbers, i.e., it exhibits a minimum reflectance for wavelengths lower than 2.5 μm, while displaying a high reflectance for wavelengths higher than that. Furthermore, they show the expected correlation between the infrared (IR) reflectance and the emittance, namely: the higher IR reflectance and the lower emittance, as indicated in Table **3**.

Interestingly, the absorption edge of the film deposited on the Fe substrate differs from those deposited on other substrates; it shifts to higher wavelengths and it means that the deposited film has $CoFe_2O_4$ instead of cobalt oxide, as previously indicated by ellipsometric characterization.

The solar parameters of a given tandem are determined by the optical properties, microstructure, phase composition and thickness of the selective film. That is, the solar absorptance increases with both the extinction coefficient and the film thickness, whereas the emittance decreases as the absorber thickness diminishes. These expected trends are shown by our experimental results (Fig. **10** and Tables **2** and **3**). Notice that $CoFe_2O_4$/Fe tandem displays the highest solar absorptance, whereas the Co_3O_4/Al has the lowest emittance.

According to Table **3**, the best tandem for photothermal applications could be the Co_3O_4/Al tandem structure, because it has the highest selectivity (S=78).

4. CONCLUSIONS

Co_3O_4 thin films were deposited on different metal substrates by the sol-gel dipping method and their optical properties were analyzed using spectroscopic ellipsometry as the main technique. From ellipsometric data analysis, the optical constants, the structure of film layers, thickness and roughness of the various characterized films were

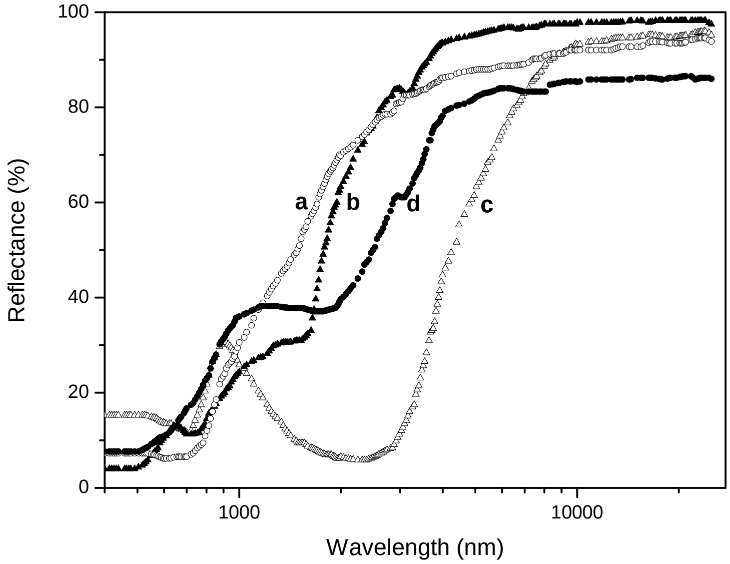

Fig. (10). UV – Vis IR reflectance spectra of the Co_3O_4/metal structures: a) SS, b) Al, c) Fe and d) Cu. The measurements were carried out in the 200 – 25000 nm wavelength range.

determined. In the 1.5–4.5 eV photon energy range, the n and k spectra of deposited films were well in accordance with those that were reported in the literature, and those that were obtained from techniques other than ellipsometry. An insight into the film phase composition was obtained from the k–spectra, indicating that Co_3O_4 predominates in the films grown on SS, Cu and Al, whereas $CoFe_2O_4$ does it in the film deposited on Fe. The obtained results show that ellipsometry is a suitable tool to study the optical properties of stratified films deposited on opaque substrates.

The photothermal parameters of the Co_3O_4/metal structures were also determined and attempts to correlate them with ellipsometric results are presented.

CONFLICT OF INTEREST

The authors confirm that this article content has no conflict of interest.

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REFERENCES

[1] Gallatt G, Pézolet M, Simard S. Optical and Physical Properties of Cobalt Oxide Films Electrogenerated in Bicarbonate Aqueous Media. J Phys Chem B 2006; 110: 6871-80

[2] Kadam LD, Pawar SH, Patil PS. Step potential analysis of cobalt oxide thin films prepared by spray pyrolysis technique. Mater Chem Phys 2001; 68: 280-2.

[3] Barrera–Calva E, Martínez-Flores JC, Huerta L, Avila A, Ortega M. Ellipsometric spectroscopy study of cobalt oxide thin films deposited by sol–gel. Solar Energy Mater Solar Cell 2006; 90: 2523-31.

[4] Ruzakowsky P, Urban FK, Tabet MF, McGahan WA. Optical properties of cobalt oxide films deposited by spray pyrolysis. J Vac Sci Technol 1996; 14(3): 685-93..

[5] Drasoven R, Monteiro R, Fortunato E, Musat V. Optical properties of cobalt oxide films by a dipping sol–gel process. J Non-Cryst Sol 2006; 352:1479-85.

[6] Barrera CE, Viveros GT, Avila A, Quintana P, Morales M, Batina N. Cobalt Oxide Films Grown by a Dipping Sol-Gel Process. Thin Solid Films 1999; 346: 138-44.

[7] Avila A, Barrera E, Huerta L, Muhl S. Cobalt oxide films for solar selective surfaces, obtained by spray pyrolisis. Solar Energy Mater Solar Cells 2004; 82:269-78.

[8] Hutchins MC, Wrigth PJ, Grebenick PD. Comparison of different forms of black cobalt selective solar absorber surfaces. Solar Energy Mater Solar Cell 1987; 16: 113.

[9] Barreca D, Massignan C, Daolio S, *et al.* Composition and microstructure of cobalt oxide thin films obtained from a novel cobalt(II) precursor by chemical vapor deposition. Chem Mater 2001; 13:588-93.

[10] Derin H, Kantarli K. Optical Characterization of thin thermal oxide films on copper by ellipsometry. Appl Phys A 2002; 75: 391-5.

[11] Forouhi AR, Bloomer I. Optical dispersion relations for amorphous semiconductors and amorphous dielectrics. Phys Rev 1986; B 34: 7018-26.

[12] Guenther RD, Guenther RB. Modern Optics. New York: John Wiley & Sons 1990.

[13] Palik ED, Handbook optical constants. New York: Academic Press 1985.

[14] Martens JW. Peters WL. An Ellipsometric and Magneto-Optical Study of Cobalt Ferrite Single Crystal. Solid Stat Commun 1982; 41(9): 667-9.

[15] Arakawa RT, Williams MW. Optical properties of aluminium oxide in the vacuum ultraviolet. J Phys Chem Solids 1968; 29: 735-44.

[16] Duffie JA, Beckman WA, Solar Engineering of Thermal Processes. New York: Wiley 1991.

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