NiO Thin Layers Prepared via Computerized Spraying System

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Abstract: Spray pyrolysis technique was employed for depositing Nickel oxide thin films onto glass substrates at 350±10 °C. An aqueous solution of NiCl2.4[H2O] within 0.01 M used for spraying. XRD examination revealed polycrystalline cubic phase of NiO thin films. The crystallinity growth along (111), (200), and (202) planes at 2θ = 37.28°, 43.29°, and 62.91°, respectively. AFM was examined and showed low roughness in the selected area. Thickness was calculated using Fizeau Fringes interferometric method that found around 175 nm. FTIR investigation endorses the vibration mode of the Ni-O bond. The absorption investigation was carried out in the range 350-750 nm, and the energy band gap was found to be about 3.68 eV. The microscopic imaging showed an adequate surface morphology with fine distribution of coating on the substrate.

1 Introduction
In recent decades, a wide variety of thin layers were deposited via famous spray pyrolysis technique (SPT) [1]. Where the fabrications would be large scale production at an affordable cost [2]. In the present research, CTS absorption layers were deposit via home-made fully computerized chemical spray pyrolysis deposition system (FCSPD) [3]. Moreover, physical and chemical techniques were also employed in the deposition of NiO thin layer [4]. The deposited layer properties depend on the type of substrate, substrate temperatures, spraying rate and droplet sizes [5]. Whereas, the droplet size was governed by the spraying rate, nozzle diameter and carrier gas pressure [6]. Nickelous oxide thin films can be fabricated via numerous physical and chemical deposition techniques [4], such as spray pyrolysis [7], chemical bath deposition [8], pulsed laser deposition [9], magnetron sputtering [10], sol-gel [11], spin coating [12], and dip-coating [13]. Furthermore, there are many chemical phases of the nickel oxide, such nickelous oxide (NiO), nickel trioxide (Ni2O3), nickel dioxide (NiO2), nickelosic oxide (Ni3O4), and nickel peroxide (NiO2).

2 Experimental
2.1 Sample Preparation
A computerized spray pyrolysis deposition system (FCSPD) was employed for deposition of NiO thin layers onto glass substrates employing a. The FCSPD has deposition part can movies in 3D. Where the platform hotplate can move in the x-y dimension during the coating process. Moreover, the holder of the nozzle moves vertically in z-axis which precisely moves the nozzle. The computerized setup has an ability of monitoring and controlling the substrate temperature within vitiation around 0.25 °C [14], as shown in Figure 1.

![Computerized Spraying system](image)

**Figure 1:** Computerized Spraying system [1].

For nickel oxide deposition, nickel di-chloride tetrahydrate NiCl₂·4[H₂O] was utilized as a raw chemical provided by Sigma Aldrich, with a 99.9% purity that dissolved in distilled water. An aqueous solution of 0.01 M concentration was used in the spraying process. The lab scale glass substrates were cleaned ultrasonically during immersing for 15 min in distilled water at 70°C. A metallic nozzle of 0.35 mm radius was used for spraying the aqua sol onto preheated substrates. The substrate temperature was kept at 350±10 °C with the average spraying flow rate around 0.25 mL per sec. The aqueous solution was sprayed on the substrate with compressed air as a carrier gas. The formation of nickel oxide thin films can be according to the chemical reaction equation [15]:

\[ \text{NiCl}_2 \cdot 4\text{H}_2\text{O (aq.)} \xrightarrow{\text{heat}} \text{NiO} + 2\text{HCl} \uparrow + 3\text{H}_2\text{O} \uparrow \]

Throughout the deposition process, the flow rate, substrate temperature, deposition period, and nozzle to substrate distance were kept unchanged throughout the deposition process. When the deposition process is done, the substrate was remained onto the hotplate for accessing room temperature.

2.2 Sample Analysis
The crystallinity was carried out via PHASER X-ray diffractometer of wavelength 1.54 Å supplied by BRUKER, Germany. In addition, the XRD data are normally used for acquiring information about the estimated crystallite size (D) using Debye-Scherer’s formula, as depicted in Equation (2-1) [16].

\[ D_{hkl} = \frac{K \lambda}{\beta \cos(\theta_{hkl})} \]  \hspace{1cm} (1)
Where; $D$ is the crystallite size; $\lambda$ is the X-ray radiation wavelength, $K$ is usually occupied as 0.94, and $\beta$ is the Full width at half-maximum (FWHM) of the diffraction peak in radians. The surface morphology was examined in 3D imaging via AFM type SPM- AA3000 from Angstrom advanced Inc., USA. Thickness of NiO thin films was measured using an optical interferometer method, employing a green laser (wavelength of 532 nm). Wherein, this method depends on the interference of the laser beam that reflected from the thin film surface and its substrate. Within, the thickness has been determined using the formula [1].

$$t = \frac{\lambda}{2} \times \frac{\Delta x}{x}$$  \hspace{1cm} (2)

Where $x$ is the fringe width, $\Delta x$ is the consecutive separation distance of fringes, and $\lambda$ is the laser wavelength. FTIR spectrum was recorded via IR Prestige-21, by Shimadzu, Japan. UV-Vis spectrum was obtained at room temperature using K-MAC SV2100 provided by Korea Material & analysis, Korea. Whereas, the energy band gap was determined by Tauc equation. An optical microscopic investigation, a digital camera of the 5 MB resolution was joined to the microscope of type MOTIC B Series, (Malaysia) that has employed for examining the surface topography of NiO thin films. The surface morphology of the deposited films was analyzed using SEM of type (Inspect S50) supplied by FEI Company, Netherlands.

3 Results and Discussion

The XRD patterns of NiO thin films are shown in Figure (1). It is noticed that samples were polycrystalline in the cubic phase. The XRD peaks were growth along (111), (200) and (202) planes, at $2\theta = 37.227^\circ$, 43.254$^\circ$, and 62.830$^\circ$, respectively. XRD patterns were compared with COD card No. (96-101-0096) [17]. In addition, the average crystallite size was calculated using Scherer’s formula which found to be about 312 nm.

Figure 2: XRD pattern of NiO thin film.

AFM was employed to study the surface roughness of the NiO thin film. Figure 2 displayed that the 3D image and particle size distribution of the deposited NiO thin film. This micrograph showed that the surface was uniformly coated with spherical particles. Whereas, the average grain size was determined by measuring the size of grains in selected area (4x4) $\mu$m of micrograph, and it was found to be about 127 nm. While, the average roughness and root mean square of the NiO thin film were found to be 8.25 nm and 9.78 nm, respectively.
Thickness of the prepared samples were found out around 175 nm for the as deposit films. FTIR was described the absorption bands that observed in the region of 430–490 cm$^{-1}$ were definitely assigned to Ni–O stretching modes [18], as illustrated in Figure 3.

Figure 3: AFM of NiO thin film in 4×4 µm.

Figure 4: FTIR spectrum of NiO thin film.

Figure 4 shows the UV–vis absorption spectra of NiO thin film. The optical absorption peak was showed at 353 nm (3.51 eV).

Figure 5: Uv-Vis spectrum of NiO thin film in range 530-750 nm.
The energy band gap of the prepared thin films was found to be about 3.68 eV, that calculated using Tauc equation.

![Energy Band Gap Diagram](image)

**Figure 6:** Energy band gap of NiO thin film in range 530-750 nm

The optical microscopic imaging was in range 850×680 µm, it shows how the fine distribution obtained by spray pyrolysis technique. Figure 6 displayed two images with different zooming scales. It is worth mentioning that, the prepared thin layers of NiO were in good adherent to glass substrates.

![Microscopic Images](image)

**Figure 7:** Microscopic images in different scale, (a) 850×680 µm, (b) 400×400 µm

### 4 Conclusions

Fully controlled spraying system has been employed for NiO thin film deposition. Whereas, spraying parameters were optimized for depositing films of Nickelous Oxide. The cubic structure has been detected using XRD studies. AFM imaging showed fine roughness. Thin film thickness was in nanoscale. FTIR spectrum was mentioned that Ni-O bond was present. Absorption was detected at UV region of spectrum, where the energy gap was found about 3.68 eV. Surface morphology was examined via optical microscopy, where a fine distribution was observed at the selected area.

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