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Properties of NiO thin films deposited by intermittent spray pyrolysis process

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Abstract

NiO thin films have been grown on glass substrates by intermittent spray pyrolysis deposition of $NiCl_2 \cdot 6H_2O$ diluted in distilled water, using a simple "perfume atomizer". The effect of the solution molarity on their properties was studied and compared to those of NiO thin films deposited with a classical spray system. It is shown that NiO thin films crystallized in the NiO structure are achieved after deposition. Whatever the precursor molarity, the grain size is around 25–30 nm. The crystallites are preferentially oriented along the (1 1 1) direction. All the films are p-type. However, the thickness and the conductivity of the NiO films depend on the precursor contraction. By comparison with the properties of films deposited by classical spray technique, it is shown that the critical precursor concentration, which induces strong thin films properties perturbations, is higher when a perfume atomizer is used. This broader stability domain can be attributed to better chlorides decomposition during the rest time used in the perfume atomizer technique.

Keywords: p-Type transparent semiconductor; NiO thin films; Spray pyrolysis

1. Introduction

Transparent conducting electrodes are now often used in different devices such as flat panel, organic light emitting diodes, solar cells and also smart windows. The oxides used to obtain such transparent conductive films are indium oxide, tin oxide (TO), indium tin oxide (ITO), ZnO [1], all these films are n-type semiconductors.

Nowadays, transparent conducting thin film coatings of p-type semiconductors are required in different applications such as transparent electrodes for optoelectronic devices. Such p-type transparent semiconductors are relatively rare. NiO is one of these oxides and last years, a growing interest has been devoted to nickel oxide thin films [2–7]. Due to its high chemical stability, as well as optical magnetic and electrical properties, NiO has a wide range of applications such as films for electrochromic devices [8], organic light emitting diodes [7], chemical sensors [9], n–p junction electrodes in dye sensitized solar cells [6] and p-type large band gap oxide [2,6,10,11]. As shown recently NiO appears to be one of the more promising anodic electrochromic materials [12]. Therefore, since NiO is one of the uncommon p-type large band gaps oxide, it is interesting to study its thin film properties. Several methods have been used to prepare nickel oxide thin films such as sputtering [4,5,13–15], electron beam evaporation [16], sol–gel [17], dip coating, spin coating, electro deposition [18], chemical bath deposition [11,19,20] and also spray pyrolysis [11,21–23]. It has been shown that NiO films with good electronic properties can be achieved by spray pyrolysis depending on growing parameters such as precursor concentration [23] and substrate temperature [22].

Smart windows, dye sensitized solar cells need, for economical reason, cheap deposition technique. In the case of n-type transparent conductive oxides a "perfume atomizer" available in cosmetic shop has been used with success [24,25].

Therefore, this very simple technique is used in the present work to grow NiO thin films. A comparison between the properties of the NiO films obtained with a perfume atomizer to

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those of NiO films achieved with a more classical spray apparatus [26] allow us to prove that perfume atomizer is useful to obtain NiO thin films with expected properties.

2. Experimental

The substrates used were bare glasses. Before deposition, the substrates were cleaned by acetone for eliminating any greasy track and then they were cleaned with soap and abundantly rinsed with distilled water. Finally, they were dried by a nitrogen flow. The substrate temperature during the deposition was around 350 °C. This temperature has been shown to be efficient to achieve NiO films [11]. Nickel chloride hexahydrate ($NiCl_2{\cdot}6H_2O$) was chosen as precursor, it was dissolved in bi-distilled water. The effect of solution molarity on the NiO thin films properties was studied (0.2–0.45 M). These molarities have been chosen because we have shown in a previous paper [26] that there is a threshold value for the different film properties when the precursor concentration varies between 0.2 M and 0.3 M. The solution was sprayed manically in air with the use of a perfume atomizer. This technique has some advantages such as an atomization based on hydraulic pressure without using any carrier gas, intermittent spraying and fine atomization. As a matter of fact during spray deposition shot, the substrate temperature was reduced from 350 °C to 330–340 °C. Therefore the spraying process was stopped during the time necessary to recover 350 °C as substrate temperature. Such conditions are complete when a shot is followed by 5 s of rest.

The volume of the solution for each deposition was 100 ml (except in the case of 0.3 M where 200 ml was also used). Only a small amount of the solution was consumed in each shot and 45 min was necessary for 100 ml. The substrate to nozzle distance was ≅30 cm.

A Siemens D-500 X-ray diffractometer using the Cu Kα radiation was employed to study the film structure.[1] It has been shown that electrochromic, but also dyes sensitized solar cells performances are related to the grain size of the films, because a small grain size implies a large surface to bulk ratio. Crystallite size can be estimated from the full width at half maximum (FWHM) of the X-ray diffraction liner. The broadening of the FWHM is inversely proportional to the average crystallite size (D) as predicted by the well-known Scherrer's formula [27] the grain size D is:

$$D = \frac{K\lambda}{\beta\cos\theta} \tag{1}$$

where β is the observed angular width at half maximum intensity of the peak with:

$$\beta^2 = \beta'^2 - \beta_0^2$$

where β' is the measured line width at half maximum and β_0 is the instrumental broadening [27]. $\beta_0 = 0.16$ with the apparatus used. K is dimension less number, which is equal to 0.9. λ is the X-ray wavelength (0.1548 nm for Cu $K\alpha_1$) and θ is the diffraction angle.

The surface topography and the cross-section of the films were observed with a field emission scanning electron microscope (SEM, JEOL F-6400). Using simple software, the thickness of the films was measured from the cross-section visualization.

Electron probe microanalysis (EPMA) was performed using a JEOL F-5800 LV, SEM equipped with a PGT X-ray microanalysis system; X-rays were detected by a germanium crystal.

The optical measurements were carried out at room temperature using a Carry spectrometer. The optical density was measured at wavelengths of 2–0.25 μm.

The majority carrier type has been checked by the hot probe technique. A n-type constantan wire was used as the reference sample. The electrical conductivity, at room temperature, was measured using gold electrodes.

3. Results

The XRD patterns were recorded for different films deposited onto glass substrate, the solution molarity varying from 0.2 M to 0.45 M. All the peaks visible belong to the cubic NiO phase (JCPDS 04-835). Only peaks corresponding the (1 1 1), (2 0 0), (2 2 0) and (2 2 2) directions are visible, there is not $NiCl_2{\cdot}6H_2O$ contribution in the XRD diffractograms (Fig. 1).

In randomly oriented powder, the most intense XRD peak is corresponding to the (2 0 0) direction. It can be seen in Fig. 1 that in the present diffractograms, the peak along the ($h\,h\,h$) direction is the strongest. It can be concluded that crystallites are mainly oriented along the ($h\,h\,h$) direction. The degree of preferential orientation along this ($h\,h\,h$) direction $F_{h\,h\,h}$ has been estimated using [28]:

$$F_{hhh} = \sum_{h=1,2} f_{(hhh)} = \frac{\sum_{h=1,2} I_{(hhh)}/I_{0(hhh)}}{\sum_{hkl} I_{(hkl)}/I_{0(hkl)}} \tag{2}$$

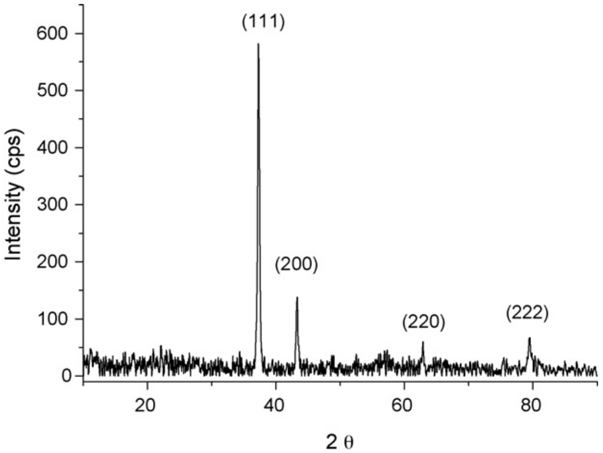

Fig. 1. Typical X-ray diffraction diagram of a NiO film, deposited from a precursor molarity of 0.35 M (solution volume 100 ml).

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[1] XRD measurements have been done at the IMN-Nantes.