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A copper(II) oxide – tin dioxide heterojunction sensor for the detection of hydrogen sulfide

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Abstract

We present a novel sensor concept for highly sensitive detection of hydrogen sulfide (H_2S) using the heterojunction copper(II) oxide - tin dioxide. Unlike other approaches, we use a thin film stack of the semiconductors where the CuO completely covers the SnO_2. The basic idea hereby is to prevent the SnO_2-layer from the contact of reactive gases in order to reduce cross sensitivities. The films were prepared by reactive electron beam evaporation of copper and tin oxide. Structural and morphological analyses of the films were carried out. The sensitivity, selectivity and stability of the device has been evaluated using several reactive gases including long term tests. The sensor is extremely sensitive to traces of H_2S. A slight cross sensitivity to NO_2 is observed.

Key words: gas sensing, hydrogen sulfide, copper(II) oxide, tin dioxide, pn-junction, selectivity

Introduction

Hydrogen sulfide (H_2S) is a highly toxic and corrosive gas whose odor is usually associated with rotten eggs. In the harsh environment of oil- / gas extraction, gas warning systems are necessary for employees safety. Typical concentration levels in applications for H_2S sensors range from sub-ppm to thousands of ppm. A review of the various detection methods can be found in [1]. However, metal oxide gas sensors, fabricated on silicon substrates provide compatibility with common microelectronics and MEMS systems and enable low cost fabrication. Copper(II) oxide (CuO) is well known for its highly specific interaction with hydrogen sulfide, namely the formation of sulfidic structures [2]: $CuO + H_2S \rightarrow CuS + H_2O$.

Beside research activities to use “pure” CuO for H_2S sensors [3], various works on copper and copper oxide as dopant or additive material in tin dioxide (SnO_2) sensors were published. The idea to markedly enhanced response of SnO_2 sensing elements towards H_2S exposure when doped with 5 w% CuO was published in 1992 [2]. Several experimental and theoretical studies followed. The term of so-called heterojunction sensor was assigned to the CuO:SnO_2 sensing effect. This originates from the effect that n-SnO_2 and p-CuO form pn-junctions and a corresponding depletion region. When exposed towards H_2S, CuO gets converted to CuS and the space charge region consequently collapses, resulting in a drastic increase of conductivity. Beside simple mixing of both materials in a thick film, SnO_2 films with CuO islands on top, heterostructures of CuO-SnO_2 thin films [4], CuO doped SnO_2 thin films and CuO modified SnO_2 nanoribbons [5] have been reported. We present an approach featuring a stack of a CuO and a highly densed SnO_2 thin film (fig 1).

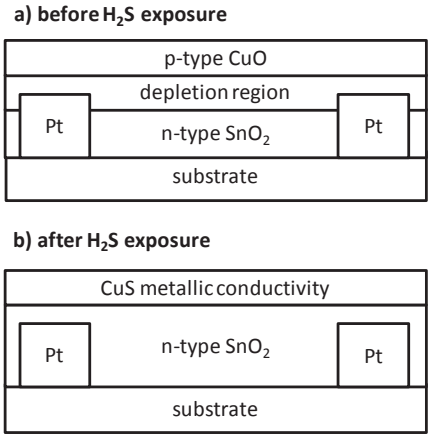

Fig.1. a) “Stack sensor” approach: P-type CuO and highly dense n-type SnO_2 thin film form a pn-junction. b) Due to H_2S exposure the CuO is converted to CuS and the depletion region collapses.

Experimental

A microscope picture of the sensor chip fabricated on silicon substrate is shown in fig 2. An oxidized silicon wafer is used as substrate. A 200 nm thick Pt film with a 25 nm Ta adhesion layer has been deposited and patterned to act as electrodes, heater and temperature sensor. The metal oxides are deposited and patterned by use of the lift-off method. The SnO_2 films, of 60 nm thickness, and the CuO films (20 nm thick) were deposited by reactive e-beam evaporation of SnO or. copper and a subsequent oxidation. The CuO:SnO_2 stack was stabilized by annealing at 700 °C for one hour in air.

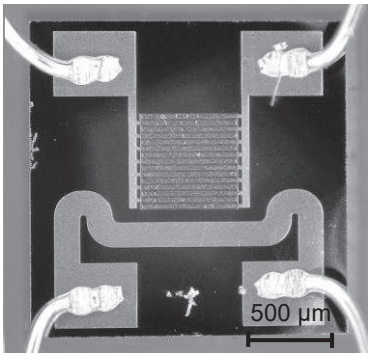

Fig.2. Microscope picture of the fabricated sensor chip (2x2 mm²). Due to the high thermal conductivity of the silicon substrate, the resistive heating via a Pt:Ta heater reveals a homogeneous temperature distribution along the gas sensitive layer. Interdigitated Pt:Ta electrodes with a spacing of 10 µm in between them provide the interface to determine the electrical conductivity of the CuO:SnO_2-layer.

The morphological characteristics of all fabricated layers were investigated with X-ray analysis and scanning electron microscopy. The processed wafers were diced. The chips are mounted into TO5-housings and are connected using a 35 µm thick gold wire by ultrasonic bonding. For a better thermal isolation of the chip against the metal housing a glass spacer is used. Each mounted sensor was preheated in air for 48 h at 300 °C before the gas measurements. The response of sensors to different concentrations of H_2S, NO_2, CO and ethanol was measured at a number of working temperatures. Fig. 3 shows the typical response of such sensors to these gases in synthetic air (50 % r.h., 25 °C). The working temperature was 290 °C. Significant changes in resistance are observed only for sensors exposed to H_2S and NO_2. The responses time (t_{90}) is 15 sec for 2 ppm H_2S with a detection limit of 0.2 ppm and a recovery time (t_{10}) of 7 min. The NO_2-response is two to three powers of ten smaller as the sensitivity to H_2S. The response to H_2S concentrations in the lower ppm range is extremly high due to the reversible transistion of CuO to CuS. The NO_2 reaction is the “normal” charge carrier exchange of oxidizing gases with p-type semiconducing metal oxide. Long term tests of the sensors over month in the gas lab and at the rooftop of the Dräger building in Lübeck reveals a slight drift of the resistance in air and the sensitivity to lower values.

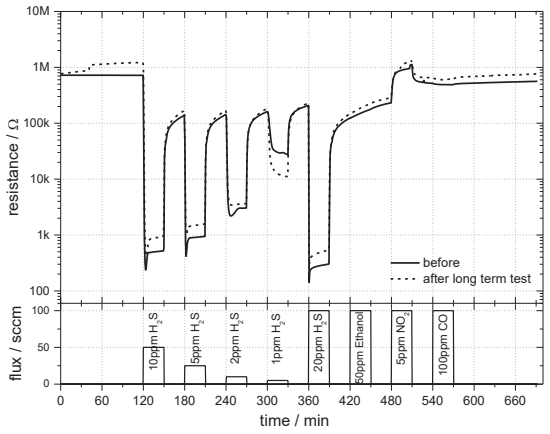

Fig.3. Gas response of CuO:SnO_2 heterojunction gas sensors at a working temperature of 290 °C exposed to different test gases in humid synthetic air (50 % r.h. @ 23 °C). Diagrammed is the gas response towards the same test gases before and after a long term test of 88 days. The lower diagram shows the test gas flow during the experiments.

Conclusion

Our research revealed that a stacked SnO_2 CuO heterojunction sensor shows a high sensitivity to H_2S. An insignificant NO_2 and O_3-response is observed. No cross sensitivity to traces of SO_2, H_2, NH_3, CH_4 are measured. Humidity (20 to 80 % r.h.@RT) has no significant influence on the sensor response.

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