Hydrogen gas sensors based on PLD grown NiO thin film structures

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NiO thin films were grown by pulsed laser deposition on (100)Si substrates at 200 °C temperature. The effect of the O2 pressure during the deposition process on the morphological, electrical and sensing properties of the films has been investigate. AFM images showed that the surface morphology of NiO films can be modified by the oxygen pressure during deposition. Electrical measurements showed that the well-known native p-type conductivity exhibits a conversion from p-type to n-type when the O2 pressure is reduced. Resistance responses of NiO-thin films towards hydrogen (H2) flow in air ambient have been measured. NiO thin film p–n homojunctions were then fabricated to investigate the electrical properties of such structures. The p–n homojunctions exhibited the distinct rectifying current–voltage (I–V) characteristics.

1 Introduction Nowadays the development of solid-state gas sensors for the detection of inflammable and toxic gases such as hydrogen, carbon monoxide, etc. is a major concern. H2 especially, is a renewable, abundant, efficient energy source, which provides zero emissions [1]. In the near future it could be used as a city gas or to power cars in the same way as natural gas is used. As H2 has a lower explosion limit (LEL) at 40000 ppm [1], a device which detects its presence at lower concentrations becomes indispensable.

A promising approach in the field of solid-state sensing devices is to use electrochemical gas sensors based on semiconducting metal oxides (MO), fabricated by using novel gas sensing materials. Gas sensors based on n-type MO semiconductors such as ZnO, SnO2, In2O3 have been widely investigated as sensing materials for the detection of toxic gases. On the contrary, p-type MO semiconductors have not yet been extensively studied for gas sensing applications.

The sensing properties of MO sensors can be enhanced by adopting methods like surface modifications, developing p–n homo- or hetero-junctions [2–4]. The hetero-junction sensors reported are mainly based on the interface properties between the oxides [4, 5]. Nevertheless, reports on homo-junction sensors based on semiconducting MO are rather rare.

Nickel oxide (NiO) is considered to be a model p-type semiconductor with a wide band-gap energy ranging from 3.6 eV to 4.0 eV [6, 7]. It has an excellent chemical stability as well as good optical, electrical and magnetic properties. It has been used as p-type transparent film [6, 8], in electro-chromic display devices [9–11] and recently it proved to be a promising functional material for applications in resistive-type gas sensors [1, 12–14].

Thin NiO films have been fabricated by various physical and chemical vapour deposition techniques, including spray pyrolysis [15–17], sol–gel process [18], reactive sputtering [19–21] and pulsed laser deposition [22, 23]. The preparation method and the deposition mode are fundamental in determining the microstructure and consequently the gas sensing properties of MO thin films, but the effective dependence of the process parameters on the film properties is not yet well demonstrated.

In this work, we investigated the influence of O2 pressure on the properties of undoped NiO thin films, grown by pulsed laser deposition (PLD) on Si substrates at 200 °C.
The conductivity type and the electrical properties of the high quality NiO thin films were controlled by changing the pressure of the reactive O$_2$ gas during film growth. The surface morphology and roughness of the films were observed by an AFM operating in air. The response of these NiO films towards H$_2$ has been demonstrated at operating temperatures in the 80–125 °C range. Finally, the fabrication of p-NiO/n-NiO homojunction structures as potential gas sensors has been achieved within a simple deposition cycle for the first time.

2 Experimental

Undoped NiO films were grown by PLD on Si substrates in a stainless steel vacuum chamber. Prior to each irradiation the vacuum chamber was evacuated down to a residual pressure of $7 \times 10^{-4}$ Pa. A Ni foil (purity 99.999%) was used as target. To avoid fast drilling, the target was placed on a movable vacuum-compatible computer-controlled XY translator.

The NiO monolayer films were deposited by using a Quantel Nd:YAG laser ($\lambda = 355$ nm, $\tau_p = 10$ ns) at a repetition rate of 10 Hz, with an estimated fluence of 2–4 J/cm$^2$. The laser beam was focused on the target with an incident angle of about 45° relative to the normal of the target surface. The (100)Si substrates were positioned at 50 mm downstream. All films were grown at 200 °C temperature and under O$_2$ pressures ranging from 5 Pa to 50 Pa. The deposition time was set at 90 min.

For the growth of the double-layer NiO structures (p-NiO/n-NiO), a Lumonics Mo. TE-861T excimer laser ($\lambda = 248$ nm, $\tau_p = 10$ ns) was used at a repetition rate of 10 Hz, and a fluence of 2–4 J/cm$^2$. The double-layer NiO structures were grown on both p-type (111)Si ($\rho = 736$ Ω cm) and n-type (111)Si ($\rho = 5.47$ Ω cm) substrates. First the p-NiO layer for 120 min was deposited on the substrate, followed by the growth of the n-NiO layer for approximately 60 min.

The effect of the deposition parameters on the electrical and sensing properties of the grown NiO films was investigated: the electrical resistivity of the samples was measured using the Van der Pauw technique, while the type of conductivity and the carrier concentration were obtained by Hall voltage ($V_H$) measurements in a magnetic field of 0.7 T. For the determination of the NiO film thickness, reflectance spectra were recorded by a Perkin–Elmer $\lambda$19 spectrometer. Thickness values ranging from 100 nm to 175 nm were estimated as proposed by Manifacier et al. [24]. Surface morphology was studied by atomic force microscopy (AFM) using a Veeco CP-II digital instrument in contact mode under normal air conditions.

Dynamic sensor response measurements were performed against H$_2$ in air flow at working temperatures between 25 °C and 125 °C in a stainless steel tube set-up. The sample holder can be resistively heated up to 400 °C with an accuracy of ±1 °C by an ITC-502 (Oxford Instruments) temperature controller. A platinum resistor measures the temperature and two mechanically-held point contacts measure the film resistance. Tests were made against 30000 ppm H$_2$ mixed with air before reaching the tube inlet. The gas flow was controlled by two calibrated flowmeters and fed into an injection point located below the sample holder. After introducing the H$_2$ gas into the tube, the film resistance versus time was recorded by a digital multimeter (Agilent 34401A) for various operating temperatures.

![Figure 1](online colour at: www.pss-a.com) AFM 3D images of two NiO thin films deposited on (100)Si substrate at 200 °C with O$_2$ pressures of a) 5 Pa and b) 50 Pa, respectively.
Results and discussion

3.1 Thin film surface characterization

Typical AFM images of the NiO film surface deposited on silicon substrates are shown in Fig. 1. The quantitative analysis of the roughness deduced from the AFM images, shows that the roughness depends on the pressure of the oxygen ambient during the deposition. The NiO film grown under 5 Pa O\(_2\) pressure showed a smoother surface with small grains and a surface roughness of 0.70 nm. On the contrary, the film surface of the NiO film deposited under 50 Pa O\(_2\) showed that the grains create relatively larger crystallites and the roughness value increased to 2.93 nm.

3.2 Electrical properties and gas sensing results of NiO thin films

The electrical properties of nickel oxide films prepared by PLD were significantly depending on the O\(_2\) pressure inside the chamber during growth. The conductivity type of the NiO thin films was determined by Hall coefficient (\(R_{H}\)) measurements at room temperature. The carrier concentration (\(n_{H}\) or \(p_{H}\)) and the Hall mobility (\(\mu_{H}\)) were obtained from the combined Hall coefficient and electrical resistivity (\(\rho\)) measurements using the well-known equations:

\[
\frac{1}{\rho} = n e \mu + \frac{1}{\rho_{H}},
\]

where \(\mu\) is the mobility and \(e\) is the electronic charge.

The carrier concentration is given by the relation \(n = r n_{H}\), where \(r\) (scattering factor) is usually assumed to be 1. Thin films grown in higher O\(_2\) pressure (>30 Pa) exhibited p-type conductivity, as expected. When the O\(_2\) pressure during the deposition is kept under 30 Pa, NiO films exhibited n-type conductivity (Table 1).

The conduction mechanism of undoped NiO film is strongly related to the nickel vacancies and interstitial oxygen existing in the microstructure [25]. The electrical properties of NiO films are connected therefore to their microstructure and composition and, consequently, are directly related to the deposition conditions [19, 20, 26].

Figure 2 shows the influence of the ambient O\(_2\) partial pressure on the conduction type of the undoped NiO films.

The relative response (sensitivity) against gas flow is determined by the formula:

\[
S_{R} = \frac{R_{g} - R_{a}}{R_{a}},
\]

where \(R_{g}\) is the film resistance in air atmosphere and \(R_{a}\) in the presence of the H\(_2\) gas. Gas sensitivity is strongly related with adsorption/desorption processes occurring at the gas-surface interface. It has been shown that for effective operation of chemical sensors, the gas-sensing materials should have a specific relation between adsorption/desorption parameters for oxygen and the detecting gas [27–29].

When the H\(_2\) molecules come in contact with the surface of a thin NiO film, they react with the adsorbed oxygen (O\(_2\) or O\(_x\)) and water molecules evaporate. The previously localized electrons are injected back into the film bulk and induce a conductivity change of the oxide. In the case of a p-type semiconductor, the resistivity of the sensor increases, as a result of the recombinant of the injected electrons with the holes (majority carriers) in the valence band. On the contrary, for a n-type semiconductor the resistance decreases when the sensor comes in contact with a reducing gas such as H\(_2\) [30].

The recording of the dynamic response of the resistance against H\(_2\) (30000 ppm) in air ambience of two undoped NiO thin films, deposited at \(T = 200^\circ\text{C}\), is shown in Fig. 3(a) and (b). The difference in behaviour of the two sensors is due to the different values of O\(_2\) pressure during their growth. In the first case, the NiO thin film was grown under low O\(_2\) pressure (5 Pa) and it exhibited a decrease in resistance (Fig. 3(a)) when exposed to a reducing gas. This suggests that the metal-oxide layer behaved like a n-type semiconductor, in agreement with the electrical measurements above. Moreover, the H\(_2\) sensing properties of the NiO thin film were strongly depending on the working temperature. In particular, the response time decreased from 20 min to 10 min and the recovery time reduced from 17 min to 9 min, when the working temperature increased. Probably the increase of the working temperature accelerates the adsorption/desorption processes on the surface of NiO films.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value for 5 Pa</th>
<th>Value for 10 Pa</th>
<th>Value for 20 Pa</th>
<th>Value for 30 Pa</th>
<th>Value for 50 Pa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickness (nm)</td>
<td>174</td>
<td>144</td>
<td>114</td>
<td>100</td>
<td>100</td>
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<tr>
<td>Surface roughness (nm)</td>
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<td>0.87</td>
<td>0.97</td>
<td>1.54</td>
<td>2.93</td>
</tr>
<tr>
<td>(\rho) ((\Omega\ cm))</td>
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<td>1.10</td>
<td>0.73</td>
<td>0.30</td>
<td>1.15</td>
</tr>
<tr>
<td>Dominant carrier type</td>
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<td>n</td>
<td>n</td>
<td>p</td>
</tr>
<tr>
<td>(p_{H}) or (n_{H}) ((cm^3))</td>
<td>(2.5 \times 10^{15})</td>
<td>(1.1 \times 10^{16})</td>
<td>(2.6 \times 10^{17})</td>
<td>(2.5 \times 10^{16})</td>
<td>(9.7 \times 10^{16})</td>
</tr>
</tbody>
</table>

Table 1 Properties of undoped NiO thin films grown on (100)Si substrate.
the NiO thin film. For this reason the maximum sensitivity of the NiO film increased from 12% to 14% with the increase of the working temperature.

In the second case, the NiO thin film was grown under higher O\textsubscript{2} pressure (50 Pa) and exhibited an increase in resistance (Fig. 3(b)) when exposed in a reducing environment. This is a typical behaviour of p-type semiconductor [31]. The maximum sensitivity of the sensor is about 76% at working temperature of 125 °C with response and recovery time of about 15 min and 10 min respectively. At the working temperature of 80 °C the maximum sensitivity of the sensor found to be around 10% with response and recovery time of 12 min and 2 min respectively. The sensitivities appear to be closely related to surface roughness as it has been measured with AFM: the sensitivity increases with the increase of the surface roughness, because the number of the active adsorption sites for oxygen or hydrogen molecules on the surface is also increased [32].

3.3 Study of the p-NiO/n-NiO structures Rectifying log \( I \)–\( V \) characteristics were recorded with a forward threshold voltage of about 0.8 Volts. Figure 4a shows the log \( I \) (current density) versus \( V \) plot, obtained at room temperature with the contact region exposed to air ambience for the p-NiO/n-NiO junction grown on a p-type Si substrate. The ideality factor of the diode was found to be ~15. Figure 4b shows the log \( I \) versus \( V \) characteristic obtained at room temperature with the contact region exposed to air ambience for the p-NiO/n-NiO junction deposited on n-type Si substrate. The ideality factor of the diode was found to be ~13.

4 Conclusion NiO thin films were grown on (100)Si substrates under various O\textsubscript{2} pressures by PLD. The O\textsubscript{2} pressure variation was shown to strongly affect the conductivity type of the NiO thin films. Very low O\textsubscript{2} pressure during the growth of undoped NiO thin films enhanced the generation of large electron populations, inverting the well-known p-type native character of NiO films and resulting in n-type conductivity.

In addition to the electrical measurements, NiO thin films have been tested as potential H\textsubscript{2} sensors. The dynamic response measurements against 30000 ppm H\textsubscript{2} in air flow confirmed the conversion of the conduction type, since in n-type NiO films the resistance decreased when exposed to H\textsubscript{2} and in p-type NiO films increased. Moreover, the sensitivity of NiO gas sensors is strongly depending on the grain size and surface morphology of the oxide.
layer, since these parameters influence the effective surface area on which gas molecules can be adsorbed [33].

Finally, novel double layer structures based on NiO p–n junctions were fabricated with PLD method.

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References