Thin Solid Films 583 (2015) 233–238

Contents lists available at ScienceDirect

Thin Solid Films

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

Tailoring the textured surface of porous nanostructured NiO thin films for the detection of pollutant gases

R. Kumar [a,b,*], C. Baratto [a,b], G. Faglia [a,b], G. Sberveglieri [a,b], E. Bontempi [c], L. Borgese [c]

[a] *CNR-INO SENSOR Lab., Via Branze 35, 25133 Brescia, Italy*
[b] *University of Brescia, Dept. of Information Engineering, Via Valotti, 9, 25133 Brescia, Italy*
[c] *INSTM and Chemistry for Technologies Laboratory, University of Brescia, Department of Mechanical and Industrial Engineering, Via Branze, 38, 25133 Brescia, Italy*

ARTICLE INFO

Article history:
Received 20 October 2014
Received in revised form 31 March 2015
Accepted 1 April 2015
Available online 10 April 2015

Keywords:
Gas sensor
Nickel oxide
p-Type semiconductor
Micro-Raman spectroscopy
Sensing response

ABSTRACT

In the present article, an experimental approach to detect pollutant gases in presence of humidity was applied for gas sensors based on p-type NiO thin films. NiO thin films were deposited by radio frequency magnetron sputtering in inert atmosphere using a NiO target. Thin films were investigated by scanning electron microscopy to observe their surface morphology. Crystal structure and vibrational study were investigated by X-ray diffraction and micro-Raman spectroscopy, respectively. It was observed that deposition temperature played a crucial role in the structural and surface morphology of NiO thin films. Sensing response of the nanostructured thin films to reducing and oxidizing gas was studied as a function of gas concentration and operating temperature. A double digit (12.3) response was observed towards ozone at 200 °C, while maximum response to ethanol and acetone was recorded at 400 °C. A correlation was established between sensing response and crystalline dimension for ozone sensing. The result showed that NiO thin films can be used as p-type metal oxide material for the fabrication of solid state gas sensors to detect low concentrations of ozone (70 ppb).

1. Introduction

After the introduction of first generation conductometric gas sensors based on thick film by Taguchi in 1960s [1], thin film metal oxide (MOX) gas sensors [2] are reported in literature. They are small size, inexpensive to tailor and needs low power consumption [3]. Different techniques are reported in literature to deposit metal oxide thin films; among them magnetron sputtering is a well known process and can be used at large scale sensor device production. NiO is an interesting p-type material that can be deposited by magnetron sputtering technique. NiO is an antiferromagnetic material with a Nèel temperature of 523 K. It has been utilized as electrode in solar cell [4,5], electrochromic material [6] and conductometric gas sensor [7]. NiO can be used for solar thermal absorber, organic light emitting diodes, catalyst for oxygen evolution, and p–n junction electrodes in dye sensitized solar cells [8]. NiO exists in rhombohedral and cubic phase [9], and is a naturally p-type binary oxide material due to Ni vacancy [10]. NiO can also be used as transparent conducting oxide by changing the preparation conditions in order to decrease the resistivity, while increasing its transmittance [11].

The aim of this work is to prepare p-type gas sensor based on NiO thin films. Different techniques such as ion assisted electron beam evaporation [12], sol–gel [13], and sputtering [14] have been reported in the literature for the preparation of NiO thin films for gas sensing application. It has been already established that NiO can sense reducing (NH_3, CH_4, and H_2 [13,15]) and oxidizing gases NO_2 [14]. However, the catalytic activity of NiO towards ozone has been predicted by theoretical work [16], and there is no report available on the sensing properties of NiO thin films towards ozone.

In this work, we investigated different deposition conditions to tailor the NiO thin films with porous nanostructured morphology using radio frequency (RF) magnetron sputtering technique. Scanning electron microscopy (SEM), X-ray diffraction (XRD), and micro-Raman spectroscopy techniques were applied to characterize the thin films. The functional characterization as gas sensors was performed towards ozone and other interfering gases (CO, ethanol, and acetone) at different working temperatures. The porous thin films obtained have a peculiar morphology with tetrahedral shaped grains. The use of such type of morphology for gas sensing application has not been reported in the literature. A correlation of microstructure with sensing properties of the thin films is discussed as well.

2. Experimental details

NiO thin films were deposited by RF magnetron sputtering from a NiO target (99.99% pure, 4″ size from CERAC). The distance between substrate and the target was about 8 cm inside the magnetron sputtering chamber. Substrate temperature was varied from room temperature (RT), 100 °C, 200 °C and 400 °C in inert atmosphere (Ar) at 100 W powers. Thin

---

* Corresponding author at: University of Brescia, Dept. of Information Engineering, Via Valotti 9, 25133 Brescia, Italy.
E-mail address: raj.kumar@ing.unibs.it (R. Kumar).

http://dx.doi.org/10.1016/j.tsf.2015.04.004
0040-6090/© 2015 Published by Elsevier B.V.

films were deposited on glass substrates for UV–Vis analysis and on Si substrates for SEM and XRD analysis. Sensing films were deposited on alumina (2 mm × 2 mm) substrates for gas sensing tests. Prior to deposition the substrates were carefully washed in acetone, dried with synthetic air and kept at the desired temperatures (RT — 400 °C) in vacuum (0.1 Pa) for 30 min. Before deposition 10 min pre-sputtering was also applied to eliminate surface contaminants. The thickness of the layers measured after deposition by a step profiler (Alpha step KLA TENCOR) varied from 240 nm to 550 nm as a function of deposition time and deposition temperature.

Transmittance spectra (300–900 nm) of thin films deposited on glass substrates were collected at RT by a PG Instruments T80 spectrophotometer.

For structural and microstructural characterization XRD experiments in Glazing Incidence (GIXRD) conditions were made. GIXRD was performed by means of a Bruker 'D8 Advance' diffractometer equipped with a Göbel mirror and a Cu K_α radiation tube ($\lambda = 0.154$ nm) (Chem4Tech, Brescia, Italy). The incidence angle was fixed at 0.5° to be more sensitive to the films.

Surface morphology was investigated by Field Emission (FE) SEM (LEO 1525). During SEM measurements the samples were observed in secondary-electron imaging mode by operating the microscope at 10 kV accelerating voltage.

Raman analysis was carried out with a modular micro-Raman confocal system from Horiba equipped with single monochromator (ihr320mst3) and Peltier cooled CCD camera. He:Cd laser at 442 nm was used as excitation source, along with interference filters on laser lines and edge filters on the signal. The samples were mounted on a motor controlled X–Y stage. The Raman spectra were collected by the instrument operating with 1800 L/mm grating and 100× objectives.

Fig. 1 shows the top view SEM image of sensing device on alumina substrate with platinum (Pt) electrode and Pt heater arrangement around the sensing film. Pt electrodes and heater were deposited by RF magnetron sputtering. The heater simultaneously serves as a Pt film thermometer to measure the sensor temperature. Au wires were used to make the connection on the transistor outline-5 pin (TO-5) case. The thin films were aged on the TO-5 case by heating the sensors at 500 °C in ambient air for two weeks prior to measurements.

Sensing tests were performed in a stainless steel test chamber (1 L) at an ambient temperature of 20 °C and at atmospheric pressure, using a constant flux (300 cm^3/min) with 50% relative humidity (RH). A constant bias (1 V direct-current) was applied to the sensing film and the electrical current was measured by a picoammeter (Keithley model 486). The system used to dynamically reproduce environmental conditions in a controlled and repeatable way is based on volumetric mixing through mass flow controllers and certified bottles. The ozonized air was produced by a thermo-stated UV lamp discharge (ANSYCO), here O_3 is generated by oxidizing O_2 molecules of dry air flow exposed to a calibrated lamp. For p-type sensors, relative response was calculated as response = $(G_{air} - G_{gas}) / G_{gas}$ for reducing gases, and as response = $(G_{gas} - G_{air}) / G_{air}$ for oxidizing gases. Response (recovery) times were calculated as the time needed to reach 90% (70%) steady state value in gas (air).

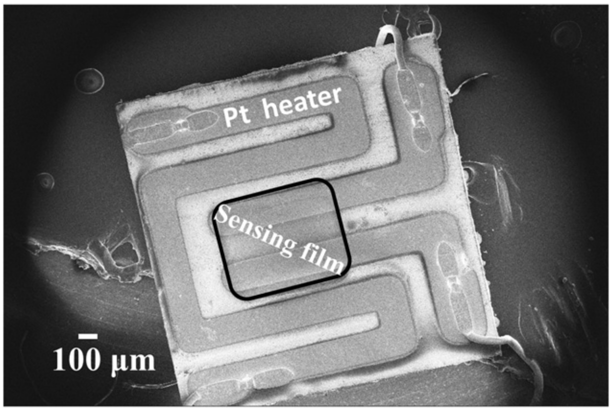

Fig. 1. SEM image shows the sensing film and the interdigitated contacts (Pt heater).

3. Results and discussion

3.1. SEM microscopy

Fig. 2 reports the surface morphology of thin films as deposition temperatures increased. Nanostructured thin films with textured surface morphology were observed by FE SEM. Triangular shaped features observed at RT (Fig. 2(a)) aggregates to form pyramidal shaped grains at 100 °C (Fig. 2(b)). Fig. 2(a–b) insets present higher magnification images. The shape of the grains remains the same from 100 °C up to 400 °C. At 400 °C (Fig. 2(d)) the dimensions of the pyramids increased with respect to what we observed at 100 °C and 200 °C. Randomly scattered cluster of nano flowers were also observed on the surface of all thin films.

3.2. X-ray diffraction analysis

Fig. 3 shows GIXRD patterns collected for all samples deposited on Si substrates. The thin film deposited at room temperature shows only a sharp peak, corresponding to (111) reflection of NiO cubic phase (JCPDF card no. 471049) in the range of measurement. Because other expected peaks of the NiO phase (at about 43.3° in 2Theta) cannot be detected for this sample, it can be concluded that the film is oriented. Being a change in deposition temperature, the (200) peak appears in the patterns. The (200) reflection which is expected to be more intense peak of NiO cubic phase increased with the increasing of the deposition temperature [17,11]. This can be attributed to a gradual decrease in the preferred orientation of the samples. Despite that the change in NiO thin film microstructure (in particular the preferred orientation effect) is generally due to the oxygen amount [18,19] in the deposition chamber, this behavior is coherent with results already reported in literature about the preferred orientation growth of NiO thin films deposited by RF magnetron sputtering [20,21].

From XRD patterns, the average grain sizes were determined using Scherrer's formula [22] applied on (111) reflection. The obtained values reported in Fig. 3 shows that thin films are nanocrystalline. At RT the crystalline dimensions was 42 nm then decreased to a minimum of 38 nm at 200 °C and then increased again.

The crystalline dimensions (Fig. 3) can be compared with the mean dimensions of the grains observed by SEM for the films deposited at RT, 100 °C, and 200 °C (Fig. 2). In the case of thin films deposited at 400 °C the grains observed by SEM are probably polycrystalline.

3.3. UV–Vis

NiO thin films were investigated by UV–Vis spectrophotometer to find the transmittance spectrum and energy band gap. Fig. 4(a) reports average transmittance data of thin films calculated in the range of 400–700 nm. Thin films are highly transparent. Average transmittance is higher than 80% at 100 °C and 200 °C while it decreases at RT and 400 °C deposition temperatures. The transmittance spectra are reported in the inset of Fig. 4(a).

We calculated the energy band gap (E_g) of NiO thin films by extrapolating the straight-line portion of $(\alpha h\nu)^n$ to the energy ($h\nu$) axis. In this plot, the intercept on energy axis gives the value of energy band gap (direct band gap n = 2). Where α = absorption coefficient = 1/d log (1 / ($T_{normalized}$)), d = thickness of thin film, T = normalized transmittance.

Fig. 4(b) shows the energy band gap values as a function of deposition temperatures. The inset figure shows the energy band gap diagram.