

# Optical properties of Co and Co–Fe–Cr thin films deposited from an aerosol on glass substrates

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## Abstract

Thin films of Co and Co–Fe–Cr metal oxide films were prepared by deposition of an aerosol generated pneumatically from aqueous nitrate solutions. As substrates commercial gray glass has been used. Thermogravimetric (TG, DTG) and DTA measurements of initial nitrate components and their homogenized mixture were performed, and optical properties of deposited films important for privacy purposes (reflectance, transmittance), in the UV–visible and near-infrared regions up to 4761 nm as well as their surface roughness were measured. The reflectance values, defined at 550 nm wavelength, were 20–30% for Co-oxide films and 20–25% for Co–Fe–Cr films compared to 10–15% reported in literature. Transmittance values were 14–28% and 24–36%, respectively. For the substrate (uncoated gray glass) also used as a reference, these corresponding values were 5 and 57%. The surface roughness  $R_a$  correlates with the main deposition parameters, such as temperature and time of deposition, and the molarity of solutions used. Crystallinity in Co-oxide films has been detected by X-ray measurements. © 1998 Elsevier Science S.A. All rights reserved.

**Keywords:** Deposition process; Pyrolysis; Glass substrates; Optical coatings; Optical properties

## 1. Introduction

Methods of tinting glass by transparent metal oxide films in order to obtain particular optical properties and colour effects have already been known for many years. For privacy purposes, two optical properties of coated glass are of primary importance, namely reflectance and transmittance of light in the UV–visible and near-infrared regions. Of the methods used to deposit these films on large glass areas so far, the most often applied is the deposition from an aerosol generated pneumatically from a solution of particular metallic salts. Nitrates, chlorides or more recently various metalorganic salts are used as starting materials, dissolved or suspended either in aqueous medium or in some of many organic solvents. As a final product, Co-oxide films are usually required as they give the highest reflectance values. The most commonly used combination of Co–Fe–Cr oxide also gives sufficient mechanical durability and chemical resistivity.

Preparation of Co-oxide films from aqueous nitrate solutions has been described by Rios et al. [1], Raymond [2],

and Michelotti and Ohlberg [3]. Their films had a visible light reflection factor below 20%, usually being 10–15%. Patil et al. [4] used an aqueous solution of cobalt-chloride to prepare Co-oxide films. For Cr-coatings, Misho et al. [5] used aqueous nitrate solution, while Abbas and Jaboori [6] applied chromium-chloride dissolved in a water–ethanol combination. It seems, there is no mention in the literature concerning the preparation of Co–Fe–Cr films from aqueous nitrate solutions. However, during the few last years, the majority of producers of coloured glass used metalorganic salts, mainly those of Co, Fe and Cr, dissolved in an organic solvent [7–9]. For privacy glazing Gulotta et al. [10] used a combination of Co–Fe–Se. When compared with those prepared from nitrates, such films have visible light reflection factors around 25–50%. Recently, to eliminate health and environmental hazard as well as the cost of organic solvents, relatively water-insoluble coating reactants (mainly acetyl-acetonates) were used chemically suspended in an aqueous medium [11–14].

From the same reason as mentioned above, e.g., to eliminate health and environmental hazards and the cost of organic

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solvents and also the cost of relatively expensive organic solutes compared to the nitrate salts, we based our experiment on the idea of using environmentally safe aqueous nitrate solutions as a source of an aerosol to deposit metallic-oxide coloured films on glass substrates. It is the purpose of this paper to show that by applying Co, Fe and Cr-nitrate salts as solutes, and aqueous medium as a solvent, we are able to obtain films deposited on glass substrates with relatively good privacy properties, having a visible light reflectance factor (defined usually at 550 nm wavelength) in the interval 20 to 30% compared to the previously reported 10–15% [2].

Perhaps it is of importance to stress that the method used is industrially scalable and may be used to coat large areas of float glass needed for instance in the car and building industries, or for any other industrial applications where colour effects applied on the glass substrates are required. If necessary, the ecologically undesirable nitrogen oxides produced during thermal decomposition of nitrates could be liquidated by a catalytic reaction similar to that used in car engines. A great advantage of the use of nitrates is also their relatively low price.

## 2. Experimental

As an aerosol source we prepared two types of aqueous nitrate solutions, the solution of Co-nitrate with 0.1 M (molarity) and that of Co-Fe-Cr nitrate mixture with 0.0025 M and 0.0005 M with the metallic cation ratio Co:Fe:Cr=12:3:1. Mallinckrodt chemicals and deionized water were used throughout. To generate an aerosol we applied a Spraying System gun with 0.4 mm fluid orifice diameter. Commercial gray glass, 4.0 mm thick and about 1 cm<sup>2</sup> in surface area, was used as a substrate for the film deposition. The working temperature of the molten-tin heater varied in the range 500 to 600°C with the substrate surface temperature controlled by a thermocouple. The drop in the substrate surface temperature during the deposition time of 5–15 s was 50 to 100°C as given by our experimental arrangement. Both flux flow and aerosol carrier gas flow used to pulverize droplets were controlled carefully by flow meters. Prior to the film deposition we performed thermogravimetric (TG, DTG) and DTA measurements on all the nitrate components as well as their homogenized mixture to find informative values of the nitrate decomposition temperatures and their transformation to oxides. The equipment used for these measurements was a Derivatograph 1500 MOM device, with initial weight of the samples being 250 mg. Measurements were performed in static air atmosphere with a heating rate of 5°C/min in the temperature interval 20 to 600°C.

Synthesized films were characterized by optical measurements of their reflectance and transmittance and by the surface roughness measurements. The UV-visible light measurements were performed by a UNICAM 8700 Spectrometer in the wavelength range 200 to 900 nm with a resolution of 1 nm. While transmittance was measured in a standard config-

uration, the reflectance was measured in a close-normal (12°) set up. The near-infrared region measurements were performed by a 750 Magna-IR NICOLET Spectrometer in the range 909 to 4761 nm with a resolution 0.16 nm ( $\sim 4 \text{ cm}^{-1}$ ). As in the UV-visible case, the transmittance was measured in a standard set up and the reflectance in the close-normal (12°) configuration. The surface roughness  $R_a$ -values were determined by a SLOAN DEKTAK II profilometer and evaluated following the formula:

$$R_a = \frac{1}{L} \int_0^L |y| dx \quad (1)$$

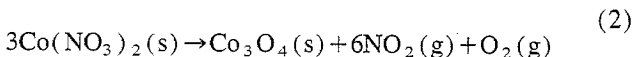
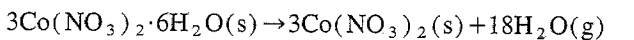
where  $L$  is the length of a measuring interval, and  $y$  is an amplitude of the particular roughness value on the length  $dx$ .

Preliminary X-ray diffraction analysis of deposited films was performed by a standard Siemens D-500 diffractometer using Cu  $K\alpha$  radiation, however, the results have shown that probably the more sensitive method of a low-angle X-ray diffraction at grazing incidence should be applied.

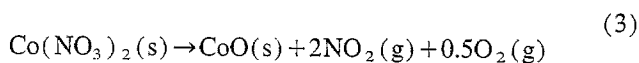
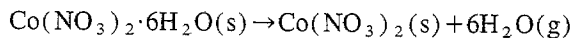
## 3. Results and discussion

From the thermogravimetric (TG, DTG) and DTA measurements we found that both Co-nitrate and the Co-Fe-Cr nitrate mixture were decomposed in a couple of endothermic steps in the interval of about 50 to 280°C. Thickness of deposited films was estimated to be 400–500 Å.

Results of TG, DTG and DTA measurements are plotted in Fig. 1 (a, b, c) for all three nitrate components. Measurements of their homogenized mixture gave similar results. Each component decomposes in two endothermic steps with the first step representing the loss of water. Cobalt nitrate, which in crystalline state forms hexahydrate  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , decomposes in static air in the temperature range 60 to 280°C according to the following chemical reactions:



The appropriate TG, DTG and DTA diagrams are shown in Fig. 1a. The first endothermic step, representing the loss of water, continues by the second one which leads to the formation of black  $\text{Co}_3\text{O}_4$ . This oxide contains Co(II) and Co(III) bound together in a spinel structure  $\text{Co}^{2+} \text{Co}_2^{3+} \text{O}_4$  [15]. The total measured weight loss at 280°C was 69.6%, calculated from Eq. (2) was 72.4%. The decomposition process may be influenced by the concentration of oxygen in the measuring environment. At reduced oxygen content, an olive-green CoO is formed according to the formula



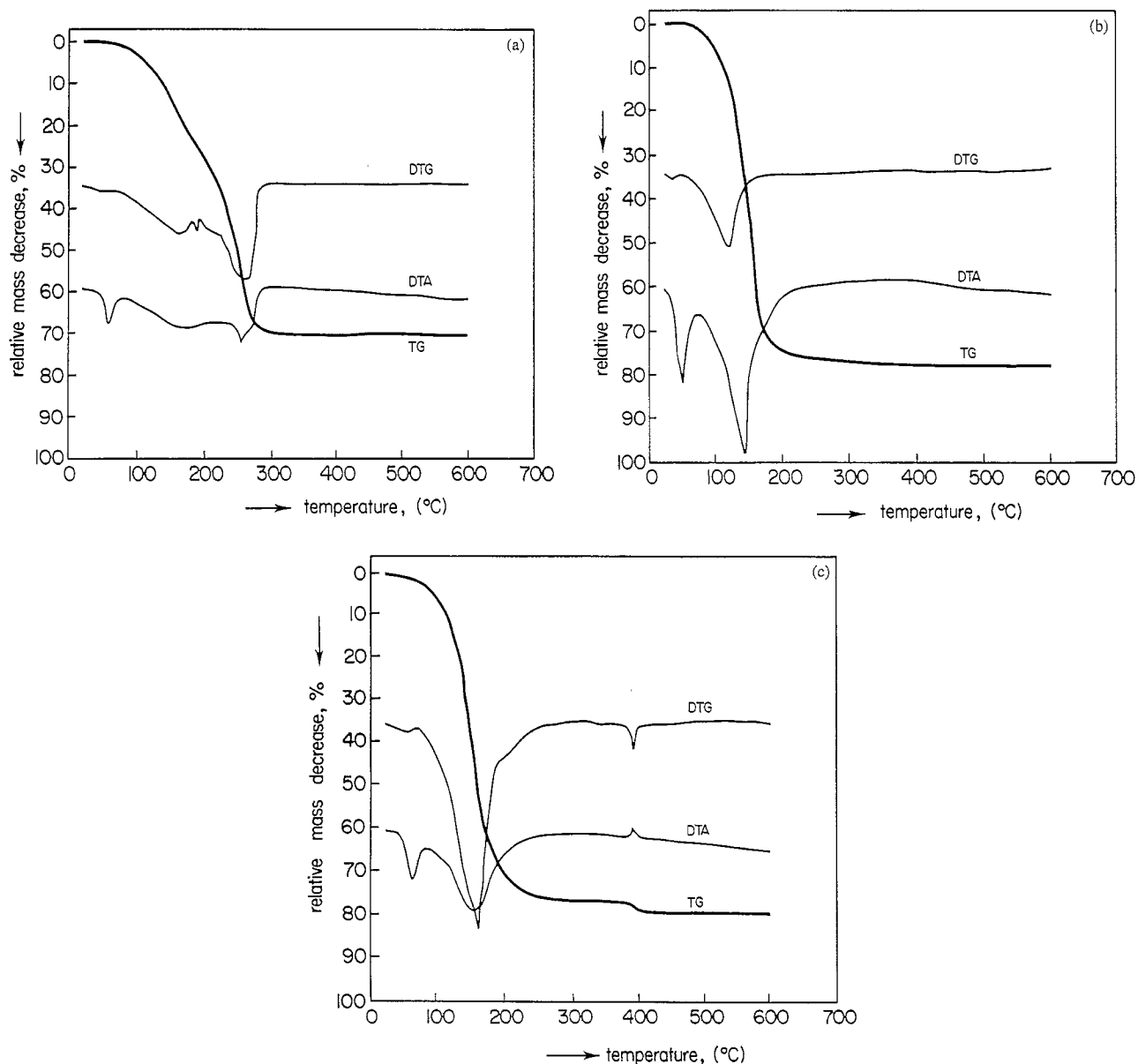
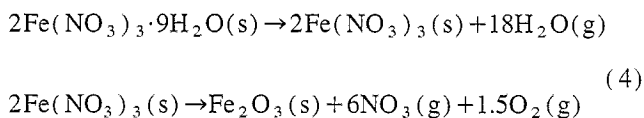


Fig. 1. Thermogravimetric (TG, DTG) and DTA data obtained by measurement in static air atmosphere, for (a) Co-nitrate, (b) Fe-nitrate, (c) Cr-nitrate.

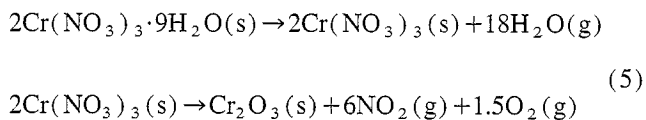
The CoO can be converted to  $\text{CO}_3\text{O}_4$  by heating it in air at  $600^\circ\text{C}$  [15].

Ferric (III) nitrate, forming in crystalline state nonahydrate  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ , decomposes in static air atmosphere within the temperature range  $60$  to  $210^\circ\text{C}$  in two reaction steps:



The TG, DTG and DTA diagrams are plotted in Fig. 1b. Again, the first endothermic step represents loss of water, the second one leads to the formation of  $\text{Fe}_2\text{O}_3$ . The measured weight loss at  $210^\circ\text{C}$  was  $77.9\%$ , the calculated one following the reactions (4) was  $80.2\%$ .

Also, chromium (III) nitrate, forming in crystalline state nonahydrate  $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ , decomposes in static air in the temperature interval  $50$  to  $280^\circ\text{C}$  in two endothermic steps:



The measured TG, DTG and DTA curves are shown in Fig. 1c. The weight loss at  $280^\circ\text{C}$  was  $76.3\%$ , the calculated one following reaction (5) was  $81.0\%$ . The origin of the exothermic reaction at  $380^\circ\text{C}$  leading to a weight loss of about  $1.7\%$  is not fully understood. One cannot rule out that the

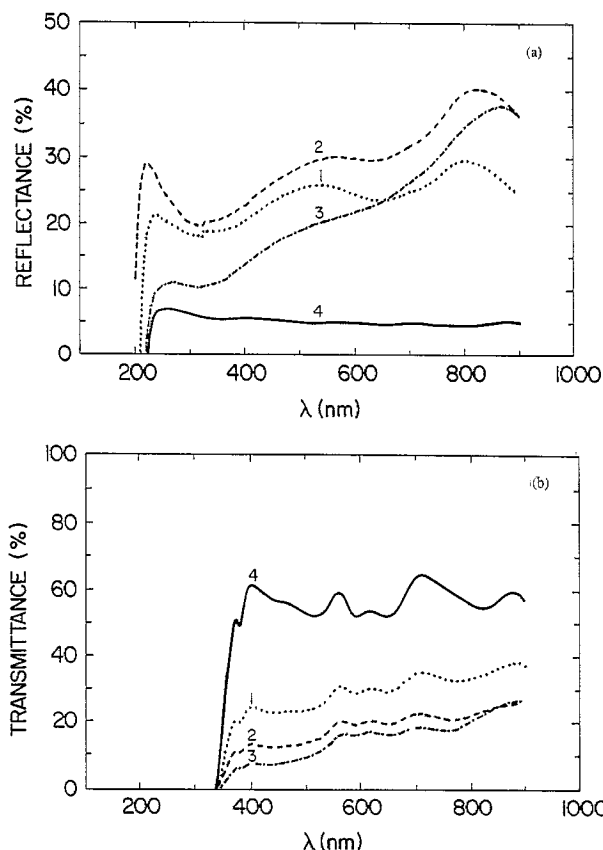
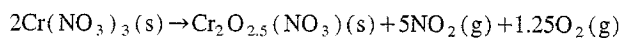
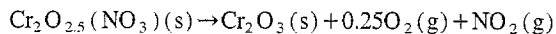


Fig. 2. Optical properties [(a) reflectance, (b) transmittance] of Co-oxide films (1,2,3) and those of uncoated gray glass (4) in the UV-visible region up to 900 nm. The temperature of substrate heater  $T_s = 550^\circ\text{C}$ , solution molarity  $M = 0.1$ , and time of deposition  $t_d = (1) 5$  s, (2) 10 s and (3) 15 s.

second of reactions (5) might be divided more precisely into the two following chemical processes:



(6)



In this case, the  $\text{Cr}_2\text{O}_{2.5}(\text{NO}_3)$  would be formed at  $280^\circ\text{C}$  and its full conversion to the  $\text{Cr}_2\text{O}_3$  will be concluded at  $380^\circ\text{C}$ .

All investigated compounds belong to the group of covalent nitrates, which, at proper deposition conditions, may even partially vaporize [16]. In such a case, the deposition takes place, at least partially, from the vapour, which is similar to the true chemical vapour deposition (CVD) process. This is also the reason why the product of nitrate decomposition, the metallic oxide film, sticks mechanically very well to the glass substrate.

Dependence of reflectance and transmittance values in the UV-visible region for Co-oxide films (1,2,3) and the uncoated gray glass (4) on the light wavelength is shown in Fig. 2a and b. In this case, films were deposited at a substrate heater temperature of  $550^\circ\text{C}$  from a 0.1 M nitrate solution for 5, 10 and 15 s. The reflectance values defined at 550 nm wavelength are in the region 20–30% for films (1–3). Reflec-

tance of reference sample (4) is 5%. It seems that from the point of view of obtained reflectance of deposited films required for privacy purposes, the optimum deposition time in this particular case is 10 s, giving the value of 30% at 550 nm. For a deposition time of 15 s the film (3) is already too thick, dark, reddish, and therefore, also the IR part of this dependence is more pronounced. The transmittance values for samples (1–3) are in the interval 14–28% with the thicker film (3) giving the lowest value of 14%. Transmittance of uncoated gray glass at 550 nm is about 57%.

Optical properties of Co-oxide films presented partially and in more detail in Fig. 1 are illustrated for the complete UV-visible and near-infrared region up to 4761 nm wavelength in Fig. 3. We may conclude that for the presented Co-oxide films deposited on gray glass we obtained a reflectance of 20–30% and transmittance of 14–28%. Reflectance of reference gray glass was 5% and transmittance 57%.

It is well known that the addition of ferric and chromic oxide to that of cobalt gives improved mechanical and chemical resistance of deposited films, however, at the same time, it may worsen the optical properties, e.g., this addition may deteriorate the reflectance and increase the transmittance of films. Therefore, the volume amount of Co-oxide in the film is usually kept at its maximum and the addition of two other elements is then optimized to obtain a compromise between

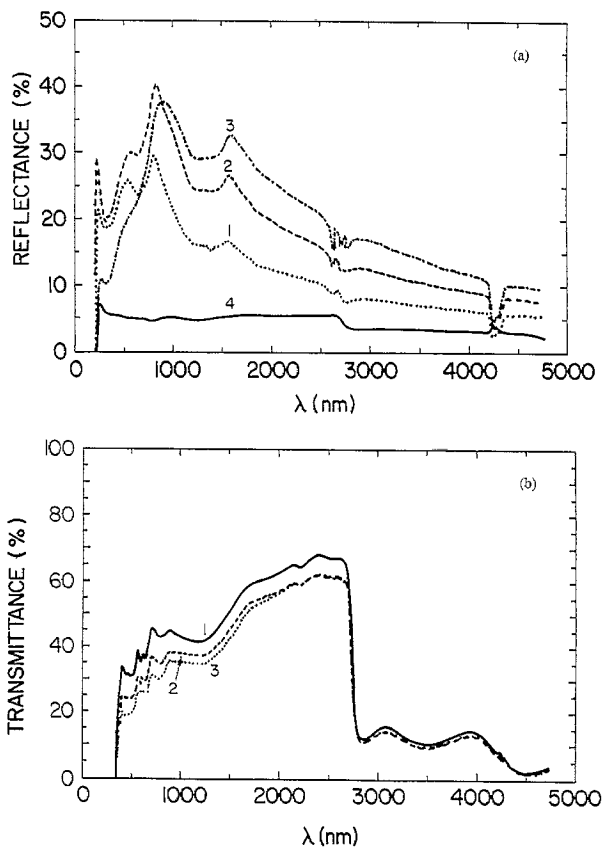


Fig. 3. Optical properties [(a) reflectance, (b) transmittance] of Co-oxide films (1,2,3) and those of uncoated gray glass (4) from Fig. 1 in a complete UV-visible and near-infrared region up to 4761 nm.

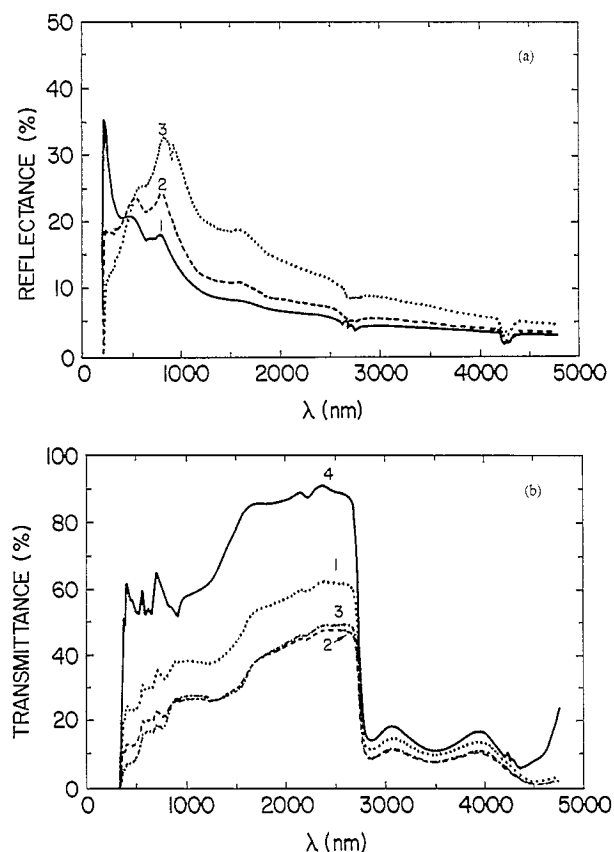


Fig. 4. Optical properties [(a) reflectance, (b) transmittance] of Co:Fe:Cr = 12:3:1 films in a complete UV-visible and near-infrared region up to 4761 nm. Curve (1)  $T_s = 600^\circ\text{C}$ ,  $t_d = 10$  s,  $M = 0.0025$ ; (2)  $T_s = 550^\circ\text{C}$ ,  $t_d = 10$  s,  $M = 0.0025$ ; (3)  $T_s = 550^\circ\text{C}$ ,  $t_d = 10$  s,  $M = 0.005$ .

good optical, mechanical as well as chemical properties. Optical properties of the oxide Co:Fe:Cr = 12:3:1 films are demonstrated in Fig. 4 for the whole UV-visible and near-infrared region up to 4761 nm. Similarly to the case of Co-films, the optimum deposition parameters are  $T_s = 550^\circ\text{C}$ ,  $t_d = 10$  s for a solution molarity in this case of  $M = 0.0025$ . The obtained reflectance values at 550 nm wavelength were 20–25% with the transmittance being 24–36%.

In all studied samples we observed some kind of 'cut-off' at about 340 nm for transmission characteristics. This phenomenon together with various peaks on the spectral characteristics are to a great extent determined by the absorption characteristics of the glass substrate as well as by the presence of various dopants introduced into the glass to obtain its gray appearance. The effect of depositing oxide films on such a type of substrate is even more evident on the reflectance characteristics, where, besides the interference undulation of curves, a glitch characteristic for the absorption edge is observed in the majority of reflectance curves.

Results of the surface roughness  $R_a$  measurements are summarized in Table 1 and they seem to correlate with the film preparation conditions. The most smooth surface is of course that of uncoated gray glass ( $R_a = 25 \text{ \AA}$ ) giving lowest reflectance and highest transmittance. Surface roughness is more

Table 1

Surface roughness  $R_a$  of prepared Co and Co-Fe-Cr metal oxide films compared to that of uncoated reference gray glass

Deposited film	Deposition parameters			Surface roughness $R_a$ ( $\text{\AA}$ )
	$T_s$ ( $^\circ\text{C}$ )	$t_d$ (s)	$M$	
Uncoated gray glass				25
Co-oxide	550	5	0.1	280
	550	10	0.1	345
	550	15	0.1	415
Co:Fe:Cr = 12:3:1	600	10	0.0025	135
	550	10	0.0025	95
	550	10	0.005	209

pronounced in the case of single Co-oxide films with the  $R_a$  values correlating with time of the film deposition.

Our preliminary X-ray diffraction measurements of synthesized films revealed peaks from Co-oxide films; however, we were not able to distinguish any peaks in the case of Co-Fe-Cr films, where apparently the volume fraction of individual oxide components was rather low. Peaks detected in the case of Co-films confirm their developed crystallinity and thus also higher reflectivity compared to Co-Fe-Cr films. However, as we have mentioned previously, to increase the sensitivity of these measurements, the low-angle X-ray diffraction at grazing incidence must be applied in future investigations.

#### 4. Conclusions

We have prepared Co, and Co-Fe-Cr metal oxide films deposited on commercial gray glass substrates from an aerosol generated pneumatically from aqueous nitrate solutions. Synthesized films were characterized by measuring their optical properties important from the point of view of privacy purposes, e.g., reflectance and transmittance, and by measuring their surface roughness. Preliminary X-ray study concerning the developed crystallinity of deposited films was also performed.

The reflectance values of Co-oxide films obtained in UV-visible 550 nm light were 20–30% compared to 10–15% known from the literature. The transmittance of these films was 14–28%. Reflectance and transmittance of reference uncoated gray glass were 5 and 57%, respectively. It seems there is no report in the literature concerning preparation of Co-Fe-Cr films from aqueous nitrate solutions. For this type of films we obtained reflectance of 21–28% and transmittance of 24–36%, both defined at 550 nm wavelength. The optimum deposition parameters giving highest reflectance seem to be similar for both types (Co and Co-Fe-Cr) of films, i.e., substrate heater temperature  $T_s = 550^\circ\text{C}$ , deposition time  $t_d = 10$  s, and a solution molarity  $M = 0.1$  for Co-oxide films and  $M = 0.0025$  for Co-Fe-Cr films.

We have also found that optical properties of deposited films are strongly influenced by properties of glass substrates

as well as by dopants used to obtain the gray appearance of glass. As far as the optical properties of deposited films are concerned, we consider our results as very preliminary and still far from being fully optimized. This work is now under way in our laboratory.

Results of surface roughness  $R_a$  measurements seem to correlate well with deposition parameters such as temperature and time of deposition, and molarity of the aqueous nitrate solutions used. Higher solution molarity and longer deposition times give film with rougher surfaces. When evaluating these results we came to the conclusion that the film surface might be smoother when instead of a pneumatic generation of an aerosol we would use ultrasonic excitation. Ultrasonic atomization, invented by Spitz and Viguie [17], is a very convenient and modern method of growing various materials either in a thin-film form (for example, semiconductors [18–21], superconductors [22,23], or in a form of ultrafine homogeneous powders [24,25], having some important advantages over the generally used conventional pneumatic nebulization. One of the main deposition parameters is the aerosol mean droplet diameter, which is about one order of magnitude less than in the case of pneumatic generation. This kind of work is under way in our laboratory and as the results show, the surface roughness of prepared films has dropped substantially. On the other hand, such smoother surfaces are also more resistant against chemical attacks. Some preliminary results of this work were published recently [26]. Chemical durability test, performed by immersing the film samples into concentrated (37%) HCl, revealed that the films prepared by deposition from an aerosol generated by ultrasonic excitation have about twice the durability of films deposited from a pneumatic aerosol, when all investigated films were deposited under otherwise similar conditions.

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### References

- [1] E. Rios, G. Poillerat, J.F. Koenig, J.L. Gautier, P. Chartier, *Thin Solid Films* 264 (1995) 18.
- [2] R.F. Raymond, U.S. Patent No. 2,688,565 (Sept. 7, 1954).
- [3] J.E. Michelotti, S.M. Ohlberg, U.S. Patent No. 4,308,319 (Dec. 29, 1981).
- [4] P.S. Patil, L.D. Kadam, C.D. Lokhande, *Thin Solid Films* 272 (1996) 29.
- [5] R.H. Misho, W.A. Murad, G.H. Fattahallah, *Thin Solid Films* 169 (1989) 235.
- [6] A.K. Abbas, E.M. Jaboori, *Phys. Stat. Sol. (A)* 116 (1989) K111.
- [7] E. Plumet, R. Posset, U.S. Patent No. 4,129,434 (Dec. 12, 1978).
- [8] J.H. Mayer, S. Guerra, U.S. Patent No. 4,294,881 (Oct. 13, 1981).
- [9] H.E. Donley, U.S. Patent No. 4,401,474 (Aug. 30, 1983).
- [10] J.A. Gulotta, J.F. Krumwiede, L.A. Kutilek, A.V. Longobardo, R.B. Heithoff, U.S. Patent No. 5,393,593 (Feb. 28, 1995).
- [11] Ch. Greenberg, *J. Electrochem. Soc.* 132 (1985) 1394.
- [12] Ch.B. Greenberg, U.S. Patent No. 4,719,127 (Jan. 12, 1988).
- [13] Ch.B. Greenberg, *J. Electrochem. Soc.* 140 (1993) 3332.
- [14] P. Ruzakowski Athey, F.K. Urban III, M.F. Tabet, W.A. McGahan, *J. Vac. Sci. Technol. A* 14 (1996) 685.
- [15] N.N. Greenwood, A. Earnshaw, *Chemie Prvku, Informatorium, Praha*, 1993, p. 1375. (Translation from English: *Chemistry of Elements*, Pergamon, Oxford, 1984).
- [16] F.A. Cotton, G. Wilkinson, *Anorganicka Chemie, Academia, Praha*, 1973, p. 836. (Translation from English: *Advanced Inorganic Chemistry*, Wiley, New York, 1996).
- [17] J. Spitz, J.-C. Viguie, French Patent No. 2,110,622 (1972).
- [18] G. Blandenet, M. Court, Y. Lagarde, *Thin Solid Films* 77 (1981) 81.
- [19] M. Langlet, E. Senet, J.L. Deschanvres, G. Delabougliose, F. Weiss, J.C. Joubert, *J. Less-Common Met.* 151 (1989) 399.
- [20] M. Langlet, D. Walz, P. Marage, J.C. Joubert, *Thin Solid Films* 221 (1992) 44.
- [21] M. Langlet, J.C. Joubert, in: C.N.R. Rao (Ed.), *Chemistry of Advanced Materials*, Blackwell, Oxford, 1993, p. 55.
- [22] M. Jergel, *Supercond. Sci. Technol.* 8 (1995) 67.
- [23] M. Jergel, A. Conde-Gallardo, C. Falcony Guajardo, V. Strbik, *Supercond. Sci. Technol.* 9 (1996) 427.
- [24] G.L. Messing, J.C. Zhang, G.V. Jayanthi, *J. Am. Ceram. Soc.* 76 (1993) 2707.
- [25] O. Milosevic, B. Jordovic, D. Uskokovic, *Mater. Lett.* 19 (1994) 165.
- [26] M. Jergel, M. García, A. Conde-Gallardo, C. Falcony, M.A. Canseco, G. Plesch, *Thin Solid Films* 305 (1997) 157.