Hydrogen Sensing Properties of Thin NiO Films Deposited by RF Sputtering

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Abstract

Electrical properties of p-NiO films fabricated by RF magnetron sputtering were studied for hydrogen sensor applications. A response of sheet resistance to hydrogen concentration in air has been measured at elevated temperature. Significant changes in sheet resistance of NiO films were observed even for H2 concentration of a few ppm in air. The sensibility of NiO films to hydrogen trace was further increased by Pd clusters deposited on the NiO surface. The best sensibility result achieved on the NiO film was: 0.3 ppm of H2 in air at 145°C.

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1. Introduction

Hydrogen is a good candidate to become an alternative fuel for clean energy generation. In this context, mass production, distribution as well as hydrogen combustion in engines will require advanced control systems to ensure secure storage and usage of the gas. Therefore, new smart sensors with high sensibility to H2 will be needed. Many works have been devoted to find adequate material for hydrogen sensors, in particular metal oxide like SnO2 [1], WO3 [2], ZnO [3] or GaN [4] were studied as sensitive thin film resistors or Schottky diodes. Almost successful use of NiO films to detect hydrogen in air was also

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reported [5], but real sensor requires optimization of sensing surface to ensure high sensibility, short response time, good repeatability and reliability. In this work we focus on sensing properties of thin semiconducting p-NiO films with the aim to develop a sensor capable of detecting hydrogen concentration in air below 1 ppm.

2. Experimental setup

Thin NiO films were deposited by radio frequency magnetron sputtering from 3” NiO target in Ar-O₂ plasma using RF power of 200 W at room temperature (RT) or 300°C. High resistivity Si(001) and quartz wafers with dimension of 10 x 10 mm² were used as substrates. The surface morphology and structural properties of the films were characterized using Scanning Electron Microscopy (SEM) and X-Ray diffraction (XRD), respectively. The compositions of the films were determined by Energy Dispersive Analysis of X-rays. Pulsed laser deposition (PLD) system was employed to ablate a Pd target for 1 min. deposition of Pd clusters on NiO surface. The scheme of the PLD apparatus is shown in Fig. 1.

![Fig. 1 Experimental apparatus for PLD deposition with Nd:YAG laser (355 nm, 10 ns pulse duration).](image)

Dynamic sensor response measurements were performed under controlled flows of H₂ and dry air at temperature range of 30°C–210°C in a stainless steel tube set-up. The current through the NiO samples was recorded in real time by a Keithley 485 picocammeter at a bias voltage of 1 V. Changes in current were monitored for various hydrogen concentrations and operating temperatures. The sensor response $S$ was calculated as the ratio of $R_g/R_o$, where $R_g$ and $R_o$ are the sensor resistance at air flow with and without hydrogen, respectively.

3. Results and discussion

As-deposited NiO films are formed with polycrystalline grains, characterized by fcc structure and texture dependent on oxygen content in plasma. <111> texture is observed for deposition at low oxygen content in plasma and <200> texture is observed for deposition in O₂. When a film is deposited in O₂-Ar mixture then both 111 and 200 are visible in the XRD spectrum. For NiO films deposited at oxygen content in plasma from 9% to 50%, the lattice parameter increased from 4.194 Å to 4.303 Å, respectively. Composition of NiO calculated from EDX analysis results in oxygen to nickel ratio changing in the range from 1.1 to 1.23, what is concurrent with well defined p-type conductivity in oxygen rich NiO compound. Electrical parameters of the NiO films after deposition and thermal treatment in Ar or O₂ were previously studied and reported in the paper [4]. Some samples were tested as hydrogen sensors and the response $S$ was measured at different temperature. The resistivity of NiO films strongly increased in the presence of H₂. We observed for the sample (NiO_2) with NiO deposited at RF power of 200 W and 32% O₂ in the
Ar-O₂ plasma, that the 90 nm thick film was able to detect hydrogen concentrations as low as 4 ppm in air kept at operating temperature of 143°C. After deposition of Pd nanoparticles, the sample can detect hydrogen concentrations of 700 ppb in air. Moreover, the response S of the sample for detection of 7 ppm hydrogen in air increases from S = 1.06 to 2 after deposition of Pd. The most remarkable effect of Pd nanoparticles is a decrease in the response time, defined as the time interval between 10% and 90% of the total signal change. The response time of the sample without Pd to hydrogen concentration of 8 ppm in air is 27 min., while for sample with Pd clusters the response time is decreased to 5.5 min.

Hydrogen sensing results for the sample NiO_8 with 100 nm thick NiO film deposited at 80% O₂ in the Ar-O₂ plasma and at RT, can be seen in Fig. 2. NiO morphology shown in Fig. 2c reveals elongated grains. Prior to Pd deposition, the sample is capable of detecting H₂ concentrations as low as 3 ppm in air, operating at 130°C. The sensitivity of the sample is further increased due to the Pd nanoparticles (Fig. 2b), because the sample can detect now 700 ppb of H₂ in air at the same operating temperature.

Fig. 2. (a) Hydrogen sensing response S of the NiO film deposited on Si(001) at RF power of 200 W, 80% O₂ in the Ar-O₂ plasma, at RT - sample NiO_8; (b) The response after deposition of Pd nanoparticles; (c) SEM of the NiO surface and the film cross-section.

Fig. 3 presents hydrogen sensing results for the sample NiO_2G with NiO deposited at 33% O₂ and 300°C - before (3a) and after (3b) Pd deposition. Prior to Pd deposition, the sample detects hydrogen concentrations as low as 4 ppm in air, while after Pd deposition, the NiO film detects H₂ trace of 300 ppb. These are the best sensing properties we obtained for the NiO films grown on Si(001) as well as probably registered on thin film semiconductor sensor and unpublished up to now. Moreover, one can observe, that a purging time to recover active surface is very short. This behavior suggests, that the NiO surface plays a dominant role in conduction, and grain boundaries' conduction is less evident in the measured current.

Fig. 3: (a) Hydrogen sensing results for the sample NiO_2G with NiO deposited at 33% O₂ in the Ar-O₂ and 300°C; (b) The response S after deposition of Pd nanoparticles; (c) SEM micrographs of morphology for NiO film deposited at 33% O₂ and 300°C.
A summary of our sensibility results is included in Tab. 1. Every NiO surface is able to detect H₂ trace of a few ppm at the low operating temperature. The sensibility of NiO to hydrogen detection is increased due to partial coverage of the surface with Pd nanoparticles. The nanoparticles catalyse the hydrogen-surface reaction thus enabling the decrease in the detectable hydrogen concentrations. Further progress in the sensor efficiency for higher sensibility and shorter response time will rely on the optimization of the NiO roughness and coverage of the NiO surface by Pd nanoparticles with suitable density.

Table 1. Minimum of H₂ concentration in air detected by NiO films deposited at different oxygen content in the Ar-O₂ plasma.

<table>
<thead>
<tr>
<th>ID</th>
<th>O₂ content in plasma (%)</th>
<th>Film thickness (nm)</th>
<th>Pd clusters</th>
<th>Sensed H₂ content (ppm)</th>
<th>T (°C)</th>
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<tr>
<td>NiO_2</td>
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<td></td>
<td></td>
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<td>No</td>
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<td>143</td>
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<td></td>
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<td>Yes</td>
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<td>145</td>
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<tr>
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<td>No</td>
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<td>130</td>
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</table>

4. Conclusions

p-NiO films were studied as hydrogen sensor resistors. H₂ concentration of a few ppm in air was detected at operating temperature ranging from 130°C to 145°C. The sensibility of the films to hydrogen trace of 0.3 ppm in air was further increased due to Pd clusters deposited by the PLD method. Moreover, Pd nanoparticles reduce by a factor of a few the response time for hydrogen detection of the NiO film.

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References