Higly Sensitive Pt-TiO₂-Pt Sandwich-type Metal Oxide Gas Sensors of Hydrogen

Influence of the electrode design on the gas sensing properties

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Abstract – In this paper, we present a metal oxide-based hydrogen gas sensor with high sensitivity and short response time, operating at room temperature. Our sensors have a sandwich-like structure with a thin metal oxide layer in between the top and bottom electrode. The electrodes are in a shape of long narrow bridges, perpendicular to each other. It has been shown that narrowing the top electrode down to ~100 nm causes the sensitivity to substantially increase and reduces the response time. The sensor response (ratio R_{Air}/R_{H2}) to 1% H_2 in synthetic air can be as high as ~10^5 at room temperature, with response time of only a few seconds. A theoretical model explaining such a behavior is also proposed. The increased sensitivity of sensors with narrow top electrode is explained by non-trivial abrupt change of the charge carrier transport mechanism from thermoemission to electron drift. This change is caused by the hot electron temperature instability induced by combination of the H_2 diffusion profile under the top electrode and high intensity of electric field between the electrodes.

Keywords-hydrogen gas sensor; metal oxide; high sensitivity; room temperature.

I. INTRODUCTION

Pursuit of alternative fuels and energy carriers causes hydrogen to attract more and more attention. However, the use of hydrogen also brings its safety risks what makes the leak detection crucial. Demand for highly sensitive, fast, stable and reasonably priced hydrogen gas sensors therefore increases [1]. Operation of the chemiresistive MOS gas sensors is based on the change of conductivity due to contact with oxidizing and reducing gases [2]. Although these devices are already being used for years, their further research and improvement is possible thanks to development in the field of nanotechnology. One of the problematic properties of the MOS gas sensors is their relatively high operating temperature, usually ranging approximately from 200 to 400 °C. Heating to such temperatures is undesirable for use in hazardous explosive environments and significantly rises the power consumption. The work presented here is therefore focused on development of highly sensitive metal oxide gas sensors operating at room temperature.

In Section 2, the sample preparation process is described. In Section 3, the results of measurements performed on the prepared samples are presented and discussed.

II. SENSOR FABRICATION

The sensors were prepared as follows: On the sapphire substrate, the 100 μm wide and 20 nm thick bottom Pt electrode was formed by lift-off photolithography and DC (direct current) magnetron sputtering. The 35 nm thick TiO₂ layer was then deposited by DC reactive magnetron sputtering. Subsequently the upper Pt electrode (width ranging from 100 nm to 1100 nm on different samples) was formed on top of the TiO₂ layer by DC magnetron sputtering followed by electron beam lithography and ion beam etching. The whole sensor structure was then annealed at 600 °C for 1 hour. During the annealing process, the TiO₂ crystallizes and ohmic contacts are formed at the metal-semiconductor interfaces. The TiO₂ grain diameter was determined by XRD (X-ray diffraction) and AFM (atomic force microscopy) to be approximately 10 nm. A sketch of the final sensor profile is shown on Figure 1.

III. RESULTS AND DISCUSSION

Responses of the sensors to presence of H₂ in technical air were measured in a closed chamber in a gas flow regime, with possible target gas concentration ranging from 300 ppm to 10 000 ppm (parts per million) regulated by two Red-y mass flow controllers. For wider (over ~300 nm) top electrodes,
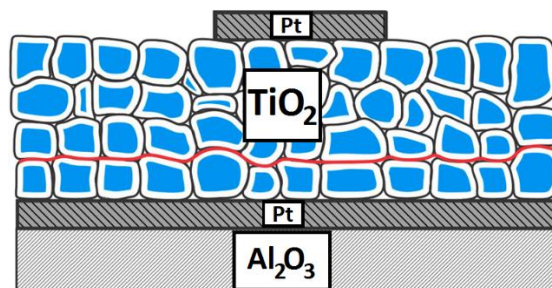

Figure 1. Illustration of the sensor cross section. Schematic figure of the sandwich-type sensor with crossed electrodes.
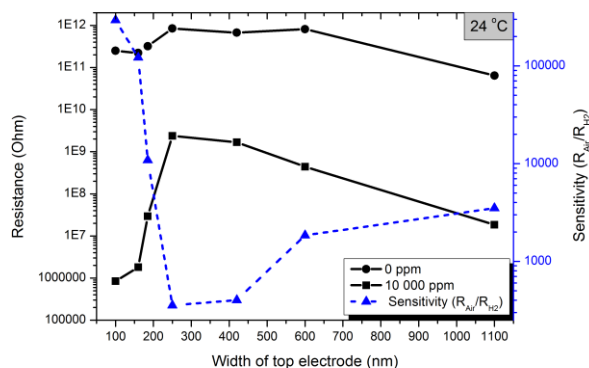
Figure 2. Dependence of the sensor resistance on the top electrode width for 0 and 10000 ppm H_2 in technical air (left y axis). Dependence of sensitivity on the top electrode width (right y axis).

Figure 3. Response of the sensor with 500-bridge top electrode on different concentrations of H_2 in technical air at room temperature.

the resistance of the sensors was observed to slightly increase with the decreasing width of the top electrode due to its smaller cross section. However, a steep decrease of the sensor resistance at 10000 ppm of H_2 was observed for sensors with the top electrode width below ~200 nm even at room temperature (Figure 2). Response of the sensor (ratio R_{Air}/R_{H2}) with 100 nm wide top electrode to 10000 ppm H_2 in synthetic air was higher than ~10^5. We explain such high response of the sensors with narrow (~ 100 nm) top electrode by a combination of two effects. First, for such narrow electrodes the diffusion length of H_2 molecules is large enough to create high concentration profile even directly under the top electrode and the height of the inter-grain energy barriers in this region is decreased. At the same time, the intensity of the electric field reaches its maximum in this region. Combination of these two effects induces the hot electron temperature instability, which will be explained further. In general, relation between the temperature of electron gas and the temperature of crystal lattice is given by the energy balance equation [3]

$$\frac{k_b T_e}{2} = \frac{k_b T}{2} + j_e F \tau_e$$

where j_e is the electron current density, F is the electric field intensity and τ_e is the energy relaxation time. The term $j_e F \tau_e$, which represents the electric field induced heating of the electron gas, is usually negligible. In our situation, this term rises significantly and the electron temperature T_e is no more equal to the temperature of the crystal lattice T.
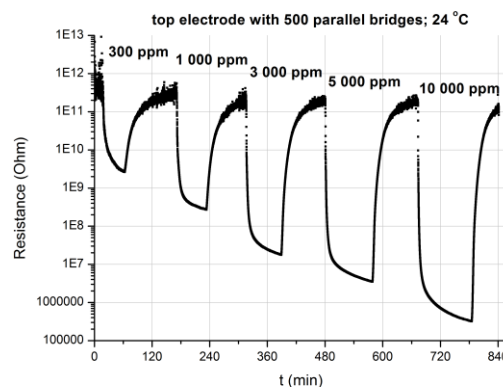
Rise of the electron gas temperature well above the level of crystal lattice temperature causes the abrupt change of the charge carrier transport mechanism from thermionic emission to electron drift [4].

Problematic is the high resistance of our sensors, which reaches values over our measurement limit of ~ 10^{11} Ohm without the presence of hydrogen. This decreases the measurable response of such sensors, especially for low H_2 concentrations. A solution for too high resistivity of TiO_2 material has been proposed through doping [5]. To solve this problem in our case, sensors with the top electrode consisting of many parallel bridges were fabricated. This type of electrode is expected to decrease the overall resistance of the whole structure and allows us to detect lower concentrations of hydrogen. Preliminary results obtained on the sensor of this type, with a 500-bridge top electrode, are shown in Figure 3.

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