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TEM INVESTIGATIONS OF Au–NiO NANOCRYSTALLINE THIN FILMS AS GAS SENSING MATERIAL

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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 transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM), selected electron diffraction (SAED) and energy dispersive X-ray (EDX) methods. NiO thin films had a polycrystalline structure (FCC NiO phase) with the size of the nanocrystals ranging from a few nanometers to 10 nm. The electrical response of NiO-based structure, as a function of hydrogen concentration has been measured.

K e y w o r d s: thin films, nanocrystals, TEM, nickel oxide

1 INTRODUCTION

Nickel oxide (NiO), as a model system for p-type materials, is attractive 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 the surfaces by catalytic metals as gold (Au) [3, 4]. Considerable efforts have been undertaken to investigate 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 to 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 the particle properties such as size and composition on a nanometer scale, allows the tight control over critical process parameters and therefore contributes greatly to the reproducibility of the nanostructure films.

We have successfully prepared nanocrystalline NiO thin films with the mean crystal size of $\sim$ 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 the 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, HRTEM, SAED and EDX. Electrical responses of the NiO-based sensors towards H_2 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 O_2-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 Au layer was measured by AFM. In order to stabilize the

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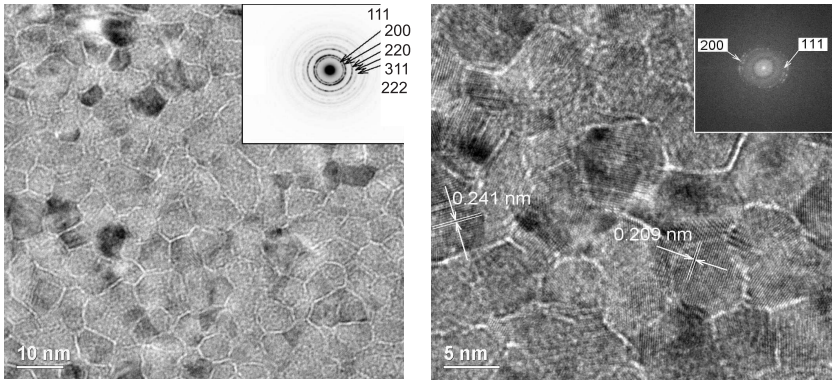
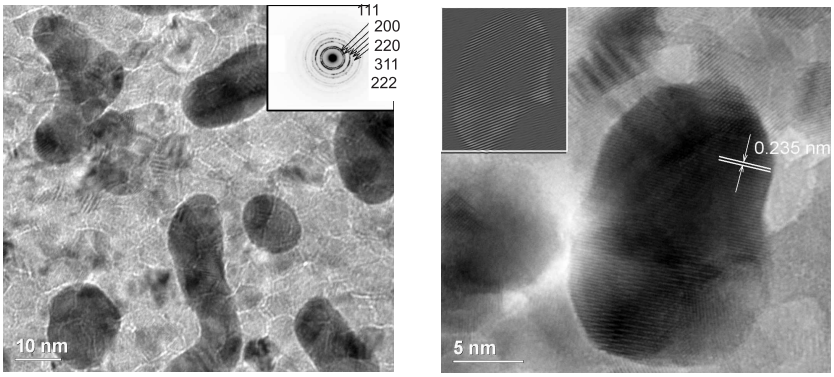


(a) (b)

Fig. 1. NiO film achieved after deposition. TEM image showing the nanostructure at lower magnification and SAED pattern in inset confirms the crystalline nature of the film (a). HRTEM image shows the nanostructure of the same NiO film in detail. Lattice fringes visible inside the selected grains are 200 and 111 planes of NiO according to PDF 4-835. FFT diffraction pattern in inset confirms the presence of both kinds of planes in the NiO grains (b).



(a) (b)

Fig. 2. TEM image of Au 1 nm formed on NiO film achieved after deposition (a), HRTEM image of Au nanoparticle on the surface of NiO film (b). The 111 planes of Au with interplane distance of 0.235 nm are marked. Inverse FFT of the same Au nanoparticle is in inset.

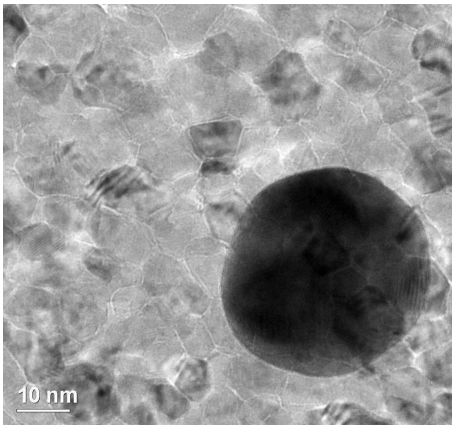


Fig. 3. TEM image of Au 1 nm formed on NiO film achieved after annealing at 400 °C. Circular morphology of Au particles is shown.

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 (SAED) 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

Nanostructural characterization of the NiO thin films has been carried out via TEM, HRTEM, SAED and EDX. TEM observations (Fig. 1) of unmodified NiO films confirmed that they were compact, polycrystalline with fine-grained nanostructure. The size of the nanocrystals forming the layer ranges from a few nanometres to 10 nanometers depending on the position in the film. We can also see

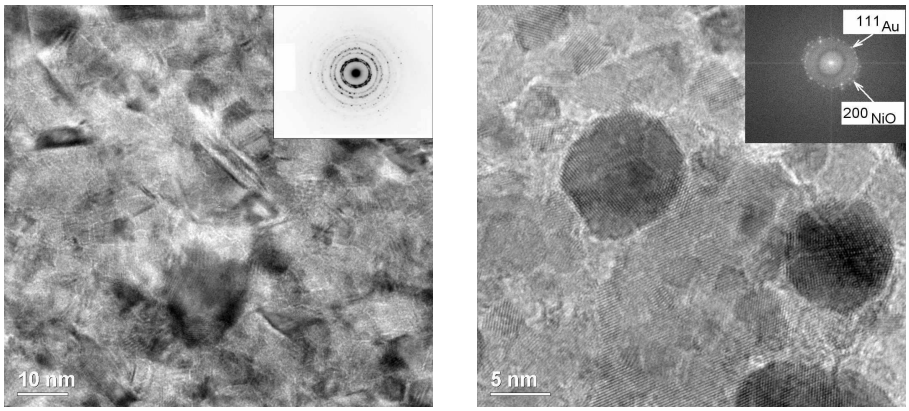


Fig. 4. TEM image of NiO film with 7 nm Au overlayer after deposition (a), HRTEM image of the same film after annealing at 400 °C (b). SAED pattern in (a) and FFT diffraction pattern in (b) confirm the presence of both Au and NiO crystallites. Dark features of circle shape are Au in (b).

Table 1. Comparison of the interplane spacings (d_{hkl}) measured from electron diffraction pattern of NiO films with theoretical d_{hkl} for NiO values (PDF 4-835).

NiO (hkl)	Theoretical d_{hkl} (nm) (PDF 4-835)	Calculated d_{hkl} (nm) for pure NiO
(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

that the samples contain small grains that are partially bonded into clusters. Straight grain boundaries separating individual grains are characteristic for phases crystallizing in face-centered cubic (FCC) structure of NiO.

Confirmation of the presence of NiO in the deposited film has been obtained from SAED and EDX analyses. An example of SAED pattern is shown in inset of Fig. 1a. The SAED pattern is of a continuous ring type indicating a polycrystalline nature of the film. The interplane spacings (d_{hkl}) calculated on the basis of the measured diffraction circle diameters in the recorded SAED patterns are shown in Table 1. A comparison between the measured and theoretical d_{hkl} for the cubic NiO phase (PDF Number 4-835) provides evidence for the formation of this oxide.

The grains in as-deposited film were not oriented randomly, but into certain prominent directions, as demonstrated by the increasing intensity at certain places of the diffraction rings. It is evident from the SAED pattern in inset of Fig. 1a that a preferential orientation can be identified for 200 planes compared with the 111 planes. The coexistence of 200 and 111 planes is evidenced by HRTEM (Fig. 1b) and by Fast Fourier Transform (FFT) diffraction is shown in inset of Fig. 1b). The FFT diffraction pattern consists of two rings, the outer one of NiO is evidently degenerated to arcs revealing the [200] preferential orientations of the nanocrystallites in the NiO film. During the annealing of the NiO film at 400 °C, a further coalescence of NiO nanocrystals has been obseerved. Therefore, the originally rather continuum-like rings in the SAED pattern recorded by as-deposited film, (inset in Fig. 1a) changed to circles formed by individual spots for annealed NiO film.

Our observations agree with the conclusions of Wang et al [2] reporting on a dense nanocrystalline NiO thin film with the mean grain size of $\sim$ 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.

A typical TEM image of the NiO film with a 1 nm thick Au overlayer is shown in Fig. 2. The presence of Au on the surface of the NiO film was confirmed by TEM, SAED and EDX. It can bee seen that the Au film after deposition (see Fig. 2a) is not continuous and close. It does not cover the NiO nanocrystalline surface completely and the Au sputtered atoms create oval and sponge-like islands or their conglomerates. Hence, the sensor surface modified by the deposition of a thin Au overlayer is created only detached Au particles partially covering the base NiO film. Steffes et al [4] fabricated very thin Ti overlayers (3 nm) on top of In_2O_3 films. They also observed that the Ti created amorphous nanoparticles and their conglomerates on the surface of the base In_2O_3 film. However, in contrast to [4], the surface of our NiO base film was covered by the crystalline Au nanoparticles (inset in Fig. 2(a)), and no amorphous Au was confirmed by SAED. The diffraction circles in SAED pattern became doubled. The outer rings belong to Au, and the inner rings are of NiO, since the interplane spacings of NiO are slightly larger than those of Au (e.g. for NiO $d_{111} = 0.241$ nm, for Au $d_{111} = 0.235$ nm). The crystalline nature of Au nanoparticles is also clearly evidenced by HRTEM (Fig. 2b) and by the inverse FFT in inset. 111 planes of Au crossing just the nanoparticle shown in Fig. 2a are evident.

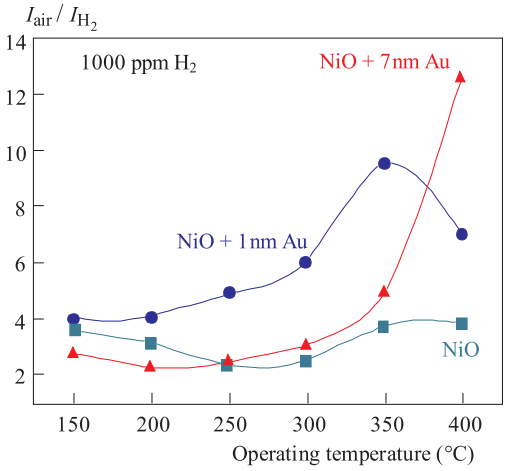


Fig. 5. Response to 1000 ppm H_2 for three NiO based sensors (*ie* unmodified and surface modified with Au 1 and 7 nm thick film).

In Figure 3 the film nanostructure with 1nm Au overlayer after annealing at 400 °C, is reported. On the background of a nanocrystalline NiO structure the agglomeration of Au nanoparticles tends to form circle shaped closed clusters with the diameter of several tens of nanometers. The Au clusters are homogeneously dispersed on the NiO surface.

Contrary to 1 nm layer, the as-deposited Au overlayer (Fig. 4a) with thickness 7 nm was continuous. The crystallinity of the layer is evidenced by the SAED pattern in inset of Fig. 4a. However, upon annealing at 400 °C evenly distributed circle shaped crystalline Au particles with diameter approaching 20 nm appeared on the surface of the NiO film, as can be seen in Fig. 4b. The FFT diffraction pattern in inset of Fig. 4b confirms the coexistence of both Au and NiO crystals. Based on the evaluated interplanar distances, the internal diffraction circle is attributed to the 111 type planes of Au and outer arcs revealing the preferential orientation is attributed to the 200 planes of NiO.

To check the gas detection properties, NiO-based sensors (unmodified and surface modified with Au 1 and 7 nm thick layers) towards 1000 ppm H_2 in dry air are reported. The calibration curves for various operating temperatures were plotted in Fig. 5. 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 catalytic effect of the Au layer. On increasing the thickness of the Au overlayers, the response to hydrogen is 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 400 °C).

4 CONCLUSIONS

Au thin films with different thickness (about 1 and 7 nm) have been sputtered on the surfaces of NiO sensing layers prepared by dc reactive magnetron sputtering. The nanostructure of unmodified and differently Au-modified NiO films have been studied by TEM, HRTEM, SAED and EDX methods. NiO thin films were polycrystalline (FCC NiO phase) with the size of nanocrystals ranging from a few nanometres to 10 nm. TEM observations of the 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.

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