

Study of the effects of heating on the physical, optical, and electrical properties of NiO thin films synthesized using a low-cost sol-gel method

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ABSTRACT

Developments in low-cost techniques for growing high-quality nickel oxide thin films (NiOTFs) are critical enablers for the fabrication of NiO-based devices, particularly solar cells, light-emitting diodes, lasers, and many other applications. In this study, it has been demonstrated that the optical, electrical, and structural characteristics of NiOTFs coated on glass substrate employing a low-cost solution method are strongly influenced by post-thermal annealing treatments in ambient air. A comprehensive study was carried out on the characteristics of the deposited NiOTFs. X-ray diffraction (XRD) measurements indicate the enhancement of the crystal quality of films after annealing. There is a noticeable change and improvement in coated NiOTFs with heat treatment at 300 and 600 °C due to clear shifts in density. During the heating temperature increment, the energy of the band gap was shifted from 3.63 to 3.44 eV, and the electrical resistance of the NiOTFs varied from 1020 to 700 Ω-cm. Furthermore, the results indicate that the low-cost sol-gel (SG) deposition technique has a greater potential for producing high-quality p-type NiOTFs with minimal defects for electronic device applications.

1. Introduction

The development in the field of nano chemistry has led to the foundation of new materials, which are synthesized by different methods [1, 2]. The most notable exception is the low-cost solution-processed synthesis of metal oxide, which is widely used to fabricate nanodevices in the photovoltaic industry [3]. In particular, NiO is recognized as an important P-type semiconductor material with a band gap of around 3.6 eV [4]. In recent years, NiO has acquired considerable attention in the investigation society owing to its significant potential applications, electrically conductive films [5], display devices [6],

anode/cathode materials in OLEDs [7], sensors [8] and so on so forth. NiOTFs have been fabricated using a wide variety of methods which include electrochemical deposition [9], SG [10], sputtering [11], thermal evaporation [12], chemical solution deposition [13], etc. Among them, the solution-processed inks converged with spin-coating coatings, an indispensable technique due to their low cost and low temperatures, and thin films can be deposited on various substances for various applications [14, 15]. According to numerous published research results, the electrical and optical characteristics of NiOTFs are restricted by the holes introduced by nickel

vacancies and interstitial oxygen atoms when the annealing temperature is increased [16].

In this study, an economical and viable strategy for the synthesis of transparent NiOTFs using the SG spin coating technique was adopted. The effects of annealing temperatures under natural conditions on the optical, electrical, and structural characteristics of NiOTFs were investigated.

2. Experimental Details

2.1 Chemicals

Absolute ethanol, nickel acetate tetrahydrate $[(C_4H_6NiO_4).2H_2O]$ and mono-ethanolamine (MEA) were used in their as-received forms without further purification or modification.

2.2 Synthesis of NiO Precursor Ink

NiO ink was synthesized using a simple SG-based method which could be found elsewhere [17], however, the process parameters were modified in the present study. In a typical synthesis procedure, 1.28 g $(C_4H_6NiO_4).2H_2O$ was added slowly to the preheated (70 °C) mixture of 50 mL absolute ethanol and 5 mM monoethanolamine (MEA) under vigorous stirring. After 12h of stirring, an emerald clear and transparent blue solution was obtained. The solution was left for further aging for 24h and thereafter filtered (filtered with a polyamide syringe filter with 0.2 μ m pore size). Absolute ethanol was chosen and $[(C_4H_6NiO_4).2H_2O]$ as a solvent, while the MEA was added as a stabilizer and the base.

2.3 NiOTFs Deposition

To deposit NiOTFs, glass substrates were repeatedly washed in ethanol, isopropyl alcohol (IPA), and deionized water for 10 minutes each. The NiO (SG) was applied dropwise to the glass substrate (uncoated) and allowed to spin at 3000 rpm for 1 min. The spin cycle was repeated ten times to achieve a film thickness of 250 nm. The substrates were immediately heated to 150 °C for five minutes for dehydration to remove solvents and residues. After the NiOTFs were deposited, they were transferred to the tube furnace for annealing in ambient air at 300 to 600 °C for 60 minutes.

2.4 Characterization

The structural studies were carried out by Field Emission Scanning Electron Microscopy (FESEM) (Hitachi S4700), and the crystallinity of the NiOTFs was measured using XRD (Rigaku) coupled with the Cu-K radiation ($= 1.54178 \text{ \AA}$) in the range of 20 – 90° at 40 kV. The elemental analysis of the NiOTFs was

analyzed by energy-dispersive X-ray spectroscopy (EDS). In contrast, a He-Cd laser with a wavelength of 325 nm was used to measure the emission spectrum of room-temperature photoluminescence (PL). Using the Hall measurement method, we measured the carrier concentration, mobility, and resistivity. The adhesion of the nanofilm to glass substrates was tested using Scotch tape and scratch tests.

3. Results and Discussion

3.1 Structural Properties of NiOTFs

The morphologies of NiOTFs were characterized by FESEM, and their results are shown in Fig. 1. Fig. 1(a) and 1(b) depict the top and side view of the thin film, which reveal uniform and dense NiOTFs. It can be further seen from both figures that the presence of monocrystalline grains is uniformly distributed onto the entire substrate surface with ~250 nm average film thickness. The distribution of chemical elements was observed by EDS, as shown in Fig. 1(c), which has two high-intensity peaks of Ni and O. In this way, it was confirmed that the NiOTFs are of high quality as they were produced. This type of film is highly suitable for efficient charge conduction and estimation of optical properties for optoelectronic devices.

To test the adhesion strength of NiO nanofilms, tape and scratch tests were used. The physical test was performed by firmly attaching adhesive tape to NiOTFs and quickly removing it. The tape left no residue, indicating good adhesive strength. To confirm the results, a pin was placed on a NiOTF with measured pressure. No damage or stress was observed on the nanofilm, indicating good adhesion ability.

Fig. 1(d) illustrates the appearance of NiOTFs that have been annealed at different temperatures (300 and 600 °C). Obtained XRD patterns exhibit very strong diffraction peaks, indicating good crystallinity since the face-centered cubic crystalline NiO structure for both of the samples was observed. Peaks at $2\theta = 37.27, 43.3, \text{ and } 62.90$ can be indexed to be (111), (200), and (220), respectively (JCPDS-ICDD no. 78-0429) [18]. In addition, there was no other impurity (nickel oxide hydrates) detected, further confirming the high purity of NiOTFs. When the annealing temperature was increased from 300 °C to 600 °C, a change in intensity and location was observed as a result of the temperature change. Moreover, the deposited material exhibited an improved crystallite size due to an increase in annealing temperature [19].

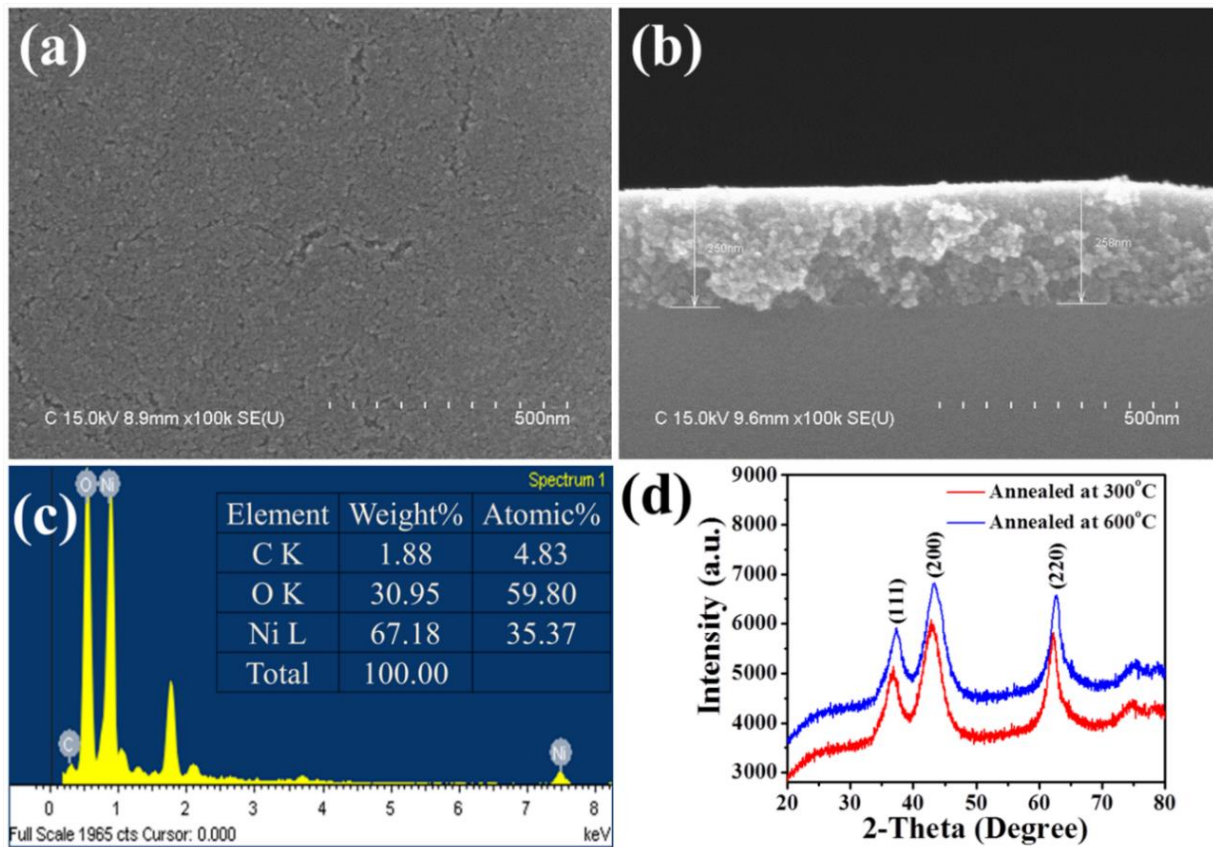


Fig. 1. FE-SEM Images of NiOTFs. (a) Top view, (b) Cross-Sectional View, (c) EDX Spectra and (d) XRD Patterns of NiOTFs Annealed at 300 °C and 600 °C

3.2. Optical Properties of NiOTFs

Comparison of the emission and transmission spectra of NiOTFs processed at 300 and 600 °C is shown in Fig. 2. Both NiOTFs showed no absorption peak in the visible wavelength range and only a clear spectrum in the UV wavelength range between 370 and 390 nm (Fig. 2). Sharp absorbance indicates the uniformity or continuity of NiOTFs with no extra peaks. The spectrum from 300 to 355 nm was originally attributed to the characteristic onset absorption of NiO. However, when annealing at higher temperatures (300 and 600 °C), a slight red shift in the absorption spectra (3.26 to 3.13 eV) was observed, indicating a slight change in the density of states for holes with increasing annealing temperature [20]. Fig. 2 (b) demonstrates the optical transmission of the NiOTFs on a glass substrate. Both the NiOTFs due to annealing treatment were found to be opaque for wavelengths below 300 nm. The maximum transmittance of 91.25 % is observed around 800 nm for both of these films. Further, when the heating temperature was raised from 300 to 600 °C, the transmittance decreased, suggesting that Ni had been transformed from a highly reflective metal to a semiconductor with a wide band gap (transmissive NiO) [21].

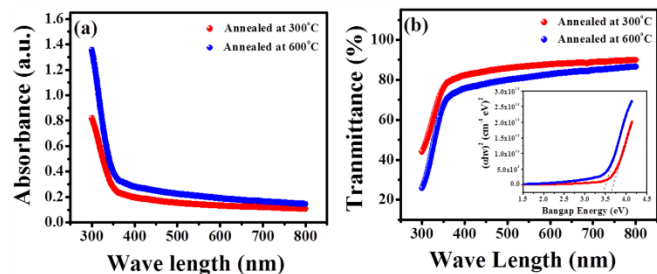


Fig. 2. (a) UV/Vis Absorption and (b) Transmittance Spectra of NiOTFs Annealed at 300 °C and 600 °C

The amount of energy contained within the optical band gap could be calculated using Tauc's graph of the optical band gap (E_g) versus photon energy. Fig. 2(b)-inset shows the optical band gap for NiOTFs can be estimated by the fact that this part of the line intersects the energy axis at zero. NiOTFs heated at 300 °C and 600 °C show energy band gaps of 3.63 eV and 3.44 eV, respectively. As a result, the optical energy band gap value (~ 0.19 eV) is reduced with a rise in heating temperature. The decrease in band gap energy with an increase in an annealing temperature due to oxygen ion vacancies occupied by electrons acting as donor centers are responsible for broadband absorption and result in a red shift of the band energy [22].

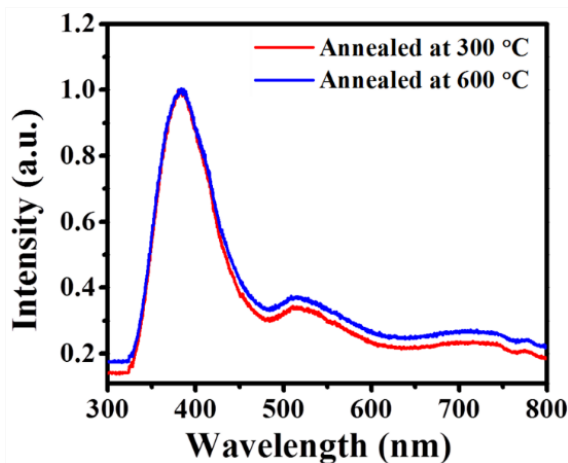


Fig. 3. PL Emission Spectra of NiOTFs Annealed at 300 °C and 600 °C

The photoluminescence of NiOTFs heated between 300 and 600 °C was examined in the wavelength range of 300 – 800 nm to determine how annealing temperature affects this behaviour (Fig. 3). Three prominent peak positions can be observed in the photoemission spectra of photoexcitation at 325 nm: 385 nm, 516 nm, and 715 nm. The peak at 385 nm can be seen to represent near-band edge UV emission (NBE). The mechanism of UV emission in NiO can be attributed to the electronic transitions of Ni²⁺ ions [23]. In the visible range, the PL peak at 516 nm correlates with green emission. Generally, metal oxide nanomaterials emit visible light due to defects in the lattice, so NiO also produces distinct peaks in visible areas, cation vacancies, oxygen trapped between gaps, and nickel holes due to charge transfer between Ni²⁺ and Ni³⁺ ions [24]. NiOTFs exhibit a slight difference in emission intensity when their annealing temperature is increased from 300 °C to 600 °C.

3.3. Electrical Properties of NiOTFs

The Hall-Effect measurement method was used at ambient to evaluate the electrical resistivity, Hall mobility, and carrier concentration of NiOTFs grown on glass substrates. As shown in Fig. 4, the electrical resistivity decreases drastically from 1020 ohm-cm to 700 ohm-cm upon increasing annealing temperature.

This is the result of a heat treatment at 600 °C under ambient (oxygen-rich) conditions. These developments in more extensive grains contribute to high crystallinity and low oxygen vacancies in SG-deposited NiOTFs, a property that is a crucial factor in low resistivity [25]. It was observed that NiOTFs heated to 300 °C had a mobility of 5.33 cm²/V.s, but a film heated to 600 °C had a mobility of 3.36 cm²/V.s. Furthermore, the carrier concentration of NiOTFs heated at 300 and 600 °C was

2.59 cm⁻³, 1015 cm⁻³ and 1.26 10¹⁶ cm⁻³, respectively. It is possible that these apparent changes ultimately contribute to the homogenization of NiOTFs and their stabilization. The reason for this is the larger grain size and the reduction of native defects caused by varying the heating temperatures [26].

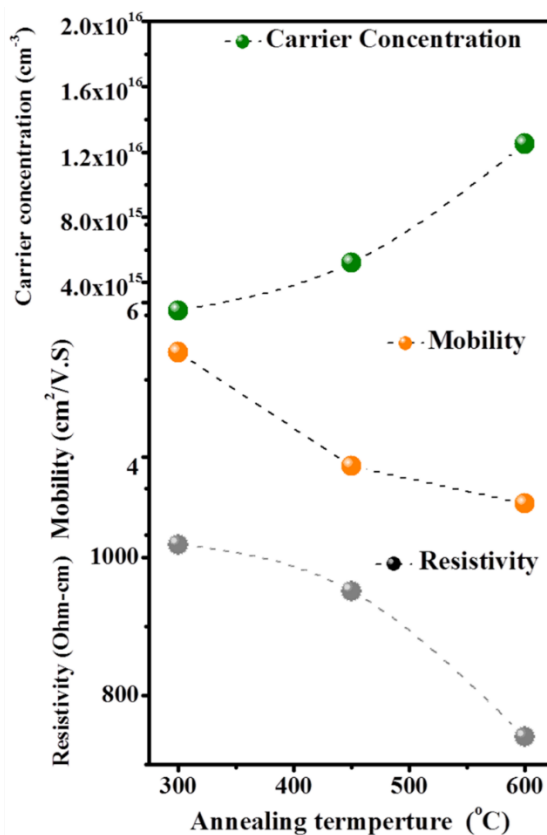


Fig. 4. Electrical Characteristics of NiOTFs

4. Conclusion

To summarize, a cost-effective spin coating technique based on SG has been demonstrated to fabricate NiOTFs on glass substrates. The films obtained in this research exhibited smooth surface morphology with good adhesion on the substrate. This was attributed to an ideal stability of NiO solution. The effects of heat treatment on the crystallinity and optical and electrical properties of NiOTFs were also investigated. Remarkably, the heat treatment enhanced the optical absorption of the NiOTFs, and XRD and SEM analyzes showed that the final products were face-centered cubic crystalline materials. Observations indicated that the band gap of the film samples was 3.63 to 3.44 eV. Under ambient conditions, the annealing temperature of the NiOTFs was increased from 300 to 600 °C, resulting in a decrease in electrical resistivity and an increase in carrier concentration. Further confirmation of the existence of defects was provided by PL measurements of NiOTFs. The present results motivate its further use in developing solar cells, LEDs, and other optoelectronic devices, as the availability of P-type substitutes currently limits its use.

5. References

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