Study of Deposition Temperature on Properties of Aged Nanostructured Nickel Oxide for Solar Cells

Ukoba, O. Kingsley*,†, Inambao, L. Freddie**, Eloka-Eboka, C. Andrew***
*†Department of Mechanical Engineering, University of KwaZulu-Natal, Durban, 4041, South Africa.
** Department of Mechanical Engineering, University of KwaZulu-Natal, Durban, 4041, South Africa.
*** Department of Mechanical Engineering, University of KwaZulu-Natal, Durban, 4041, South Africa.
(ukobaking@yahoo.com, inambao@ukzn.ac.za, fatherfounder@yahoo.com)
†
Corresponding Author; Tel: +27640827616, +2348035431913

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Abstract- Nanostructured nickel oxide (NiO) films were deposited on preheated glass substrate using spray pyrolysis technique. This study examined the influence of deposition temperature on properties of aged nickel oxide thin films. A preferred orientation along the (1 1 1) plane was observed with a polycrystalline cubic structure. Films were formed with a stoichiometric ratio at higher deposition temperatures. It was revealed that the surface morphology and elemental composition of NiO films can be optimized by deposition temperature. The optical band gap grew as deposition temperature increased. Refractive index decreased with increasing deposition temperature. Optical band gap varied from 3.31 eV to 3.69 eV as deposition temperature increased. The deposition temperature has an influence on properties of aged NiO films. These results may be of interest in the development of affordable and efficient solar cell fabrication especially in developing countries.

Keywords- NiO; solar cell material; deposition temperature, developing countries, aged.

1. Introduction

Provision of affordable and efficient energy is a major human challenge [1]. Electricity is nonexistent for 20 % of the world’s population with developing countries comprising 99.8 % of that figure [2]. Several developing countries lack access to electricity [3] while many others have highly disrupted supply with less than four hours of power supply per day [4]. Optimized techniques and materials are being researched to solve this energy problem. Interest is on development of renewable energy due to their vast advantage [5-7]. Energy from the sun has been proposed as a viable solution for power supply [8-9]. Photovoltaic is one way of using the solar energy [10-14]. Solar energy can be converted to useful direct current electricity using solar cells [15]. The focus of current solar cell research is on affordability and efficiency. Most of the equipment used for thin film deposition is expensive [16] and vacuum-based [17]. This has caused researchers in developing countries look for in-country resources, resulting in research on inexpensive materials and methods requiring only a small power supply.

Nanostructure metal oxides are reported to offer improvement for solar cells [18]. Nickel oxide (NiO) is a unique metal oxide with several uses [19-24]. It is a p-type metal oxide and is an inexpensive material. It can be manufactured by several techniques such as sputtering [25], sol-gel [26], laser ablation [27], electron beam deposition [28] and chemical bath deposition [29]. Studies have been conducted on the effect of ageing and the effect of deposition temperature on NiO films [30-32], showing that ageing and deposition temperature improved NiO film properties. However, most of the studies focused on the influence of substrate temperature on sensing properties, electrochromic properties [33] and photovoltaic cells [34]. There is little or no systematic study of the influence of deposition temperature on aged NiO film properties. Therefore, there is a need to study their combined effect on NiO films.

This research will help to ascertain if deposition of nickel oxide at either low temperatures or temperatures above 350 °C give the same optimal properties. This temperature was reported to be the optimal range for pyrolytic decomposition of NiO [35]. Therefore, this research will study the influence of deposition temperature below 350 °C and above 350 °C on properties of aged NiO films. Morphological, structural, elemental, and optical properties will be examined with a view to optimizing NiO film for efficient and affordable solar cells application.
2. Experimental Procedure

2.1 Deposition

Pure nickel (II) acetate tetrahydrate Ni(\(\text{CH}_3\text{CO}_2\))\(_2\cdot4\text{H}_2\text{O}\) of 0.05 M was mixed and stirred in 50 mL distilled water. The solution was left for one week after mixing to age before deposition. This was spray deposited using the set-up in Fig. 1. Thereafter, it was deposited at different temperatures \(T_d\) (< 350 °C and ≥ 350 °C). The samples were sprayed from 270 °C to 325 °C for \(T_d\) < 350 °C samples and done at 350 °C to 400 °C for \(T_d\) ≥ 350 °C. The glass substrate was chemically and ultrasonically cleaned before usage for deposition of the solution. Other deposition parameters were maintained to obtain uniform film thickness.

![Fig. 1. Experimental set-up of Spray pyrolysis technique.](image)

The optimum deposition parameters of spray deposited NiO films are shown in Table 1. Each droplet was 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 was obtained as a final product [36].

\[
\text{Ni(}\text{CH}_3\text{CO}_2\))\(_2\cdot4\text{H}_2\text{O}\)_{\text{red}} \rightarrow \text{NiO} + 7\text{H}_2\text{O} \uparrow +4\text{CO}_2 \uparrow
\]

(1)

The colour of prepared thin films was observed to be gray, uniform and strongly adherent to the glass.

Table 1. Optimum deposition parameter of SPT NiO film.

<table>
<thead>
<tr>
<th>Deposition parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Height of spraying nozzle to substrate distance</td>
<td>20 cm</td>
</tr>
<tr>
<td>Spray rate</td>
<td>1 ml/min</td>
</tr>
<tr>
<td>Spray time</td>
<td>1 min</td>
</tr>
<tr>
<td>Time between sprays</td>
<td>30 sec</td>
</tr>
<tr>
<td>Carrier gas</td>
<td>Filled</td>
</tr>
<tr>
<td></td>
<td>compressed air</td>
</tr>
<tr>
<td></td>
<td>of 1 bar</td>
</tr>
</tbody>
</table>

2.2 Characterization

The morphology of deposited NiO film was studied using Scanning Electron Microscope ZEISS EVO MA15VP. An Energy Dispersive X-ray Spectrometer (EDS or EDX: “GENESIS XM2”) was used for elemental composition. An EMPYREAN (PANalytical) X-ray powder diffractometer model was used for structural properties of deposited NiO films from 5 ° to 90 ° 20 angles. The absorption of the film was measured with a Perkin Elmer Spectrum 100 Fourier Transform Infrared Spectrometer (FTIR). The measured film thickness was compared with the calculated values 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.

3. Results and Discussion

3.1 Morphological studies

SEM micrographs are represented in Fig. 2. These micrographs reveal homogeneous, smooth, well adherent films devoid of pinholes and cracks. The film of \(T_d\) ≥ 350 °C has better distribution of grains than \(T_d\) < 350 °C, although it has almost the same particle size and shape as \(T_d\) < 350°C. This may be ascribed to the ageing of the films and optimized deposition parameters. This shows that deposition temperature influences structural properties of aged NiO films by increasing grain on the film. These micrographs are an improvement on earlier results reported by Chen et al. [37] using radio-frequency (RF) magnetron sputtering.

![Fig. 2. SEM micrographs of aged (one week) nickel oxide (NiO) film on glass substrate at (a)Td < 350 °C and (b)Td ≥ 350 °C](image)

3.2 Elemental composition analysis

Fig. 3 shows the EDX for the different deposition temperatures for NiO thin films. Both spectra confirm presence of Ni and O elements in NiO thin films. Oxygen concentration in deposited NiO films decreases as deposition temperature increases. This may be due to increased film growth on the glass substrate as seen from Fig. 2 thereby making less of the glass (oxygen) visible.
Related results were reported by Lu et al. [38]. An additional Si element was also observed from the EDX. This is because Silicon (Si) is a major material in the soda-lime glass substrate used [39].

![EDX spectra for one week aged nickel oxide (NiO) film on glass substrate at (a) Td < 350 °C and (b) Td ≥ 350 °C](image)

**Fig. 3.** EDX spectra for one week aged nickel oxide (NiO) film on glass substrate at (a) Td < 350 °C and (b) Td ≥ 350 °C

### 3.3 Structural studies

The phase and preferred orientation of deposited nanostructured NiO films was determined using an x-ray diffractometer. Fig. 4 gives XRD patterns of deposited nanostructured NiO films at Td < 350 °C and Td ≥ 350 °C.

The peak diffraction for Td < 350 °C is at (2θ = 43.36° and 50.54°) for the (1 1 1) and (2 0 0) planes respectively. At Td ≥ 350 °C, peak diffraction is (2θ = 36.96° and 43.14°) for the (1 1 1) and (2 0 0) planes respectively. The XRD analysis confirms Bunsenite which correspond to JCPDS card: 04- 0835 for NiO [40]. A high intensity was recorded for Td ≥ 350 °C in both planes, which may be due to better alignment of the grains. This led to increased grain growth at higher deposition temperature. It can also be ascribed to increased crystallinity as deposition temperature increased. This is related to the reported value of 37.3° for the (1 1 1) plane by Sharma et al. [30].

The XRD spectra shows that films prepared at Td < 350 °C have weak and broadened (1 1 1) diffraction peaks, which implies poor crystallinity. However, those at Td ≥ 350 °C have good crystallinity and the (1 1 1) preferred orientation. These are pointers that the microstructure of NiO films are influenced by deposition temperature as evidence from the grain growth at higher deposition temperature. NiO films with either a (1 1 1) or (2 0 0) preferred orientation are recommended for optoelectronic applications [41].

There is separate colliding of Ni²⁺ and O²⁻ on the growing aged NiO films surface at lower deposition temperature, thereby making it difficult for Ni²⁺ and O²⁻ to recombine due to insufficient energy or oxygen. There is a tendency for non-stoichiometric ratio films to be formed which are electrostatically polar. Ni²⁺ and O²⁻ strike, simultaneously, on the growing aged NiO films at higher deposition temperature, producing film formation with stoichiometric ratios that are electrostatically neutral [42]. This is corroborated with a higher intensity for the (1 1 1) preferential orientation for low deposition temperature [43].

![XRD patterns of one week aged nanostructured NiO films at different deposition temperature](image)

**Fig. 4.** XRD patterns of one week aged nanostructured NiO films at different deposition temperature

The Debye-Scherer relationship [44]; [45] in equation (2) was used to obtain the average crystallite size.

\[
D = \frac{k\lambda}{\beta\cos\theta}
\]  

(2)

Where B represents the Full Width at Half Maximum (FWHM) peak intensity (in Radian), \(\lambda\) denotes wavelength, \(\theta\) represent Bragg’s diffraction angle and \(k\) is 0.89.

Other structural parameters are shown in Table 2.

<table>
<thead>
<tr>
<th>Deposition Temperature</th>
<th>hkl</th>
<th>Diffraction angle</th>
<th>FWH M</th>
<th>Relative Intensity</th>
<th>d-spacing</th>
</tr>
</thead>
<tbody>
<tr>
<td>Td &lt; 350 °C</td>
<td>(1 1 1)</td>
<td>43.3641</td>
<td>0.5038</td>
<td>100</td>
<td>2.42290</td>
</tr>
<tr>
<td></td>
<td>(2 0 0)</td>
<td>50.5425</td>
<td>0.7557</td>
<td>81.78</td>
<td>2.09685</td>
</tr>
<tr>
<td>Td ≥ 350 °C</td>
<td>(1 1 1)</td>
<td>36.9621</td>
<td>0.5510</td>
<td>62.14</td>
<td>2.43190</td>
</tr>
<tr>
<td></td>
<td>(2 0 0)</td>
<td>43.1404</td>
<td>0.3149</td>
<td>100</td>
<td>2.09688</td>
</tr>
</tbody>
</table>

The average crystallite size of NiO film index for the (1 1
1) and (2 0 0) planes for \( T_d \geq 350 \, ^\circ C \) as observed from XRD are 26 nm and 47 nm respectively. Those of \( T_d < 350 \, ^\circ C \) are 34 nm and 23 nm for the (1 1 1) and (2 0 0) planes respectively.

3.4 Optical properties

The film thickness was considered for the NiO films at deposition temperatures below \( (T_d < 350 \, ^\circ C) \) and above \( (T_d \geq 350 \, ^\circ C) \). The measured data is depicted in Fig. 6. This was compared with the calculated value. The calculated value was obtained using the weight difference method expressed in Equation (3) [46]:

\[
 t = \frac{m}{A \rho} 
\]  

(3)

Where \( t \) denotes film thickness, \( m \) represents the actual mass deposited, \( A \) denotes thin film area while \( \rho \) represents the density of material.

Fig. 7 shows the calculated values. Both measured and calculated values are in good agreement. Film thickness grew as deposition temperature increased. The NiO film thickness was controlled by keeping deposition parameters constant. NiO thin film average thickness was between 11.85 µm and 12.55 µm.

Fig. 8 gives FTIR spectra used to identify molecular components and the structure of NiO films. It gives the spectrum of aged (one week) 0.05 M NiO films at \( T_d \geq 350 \, ^\circ C \) alone, in the range of 400 cm\(^{-1}\) and 4000 cm\(^{-1}\). The NiO stretching vibration mode was recorded in the broad absorption band region of 432 cm\(^{-1}\) to 698 cm\(^{-1}\). This is similar to the earlier reported NiO absorption range [47]. The broadness confirms that the NiO are nanocrystalline. The NiO film FTIR absorption is blue-shifted due to their nanostructure size. Other significant absorption bands were also recorded. The band at 3475 cm\(^{-1}\) reveals an O-H (hydroxyl group or hydroxide ion) stretching vibration. This is the natural portion of water due to a self-ionization reaction [48]. An H-O-H bending vibration mode was observed at 1630 cm\(^{-1}\). This shows that there is a negligible quantity of water in the NiO film. This may be attributed to adsorption of water from the air since the experiment was conducted in open air [49]. This is corroborated by the EDX result in Fig 3. The region between 1000 cm\(^{-1}\) to 1500 cm\(^{-1}\) with band centre at 1210 is assigned O-C=O symmetric and non-symmetric stretching vibration. This accounts for the traces of H\(_2\)O and CO\(_2\) in the reaction of Equation (1) which were burnt off. There is no band indicating the presence of other groups, confirming that there is no impurity in the film and that the sample was washed and well cleaned. This result agrees with the standard FTIR data for NiO films as reported by [50]. The NiO film deposited at \( T_d < 350 \, ^\circ C \) did not give FTIR. This may be due to non-absorption of the film.
Fig. 9 represents measurement of transmittance and wavelength for deposited NiO films at the deposition temperatures. Transmittance grew from 70.70 % to 76.41 % as deposition temperature increased. However, both films exhibited high transparency in visible and near IR regions. This occurred at wavelengths of 1000 nm and 611 nm respectively. This may be due to an increase in film thickness and absorbance (shown in Fig. 10) as deposition temperature increases, making the scattered radiation more pronounced because of surface roughness [51]. These results exceed previously reported values of less than 70 % by Ismail et al. [52].

Absorption coefficient, $\alpha$ was obtained using Equation (4) [53]:

$$\alpha = \frac{(2.303 \times A)}{t}$$  \hspace{1cm} (4)

Where $t$ is film thickness and $A$ is absorbance. The relationship between optical absorption and optical energy band gap is expressed in Equation (5) [54]; [55]:

$$\alpha^2 = C(\hbar \nu - E_g)$$  \hspace{1cm} (5)

Where $C$ has constant value, $h$ denotes Planck’s constant, $\nu$ represent incidence light frequency, and $E_g$ denotes optical energy band gap.

Fig. 10. Plot of absorbance against wavelength of deposition temperature of NiO films

Fig. 11. Graph of $(\alpha h \nu)^2$ against $h \nu$ for NiO films

Fig. 11 shows a graph of $(\alpha h \nu)^2$ against $h \nu$ for aged NiO films spray deposited at both deposition temperatures. Extrapolation of Fig. 11 to $h \nu$ axis for $(\alpha h \nu)^2 = 0$ gives the optical band gap. A decrease in slope of the plot is observed as deposition temperature increases. A shift towards lower energy is observed for value optical band gap. The reduction is attributed to the Moss-Burstein shift [56, 57]. Optical energy band gaps are 3.31 eV and 3.69 eV for $T_d < 350$ °C and $T_d \geq 350$ °C respectively. This gives a better optical band gap compared to the existing reported value of 3.5 eV [58]. This may be ascribed to crystallite size increment [59]. The quantum size effect may be responsible for the large value of the band gap of NiO films [60]. Careful and well optimized deposition parameters also help in obtaining a better optical band gap.
Fig. 12 shows the refractive index of the NiO films. The refractive index of deposited films was calculated using refractive index and optical band gap expression as shown in Equation 6 [61]:

$$\eta = \sqrt{(12.417 / (E_g - 0.365))}$$

(6)

Where $\eta$ denotes refractive index while $E_g$ represents optical band gap.

Refractive indices were found to be 2.0533 and 1.9324 for $T_d < 350$ °C and $T_d=350$ °C respectively. This is an improvement on reported values of 1.99 by Sriram and Thayumanavan [32].

4. Conclusion

This study reported spray pyrolysis deposition of aged nanostructured NiO films on glass substrate. The influence of deposition temperature on aged NiO films on elemental, morphological, structural and optical properties was studied with a view to optimizing deposition temperature for solar cell application.

This study contributed new results relating to surface morphology, structural, film thickness and optical of NiO films using spray pyrolysis.

Deposition temperature only affected the surface morphology of aged NiO films by producing a grainier surface. It does not affect the shape and size. Elemental composition using EDX confirmed the presence of Ni and O elements in NiO films. It was observed that the film thickness grew as deposition temperature increased.

NiO films are formed with a non-stoichiometric ratio at lower deposition temperatures, but are electrostatically neutral at higher deposition temperatures.

Transmittance grew from 70.70 % to 76.41 % as deposition temperature increased. This resulted in a reduction in the refractive index of the aged NiO films as deposition temperatures increased. Optical band gap varied from 3.31 eV to 3.69 eV as deposition temperature increased. This study produced better optical band gaps than existing reported values. The new findings were a result of well optimized deposition parameters. Therefore, deposition temperature does affect the properties of aged nanostructured NiO thin films. This optimized result may be explored further for affordable, durable and efficient solar cell fabrication and research in developing countries by ageing the precursor for longer period and at different concentrations, it can also be doped with another material or this result used directly to fabricate a solar device using a pn heterojunction technology. This optimized results will help in affordable and sustainable solar cells fabrication as it will be useful as p-type material in a pn heterojunction solar cells.

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References


