Applied Surface Science xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Applied Surface Science

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

Structural, optical and electrical properties of sputtered NiO thin films for gas detection

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ARTICLE INFO

Article history:
Received 29 February 2016
Received in revised form 4 May 2016
Accepted 5 May 2016
Available online xxx

Keywords:
Nickel oxide
Structural evolution
Optical parameters
Activation energy

ABSTRACT

This study systematically investigates the nanostructural evolution, optical and electrical properties of sputtered nickel oxide films prepared at room temperature. The films with 50 and 100 nm thicknesses were deposited by DC reactive magnetron sputtering. After annealing at 500 °C, the films had a polycrystalline (fcc) NiO phase structure. The size of crystallites was from 8 to 28 nm for NiO films with 50 nm thickness and from 7 to 26 nm for those with 100 nm thickness. The grains in both of the annealed NiO thin films exhibited polyhedral morphology with regular and flat edges. It was observed that annealed NiO films were highly transparent, about 70–90% in the spectral range from 500 to 900 nm. A double Schottky barrier was found between two adjacent grains which affects the conductivity of NiO thin films on exposing to different gas atmospheres. NiO thin films with 50 nm thickness exhibit bigger differences of the conductivity to hydrogen in comparison with NiO films with 100 nm thickness in the temperature range from 100 to 250 °C.

1. Introduction

Nickel oxide (NiO) is one of the versatile and technologically important p-type semiconducting materials with the band gap energy in the range of 3.6–4 eV [1–3]. It is an attractive material, well-known for its excellent optical and electrical properties. Recently, NiO has been investigated for applications such as catalyst in fuel cells [4], electrode materials for lithium ion batteries [5], electrochromic devices [6], supercapacitors [7], hole transporting layer in solar cells [8] and also as a functional layer in metal oxide gas sensors due to its chemical stability and non-toxicity [9–19]. These thin films have been prepared by several methods such as spray pyrolysis [20], high temperature oxidation [21], sol-gel process [11], pulsed laser deposition [22], electrochemical deposition [23], hydrothermal method [16,19] and reactive magnetron sputtering [2,3,12–15]. The selection of the deposition method facilitates the control of particle properties in nanometer scale, allows exact control over the critical process parameters and contributes greatly to the reproducibility of the prepared nanostructured films. In addition to standard crystalline structures formed by grains, NiO can be synthesized into novel progressive structures such as nanowires and nanofibres [9,16,18], nanotubes [24], hollow hemispheres [25], nanoflowers [26], cactus-like structures [19] and nanosheets [27].

Nanostructured thin films have often more attractive properties than routinely prepared materials. They consist of very small particle sizes, have large exposed surface areas and posses high surface energies. It is well-known that gas sensing properties of metal oxides are more or less related to the surface morphology, their high porosity and the nanostructure with small particles. Based on study [11] of NiO films prepared by sol-gel method it was observed that the grain sizes were in the range from 10 to 22 nm. In addition, the authors found that their NiO sensors can operate at 175 °C and they are able to detect hydrogen with concentration under 3000 ppm. In general, there is an effort of scientists to fabricate gas sensors with high sensitivity, repeatability, good selectivity towards different gasses and operating at relatively low temperatures under 200 °C. It has been found that the thickness of NiO thin films is an important parameter which influences the structural, electrical, optical and the gas sensing properties [2,3,11,12,14,15,28,29]. Steinbach et al. [12] reported that sputtered NiO films with a thickness from 30 to 130 nm recorded the gas response in the range from 1 to 170 for minimal hydrogen concentration of 5000 ppm at the operational temperature higher than 400 °C.

Only few studies [2,28,29] are focused on the influence of thickness on the structural, optical and electrical properties of NiO thin

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http://dx.doi.org/10.1016/j.apsusc.2016.05.028
0169-4332/

Please cite this article in press as: M. Predanocy, et al., Structural, optical and electrical properties of sputtered NiO thin films for gas detection, Appl. Surf. Sci. (2016), http://dx.doi.org/10.1016/j.apsusc.2016.05.028

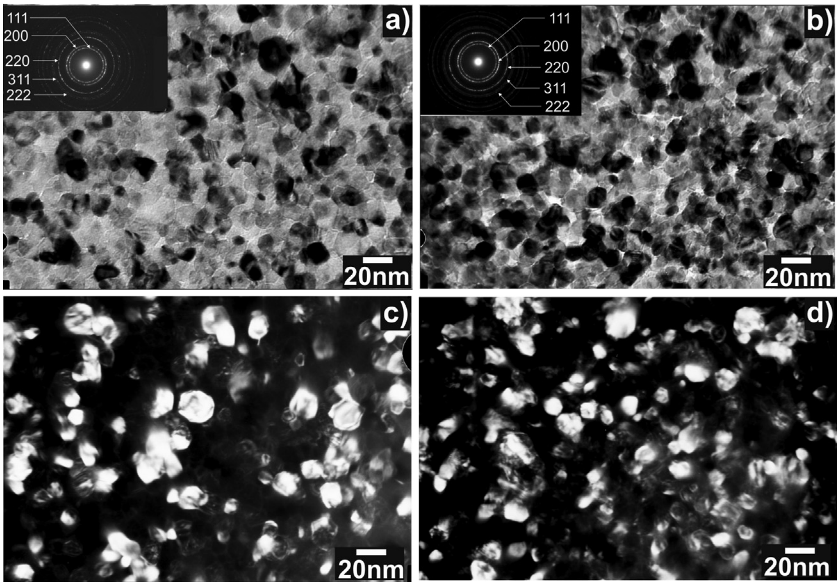

Fig. 1. Bright field (a,b) and dark field (c,d) TEM micrographs with the relevant SAED patterns of 50 (a,c) and 100 nm (b,d) of annealed NiO films at magnification of 250k×.

films prepared by DC reactive magnetron sputtering at constant deposition parameters. In our study, detailed nanostructural and morphological evolution of NiO parameters such as the grain size distribution, the orientation of crystal planes, structure phases, and surface morphology are presented. Electrical and optical properties of NiO films prepared with two different thicknesses were systematically investigated. For better understanding of NiO gas sensing behaviour a correlation of these properties with the film thickness of sputtered NiO is discussed as well.

2. Experimental procedure

Nanocrystalline nickel oxide films were deposited by DC reactive magnetron sputtering from a Ni target (4 in. in diameter, 99.99% pure) in a mixture of oxygen and argon at room temperature. A sputtering power of 600 W was used. The relative partial pressure of oxygen in the reactive mixture O_2-Ar was 30%. The distance between the substrate and the target was approximately 75 mm. The sputtering vacuum chamber was evacuated to a pressure bellow 10^{-4} Pa before starting deposition. The total working sputtering gas pressure was kept at 0.5 Pa and adjusted by a piezoceramic valve. Details of these sputtering deposition conditions had been described elsewhere [30]. The film thicknesses measured by Talystep were 50 and 100 nm for all examined samples. The two thicknesses of the deposited NiO films were achieved only time duration of sputtering process. The NiO thin films were prepared on an unheated alumina substrate, KCl and glass – corning 1737 substrate. In order to stabilize the properties of NiO thin films, all samples were annealed in a furnace at 500 °C in nitrogen atmosphere for 2 h.

The structural features of the films prepared on KCl substrate were investigated by means of a JEOL JEM 2000 FX transmission electron microscope (TEM) operating at accelerating voltage 160 kV. Selected area electron diffraction (SAED) patterns were recorded together with bright and dark images of the film structure. Detailed study of crystallites was performed by the high resolution TEM (HRTEM) device Philips CM 300. The surface morphology of annealed NiO thin films was examined using secondary electrons in the scanning electron microscope (SEM) JEOL FESEM 7600F.

Both electrical and optical properties of NiO films were investigated on glass – corning 1737 substrates. The electrical properties of the NiO films were examined by Hall measurements in Van der Pauw geometry using the source meter unit Agilent B2902A and the multimeter Agilent 34410A. The Hall voltage developed in the films was measured by applying a magnetic field of 0.5 T and used for determination of the Hall mobility and the carrier concentration. The values of optical transmittance of NiO films were measured in the wavelength range 300–900 nm using spectrometer OceanOptics. The temperature variation of conductance prepared NiO films was measured in the special vacuum chamber PLV-50 fy CascadeMicrotech under measured gasses in the temperature range from 25 to 250 °C. The gas sensing structures prepared on alumina substrate contained interdigitated Pt electrodes and a NiO sensitive film. The mass flow meters and the controllers with a nominal flow of 25 and 1000 sccm were used to set the nominal concentration of the tested gasses in the vacuum chamber PLV-50.

3. Results and discussion

3.1. Structural and morphological analyses

In order to confirm the NiO phase structure and to study the degree of crystallization of the films, SAED and HRTEM observations were carried out. Identification of NiO films was based on the observed SAED patterns (inset in Fig. 1a and b) recorded from annealed films consisting of the dotted rings of different intensity. The measured lattice spacings are shown in Table 1. A comparison can be made with the tabulated *d*-spacing for the cubic NiO phase given by PDF Number 4-835. It provides a further evidence for the formation of this oxide. Table 1 demonstrates good correlation between the examined samples. It is seen that the measured *d*-spacings for both NiO thin films show lower values than expected. We suppose that this fact indicates the stress in the volume of the thin film material and the presence of small defects. The SAED patterns recorded from both of the annealed NiO films consisted of spots creating continuous rings indicating a polycrystalline nature of the film with high crystallinity of individual grains for cubic NiO. The texture of the prepared NiO films mainly depends on oxygen content, deposition temperature and post-annealing process [31]. The SAED patterns shown in Fig. 1a and b does not imply the presence of a texture in the two observed films. The values of intensity distribution in SAED patterns of NiO films under the same measuring conditions are also compared in Table 1. Unlike in 100 nm thick

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