The Influence of Oxygen Flow Ratio on the Optoelectronic Properties of p-Type Ni$_{1-x}$O Films Deposited by Ion Beam Assisted Sputtering

Hui Sun $^{1}$, Sheng-Chi Chen $^{2,3,*}$, Wen-Chi Peng $^{2}$, Chao-Kuang Wen $^{4}$, Xin Wang $^{5}$ and Tung-Han Chuang $^{4}$

$^{1}$ School of Space Science and Physics, Shandong University at Weihai, 180 Wenhuaxi Road, Weihai 264209, China; huisun@sdu.edu.cn

$^{2}$ Department of Materials Engineering and Center for Thin Film Technologies and Applications, Ming Chi University of Technology, Taipei 243, Taiwan; n58011120@mail.ncku.edu.tw

$^{3}$ Department of Electronic Engineering, Chang Gung University, Taoyuan 333, Taiwan

$^{4}$ Institute of Materials Science and Engineering, National Taiwan University, Taipei 106, Taiwan; d04527007@ntu.edu.tw (C.-K.W.); tunghan@ntu.edu.tw (T.-H.C.)

$^{5}$ Institute of Materials Science and Engineering, Ocean University of China, 238 Songling Road, Qingdao 266100, China; wangxinhd@ouc.edu.cn

* Correspondence: chensc@mail.mcut.edu.tw; Tel.: +886-2-2908-9899 (ext. 4679)

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Abstract: In this work, p-type non-stoichiometric Ni$_{1-x}$O thin films were deposited by oxygen ion beam assisted RF sputtering on glass substrates. The influence of the oxygen flow ratio (0–100%) on the films' optoelectronic properties was investigated. In our experimental conditions, all the films are crystallized in the cubic NiO phase. However, their crystallinity and mean grain size decreases with increasing oxygen flow ratios. Meanwhile, the films' conductivity improves from 9.1 to 25.4 S·cm$^{-1}$. This is due to the fact that the nickel vacancies along with hole carriers can be introduced into NiO films when they are deposited under higher oxygen flow ratio conditions. Thus, the O-rich environment is beneficial in enhancing the films' carrier concentrations. In addition, with an increasing oxygen flow ratio, the film's transmittance degrades. The direct optical band gap of Ni$_{1-x}$O films declines slightly from 3.99 to 3.95 eV, with the oxygen flow ratio increasing from 0% to 100%.

Keywords: NiO thin films; optoelectronic properties; oxygen flow ratio; ion source assisted sputtering; p-type conduction

1. Introduction

Transparent conductive oxides (TCOs) have aroused people’s attention due to their potential applications in the fields of flat panel displays, light emitting diodes, solar cells, smart windows, and photocatalysts [1–5]. They possess a wide band gap, generally greater than 3.0 eV, and so are transparent in the visible light spectrum. To date, the traditional TCOs, including In$_2$O$_3$, ZnO, and SnO$_2$, have been widely employed in commercial applications [6–9]. All of them present good n-type conductivity. However, producing p-type TCOs with high resistivity and low transparency has proven to be more elusive in contrast with n-type TCOs [10–12]. The slow development of p-type TCOs has limited the implementation of the transparent p–n junctions, which is of interest for use in photovoltaics and invisible electronic devices.

Generally, due to the top valence band of TCOs being predominantly composed of O 2$p$ states, it is difficult to introduce free holes into a valence band of oxides owing to their strong localization
by O 2p [13,14]. Thus, most TCOs are intrinsic n-type semiconductors. Currently, the extensively studied intrinsic p-type TCOs are mainly focused on Cu-based oxides and Ni-based oxides [15–18]. In particular, NiO is considered an attractive candidate due to its wide band gap above 3.6 eV, intrinsic p-type conductivity, abundant availability, chemical stability, non-toxicity, low-cost, the fact that its easily producible, etc. [19–21]. To date, NiO has been widely studied in various domains, such as photoanodes [22], electrochromic materials [23], gas sensors [24], and photoelectrochemical cells [25,26]. The reported optoelectronic properties of NiO films are compared in Table 1. Recently, nickel vacancies (V_{Ni}) were proven to play an important role in NiO films’ electrical properties. These can be spontaneously formed under oxygen-rich conditions [27,28]. Holes can be generated from nickel vacancies and are responsible for the films’ p-type conductivity. Thus, the dilemma of how to introduce nickel vacancies into NiO films has become a hot topic for researchers.

Table 1. The reported optoelectronic properties of NiO films.

| Film | Thickness (nm) | Transmittance (%) | Conductivity (S·cm\(^{-1}\)) | Carrier Concentration (cm\(^{-3}\)) | Carrier Mobility (V·cm\(^{-1}\)·s\(^{-1}\)) | Ref. |
|------|---------------|-------------------|-----------------------------|----------------------------------|----------------------------------|------|
| NiO  | 100           | ~20–50 (visible region) | 0.5                         | 7.26 \times 10^{16}              | 45.1                             | [21] |
| NiO  | 50            | ~83–88 (visible region) | –                           | ~4.4 \times 10^{18}             | –                                | [25] |
| NiO  | 35            | 39 (at 550 nm)       | 21.74                       | 1.1 \times 10^{21}              | 0.1                              | [29] |
| NiO  | 100           | 73.4 (at 550 nm)     | 2.86 \times 10^{-5}        | 1.13 \times 10^{13}             | 6.41                             | [30] |
| NiO  | –             | ~40–50 (visible region) | –                           | 3.8 \times 10^{17}              | –                                | [31] |

In our previous work, oxygen ion beam assisted RF sputtering was employed to deposit NiO thin films in pure Ar conditions [32]. The films’ electrical properties are significantly improved compared with the films prepared by RF sputtering without oxygen ion beam assistance. As mentioned above, an oxygen-rich deposition environment is beneficial for the formation of Ni vacancies and holes. Thus, in the current work, oxygen flow is added into the sputtering system in order to further improve the films’ electrical conductivity. The influence of the oxygen flow ratio (f_{O2}) on the films’ optoelectronic properties is studied here.

2. Materials and Methods

Ni_{1-x}O thin films with a thickness of around 100 nm were deposited on rotating (10 rpm) Corning 1737F glasses at room temperature via in-line magnetron sputtering system (PSUVHL-200C, HOPE Vacuum Technology Co., Ltd., Taiwan). This system consists of a load-lock chamber and a main sputtering chamber, where the substrates loaded on the carrier can be moved horizontally from one chamber to another. The main advantage of this set-up is to enable the process of loading and unloading samples in the load-lock chamber while maintaining the vacuum in the main chamber. The illustration of the deposition system is shown in Figure 1. The ion gun is located perpendicular to the substrate holder, and the target is positioned next to the ion gun. The distance between the target and the substrate was kept at 20 cm. The sputtering chamber was pre-pumped until a base pressure higher than 6.7 \times 10^{-5} Pa was achieved. Oxygen and argon were used as reactive gas mixtures. The working pressure was fixed at 0.67 Pa, while the oxygen flow ratios O_{2}/(O_{2} + Ar) varied from 0% to 100%. A NiO target (purity 99.95%) with a diameter of 152.4 mm and a thickness of 3 mm was supplied by Ultimate Materials Technology Co., Ltd. (Taiwan) and powered by a radio frequency supply during the deposition process. The target power was set at 400 W. An assistance oxygen ion beam was powered using a DC supply (150 W) which bombarded the substrates during the deposition process. Other experimental parameters are summarized in Table 2.
The films’ thicknesses were examined using a surface profiler (Kosaka Surfcoder). The films’ compositions were measured using a JEOL JXA-8200 (JEOL, Tokyo, Japan) electron probe X-ray microanalyzer (EPMA). The films’ structural properties were detected with X-ray diffractometry (XRD, Philips PANalytical—X’Pert PRO MPD, Almelo, The Netherlands) in the 30°–70° angle range. The surface morphologies were observed via a JEOL JSM-6701F field emission scanning electron microscope (FE-SEM). The films’ carrier concentrations, carrier mobilities, and conductivities were analyzed using the Hall effect system (AHM-800B, Agilent Technologies, Santa Clare, CA, USA). Finally, the films’ optical properties were determined using an ultraviolet–visible-near infrared (UV–VIS-NIR) double beam spectrophotometer (JASCO-V670, JASCO, Tokyo, Japan) (λ = 200–900 nm).

### Table 2. Sputtering parameters maintained during the deposition of Ni$_{1-x}$O thin films.

| Parameters                          | Value       | Parameters               | Value       |
|-------------------------------------|-------------|--------------------------|-------------|
| Background pressure (Pa)            | <6.7 × 10$^{-5}$ | Substrate                | Corning 1737F glass |
| Working pressure (Pa)               | 0.67        | Ion source               | O$_2$       |
| Working gas                         | Ar, O$_2$   | Ion source power (W)     | 150         |
| Target                              | NiO         | Target power (W)         | 400         |
| Hot substrate                       | No          | Oxygen flow ratio (%)    | 0, 10, 50, 100 |
| Films thickness (nm)                | 100         |                          |             |
| Oxygen flow ratio (%)               |             |                          |             |

Figure 1. (a) Schematic of an in-line magnetron sputtering system; (b) An external-view of an in-line magnetron sputtering system. The arrow shows the direction of the sample delivery from the load-lock chamber to the main chamber. (c) An internal-view of the main chamber. An ion gun is positioned perpendicularly to the substrate holder.

### 3. Results and Discussion

Figure 2 shows the variation of the oxygen content as a function of the oxygen flow ratio. With oxygen ion beam assistance, oxygen content is always higher than 50 at.%, indicating that all the films are non-stoichiometric. The oxygen-rich state contributes to the production of nickel vacancies, which has been confirmed to promote the films’ p-type conductivity [33,34]. With the oxygen flow ratio rising from 0% to 100%, the oxygen content gradually increases from 69.1 to 70.1 at.%. 

\[ \text{Oxygen content (at.%) = 100 \times \frac{[O]}{[Ni]+[O]} \]
Compared with our previous work [32], where Ni$_{1-x}$O thin films were deposited with oxygen ion beam assistance in pure Ar atmosphere, the effect of the oxygen flow ratio on the oxygen content is less important than that of ion source power. The variation of oxygen content in Ni$_{1-x}$O films deposited at various ion source powers reported in our previous work is summarized in Table 3.

![Graph showing the variation of oxygen content in Ni$_{1-x}$O films with oxygen flow ratio.](image1)

**Figure 2.** Oxygen content in Ni$_{1-x}$O films deposited with various oxygen flow ratios.

**Table 3.** The variation of oxygen content in Ni$_{1-x}$O films deposited with various ion source powers [32].

| Ion Source Power (W) | Oxygen Content (at.%) |
|----------------------|------------------------|
| 80                   | 59.5                   |
| 100                  | 67.5                   |
| 120                  | 68.6                   |
| 150                  | 69.1                   |

Figure 3 shows the X-ray diffraction patterns of Ni$_{1-x}$O films deposited on glass substrates at various oxygen flow ratios. All the films are crystallized in cubic NiO phase. The diffraction peaks at around 37°, 43°, and 62° correspond well to the (111), (200), and (220) orientations of NiO. The relatively wide diffraction peaks imply that the films possess poor crystallization. In addition, the film’s crystallinity degrades with increasing oxygen flow ratio. This is attributed to more point defects such as nickel vacancies introduced into Ni$_{1-x}$O films when they are deposited in higher f$_{O2}$ conditions. A similar phenomenon is also reported by other groups, where Ni$_{1-x}$O films were prepared by DC reactive magnetron sputtering and plasma-enhanced metalorganic chemical vapor deposition [35,36].

![Graph showing X-ray diffraction patterns of Ni$_{1-x}$O films.](image2)

**Figure 3.** Oxygen content in Ni$_{1-x}$O films deposited with various oxygen flow ratios.
From XRD patterns, the crystallite size of Ni$_{1-x}$O films can be calculated using Scherrer’s formula [37]

$$\beta_{hkl} \cos \theta_{hkl} = K \lambda / D$$

where $\beta_{hkl}$ is the full width at the half maximum (FWHM) of the diffraction peak, $K$ is the shape factor, and $D$ is the crystallite size corresponding to the reflective planes. The relationship between the grain size and the oxygen flow ratio is shown in Figure 4. The grain size of Ni$_{1-x}$O films decreases from 7.63 to 5.77 nm with increasing oxygen flow ratios, implying that the excess oxygen can introduce some kinds of defects into NiO films, which affects the nucleation and growth of NiO grains. The decrement in the grain size reveals a degradation of the films’ crystallinity. It is identical with the broadening of NiO peaks shown in XRD analysis (Figure 3).

**Figure 4.** The variation of the grain size of Ni$_{1-x}$O films deposited with various oxygen flow ratios.

SEM observations of the top surfaces of Ni$_{1-x}$O films are shown in Figure 5. The evolution of the films’ morphologies is evident. With the increment in oxygen flow ratios, the particle size gradually decreases. From the change in the size distribution versus the oxygen flow ratio (Figure 5a–d), the main diameter of the NiO particles for the film deposited without oxygen flow is about 22.5 nm. It then decreases from 18.0 to 15.0 nm and further decreases to 9.0 nm with $f_{O_2}$ increasing from 10% to 50% and then to 100%. With increasing oxygen flow ratios, the formation of Ni$^{2+}$ defects contribute to the degradation of a film’s crystallinity, which further leads to the refinement of the NiO particles. This is consistent with the XRD results shown in Figure 3.

The relationship between the carrier concentration, Hall mobility, and electrical conductivity of Ni$_{1-x}$O films and oxygen flow ratio is illustrated in Figure 6. Through Hall measurement, the p-type conductivity of Ni$_{1-x}$O films is confirmed, regardless of the oxygen flow ratio. For the film deposited without oxygen, a relatively low carrier concentration of about $8.8 \times 10^{18}$ cm$^{-3}$ is obtained. This value monotonically increases to $8.1 \times 10^{19}$ cm$^{-3}$ when the oxygen flow ratio reaches 100%. The generation of the holes in O-rich Ni$_{1-x}$O films is considered to originate from the following reaction:

$$1/2 \text{O}_2 + V_{\text{Ni}^{''}} + 2 \text{Ni}_{\text{Ni}}^{*}$$

where $V_{\text{Ni}^{''}}$ represents Ni$^{2+}$ vacancies and $\text{Ni}_{\text{Ni}}^{*}$ denotes the formation of Ni$^{3+}$ cations at Ni$^{2+}$ sites. Nandy et al. [38] has reported that Ni$^{2+}$ vacancies along with Ni$^{3+}$ cations can be formed in non-stoichiometric Ni$_{1-x}$O films deposited under O-rich conditions. Two holes associated with each cation vacancy can then be generated. In our case, with increasing oxygen flow ratios, more oxygen is introduced into the deposition system. Therefore, more Ni$^{3+}$ cations and more positive carriers emerge. Thus, the carrier concentration increases. Meanwhile, the carrier mobility of Ni$_{1-x}$O films decreases from 6.12 to
1.96 V·cm⁻¹·s⁻¹ with increasing oxygen flow ratios. This decrement is mainly caused by the degradation of the films’ crystallinity. The diminution in the grain size results in more grain boundaries in the films, which significantly obstruct the carrier movement and enhance the carrier scattering.

Regarding the films’ electrical conductivity (Figure 6b), the NiO film deposited without oxygen presents a conductivity of about 9.1 S·cm⁻¹. As we have previously mentioned, all the films produced in the current work are oxygen enriched. The oxygen content in an Niₓ₋ₓO film can reach 69.12 at% even through there is no oxygen input. Hence, the holes originating in oxygen rich environments contribute to the films’ p-type conduction. With increasing oxygen flow ratios, a film’s conductivity is enhanced under the combined influence of carrier concentration and carrier mobility, indicating that the variation of carrier concentration plays a more important role in the films’ electrical properties. The film’s highest conductivity at around 25.4 S·cm⁻¹ can be realized when fₒ₂ reaches 100%.

Figure 5. Top surface SEM micrographs of Niₓ₋ₓO films deposited on glass substrates at various oxygen flow ratios and their corresponding size distribution of NiO particles: (a,a₁) 0%, (b,b₁) 10%, (c,c₁) 50%, and (d,d₁) 100%. 
The variation of films’ transmittance as a function of oxygen flow ratio is shown in Figure 7. As reported by Reddy [39] and Sun [21], the transmittance of off-stoichiometric NiO film is not ideal. All the films are pale brown or dark brown. With increasing oxygen flow ratios, more grain boundaries and point defects such as Ni$^{2+}$ vacancies exist in the films. They can cause a large amount of visible light scattering, thereby reducing a film’s transmittance. Besides this, an absorption edge is observed at around 300 nm, originating from the charge transfer from the valence band to the conductive band. This absorption edge presents a red-shift to longer wavelengths with increasing oxygen flow ratio, implying a decrement in the films’ band gaps. A film’s optical band gap $E_g$ can be calculated through the following equations [40,41]

$$\alpha = (1/d) \ln(1/T)$$  \hspace{1cm} (3)

$$\alpha h v = A (h v - E_g)$$  \hspace{1cm} (4)

where $\alpha$ is the absorption coefficient, $d$ is the film thickness, $T$ is the film’s transmittance, $h v$ is the incident photon energy, and $A$ is a constant. The exponent $n$ depends on the type of transition. $n = 1/2$ and 2 for direct and indirect transition, respectively. The films’ direct band gaps versus oxygen flow ratio is depicted in Figure 8. A slight reduction in the films direct band gap from 3.99 to 3.95 eV is noted. This is consistent with the red-shift of the absorption edge shown in Figure 7. Generally, the fundamental band gap of NiO of about 3.9 eV is believed to correspond to the charge transition from valence band maximum to the unoccupied Ni 3$d$ orbital [42–45]. This value is comparable to our results.
By comparing Figures 7 and 8, it can be seen that a film’s transmittance obviously varies even though its band gap just present minor changes. We suspect that this behavior is mainly caused by the changes of the films’ crystallinity. As oxygen content increases in the film, the film’s crystallinity degrades (Figure 3), and the grain size evidently decreases (Figures 4 and 5). Thus, more grain boundary scattering of the visible light occurs in the films deposited with a higher oxygen flow ratio. The films’ transmittances then deteriorate greatly.

![Figure 8. The variation of the films’ direct band gaps as a function of the oxygen flow ratio.](image)

### 4. Conclusions

Ni$_{1-x}$O films have been prepared by oxygen ion beam assisted RF sputtering, and the influence of the oxygen flow ratio on the structural, morphological, and optoelectronic properties has been investigated. The XRD results indicate that all the films are crystallized in a cubic NiO structure. With an increase in the oxygen flow ratio, a degradation in films’ crystallization is detected. It is assumed to be caused by the introduction of point defects, such as nickel vacancies. Meanwhile, with increasing oxygen flow ratios, the carrier concentration is enhanced and the carrier mobility reduces. Films’ conductivity then improves. The holes originating from Ni$^{2+}$ vacancies in O-rich conditions contribute to films’ p-type conductivity, whereas a film’s optical transmittance decreases when the oxygen flow ratio rises. This is attributed to more scattering of the visible light in the films with poor crystallinity deposited under higher $f_{O2}$. When the oxygen flow ratio reaches 100%, the highest p-type conductivity of about 25 S·cm$^{-1}$ is realized. In this condition, the films’ optical band gap is around 3.95 eV.

**Author Contributions:** Sheng-Chi Chen and Hui Sun conceived and designed the experiments; Wen-Chi Peng and Chao-Kuang Wen performed the experiments; Hui Sun and Xin Wang analyzed the data; Sheng-Chi Chen and Tung-Han Chuang contributed reagents, materials, and analysis tools; Hui Sun wrote the paper.

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