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Spectral and Electrical Characteristics of Nanostructured NiO/TiO$_2$ Heterojunction Fabricated by DC Reactive Magnetron Sputtering

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Abstract
In this work, p-n junctions were fabricated from highly-pure nanostructured NiO and TiO$_2$ thin films deposited on glass substrates by dc reactive magnetron sputtering technique. The structural characterization showed that the prepared multilayer NiO/TiO$_2$ thin film structures were highly pure as no traces for other compounds than NiO and TiO$_2$ were observed. It was found that the absorption of NiO-on-TiO$_2$ structure is higher than that of the TiO$_2$-on-NiO. Also, the NiO/TiO$_2$ heterojunctions exhibit typical electrical characteristics, higher ideality factor and better spectral responsivity when compared to those fabricated from the same materials by the same technique and with larger particle size and lower structural purity.

Keywords: Multilayer structure; Magnetron sputtering; Nanostructures; Metal oxides
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1. Introduction

For more than six decades, semiconductor heterojunctions attract the research interest due to their effectiveness in photonics and optoelectronics applications, especially solar cells, photodetectors and gas sensors. With a wide range of semiconductors and variety of their properties, heterojunctions can cover wide range of uses. As well, the transfer from micro to nanoscale structures allowed to discover new uses of heterojunctions with relatively different characteristics [1-3].

The formation of a heterojunction from two different semiconducting materials allows to invest the properties of both materials to serve some important practical applications in addition to new possible properties of the junction to serve new applications [4,5].

The structural purity of the semiconducting materials forming the heterojunction plays a key role in its performance as no contributions are expected due to the existence of impurities or other compounds within the crystalline structures of both materials [6]. Synthesis of highly-pure semiconductors is one of the most requiring processes to take care of preparation conditions and parameters. Among many methods and techniques used to synthesize semiconductors, plasma sputtering is one of the most important due to its low cost, open technology, reliability and good control of preparation parameters to ensure the production of highly-pure structures [7,8]. Also, this technique allows to produce nanostructures from semiconducting materials with high structural purity and distinguished specifications [9].

Nickel oxide (NiO) and titanium dioxide (TiO$_2$) are categorized as wide semiconductors (3.2 and 3.85 eV, respectively) and excellent candidates for many applications of semiconductors. TiO$_2$ is an important semiconductor for photocatalysis and the first candidate to fabricate efficient photocatalyst devices [10,11]. As well, NiO is an excellent candidate to fabricate gas sensors, dye sensitized photocathodes, electrodes in alkaline batteries, resistive switching, and electrochromic smart windows [12-14]. The energy outline of the heterojunction made from NiO and TiO$_2$ can be shown in Fig. (1).

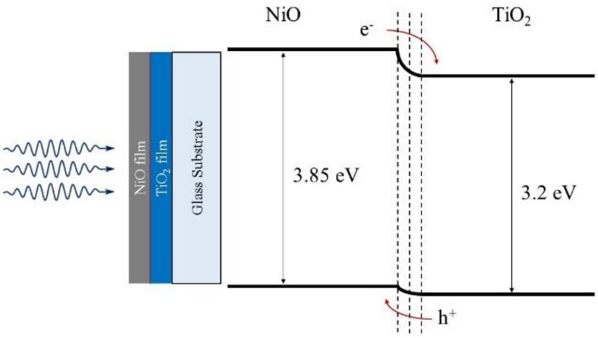

Fig. (1) Energy outline of the nanostructured NiO/TiO_2 heterostructure

The small difference between valence and conduction bands in both materials makes it easy for charge carriers to transfer from one side of the heterojunction to the other. The depletion region formed at the junction may exhibit new characteristics while both sides keep their original properties [15].

In this work, p-n heterojunctions were fabricated from highly-pure nanostructures of NiO and TiO_2 by dc reactive magnetron sputtering technique and their spectroscopic and optoelectronic characteristics were determined.

2. Experimental Part

A home-made dc reactive magnetron sputtering system was used in this work. Two highly-pure Ti and Ni targets (99.99%) were sputtered in presence of oxygen to deposit TiO_2 and NiO thin films on glass substrates. The deposition chamber was initially evacuated down to 0.001 mbar and then filled with gas mixture of argon and oxygen with mixing ratio of 1:1. The pressure of gas mixture was about 0.8 mbar and the discharge current was 20 mA. More details on the sputtering system and its operation parameters can be found elsewhere [16-21]. The optimized conditions to prepare nanostructures from both materials were presented in previous studies on the same system [22-24].

The deposited thin films were extracted as powders by a novel technique known as conjunctional freezing-assisted ultrasonic extraction method [7,8].

The two possible configurations of the multilayer structure (NiO-on-TiO_2 and TiO_2-on-NiO) were compared and the results showed that the first configuration exhibits higher absorbance than the second one. Therefore, all results were presented for the first configuration shown in Fig. (2).

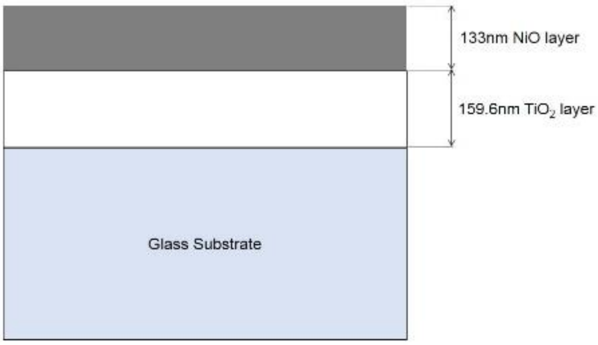

Fig. (2) The configuration of multilayer NiO/TiO_2 thin film structure prepared in this work

The spectroscopic characteristics were determined by a KMAC S2100 UV-visible spectrophotometer in the spectral range of 200-900 nm with a resolution of 0.2 nm. The optoelectronic characteristics were determined by using a dc voltage supply (DHF-1502DD) and a Keithley480 picoammeter. The light characteristics were measured by illuminating the fabricated device with a 10 mW light source. The structural characteristics were determined by the x-ray diffraction (XRD) patterns recorded using a Philips PW1730 diffractometer with Cu source (λ=1.54060Å).

3. Results and Discussion

Figure (3) shows the XRD pattern of the multilayer structure fabricated from the NiO thin film deposited on the TiO_2 thin film deposited on glass substrate. The film thickness of NiO and TiO_2 films was 133 and 159.6 nm, respectively. Referring to the JCPDS cards [25] of both NiO and TiO_2, all peaks observed in this pattern are belonging to NiO and TiO_2 compounds only without any peak belonging to the free metal (Ni or Ti) neither to other compounds. This initially highlights the structural purity of the prepared multilayer structure.

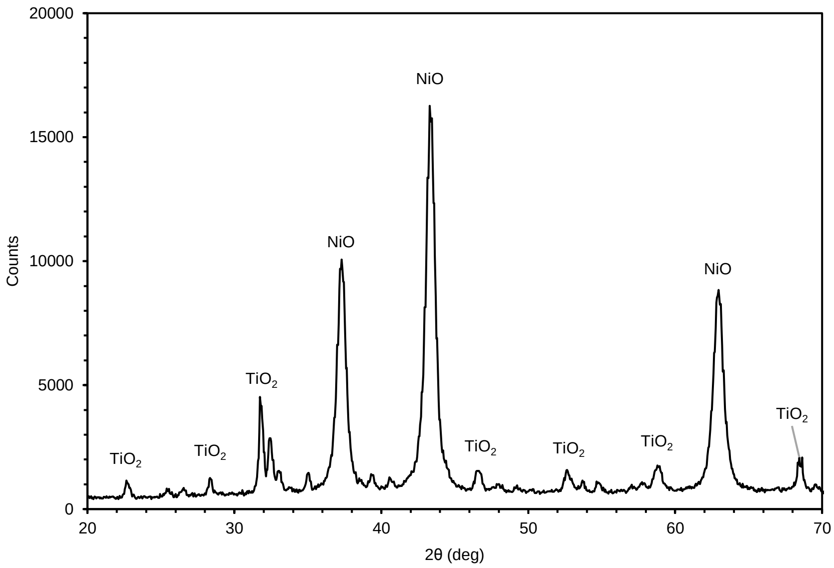

Fig. (3) XRD pattern of multilayer NiO/TiO_2 structure prepared in this work

To confirm the formation of the required compounds (NiO and TiO_2) as well as the structural purity of the prepared samples, the FTIR spectra were recorded for each sample individually, in the spectral range of 400-4000 cm^{-1}, as shown in Fig. (4). The band assigned at 1064 cm^{-1} is ascribed to the vibration of the Ni-O bond [26] 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) [26]. 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). However, the O-H bands are unavoidable due to the adsorption of water from the environment.

Figure (5) shows the absorption spectra of the NiO/TiO_2 heterojunction fabricated in this work as compared to the summation of absorbance of both materials when deposited individually. The difference reaches its maximum of about 850% at 461 nm. It is clear that the increase in absorbance is attributed to the formation of the heterojunction and its characteristics. Also, the heterojunction structure shows high absorption in the UV region and an absorption edge at about 490 nm is observed while both materials show such high absorption at wavelengths shorter than 440 nm. This red shift in absorption spectrum can be invested for better absorption of the visible radiation and hence using this heterojunction in the fabrication of photodetectors and solar cells.

Figure (6) shows the I-V characteristics in dark and under 10mW illumination for the NiO/TiO_2 heterojunction fabricated in this work. As shown, typical behavior is observed as the dark current is about 3.5μA while the photocurrent reaches a maximum at about 107μA. Accordingly, the ideality factor of this heterojunction can be determined to be 3.02.

Figure (7) shows the spectral responsivity of the nanostructured NiO/TiO_2 heterostructure fabricated in this work. The heterostructure shows relatively low responsivity (<0.3) to the wavelengths shorter than 300 nm (UV). Similarly, this heterostructure shows low responsivity (<0.4) to the wavelengths longer than 800 nm (NIR). The responsivity of this heterostructure exceeds 0.6 for the wavelengths in the visible region (400-700 nm). Therefore, this heterojunction device can be successfully used to fabricate photonic and optoelectronic devices like photodetectors and solar absorbers with relatively better characteristics than those of the thin film NiO/TiO_2 heterojunction with larger particle size.

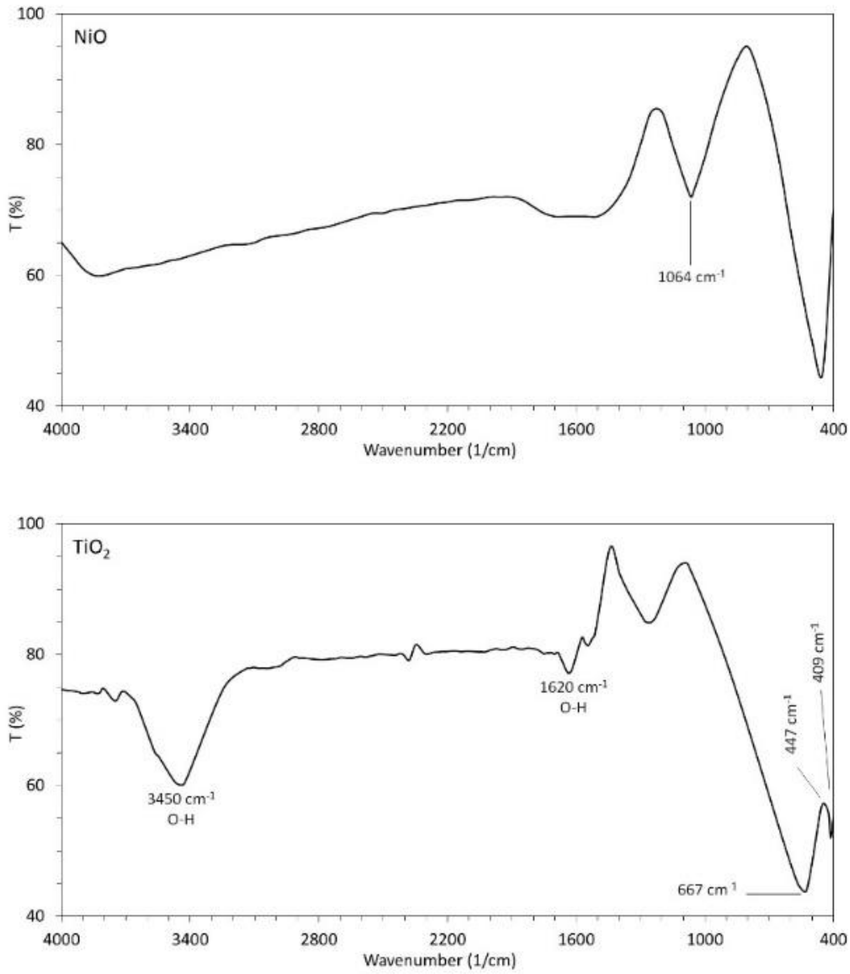

Fig. (4) FTIR spectra of NiO and TiO_2 samples prepared in this work

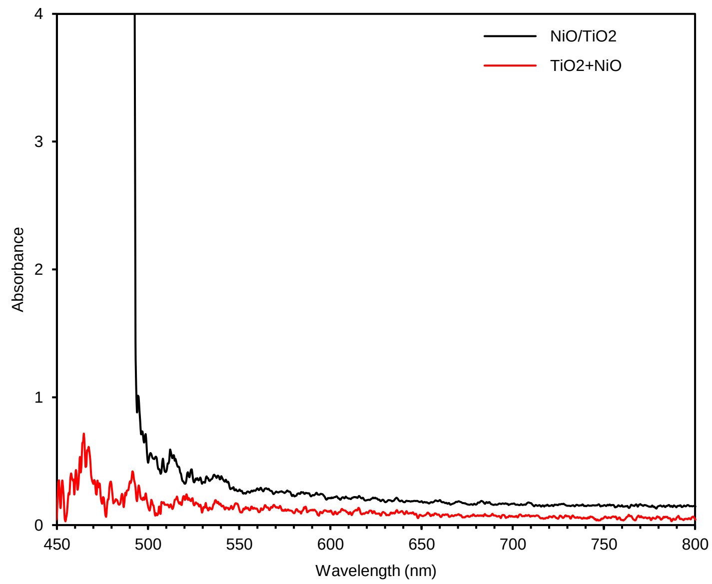

Fig. (5) Absorption spectra of nanostructured NiO/TiO_2 heterostructure fabricated in this work

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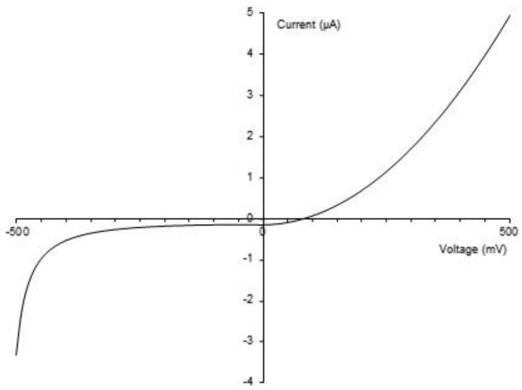
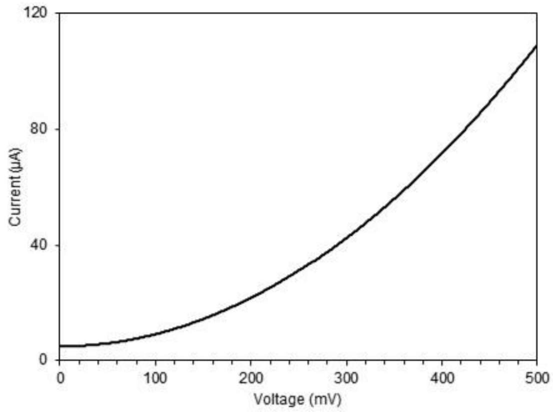


(a)



(b)

Fig. (6) The I-V characteristics in dark (a) and under 10mW illumination (b) for the NiO/TiO_2 heterojunction fabricated in this work

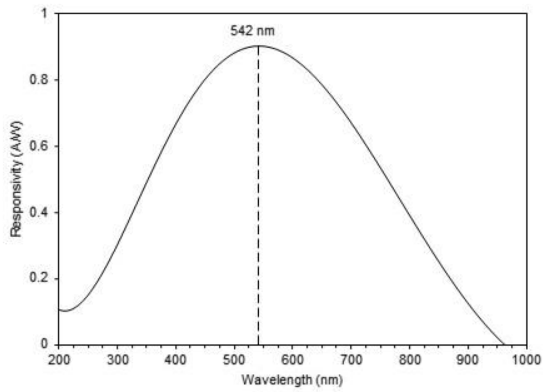


Fig. (7) Spectral responsivity of the nanostructured NiO/TiO_2 heterostructure fabricated in this work

4. Conclusions

In concluding remarks, an efficient p-n heterojunction was fabricated from NiO and TiO_2 nanostructures synthesized by dc reactive magnetron sputtering technique. This heterojunction shows better spectroscopic and electrical characteristics than the similar structures fabricated from the same materials (NiO and TiO_2) of larger particle size. The photocurrent obtained at the same levels of applied voltage is relatively lower, however, the ideality factor is reasonably higher. The spectral responsivity of this heterojunction in the visible region encourages to use it in the fabrication of nanostructured thin film optoelectronics such as photodetectors and solar cells.

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