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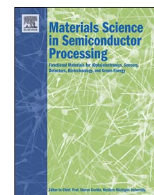

Influence of annealing temperature on nickel oxide thin films grown by chemical bath deposition

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ABSTRACT

Nickel oxide thin films were prepared with a simple formulation using nickel sulfate and triethanolamine aqueous solutions via chemical bath deposition. After deposition, the films were subjected to annealing in an O_2/N_2 atmosphere for two hours at 200, 300, and 400 °C. X-ray diffraction patterns indicated that the as-deposited NiO_x films were amorphous. After annealing, the NiO_x crystallizes into a cubic phase. The X-ray photoelectron spectroscopy analysis confirms the presence of NiO_x with an FCC phase that yields a chemical composition of $NiO_{1.17}$, without the appearance of other Ni compounds. The band gap for the NiO_x films is determined to lie between 4.0 and 3.4 eV. Scanning electron micrographs exhibit a compact deposition and worm-like structure morphology. Hall effect measurements indicate a *p*-type conductivity and the resistivity is found to vary from 1.73×10^3 to 0.89×10^6 Ω cm due to oxygen incorporation. Employing Kelvin probe microscopy and photoemission spectroscopy, the NiO_x films present a work function between 4.70 and 5.48 eV and an ionization energy of ~ 5.6 eV. From the work function, ionization energy, and the band gap results, we propose a band diagram for the films at different annealing temperatures.

1. Introduction

Transparent conductive oxides (TCOs) have been widely used in the form of thin films in different electronic devices and are key components in technologies such as touch screens and transparent electronics [1,2]. Zinc oxide (ZnO) [3], titanium oxide (TiO_2) [4], and tin oxide (SnO_2) [5] are some of the most utilized TCOs. These TCOs are characterized by a wide band gap (E_g) and typically they present *n*-type conductivity due to intrinsic defects such as vacancies and interstitial ions [4,6]. There are also TCOs with a *p*-type conductivity such as copper aluminum oxide ($CuAlO_2$) [7], copper gallium oxide ($CuGaO_2$) [8] and nickel oxide (NiO_x)[9]. However, the *p*-type TCOs reports are much lower in number with respect to the works related with *n*-type TCOs; this has limited the development of transparent devices where a *p-n* junction is needed [10,11]. For this reason, the development of TCOs with a *p*-type conductivity, by chemically modifying those utilized as *n*-type, has been attempted [12,13]. Nonetheless, this modification makes these materials unstable which hinders obtaining them [6,11].

NiO_x is a binary *p*-type TCO of great interest due to its electrical, optical, and physicochemical properties, such as a good chemical stability [14], a face-centered cubic crystalline structure [15], a controllable E_g of 3.5–4.0 eV [16], a high optical transmittance in the visible region [17], and also being inexpensive to produce [18]. The aforementioned properties make NiO_x attractive for applications, including UV photodetectors [19], gas sensors [20], light emission diodes (LEDs) [21,22], batteries [23], electrochromic windows [24] and solar cells [25]. One of the recent applications for NiO_x has been as a hole transport layer (HTL) in hybrid solar cells based on perovskite. On the other hand, in an ITO/NiO/perovskite/ZnO/Al structure, the NiO_x acts as an electron blocker in the structure of the device. It also enhances the stability of the perovskite-based solar cells in comparison to an organic HTL, such as poly (3-hexylthiophene) (P3HT) and poly (3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT: PSS)[26,27].

NiO_x has been obtained as a thin film by both physical and chemical methods. Some of the physical methods include sputtering [28], pulsed laser deposition (PLD) [29,30], electron beam evaporation [31,32], among others. On the other hand, chemical methods include spray pyrolysis [33], successive ionic layer adsorption reaction (SILAR) [34], sol-gel [35,36], electrodeposition [37,38], and chemical bath

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deposition (CBD) [39,40]. CBD is very popular due to it being a low-cost process, it is possible to make deposition in large areas, and it is performed at low temperatures without the use of high vacuum [41]. One of the main components in the CBD process is the use of complexing agents which provide better control of the deposition of thin films [42]. However, reports of NiO_x films by CBD employing complexing agents are scarce. Generally, the reported formulations employ a nickel salt and urea without the use of a complexing agent [43,44]. On the other hand, reports of NiO_x with the use of complexing agents, such as ammonium, use long deposition times or complex formulations [45].

This paper presents the study of the chemical composition of NiO_x films obtained by CBD. The chemical composition was determined through X-ray photoelectron spectroscopy (XPS), from which it is found that the films present a Ni^{2+} oxidation state that corresponds to the formation of NiO_x; it is also determined that there is a slight enrichment of oxygen without the presence of Ni_2O_3 or other nickel compounds. The enrichment with oxygen was related with the behavior of the structural, optical, and electrical properties of the NiO_x films when they are subjected to annealing at different temperatures. From the determination of the work function, ionization energy, and E_g, a band diagram for NiO_x was proposed in function of the annealing temperature. The data that the band diagram bears is of great importance for the incorporation of NiO_x to different optoelectronic devices.

2. Experimental details

2.1. Film deposition

The NiO_x films were deposited on LAUKA® glass substrates. The metallic ion source was nickel sulfate ($NiSO_4{\cdot}6H_2O$, 99% purity) and the complexing agent was triethanolamine (TEA) ($C_6H_{15}NO_3$, 99.8% purity).

The substrate was washed with Alconox® detergent and rinsed with tap water followed by distilled water. All the solutions were prepared using distilled water. For the synthesis of the NiO_x films, 25 mL of 0.075 M $NiSO_4{\cdot}6H_2O$ and 1.5 mL of 3.7 M TEA were firstly prepared and mixed with distilled water reaching a mixed solution final volume of 100 mL. The pH value of the solution was ~ 9.

The deposition time was about 1 h with a temperature of 50 °C. It is noteworthy that the formulation employs a small quantity of reactants and thus produces minor residues.

Based on the mechanism reported by Ezema et al. [46], who employed the complex ion $[Ni(NH_3)_6]^{2+}$, a mechanism is proposed through a series of steps using the $[Ni(TEA)]^{2+}$ ion complex. The first step consists of the dissociation of $NiSO_4$ in the presence of water, which produces the free ion Ni^{2+} (Eq. (1)), subsequently the free ions form a complex with the TEA molecules forming a complex ion $[Ni(TEA)]^{2+}$; Ni^{2+} ions are released gradually according to an equilibrium reaction (Eq. (2)). Then, a $Ni(OH)_2$ film is formed on the surface of the substrate by the adsorption and growth of this nickel species on the substrate (Eq. (3)) [47], and finally by annealing we obtain NiO_x (Eq. (4)).

$$NiSO_4 + H_2O \rightarrow Ni^{2+} + SO_4^{2-} \quad (1)$$

$$Ni^{2+} + TEA \leftrightarrows [Ni(TEA)]^{2+} \quad (2)$$

$$Ni^{2+} + 2OH^- \leftrightarrows Ni(OH)_2 \quad (3)$$

$$Ni(OH)_2 \xrightarrow{HEAT} NiO + H_2O \quad (4)$$

2.2. Annealing of the NiO_x thin films

After the chemical bath deposition process, the films were dried at room temperature and annealed in a quartz tube in O_2/N_2 atmosphere containing 10% and 90%, respectively. In the case of ZnO, this gas ratio is considered to enable the formation of a low resistivity *p*-type semiconductor oxide [48,49]. The annealing temperatures were 200, 300, and 400 °C, and the reaction time was 2 h.

2.3. Characterization of the NiO_x films

The crystalline structure of the films was determined by X-ray diffraction using a Rigaku Ultima III diffractometer with a Cu K_α (λ = 0.154 nm) radiation source. The optical transmittance and E_g were obtained from UV–visible spectra with a Black Comet and Stellar Net spectrometer. The morphology and thickness of the films were studied using a scanning electron microscope (SEM) Zeiss Supra-40. Electrical measurements were performed in a CASCADE SUMMIT 11741B-H probe station; circular transmission line model (CTLM) was employed to assess the sheet resistance, while Hall effect measurements were done in a Lakeshore series 8400 AC/DC Hall effect equipment. The work function was determined by a Scanning Kelvin Probe SKP 5050 KP Technology tool. The value of the ionization energy was obtained by photoemission spectroscopy in air using a Riken Keiki AC-2 Photoelectron Spectrometer system with a deuterium lamp and an energy scan from 4.4 to 5.8 eV with 0.05 eV steps.

XPS was employed to assess the oxidation state and chemical composition of the nickel oxide films. In the present work, the XPS analysis performed is especially peculiar because it enabled not only the chemical assessment of the films, but it incorporated important structural details of our films. The system consisted of a PHOIBOS WAL electron energy analyzer and a monochromatic Al $K\alpha_1$ (1486.7 eV) light source provided by SPECS. A constant pass energy of 15 eV was used in data acquisition. Energy calibration was done respecting the main O 1*s* peak located at 529.4 eV [50]. The analysis of the experimental XPS data was done by constructing peak envelopes composed of several Voigt and Gaussian profiles; the determination of peak parameters, like peak positions, widths, and areas, was done via peak-fitting [51]. The fitting procedure had the theoretical branching ratio [52] as the single constraint. Background modeling was performed employing the active background approach [53], where the contributions of a Shirley-type [53] and Tougaard-type [54] background are considered within the fitting procedure. A rigorous approach is employed to assess the uncertainty in the integrated peak areas [55]. The chemical assessment of the nickel oxide films was done by using the integrated peak areas as a mean to evaluate the intensity of the photoemission signal for each component present in the surface of the film. This quantitative approach has been recently proven to be satisfactory for assessing the chemical composition of a couple of transition metal oxides [56,57]. The expression for homogeneous materials yield [58,59]:

$$\rho_n \sim \frac{I_n K_n}{\frac{d\sigma_n}{d\Omega} \lambda_n \sin\theta} \quad (5)$$

where ρ_n is the atomic density of each component n (n = Ni, O), I_n is the assessed peak area of each core level, K_n is the photoelectron kinetic energy, $d\sigma_n/d\Omega$ is the differential photoelectric cross section for each core level [60], θ is the electron escape angle and λ_n is the effective attenuation length at the corresponding kinetic energy. The input parameters were obtained from reference tables [60–63].

3. Results and discussion

3.1. X-ray diffraction

Fig. 1 shows the diffractogram of the NiO_x films at different annealing temperatures. The XRD patterns of the films indicate an amorphous phase for the as-deposited film and even after an annealing at 300 °C the amorphous phase is still present. The amorphous behavior

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