Au-NiO nanocrystalline thin films for sensor application

I Hotovy1, J Huran2, L Spiess3, H Romanus3, S Capone4, V Rehacek1, A M Taurino4, D Donoval1 and P Siciliano4

1 Department of Microelectronics, Slovak University of Technology, Ilkovicova 3, 812 19 Bratislava, Slovakia
2 Institute of Electrical Engineering, Slovak Academy of Sciences, Dubravska cesta 9, 842 39 Bratislava, Slovakia
3 Department of Materials Technology, Technical University Ilmenau, PF 100565, D-98684 Ilmenau, Germany
4 Institute of Microelectronics and Microsystems I.M.M.-C.N.R., Via Arnesano, 73100 Lecce, Italy

E-mail: ivan.hotovy@stuba.sk

Abstract. Nanocrystalline NiO thin films were deposited by dc reactive magnetron sputtering in a mixture of oxygen and argon and subsequently coated by Au on a NiO film surface. Very thin Au overlayers with a thickness of about 1 and 7 nm have been prepared by magnetron sputtering. Then, the surface modified NiO films have been analysed by TEM, EDX and SEM. NiO thin films showed a polycrystalline structure with the size of nanocrystals ranging from a few nanometers to 10 nm. Electrical responses of NiO-based structure towards hydrogen have been measured.

1. Introduction

Nickel oxide (NiO), which belongs to metal oxides, is usually taken, as a model for p-type materials, is an attractive material well known for its chemical stability as well as for its excellent optical and electrical properties. Indeed, NiO thin films have been studied for applications in electrochromic devices and also as functional layers for solar cells [1,2]. In particular, the field of gas sensing has benefited from the production of prospective materials characterized by a high surface-to-volume ratio. The gas-sensing properties of metal oxides are more or less related to the material surface, its high porosity and a nanostructure with small particles. Also, these properties can be essentially improved by doping of their surfaces by catalytic metals as gold (Au) [3,4]. These efforts have been made to investigate the prospective thin film materials based on metal oxide, but there is no available information about nanostructured films with surface modification for gas detection. The approach is different from the heuristic one, because our purpose was not obtain the best sensors, but to modify and control the metal oxide surface by fabricating small Au particles or clusters using magnetron sputtering. This fabrication technique, which facilitates the control of particle properties such as size and composition on a nanometer scale, allows tight control over critical process parameters and so contributes greatly to the reproducibility of the nanostructure films.

We have successfully prepared nanocrystalline NiO thin films with the mean crystal size of ~10 nm by dc reactive magnetron sputtering from a metallic Ni target in a mixture of oxygen and argon. To improve the sensing characteristics of nanocrystalline NiO films, we deposited very thin Au overlayers...
with a thickness of about 1 and 7 nm on top of the NiO surface by magnetron sputtering. Then, the modified NiO films have been analyzed with TEM, EDX and SEM. Electrical responses of the NiO-based sensors towards H₂ concentration have been measured.

2. Experimental details
The NiO films were deposited by dc reactive magnetron sputtering from a Ni target (101.2 mm in diameter, thickness of 3 mm and 99.95% pure) in a mixture of oxygen and argon. A sputtering power of 600 W was used. Both the inert argon flow and reactive oxygen flow were controlled by mass flow controllers. The relative partial pressure of oxygen in the reactive mixture O₂-Ar was 20%. The total working sputtering gas pressure was kept at 0.5 Pa and adjusted by a piezoceramic valve. The films thickness as measured by a Talystep were about 100 nm for all the samples. NiO films were deposited onto unheated KCl for physical characterization. On top of these base films, thin Au overlayers (1 and 7 nm thick) were deposited by magnetron sputtering. The amount of Au deposited on the surface of NiO thin films was controlled by measuring the sputtering time and the thickness of the very thin Au layer was determined by AFM. In order to stabilize the properties, all films have been annealed in a furnace at 400°C in dry air for 2 hours.

The structural features of the films were investigated by means of a Tecnai 20 S-TWIN transmission electron microscope (TEM) operated at 200 kV. It is equipped with energy dispersive X-ray (EDX) facility for high resolution chemical analysis. Selected electron diffraction patterns have been recorded together with bright and dark field images of the film structure. The NiO-based sensor devices prepared over alumina substrates were mounted as suspended devices onto standard TO-8 packages and introduced into a test chamber for the sensing tests in controlled ambient. A constant dc voltage of 2 V was applied across the sensing films and the electrical current was measured by an electrometer (Keithley mod. 6517A) equipped with a multiplexer.

3. Results and discussion
The structural properties of the NiO thin films have been examined using TEM (figure 1). Identification of the deposited films was based on the observed electron diffraction patterns. The measured lattice spacings are shown in table 1. Comparisons can be made with the tabulated d-spacing for the cubic NiO phase (PDF Number 4-835) and this provides further evidence for the formation of this oxide. The diffraction pattern was of a continuous ring type indicating a polycrystalline film. The grains were not oriented homogeneously, but into certain prominent directions. TEM observations (figure 1) of unmodified NiO films confirmed that the films were formed by nanocrystals and showed a fine-grained structure. The size of the nanocrystals ranges from a few nanometres to 10 nanometers depending on the position in the film. We can see that the samples contain small grains that are partially bonded into clusters. Our observations agree with conclusions of Wang et al [2] who report on a dense nanocrystalline NiO thin film with the mean grain size of ~ 30 nm analysed by TEM and XRD. According to Xuping et al [5], NiO films deposited also at room temperature by dc reactive magnetron sputtering showed the texture of (111) plane and the average grain size was about 12 nm.

| NiO (hkl) | d (nm) expected | pure NiO measured |
|----------|----------------|------------------|
| (111)    | 0.2410         | 0.2441           |
| (200)    | 0.2088         | 0.2115           |
| (220)    | 0.1476         | 0.1489           |
| (311)    | 0.1259         | 0.1281           |
| (222)    | 0.1206         | 0.1218           |
A typical TEM images of the NiO film with a 1 nm thick Au film is shown in figure 2. It can see that Au film after deposition (see figure 2a) is not continuous and close. It does not cover the NiO nanocrystalline surface completely and the Au sputtered atoms create areas of islands and conglomerates. Hence, the sensor surface modified by the deposition of a thin Au overlayer is porous and these Au particles cover the base film as an amorphous phase. Steffes et al [4] formed very thin Ti overlayers (3 nm) on top of In\textsubscript{2}O\textsubscript{3} films. They also observed that the conglomerates of amorphous Ti covered the In\textsubscript{2}O\textsubscript{3} surface and no crystallites were seen. Figure 2b shows the film nanostructure after annealing at 400°C. On the background of a well nanocrystalline NiO structure the agglomeration of
Au nanoparticles tend to form circle shaped closed clusters in diameter of several tens nanometers. The presence of Au was confirmed by EDX analysis recorded during TEM observation. The Au clusters were homogeneously dispersed on the NiO surface.

To check the gas detection properties, NiO-based sensors (unmodified and surface modified with Au 1 and 7 nm thick layers) towards 1000 ppm H₂ in dry air are reported. The calibration curves for various operating temperatures were plotted in figure 3. Both the Au-modified NiO samples showed higher responses compared to the sensor element with an unmodified NiO thin film in the whole operating temperature range thus confirming the promoting catalytic effect of the Au layer.

![Figure 3. Response to 1000 ppm H₂ for three NiO based sensors (i.e. unmodified and surface modified with Au 1 and 7 nm thick film).](image)

In figures 4 and 5, SEM images of Au-modified (1 and 7 nm thick) NiO surface are shown. Well defined Au clusters on the NiO films are clearly seen. On increasing the thickness of the Au overlayers, the responses to hydrogen were still dependent on the catalytic material but some new characteristics appear due to the higher amount of sputtered metals but also to different morphologies of the catalytic layers subject to changing when the sensor operating temperature increases (up to 400ºC).

![Figure 4. SEM image of Au-modified (1 nm thick) NiO surface for a sample (a) as-deposited, (b) a sample after sensor measurement at 400ºC (b).](image)
4. Conclusions

Very Au thin films with different thickness (about 1 and 7 nm) were sputtered on the surfaces of NiO sensing layers prepared by dc reactive magnetron sputtering. The surface structure and morphology of unmodified and differently Au-modified NiO films have been studied by TEM, EDX and SEM.

NiO thin films had a polycrystalline structure (f.c.c. NiO phase) with the size of nanocrystals ranging from a few nanometres to 10 nm. TEM observations of Au-modified NiO films revealed that the films were formed by NiO nanocrystals and Au clusters homogeneously dispersed on the NiO surface. The hydrogen gas-sensing property was improved by the catalytic activity of the thin Au overlayers and depends also on the step of Au coverage of NiO surface.

5. Acknowledgements

This work was supported by the Scientific Grant Agency of the Ministry of Education of the Slovak Republic and the Slovak Academy of Sciences, No.1/3095/06 and by Science and Technology Assistance Agency under the contract No. APVT-20-021004.

References

[1] Magana C, Acosta D, Martinez A, Ortega J 2006 Solar Energy 80 161
[2] Wang Y, Zhang Y, Liu H, Yu S, Qin Q 2003 Electrochimica Acta 48 4253
[3] Schweizer-Berberich M, Zheng J, Weimar U, Gopel W, Barsan N, Pentia E, Tomescu A 1996 Sensors and Actuators B 31 71
[4] Steffes H, Imawan C, Solzbacher F, Obermeier E 2001 Sensors and Actuators B 78 106
[5] Xuping Z, Guoping Ch 1997 Thin Solid Films 298 53

Figure 5. SEM image of Au-modified (7 nm thick) NiO surface for a sample (a) as-deposited, (b) a sample after sensor measurement at 400°C (b).