IRAQI JOURNAL OF MATERIALS
Volume (3) Issue (4) October-December 2024, pp. 1-8

Characterization of Multilayer Highly-Pure Metal Oxide Structures Prepared by DC Reactive Magnetron Sputtering

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Abstract

In this work, multilayer nanostructures were prepared from two metal oxide thin films by dc reactive magnetron sputtering technique. These metal oxide were nickel oxide (NiO) and titanium dioxide (TiO_2). The prepared nanostructures showed high structural purity as confirmed by the spectroscopic and structural characterization tests, mainly FTIR, XRD and EDX. This feature may be attributed to the fine control of operation parameters of dc reactive magnetron sputtering system as well as the preparation conditions using the same system. The nanostructures prepared in this work can be successfully used for the fabrication of nanodevices for photonics and optoelectronics requiring highly-pure nanomaterials.

Keywords: Magnetron sputtering; Reactive sputtering; Multilayer structures; Nanostructures
Received: 18 April 2024; **Revised:** 20 July 2024; **Accepted:** 27 July 2024; **Published:** 1 October 2024

1. Introduction

Several decades ago, the multilayer structures have attracted the research interests due to their advantages and features for both research and industrial purposes. These structures have mostly presented a mixture of advantages of all constituents included in the multilayer structure. However, they may show new features and characteristics not observed for the constituents individually [1-4]. This can be reasonably observed in spectroscopic studies as the multilayer structures can exhibit absorption higher than the individual absorption characteristics of their constituents in addition to new absorption peaks or edges in the regions of weak absorption [1].

Drastic developments were seen in the physics and technology of photonics and optoelectronics devices such as photodetectors, solar cells, gas sensors, photocatalysts, etc. [5-9]. Such devices represent the skeleton of the modern technologies, therefore, the research works are intensively focused on development and enhancement of their characteristics and performances [1,3,10]. Recently, nanotechnology has added more routes to develop them with new properties and characteristics [4].

Thin film deposition techniques made it easy to fabricate multilayer structures by consequent deposition of layers from different materials but most of these techniques may include a chemical reaction or physical changes in the properties of the lower layer when a new layer of different materials is deposited upon [3]. This problem may have negative effects on the outcome expected from a multilayer structure. Among all physical vapor deposition (PVD) methods and techniques, the reactive magnetron sputtering shows very good features in fabrication multilayer structures as no reactions that may change the properties of the lower layers are included [11,12]. As well, no mechanical or thermal processes exist to affect negatively the grown layers [13,14]. Therefore, high-quality multilayer structures can be successfully fabricated by reactive magnetron sputtering in addition to the advantages of low-cost large-scale production, reliability and reproducibility [15-18].

In this work, multilayer structures were fabricated from nickel oxide and titanium dioxide thin films prepared by dc reactive magnetron sputtering technique. The structural characteristics of the fabricated structures were introduced and analyzed.

2. Experiment

Highly-pure sheets of titanium (99.99%) and nickel (99.99%) were used as sputtering targets. The target was maintained inside the deposition chamber on the cathode. Pure oxygen was used as reactive gas required to form the metal oxides. The quartz substrates on which the metal oxide thin films are to be deposited were carefully cleaned and then put on the surface of the anode. The temperature of the anode (and the substrate as well) could be controlled and a thermocouple was used to measure it. More details on the magnetron sputtering system used in this work and shown in Fig. (1) can be found elsewhere [19-23].

Fig. (1) A photograph of the dc reactive magnetron sputtering system used in this work

The deposition chamber was first evacuated down to 10^{-3} mbar before filled with the gas mixture of argon and oxygen at a pressure of 0.1 mbar. The plasma required for sputtering was generated by the electric discharge of argon. Electrical power was provided by a high-voltage dc power supply. Several parameters of sputtering system, such as inter-electrode distance, deposition time, substrate temperature, total gas pressure and Ar:O_2 ratio, could be varied to determine their effects on the deposition process.

The fabricated multilayer structures were characterized by the Fourier-transform infrared (FTIR) spectroscopy, x-ray diffraction (XRD), scanning electron microscopy (SEM), energy-dispersive x-ray spectroscopy (EDX) and atomic force microscopy (AFM).

3. Results and Discussion

Figure (2) shows the FTIR spectrum of the multilayer sample prepared using Ar:O_2 gas mixture of 1:1 after deposition time of two hours. All peaks assigned for the vibration bands of M-O bonds were seen as shown in table (1). These bonds are distinctly recognized as both materials are metal oxide (NiO and TiO_2). The band assigned at 1064 cm^{-1} is ascribed to the vibration of the Ni-O bond [24] while three bands are observed for the TiO_2 sample at 409, 447 and 667 cm^{-1}, which ascribed to the vibration modes of the triatomic molecule (TiO_2) in addition to the peak assigned at 709 cm^{-1}, which is ascribed to the bridging stretching mode of Ti-O-Ti [25].

Table (1) Vibration bands observed on the FTIR spectrum of the fabricated multilayer structure

Wavenumber (cm^{-1})	Assigned bond	Material
409	Ti-O-Ti	Bending
447	Ti-O	Symmetric stretching
667	Ti-O	Asymmetric stretching
709	Ti-O-Ti	Bridging
1064	Ni-O	Stretching

No bands ascribed to compounds other than O-H were observed, which confirms the structural purity of both types of samples (NiO and TiO_2) [26]. However, the O-H bands are unavoidable due to the adsorption of water from the environment. When compared to the individual FTIR spectra of NiO and

TiO_2 samples prepared by the same technique, it is confirmed that no other phases were formed (e.g., Ni_2O_3, NiO_2, TiO or Ti_2O_3) nor new compound, such $NiTiO_3$ [27]. This is significant evidence for the advantage of reactive magnetron sputtering in fabrication of highly-pure multilayer structures.

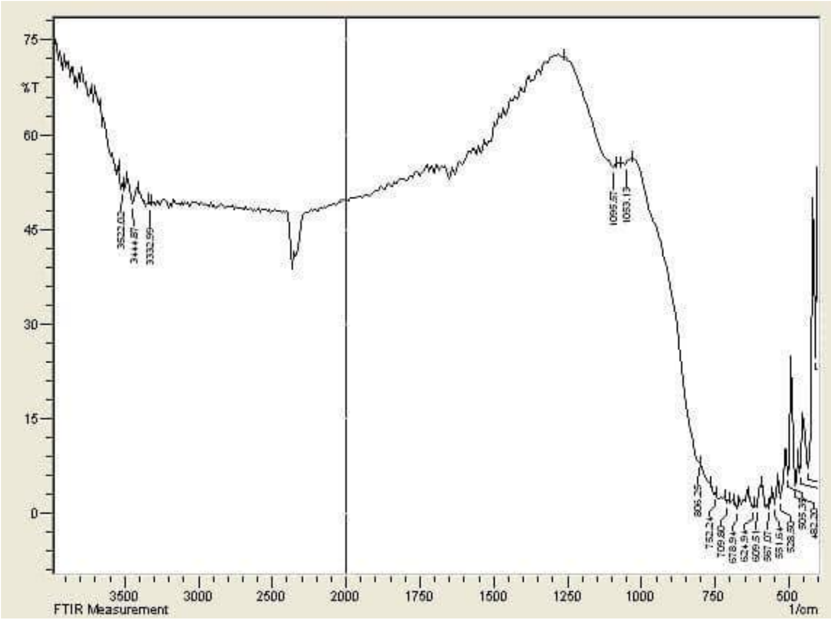


Fig. (3) The FTIR spectrum of the multilayer NiO/TiO₂ structure prepared in this work using 1:1 gas mixture after deposition time of 2 hours

Figure (3) shows the XRD pattern of the multilayer structure prepared in this work using $Ar:O_2$ gas mixture of 1:1 after deposition time of two hours. As seen, two sharp and intensive peaks are observed at 2θ of 35.22° and 38.46°, which corresponding to the crystal planes of (111) and (200), respectively, of NiO. The peak assigned at 62.52° is belonging to the (220) crystal plane of NiO as well. Other lower peaks are all belonging to crystal planes TiO_2 [28-30]. As previously confirmed by the FTIR result, no peaks corresponding to reflection from crystal planes belonging to other compounds were observed. Table (2) shows the calculations of grain size based on the XRD results.

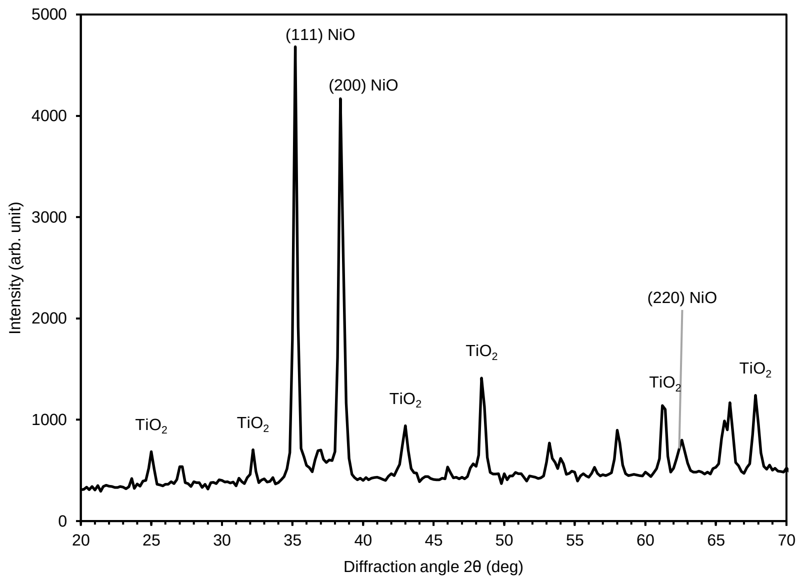


Fig. (2) XRD pattern of the NiO/TiO₂ multilayer structure prepared in this work using 1:1 gas mixture after deposition time of 2 hours

Table (2) Calculations of grain size based on the XRD results

2θ	d (Å)	D (nm)	Material
25.0162	3.55669	15.413	TiO_2
32.2164	2.77633	13.483	TiO_2
35.2254	2.54576	12.410	NiO
36.8363	2.43805	8.231	TiO_2
38.4639	2.33854	10.469	NiO
42.9806	2.10267	8.112	TiO_2
48.4665	1.87671	8.667	TiO_2
53.2587	1.71859	6.964	TiO_2
58.0355	1.58798	7.060	TiO_2
61.2700	1.51168	7.005	TiO_2
62.5275	1.48426	4.709	NiO
65.7933	1.41827	3.635	TiO_2
67.7970	1.38115	5.696	TiO_2

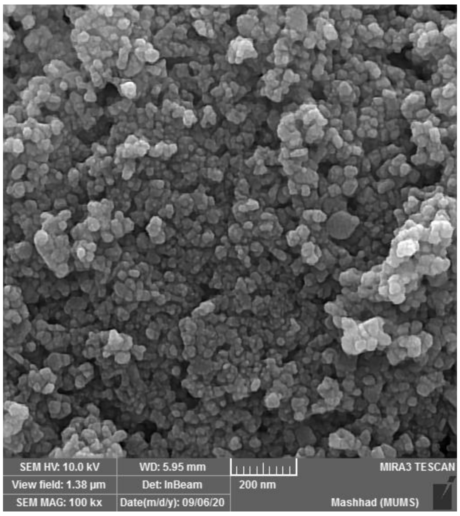
The formation of nanostructures in the prepared samples was identified by the SEM results as shown in Fig. (3). A minimum particle size of about 40 nm can be seen while no large aggregation is observed. As compared to the SEM results of NiO and TiO_2 samples individually, the surface morphology of the multilayer sample is similar to that of the TiO_2 sample. This can be attributed to the larger particle size of TiO_2 particles as the NiO nanoparticles of lower sizes are deposited on the vacancies among the larger particles. The spherical shape of NiO nanoparticles seen in Fig. (3a) approximately disappeared in the multilayer sample. Instead, larger particles appear with a possibility to be a combination of NiO nanoparticles attached to TiO_2 nanoparticles. If this is the situation, then the assumption of formation of nano-heterojunctions can be reasonably possible. Such assumption encourages to synthesize nanophotonics and nano-devices based on the optoelectronic characteristics of such heterojunctions.

With assumption of forming nano-heterojunctions from NiO and TiO_2 nanoparticles, and considering the concentrations of solid species that may reach up to 10^{18} cm^{-3}, the formation of up to 10^{12} nano-heterojunctions is very likely. When compared to conventional thin film structures (NiO/TiO_2), these multilayer structures are much more efficient by about 1000%. Therefore, the tiny contributions of such nano-devices can produce a huge amount of outcome (energy, current, voltage, etc.). Accordingly, a drastic development in their applications can be expected with further control of the nanoparticle size and distribution [31-35].

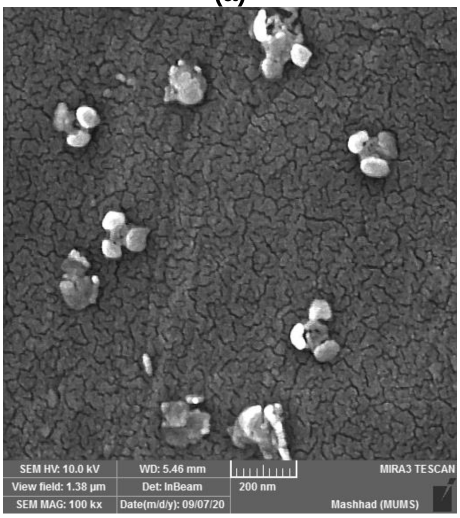
The elemental constitution of each sample (NiO and TiO_2) as well as the fabricated multilayer structure was individually characterized by EDX, as shown in Fig. (4). Both structures can be considered highly pure as no traces for other elements other than Ni, Ti and O were seen. In addition, the multilayer structure has confirmed that its formation processes did not include any opportunity for other elements to be exist in the final sample as dopants or contaminants. This result additionally supports the advantage of reactive magnetron sputtering technique in production of highly-pure nanostructures.

Multilayer structures – like those fabricated in this work – can be successfully employed in photonics, optoelectronics, spectroscopic and other applications including an interaction between the electromagnetic radiation and matter. As well, gas sensors for more than one gas can be fabricated from such structures [36,37]. Therefore, the surface roughness is an important parameters to make such interaction much more efficient. The topography of the synthesized multilayer structures was introduced by the AFM as shown in Fig. (5) showing the 2D and 3D images of their surfaces.

The average roughness was determined to be 16.7 nm while the root-mean-square roughness was about 19.5 nm. These surfaces can also be considered highly homogeneous with a surface skewness of about 0.0224. It is known that lower values of surface skewness correspond to rougher surfaces while higher values (up to ∞) correspond to smoother surfaces [38,39]. These values reflect the high surface area that can be available for the interaction between these nano-surfaces and electromagnetic radiation or gas species to be sensed.



(a)



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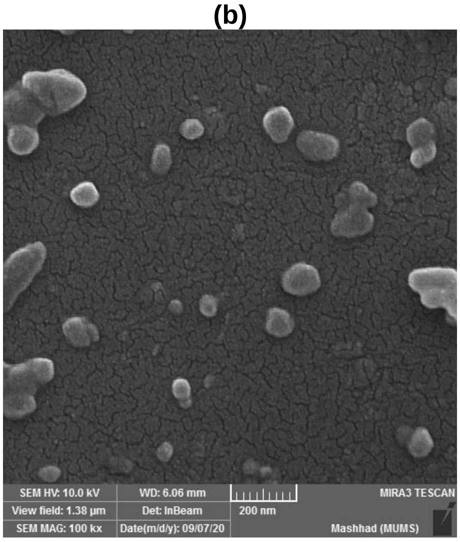

(c)

Fig. (3) The SEM image of the NiO sample (a), TiO2 sample (b) and multilayer NiO/TiO_2 structure (c) prepared in this work using 1:1 gas mixture after deposition time of 2 hours

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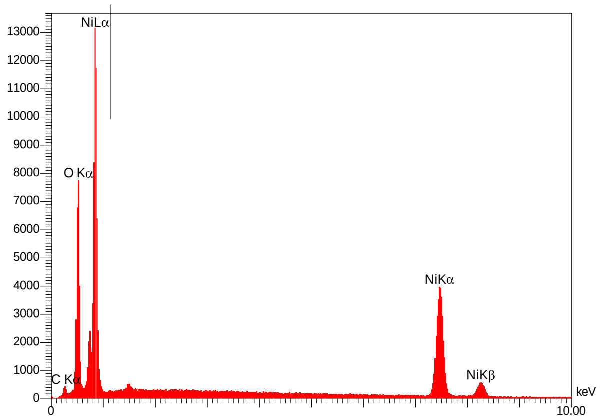
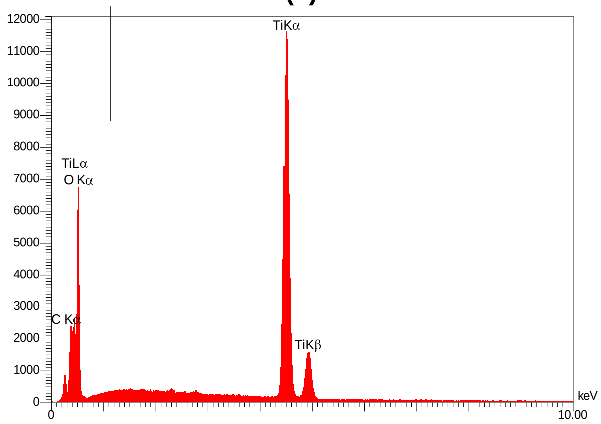
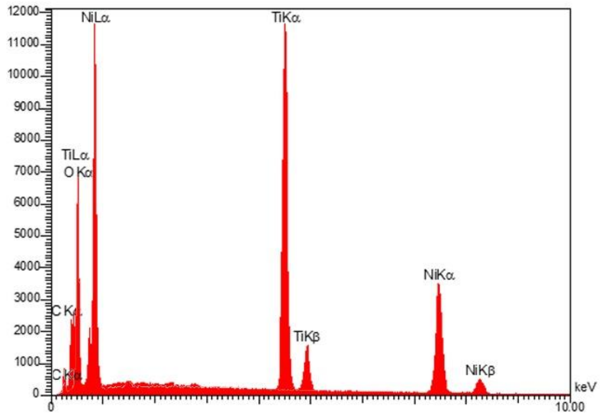
Volume (3) Issue (4) October-December 2024, pp. 1-8



(a)



(b)



(c)

Fig. (4) Results of EDX of the NiO (a), TiO_2 (b) and multilayer (c) samples prepared in this work using 1:1 gas mixture after deposition time of 2 hours

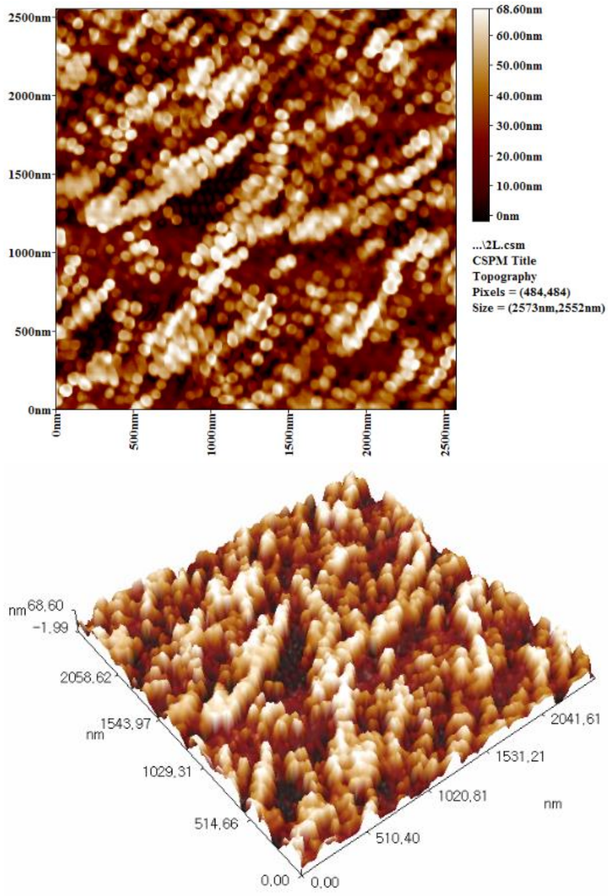


Fig. (5) The 2D and 3D AFM images of the multilayer NiO/TiO_2 structure prepared in this work using 1:1 gas mixture after deposition time of 2 hours

4. Conclusion

In concluding remarks, the fabrication and characterization of multilayer nanostructures from NiO and TiO_2 by dc reactive magnetron sputtering technique were presented. These nanostructures showed high structural purity with no imperfections or degradation when compared to the nanostructures of NiO and TiO_2 individually as well as to the thin film NiO/TiO_2 structures. These results encourage to employ such multilayer structures in many photonics and optoelectronics applications due to their advantages as low-cost highly-pure nano-surfaces.

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