IOP Conf. Series: Journal of Physics: Conf. Series **1319** (2019) 012014 doi:10.1088/1742-6596/1319/1/012014

NiO gas sensing element prepared on needle-shaped silicon substrate

M Predanocy[1], I Hotový[1], M Mikolášek[1], R Botcher[2] and L Spiess[2]

[1] Institute of Electronics and Photonics, Slovak University of Technology, Ilkovicova 3, 81219 Bratislava, Slovakia
[2] Institut für Mikro- und Nanotechnologien, Technische Universität Ilmenau, Gustav-Kirchhoff Str. 5, D-98693 Ilmenau, Germany

martin.predanocy@stuba.sk

Abstract. This study presents a new approach to enhancing the gas sensor properties based on increasing the sensing area by a structured substrate. Two types of needle-shaped silicon substrates with surface areas of 40 and 14 μm^2 were used as substrate for the preparation of NiO gas sensing element with a thickness of 25 nm. The surface morphology and composition of the prepared samples were examined by SEM, FIB-SEM, and GD OES methods. Deposited NiO films were continuous consisting of an agglomeration of small nanosized grains with arbitrary forms created on each Si needle. It was found that NiO had a polycrystalline nature. The gas sensing measurements revealed that hydrogen responses were better for NiO sensing elements prepared on needle-shape Si substrates with 40 μm^2 surface area than those with 14 μm^2 for all investigated concentrations and temperatures. The maximum relative sensitivity of 26% was measured at 250 ppm of hydrogen.

1. Introduction

Recently, there has been increased interest in the effort in miniaturization, reliability improvement of microfabrication of novel microelectronic devices. Micro-devices are becoming increasingly important in portable electronic applications where low power designs and long life of devices are required. New approaches in miniaturization can show the way to improving the properties of micro/nano devices. Attention of scientists is focused on altering the surface morphology of high aspect ratio structures so that the real surface area is greater than the geometrical area [1, 2, 3]. Then the increase of surface morphology often enhances the element functionality and reliability. A large real surface area can be achieved either by preparing small particles or clusters of particles (clusters) or by creating materials with pores in the surface [1]. This issue can also be widely applied in the field of metal oxides gas sensors for improving sensitivity and getting better gas responses [1]. Scientists and engineers are active in designing a new generation of gas microsensors, and their mission is to identify gases, recognize different types of gases in gaseous mixtures as well as ensure sensitivity to a wide range of chemicals in gaseous state. Consequently, such sensor elements may form part of intelligent microsystems. Necessary requirement is miniaturization and integration of these sensors to micro-electro-mechanical components and systems (MEMS) using standard production processes and methods used in integrated circuit technology and the use of micro-patterning methods to create three-dimensional micromechanical structures from a semiconductor substrate or directly on the substrate.

Content from this work may be used under the terms of the Creative Commons Attribution 3.0 licence. Any further distribution of this work must maintain attribution to the author(s) and the title of the work, journal citation and DOI.
Published under licence by IOP Publishing Ltd

We present a new approach to enhancing the gas sensing properties using two types of needle-shaped Si substrates. Our paper describes the preparation of NiO gas sensing element with a thickness of 25 nm. The sensor structures containing of NiO and Si_3N_4 films were analyzed with SEM, FIB-SEM and GDOES. Gas sensing behaviour of NiO elements operating at temperatures 200 and 350°C towards hydrogen concentrations less than 1000 ppm was studied.

2. Experimental details

As the base material for needle-shaped silicon formation and as the substrate for the analyzed layers a p-type standard 4-inch silicon wafer (SiegertWafer GmbH) with specific resistivity of 5-10 Ωcm, [100] - orientation and 525 μm thickness was used. Dry etching was performed in an Oxford reactor (Oxford RIE PlasmaLab100) operated at 13.56 MHz. Silicon wafers were etched in SF_6/O_2 plasma with variable process parameters. Two sets of the parameters were selected for the preparation of NiO gas sensing elements:
S 3: Oxford process, SF6=84 sccm, O_2=60 sccm, Ra=145 nm
S 7: Oxford process, SF6=80 sccm, O_2=70 sccm, Ra=35 nm
Typical surface morphology of needle-shaped silicon is shown in figure 1. The silicon needles have a height of 0.8 and 0.5 μm, respectively.

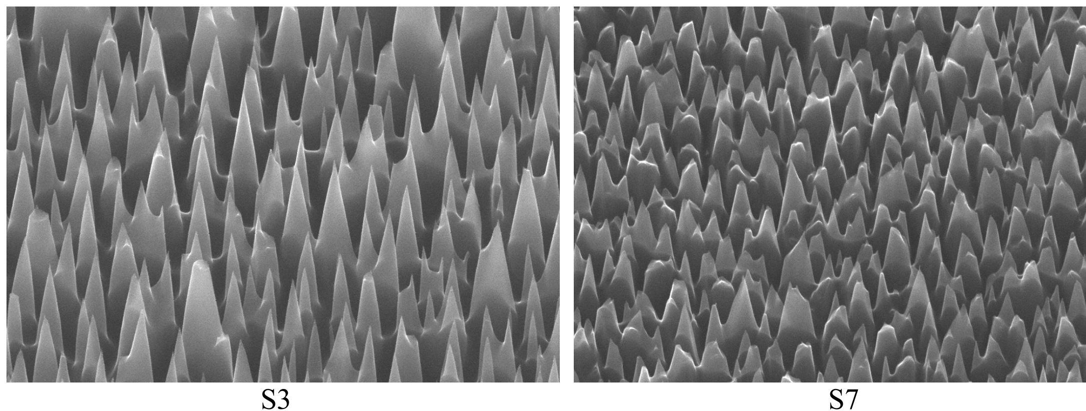

Figure 1. SEM observation of the surface area after etching process for samples S3 and S7.

Silicon nitride as an electrical barrier layer with a thickness of about 200 nm was deposited onto the needle-shaped Si surface by PE CVD method. Consequently, NiO layers with a thickness of about 25 nm were sputtered onto two types of needle-shaped silicon substrates [4]. The NiO films were deposited by DC reactive magnetron sputtering from a Ni target in a mixture of oxygen and argon. The relative partial pressure of oxygen in the reactive mixture O_2-Ar was 30%. In the next step, several selected samples were coated by Au contact films through a shadow mask for electrical and gas sensing characterization.

Fabricated samples were analyzed with SEM, FIB-SEM, and GDOES methods. The electrical properties of the prepared films were investigated in Van der Pauw geometry. The responses from NiO elements towards hydrogen were obtained by measuring the electrical resistance. The gas sensing measurements of NiO layers were carried out in the vacuum chamber CascadeMicrotech PLV50. The sensor resistance was measured every 0.5 s by an SMU multimeter and recorded using a GPIB interface for communication with a computer by LabVIEW language [4].

3. Results and discussions

3.1. Surface morphology and composition

Since the gas sensing elements were prepared on needle-shape Si substrates, SEM observation were also done on this type of substrate to identify the effective morphology. It was observed that NiO surface reflected the needle-shaped Si substrate morphology for both examined samples. The NiO film consisting of an agglomeration of small nanosized grains with arbitrary form was created on each Si needles (figure 2). Nanostructured NiO film consistently covers every available plane of matchless larger Si needles. NiO grows not only on top of the Si needles but also on the needle sides and is filling the space between Si needles.

FIB-SEM cross sectional images showed the polycrystalline nature of NiO. In this case, NiO thin film is continuous and is created by repeated nanocrystals which homogenously cover the needle-shaped Si surface (figure 3). The main difference between samples S7 and S3 consists in the higher needle height for the S3. The calculated surface area on the 1 μm^2 projected area was 40 and 14 μm^2 for samples S3 and S7, respectively.

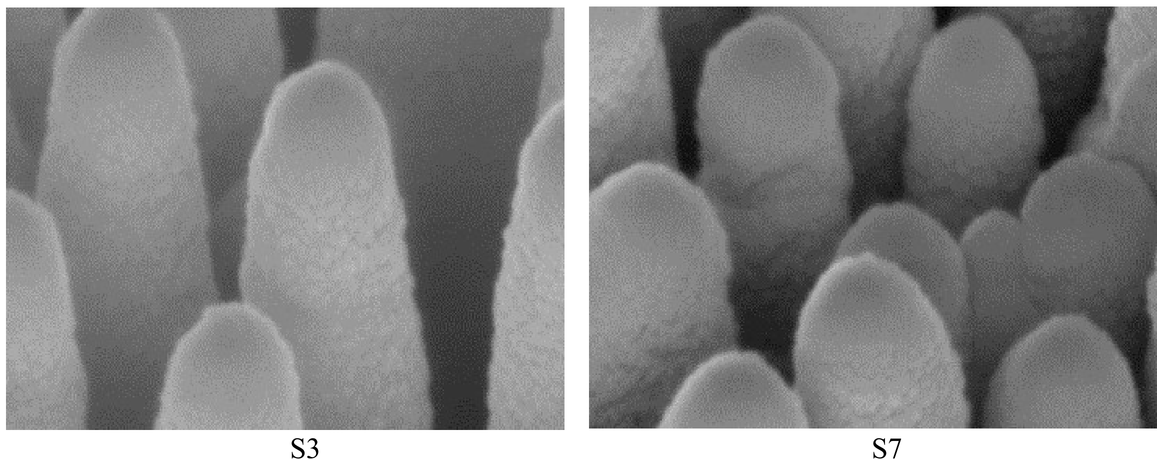

Figure 2. SEM images of S3 and S7 morphology.

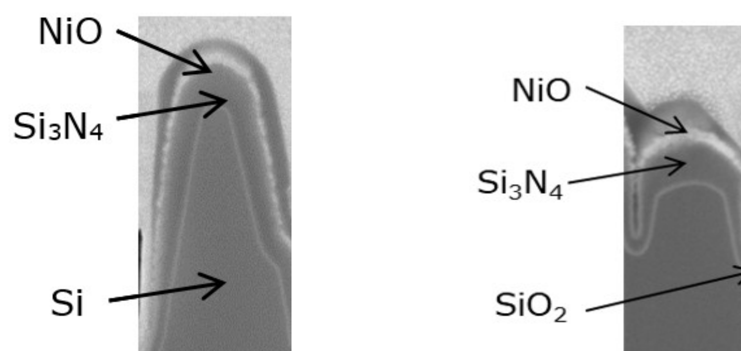

Figure 3. FIB cross section of NiO gas sensing element of samples S3 and S7.

The in-depth GD OES profiles of both investigated samples showed a similar depth material profile. Figure 4 shows a typical GD OES profile for prepared sample S3. We can note an approximately correct stoichiometry of the layer itself and the barrier layer Si_3N_4 between NiO and silicon micro-needles. The absence of the sharp interface between these layers is due to the needle-shaped profile of the substrate.

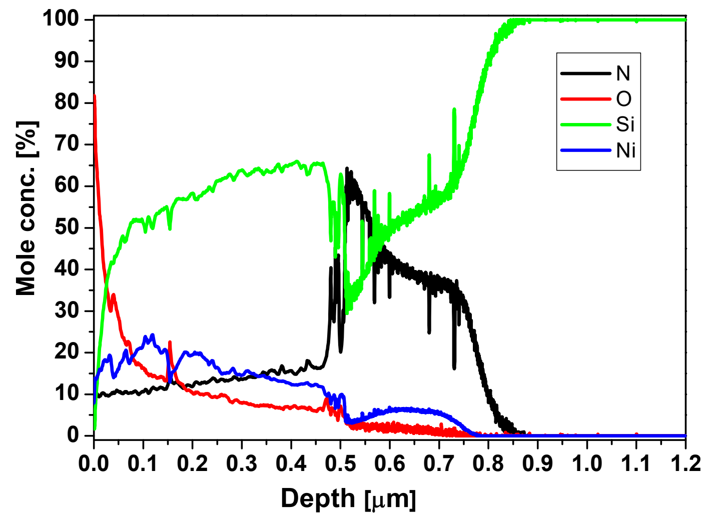

Figure 4. Typically, GD OES profiles for sample S3 prepared on a needles-shaped silicon substrate with Si_3N_4 insulating layer and sputtered NiO layer.

3.2. Electrical characterization

The square resistance measured on samples is 298 and 395 Ω/sq for samples S3 and S7, respectively. Taking into account the thickness of the NiO layer 25 nm, the specific resistance is 1.49×10^{-3} and 1.98×10^{-3} Ωcm for samples S3 and S7, respectively. The measured specific resistances are too low for NiO layers. The main part of the current flows under the metal contacts perpendicular through NiO layer to the needle-shaped silicon substrate and between the metal contacts through the silicon substrate. Due to this, the measured resistivity reflects the resistivity of the silicon substrate. Taking into account the thickness of silicon substrate ~500 μm, the specific resistivity is calculated as 14.9 and 19.8 Ωcm for substrates S3 and S7, respectively. These are realistic values for specific resistivity of common silicon substrates. The leakage currents through the silicon substrate present a problem for utilization of Si/NiO structure for gas sensor applications because the resistivity of the structure is significantly defined by the resistivity of the silicon substrate. To suppress such leakage currents, it is necessary to insert an electro-insulating layer between the needle-shaped silicon substrate and the active NiO layer.

Therefore, we decided to examine silicon nitride as a potential electrical barrier. The measurements showed that the square resistance increased more than 10 times for Si_3N_4 insulating material. The final sensitivity of the active sensing layer prepared on such structures will be the trade-off between the current league through the insulating layers and silicon substrate and increased gas sensing sensitivity provided by the larger area of the active NiO layer.

Figure 5 presents the substitute electrical circuits of the sensing element for our realized electrical measurements. In the case of Si needles without an insulating layer the resulting resistance is determined by R_{Si} (figure 5a). In the second case, Si needles and NiO layer are separated by Si_3N_4 insulating layer (figure 5b) and the value of the resistance is given as:

$$R = R_{Si} + 2\times R_i \ \ (for\ R_L = \infty), \qquad (1)$$

where R_L is the leakage resistance. Then the measured results respond mainly to the resistance of NiO sensing film R_{NiO}.

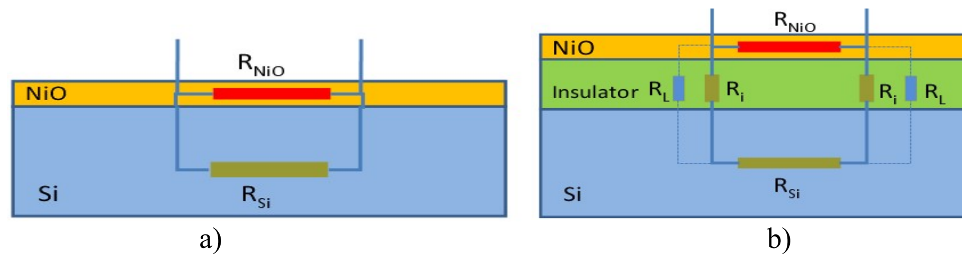

Figure 5. Substitute electrical circuit for gas sensing element: a) (Si/NiO), b) ($Si/Si_3N_4/NiO$).

3.3. *Hydrogen sensing properties*

The gas sensing responses of NiO on the needle-shaped silicon with an insulating layer were measured to hydrogen with different concentrations in the range from 100 to 1000 ppm. The working temperatures 200 and 250°C were optimized for sputtered NiO films in our previous work [4]. Figure 6 shows a typical behavior of the investigated NiO sensing elements at the optimal operational temperatures. It can be seen that sample S3 exhibits significantly better hydrogen responses in comparison with sample S7. We suppose that the improvement in the sensing properties of NiO in the case of S3 is caused by the larger surface area. This phenomenon is significantly greater for 250°C operational temperature. The highest values were recorded for hydrogen concentration of 1000 ppm for sample S3. A similar effect of increasing gas responses was not observed in the case of sample S7. Both types of sputtered NiO films exhibited good reversibility after many measuring cycles.

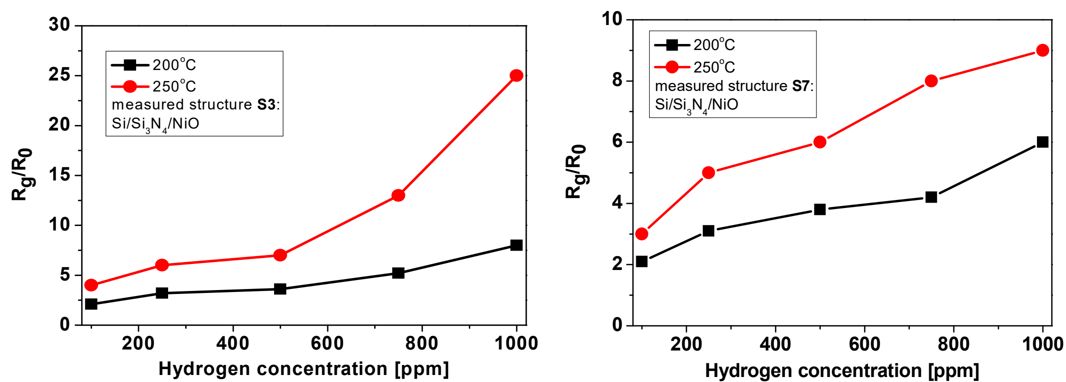

Figure 6. The relative sensitivity of NiO thin films for different hydrogen concentrations at examined temperatures 200 and 250°C.

4. Conclusion

A new approach to enhancing the gas sensing properties for metal oxides was presented. Gas sensor elements with a 25 nm thick NiO film and Si_3N_4 insulating layer prepared on needle-shaped silicon substrates were successfully fabricated. SEM and FIB-SEM observations showed that NiO surface reflected the needle-shaped Si substrate morphology for both examined samples. The NiO film consisting of an agglomeration of small nanosized grains with arbitrary form was created on Si needles. The performed electrical measurements confirmed the need of an insulating layer between the active NiO film and needle-shaped Si substrate. It was found that the sample with a surface area of 40 μm^2 exhibited 3.1 times higher hydrogen responses in comparison with the sample having only 14 μm^2 for hydrogen concentration of 1000 ppm at the operating temperature of 250ºC.

Acknowledgements
This work was supported by grants VEGA 1/0828/16, APVV-16-0266 and APVV-17-0169. This work was also supported by the European project "IoSENSE: Flexible FE/BE Sensor Pilot Line for the Internet of Everything". This project has received funding from the Electronic Component Systems for European Leadership Joint Undertaking under grant agreement No 692480. This Joint Undertaking receives support from the European Union Horizon 2020 research and innovation programs of Germany, Netherlands, Spain, Austria, Belgium, and Slovakia.

References

[1] Yan D, Li S, Hu M, Liu S, Zhu Y and Cao M 2016 *Sens. and Act. B: Chemical* **223** 626
[2] Leber M, Shandhi M M H, Hogan A, Solzbacher F, Bhandari R and Negi S 2016 *Appl. Surf. Science* **365** 180
[3] Stubenrauch M, Fischer M, Kremin C, Stoebenau S, Albrecht A and Nagel O 2006 *J. of Micromech. and Microengineering* **16** 82
[4] Predanocy M, Hotový I and Čaplovičová M 2017 *Appl. Surf. Science* **395** 208