

THE COMPOUND OXIDES BASED ON TiO₂ AND NiO THIN FILMS FOR LOW TEMPERATURE GAS DETECTION

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The multilayer compound thin films, consisted of metal oxides (TiO₂ and NiO) prepared by dc magnetron sputtering technique, have been studied. The structural, compositional, electrical and gas sensing properties have been investigated by XRD, GDOES and Van der Pauw method considering changes in layout, annealing temperature and addition of Au noble metal catalyst. The Au modified compound oxides exhibit fast response and enhanced sensitivity to hydrogen at low operating temperatures.

1. Introduction

It is well-known that the adsorption of gases on metal oxide films causes electrical conductivity changes, so a measurement of electrical resistance allows us to detect the presence of specific gases. Nanostructured compound materials exhibit unusual and often enhanced properties with respect to single oxides [1]. Under normal conditions, it is well known, that TiO₂ has high resistivity. For usage of the TiO₂ layers at low temperature it is needed to build in material that causes lowering of the resistivity of the whole complex. It seems that NiO is great material for incorporation into complex compound layers based on TiO₂. Under some conditions it is expected that the oxide at lower concentration restrains the growth of the other oxide and stabilizes it, avoiding the well-known grain growth that takes place when the sensor is heated [2]. This circumstance together with fast response time and good sensitivity to concentrations of hydrogen below environmental monitoring limits make investigated compound mixed oxides new promising candidates for gas sensing materials.

2. Thin films preparation and characterization

Two main layouts of compound oxides were prepared (Fig. 1). The difference between

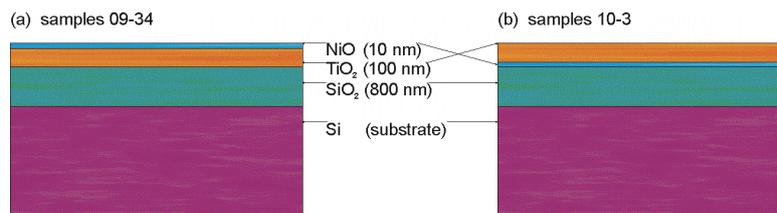


Fig. 1 The cross-section of deposited structures; NiO film on the top – first layout (a), TiO₂ film on the top of the structure – modified layout (b).

the layouts is in sequence of the top two functional layers: TiO₂ and NiO. In the first layout (sample code 09-34) the compound structure was deposited as multilayer complex of films in order Si/SiO₂/TiO₂/NiO (Fig. 1a). Afterwards the sequence of thin films was altered: Si/SiO₂/NiO/TiO₂ (Fig. 1b) so as to get the modified layout (sample code 10-3).

Deposition of the TiO₂ and NiO thin films in both layouts undergoes the same settings and parameters. The TiO₂ thin films were prepared by dc reactive magnetron sputtering from a Ti target in a mixture of Ar and O₂. Sputtering power of 600W was used. The apparatus was initially evacuated to a pressure below 0.5 mPa. The relative partial pressure of O₂ in the reactive mixture O₂-Ar was 25%. The 10 nm thick NiO films were also deposited by dc magnetron sputtering in a mixture of Ar and O₂. The total gas pressure was kept at 0.6 Pa.

To obtain enhancement in the structure of deposited layers samples were post-annealed by rapid thermal annealing at 500°C, 600°C, 700°C and 900°C for 10 seconds in a mixture of argon and hydrogen. The relative partial pressure of hydrogen in the mixture Ar-H₂ was 5%. After annealing process representative set of samples from the both layouts was chosen and underwent 30 s of the pulsed laser deposition (PLD) of the gold catalyst.

The glow discharge optical emission spectrometry (GDOES) was used to find the depth profiles of investigated structures. The crystal structure was identified with a Theta-Theta X-ray diffractometer (XRD) D5000 with Goebel mirror oriented into grazing incidence focusing with Cu K α radiation. The diffraction patterns were recorded for values between 15° and 60°. The electrical measurements were performed using the linear four probe Van der Pauw method at room temperature in order to obtain the resistivity and sheet resistance.

Samples of both layouts were then tested as hydrogen gas sensors in an apparatus that consists of aluminium vacuum chamber. The testing procedure began with initial chamber evacuation down to 1 Pa and thereafter the apparatus was filled with synthetic air to level of atmospheric pressure. The films were tested in the operating temperature range of 180 °C to 200 °C at hydrogen concentrations from 10000 to 1000 ppm. The hydrogen concentration was calculated on the basis of the partial pressures of the sensing gas and air inside the chamber. The pressure was measured by a MKS Baratron gauge. A 1 V bias was applied by two gold-coated electrodes mechanically pressed on the sample surface. The current *I* through the film was measured with a Keithley Mo. 485 Pico-ammeter. Current changes helped to monitor the gas sensing in real time. The relative response is defined as:

$$R = \frac{I_a - I_g}{I_a} = \frac{R_g - R_a}{R_g} \quad (1)$$

where *R_a* (*I_a*) is the resistance (current) in air and *R_g* (*I_g*) the resistance (current) in the presence of the gas.

3. Structural and compositional properties observation

GDOES depth profiles yield exact knowledge about the type and position of every element in compound structure. Figure 2 delineates depth profiles of the samples 09-34. Zero level on the x-axis, which corresponds to the surface, shows only small amount of oxygen in the near sub-surface area. Low oxygen content and almost parallel tendency of slope of oxygen and Ti indicates pure Ni covering of sensing film in the case of the first layout. In addition the depth profiles displays dependency of moving and inter-diffusion of incorporated layers in the volume of investigated structure on the parameters of annealing temperature.

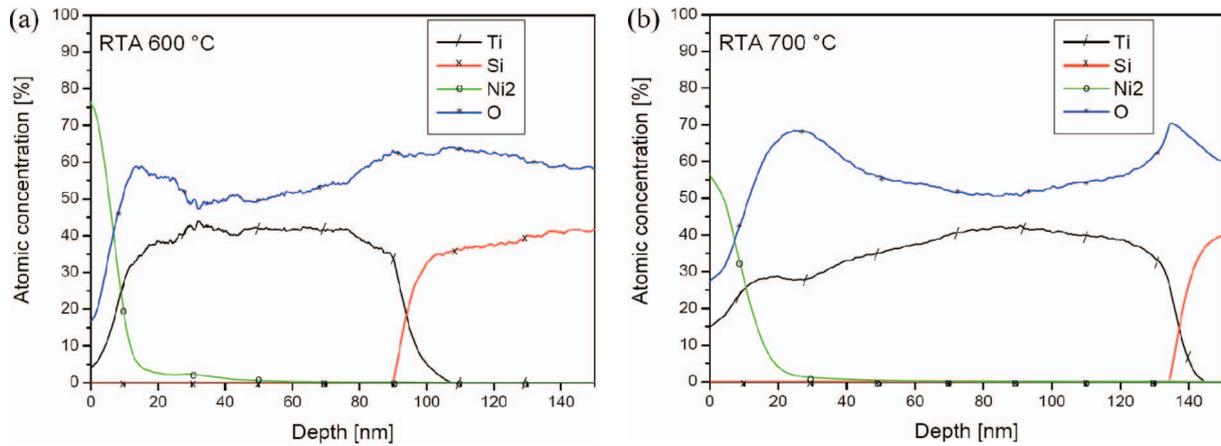


Fig. 2 GDOES depth profiles of samples 09-34 after rapid thermal annealing in chamber heated up to 600 °C (a) and 700 °C (b).

The XRD diagrams (Fig. 3) showed that as-deposited and annealed samples at 500 °C were amorphous, whereas annealed samples at 600 °C and 700 °C were found to be polycrystalline. Diffraction patterns from samples annealed at 600 °C and 700 °C delineate presence of diffraction peaks that appertain to anatase TiO_2 lattice, as referred in JC-PDS 21-1272. In samples 09-34 the rest of the diffraction peaks belongs to cubic Ni lattice, as referred in JC-PDS 4-0850. This fact also indicates presence of pure Ni on the top the 09-34 films.

Sample:	RTA	R_s [Ω/sq]	Thickness [nm]	ρ [Ωcm]
09-34/1	as-dep	2.0×10^6	110	21.7
09-34/3	500 °C	1.9×10^7	100	186.7
09-34/5	600 °C	4.7×10^5	70	3.3
09-34/7	700 °C	5.8×10^3	105	0.1
10-3/1	as-dep	1.3×10^{10}	100	1.3×10^5
10-3/1	500 °C	1.0×10^{10}	100	1.0×10^5
10-3/1	600 °C	9.7×10^9	100	9.7×10^4
10-3/1	800 °C	9.2×10^9	100	9.2×10^4

Tab. 1 Electrical properties of as-dep and annealed samples 09-34 and 10-3.

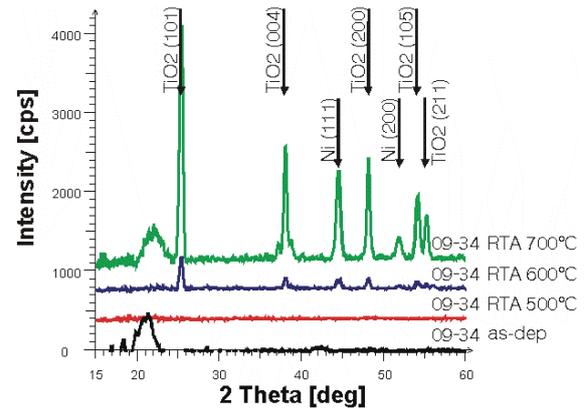


Fig. 3 XRD patterns of as-dep and annealed samples 09-34.

4. Electrical measurements and hydrogen sensing properties

The sheet resistance R_s and resistivity ρ of the investigated thin films were obtained by linear four probe Van der Pauw method. Table 1 depicts decreasing trend of R_s and ρ with raising annealing temperature. According to our previous experiments, R_s of TiO_2 in presence of top Ni layer (09-34) is lowered in three orders of magnitude down in comparison to pure TiO_2 layer. This shift of samples 09-34 can be seen also in comparison to modified samples 10-3. It is assumed that pure Ni on top acts as metal clusters (nanoelectrodes) that causes significant change in conductivity of the sensing film [3].

Compound mixed oxides of the both layouts were tested as potential gas sensors for low temperature (under 200 °C) hydrogen sensing. The best results were obtained for the modified layout (samples 10_3) together with afterwards Au catalyst deposition (Fig. 4). It is known that for pure TiO_2 it is not possible to extract appreciable responses until operating

temperature lower than 200 °C [4]. Novel NiO/TiO₂ compound oxides together with noble metal catalyst overcome this temperature limitation and provide enhanced sensitivity and very fast response. Over and above these findings indicate possibility of further lowering of the operating temperature and consequential reduction of energy consumption of the final device.

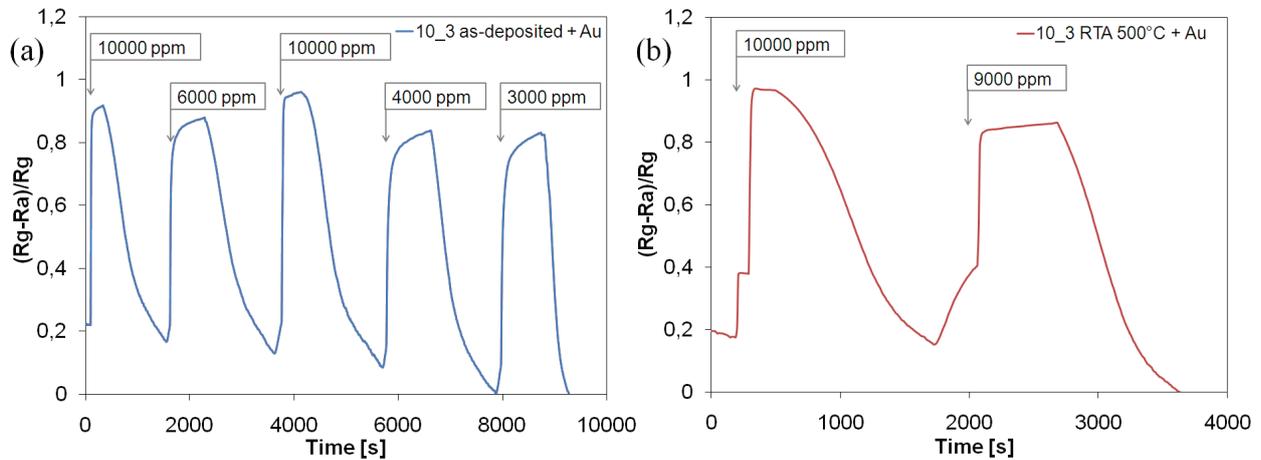


Fig. 4 Relative response of as-dep (a) and annealed at 500 °C (b) compound oxides with Au clusters in time. Operating temperature was for the both measurements 200 °C.

5. Conclusion

Investigation of sputtered and subsequently annealed thin compound films revealed absence of surface NiO phase in the first layout samples (09-34) and presence of pure Ni. This fact influenced electrical Van der Pauw and hydrogen gas measurements. Ni layer situated on the surface caused notable decrease of resistivity of the film, but with and also without of the noble metal catalyst addition, the first layout structures were insensitive to hydrogen in low operating temperatures. We expect full covering of the sensitive layer by pure Ni thereby no response to hydrogen was observed.

On the other side, samples 10-3 with 10 nm thin NiO layer under 100 nm TiO₂ layer showed some response to hydrogen, which was afterwards greatly enhanced by Au catalyst. Au modification brought shift of the working temperature down to lower values - under 200 °C desirable for revealing the improved sensitivity and response time of the multilayer compound oxides.

Acknowledgement

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