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# Deposition of p-type NiO films by chemical spray pyrolysis

M. Krunks [a,*], J. Soon [a], T. Unt [a], A. Mere [a], V. Mikli [b]

[a] Department of Materials Science, Tallinn University of Technology, Ehitajate tee 5, Tallinn 19086, Estonia
[b] Centre for Materials Research, Tallinn University of Technology, Ehitajate tee 5, Tallinn 19086, Estonia

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ABSTRACT

NiO films were fabricated by spray pyrolysis method using aqueous and alcohol based solutions of Ni chloride and acetate, and growth temperatures in the range of 350–500 °C. Films are of cubic NiO phase, the crystallite size increases and film thickness decreases with the film growth temperature. When NiO films are prepared from chloride solutions the crystallites grow along the (111) plane parallel to the substrate while, by contrast, they grow with no preferred orientation when grown from nickel acetate solutions. Spray of $NiCl_2$ results in films with uneven thickness, rough surface and porous microstructure while smooth films with uniform thickness can be obtained spraying Ni acetate solutions. Effect of Li-doping has been studied with NiO films from acetate solutions, LiCl and $LiNO_3$ were used as dopant sources. According to XRD, sprayed NiO:Li films are of NiO phase where the lattice parameter decreases with increasing Li concentration in solution indicating the incorporation of Li atoms into NiO lattice. NiO and NiO:Li films show p-type conductivity, Li-doping decreases resistivity by two orders of magnitude, from ca. 300 to some Ω cm, as the carrier concentration increases from $10^{16}$ to $10^{18}$ $cm^{-3}$ ($[Li^+] = 25$ at.%, $LiNO_3$). At similar doping rates $LiNO_3$ is more efficient dopant source compared to LiCl.

## 1. Introduction

Nickel oxide (NiO), a stable compound with wide band gap of 3.6–4.0 eV [1] is a promising candidate for transparent conductive oxide with p-type conductivity. Undoped stoichiometric NiO exhibits high electrical resistivity of the order of $10^{13}$ Ω cm at room temperature [2]. NiO p-type conductivity can be significantly increased by doping with monovalent Li ions, appearance of nickel vacancies and/or interstitial oxygen in crystallites [3,4]. NiO films have wide range of applications such as electrochromic material in smart windows [5], active material in chemical sensors [6], photocathode in dye sensitized solar cells [7,8], an anode interfacial layer in polymer solar cells [9], component of p-n junction diode [10] and random access memory devices [11].

NiO films can be prepared by various methods including chemical deposition in solution, atomic layer deposition, sputtering, electron beam evaporation, pulsed laser deposition, chemical spray deposition, sol–gel and others. The most popular physical method used up to now is sputtering [3] which is a well understood process [12]. At the same time the less expensive manufacturing processes should be considered and here the atmospheric spray pyrolysis method offers the promise of less expensive fabrication for large area coatings due to elimination of vacuum systems [12,13]. NiO films are obtained by spraying of solutions of nickel chloride [4,14,15], nickel nitrate [13,14,16–18], nickel acetate [19,20] or nickel acetylacetonate [21] over preheated substrates. The lowest resistivities in the order of 1 Ω cm are obtained by spraying of $Ni(NO_3)_2$ solutions using LiCl or $LiNO_3$ as dopant sources [13,16].

Comparative study on the effect of Ni source on properties of NiO films made by spray pyrolysis technique is few [14] and therefore, in this study we focus on comparison of structural properties and morphology of NiO films grown at different temperatures from Ni chloride and Ni acetate solutions. As there is very little known about the properties of doped NiO films from Ni acetate solutions, we aim to study the effect of Li-doping on the structure and electrical properties of sprayed NiO films.

## 2. Material and methods

Nickel acetate tetrahydrate ($Ni(CH_3COO)_2 \cdot 4H_2O$, ≥ 99.0%, Aldrich) and nickel chloride hexahydrate ($NiCl_2 \cdot 6H_2O$, 99.95%, Alfa Aesar) were used as nickel sources dissolved in deionised water. The concentration of a nickel salt was 0.05 mol/L in an aqueous spray solution, and 0.1 mol/L in an alcoholic spray solution (isopropanol:$H_2O = 3:2$, by volume). LiCl (99%, Sigma Aldrich) and $LiNO_3$ (99%, Alfa Aesar) were used as dopant sources added into the

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* Corresponding author. Tel.: +372 6203363; fax: +372 6202020.
*E-mail address:* malle.krunks@ttu.ee (M. Krunks).

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spray solution, the concentration of Li ions ($[Li^+]/([Li^+]+[Ni^{2+}])$) in a solution was 10 and 25 at.%. The volume of the solution for each deposition was 50 mL and the solution deposition rate was 2 mL/min. The solution was sprayed with the help of compressed air as carrier gas onto cleaned glass substrates with a size of $20 \times 15 \times 1$ mm$^3$ placed on a molten tin bath used as a heater. The film deposition temperature (Ts) was varied from 350 °C to 500 °C and kept with accuracy of ±5 °C using a feedback control system for the heater power supply. The spray set-up is described in detail elsewhere [22].

The sprayed films were characterized by X-ray diffraction (XRD) measurements on Rigaku Ultima IV diffractometer with monochromatic Cu Kα radiation ($\lambda = 0.1540$ nm), a tube voltage of 40 kV, a current of 40 mA and using a D/teX Ultra silicon strip detector. The crystallite size was calculated using the Debye Scherrer method and a Scherrer constant of 0.94. Scanning electron microscopy (SEM) was applied to study the film surface morphology and film thickness on a Zeiss EVO-MA15 microscope at an operating voltage of 10 kV. The elemental composition of the films was evaluated by energy dispersive X-ray (EDX) analysis using a Röntec EDX Xflash 3001 detector and an Oxford Instruments INCA Energy system. The charge carrier type was measured with the help of hot probe technique and the electrical properties of thin films (resistivity, charge carrier concentration, and mobility) were measured at room temperature using MMR's Variable Temperature Hall System supplied with Hall, Van der Pauw Controller H-50. The contact material used for the Van der Pauw and Hall measurements was graphite.

## 3. Results and discussion

### 3.1. *Structure and morphology of NiO films obtained by spray of $NiCl_2$ and $Ni(CH_3COO)_2$ solutions*

The XRD patterns of thin films deposited from $NiCl_2$ and $Ni(CH_3COO)_2$ (further marked as $Ni(ac)_2$) aqueous solutions at substrate temperatures (Ts) in the interval of 350–500 °C are presented in Fig. 1 and Fig. 2, respectively. According to XRD study all the diffraction peaks are belonging to NiO with cubic structure (JCPDS 00-047-1049) [23], no other crystalline phases were detected. NiO films from chloride precursor exhibit the (111) reflection as the strongest peak on the diffractogram (Fig. 1). The ratio of the intensities of the (111) and (200) diffraction peaks ($I_{(111)}/I_{(200)}$) decreases from 16 to 2 increasing the substrate temperature from 350 to 500 °C. A comparison with the intensity of XRD reference lines of NiO powder ($I_{(111)}/I_{(200)} = 0.6$) refers that all the films grown from chloride solution show preferential growth of the crystallites along the (111) plane parallel to the substrate. This result corresponds to that reported in literature [14,15]. According to the results of present study, the preferred orientation along the (111) plane weakens with temperature. Reguig et al. [15] and Cattin et al. [14] observed weakening of the (111) orientation by spraying more concentrated solutions (C > 0.3 M) at fixed temperature. Full width at half maximum (FWHM) of the diffraction peaks decreases with temperature and indicates the growth of crystallites. The mean crystallite size (calculated according to the Scherrer formula from the FWHM of the (111) reflection) increases from 16 to 26 nm (Table 1).

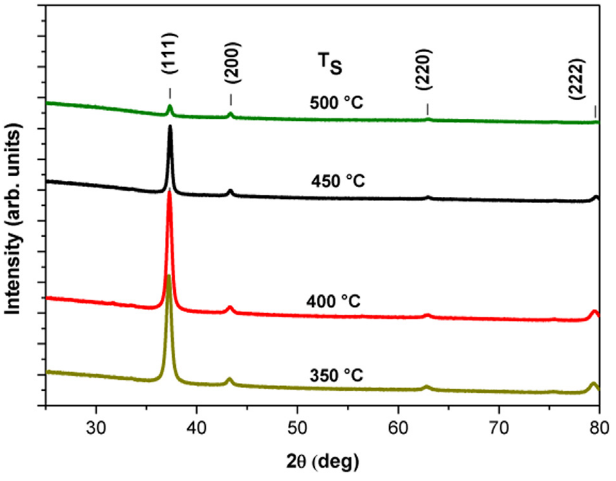

**Fig. 1.** XRD patterns of NiO film grown by spray of $NiCl_2$ 0.05 mol/L aqueous solutions at different substrate temperatures in the range of 350–500 °C.

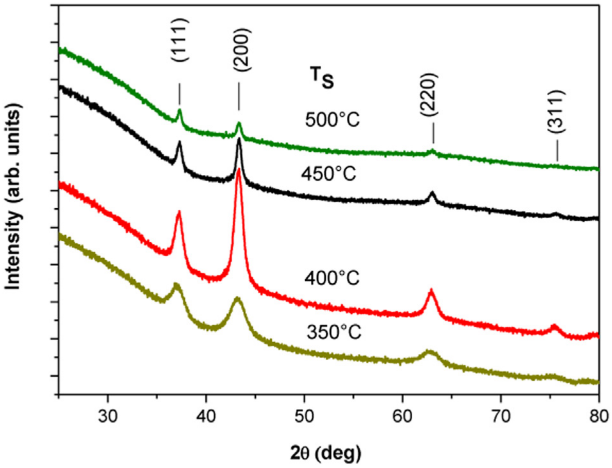

**Fig. 2.** XRD patterns of NiO film grown by spray of $Ni(CH_3COO)_2$ 0.05 mol/L aqueous solutions at different substrate temperatures in the range of 350–500 °C.

Fig. 2 shows that the crystallinity of NiO films from $Ni(ac)_2$ solutions is lower compared to the films from $NiCl_2$ solution as the diffraction peaks are significantly wider. The crystallites do not show preferential growth as the $I_{(111)}/I_{(200)}$ varies between 0.5 and 0.7 which is close to that of powder reference [23]. The crystallite size (calculated from the FWHM of the strongest (200) diffraction peak) changes from 6 nm to 10 nm increasing the Ts from 400 °C to 500 °C (Table 1).

Thinner films are obtained at higher Ts, the film thickness decreases from ∼ 600 nm to ∼ 50 nm and from 1000 nm to 75 nm increasing the Ts from 400 °C to 500 °C when spraying $NiCl_2$ or $Ni(ac)_2$ solutions, respectively (Table 1). Much lower film thicknesses at higher growth temperatures is a commonly known characteristic of the spray process as the solution droplets are repelled from the reaction zone at higher temperatures and less precursor material reaches the substrate [24]. According to EDX, the chlorine concentration in NiO films grown at 400 °C from $NiCl_2$ solution is 1.6 at.%, and drops to 0.3 at.% when grown at Ts of 500 °C (Table 1). Thus, higher growth temperatures are preferable if contamination with chlorine residues is aimed to keep possibly low. Independent of the starting chemical, Si and Na are detected by EDX in films grown at 500 °C (See Table 1). It is likely that signals of Si and Na originate from a glass subtrate as the film thicknesses are relatively low, ca. 50–75 nm (Table 1).

The SEM images reported in Fig. 3 clearly show remarkable different characteristics between the NiO films prepared from chloride and acetate solutions. NiO films from $NiCl_2$ solution exhibit uneven thickness, irregular rough surface and porous microstructure (Fig. 3(a)). Coarse grained surface of NiO films grown from Ni chloride solutions has been reported also in literature [14,15].