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www.elsevier.com/locate/ceri

PII: S0272-8842(18)31394-4
DOI: <https://doi.org/10.1016/j.ceramint.2018.05.246>
Reference: CERI18421

To appear in: *Ceramics International*

Received date: 20 April 2018
Revised date: 28 May 2018
Accepted date: 29 May 2018

Cite this article as: Umesh T. Nakate, Gun Hee Lee, Rafiq Ahmad, Pramila Patil, Dhanaji P. Bhopate, Y.B. Hahn, Y.T. Yu and Eun-kyung Suh, Hydrothermal synthesis of p-type nanocrystalline NiO nanoplates for high response and low concentration hydrogen gas sensor application, *Ceramics International*, <https://doi.org/10.1016/j.ceramint.2018.05.246>

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Hydrothermal synthesis of p-type nanocrystalline NiO nanoplates for high response and low concentration hydrogen gas sensor application

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Abstract

High quality nanocrystalline NiO nanoplates were synthesized using surfactant and template free hydrothermal route. The gas sensing properties of NiO nanoplates were investigated. The nanoplates morphology of NiO with average thickness ~20 nm and diameter ~100 nm has been confirmed by FE-SEM and TEM. Crystalline quality of NiO has been studied using HRTEM and SAED techniques. Structural properties and elemental compositions have been analysed by XRD and energy dispersive spectrometer (EDS) respectively. The detailed investigation of structural parameters has been carried out. The optical properties of NiO were analyzed from UV-Visible and photoluminescence spectra. NiO nanoplates have good selectivity towards hydrogen (H₂) gas. The lowest H₂ response of 3 % was observed at 2 ppm, whereas 90 % response was noted for 100 ppm at optimized

temperature of 200 °C with response time 180 s. The H₂ responses as functions of different operating temperature as well as gas concentrations have been studied along with sensor stability. The hydrogen sensing mechanism was also elucidated.

Keywords: Hydrogen sensor; Nanoplates; NiO; High response; XRD; Structural analysis

1. Introduction

The hydrogen is one of the combustible gases and known as renewable, abundant, and clean energy source [1]. Considering limited natural fuel energy sources and increasing air pollution, researchers are actively working on hydrogen production and storage for clean energy source [2]. Nowadays, hydrogen gas is being widely used at various areas such as in food products, medicine, steel manufacturing, chemical industries, laboratories, [3-5]. Hydrogen is highly inflammable and may lead to major fire accidents on leakage. Hydrogen gas monitoring is extremely essential in order to prevent such fire accidents [6] and hence there is need to develop hydrogen sensors with higher sensitivity or response and low concentration detection capacity with good selectivity and stability.

Various semiconducting metal oxide materials such as ZnO, SnO₂, WO₃, Fe₂O₃, In₂O₃, CuO, CdO, TiO₂, and NiO have been studied for gas sensor application due to their advantages such as low cost, small dimension, easy operation and good compatibility with electronic processing [7-12]. Among these materials, p-type semiconducting material, e.g. NiO, has been relatively less studied, only around ~ 9.41% [13]. NiO is a wide band gap, nontoxic material having good electrical properties and chemical stability [14]. The two dimensional (2-D) nanostructures such as nanoplates offer large surface area with remarkable active sites for adsorption of gas molecules and good electron transport properties [15]. Among various synthesis methods for NiO nanostructures such as electrodeposition (ED) [16], laser deposition [17], thermal oxidation [18], sputter deposition [19], microwave-assisted chemical synthesis [20], and so on but hydrothermal synthesis method has potential to produce nanostructures with high quality materials [21-23]. NiO nanostructures such as nanowires, nanoparticles, nanoflower, nanorods, nanotubes, have been explored for gas

sensor application [24-28], however nanoplates like morphology of NiO has not been investigated for hydrogen gas sensor application as per our best of the knowledge.

In the present work, NiO nanoplates powder was synthesized via economical hydrothermal method and characterized using XRD, FESEM, EDS, TEM, PL, and UV-Visible spectroscopy. Structural parameters such as average crystallite size measured using Scherrer's formula and Williamson Hall (W-H) plot, interplanar distance (d), dislocation densities, texture coefficient (TC), micro strain, stacking fault (SF) were estimated from XRD data. Electrical properties as functions of temperature and Hall measurement for semiconducting properties of NiO were elucidated. The H₂ sensing response for NiO sensor was recorded as a function of operating temperature and gas concentration was estimated. The transient gas response and selectivity of NiO sensor were also measured. The gas sensing mechanism is discussed and sensor stability is verified.

2. Experimental:

The NiO nanoplates were synthesized via hydrothermal method. Initially, aqueous solution of 0.6 mM Nickel nitrate (Ni(NO₃)₂·6H₂O) was prepared in deionized (DI) water in one beaker whereas second solution of 1.2 mM sodium hydroxide (NaOH) was prepared in another beaker. These solutions were mixed and kept for stirring for 30 min in order to get uniform mixed solution at 600 rpm. The obtained mixed solution was transferred in Teflon coated stainless steel autoclave. The autoclave was maintained at 200 °C temperature for 10 h. The solution was washed out several times using DI water and powder product was collected after centrifugation. The obtained powder was dried in oven at 60 °C. Finally, powder was annealed at 450 °C for 1 h in air to remove impurities and to achieve good crystallinity.

Fabrication of sensor devices was carried out using drop casting method. Sensor powder material was added to ethylene glycol. The prepared solution was ultrasonicated for 10 min for uniform dispersion. The sensor material dispersed solution was drop casted using micro pipette on platinum (Pt) inter digital pattern designed in 1 cm² area on alumina substrate as shown in schematic in Fig. 1 (a). After drop casting sensor material on substrate, it was heated at 300 °C for removal of ethylene glycol and for good adhesion. The electrical contacts were made to fabricate sensor device using gold coated wires. The schematic of gas sensing testing system is shown in Fig. 1 (b). Sensing system consists of gas cylinders of air, nitrogen, and target gas, testing space in furnace, mass flow meters and Keithley electrometer. The gas response formula for sensor is defined as [29]

$$S(\%) = \frac{R_g - R_a}{R_a} \times 100 \quad 1)$$

where S is the response or sensitivity, R_a is the stabilized resistance of sensor material for 2 h in the air, and R_g is the resistance of sensor material in target gas.

3. Results and discussions:

3.1 Structural properties:

The XRD pattern of our material is shown in Fig. 2 (a) which confirms the cubic face-centered crystal structure of NiO Joint Committee on Powder diffraction Standards (JCPDS) card no. 047-1049 [30]. The sensor performance of semiconductor metal oxide device is governed by structural properties such as grain size, texture coefficient (TC), and dislocation densities [31-34]. Hence detailed structural parameters investigation of a given sensor material is necessary. The structural parameters from NiO XRD pattern are tabulated in Table 1. The Scherrer's formula has been used to determine average crystallite size from each XRD peak which has been indicated in Table 1. The average crystallite size was estimated to be ~

6.8 nm from all XRD peaks. The measured 'd' values from all diffraction peaks were higher than standard values. The obtained XRD peak positions 2θ were observed to be shifted at lower values than JCPDS data as shown in Table 1. The dislocation densities in NiO were calculated from every diffraction peak as shown in Table 1. The TC values were estimated for each XRD peaks (hkl). The TC value of greater than one indicates the preferred orientation of material growth random orientation is shown by TC value ~ 1 . The TC value of 1.26 associated with (111) plane is the highest among all which confirms the NiO growth preference along (111) plane. The deconvoluting size and micro strain induced broadening were utilized from W-H plot to calculate the average crystallite size and the strain in NiO particles. The line fit was performed on data points given in W-H plot as shown in Fig. 2 (b). The negative slope value in W-H plot reveals the compressive micro strain -0.58% in NiO particles. The average crystallite size estimated from the line intercept from W-H plot is about 6.4 nm, in close agreement with value obtained using Scherrer's formula, 6.8 nm. The stacking fault (SF) for NiO was also calculated and shown in Table 1. The observed micro strain may be attributed to the change in interplanar distance and dislocation densities in NiO crystal.

3.2 NiO nanoplates formation:

The dissociation of nickel nitrate salt ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) into nickel cations (Ni^{2+}) and nitrate anion radicals (NO_3^{2-}) with formation of grey color solution was observed when salt was added to distilled water as in Eq. 2. Similarly, transparent solution was seen after dissociation of sodium hydroxide (NaOH) to sodium cations (Na^+) and hydroxide anions (OH^-) when added to distilled water as in Eq. 3.

The nickel cation and hydroxyl anions react with each other forming very small solid particles of nickel hydroxide ($\text{Ni}(\text{OH})_2$), termed as nuclei in Eq. 4. The precipitate formed was whitish gray in colour.

The general reaction between nickel nitrate and sodium hydroxide gives rise to nickel hydroxide and sodium nitrate as in Eq. 5. The formed nickel hydroxide leads to oxidation of reactant by the thermal treatment, giving rise to nickel oxide (NiO) as in Eq 6.

In the first stage, the primary nuclei were formed uniformly in the precursor solution. After nuclei reaches a critical size, further growth starts on every nuclei in order to minimize interfacial surface free energy. The quasi equilibrium growth of nuclei to 2-D hexagonal shape nanoplates is initiated along the textured or orientation plane. The obtained product was calcined for excess hydroxyl impurity and re-crystallized. The schematics of growth mechanism have been shown in Fig. 2 (c).

3.3 Surface morphology and elemental studies:

The FESEM micro graph images with different magnifications and TEM images of obtained NiO are shown in Fig. 3 (a) – (d). The nanoplates-like morphology was confirmed by electron microscopy images. The average thickness and diameter of nanoplates structures were measured to be ~ 20 and ~ 100 nm. During the NiO annealing, the hexagonal shape of nanoplates may be transformed into circular shape due to excessive heat treatment. The high resolution transmission electron microscope (HR-TEM) image of NiO is shown in Fig. 3 (e). The crystallinity of NiO can be observed from HR-TEM that confirms nanoplates structure. The selected area electron diffraction (SAED) pattern of NiO is shown in Fig. 3 (f).

The characteristic electron annular diffraction pattern also confirms the crystal structure or phase formation of NiO [35]. The nanoplates morphology and high specific surface area predict high adsorption of target gas, which may contribute achieving high gas response of sensor.

The elemental composition was confirmed using EDS measurement. The EDS spectrum of NiO is shown in inset of Fig. 3 (d). The presence of Ni and O elements were confirmed in EDS spectrum. The atomic and weight percentage values of Ni and O elements are given in inset of Fig. 3 (d).

3.4 Optical properties:

The UV-Visible absorption spectrum for NiO was recorded and shown in Fig. 4 (a). The absorbance peak was observed in ultra violet electromagnetic region. The increasing absorbance broad shoulder of absorbance peak may be due to the particle size distribution and defects. The optical energy band gap of NiO estimated from Tauc's plot is shown in the inset of Fig. 4 (a). The Tauc's relation of absorption coefficient (α) and photon energy ($h\nu$) is given by [36]

$$\alpha = \frac{\alpha_0 (h\nu - E_g)^n}{h\nu} \quad (7)$$

where E_g is the Energy band gap, α is the absorption coefficient, and α_0 is the constant. The power factor can be determined by the type of electronic transition. For the NiO material, the 'n' has value 1/2. The energy band gap of NiO was estimated to be 3.2 eV, using Eq 7.

The photoluminescence (PL) spectrum for NiO was recorded at room temperature and shown in Fig. 4 (b). The excitation wavelength was 300 nm. A strong emission peak around

366 nm is due to the free-exciton recombination. The broadening in the emission peaks of the materials may be attributed to the size distribution of particles and defects level.

3.5 Electrical and hydrogen sensing properties:

The electrical properties were studied via Hall experiment and measuring the resistance of NiO nanoplates as a function of temperature. The Hall measurement confirms 'p type' semiconducting nature of NiO. The charge carrier concentration of NiO is $2.5 \times 10^{16} \text{ cm}^{-3}$, and the mobility $4.68 \times 10^2 \text{ cm}^2/\text{Vs}$. The resistance of NiO was measured as a function of temperature as shown in Fig. 5 (a). The NiO resistance dropped with temperature. This resistance drop may be due to the electron hole pair formation leading increased net holes for current conduction.

The hydrogen gas response of NiO sensor was measured as a function of operating temperature as shown in Fig. 5 (b). The hydrogen gas response increases with temperature up to 200°C the optimum temperature, and then decreases above it. The high hydrogen gas response for increased operating temperature may be attributed to the gain in catalytic energy which lead to enhancement in chemical sensing reaction at the sensor surface. The adsorption of gas molecules is restricted for higher operating temperature ($> 200^\circ\text{C}$) and hence less gas molecules participate in sensing reaction resulting in drop in response. The operating temperature of the sensor is determined by the type of target gas as well as on chemical composition of the oxide sensor material.

3.6 Transient gas response and selectivity study:

The transient gas response for NiO sensor was studied at different gas concentration and operating temperatures. The dynamic sensor resistance was recorded as a function of time for various hydrogen gas concentrations of 100 down to 2 ppm, at operating temperature of 200 °C as shown in Fig. 5 (c). The sensor resistance increased with the target gas exposure time and decreased due to recovery after removing target gas with pure air flush. The change in sensor resistance was smaller for low gas concentration. The dynamic hydrogen gas response of NiO sensor at different operating temperatures is shown in Fig. 5 (d). The response and recovery times decreased with increasing temperature due to increased chemical catalytic reaction at the sensor surface. The highest gas response was recorded as operating temperature of 200 °C. The selectivity study for NiO sensor is shown in Fig. 5 (e). The NiO sensor exhibits high selectivity towards hydrogen gas at 200 °C. The selectivity of sensor for any specific gas is determined by the amount of effective chemical catalytic reaction and structural as well as chemical nature of the sensor material.

3.7 Hydrogen sensing mechanism:

Metal oxide semiconductor gas sensor deals with chemical sensing reaction taken place at the interface of sensor material's surface and gas. The gas response was measured by the change in resistance of sensor material in the presence of pure air of oxidation and after the exposure of target gas in air. The change in resistance mainly depends on the amount of chemisorbed oxygen and target gas molecules on the sensor surface. The typical hydrogen gas sensing chemical reaction can be shown via following equations [29].

I) *Oxidation*, corresponding resistance R_a

II) *Reduction*, corresponding resistance R_g

The proposed gas sensing mechanism for NiO sensor has been shown schematically in Fig. 6. At first stage, oxidation takes place in pure air due to chemisorption of air oxygen creating hole-accumulation layers (HAL) at the sensor surface. The adsorbed air oxygen captures electron from the metal oxide sensor and forms reactive oxygen anion species as in Eq. 10 and as shown in Fig. 6 (a). The electric current flows via holes transport in the 'p type' semiconductor. The current conducts through HAL of the sensor. Hence the hole concentration determines current or resistance in the NiO semiconductor material. The measured sensor resistance R_a in the presence of pure air at equilibrium oxidation reaction depends on the net or total holes present at that time. At second stage, hydrogen gas molecules get adsorbed on the sensor surface leading to chemical reduction process. Electrons are released to the sensor during the reduction shown in Eq. 11 and as shown in Fig. 6 (b). These electrons combine with holes present in HAL of NiO sensor material. Hence the net or total number of holes and hence the charge concentration are reduced in the sensor material leading to the increase in resistance R_g . The change in sensor resistance before and after target gas exposure contributes to the sensor response calculated using Eq. 1.

3.8 Concentration effect and stability studies:

The measured hydrogen gas response of NiO sensor for 2-100 ppm concentration at optimized operating temperature at 200 °C is shown in Fig. 6 (c). The gas response for low hydrogen gas concentration was linear whereas it becomes non-linear for high

concentration. Different rate of gas response for different gas concentration may depend on diffusion and adsorption of target gas molecule in the testing system. The lowest hydrogen gas concentration detected was 2 ppm with 3 % response whereas 90 % gas response was noted for 100 ppm concentration at 200 °C operating temperature. The capacity of the sensor is restricted by its saturation level and limited active area of the sensor device. The stability study for NiO sensor is shown in Fig. 6 (d). The NiO sensor was found to be quite stable. The repeatability of the sensor was confirmed several times. The performance of NiO sensor for hydrogen gas sensing was compared with previously reported data and shown in Table 2. It was observed that NiO nanoplates structure sensor has better performance with low hydrogen gas detection ability.

4. Conclusions:

In summary, high quality NiO nanoplates material was prepared via easy solution processed method. The phase confirmation as well as detailed structural parameters was investigated using XRD analysis. Nanoplates like morphology having average thickness and diameter of ~ 20 nm and ~ 100 nm respectively, was confirmed using FESEM and TEM images. The Hall measurement and increased electrical conduction with temperature, confirm good semiconducting nature of NiO material. The NiO sensor has shown high response and selectivity towards hydrogen gas at operating temperature of 200 °C. The highest hydrogen response was recorded as 90 % for 100 ppm gas concentration with fast response time of 180 s. NiO nanoplates structure can be potential materials for future advanced hydrogen gas sensor.

Acknowledgements

This work was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education (NRF-2018R1A2B6002316).

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Fig. 1: a) Schematics of sensor device,
b) Schematics of gas sensor testing set up,

Fig. 2: a) XRD pattern of NiO,
b) W-H plot for NiO,
c) Schematics of NiO nanoplates synthesis and growth mechanism.

Fig. 3: a) FESEM image of NiO with 300 nm scale bar,
b) FESEM image of NiO with 100 nm scale bar,
c) TEM image of NiO with 200 nm scale bar,
d) TEM image of NiO with 100 nm scale bar, The inset shows EDS spectrum.
e) HR-TEM image of NiO with 5 nm scale bar
f) SAED pattern for NiO.

Fig. 4: a) UV-Visible absorption spectrum of NiO, The inset shows Tauc's plot.
b) PL spectrum of NiO.

Fig. 5: a) NiO sensor resistance as a function of temperature,
b) the hydrogen gas response of NiO sensor for 100 ppm concentration at different operating temperatures,
c) Transient hydrogen gas response of NiO sensor at different gas concentrations at 200 °C,
d) Transient hydrogen gas response at different operating temperatures for 100 ppm concentration,
e) Selectivity study of NiO sensor for 100 ppm concentration at 200 °C.

Fig. 6: a) and b) Schematics of hydrogen gas sensing mechanism for NiO sensor,
c) Hydrogen gas concentration effect on NiO sensor response at 200 °C,
d) Stability of NiO sensor for 100 ppm at 200 °C.

a)

b)

Table 1: Structural parameters of NiO nanoplates

Parameter	Standard values/Formula	(hkl) / 2θ	Estimated values
Crystallite size (D) (nm) Scherrer's formula	$D = \frac{K \cdot \lambda}{\beta \cdot \cos \theta}$	111 200 220 311 222	8 5 7 5 9
d – spacing (Å) JCPDS - Card no. 47-1049	2.4120 2.0890 1.4768 1.2594 1.2058	111 200 220 311 222	2.4279 2.0970 1.4825 1.2668 1.2084
Diffraction peak 2θ (degree)	37.249 43.276 62.879 75.416 79.409	111 200 220 311 222	37.01 43.12 62.64 74.94 79.25
Dislocation density (lines/m ²) X 10 ¹⁵	$\delta = 1/D^2$	111 200 220 311 222	16 40 20 40 12
Texture coefficient TC	$TC_{hkl} = \frac{I_{hkl}/I_0}{\frac{1}{N} \sum I_{hkl}/I_0}$	111 200 220 311 222	0.75 0.77 1.26 0.97 1.23
Micro strain (ϵ)	$\frac{\beta \cos \theta}{\lambda} = \frac{1}{D} + \frac{\epsilon \sin \theta}{\lambda}$		-0.60%
Stacking fault (SF)	$SF = \frac{2\pi^2}{45(3 \tan \theta)^{1/2}} \beta$	111 200 220	0.0056 0.0114 0.0073

311	0.0093
222	0.0055

Table 2: Comparison on hydrogen sensor

Material	Operating temperature	Synthesis method	Gas Response S (%)	Concentration (ppm)	Ref
NiO	200 °C	Sol-gel	63	3000	[29]
MoO ₃ -SnO ₂	240 °C	Sol-gel	10	1000	[37]
ZnO@SnO ₂	400 °C	MBE/PLD	70	500	[38]
ZnO –SnO ₂	200 °C	Chemical route	45	1000	[39]
ZnO	350 °C	Solution deposition	60	1660	[40]
SnO ₂	250 °C	Sonochemical	32	1000	[41]
WO ₃	300 °C	Self assembled	20	200	[42]
In ₂ O ₃ /graphene	250 °C	Facile synthesis tech.	9	250	[43]
NiO	200 °C	hydrothermal	90	100	This work