New Advanced Model of Lithium-Doping along with Spray Pyrolysis Technique for Development of Electrochromism in Nickel Oxide Thin Films

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Abstract: ***In case of nickel oxide thin films electrochromic materials possess specific optical properties that can be switchable and are used in distinct fields-specially smart windows. The optical properties of EC materials can be altered with electrical voltage. In recent times, the research on electrochromism is more frequent mainly with Nickel Oxide and Tungsten Oxide. In this paper we have showed a new doping model with spray pyrolysis.***

Keywords: electrochromism, doping, spray pyrolysis technique, nickel oxide film

1. Introduction

For past few years, electrochromic (EC) devices have been widely investigated for their promising application in large area glazing, high-contrast displays and automotive glazing. Also, electrochromic devices have applications in smart windows in order to balance lighting and air conditioning needs, and anti-dazzling devices for vehicles [1]. Nickel oxide (NiO) is the most exhaustively investigated transition metal oxide exhibiting semiconducting properties. It offers promising candidature for many applications such as electrocatalysis or electrosynthesis. Certain oxides (viz. tungsten oxide) have high transparency in the bleached state, whereas nickel oxide has a residual brown tint in the bleached state which can be reduced using additives such as Mg, Al, Si, Zr, Nb or Ta [2].

This paper contains new advanced doping model of electrochromic materials. Mainly this type of mood of electrochromism technique in Nickel Oxide Films is done in order to get an advanced performance. Also, spray pyrolysis technique is discussed here.

2. Electrochromic Behavior of Nickel Oxide Film

The electrochemistry of nickel oxide has been extensively studied due to its technological importance as the active material of nickel battery systems. Now, the electrochromic processes observed during charge/ discharge cycle suggest that nickel oxide can be very attractive materials in view of their potential application in "smart windows" [3]. A smart window consists of a number of layers: EC thin films (one anodic and one cathodic), electron conductive layers and an ion containing electrolyte. When a potential is applied over the smart window, ions in the electrolyte are transported between the EC layers and the transparency changes. In recent years materials development in this field has frequently been directed to the study of mixed oxides [4]. Such windows have variable light transmission characteristics and may be useful for applications in buildings or car industries. In this case, nickel oxide is deposited as a thin layer on a transparent substrate: glass plate covered by a film of conductive oxide, i.e, SnO_2 or ITO: another electrochromic application being the display panels or rearview mirrors in which the substrate is, on the contrary, reflecting. The electrochromic process in the case of nickel oxides is due to a reversible redox reaction in which the reduced state is transparent and the oxidized state is dark brown. A charge cycle is not completely reversible, and there are several significant processes which influence the electrode performance and degradation [3]. Transparent conducting nickel oxide films have a wide range of applications in optoelectronic and thermal devices. In the area of optoelectronics, nickel oxide is well known as an electrochromic material. Another area where NiO films are of great interest is in the new optical recording material of a NiO heterogeneous system that would realize a portable medium by using a laser diode beam for recording and reading [6].

3. Spray Pyrolysis Technique

Nickel oxide thin films have been prepared by various techniques that involve: vacuum evaporation, electron beam evaporation, rf-magnetron sputtering, anodic oxidation, chemical deposition, atomic layer epitaxy, sol–gel and spray pyrolysis technique (SPT). Although SPT has been employed in the past to deposit NiO films through acetylacetonate and nitrate routes, their characterization have sparsely been carried out [5]. The interest in metallic oxide thin films is growing fast due to their importance in many applications in science and technology. One formerly used process was that preparing NiO films with the solutions of $Ni(NO_3).6H_2O$ using the chemical spray pyrolysis technique [7]. But this procedure is not widely used in recent times.Aqueous solutions are commonly used in SP system to deposit thin films due to ease of handling, safety, low cost and availability of a wide range of water-soluble metal salts. The solute must have high solubility to increase the yield of the process. Other metal salts such as nitrates, acetates and sulfates can also introduce impurities, which may adversely affect subsequent processing or properties and phase development. The low solubility of metal acetates and high decomposition temperature of metal sulfates limit the use of these salts [5].

3.1 Setup of Spray Pyrolysis

Spray pyrolysis does not require high-quality substrates or chemicals. The method has been employed for the deposition of dense films, porous films, and for powder production. Even multilayered films can be easily prepared using this versatile technique [9]. The experimental configuration used is shown in Fig. 1, comprising air compressor, temperature controller, heater, exhaust fan and pipe, and spray gun with attached container. The container houses the precursor solution. A hose connects the air compressor to the spray gun. A temperature of 350°C was attained and read by a thermocouple attached to the heater before commencing deposition.

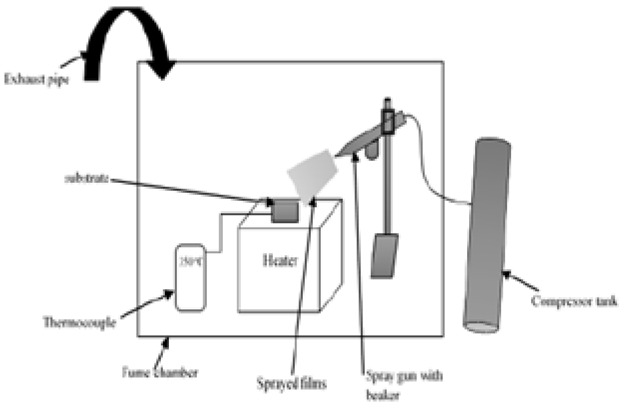

Figure 1: Set-up of spray pyrolysis technique

3.2 Decomposition of Precursor

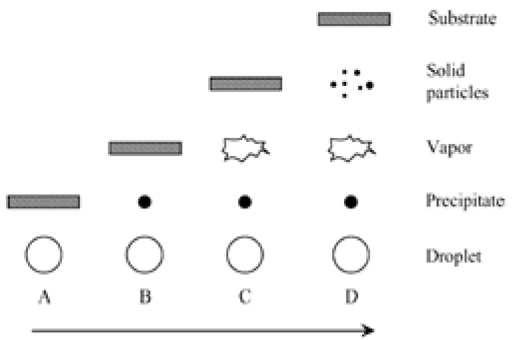

Figure 2: Deposition starting with temperature increment

Precursor solution was nickel acetate tetrahydrate of concentration 0.025 M, 0.05 M, 0.075 M and 0.1 M. This was mixed and stirred in 50 mL distilled water for 10 min. Thereafter the solution was poured into the spray gun container. The glass substrate was chemically and ultrasonically cleaned before usage. The glass substrate was heated at a constant temperature of 350°C on a heater. Other deposition parameters were maintained to obtain uniform film thickness. The optimum deposition parameters of spray deposited NiO film are shown. Each droplet is found to be smaller than micro-sized particles. The sprayed solution on the preheated substrate glass experiences evaporation and solute precipitation before pyrolytic decomposition as shown in Equation (1). Nickel oxide is given off as a final product [8].

$$Ni(CH_3COO)_2.4H_2O \longrightarrow NiO + 7H_2O\uparrow + 4CO_2\downarrow \quad (1)$$

3.3 Characterization

The morphology of deposited NiO film was studied using a ZEISS ULTRA PLUS Field Emission Gun Scanning Electron Microscope (FEGSEM). Elemental analysis was performed using an Energy Dispersive X-ray Spectrometer (EDX: "AZTEC OXFORD DETECTOR"). Structural properties of the deposited NiO films were investigated using an EMPYREAN (PANalytical) X-ray powder diffractometer for a range of 5 ° to 90 ° 2θ angles. Measured film thickness was compared with calculated film thickness obtained using the weight difference method. Optical properties were studied in wavelengths of 300 nm to 1000 nm with a SHIMADZU UV-3600UV-VIS Spectrometer model [8]. The atomizers mentioned in the "Setup of Spray Pyrolysis" section are usually used in spray pyrolysis technique: air blast (the liquid is exposed to a stream of air), ultrasonic (ultrasonic frequencies produce the short wavelengths necessary for fine atomization) and electrostatic [9].

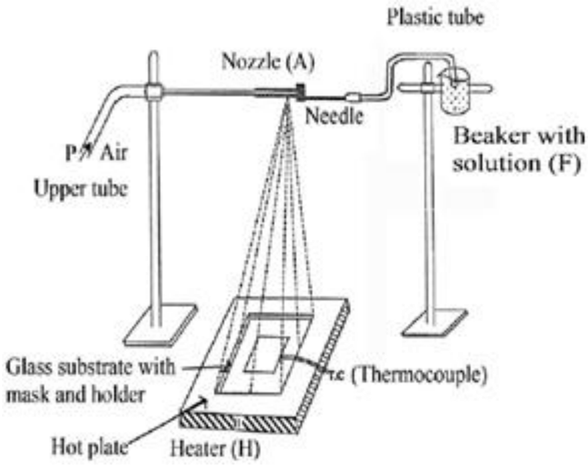

Figure 3: Spray pyrolysis technique characterization

3.4 Influence of Temperature

Spray pyrolysis involves many processes occurring either simultaneously or sequentially. The most important of these are aerosol generation and transport, solvent evaporation, droplet impact with consecutive spreading, and precursor decomposition. The deposition temperature is involved in all mentioned processes, except in the aerosol generation. Consequently, the substrate surface temperature is the main parameter that determines the film morphology and properties. By increasing the temperature, the film morphology can change from a cracked to a porous microstructure. In many studies the deposition temperature was reported indeed as the most important spray pyrolysis parameter. The properties of deposited films can be varied and thus controlled by changing the deposition temperature, for instance, it influences optical and electrical properties [9].

3.5 Atomization of Precursor Solution

Atomization of liquids has been investigated for many years. The key is to understand the basic atomization process of the atomization device in use. In particular, it is important to know which type of atomizer is best suited for which application and how the performance of the atomizer is affected by variations in liquid properties and operating conditions. Air blast, ultrasonic, and electrostatic atomizers are normally used in spray pyrolysis techniques. Numerous reports were published on the mechanism of liquid atomization. Rizkalla and Lefebvre examined the influence of liquid properties on air blast atomizer spray characteristics. Lampkin presented results concerning the application of the air blast atomizer in a spray pyrolysis set-up. Recently, a theory of ultrasonic atomization was published. Ganan-Calvo et al. have studied the electrostatic atomization of liquids and derived scaling laws for droplet size from a theoretical model of charge transport [9].

3.6 Structural Studies and Elemental Composition Analysis

The phase and the preferred orientation of the deposited nanostructured NiO films were determined using an x-ray diffractometer. The XRD patterns of the deposited nanostructured NiO films at different precursor concentrations. The patterns have peak diffractions at (2θ = 37^{o} and 43^{o}) for and planes respectively and 64^{o} for the plane for 0.1 M. The XRD analysis confirms Bunsenite which corresponds to the JCPDS card: 04- 0835 for Nickel oxide. The highest intensity was recorded for the plane with a strong peak of 2θ = 37^{o} for precursor solutions of 0.05 M, 0.075 M and 0.1 M which is an improvement. This could be due to an increase in grain growth caused by greater thickness. It can also be due to an increase in crystallinity as the concentration of the precursor solution increases. These results confirm the polycrystalline with cubic crystalline structures of deposited NiO film also observed polycrystalline with cubic structures when they varied concentrations of NiO films using SPT with a perfume atomizer but this seemed to have more intensity. The lower intensity peak increased gradually as the precursor solution increased from 0.05 M to 0.1 M with emergence of a third peak of for 0.1 M. The average crystallite size was obtained using the Debye-Scherrer formula. An additional silicon (Si) element was also observed. This is because Si is present in soda-lime glass or soda-lime-silica glass substrate [8].

4. New Lithium- Doping Procedure

4.1 Synthesis of Li Doped NiO Nanoparticles

Nickel nitrate and lithium nitrate solutions are mixed thoroughly using magnetic stirrer followed by the dropwise addition of sodium hydroxide under constant stirring. The solution is washed with double distilled water and ethanol for several times. Then it is dried in hot air oven for about 100^{o}C for 24 hours [10].

4.2 Processes in Steps with Cross Section

Firstly, Spray pyrolysis has been employed deposition of electrochromic films which may be approximately 250 nm thick. Targeting Ni metal, Li-Ni alloy target and $LiNO_3$ ceramic target supported on a Mb backing plate was brought. The gun power for metallic target was 150. The $LiNO_3$ pyrolysis process is hereafter noted. It is also observed that $LiNO_3$ spray pyrolysis process is denoted as intercalation lithiation. The electrochromic films were deposited onto F-doped substrate and glass particles. To sum up, the entire function was done in an ultra violet surface decontamination system which was beset with a heat controller. The base pressure was 10^{-5} Torr. The sample chamber was purged with pure oxygen for 35 sec. before initiating heating and UV irradiation.

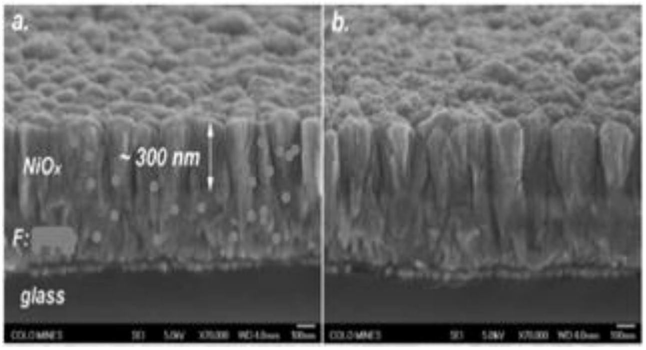

Figure 4: (a) Deposited electrochromic film cross-section (NiO), (b) Deposited electrochromic film cross-section ($LiNO_3$)

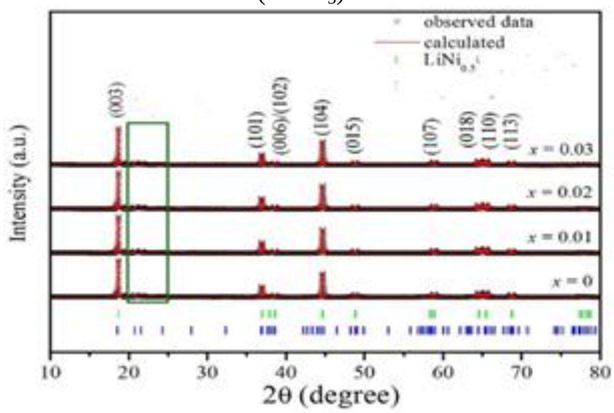

Figure 5: Observed data calculated in case of Li-Ni particles

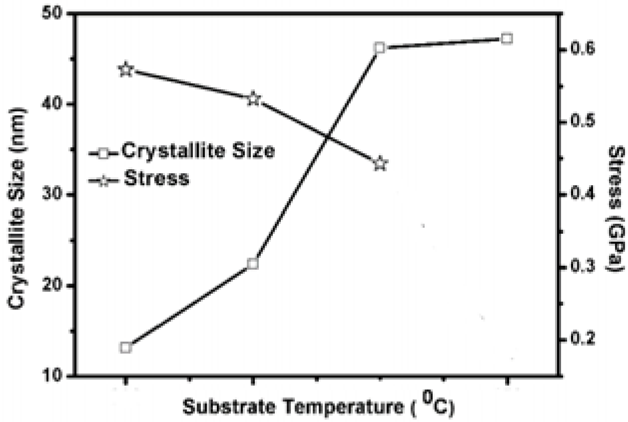

Figure 6: Influence of temperature in precursor ecomposition

Table 1: NiO nanoparticles' dislocation density ($LiNO_3$)

Serial No.	Nanopowder Samples	Dislocation Density (10^{18} lines/m^2)
1	0.05M Li Doped NiO	0.02385
2	0.08M Li Doped NiO	0.08476
3	0.14M Li Doped NiO	0.09533

5. Results and Discussions

It can be observed from figure 5,6 and from the table above, for $LiNO_3$ dislocation density with 0.05 M nanoparticle samples is 0.02385, for 0.08 M nanoparticles 0.08746 and for 0.14 M nanoparticles 0.09533. In addition, substrate stress also increased from 0.2 to 0.6 GPa and crystalline size from 5 to 45 nano metre. All these outcomes depict that it was a successful experiment which shows an advancement in Lithium doped process along with spray pyrolysis technique. Overall, the process was done perfectly and the output values are accurate.

6. Conclusion

Despite having several options to continue our research on development of electrochromism in Nickel Oxide films like rf-magnetron sputtering, anodic oxidation etc., spray pyrolisis included with Lithium Nitrate substrate was used. The reason behind this was to get more effectiveness with a newer model of doping procedure.

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References

[1] S.A. Mahmoud*, S.A. Aly, M. Abdel-Rahman, K. Abdel-Hady, "Electrochromic characterisation of electrochemically deposited nickel oxide films," Physica B 293 (2000) 125}131, Received 7 December 1999; received in revised form 31 March 2000.

[2] A.C. Sonavanea, A.I. Inamdara,b, P.S. Shindea, H.P. Deshmukhc, R.S. Patil a, P.S. Patil, "Efficient lectrochromic nickel oxide thin films by electrodeposition," Journal of Alloys and Compounds, GModel, JALCOM-20757.

[3] F. DECKER, S . PABBERINI, R. Plcacct and B. ScaosAn, "The Electrochromic Process In Non Stoichiometric Nickel Oxide Thin Film Electrodes," kcsmhkmlm Act.,, Vol. 37, No . 6, pp . 1033 10311,1992 0013-4686/9215.00+0 .O0 Panted in Great Britain . 0 1992.

[4] S. Green1, J. Backholm1, P. Georén2, C.G. Granqvist1, G. A. Niklasson1, "Electrochromism in Nickel Oxide and Tungsten Oxide Thin Films: Ion Intercalation from Different Electrolytes," Solar Energy Materials and Solar Cells, 2009, Vol. 93, Issue 12: 2050-2055.

[5] P.S. Patil*, L.D. Kadam, "Preparation and characterization of spray pyrolyzed nickel oxide (NiO) hin films, Applied Surface Science 199 (2002) 211-221

[6] P. Pushpharajah, S. Radhakrishna, " Transparent conducting lithium-doped nickel oxide thin films by spray pyrolysis technique," JOURNAL OF MATERIALS SCIENCE 32 (1997) 3001Ð3006.

[7] R.H. Misho, W.A. Murad, G.H. Fatahalah, "Preparation and optical properties of thin Nickel Oxide Solid Films," phys. stat.sol. a(109), K101, 1988.

[8] 1aUkoba, O.K, aInambao, F.L. and aEloka-Eboka, A.C, "Experimental Optimization of Nanostructured Nickel Oxide Deposited by Spray Pyrolysis for Solar Cells Application," International Journal of Applied Engineering Research ISSN 0973-4562 Volume 13, Number 6 (2018) pp. 3165-3173.

[9] Dainius Perednis & Ludwig J. Gauckler, "Journal of Electroceramics, 14, 103–111, 2005.

[10] S. Irudaya Sahaya Lancy, M. Priya Dharshini, V. Shally, Sr. Gerardin Jayam, "Effect of lithium doping concentration on the structural, morphological and optical properties of NiO nanoparticles," International Research Journal of Advanced Engineering and Science, Volume 1, Issue 2, pp. 55-58, 2016.