Optimization and characterization of NiO thin film and the influence of thickness on the electrical properties of n-ZnO nanorods/p-NiO heterojunction

Ahmad Echresh, Mazhar Ali Abbasi, Morteza Zargar Shoushtari, Mansoor Farbod, Omer Nur and Magnus Willander

Linköping University Post Print

N.B.: When citing this work, cite the original article.

Original Publication:

Ahmad Echresh, Mazhar Ali Abbasi, Morteza Zargar Shoushtari, Mansoor Farbod, Omer Nur and Magnus Willander, Optimization and characterization of NiO thin film and the influence of thickness on the electrical properties of n-ZnO nanorods/p-NiO heterojunction, 2014, Semiconductor Science and Technology, (29), 11, 115009.

<http://dx.doi.org/10.1088/0268-1242/29/11/115009>

Copyright: IOP Publishing

<http://www.iop.org/>

Postprint available at: Linköping University Electronic Press

<http://urn.kb.se/resolve?urn=urn:nbn:se:liu:diva-112474>

Optimization and characterization of NiO thin film and the influence of thickness on the electrical properties of n-ZnO nanorods/p-NiO heterojunction

Ahmad Echresh ^{a,b}, Mazhar Ali Abbasi ^a, Morteza Zargar Shoushtari ^b, Mansoor Farbod ^b,

Omer Nur ^a and Magnus Willander ^a

^a Department of Science and Technology, Physical Electronics and Nanotechnology Division, Campus Norrköping, Linköping University, SE-601 74 Norrköping, Sweden

^b Department of Physics, Shahid Chamran University of Ahvaz, Ahvaz, Iran

E-mail of corresponding author: Ahmadechresh@gmail.com

Abstract

In this study, we report on the synthesis optimization of NiO thin film to grow preferentially along the (111) direction. The x-ray diffraction (XRD) pattern revealed that the NiO film with 200 nm thickness annealed at 600 °C temperature has the best preferential orientation along the (111) direction. Also, atomic force microscope (AFM) images show that the grain size of NiO increases at higher temperatures. Then, ZnO nanorods were grown on the NiO thin film with 100, 200 and 300 nm thickness grown at 600 °C. The XRD pattern and scanning electron microscope (SEM) images indicate that the well aligned ZnO nanorods with hexagonal face have a preferential orientation along the c-axis (002). The current-voltage measurements of the n-ZnO nanorods/p-NiO heterojunctions showed a clear rectifying behavior for all diodes. The threshold voltage of the heterojunctions was increased by increasing the thickness of the NiO thin film which was attributed to the increasing of the series resistance (R_s) of the diodes.

Keywords: NiO thin film, ZnO nanorods, Heterojunction, Electrical properties

1. Introduction

Recently, zinc oxide (ZnO) has attracted a great deal of attention due to its wide direct band gap (3.37 eV) and relatively large exciton binding energy (60 meV) and because of these unique properties, ZnO has been recognized as a promising material for the optoelectronic devices [1,2]. Specially one dimensional ZnO nanostructures are well known for a variety of attractive properties and have been used successfully in different optoelectronic devices and UV photo detectors [3, 4]. Due to instability and low carrier concentration and mobility of holes in ZnO, p-type ZnO based nanodevices are still in challenge [1]. To realize the ZnO-based p-n heterojunctions, some researchers have grown n-ZnO nanostructures on other p-type substrates such as GaN [5-7], SiC [8, 9], GaAs [10, 11], Si [12]. Because of the similarity between the hexagonal and the cubic crystal forms, good lattice matching conditions may be expected if the cubic lattice edge is $\sqrt{2}$ times the hexagonal lattice constant (a-axis) and the c-axis is grown perpendicular to the (111) plane [13]. Since NiO thin film has relatively stable p-type semiconductor characteristics, wide direct band gap (3.7 eV) and cubic structure, n-ZnO/p-NiO heterojunctions have been reported as a suitable p-n heterojunction for fabricate the UV detector [14-16]. Sputtering, chemical vapour deposition and thermal evaporation methods have been used to synthesis NiO thin films [17-19]. According to the best of our knowledge, few researchers have used thermal evaporation method to synthesis NiO thin film [19] and there have been no detailed investigations reported about the optimization of the preferential orientation growth and the effect of NiO film thickness on the electrical properties of the ZnO nanorods/p-NiO heterojunction.

In this study, we have optimized the NiO thin film synthesized via thermal evaporation method and then fabricated and characterized n-ZnO nanorods/p-NiO

heterojunction using the optimized NiO thin film. In addition, we have investigated the effect of the NiO film thickness on the electrical properties of n-ZnO nanorods/p-NiO heterojunction. The devices were characterized by the X-ray diffraction (XRD), atomic force microscope (AFM), field emission scanning electron microscope (FESEM), UV-visible spectroscopy (UV-vis) and semiconductor parameter analyzer.

2. Experimental method

Commercially available p type Si substrate was used in this study and all chemicals were purchased from Sigma Aldrich with high purification. First, Ni film with different thickness (100, 200 and 300 nm) was deposited by thermal evaporation in a vacuum chamber with a pressure of 2×10^{-6} mbar on the Si substrates. Then to oxidize the Ni films, the substrates were annealed in oxygen ambient at a temperature of 400-1000 °C for several hours. The prepared substrates were spin coated few times with a seed solution of ZnO nanoparticles [20] to obtain a uniform growth and then were annealed at 120 °C for 20 min. For the growth of ZnO nanorods, an equimolar concentration of hexamethylenetetramine (HMT) and zinc nitrate hexahydrate solutions (0.075 M) were separately prepared and mixed together. Then the final solution was poured in a beaker and the pre-treated substrates were immersed in the solution with the growth side facing downward. Then the beaker was sealed and heated in a laboratory oven at 95 °C for 5 hours and after that was allowed to cool down to room temperature. After the growth process, the samples were rinsed with deionized water in order to remove the residual salts and dried with nitrogen blow. For devices processing, an insulating layer of Shipley 1805 photo resist (Marlborough, Ma, USA) was coated to fill the vacant spaces between the nanorods. Reactive ion etching with oxygen plasma was used to expose the tips of ZnO nanorods before the deposition of Al

top ohmic contact. The Ag was deposit by thermal evaporation method as bottom ohmic contact for p-NiO.

3. Results and discussion

3.1. *Structural and morphological properties of NiO thin films*

First, Ni was deposited on the Si substrate with 200 nm thicknesses and then annealed in oxygen ambient at different temperatures (400–1000 °C) to get the NiO thin film. The XRD pattern of samples is shown in Fig. 1(a). These patterns display diffraction peaks that correspond to the NiO cubic structure (JCPDS No. 01-1239). The lattice parameters and texture coefficient (TC) that represents the preferential crystallite orientation are given in Table 1. TC is defined by the following equation [21]:

$$TC(hkl) = \frac{\frac{I(hkl)}{I_0(hkl)}}{\sum \frac{I(hkl)}{I_0(hkl)}} \times 100$$

Where $I(hkl)$ and $I_0(hkl)$ are the measured and standard relative intensities of different peaks, respectively. It is to be noted that the patterns have preferential orientation along the (111) direction by increasing the temperature up to 800 °C but at higher temperature the sample doesn't have special preferential orientation. The grown NiO film at 600 °C has the best preferential orientation along the (111) direction. In the second step, Ni was deposited with 100, 200 and 300 nm thickness and annealed at 600 °C. Fig. 1(b) shows the XRD pattern for these samples. It can be seen that the preferential orientation takes place along the (111) direction by increasing the thickness up to 200 nm but preferentiality is vanished by increasing the thickness. It has been reported that the development of preferential oreintation

in NiO is governed by surface energy [22]. The (111) reduces the surface free energy of growing NiO film as it deposited in an oxygen rich ambient. It seems that at low temperature because of oxygen rich ambient, NiO film might be controlled by the arrangement of O^{2-} , resulting in a preferential orientation (111) since the (111) plane is most densely packed plane of O^{2-} for NiO structure. By increasing the temperature Ni^{+2} has more kinetic energy migrating to the equilibrium position which leads to decrease Ni vacancy defects and result in increase the (200) plane intensity that attributed to the densely packed plane of Ni^{+2} . Typical AFM images of the samples with 200 nm thickness that annealed at different temperatures (400-1000 °C) are shown in Fig. 2. One can observe that at low temperatures the surface consisted of small grain with unclear grain boundaries but by increasing the temperature the size of grains increased and grain boundaries became clear.

3.2. *Structural and morphological properties of the grown ZnO nanorods*

Typical SEM image of the grown ZnO nanorods on the optimized NiO thin film is shown in Fig. 3 (a). It can be seen that relatively well aligned ZnO nanorods has hexagonal faces and average diameter about 100 nm. Fig. 3(b) shows the XRD pattern of the ZnO nanorods and as can be observed that it has achieved a preferential orientation along the c-axis (002) (JCPDS No. 36-1451).

3.3. *Optical absorption properties*

Fig. 4 (a, b) displays the UV-visible absorption spectra and the plot of $(\alpha h\nu)^2$ versus $h\nu$ for ZnO nanorods and NiO thin film. The optical band gap of samples was measured using the following formula [23]:

$$(\alpha h\nu) = A (h\nu - E_g)^{1/2}$$

Where α is an optical absorption coefficient, $h\nu$ is the photon energy, A is a constant coefficient and E_g is the optical band gap energy. The optical band gap values of ZnO and NiO, obtained by extrapolation method, were 3.25 and 3.8 eV, respectively. According to the electron affinity (χ) of ZnO (4.35 eV) and NiO (1.46 eV) the energy band diagram can be drawn via Anderson model [13] that is shown in Fig. 4 (c). The conduction band and valence band offsets for p-NiO/n-ZnO were calculated to the 2.89 eV and 2.34 eV, respectively

3.4. *Electrical properties of n-ZnO nanorods/p-NiO heterojunction*

The schematic diagram of the n-ZnO nanorods/p-NiO heterojunction structure is shown in Fig. 5(a). Electrical properties of the n-ZnO nanorods/p-NiO heterojunctions with different NiO film thickness (100, 200 and 300 nm) were investigated by current-voltage (I-V) measurement. Fig. 5(b, c) shows the current-voltage and the semi-log current density–voltage (J-V) characteristics of the diodes. It can be seen that all diodes show nonlinear and obvious rectifying behavior. The threshold voltage and leakage current under reverse bias (-5 V) for n-ZnO nanorods/p-NiO heterojunctions with 100 nm, 200 nm and 300 nm NiO thickness were 3.6 V and 1.09 mA, 4.7 V and 0.19 mA, 5 V and 0.10 mA, respectively. The series resistance (R_s) of the n-ZnO nanorods/p-NiO (100, 200 and 300 nm) heterojunctions that can be obtained from the $I/(dI/dV)$ vs. I plot was 286.09 Ω , 365.60 Ω and 420.27 Ω , respectively, as shown in Fig. 5(d). The threshold voltage and R_s of heterojunctions were lower than those reported by Byung et al [15]. As can be observed by increasing the thickness of NiO thin film, the threshold voltage increased and the leakage current decreased that this

attributed to the increasing of the R_s . Also, the I_F/I_R ratio of the n-ZnO nanorods/p-NiO (100, 200 and 300 nm) heterojunctions was 18.32, 51.84 and 21.43, respectively, where I_F and I_R is the current under forward bias (5 V) and the current under reverse bias (-5 V), respectively. It can be seen that n-ZnO nanorods/p-NiO heterojunction with 200 nm of NiO film thickness, which has better preferential orientation along (111) direction than other heterojunctions with 100 nm and 300 nm of NiO film thickness, has the highest value of I_F/I_R ratio which is attributed to high quality of heterojunction.

4. Conclusion

In summary, we optimized the NiO thin film synthesized via thermal evaporation method. The structural measurement show that the NiO thin film with 200 nm thickness annealed at 600 °C has the best preferential orientation along the (111) direction. Then, ZnO nanorods were grown via hydrothermal method to fabricate n-ZnO nanorods/p-NiO heterojunction. The XRD pattern revealed that ZnO has wurtzite structure with preferential orientation along the c-axis (002). Also, we investigated the effect of NiO thickness on the electrical properties. Current-voltage measurements show that the series resistance (R_s) is enhanced by increasing the thickness which this led to increase the threshold voltage and decreased the leakage current of the diode. The n-ZnO nanorods/p-NiO heterojunction with 200 nm NiO film thickness has the highest value of I_F/I_R ratio (51.84) which is attributed to high quality of heterojunction.

Acknowledgment

The authors acknowledge Linkoping University and Shahid Chamran university of Ahvaz for financial support of this work.

References

- [1] Echresh A, Shoushtari M Z and Farbod M 2013 Effect of growth angle and post-growth annealing on the structural and optical properties of ZnO nanorods grown hydrothermally on p-Si substrate J. Materials Letters **110** 164.
- [2] Park S, Mun Y, An S, Lee W I and Lee C 2014 Enhanced photoluminescence of Au-functionalized ZnO nanorods annealed in a hydrogen atmosphere J. Luminescence **14** 75.
- [3] Soh C B, Tay C B, Chua S J, Le H Q, Ang N S S and Teng J H 2010 Optimization of hydrothermal growth ZnO nanorods for enhancement of light extraction from GaN blue LEDs J. Crystal Growth **312** 1848.
- [4] Abbasi M A, Ibupoto Z H, Khan A, Nur and Willander M 2013 Fabrication of UV photo-detector based on coral reef like p-NiO/n-ZnO nanocomposite structures J. Materials Letters **108** 149.
- [5] Abbasi M A, Ibupoto Z H, Hussain M, Nur O and Willander M 2013 The fabrication of white light-emitting diodes using the n-ZnO/NiO/p-GaN heterojunction with enhanced luminescence J. Nanoscale Research Letters **8** 320.
- [6] Nandi R, Joshi P, Singh D, Mohanta P, Srinivasa R S and Major S S 2014 Structural and optical properties of ZnO nanorods grown chemically on sputtered GaN buffer layers J. Thin Solid Films **555** 122.
- [7] Naisen Y u, Lifang D u, Haiying D u, Danyang H u, Zhangwen M a o, Yong W, Yunfeng W u and Dongping L i u 2014 Synthesis of ZnO film on P-GaN/Si(111) by one-step hydrothermal method J. Thin Solid Films **550** 206.

- [8] Asharfi A 2010 Band Offsets at ZnO/SiC heterojunction: Heterointerface in band alignment J. Surface Science **604** L63.
- [9] Phan D T and Chung G S 2011 Comparison of ZnO thin films grown on a polycrystalline 3C-SiC buffer layer by RF magnetron sputtering and a sol-gel method J. Applied Surface Science **257** 3285.
- [10] Koc P, Tekmen S, Baltakesmez A, Tuzemen S, Meral K and Onganer Y 2013 Stimulated electroluminescence from n-ZnO/p-GaAs:Zn heterojunctions fabricated by electro-deposition J. AIP Advances **3** 122107.
- [11] Tekmen S, Gur E, Asil H, Cinar K, Coskun C and Tuzemen S 2010 Structural, optical and electrical properties of n-ZnO/p-GaAs heterojunction J. Phys. Status Solidi A **207** 1464.
- [12] Keskenler E F, Tomakin M, Dogan S, Turgut G, Aydin S, Duman S and Gurbulak B 2013 Growth and characterization of Ag/n-ZnO/p-Si/Al heterojunction diode by sol-gel spin technique J. Alloy and Compounds **550** 129.
- [13] Milnes A G and Feucht D L 1972 Heterojunctions and Metal Semiconductor Junctions Carnegie-Mellon University Academic Press **1** 1-33.
- [14] Hoa L T, Tien H N and Hur S H 2014 A highly sensitive UV sensor composed of 2D NiO nanosheets and 1D ZnO nanorods fabricated by a hydrothermal process Sensors and Actuators A: Physical **207** 20-24.
- [15] Jung B O, Kwon Y H, Seo D J, Lee D S and Cho H K 2013 Ultraviolet light emitting diode based on p-NiO/n-ZnO nanowire heterojunction Journal of Crystal Growth **370** 314-318.

- [16] Long H, Ai L, Li S, Huang H, Mo X, Wang H, Chen Z, Liu Y and Fang G 2014 Photosensitive and temperature-dependent I – V characteristics of p -NiO film/ n -ZnO nanorod array heterojunction diode J. Materials Science and Engineering: B **184** 44.
- [17] Mistry B V , Bhatt P, Bhavsar K H, Trivedi S J, Trivedi U N and Joshi U S 2011 Growth and properties of transparent p -NiO/ n -ITO ($\text{In}_2\text{O}_3\text{:Sn}$) p – n junction thin film diode J. Thin Solid Films **519** 3840–3843.
- [18] Zhang X L, Hui K S and Hui K N 2013 High photo-resposivity ZnO UV detector fabricated by RF reactive sputtering J. Materials Research Bulletin **48** 305-309.
- [19] Chrissanthopoulos A, Baskoutas S, Bouropoulos N, Dracopoulos V, Pouloupoulos P and Yannopoulos S N 2011 Synthesis and characterization of ZnO/NiO p – n heterojunctions: ZnO nanorods grown on NiO thin film by thermal evaporation J. Photonic and Nanostructures – Fundamental and Application **9** 132-139.
- [20] Greene L E, Law M, Tan D H, Montano M, Goldberger J, Somorjai G and Yang P 2005 General route to vertical ZnO nanowire arrays using textured ZnO seeds J. Nano Letters **5** 1231.
- [21] Ilıcan S, Caglar M and Caglar Y 2007 Determination of the thickness and optical constants of transparent indium-doped ZnO thin films by the envelope method J. Material Science – Poland **25** 709.
- [22] Ryu H W, Choi G P, Hong G J and Sark J 2004 Growth and Surface Morphology of Textured NiO Thin Films Deposited by Off-Axis RF Magnetron Sputtering Japanese Journal of Applied Physics **43** 5524.
- [23] Echresh A and Shoushtari M Z 2013 Synthesis of Al-doping ZnO nanoparticles via mechanochemical method and investigation of their structural and optical properties J. Materials Letters **109** 88.

Table 1. The lattice constant and texture coefficient of the grown NiO films.

Sample	a(Å)	TC₁₁₁(%)	TC₂₀₀(%)	TC₂₂₀(%)
400 C, 200 nm	4.1627	46.20	36.08	17.72
600 C , 100 nm	4.1721	44.19	28.68	27.13
200 nm	4.1689	50.27	33.34	16.39
300 nm	4.1743	38.70	37.19	24.11
800 C, 200 nm	4.1830	48.02	36.16	15.82
1000 C, 200 nm	4.1728	41.17	47.07	11.76

Fig. 1: XRD patterns of grown NiO thin films (a) with 200 nm thickness at different temperatures and (b) with different thickness at 600 °C.

Fig. 2: Atomic force microscope (AFM) 2D images of the surface of the NiO with 200 nm thickness annealed at (a) 400 °C, (b) 600 °C, (c) 800 °C and (d) 1000 °C.

Fig. 3: SEM image (a) and XRD pattern (b) of ZnO nanorods grown on the NiO film.

Fig. 4: UV-visible absorbance of ZnO (a) and NiO (b) and band diagram of p-NiO/n-ZnO diode(c).

Fig. 5: (a) schematic diagram, (b) Current-voltage, (c) semi-log current density – voltage and (d) $I/(dI/dV)$ vs. I characteristic curve of the n-ZnO nanorods/p-NiO heterojunctions.