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Properties of NiO thin films deposited by chemical spray pyrolysis using different precursor solutions

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ABSTRACT

NiO thin films have been deposited by chemical spray pyrolysis using a perfume atomizer to grow the aerosol. The influence of the precursor, nickel chloride hexahydrate ($NiCl_2{\cdot}6H_2O$), nickel nitrate hexahydrate ($Ni(NO_3)_2{\cdot}6H_2O$), nickel hydroxide hexahydrate ($Ni(OH)_2{\cdot}6H_2O$), nickel sulfate tetrahydrate ($NiSO_4{\cdot}4H_2O$), on the thin films properties has been studied. In the experimental conditions used (substrate temperature 350 °C, precursor concentration 0.2–0.3 M, etc.), pure NiO thin films crystallized in the cubic phase can be achieved only with $NiCl_2$ and $Ni(NO_3)_2$ precursors. These films have been post-annealed at 425 °C for 3 h either in room atmosphere or under vacuum. If all the films are p-type, it is shown that the NiO films conductivity and optical transmittance depend on annealing process. The properties of the NiO thin films annealed under room atmosphere are not significantly modified, which is attributed to the fact that the temperature and the environment of this annealing is not very different from the experimental conditions during spray deposition. The annealing under vacuum is more efficient. This annealing being proceeded in a vacuum no better than 10^{-2} Pa, it is supposed that the modifications of the NiO thin film properties, mainly the conductivity and optical transmission, are related to some interaction between residual oxygen and the films.

1. Introduction

Transparent conductive oxide films, such as indium tin oxide (ITO), zinc oxide, etc., are widely used for transparent electrode, window coating, etc. All of them are n-type. However p-type transparent conducting thin films are also required in applications such as transparent electrode for optoelectronic devices, smart windows, transparent electronic devices, etc. [1]. Indeed not many oxides are easily p-type. Usually the p-type conductivity is due to the metal deficit or oxygen excess.

The nickel oxide, NiO, is a good example of p-type semiconductor. It has already been probed in different devices. Nickel oxide films show anodic electrochromism and are well suitable for device operations in conjunction with tungsten oxide films [2–4]. NiO, which should exhibit a higher work function than ITO, is more favourable for the hole injection into the organic, in organic light emitting diodes (OLEDs) [5]. It is possible to improve diode performance and stability by inserting a thin NiO buffer layer between the ITO and the organic material [6]. NiO can be used in the fabrication of n–p junction electrodes made of n-type SnO_2 and p-type NiO for control of charge recombination in dye-sensitised solar cells [7] and as a photocathode in a tandem dye-sensitised solar cell [8].

Another important field of possible of NiO thin film application is the solar energy conversion. In the dye-sensitised solar cells (DSSCs), in its classical configuration, i.e. with TiO_2 as dye sensitiser, light is absorbed by the sensitising dye, and then the created electrons are transferred from the excited state of the dye to the conduction band of the large band gap semi semiconductor. The oxidized dye recovers its electrical neutrality by electron transfer from reduced specie, often iodine, in the electrolyte dye [9]. In such DSSC devices the sensitiser should be a porous film thick of some microns. Up to now a lot of works have been devoted to DSSC using TiO_2 or another n-type semiconductor oxide but not to p-type porous semiconductor oxide. Therefore it is of interest to study the possibility of growing p-NiO porous thin films thick of some microns with acceptable conductivity and transmission, i.e. in the same order of magnitude as that of TiO_2.

NiO thin films have been fabricated by various techniques such as reactive sputtering [10], annealing treatment of vacuum

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deposited thin nickel films [11], chemical bath deposition [12,13] spin coating, dipping and electrochemically [14]. Spray pyrolysis has also been used with success [15–17]. In a recent paper we have studied the influence of the $NiCl_2$ precursor concentration on the NiO thin film properties [15] and we have shown that NiO thin films can be grown on glass substrates by intermittent spray pyrolysis deposition of $NiCl_2{\cdot}6H_2O$ diluted in distilled water, using a simple "perfume atomizer" [16]. 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 has been attributed to better chlorides decomposition during the rest time used in the perfume atomizer technique. Such original behaviour opens interesting new possibilities for spray pyrolysis. Therefore the purpose of this study is to investigate the changes observed in the NiO thin films properties when different chemical precursor solutions are deposited by intermittent spray pyrolysis ("perfume atomizer"), with the goal of enhancing their transmittance and reducing their resistivity. Effectively, the transmittance of the NiO films is rather low while the resistivity is rather high for the purpose of being a p-type transparent oxide. Finely attempts are made to explain the observed phenomena.

2. Experimental

The substrates used are bare glasses. Before deposition, the substrates were first cleaned by acetone, for eliminating any greasy track, then with soap and at last 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 [15]. Nickel chloride hexahydrate ($NiCl_2{\cdot}6H_2O$), nickel nitrate hexahydrate ($Ni(NO_3)_2{\cdot}6H_2O$), nickel hydroxide hexahydrate ($Ni(OH)_2{\cdot}6H_2O$), nickel sulfate tetrahydrate ($NiSO_4{\cdot}4H_2O$), were chosen as precursor. They were dissolved in bi-distilled water. The solutions were sprayed manically in air with the use of a perfume atomizer. The perfume atomizer 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 to 330–340 °C. Therefore the spraying process was stopped during the time necessary to recover 350 °C as substrate temperature. Such conditions are completed when a shot is followed by 10 s of rest.

The volume of the solution for each deposition was 60 ml. Only a small amount of the solution was consumed in each shot and 30 min was necessary for 60 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 (XRD measurements have been done at the IMN-Nantes).

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 (measurements have been carried out at the "Centre de microcaracterisation-Université de Nantes").

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 0.15–2 μm.

The majority carrier type has been checked by the hot probe technique. Two copper wires pasted onto two copper electrodes placed at a distance of 1 cm from each other create a closed loop circuit with a digital multimeter. A thermo-couple equipped heater is attached to one of the electrodes to warm it up to around 100 °C. The majority carrier type is deduced from the sign of the measured voltage. A n-type constantan wire is used as the reference sample.

The electrical conductivity, at room temperature, was measured using copper electrodes.

In order to check the influence of a post-deposition annealing on the properties of the films, they have been heated 3 h at 425 °C under vacuum and in room atmosphere.

3. Results

The films have been systematically characterized before and after annealing in vacuum and in room atmosphere.

Fig. 1 shows X-ray diffraction diagrams of the deposited films as a function of the precursor solutions. All the peaks visible in Fig. 1a–e belong to the cubic NiO phase (JCPDS 04-0835). While, there is neither precursor nor Ni_2O_3 [10] contribution in these XRD diffractograms, the peaks visible in Fig. 1f correspond to $NiSO_4$ (inset Fig. 1f). The SEM photographs of these deposited films shown in Fig. 2 corroborate these results. It can be seen that the morphology of the films depends more of the precursor nature than of its concentration. Films achieved from $NiCl_2$ or $Ni(NO_3)_2$ have quite similar aspect even if the films issued from the former precursor appear more porous (Fig. 2a–d). In the case of $Ni(OH)_2$ (Fig. 2e) the films are highly inhomogeneous, randomly shaped heaps are distributed onto a very smooth layer. In Fig. 2f the films issued from $NiSO_4$ exhibit a more compact morphology. These different morphologies are in good agreement with EPMA qualitative study. Table 1 shows that, in the precision range of the technique, the films issued from $NiCl_2$ and $Ni(NO_3)_2$ are stoichiometric, whatever the precursor concentration. Moreover, it can be seen that the oxygen/nickel ratio does not vary significantly whatever the annealing process used. As said above, the measurements of films composition have been done by EPMA analysis. This technique allows estimating oxygen. However, the precision of the measure decreases with the atomic weight of element. Therefore, if no significant evolution after annealing is put in evidence it does not prove that there is not a small oxygen/nickel ratio modification. It should be noted that the chlorine present in the films issued from $NiCl_2$ nearly disappears only from the samples annealed under vacuum.

The two others precursors do not give stoichiometric NiO films, in the case of $Ni(OH)_2$ there is a strong excess of oxygen, claiming that pyrolytic reaction was not favourable in such temperature ranges ($T_s = 350$ °C). The XRD and EPMA results allow discussing more precisely the morphology of these films. The NiO put in evidence by XRD should correspond to the heaps randomly distributed onto a smooth amorphous film of $Ni(OH)_2$, which justifies the EPMA results. After annealing, even if the ratio nickel/oxygen increases, mainly in the case of vacuum annealing, pure NiO films cannot be achieved. Moreover the NiO crystallites adhere poorly to the films. When the $NiSO_4$ is used there is not any pyrolysis reaction, even if there is some beginning of the reaction during vacuum annealing. It appears from Table 1 that the annealing under vacuum seems more efficient in improving the thin films properties, since the decrease in oxygen excess is higher for these both precursors, even if pure NiO is not achieved.

As it can be seen in Fig. 3, in the case of $NiCl_2$ precursor, if there is no clear modification of the NiO thin film morphology after annealing in room atmosphere, after annealing under vacuum, the roughness of the thin film surface increases, it means that the