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Ellipsometric spectroscopy study of cobalt oxide thin films deposited by sol–gel

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Abstract

Due to their unique optical properties, solar selective coatings enhance the thermal efficiency of solar photothermal converters. Hence it seems to be interesting to study the optical properties of promising materials as solar selective coatings. In an earlier work, it was demonstrated that sol–gel deposited cobalt oxide thin films possess suitable optical properties as selective coatings. In this work, cobalt oxide thin films were prepared by same technique and their optical properties were analyzed as a function of the dipping time of the substrate in the sol, using the spectroscopy ellipsometry, atomic force microscopy and X-ray photoelectron spectroscopy techniques. The optical constants (n and k) for these films, in the 200–800 nm range, are reported as a function of the dipping time. The fitting of ellipsometric data, I_s and I_c, for the glass substrate and the cobalt oxide thin film, as modeled with the Lorentz and Tauc–Lorentz dispersion relations, indicated that the film microstructure resembles a multilayer stack with voids. From these results, the Co_3O_4 and void percentages in the film were estimated. Both, thin film thickness and void/Co_3O_4 percentage ratio, were determined to be strongly dependent on the immersion time. Furthermore, the total thickness of a multilayered film was found to be the sum of thickness of each individual layer.

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1. Introduction

Selective coatings are currently used for improving the thermodynamic efficiency of the solar photothermal converters [1]. It has been reported that cobalt oxide has desirable optical properties to harvest the solar energy in an efficient way, when used as the selective coating in photothermal devices [1–3]. In spite of this, there are rather few studies on the optical properties of cobalt oxide, particularly, when it is prepared by the dipping sol–gel technique.

It is well known that, the physical properties and the chemical composition of sol–gel deposited thin films are strongly affected by the experimental parameters involved in this technique. In particular, withdraw rate, room relative humidity, sol viscosity and so on, are considered as the main parameters which determine the physicochemical properties, but the dipping time has been considered as a minor one. Hence there is no research addressed to analyze how the above properties could be affected by the dipping time.

In the present work, cobalt oxide thin films were prepared by the dipping sol–gel technique and their optical properties were analyzed as a function of dipping time. Our results showed that dipping time could be an important parameter because it determines the film microstructures, and then the film optical properties.

2. Experimental

2.1. Film preparation

Cobalt oxide thin films were grown on pyrex substrates using the dipping sol–gel technique. Prior to deposition process, the substrates were scrupulously cleaned with detergent, rinsed in deionized water, and soaked in absolute ethanol under ultrasonic agitation for 5 min.

In this work a particulate Co-propionate (0.1 M) based sol was used. Details on the sol preparation can be found elsewhere [1,2].

The films were grown in a closed chamber, maintaining the relative humidity at 55%. The deposition process was as follows: a precleaned substrate was immersed in the sol for a given dipping time, taken out from the sol at the withdraw rate of 1 mm/s, and then dried at room temperature. Dipping times of 3, 5, 10, 30 and 180 min were essayed.

Cobalt oxide thin films were obtained from the as-grown films after an annealing process in air at temperatures in the 300–500 °C range for 2 h.

2.2. Characterization techniques

The surface chemical composition of the as-grown and annealed films was analyzed by the X-ray photoelectron spectroscopy (XPS) technique, using a UHV VG Microtech MultiLab ESCA 2000 apparatus, equipped with an X-ray source with Al-target (K_{α}, 1486.6 eV) and a CLAM4 MCD photoelectron detector. The XPS measurements were carried out on representative samples and the surface chemical composition was determined before and after an erosion process with Ar-ions.

The surface morphology was studied with a Park Scientific Instruments atomic force microscope (AFM).

The optical properties were obtained from transmittance and spectroscopic ellipsometry (SE) measurements in the UV-Vis, using a UV-VIS Shimadzu 3101-PC double beam automatic scanning spectrophotometer and a phase modulated Jobin Yvon Uvisel DH10 ellipsometer, respectively. All ellipsometric data were recorded at an incidence angle of 70° and were analyzed using the Delta-Psi software Version 2.0.

3. Results and discussion

The chemical characterization of the films were made by the X-ray diffraction technique [2], being the main phase found to correspond to Co_3O_4 with a cubic symmetry. In this work, an XPS analysis was made for typical samples before and after a 10-s process of argon particles erosion. Such small erosion time indicates that the Co_3O_4 on glass substrate are very thin, because the signals of the substrate were observed immediately after this treatment. The XPS spectra of a representative sample of treated Co_3O_4/glass (3 min dipping time) at 400 °C, before and after surface erosion, is shown in Fig. 1. Peaks corresponding to Co 3p and O 1 s spectral lines appear clearly. After deconvoluting the O 1 s and Co 3p peaks, several phases corresponding to the substrate and the Co_3O_4 are identified, respectively. These results are summarized in the insets of Fig. 1.

AFM was used to observe the morphological characteristics of the Co_3O_4/glass films. The samples grown as a function of the dipping time (3, 5, 10 and 30 min) and annealed at 400 °C exhibit a significant difference in surface morphology according to the three-dimensional AFM images shown in Fig. 2. On the contrary, at first glance, these samples do not show any difference at all. A quantitative analysis of the surface roughness upon small scale images (Fig. 2) using the RMS function of the Quesant software led to RMS

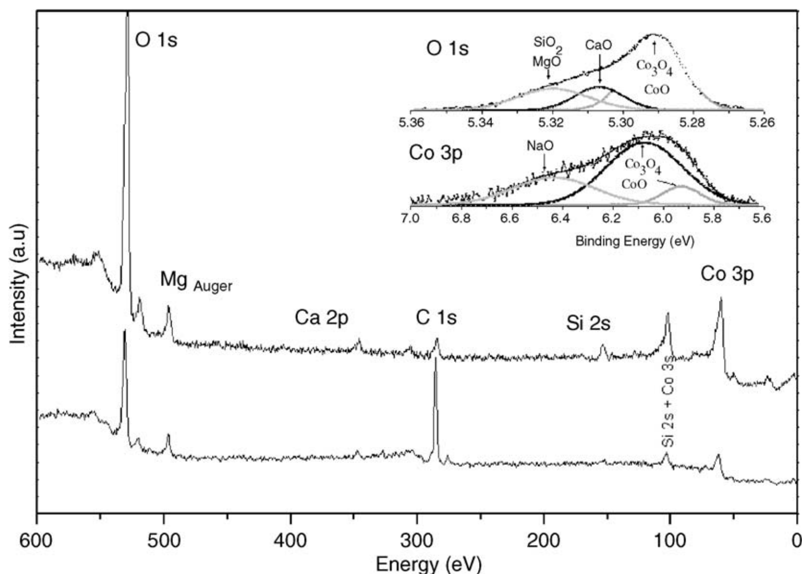

Fig. 1. XPS spectra of Co_3O_4/glass (3 min dipping time) at 400 °C before and after a surface erosion. The deconvolution analysis of O 1 s and Co 3p peaks are summarized in the insets.

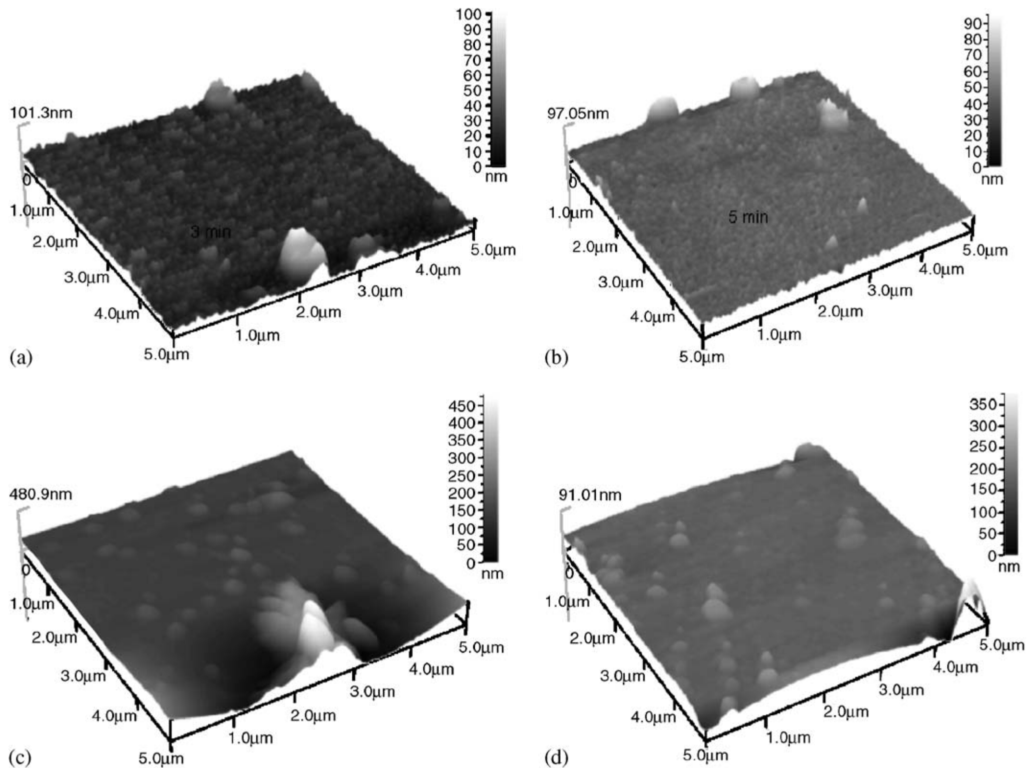

Fig. 2. Three-dimensional AFM view of Co_3O_4/glass, deposited by the dipping sol–gel process (a) 3, (b) 5, (c) 10 and (d) 30 min dipping time, 400 °C.

values in nm of 8, 2, 4 and 3 for the samples with 3, 5, 10 and 30 min dipping time, respectively.

A slice statistical analysis in the most representative sections of the samples was made too. This analysis provides data on the approximate film thickness and the void material ratio, which are useful in the SE analysis.

Transmittance: Fig. 3 shows the transmittance spectra of three representative samples, 3, 5 and 10 min dipping times. All the samples exhibit a similar optical behavior over entire spectral range 300–1100 nm, but there is a noticeable decrease in transmittance as the dipping time increases. This result indicates the same chemical composition of the films, in accordance with the XPS results, with the only change occurring in the thin film thickness as a function of a dipping time, as expected.

Spectroscopic Ellipsometry (SE): The SE analysis of Co_3O_4/glass films allows determining the basic optical properties, film thickness and surface roughness stated as the void material ratio. Therefore, two dispersion models, one (Lorentz) to simulate the glass substrate and the other (Tauc–Lorentz), the optical properties of the film, are proposed.

Glass substrate: To know the optical properties of Co oxide, it is necessary to determine and model the substrate, in order to fix its optical properties. Thus, the rear face of the substrate is polished in order to avoid the incident radiation leakage leading to erroneous

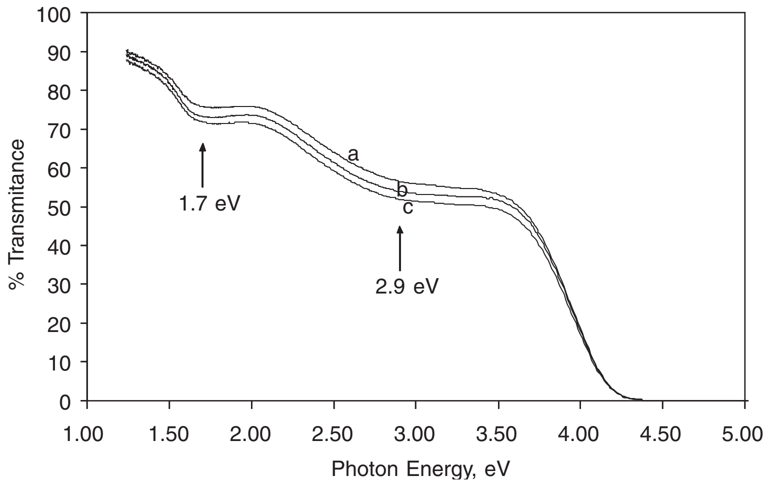

Fig. 3. Transmittance curves for Co_3O_4/glass with (a) 3, (b) 5 and (c) 10 min dipping time. Arrows designate the Co_3O_4 absorption bands.

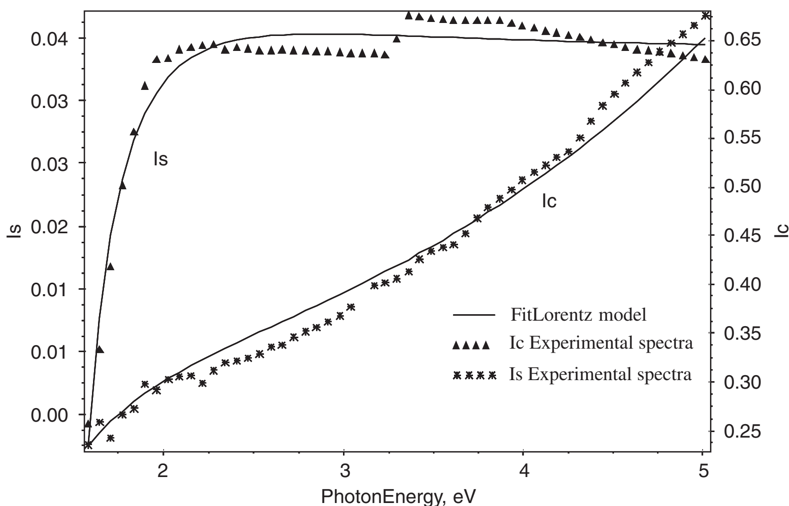

Fig 4. Ellipsometric parameters I_s and I_c and calculated adjustment (Lorentz dispersion model, continued line) as a function of wavelength, for the glass substrate.

readings. After choosing the right range wavelength, the incident polarized beam is directed to the unpolished glass surface. The glass substrate shows a slightly absorbent behavior as the wavelength grows, thus, a Lorentz oscillator dispersion model, to obtain a good fitting to the experimental data, was used.

The ellipsometric parameters I_s and I_c determined from the measurement of the glass substrate are shown in Fig. 4. A Lorentz dispersion model is used to model the glass substrate by means of the Delta-Psi software. Fig. 4 also depicts the adjustment of the

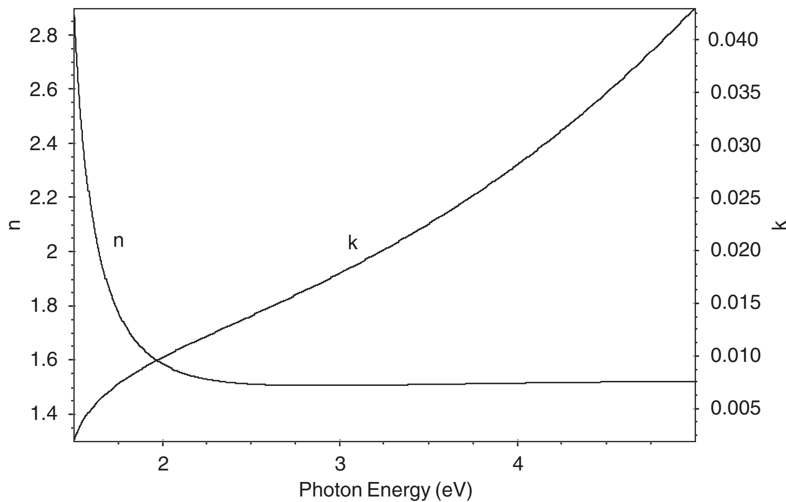

Fig. 5. Refractive index, *n*, and the extinction coefficient, *k*, as a function of wavelength, for glass substrate, obtained by SE.

Lorentz model to the experimental ellipsometric data, obtaining a good correlation, $\chi^2 = 1.2$ (a value χ^2 nearly 1 means a good adjustment).

When inverting the calculated I_s and I_c glass values, the real and imaginary components of the complex refractive index (refractive index, *n*, and the extinction coefficient, *k*) are obtained and depicted in Fig 5. The *n*, average value in almost all the wavelength range is 1.53 in accordance with the literature values. A slight absorption with the wavelength explains the growth of extinction coefficient proportionally to the photon energy. This shows that the substrate is not completely transparent and justifies the use of an absorbent model for the substrate characterization.

Cobalt oxide on glass substrate at different dipping times: Once the substrate has been properly fitted, the Co_3O_4 film on glass can also be modeled using a methodology similar to that used with a glass substrate. Due to the nature of the characterized material, Co_3O_4, which behaves as optically absorbent at different wavelengths, it is necessary to make use of one dispersion model capable of predicting these absorptions. A tandem structure of a glass substrate and Co_3O_4 film and, if necessary, a surface layer containing both Co_3O_4 and voids must also be proposed. The mixture of Co_3O_4 and voids has an average surface thickness and therefore this percentage fraction is associated with the roughness parameter, determined from the SE and corroborated by AFM.

The I_s and I_c experimental values for a representative (3-min dipping time) Co_3O_4/glass tandem are shown in Fig. 6 along with the fitted curve. This curve was obtained assuming certain percentage of voids in the Co_3O_4 surface film. A Tauc–Lorentz dispersion model for the Co_3O_4 film was used and a good correlation factor was again obtained ($\chi^2 = 0.85$).

Fig. 7 outlines the microstructure obtained by means of the Tauc–Lorentz dispersion model and the experimental evidence of AFM. Here, the layer of glass substrate of fixed optical properties, determined previously, together with a layer of compact Co_3O_4 and a surface layer made up of Co_3O_4 and a void fraction (indicative of surface roughness) were also determined. The surface roughness determined by the Co_3O_4 void ratio was estimated

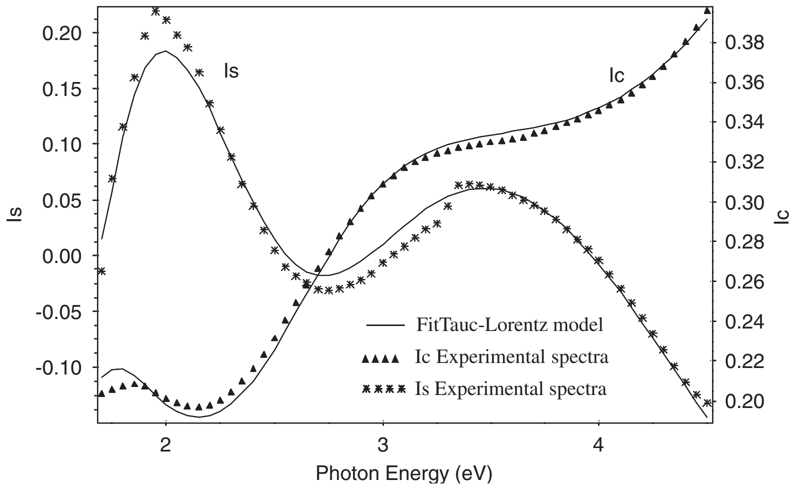

Fig. 6. Ellipsometric parameters I_s and I_c and calculated adjustment (Tauc–Lorentz, continued line) as a function of wavelength (1.65–4.5 eV), for the Co_3O_4/glass tandem.

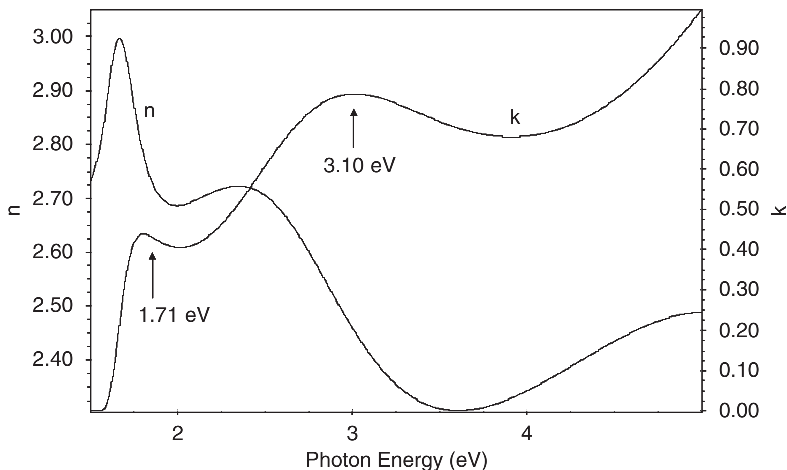

Fig. 7. Proposed tandem structure for the Co_3O_4 in glass, obtained for a representative sample, 3 min dipping time.

by SE and validated by the AFM results. Once the Co_3O_4/glass tandem ellipsometric data are adjusted, it is possible to determine the basic optical properties, *n* and *k*, of the Co_3O_4 film. Fig. 8 depicts the optical properties (*n*, *k*) for a representative sample, Co_3O_4/glass, 3-min dipping time. The spectra relative to the extinction coefficient show characteristic edges of absorption band (1.71 and 3.10 eV), corresponding to the Co_3O_4 phase, previously reported by other authors [4–7].

In Table 1, the main structure characteristics obtained by the SE studies, for the Co_3O_4/glass with different dipping times, are presented. In general, a proportional increase of the total film thickness as a function of the dipping time is observed. The Co_3O_4 film thickness practically stays constant in all cases, while the outer rough surface film increases

21% Co_3O_4	79% Voids	138 A Model dispersion of Tauc-Lorentz and air
100% Co_3O_4		87 A Model dispersion of Tauc-Lorentz
Glass substrate		Model dispersion of Lorentz

Fig. 8. Fundamental optical properties (n, k), obtained after fitting as a function of wavelength, for a representative sample, Co_3O_4/glass, 3 min dipping time, excluding the substrate contribution.

Table 1
Co_3O_4/glass film structure model results, as a function of dipping time, obtained by a spectroscopic ellipsometry study

Dipping time (min) Co_3O_4/glass	Co_3O_4 thin film thickness (Å)	Roughness layer thickness (Å)	Total thickness (Å)	Fractions % Co_3O_4 + % voids
3	85	125	210	21 + 79
5	86	131	217	24 + 76
10	87	138	225	21 + 79
30	89	153	242	23 + 77

continually. In the outer film, the material:void ratio practically stays constant in a volume proportion 21%:79%, respectively. These SE results agree with the AFM analysis, because, for instance, a typical AFM slice analysis of a 30-min dipping time sample indicates that the surface layer has a 150 Å film thickness with a 21.2%:78.8%, material:void ratio, respectively. These values are in tight correspondence with the SE results, Table 1.

In this work, the optical properties of Co_3O_4 thin film, prepared by the dipping sol–gel process, were determined. This result is in agreement with the optical properties of Co_3O_4 film, prepared with other experimental procedure, previously reported [4–7]. On the contrary, the Co_3O_4 thin film optical properties of a similar work [2] widely differ from this one, because its authors based their analysis on the Co_3O_4 transmittance spectra, and interpreted some of the absorption bands of this material like optical interferences, which lead them to commit an error in the calculation of the fundamental Co_3O_4 optical properties.

4. Conclusions

The influence of dipping time on the thin film thickness and optical properties of Co_3O_4/glass film, prepared by the sol–gel process, was studied. For a cobalt propionate 0.1 M sol solution, the film thickness, FT (Å), increases proportionally as a function of the dipping time, DT (min), according to the following relation, $FT = 196.3DT^{0.06}$, see Table 1. In general, it is observed that the film thickness does not grow as quickly as the dipping time increases, and probably this is the reason why the practical dipping time in sol–gel process is not taken into account as a practical and important process variable.

In some applications of solar materials, such as the preparation of photothermal coatings, it used to be necessary to have thicker thin films of more than 1000 Å. At the date, the typical procedure to grow up thicker thin films using the dipping sol–gel process consists of simultaneous dipping, withdrawal, drying and annealing, as many times as desired. Notwithstanding the unsurprising actual results, other sol systems must be studied in order to analyze the possibilities to grow films to the desirable thickness using only the dipping time as a main variable.

Optical constants, $n(\lambda) = (1.6-2.8)$ and $k(\lambda) = (0.005-0.04)$ and total film thickness, can be determined for thin absorbing Co_3O_4 films deposited by the dipping sol–gel process onto a slightly absorbing substrates. The SE fitting procedure uses a Tauc–Lorentz dispersion model for the modeling of Co_3O_4 films.

The Co_3O_4 film thickness determined by SE is made up of a solid layer and other rough one, Table 1. The rough surface layer is typically composed of a Co_3O_4:void ratio (21%:79%) (indicative of surface roughness), and was determined by SE and validated by the slice AFM analysis for representative samples.

The spectroscopic ellipsometry has been used to determine the Co_3O_4 optical properties and the film thickness as a function of the dipping time in a kind of sol–gel process. This result led to the conclusion that SE is a powerful tool to control and develop new thin film coatings.

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