Comparative studies on the morphological, structural and optical properties of NiO thin films grown by vacuum and non-vacuum deposition techniques

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Keywords: radio frequency magnetron sputtering, spray pyrolysis, NiO, thin film, nickel oxide

Abstract
The structural and optical characteristics of Nickel oxide thin films (NiOTF) formed on the soda-lime glass substrate (SLG) under vacuum and non-vacuum conditions are investigated in this work. The difference between RFMS (Radio Frequency Magnetron Sputtering; vacuum) and SP (spray pyrolysis; non-vacuum) was helpful in the development of NiOTF. Deposited films data for this study were characterized by using x-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), scanning probe microscopy (SPM), and optical spectrophotometer. Structural studies disclosed that NiOTF developed via RFMS technique was more uniform with large crystals and lower surface roughness in contrast to that of developed via SP technique. Transmittance spectrum divulged that the transmittance of spray pyrolyzed NiO films are \(
\sim 10\%\) less than that of ones produced by RFMS. Urbach energy analysis of NiOTF developed by RFMS and SP affirmed the findings of structural studies.

1. Introduction

The use of metal oxides has been studied extensively for over a century due to scientific interest in their potential technical value and properties [1]. During these studies, the remarkable chemical, electrical, and optical properties of metal oxide and oxide semiconductors have recently received a lot of attention. The aforementioned developments within metal oxide and oxide semiconductors over the previous decade have made a significant impact on the variety of electronic devices in which oxide semiconductors are found, including photovoltaics, thin-film transistors, sensors, LED, nonvolatile memory devices, and catalysts, among other uses. Nickel oxide (NiO) has been widely researched during the last two decades due to its striking connections [2–5]. Because NiO is used in many diverse applications, such as p-type transparent semiconductors, gas sensors, electrochromic devices, and photovoltaics, this revival of interest began gradually [6]. Many NiO-related problems, especially ones pertaining to the electrical conduction process, persist to this day. For many years, researchers have thought about NIO as a high-resistance charge transfer insulator known as Mott-Hubbard insulator. At the present time, photosensor applications utilize the photo conductance of metal oxides, such as ZnO, NiO, V_2O_5, Co_2O_4, Ga_2O_3, and WO_3 thin films, ZnO, TiO_2, SnO_2 and W_18O_49 nanowires, Nb_2O_3 nano moss, and TiO_2 nanorod arrays Metal oxide materials are affordable, stable, and simple to manufacture [7]. Therefore, metal oxide-based materials are considered as potential candidates for photodetector applications in the near future [8].

Nickel oxide (NiO) is one of the most popular p-type semiconductors due to wide band gap (3.6–4.0 eV), switchable optical and electrical properties, non-corrosiveness towards transparent conductive oxide (TCO)
substrate along with good chemical stability. Thus NiO is considered as a potential candidate for applications in photovoltaic devices \cite{9}, electro-chromic devices \cite{10}, and ultraviolet (UV) photo-detectors \cite{11}, etc. Different approaches, such as radio frequency magnetron sputtering (RFMS) \cite{12}, Spray pyrolysis (SP) \cite{13}, electron beam evaporation \cite{14}, and sol-gel method \cite{15}, etc, have been considered for successful growth of NiOTF. All of these deposition methods offer unlike benefits depending on the application of interest, and great effort has gone into obtaining films with the desired physical or chemical properties. However, RFMS and SP are the most common methods for the deposition of NiOTF. Among the various film deposition methods, RFMS method delivers high-uniformity and pinhole-free films owing to high kinetic energy of the sputtered atoms adhering better with the substrate and covering large surface area \cite{12}. In contrast, SP also gained massive acceptance because of being a simple, applicable to high-volume production processes, safe and cost-effective technique but control of morphology is very difficult \cite{13}. The optical properties of thin films depend on the deposition method, deposition conditions, and post-deposition process. In this work, we have studied the morphological, structural and optical properties of NiOTF deposited by SP and RFMS techniques (denoted as SP-NiOTF and RFMS-NiOTF, respectively, from here on). This study was aimed at understanding, with a view to designing suitable experimental conditions, as to how vacuum and non-vacuum deposition techniques affect the properties and qualities of NiOTF.

2. Experimental

NiOTF deposited to Ultrasonically purify the soda-lime glass substrates (30 × 30 × 1.1 mm) could be done in several ways: detergent water, deionized water, methanol, isopropanol, deionized water. Finally, the substrates were dried under a stream of N2 gas and then rinsed with acetone. In RFMS—carried out at room temperature—NiO (CRM, China) sputtering target with 99.99% purity was used as a source material. Base pressure, working pressure, sputtering power and deposition time were maintained at 5 × 10⁻⁶ Torr, 28 mTorr, 50 W and 90 min, respectively. After RFMS deposition, the NiOTF was annealed at 350°C for 20 min. In SP, spraying was carried out in 10 min followed by annealing at 350°C for 20 min. In both cases film thickness was maintained 106–118 nm. A precursor solution of SP was prepared using nickel chloride (Merck, Germany) and deionized water. The optical, structural and morphological characterizations were conducted by using UV/Vis/NIR spectrophotometer (Perkin Elmer Lambda 950, USA), XRD (D8 Advance, AXS Bruker, CuK 1 radiation (\(\lambda = 0.15406\) nm), Karlsruhe, Germany) was used to check the phase structure of the thin films) and FESEM (Zeiss Supra 55 VP, Germany), respectively. The surface topography and roughness of NiOTF were investigated in a non-contact mode using a scanning probe microscope (SPM; INTEGRA PRIMA, NTMDT, Russia).

3. Results and discussion

It is clear from the results in figure 1 that the x-ray diffraction patterns of SP-NiTF and RFMS-NiTF vary from 20° to 80°. The diffraction pattern of RFMS-NiOTF exhibits only one diffraction peak corresponding to NiO (200) orientation at 43.3°, which is in accordance with the standard XRD spectrum (JCPDS card No. 00-047-1049), indicating that the grown crystalline NiOTF layer crystallizes in cubic structure. In addition, the (200) peaks intensity also increases with thermal oxidation temperature suggesting an improvement of the film’s

![Figure 1. XRD patterns of NiOTFs deposited by SP and RFMS techniques.](image-url)
crystallinity. In contrast, SP-NiOTF seems to be consisting of mainly amorphous regions and some crystalline regions. In the XRD pattern of SP-NiOTF, a dominant peak and another small peak corresponding to NiO (111) at 37.3° which (111) phase is related to NiO amorphous phase, [16] and NiO (200) at 43.3° crystalline, respectively, were observed. The higher peak intensity of RFMS-NiOTF corresponding to NiO (200) orientation at 43.3° indicates its better crystallinity compared with SP-NiOTF. The Debye–Scherrer equation (equation (1)), was used to calculate the average crystallite size \( d_{\text{hkl}} \), where is the x-ray wavelength, is the Full-Width Half-Maximum intensity of the major peak detected at 2\( \theta \) in radian, \( \theta \) is the Bragg’s angle of diffraction, and \( k \) is a constant. Crystallite sizes of SP-NiOTF and RFMS-NiOTF were calculated to be 37.6 and 28.08 nm, respectively, which are supported by the findings of Patil et al [17] and Ahmed et al [18].

\[
d_{\text{hkl}} = \frac{k\lambda}{\beta \cos(\theta)}
\]

Figure 2. Surface morphology of (a) SP-NiOTF and (b) RFMS-NiOTF and surface topography of (c) SP-NiOTF and (d) RFMS-NiOTF.

The surface morphology and topography of SP-NiOTF and RFMS-NiOTF are displayed in figure 2. The surface of NiOTF developed via SP seems to be consisting of non-uniform, island-like NiO crystals, whereas that of NiOTF developed via RFMS looks grain-like, uniform and pinhole-free. This may be due to high kinetic energy of the sputtered atoms leading to high deposition rates and adhesion of films. The root mean square (RMS) surface roughness of NiOTFs deposited via SP and RFMS are 5.639 and 1.046 nm, respectively, indicating that the latter technique produces better quality film.

Figure 3 represents the optical properties of NiOTFs deposited by SP and RFMS. Figure 3(a) shows the optical transmittance of the films calculated across a wavelength range of 200–1000 nm. The transmittance of the SP-NiOTF and RFMS-NiOTF in the visible range was 73.46%, 83.69%, correspondingly. It was observed that the transmittance of SP-NiOTF reduced ~10% as compared to that of RFMS-NiOTF within the visible range. This variation of transmittance may be attributed to the increase of Ni content in NiOTF due to annealing at high temperature [19]. Light scattering of SP-NiOTF can also be expected to be more pronounced because of having large amount of grain boundaries and point defects that reflect the incident light [19]. The optical bandgap (\( E_g \)) of SP-NiOTF and RFMS-NiOTF has been calculated from the transmission spectra using the following equation (equation (2)) [20], where, \( \alpha \) is the absorption coefficient, \( h \) is the Planck’s constant, \( \nu \) is the incident photon frequency, \( A \) is the constant and \( E_g \) is the optical band gap.
From figure 3(b), we can see that Study resulted in the lowest band gap of SP-NiTF at 3.35 eV and the highest band gap of RFMS-NiTF at 3.45 eV, which could be attributed to the change in stoichiometry and crystallinity of the NiOTF. Interestingly, the bandgap can be modified by a shift in the absorption edge and variations in carrier concentration. According to Burstein-Moss effect, when the states close to the conduction band of a semiconductor get populated, its absorption edge is pushed to higher energies leading to increased band gap [21].

The exponential section of the absorption coefficient curve at the optical band edge is known as the Urbach tail. Urbach tails form in defective crystalline, disordered, and amorphous materials due to localized states of these materials that extend or narrow the band gap [22].

The following equation (equations (3) and (4)) can be used to describe the Urbach empirical rule (equations (3) and (4)) [23], (where $\alpha$ is absorption factor, $h\nu$ is the photon energy, $\alpha_o$ is steady, and $E_u$ stands for the Urbach energy, that is a depending on temperature).

$$\alpha = \alpha_o + \exp(\frac{h\nu}{E_u})$$

$$\ln \alpha = \ln \alpha_o + \frac{h\nu}{E_u}$$

Urbach energy of SP- and RF-NiOTF computed from the inclines of $\ln \alpha$ as compared to photon energy ($h\nu$) plots that were drawn following equation (4) and is shown in the figure 3(c). It has been noted that Urbach energy of spray pyrolysis NiOTF is a bit higher that are associated with RFMS-NiOTF, indicating that the latter has superior film quality. Figure 3(d) shows the optical density (OD) of SP- and RFMS-NiOTF in the wavelength range of 200–1000 nm. The OD of both films decreases almost in the same fashion until pretty much the onset of visible light and then remains steady until the end. If looked closely, the OD of RFMS-NiOTF actually decreases slightly more than that of SP-NiOTF, confirming the finding of transmittance study depicted in figure 3(a).

4. Conclusions

In summary, NiOTFs have been successfully deposited by SP (non-vacuum) and RFMS (vacuum) techniques on SLG substrate. XRD study confirmed the higher crystallinity of RFMS-NiOTF. FESEM and SPM study showed the surface of RFMS-NiOTF to be relatively more uniform and less rough. Transmittance of RFMS-NiOTF was higher than that of SP-NiOTF. Band gap of SP-NiOTF was found to be slightly narrower than that of RFMS-NiOTF. In comparison to RFMS-NiOTF, SP-NiOTF has a higher urbach energy, suggesting poor crystallinity.
and a higher standard of impurities. This study demonstrated that the NiOTF produced by RFMS under vacuum condition was superior to SP-NiOTF in quality. As NiO nanomaterials have applications in many areas, this study can act as a guide to better deposition of NiO nanomaterials on other substrates as well.

Acknowledgments

This research was supported by Prince of Songkla University and the Ministry of Higher Education, Science, Research and Innovation, Thailand, under the Reinventing University Project (Grant Number REV64011).

Data availability statement

No new data were created or analysed in this study.

Conflicts of interests

The authors have no conflicts of interest to declare that are relevant to the content of this article.

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