Nickel Oxiide Thin Films Grooved by Laser Processing

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Abstract. Nickelous oxide thin films were successfully deposited onto glass substrates via a fully computerized system of Spray pyrolysis technique. The substrate was maintained at 350°C. Dichloronickel tetrahydrate was used as the raw chemical material. XRD investigation revealed a cubic phase of NiO crystal structure. XRD diffraction patterns were found peaks at 2θ = 37.280°, 43.297°, 62.916 and 79.542°, respectively. The FTIR certified vibration mode of Ni-O bonds. Debye-Scherrer’s formula found out the grains at 21 nm. Absorption spectrum recorded in the wavelength range of 350-850 nm. Morphology of NiO films was uniformly coated with good surface distribution. The fabricated film was grooved by a blue laser source of 500mW power. Laser grooving process produced a groove width of about 34 µm.

Keywords: Fully computerized Spray pyrolysis, NiO, Laser grooving.

1 Introduction
Thin films of Nickel oxide have been magnificently deposited onto a glass substrate using economical spray pyrolysis technique SPT [1]. As mentioned in the literature, SPT could be classified as solution-based chemistry that is based on the nature of the deposition [2]. Moreover, deposition processes started with a solution have been more popularity [3]. SPT starts via simple available materials, which has been offered products at low-cost within high purity [4]. NiO thin films might be deposit via a number of physical and chemical techniques [4]. Numerous deposition techniques were employed for NiO thin films fabrication on different substrates [5]. Such as thermal evaporation [6], electron beam deposition [7], metal organic chemical vapor deposition [8], chemical bath [9], spray pyrolysis [10], sol-gel [11], spin-coating [12] and reactive sputtering [13], and RF magnetron sputtering [14]. Due to the noteworthy properties of NiO thin films, where are considered to be promising for solar cells applications [15]. Inorganic semiconducting materials can classify as inexpensive, eco-friendly and viable sources for solar cell fabrication [16]. The deposited film be subject to substrate type, substrate temperature, spraying frequency and droplet sizes [17]. Droplet size depended on the spray rate, nozzle diameter, carrier gas, and gas pressure [18]. Recently, lasers have employed in a number of common manufacturing applications, such as welding, drilling, cutting, and grooving processes [19].
2 Specimen preparation

Fully computerized chemical spray pyrolysis system [20], [21] was employed in the deposition process of NiO thin films on glass slide of dimensions (75×25×1.5) mm as a substrate. Dichloronickel tetrahydrate (NiCl$_2$·4H$_2$O) was exploited as raw material for spraying solution, which supplied by Sigma Aldrich (purity, 99.9%). The distilled water used as a solvent for preparing 0.01 mol concentration at 2.2 pH. An airbrush with the metal nozzle of radius 0.35 mm was used for the sparing process. For uniform thin film deposition, the equipped solution was sprayed onto preheated glass substrates. Where the nozzle was fixed at 30 cm over the substrates. Therein, evaporation of solvent and decomposition on the substrate were happened, that fabricate the nickel oxide thin film as described by the chemical reaction below [2]:

$$\text{NiCl}_2\cdot4\text{H}_2\text{O} \xrightarrow{\text{heat}} \text{NiO} + 2\text{HCl} \uparrow + 3\text{H}_2\text{O} \uparrow$$

During deposition, the substrate temperature was retained at 350±5 °C. So that, each of flow rate, air pressure, nozzle to substrate distance were preserved unchanged. The solution flow rate has an average value of around 0.2 mL per sec, for each spray pulse. An aqueous solution was sprayed on the substrate with compressed air as a carrier gas. The substrate was held onto a preheated plate for reaching room temperature, as crystal nucleation growth. Additionally, a focusable laser pointer source was employed in the grooving process with wavelength 410 nm at 500mW). In the current work, the laser source was joined with CNC homemade machine [21] at the optimum height, as the smallest spot size was obtained. The main idea of using a laser grooving process is for increasing the surface area deposit thin films. So that, absorption improved with the grooving process.

3 Instruments

The crystallography was examined via X-ray diffractometer (D2 PHASER, by BRUKER, Germany), with incident wavelength $\lambda = 1.54056$ Å (CuK$_{\alpha1}$). In the interim, Debye-Scherer’s formula was employed for calculation the crystallite size, as in (eq.1) [22]

$$D = \frac{K \lambda}{\beta \cos(\theta)}$$

Where; $D$ is denoted to the grain size, $K = 0.9$ which is a numerical factor, $\lambda$ is the X-rays wavelength, $\beta$ refers to the width (full-width at half-maximum) of the diffraction peak in radians, and $\theta$ is the Bragg angle. Meanwhile, the FTIR was examined using IR Prestige-21, (Shimadzu, Japan). UV-Vis spectroscopy was realized at room temperature via K-MAC SV2100 spectrophotometer (Korea Material & analysis, Korea). The thickness of the prepared NiO thin film was measured by the interferometer process. Whereas a green laser was employed (532 nm), thickness has been determined using formula as in equation 2 [23].

$$t = \frac{\lambda}{2} \times \frac{\Delta x}{x}$$

This optical method directly depended on the interference of the reflected light from the thin film within the substrate. The optical microscopic investigation was investigated via a MOTIC-B microscope (Malaysia), with a digital camera of 5MB resolution. And also, the micrograph images were enhanced via image processing software.
4 Results and discussion

The most intense peaks of NiO seen on the XRD pattern were diffracted from planes (111), (200), (220) and (222) which corresponding to diffraction angles such 37.280°, 43.297°, 62.916 and 79.542°, respectively. The XRD patterns of NiO films are shown in Figure (1), where the samples are a polycrystalline cubic phase.

![Figure (1): XRD patterns of NiO thin film.](image)

XRD patterns were certified with ICDD card No. (PDF#040835) [24]. Also, the d-spacing was examined too, as listed in the table (1).

| hkl | Theoretical | Empirical |
|-----|-------------|-----------|
| 2θ  | d<sub>hkl</sub> | 2θ  | d<sub>hkl</sub> |
| 111 | 37.280      | 2.4100    | 37.352      | 2.4056 |
| 200 | 43.297      | 2.0880    | 43.261      | 2.0896 |
| 220 | 62.916      | 1.4760    | 62.896      | 1.4765 |
| 222 | 79.391      | 1.2060    | 79.542      | 1.2041 |

As seen in the table above, about 99% of precision was ensured in matching the empirical data of XRD with the database. So, the NiO thin film identity was confirmed. Whereas, the grain size that calculated via Scherer’s formula, was found to be approximately about 21 nm as an average. FTIR examined the absorption region 430–490 cm<sup>−1</sup> corresponded to Ni–O stretching modes [25]. The band around 435 cm<sup>−1</sup> has basically revealed the existence of NiO bond [26].
The spectroscopic investigation of UV-vis has observed absorption peaks in the range of 350-750 nm [25]. Where the energy of the absorbed photon decreased gradually with wavelength increasing, as depicted in figure (3).

Moreover, the thickness was measured to be approximately about 151 nm using fringes interferometer method as depicted in equation (2). Additionally, the surfaces morphology of the fabricated film was displayed in figures (4 and 5). Whereas, Figure (4-a) displayed a morphology within dimensions (400×400) µm as a fine absorber roughness. Zoomed image (40×40) µm as mentioned in Figure (4-b). According to surface topography, a good distribution could be observed, where an adequate morphology is SPT advantage.
Figure (4): 3D surface morphology, (a) morphology within (400×400) µm, (b) zoomed morphology within (40×40) µm.

Figure (5): Up view of 3D surface morphology, (a) morphology within (400×400) µm, (b) morphology.

The surface roughness profile gives a notation about the material distribution on the thin film surface, as seen in Figure (6)
As illustrated in Figure (7), the microscopic image was zoomed in (100×100) µm from its original scale (850×680) µm. Using image processing software were employed to deal with the microscopic image. Figure (7) shows the grooved width that found to be about ≈ 18 µm.

Absorption was raised when the surface area increased by grooving. Which, it is the main wanted reason for solar absorber manufacturing. A 3D image is displayed in figure (8). Which clarify how the area of absorber increased by engraving the surface.
Figure (8): 3D image of the grooved line in scale (100×100) µm.

Figure (9) shows the spectrum color distribution of the groove line. There are two observable curve lines that explain the color variation at the selected regions, as mention in figure (9-a). At the selected image scale (100×100) µm, these lines describe the surface distribution when peaks are referring to the groove depth. Meanwhile, figure (9-b) elucidate the spectrum color distribution in the same selected section that shows groove clearly.

Figure (9): Surface image of the grooved line in scale (100×100) µm, (a) groove width determination, (b) groove line.

5 Conclusion

Spray pyrolysis deposition was adjusted for fabricating NiO films, where the prepared films are in good adhesion onto substrates. XRD examination reveals a cubic structure. Grain size was depicted around nanoscale. Ni-O bond was detected via FTIR studies. Groove width was in micro range. In fact, the original image had an individual groove line, and the experiments still dealt with in the future. So, a number of grooves could be shown in further works.

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