Materials Science in Semiconductor Processing 75 (2018) 26–30

Contents lists available at ScienceDirect

Materials Science in Semiconductor Processing

journal homepage: www.elsevier.com/locate/mssp

# Substrate temperature dependent structural orientation of EBPVD deposited NiO films and its influence on optical, electrical property

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## ARTICLE INFO

*Keywords:*
NiO
Thin films
EB-PVD
Electrical properties
Orientation

## ABSTRACT

The structural, electrical and optical property of nickel oxide thin films deposited by electron beam physical vapour deposition were investigated with respect to substrate temperature ($T_s$ = 100, 300, and 450 °C). In spite of the amorphous nature of the substrate (quartz), depending on the substrate temperature either a preferred or polycrystalline NiO growth was observed. A (200) preferential orientation resulted at 100 °C while at 300 and 450 °C the NiO films were oriented along (111) and (220) planes. The NiO films obtained at $T_s$ = 100 °C was highly transparent compared to the polycrystalline films due to the low light scattering of (200) film. The conductivity of NiO films measured at 100 °C was found to be three orders higher than the films obtained at $T_s$ = 450 °C. Thus, the orientation was found to be influencing optical and electrical properties of NiO films.

## 1. Introduction

Thin films of nickel oxide (NiO) are of great interest in a wide range of applications like electrochromic devices, smart windows and automobile mirrors [1], gas sensors [2,3], electrode material for solar cells [4], fuel cell [5], photocatalysis [6–8] and batteries [9] etc. owing to its low cost, good chemical stability with excellent structural, optical, magnetic and electrical properties. At present various techniques have been employed to fabricate NiO thin films which include sputtering [2], chemical vapour deposition [10], chemical bath deposition [11], spray pyrolysis [12], pulsed laser ablation [13] and electron beam physical vapour deposition [5] and so on. The NaCl type cubic NiO with a band gap value of 3.6–4.0 eV is a wide bandgap p-type semiconductor [6,8]. However, the orientation of NiO films in either (111) or (200) has a strong influence on the optical and electrical properties. NiO (200) surfaces are thermodynamically more stable than other crystallographic orientations due to its stoichiometric nature [14–16]. The presence of less stable mixed orientation such as (111) accelerates electrical aging and instability in conductivity in NiO films [17]. Thus, fabrication of NiO (200) is important to preserve stability and conductivity.

The preferential growth of NiO film depends on the coating technique as well as the deposition environment. Several approaches have been followed so far to prepare NiO thin films, such as pulsed laser deposition, sputtering, electrochemical method, sol-gel method *etc*. In spite of the several attempts, fabrication of highly oriented NiO (200) and its impact on the electrical property remains unexplored [2,12,13]. Ismail et al. attributed the increase in electrical resistivity of spray pyrolysis deposited NiO films to the emergence of (111) plane [18]. Fasaki et al., observed an increase in resistivity for the pulsed laser deposited NiO (111) [19]. However, Chen et al., noticed a higher resistivity in NiO (200) due to stoichiometric nature. But none of the above works managed to fabricate highly oriented NiO (200) films [20].

Electron Beam Physical Vapor Deposition (EB-PVD) possess the advantage of fabricating dense, high pure films with the flexibility to vary the orientation by tuning the deposition parameter. Our earlier work showed the influence of substrate temperature on the orientation of samarium doped ceria [21]. Here, we report the effect of substrate temperature on the growth of NiO deposited on amorphous quartz by the EB-PVD method and its effect on the structural, optical and electrical property. To the best of the author's knowledge, there is no report available so far to investigate the electrical behaviour of preferentially oriented NiO (200) film.

## 2. Experimental method

### 2.1. Material preparation

NiO nanoparticles were synthesized by a co-precipitation method using nickel nitrate hexahydrate ($Ni(NO_3)_2{\cdot}6H_2O$, Himedia) and ammonia (Merck, India) as precursors. Typically, to 200 ml solution of 0.5 M $Ni(NO_3)_2{\cdot}6H_2O$, 1 N ammonia solution was added dropwise under vigorous stirring in order to maintain the pH at 11. After stirring the solution for 6 h, the precipitate was centrifuged and washed four

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https://doi.org/10.1016/j.mssp.2017.11.013
Received 4 October 2017; Received in revised form 7 November 2017; Accepted 10 November 2017
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times with deionized water to remove any impurities. The resultant precipitate was subsequently filtered, dried at 80 °C overnight and calcined at 300 °C for 2 h. The calcined powder was uniaxially pressed into a cylindrical pellet using a hydraulic press with 5 t pressure.

### 2.2. Deposition of NiO thin films

The thin film deposition was carried out using NiO pellet (discussed above) as the target using BC-300 Vacuum box coater (M/s Hindhivac, India) on ultrasonically cleaned quartz substrates (Ant labs, 99.99%, amorphous). To assess the effect of substrate temperature on structural, optical and electrical properties, the NiO thin films were deposited at a various substrate temperature ($T_s$ = 100, 300, and 450 °C). The thickness of NiO film was maintained at 1 µm through an in situ digital thickness monitor for all the samples in order to neglect the thickness contributions to the conductivity. The base pressure was maintained at $\sim 1 \times 10^{-6}$ mbar while the deposition was carried out at a chamber pressure of $\sim 5 \times 10^{-6}$ mbar. The acceleration voltage and deposition rate was maintained constant at 5 keV and 5 Å/s, respectively. The substrates were rotated at 20 rpm to get the uniform thickness of the films and for all coatings the target-substrate distance were kept the same as 120 mm.

### 2.3. Characterization

The crystallographic phase identification of films was carried out by X-ray diffractometer (XRD, Rigaku Ultima IV) operated at 40 keV using monochromatic Cu $K_\alpha$ ($\lambda$ = 0.15418 nm) radiation with a scan rate of 2° per minute. Raman spectra were recorded in the range of 300–1500 $cm^{-1}$ at room temperature using Renishaw Laser confocal micro-Raman spectrometer (Renishaw, RM 2000) with 514 nm laser excitation. The optical absorption and reflectrance spectra of the films were recorded using UV–visible Diffused Reflectance Spectrophotometer (DRS, Varian, 5000) in the range of 200–800 nm with a resolution of 1 nm. The impact of substrate temperature on the conductivity was investigated by electrochemical impedance spectroscopy (Novocontrol Technologies, Concept 80). The in-plane conductivity measurement was carried out with two-probe configuration with the help of platinum wires. The conductivity was measured from 200 to 700 °C at a temperature interval of 50 °C in the frequency range of 1 Hz to 10 MHz by applying a bias voltage of 1 V. A soaking time of 15 min was provided at each temperature in order to achieve the thermal equilibrium before recording the conductivity data. The resistivity and conductivity values from the EIS spectra of the NiO films were determined by fitting with the analog equivalent circuit using Brick Layer model (BLM).

## 3. Result and discussion

### 3.1. XRD analysis of NiO films

XRD pattern of the NiO films deposited at different substrate temperatures ($T_s$ = 100 °C, 300 °C and 450 °C) over the amorphous quartz substrate is shown in Fig. 1. The peaks observed at 37.4°, 43.5° and 63.7° corresponds to the (111), (200) and (220) planes of the cubic rock-salt NiO structure with a space group of *fm3m* (ICDD # 04-002-0665) respectively. The XRD pattern of the NiO films shows preferentially oriented films at different substrate temperature. At lower substrate temperature ($T_s$ = 100 °C), a single narrow peak was observed at 43.5° corresponding to the growth of preferentially oriented NiO (200) plane. On increasing the substrate temperature to 300 °C and 450 °C, additional peaks were observed corresponding to pure NiO phase without any secondary or impurity phases.

The lattice parameter of bulk rock-salt structured NiO is reported to be 4.177 nm [22]. The calculated lattice parameters of the films are close to the reported value and found to be varying with the films deposited at different temperature. The estimated lattice strain values of the NiO films presented in Table 1 were calculated using Williamson-Hall equation [23],

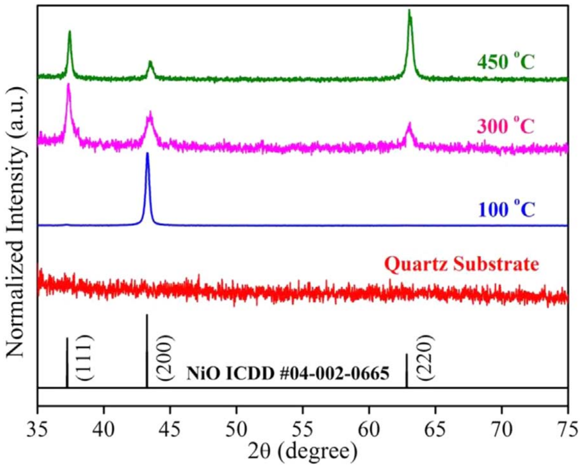

Fig. 1. XRD spectra of NiO thin films deposited at different substrate temperature ($T_s$ = 100, 300 and 450 °C).

$$\beta \cos\theta = \frac{k\lambda}{D} + 4\varepsilon \sin\theta \tag{1}$$

where $\beta$ is the full width at half maxima (FWHM), $k$ is the Scherrer's constant ($k$ = 0.91), $\varepsilon$ is the lattice strain, $\theta$ is the Bragg's angle, $\lambda$ is the wavelength of X-ray (0.14517 nm) and $D$ is the crystallite size (nm). The lattice strain values were decreasing on increasing the substrate temperature from 300 to 450 °C. Strain values could not be calculated $T_s$ = 100 °C films using Williamson-Hall method due to the presence of a single peak. From the XRD pattern, a single peak corresponding to (200) plane at $T_s$ = 100 °C was observed. On the other hand, the peaks corresponding to (111) and (220) planes dominate the spectrum at 300 °C and 450 °C, respectively, indicating the preferential orientation of NiO crystallographic planes at different substrate temperatures. The degree of preferential orientation of different crystalline planes can be quantified by calculating the texture co-efficient (TC) using Harris equation [3],

$$TC(hkl) = \frac{I(hkl)/I_o(hkl)}{\frac{1}{N}\sum (I(hkl)/I_o(hkl))} \tag{2}$$

where $I(hkl)$ and $I_o(hkl)$ denote the integrated intensity of thin film XRD and the ICDD intensity of the corresponding planes, respectively, $N$ is the number of reflections considered in the calculation.

Fig. 2. shows the texture coefficient (TC) plot of NiO films deposited at various substrate temperature. A TC value less than one indicates the crystal orientation is random and a value of one or more than one represents the preferential orientation towards the particular (*hkl*) plane [21]. When $T_s$ = 100 °C, the calculated TC value of 2.9 confirms the preferential orientation along (200) plane. However, TC value for (200) became less than one on increasing the $T_s$ to 300 and 450 °C with the increase in (111) and (220), respectively. The TC value of (111) plane decreased when the substrate temperature increased similar to the TC value of (200) plane. Conversely, the TC values of (220) plane increased on increasing the substrate temperature from 300 to 450 °C.

EBPVD technique is an atom-by-atom evaporation process. The growth of the preferentially oriented thin films by EBPVD technique can be affected by many parameters like chamber pressure, E-beam gun power, substrate temperature, substrate orientation, deposition rate, crystallinity of the substrate [24] etc., In the present work, all the samples show preferential orientation along different planes at different substrate temperature. As the deposition rate, pressure and target material are the same, the crystallite size and phase formation now depend

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