Structural and Optical Characterization of Nickel Oxide Thin Films Prepared by Spray Pyrolysis Technique

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ABSTRACT

In this research, Nickel oxide (NiO) thin film were prepared by using nickel chloride ( NiCl₂.6H₂O) on glass substrate by using Spray Pyrolysis technique. The Structural and optical properties were studied for the growth thin films under influence different molarities (0.5,1,2 M) by XRD , SEM . The optical properties studied in the wavelength range from 200-1100nm measured by UV-VIS Spectrometer device.

The X-ray diffraction studies indicated that intensity was increased with molarities increase and had cubic structure , these films has grain size values (4.13-11.95 nm) with different molarities (0.5, 1 , 2M) , SEM found  the films has smooth surface with grains scattered throughout the surface and the surface the films filled with the clusters of the larger grains the at increase molarities and AFM  it is found  the (RMS) of NiO films increased from 7.77 to 20.7 nm and the roughness average increased from 5.73-15.6 nm with the increase of molarities from 0.5-2 M.

From the optical studies it is found the film thickness increased with molarities increase, while the transmittance decreased from approximately 75% to approximately 54% and the energy gap for the NiO films varies from ( 3.65 to 3.1eV) as the molarities increase.

Keywords – nickel oxide, spray pyrolysis technique, thin films, Structural, optical properties.

الخصائص التركيبية والبصرية لأغشية أوكسيد النيكل الرقيقة المحضرة بطريقة الرش الحراري

في هذا البحث حضر أوكسيد النيكل باستخدام كلوتيدات النيكل على قاعدة زجاجية باستخدام تقنية الرش الحراري , درست الخصائص التركيبية والبصرية للأغشية النانوية تحت تأثير المolarity بواسطة فحص حيود الأشعة السينية والمجهر الإلكتروني الماسح ومحجر القوة الذرية , الخصائص البصرية UV-VIS -VIS درست عند طول الموجي من 200-1100 نانومتر مقاسة بواسطة استخدام جهاز مطياف 

إن فحص حيود الأشعة السينية أشار إلى أن الشدة تزداد بزيادة المolarity وتمتلك تركيب مكعب . هذه الغشاء ئها حجم حبيبي قيمة تغيرة من (11, 4.95-11.95) مع تغيير التركيز (0.5،1،2) مولارية , وجد المجهر الإلكتروني الماسح الأشعة تمتلك سطح ناعم مع انتشار الحيوانات في كافة أنحاء السطح , وسطح الأشعة السينية ملائماً بفضل الحيوانات المكعبة وزيادة المolarity ومحجر القوة الذرية وان قيمة مربع المتوسط الجذر تزداد من (7.77 إلى 20.7) مع ارتفاع الطاقة يزيد من (5.73 إلى 15.6) عندما تغيرة قيمة المolarity من (0.5 إلى 2) من دراسة الخصائص البصرية وجد ان السمك يزداد مع زيادة المolarity بينما النفاذية قلت ترقياً من 75% إلى 54% وفوجة الطاقة لأغشية أوكسيد النيكل تتغير من (3.65 إلى 3.1) الكترون فولت عند زيادة المolarity.

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INTRODUCTION

Nickel oxide thin film (NiO) is an attractive material due to its excellent chemical stability as well as optical, electrical and magnetic properties. It is a group VIII-VI semiconductor which has a polycrystalline of cubic structure. The interesting in nickel oxide (NiO) thin films is growing fast due to their importance in many applications in science and technology. It was a versatile wide band gap semiconductor material. These films are n-type. However p-type conducting films are required as optical windows for the devices where hole injection is required. NiO is a p-type semiconductor with a band gap ranging from (3.6 to 4.0) eV. NiO films have a wide range of applications, such as transparent conductive films, electrochromic display devices, anode material in organic light emitting diodes, and functional layer material for chemical sensors.

Nickel oxide films have been fabricated by various kinds of techniques, including thermal evaporation, plasma enhanced chemical vapor deposition, sol-gel, sputtering, RF magnetron sputtering, and spray pyrolysis.

The optical properties of thin films are very important for many applications, including interference devices (such as antireflection coatings, laser mirrors, and monochromatic filters), as well as optoelectronics, integrated optics, solar power engineering, microelectronics, and optical sensor technology.

In this work we study the effect of molarities on the structural and optical properties of Nickel oxide thin films.

Experimental

The NiO thin film prepared by cleaning the glass substrate by using ethanol in ultrasonically cleaner, kept the nozzle for spray pyrolysis at a distance of 25cm from the substrate during deposition, solution prepared by dissolving a certain amount (0.5, 1, 2 M) of nickel chloride (NiCl₂.6H₂O) in (200 ml) of distilled water, then the resulting solution was sprayed on preheated glass substrates to 400°C by an electrical heater, when the solution is sprayed the following reaction takes place at the surface of the heated substrate. The deposition parameters applied for the preparation of nickel oxide thin films are presented in table (1).

<table>
<thead>
<tr>
<th>Table (1) deposition parameters applied in this research</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiCl₂.6H₂O solution concentration</td>
</tr>
<tr>
<td>Substrate temperature(°C)</td>
</tr>
<tr>
<td>Nozzle to substrate distance</td>
</tr>
<tr>
<td>Solvent</td>
</tr>
<tr>
<td>Deposition time (minutes)</td>
</tr>
<tr>
<td>Time interval between successive sprays</td>
</tr>
<tr>
<td>Spray time during each cycle</td>
</tr>
</tbody>
</table>

X-ray diffraction (XRD) was used to determine the phase present and the preferred orientation of the deposits. Using Philips PW 1050 with following specifications are target is CuKα with radiation of wavelength λ =1.5406Å, Target:
Cu, Current=30mA, Voltage = 40 kV, scanning speed = 5 deg /min) over the diffraction angle range 2θ = 20-50°

XRD is used to calculate different parameters which could be used to clarify the studies of the deposited films. The average grain size (D) of nickel oxide films samples were calculated by using the Scherrer equation:

\[ D = \frac{0.9 \lambda}{\beta \cos \theta} \] … (1)

Where:
\( \lambda \): wavelength, \( \beta \): the full width at half maximum (FWHM) of the diffraction peak, and \( \theta \): Bragg’s diffraction angle, respectively.

The Bragg condition:

\[ 2d \sin \theta = n \lambda \] … (2)

Where \( d \): the spacing between the planes under consideration, \( n \): the order of the corresponding reflection.

The lattice parameter ‘a’ can be evaluated from the relation:

\[ d = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \] …(3)

The micro strain was produced through growth of thin films can be calculated from the follows formula:

\[ \delta = \frac{|a_{ASTM} - a_{XRD}|}{a_{ASTM}} \times 100\% \] …(4)

Where : \( a \) is the lattice constant.

The NiO thickness was measured by using an optical interferometer method employing He-Ne laser (0.632μm) with incident angle 45°. This method depends on the interference of the laser beam reflected from thin film surface and then substrate. The films thickness was determined using the following formula:

\[ d = \frac{\Delta x}{x} \times \frac{\lambda}{2} \] …(5)

Where: \( x \) is fringe width, \( \Delta x \) is the distance between two fringes and \( \lambda \) is the wavelength of the laser light.

The optical transmittance of NiO thin films was studied in the wavelength range from (200 – 1100)nm measured by UV-VIS Spectrometer device.

The absorption coefficient (\( \alpha \)) calculated according to the following equation:

\[ \alpha = \frac{1}{d} \ln \frac{1}{T} \] …(6)

Where (d) is the thickness of thin film and (T) is the transmission.

The optical absorption coefficient is related with the energy band gap and it is given by the equation:

\[ a h \nu = A (h \nu - E_g)^n \] …(7)

Where \( a \) (cm\(^{-1}\)) is the absorption coefficient, \( h \) (J.s) is Planck’s constant, \( \nu \) (Hz) is the photon frequency, \( A \) is constant, \( E_g \) (eV) is the band gap energy, and \( n \) has different values depending on the nature of the absorption process. The plot of \((a h \nu)^2\) versus \(h \nu\) gives the best fit results, by extrapolating the liner part down to \( a = 0 \), the value of \( E_g \) could be determined.
Results and Discussion

X-Ray Diffraction (XRD) for NiO thin films

Figure (1) shows the X-ray diffraction (XRD) for NiO thin films with different molarities at 400°C, from (XRD) analyses it is found that two peaks at 37.40° and 43.45° corresponding to the (111) and (200) planes of the cubic structure. The most intensity peak is at $2\theta = 37.40°$ with the preferential orientation of the films being (111). That intensity for the films increases with increasing molarities, these films have grain size values (4.13-11.95 nm) with different molarities (0.5, 1, 2M). This may be due to increasing in the grain growth associated with largest thickness or increasing in the degree of crystallinity as the molarity increases as shown in fig. (2). The obtained results of the XRD for the structural properties on the NiO films are presented in table (2).

Table (2): The obtained results of the XRD for the structural properties on the NiO films.

<table>
<thead>
<tr>
<th>Molarities (M)</th>
<th>$2\theta$ (deg)</th>
<th>hkl</th>
<th>d(nm) XRD</th>
<th>d(nm) ASTM</th>
<th>a(nm) XRD</th>
<th>a(nm) ASTM</th>
<th>Grain Size Gs(nm)</th>
<th>Micro Strain ($\delta$)%</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>37.40</td>
<td>111</td>
<td>2.402</td>
<td>2.4066</td>
<td>4.1603</td>
<td>4.1684</td>
<td>4.131</td>
<td>0.194</td>
</tr>
<tr>
<td></td>
<td>43.45</td>
<td>200</td>
<td>2.081</td>
<td>2.0842</td>
<td>4.162</td>
<td>4.1684</td>
<td>5.78</td>
<td>0.1535</td>
</tr>
<tr>
<td>1</td>
<td>37.34</td>
<td>111</td>
<td>2.405</td>
<td>2.4066</td>
<td>4.1655</td>
<td>4.1684</td>
<td>6.57</td>
<td>0.0695</td>
</tr>
<tr>
<td></td>
<td>43.51</td>
<td>200</td>
<td>2.078</td>
<td>2.0842</td>
<td>4.156</td>
<td>4.1684</td>
<td>7.42</td>
<td>0.295</td>
</tr>
<tr>
<td>2</td>
<td>37.41</td>
<td>111</td>
<td>2.4019</td>
<td>2.4066</td>
<td>4.1602</td>
<td>4.1684</td>
<td>9.55</td>
<td>0.196</td>
</tr>
<tr>
<td></td>
<td>43.47</td>
<td>200</td>
<td>2.0802</td>
<td>2.0842</td>
<td>4.1604</td>
<td>4.1684</td>
<td>11.95</td>
<td>0.1919</td>
</tr>
</tbody>
</table>

Figure (1) XRD of NiO films with different molarities (0.5, 1, 2 M)
Surface Morphology
The SEM micrographs of the surfaces Nickel oxide thin films with different molarities at 400°C as shows in Figure (3) at different magnification. The SEM micrograph clearly indicate that Nickel oxide film with 0.5M molarities has smooth surface with grains scattered throughout the surface. With 1 M molarities, it is found that the particles size increases for grains scattered throughout the surface. And this when the molarities is increased to 2 M, the surface filled with the clusters of the larger grains. The SEM micrographs are observed that as the high molarities of spray solution increases grain size this which agreement to the XRD results.
The atomic force micrographs (AFM) of the surfaces nickel oxide thin films with different molarities shows in Figure (4 A,B). This Figure shows the typical two-dimensional and three-dimensional AFM image of NiO films deposited at temperature 400°C, by using spray pyrolysis technique. It is found that the root mean square (RMS) of NiO films increases from 7.77 to 20.7 nm and the roughness average increases from 5.73-15.6 nm with the increasing of molarities from (0.5-2 M). The variation of surface roughness with different molarities for the NiO thin films illustrate in table (3).
Table (3) Variation of surface roughness and root mean square (RMS) at different molarities for the NiO thin films

<table>
<thead>
<tr>
<th>Molarities (M)</th>
<th>The root mean square (RMS) (nm)</th>
<th>Roughness average (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>7.77</td>
<td>5.73</td>
</tr>
<tr>
<td>2</td>
<td>20.7</td>
<td>15.6</td>
</tr>
</tbody>
</table>

Optical Properties

Figure (5) shows the thickness for the films with different molarities at 400°C, it was observed that the increases in molarities for the films lead to increasing thickness (147, 189 to 210 nm) and this is because the amount of material that participates in forming the deposited film increases.

![Figure (5) thickness of NiO films with different molarities](image1)

Figure (6) shows that the variation of transmittance for the films with different molarities at 400°C, it is found that the transmittance decreases from approximately 75% to approximately 54% with increasing molarities at (0.5, 1 and 2 M) of the solution. And this can be attributed to the increasing in the film thickness.

![Figure (6) show the optical transmittance spectra of the NiO thin films with different molarities (0.5, 1 and 2 M)](image2)
Figure (7) shows the absorption coefficient ($\alpha$) for NiO thin film on glass substrate, it is found that the absorption coefficient decreases with increasing the molarities with increasing wavelength and this attributed to the effect of the thickness which was thicker with increasing molarities.

Figure (7) show the absorption coefficient of the NiO thin films Vs wavelength at different molarities (0.5, 1 and 2 M).

Figure (8) shows the energy gap (Eg) of the NiO films at different molarities on preheated glass substrates to 400°C. The energy gap for the NiO films varies from 3.65eV to 3.1eV as the molarities varies from 0.5M to 2M. It is found that the energy gap value decreases at molarities increasing, this decreases in the energy gap can be related to the increasing in the thickness of the films which due to the increasing in the molarities.

Eg=3.65eV

Eg=3.4eV
**CONCLUSIONS**

Nickel oxide (NiO) thin films were prepared by using Spray Pyrolysis technique. They have cubic structure and the grain size increases with increasing molarities. SEM it is found that increases in the particles size for grains scattered throughout the surface when the molarities increase. For AFM, it is found that the (RMS) of NiO films increases from (7.77 to 20.7) nm and the roughness average increases from (5.73-15.6 nm) with the increasing of molarities from (0.5-2 M). From the optical properties of thin films it is found the transmittance decreases with molarities increasing and the energy gap varies from (3.65 to 3.1eV) as the molarities increase.

**REFERENCES**