Magnesium, nitrogen codoped Cr_2O_3: A p-type transparent conducting oxide

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A p-type Transparent Conductive Oxide (TCO) was synthesised by codoping of poorly-conducting chromium oxide (Cr_2O_3) with magnesium and nitrogen. We demonstrated that the codoping produced a TCO with good figure of merit despite using spray pyrolysis for deposition. The nitrogen enhances the specular transparency of the films in the visible range (400-700 nm) and, Mg improves the conductivity while retaining the p-type character of the material. Co-doping with both elements produces a p-type oxide with a low resistivity of $3\,\Omega$cm and transmission up to 65% for a 150 nm thick film. A comparison with other known p-type materials is given.

p-type transparent conducting oxides (TCOs) have attracted much attention since the deposition of thin films of $CuAlO_2$ delafossite structure was reported in 1997.[1] Producing p-type thin films with both good transparency and high conductivity represents a key challenge in the development of optoelectronics devices such as organic light emitting devices, transparent thin film transistors and solar cells.[2] Compared to conventional n-type TCOs, p-type oxides are generally less conductive and less transparent[2–5], with the lowest resistivity reported to be $0.45\ 10^{-2}\ \Omega$cm (transmission 30%)[6] and the highest transmission not exciding 70% for oxides. Better properties were reported for oxy-chalcogenides material[7,8] or CuS-quantum dots[9]. However, cost-effective production of these materials on a large scale is challenging.

Most p-type TCOs reported so far have a delafossite structure with a composition $CuMO_2$ where M is a trivalent cation such as Al, In, Ga or Cr.[2–4,10] Properties of such materials improve as a result of substitution of the trivalent element (M) for a divalent cation such as Mg, Fe, Ca. Other p-type TCO are the $CuScO_{(2+x)}$[11], $CuSr_2O_2$[12], some spinel structures such as $ZnRh_2O_4$[13] and their modifications.

In this study, we adopted a different approach. A poorly conducting p-type material, chromium oxide, (Cr_2O_3, Eskolaite) was chosen as host matrix and both cation and anion doping were performed symoltaneously in order to improve the conductivity and enhance the transparency. Spray-pyrolysis was used as deposition technique due to its robustness and versatility enabling the screening of multiple precursors. However,this technique has the drawback of producing films with lower quality and properties in comparison to the same material deposited by more advanced techniques such as sputtering, chemical vapour deposition (CVD) or pulsed laser deposition (PLD).[14,15] Details of the spray pyrolysis set-up are given elsewhere.[16] Films were deposited on glass substrates (Roth cover slips, thickness 0.17 mm). For the deposition, $Cr(NO_3)_3$ has been used as Cr precursor, deionised water as solvent and oxygen as a carrier

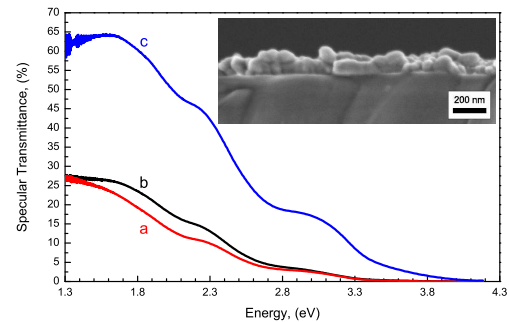FIG. 1. UV-VIS transmittance of (a) Cr_2O_3, (b) Cr_2O_3:Mg and (c) Cr_2O_3:(Mg,N) grown with precursor ratios of Cr:Mg 9:1 and Cr:N of 1:4. The inset shows an examplary SEM crossection used to determine film thickness

gas. Doping has been carried out using $MgCl_2 \cdot 6(H_2O)$ as cation dopant and $NH_4CH_3CO_2$ as anion dopant. All films were deposited by using 0.1 M concentration of Cr in solutions. N and Mg concentrations were changed over a range of 0.2 to 0.5 M and from 0.005 to 0.02 M respectively. The high nitrogen concentration in the solution was required due to a low nitrogen incorporation rate. For each precursor solution the pH was adjusted to 0 by adding HCl.

Nitrogen incorporation has mainly an effect on the optical properties of the film as measured by UV-Visible Cary 50 spectrophotometer (Fig. 1). The optical properties of the film do not change upon doping with only Mg, while an increase in transmission has been observed as the nitrogen concentration in the solution was increased. The actual incorporation of nitrogen was confirmed by X-ray photoelectron spectroscopy (XPS), by using an Omicron MultiprobeXP system (Mg X-ray source, E125 Analyser). Experimental data were analysed using the CasaXPS software. The N 1s state was identified at the characteristic binding energy (E_b=397 eV). A quantitative analysis is however difficult due to the poor signal to noise ratio and the removal of N during surface cleaning (Ar sputtering). Therefore the upper limit of the nitrogen within the sample was esthimated to be 5-10%.

There could be several reasons for the increased trans-
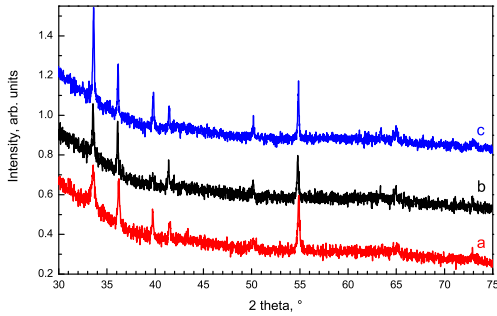
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FIG. 2. Xray Powder diffraction patterns of (a) undoped, (b) Mg doped and (c) Mg,N codoped Cr_2O_3.

FIG. 3. Figure of merit for Cr_2O_3 doped with Mg and N. Magnesium concentration [Mg] has been screen at a fixed nitrogen concentration [N] in the solution and fixed temperature: (▲) [N]=0 M T=480-510°C (■) [N]=0.4 M and T=480°C, (□) [N]=0.4 M and T=510°C. The inset shows the figure of merit for Cr_2O_3:(Mg,N) samples grown using [Mg]=0.01 M and T=510° for different [N] concentration.

mittance. The formation of a different phase, a systematic decrease in the thickness or a systematic difference in the surface roughness were all excluded as causes for increased transmittance as follows. The crystallographic phase, as determined by X-ray diffraction (Bruker D8 Discovery) is the same for all the samples (Fig. 2). Patterns were analysed by numerical reconstruction of line profiles according to the Rietveld method using the MAUD software package and only a single phase, Cr_2O_3, with a corundum structure (PDF number 01-072-3533) was found (Fig. 2). No significant difference was found in lattice parameters for undoped and doped samples (a=4.956±0.005 Å, c=13.598±0.005 Å).

Thickness of the samples was determined by cross-sectional scanning electron microscopy (SEM). No significant difference in the thickness was found between undoped and doped samples. Also the microscopic surface roughness, as determined by atomic force microscopy is comparable for all the samples and independent of the nitrogen concentration. There are two more possible reasons for the increased transmittance. Profilometer measurements show the presence of a macroscopic structure in the order of 10-50 μm scale caused by the impact of larger, not fully evaporated droplets. This is a known limitation of spray pyrolysis, using water and air blast nozzles.[16] Samples grown with nitrogen show less prominent structures and thus they are more homogeneous. However this cannot fully explain the higher transmission, especially if one takes into account that a similar increase in transmission has been noted for amorphous Cr_2O_3 grown by magnetron sputtering in nitrogen rich conditions[17]. This suggests that presence of Cr-N bonds is a contributing factor. It is possible that the N-Cr bond produces a different crystal field around the Cr atom, determining a systematic change in the absorption coefficient. All nitrogen-only doped samples are poorly conducting or insulating. To increase the conductivity of the oxide several cations such as Li, Mg, Ca, In and Zn were tested as doping elements. Li or Ca or In incorporation leads to insulating samples. Doping with Mg and Zn leads to conductive samples, but in the case of Zn only a marginal improvement were observed. In con-
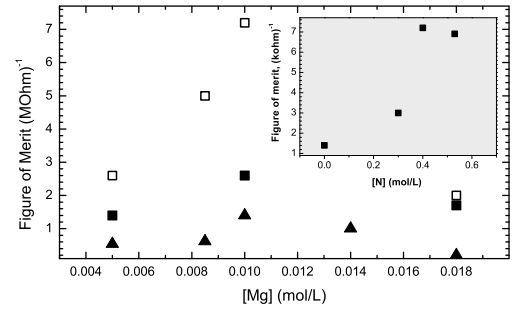
trast doping with Mg produced a remarkable improvement in the electrical properties while maintaining the p-type character of the current carriers. Mg doping of Cr_2O_3 alone has previously shown to lead to p-type conductive samples.[18] However, in that report, the presence of Mg was directly linked to a *reduction* in transmission, likely due to the formation of deep level defects leading to an unwanted broad band absorption. In this study we have shown that by employing a simultaneous (Mg,N) codoping, the transmittance of films can be significantly *improved*, while samples remain conductive. This makes this material interesting in the context of p-type transparent conducting oxides for the first time.

To find the optimum growth conditions, screening experiments have been performed to maximise the figure of merit $F=\sigma/\alpha = -1/(R_{sh}\ln(T+R))$[19], with conductivity σ, absorption coefficient α, sheet resistance R_{sh}, **average** transmittance T, and reflectance R. The latter two were calculated from values at different energies in the visible range (E=1.77, 2.0, 2.25, 2.48, 2.75, 3 eV). As often only transmission data have been published an approximate value of $F = -1/(R_{sh}\ln T)$ has been used here. Growth temperature as well as N and Mg concentrations were screened in order to get the best figure of merit for the Cr_2O_3:(Mg,N) co-doped system as shown in Fig. 3. The best F for Cr_2O_3 with only cation doping was found at Cr:Mg 9:1 and deposition temperature in the range 480–510°C The resistivity decreased from 400 Ωcm for plain Cr_2O_3, to 15 Ωcm for Cr_2O_3:Mg at a ratio Cr:Mg of 9:1. The value of resistivity we observed is slightly higher than those reported in literature for Cr_2O_3:Mg[18]. This has to be attributed to the use of a different deposition technique, spray pyrolysis, producing films with lower quality. The actual incorporation of Mg and its ratio with respect to Cr were confirmed by XPS measurements. The carrier type was confirmed by measurements of the Seebeck coefficients (+70±20 μVK⁻¹). Resistivity measurements were performed over a temperature range 50-150°C and

a carrier activation energy of 200 meV was derived from the Arrhenius plot. F improves drastically upon (Mg,N) co-doping as a result of a major enhancement of both electrical and optical properties. Best conditions were found at Cr:Mg 9:1 and Cr:N 1:4 (ratios in solution) and deposition temperature of 510°C. The transmission for these samples was as high as 65%, and resistivity as low as 3 Ω cm for films with thickness of about 150 nm. According to the Hall coefficient ($+1 cm^3 C^{-1}$) these samples are p-type conductors. The Seebeck coefficient was similar to the Mg doped case ($+70 \pm 20 \mu VK^{-1}$). Typical Hall mobility values were around $0.1 cm^2 V^{-1}s^{-1}$ and carrier concentration was in the order of $10^{19} cm^{-3}$. The carrier activation energy was 190 meV as determined by the Arrenhius plot. This is an improvement by almost two orders of magnitude with respect to the undoped Cr_2O_3 and by a factor of 3 with respect to doping with Mg only.

In order to understand how this material compares with other known p-type TCOs, we calculated the figure of merit in the same way from published work (see Table I). The best figure of merit is that of $CuCrMgO_2$ grown by sputtering. However, the same material grown by spray pyrolysis has only a slightly higher figure of merit than Cr_2O_3:(Mg,N). Furthermore Cr_2O_3:(Mg,N) has a higher figure of merit than both the only-Mg doped and only-N doped Cr_2O_3 reported so far in literature despite the limitations in the deposition technique used in this study. Cr_2O_3:(Mg,N) has also a higher figure of merit than many other p-type TCOs reported so far. We also have to note that plain Cr_2O_3 is long been known to be an exceptionally hard and durable material, which promises good stability of films in devices.[23,24] There are also reports of the possibility of n-type doped Cr_2O_3[25], which may open up prospects of fully transparent homojunctions, if the anionic co-doping approch with nitrogen can equally be employed to enhance transparency. In addition it has already been shown that amorphous Cr_2O_3:N can improve organic solar cell performance.[17]

In summary, we have synthesized a p-type TCO, with performance comparable to those of other oxide materials, despite poor film quality due to using spray pyrolysis as deposition technique. This material is based on Cr_2O_3 and it has been co-doped with Mg and N in order to enhance transmission and increase conductivity. The figure of merit of the co-doped material is higher than the Cr_2O_3 doped with only one of either Mg or N. Cr_2O_3:(Mg,N) is thus a promising material which could be further improved by applying more refined deposition techniques.

TABLE I. Comparison of the figure of merit F for Cr_2O_3:(Mg,N) with published data for other p-type TCOs. For the evaluation the **average** transmission of films in the **visible** spectral range was used.

Material	F ($M\Omega^{-1}$)	Growth technique	Ref.
$CuAlO_2$	50	PLD	1
$CuAlO_2$	11	PLD	3
$CuCr_{1-x}Mg_xO_2$	5000	Sputtering	6
$CuCr_{0.93}Mg_{0.07}O_2$	15-28	Spray pyrolysis	20
$CuScO_{2+x}$	270	Sputtering	11
$CuYO_2$	1	Co-evaporation	21
$CuY_{1-x}Ca_xO_2$	36	Co-evaporation	21
$CuGaO_2$	14	PLD	22
$CuGa_{1-x}Fe_xO_2$	29	Sputtering	10
$AgCoO_2$	4.4	Sputtering	10
$SrCu_2O_2$	0.2	PLD	12
$SrCu_2O_2$:K	2	PLD	12
Cr_2O_3:Mg	2	Spin coating	18
a-Cr_2O_3:N	0.2	Sputtering	17
Cr_2O_3:(Mg,N)	7.2	Spray Pyrolysis	here

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