

IMPEDANCE MEASUREMENT OF GAS SENSORS WITH NICKEL(II)- AND COPPER(II)- OXIDE ACTIVE LAYERS

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Abstract

The contribution deals with semiconductor gas sensor whose active layer is based on transition-metal oxides. Thin layers (90 nm) of nickel(II)- and copper(II)- oxide were deposited onto ceramic sensor substrates equipped with interdigital electrodes for signal reading. The deposition was carried out in two or three steps: (i) sputtering by means of Ar ion beam from pure (99.99%) metal targets, (ii) following thermal oxidation (400 °C for 5 h) in air, (iii) in some cases - sputtering of Pd catalyst to the surface. Then the impedance response of produced sensors (NiO, NiO+Pd, CuO, CuO+Pd) to 1000 ppm of hydrogen and 1000 ppm of methanol vapor was measured. Impedance measurements were performed in the frequency range from 40 Hz to 100 MHz. The obtained data were depicted in Nyquist representation (i.e. imaginary vs. real part of complex impedance). These diagrams have a character of one complete and one incomplete semicircle, each of them corresponding to a parallel RC-element. It was proved, that both NiO and CuO behave like p-type semiconductors; the sensor impedance increases on exposure to reducing gases. The best sensitivity was achieved on NiO+Pd sensor - during detection of hydrogen (1000 ppm) the real part of complex impedance measured at 40 Hz increased from 120 to 350 Ω.

Keywords:

gas sensor, impedance measurement, nickel(II) oxide and copper(II) oxide

1. INTRODUCTION

Metal oxide based sensors represent widely employed group of chemical sensors used for gas sensing purposes. Working principle of a chemiresistive gas sensor is based upon the reversible interaction of the semiconductor surface with the surrounding gas resulting in significant change in electrical properties of the sensing layer. This effect can be measured as a change of the electric output quantity - the layer resistance, capacitance or work function [1]. The effect of the metal oxide – gas reaction was discovered in 50's and since then metal oxide based semiconductor sensors became industrial product with large number of manufacturers [2]. Many materials are used for the active (sensing) layer like traditional and thoroughly researched SnO₂, WO₃, TiO₂, α-Fe₂O₃ and γ-Fe₂O₃ as n-type semiconductors. P-type semiconductors like CuO, Cr₂O₃ and NiO were much less studied in the past than n-type semiconductors but currently the interest is growing.

Both nickel and copper oxides behaves like a p-type semiconductor due to intrinsic defects in the oxide structure [3,4] and both are abundant in nature. In this work we test the gas sensing properties of nickel and copper oxide films prepared by ion beam sputtering with subsequent thermal oxidation and role of surface sputtered Pd as a catalyst.

2. EXPERIMENTAL

The nickel(II)- and copper(II)- oxide layers were prepared by deposition of thin metal films followed by thermal annealing in air. The Ni and Cu layers were prepared by ion beam sputtering of the Ni and Cu target. The 99.99% pure, 1 mm thick, nickel (MaTeck GmbH, Germany) and copper (Sigma Aldrich) foils were bombarded by an intense Ar⁺ (Ar gas 99.995%, SIAD Czech limited) ion beam. Thin films were subsequently annealed in the furnace opened to air at temperature 400°C for 5 hours. Selected nickel(II)- and copper(II)-oxide films were further modified by sputtering Pd catalyst to the surface. The ion source, used for the thin film and Pd deposition, was a classical Duoplasmatron of the Von Ardenne type. Parameters of the deposition were following: external voltage (bias between anode and ground electrode) $U_E = 25$ kV, background pressure $p_B = 8 \cdot 10^{-4}$ Pa, working pressure $p = 5 \cdot 10^{-3}$ Pa, Ar⁺ ion current $I_i = 400$ μ A, time of sputtering/deposition $t = 120$ minutes and $t = 80$ minutes for Ni and Cu, respectively. Distance between the target and the substrate was 5 - 6 cm. Thickness of the resulting (as-deposited) films was estimated by RBS (Rutherford Back-Scattering) using Tandetron 4130. This work was carried out at the CANAM infrastructure of the NPI ASCR Řež. The thickness was ca 92 nm in both cases. Crystallinity of the nickel(II)- and copper(II)- oxide oxide films was analyzed by X-ray Diffraction (PAN-alytical X'Pert Pro MRD) with a parallel-beam geometry, X-ray mirror in the primary beam and long Soller slits with a flat monochromator on the diffracted beam using the Cu K α radiation. For XRD measurements the films were deposited on Si substrate.

For gas sensing experiments the Ni and Cu films were deposited on the prefabricated alumina (Al₂O₃) substrates equipped with interdigital Pt electrodes placed on the front side and Pt heating meander on the back side of the substrate. The size of the substrate was 2.5 x 2.5 mm. The impedance response of produced sensors (NiO, NiO+Pd, CuO, CuO+Pd – when present Pd acts as a catalyst) to 1000 ppm of hydrogen, 1000 ppm of methanol vapor and to saturated water vapor was measured at temperatures 300 °C and 350°C. These measurements were carried out in a gas-flow system (40 ml.min⁻¹) by ac-signal with the frequency range from 40 Hz to 100 MHz and amplitude of 100 mV. The impedance response is depicted in the form of Nyquist plots, i.e. real part of complex impedance vs. imaginary part of complex impedance, where measuring frequency is a parameter of the points in diagram. For quantification of sensing properties, a quasi-dc-sensitivity was defined as

$$S = \frac{R_{gas} - R_{air}}{R_{air}}, \quad (1)$$

where R_{air} and R_{gas} are sensor resistances obtained at frequency of 40 Hz.

3. RESULTS AND DISCUSSION

3.1 Characterization of deposited layers

Prepared metal oxide layers were analyzed by the XRD technique in the range 30 – 120°. Obtained nickel(II)-oxide spectrum is presented on the Fig. 1 where dominant NiO diffraction peaks are identified. After 5 h annealing at 400°C the amount of nickel is below detectable limit and only nickel oxide diffraction peaks are present. Polycrystalline character of the film is clearly visible with (200) as the most intense diffraction peak. By evaluating the spectrum by the Rietveld method a value of cubic nickel(II)-oxide lattice parameter was found to be $a = 4.177$ Å was obtained. Also particle size was obtained and was found to be 17.5 nm. The peak located between 50 and 60° is caused by the SiO₂/Si substrate. Similar film structure was obtained by Makhlof et al. [5] after annealing layers, prepared by spray pyrolysis from Ni(OH)₂ precursor, at 400°C for 3 hours.

In case of copper(II)-oxide 5 hour annealing at 400°C, XRD spectrum depicted on the Fig. 2, also produce polycrystalline layer. No unoxidized copper is visible. The most intense diffraction peak is diffraction from CuO (111) plane. Lattice parameters of the monoclinic copper(II)-oxide were measured to be $a = 4.678(2)$,

$b = 3.428(2)$ and $c = 5.128(2)$ Å with particle size 21.0(5) nm. Similar structure was obtained e.g. by Oral et al. [6] for copper oxide layer prepared by the sol-gel method.

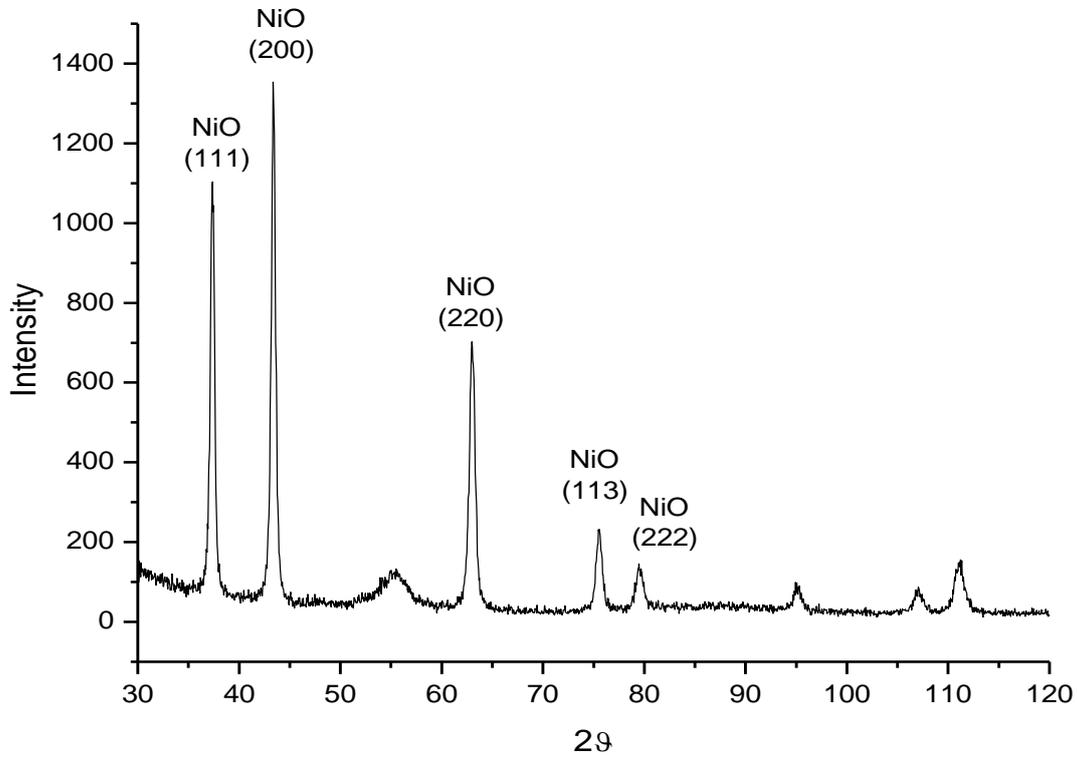


Fig. 1 The XRD spectrum of Ni thin film annealed at 400°C for 5 hours.

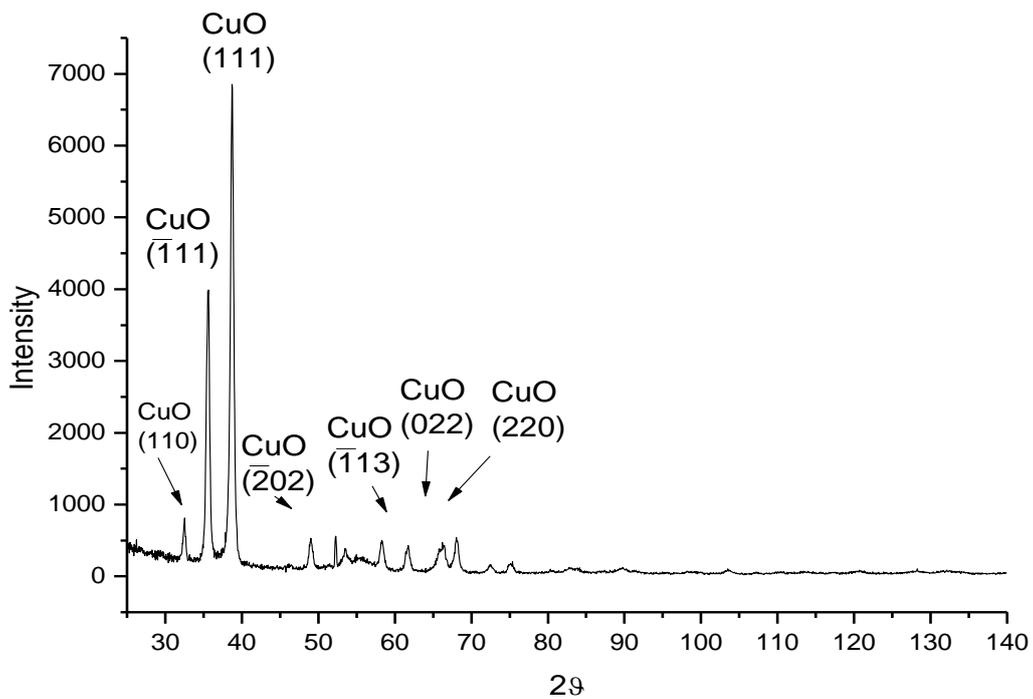


Fig. 2 The XRD spectrum of Cu film annealed at 400°C for 5 hours.

3.2 Gas sensing properties

The gas sensing properties of prepared oxidic layers are summarized in selected Nyquist plots (Figs.3 - 4) and also in calculated quasi-dc-sensitivities (Tab.1). The basic fact is that both NiO and CuO act as p-type semiconductors, i.e. in the presence of reducing gases their impedance increases. In all Nyquist diagrams there are two semicircles corresponding to a parallel RC-element in sensor equivalent circuit. Except of the cases of the lowest impedance (represented by response to air in Fig.4) the Nyquist diagrams are situated in the IV. quadrant of complex plane. It is also apparent, that there is certain drift of sensor properties - the impedance of sensor slowly increases in time. To eliminate this non-stability, longer "cycling" of sensor carried out by switching *reference gas* ↔ *detected atmosphere* would be necessary.

Table 1 Obtained sensitivities S for selected temperatures and gases; the sensitivity values were calculated using the equation (1)

Material	Temperature			
	300 °C		350 °C	
	H ₂	CH ₃ OH	H ₂	CH ₃ OH
CuO	1.07	0.52	1.10	0.70
CuO + Pd	1.77	1.55	0.87	0.88
NiO	0.29	0.08	0.42	0.19
NiO + Pd	2.85	0.24	1.45	0.30

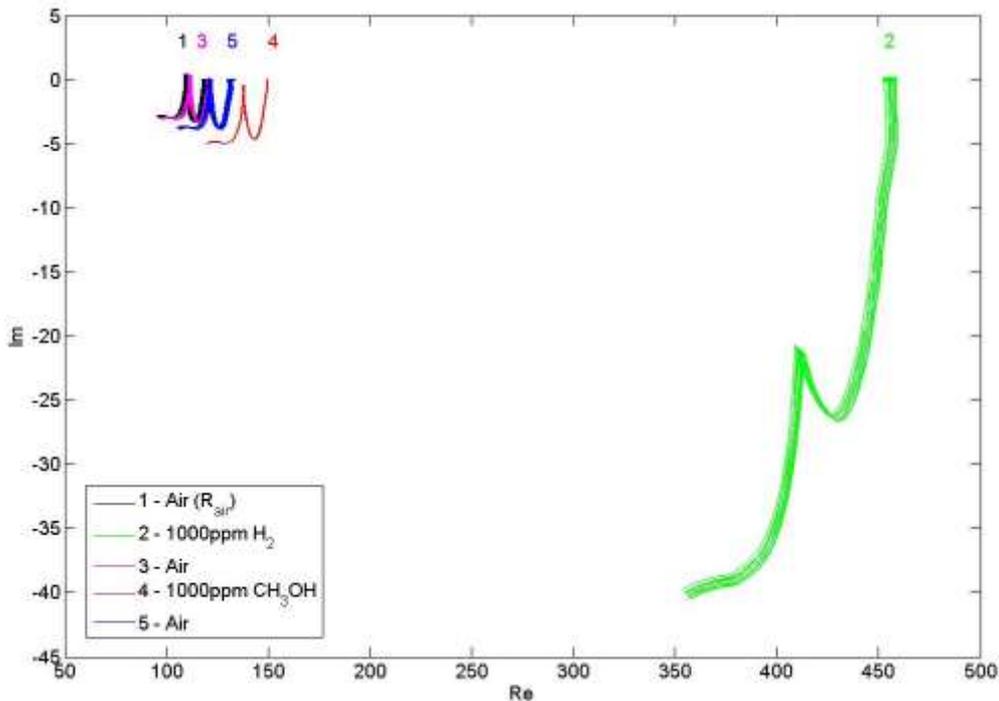


Fig. 3 Nyquist plot of NiO+Pd sensor which summarizes sensor response to 1000 ppm of hydrogen and methanol vapours at temperature 300 °C.

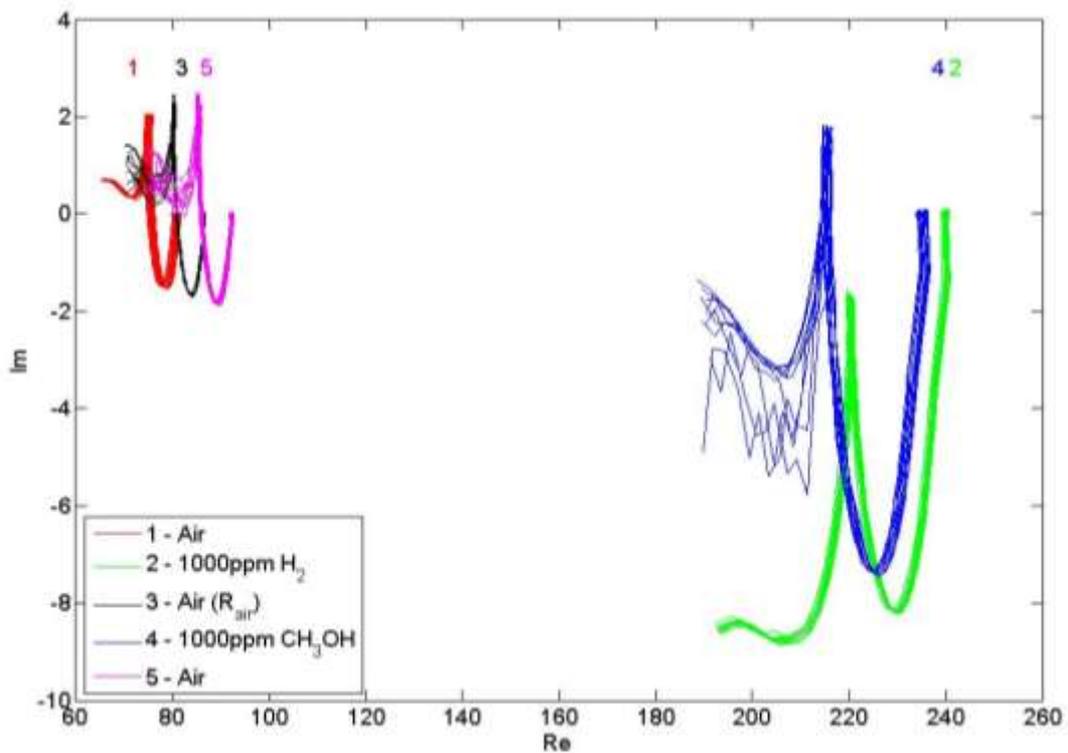


Fig. 4 Nyquist plot of CuO+Pd sensor which summarizes sensor response to 1000 ppm of hydrogen and methanol vapours.

3.3 Comparison of gas sensing properties with results published elsewhere

Effect of catalyst was on performance of nickel oxide layers was tested e.g. by Hotovy et al. [7]. Authors employed DC-magnetron sputtering for preparation of 100 nm thick NiO layers and Pt catalyst of equivalent thickness 3 nm and 5 nm was added to the surface. Maximum increase in sensitivity caused by the addition of Pt catalyst was found to be 9 times higher (for 5000 ppm H₂ at 325 °C) comparing to unmodified case. In this study an increase by factor of 9.8 at 300 °C for 1000 ppm H₂ was obtained suggesting that both Pt and Pd are very useful catalyst to optimize the nickel oxide performance.

To compare the results for methanol sensing properties of nickel oxide only one similar study was found. Dirksen et al. [8] studied effect of Li doping on sensing properties of dip coating prepared NiO. The response of both NiO and Li-doped NiO was studied in the temperature range 450 – 600 °C where maximum sensitivity to methanol was obtained at 600°C (1.094 mV.ppm⁻¹). This result cannot be easily re-calculated to sensitivity expressed according to (1), because it was evaluated as the voltage drop over a "reference" resistor connected in parallel with the studied sensor. Hence it is the property of the unique measuring configuration.

For copper oxide thin films also only few studies were published concerning the gas sensing response (significant amount of articles was, however, published for special copper oxide nanostructures like nanowires, nanorods, flower-like structures, cubes, leaflets, polyhedrons etc. prepared mostly by chemical methods). The hydrogen sensing response was reported by Nguyen et al. [9] for copper oxide layers prepared by post annealing of 100nm thick DC sputtered Cu layers. Maximum response of 3.7 for 6 % H₂ was obtained for films annealed at 400 °C. The gas response was, however, measured at 250 °C.

The methanol sensing properties were published by Parmar et al. [10]. Authors used DC-magnetron sputtering for preparation of copper oxide thin (85 nm) films. The sensitivity was defined in the same way, i.e

the equation (1) multiplied by 100. Maximum sensitivity observed was 29 % for 2500 ppm methanol at 350 °C. This is significantly lower than results presented in table (1).

4. CONCLUSIONS

Nickel and copper oxides were prepared by ion beam sputtering with subsequent thermal oxidation at 400°C for 5 hours in furnace opened to air. Both nickel(II)- and copper(II)-oxide films are of polycrystalline nature. Gas sensing properties of the films were tested using hydrogen and methanol vapors in concentration of 1000ppm at temperatures 300 °C and 350°C. Copper oxide showed overall better response for methanol than nickel oxide. Also as-annealed copper oxide showed better response than nickel oxide at both temperatures. It was shown that by addition of Pd catalyst to the surface of metal oxide the sensitivity is significantly increased. Further, optimal temperature decreased from 350°C to 300°C for hydrogen detection for both oxides.

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