SYNTHESIS AND CHARACTERIZATION OF NICKEL COBALT OXIDE THIN FILMS

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Abstract

p-Type transparent and conductive cobalt–nickel oxide films of 130 nm thickness, have been deposited by spin coating method on glass substrates. The electrical and optical properties of the oxides have been studied as a function of the $x=\text{Co/(Co+Ni)}$ ratio. A combination of x-ray diffraction, x-ray photoelectron spectroscopy and Raman spectroscopy was used in order to investigate thin film structures. Thin films of mixed oxides: NiCo$_{2}$O$_{4}$, Ni$_{0.71}$Co$_{0.29}$O$_{4}$; NiO were obtained for $x>0.60$. The electrical conductivity of these films reaches a maximum conductivity at this stoichiometry.

Keywords: p-type TCO, structure, optical properties, electrical properties, Raman spectroscopy.

1. INTRODUCTION

Transparent conducting oxides (TCO) are well known and have been widely used in optoelectronics and transparent electronics as well as in different research fields. Most of the existing TCOs are n-type, whereas it is very difficult to prepare binary metal oxides with p-type conductivity [1]. Two p-type materials that were studied extensively were Co$_{2}$O$_{4}$ and NiO. It was found that mixed oxides of Co and Ni gave higher conductivities up to five orders of magnitude more than either of the two end members.

Spinel films (with an AB$_{2}$O$_{4}$ type general formula) of cobalt nickel oxide (NiCo$_{2}$O$_{4}$) with p-type conductivity and reasonable visible transparency (40% to 60%) have been synthesized by Windisch et al. [1]. They observed a variation in the conductivity with a change in the Ni:Co ratio in the film and at Ni:Co = 1:2, the highest conductivity in these films was observed (16 Scm$^{-1}$). They proposed that Ni$^{3+}$ ions located on octahedral sites within the spinel lattice enhance the conductivity of the film. These films also showed good transparency in the infrared region, extending its application into infrared optics.

Despite the numerous studies on the electrical and magnetic properties of Ni-containing Co oxides, there is still wide disagreement on the electrical conduction mechanism and on structural details. In this paper we report our results on the study of structure, optical and electrical properties of some Ni-Co-O thin films with different compositions ($x=\text{Co/(Ni+Co)} = 0.00 - 0.70$), deposited by using a spin-coating method.

2. METHODS

Cobalt–nickel oxide films of known stoichiometry were deposited from precursor solutions containing the respective metal acetates ((CH$_{3}$COO)$_{2}$•4H$_{2}$O; Co(CH$_{3}$COO)$_{2}$•4H$_{2}$O) and an organic complexant, dimethylformamide (DMF). Subsequent thermal annealing induced oxide formation during which the organic component was fully oxidized to gaseous products.

Thin films were prepared by spin casting these solutions at 1500 rpm for 30 s onto clean optical quality fused silica substrates. After every spin coating deposition, the films were heated in air at 100 °C for 10 min to initiate oxidation that converted the precursors to an oxide phase. The procedure was repeated 5 times, and a final annealing was performed at 300 °C for 2h. Thin film thickness, $d$, was investigated by using a DEKTKAK profilimeter, and was found around 130 nm.

<table>
<thead>
<tr>
<th>Code</th>
<th>$x = \text{Co/(Co+Ni)}$</th>
<th>Deposition conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>$\omega = 1500 \text{ rot/min}$; $T_{1}=273 \text{ K, } t_{1}=10 \text{ min}$; $T_{2} = 573 \text{ K, } t_{2}=2h$; $d = 130 \text{ nm}$</td>
</tr>
<tr>
<td>2</td>
<td>0.30</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>0.40</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>0.50</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>0.60</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>0.70</td>
<td></td>
</tr>
</tbody>
</table>

The structure and morphology of films were characterized using several techniques including x-ray diffraction (CuK$_{\alpha}$ standard and Grazing angle X-Ray diffraction, SHIMADZU XRD LabX 6000), scanning electron microscopy (SEM, VEGA II LSH), x-ray photoelectron spectroscopy, and Raman spectroscopy.
spectroscopy (XPS, VERSA PROBE 5000, AlK$_\alpha$), Raman spectroscopy (LabHR 800, Ar laser - 514 nm). Elemental chemical composition was determined from x-ray energy dispersive spectra (EDX, QUANTAX QX2) and XPS.

3. RESULTS

Sample XRD standard investigations (Fig.1.a) evidenced that all samples are amorphous. These results can be related to the fact that thin films have a thickness smaller than 200 nm (130 nm) and the standard method is not anymore efficient for structural analysis. In order to have a better structural analysis we made some GAXRD investigations (Fig.1.b), at an angle of 0.5°.

GAXRD patterns evidenced that all the samples are nanocrystalline, and that as the x value increases (x > 0.50) the predominant phase becomes NiCo$_2$O$_4$ (spinel type). Small quantities of other phases, like Ni$_{1.71}$Co$_{1.29}$O$_4$; NiO are also visible.

Deconvolution of XRD peak, located around 2θ=36.50 degree, in its Gaussian components evidenced that the content in these phases is 44%, 22% and 35% respectively. For the used registration conditions, the grain sizes can be approximated by using the Sherrer formula (Table 2) [2, 3]:

$$D = \frac{0.9 \cdot \lambda}{w \cdot \cos \theta} \quad (1)$$

where λ is the X-ray wavelength, θ is the Bragg angle and w is the full width at half-maximum of diffraction peak.

<table>
<thead>
<tr>
<th>Code</th>
<th>D nm</th>
<th>Content w%</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiO</td>
<td>13</td>
<td>35</td>
</tr>
<tr>
<td>Ni$<em>{1.71}$Co$</em>{0.29}$O$_4$</td>
<td>18</td>
<td>22</td>
</tr>
<tr>
<td>NiCo$_2$O$_4$</td>
<td>10</td>
<td>44</td>
</tr>
</tbody>
</table>

SEM analysis showed that all thin films were smooth, with a nanocrystalline morphology. Some white globules become more evident as x value increases (Fig.2). EDX investigation enabled to check the elemental chemical composition of thin films and confirmed the calculated x values, presented in Table 1. No visible differences in chemical composition of white and dark phases were put in evidence.

XPS spectra (Fig.3a, b) showed the peaks characteristic to Ni and Co species in different chemical neighborhoods, supporting the XRD results. The intensities of XPS peaks with lower binding energy are increasing with x value.

The Raman spectra, in the 50-4000 cm$^{-1}$ wavenumber range, were recorded using LabHR 800 from Horriba at 512 nm laser excitation, through a confocal microscope. The beam diameter was of ~0.8 μm for Ar laser. The laser beam was focused on the sample by a 100x microscope objective lens [0.9 NA numerical aperture (N.A.)] and the measurements are

![Sample XRD patterns: a) standard; b) GAXRD pattern of sample 5 (CuK$_\alpha$); c) Deconvolution of XRD peak located at 2θ=36.5 degree.](image-url)
performed at low incident power (<5 mW) to avoid sample damage or laser induced heating.

The Raman spectra of the films also varied with composition as shown in Fig. 4a, b.

A dependence of the intensity of Raman band, observed at 655 cm\(^{-1}\), on Co content was established (Fig.4.b). The results can be correlated with the Raman studies of Charles F. et al [4].

All the cobalt–nickel oxide films were optically clear but darkened slightly as x increased up to x = 0.70 (Fig.5b). The energy band gap is determined using absorption spectra with the help of relation:

\[
(\alpha \cdot h\nu)^2 = A^2 (h\nu - E_g)
\]  

where \(\alpha\) is the absorption coefficient, \(h\nu\) is the photon energy, \(E_g\) is the optical band gap energy, \(A\) is a constant [2]. Using this relation, a graph is plotted between the square of \((\alpha h\nu)\) and \(h\nu\) to obtain a straight line (Fig.5b). The extrapolation of straight line to \((\alpha h\nu)^2 = 0\) axis gives the value of the band gap.

As is shown in Fig. 5.b, for some thin films, three different regions were put in evidence, corresponding to different phases. It was proved that \(E_g\) values, corresponding to these phases, are dependent on \(x\) value (Fig.5,c).

Electrical conductivities of thin films were
investigated as a function of temperature (Fig. 6). The electrical conductivity of the cobalt–nickel oxide films varied with composition as shown in Fig. 6, exhibiting a maximum for x=0.70. Apparently, conductivity is maximum for the stoichiometric compound NiCo$_2$O$_4$ (x=0.70), and decreases when Ni replaces Co in the spinel lattice or when NiO is present.

Compounds in this series have been variously described as p type, semimetallic-to-metallic suggesting n type, and p type with doping by Ni$^{3+}$. Further work is necessary to characterize the conduction mechanism and provide a better understanding of the role of Ni$^{3+}$ in perturbing the conductivity of the Ni-containing spinel oxide films.

![Graph](image)

**Fig. 6.** Temperature dependence of the electrical conductivity

### 4. CONCLUSIONS

Thin films of cobalt–nickel oxide were synthesized by using a spin-coating method and characterized using a variety of techniques. The films became conductive largely, at x> 0.6 due to the presence of a spinel, NiCo$_2$O$_4$, phase. The transmittance of thin films is over 30%, which is quiet good for a thin film thickness of 130 nm.

### ACKNOWLEDGEMENT

This work was supported by the PNII contract No. 12-128/2008 - ELOTRANS.

### REFERENCES