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Gas Sensing Performance of CuO Sensors Functionalized with Different Stabilized Au-NP

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Summary:
In this work, we present chemical nanosensors based on ultrathin CuO/Cu_2O films, which are fabricated by thermal evaporation and subsequent oxidation on SiN-based micro-hotplate chips. The sensors are tested against various target gases like carbon monoxide (CO), carbon dioxide (CO_2), and hydrocarbons (HC_{mix}). The CuO/Cu_2O films are functionalized with Au nanoparticles (Au-NPs) stabilized with different types of ligands: PEG-MUA, MPA and citrate. While the Au-NPs clearly increase the sensor performance in particular for CO_2, we have found that the ligands have a significant impact.

Keywords: metal oxide, CuO, nanomaterials, nanoparticles, ligands, gas sensors

Introduction

Chemical sensing of harmful or toxic gases, such as Volatile Organic Compounds (VOCs), CO_2, or CO, which have a significant negative impact on human health, has become a vital necessity for indoor and outdoor air quality (AQ) monitoring. Conductometric gas sensors rely on changes of the electrical conductance of a gas sensitive material due to the surrounding gas. Mostly, metal oxides like SnO_2, ZnO or CuO are used because of their high sensitivity to a large variety of gases [1]. The response of such sensors can be tailored by surface functionalization with metallic nanoparticles (e.g. Au, Pd, or Pt) which is a very promising approach to achieve a high degree of selectivity [2, 3]. Recently, we have successfully employed Au-NPs solutions for functionalization of CuO-based gas sensors for improved CO_2 sensing [4]. In this paper we evaluate the impact of three different types of ligands used for stabilizing the Au-NPs on the sensor performance for CO, CO_2, and HC_{mix}.

Sensor Fabrication

The gas sensors are fabricated by means of photolithography, thermal evaporation of a Cu-layer with a thickness of 500 nm, and a lift-off process on a micro-hotplate chip (see Fig.1). The circularly shaped (diameter 450 µm) Cu layer is thermally oxidized on a hotplate at 450 °C for 4 h leading to a stoichiometric mixed phase of CuO/Cu_2O-films.

Au-NP Functionalization

The Cu_xO gas sensing films have been functionalized with Au nanoparticles (average diameter 13 nm, synthesized by Fraunhofer CAN) to improve the sensor performance. The Au-NPs are dissolved in water and have been stabilized with three different types of ligands: (i) MPA (3-mercaptopropionic acid) (ii) citrate, and (iii) PEG-MUA (polyethylene glycol, 11-mercaptoundecanoic acid). The functionalization is performed by drop coating (0.2 µl) the Cu_xO-sensors with the NP solutions.

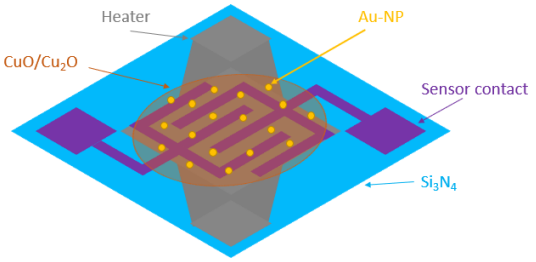

Fig. 1 Illustration of an Au-NP functionalized Cu_xO film-based gas sensor.

Sensor Characterization & Results

The sensor devices have been operated at 300 °C and tested against CO, CO_2 and HC_{mix} (equal mixture of 500 ppm of acetylene, ethane, ethene and propene). Synthetic air with 50 % relative humidity (r.h.) has been employed as

background gas. Bare Cu_xO-sensors, and Cu_xO sensors functionalized with MPA, citrate, and PEG-MUA stabilized Au-NPs have been compared. Fig.2 shows exemplarily the electrical resistance behavior of all sensors when exposed to 1000, 2000, and 4000 ppm CO_2.

Fig.3 compares the responses of all sensors towards 20 ppm CO, 4000 ppm CO_2 and 20 ppm HC_{mix}. The response to CO is slightly increased in case of citrate and PEG-MUA. Cu_xO sensor functionalized with citrate stabilized Au-NPs exhibits the highest response (39 %) towards CO_2. MPA stabilized Au-NP result in a significant response (10 %) to CO_2; the PEG-MUA stabilized Au-NP show a small (2 %) CO_2 response. Bare, unfunctionalized Cu_xO sensors have no CO_2 response at all. All Au-NP functionalized sensors exhibit a significantly increased response (18 – 22 %) towards HC_{mix}.

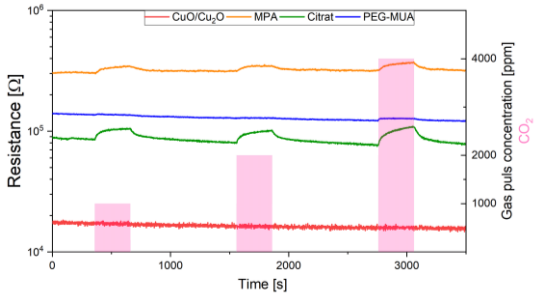

Fig. 2 Resistance measurement during exposure to 1000 / 2000 / 4000 ppm CO_2 at 300 °C operation temperature and 50% r.h.

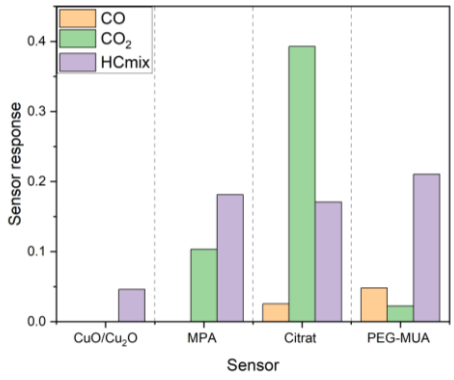

Fig. 3 Sensor response towards 20 ppm CO, 4000 ppm CO_2 and 20 ppm HC_{mix} at 300 °C operation temperature and 50% r.h.

Discussion & Conclusion

While the Au-NPs clearly increase the sensor performance in particular for CO_2, also the ligands have a significant impact. on the sensing behavior of Cu_xO-based sensors. For the test gas mixture HC_{mix} the response is almost the same for all three types of ligands, while the citrate stabilized Au-NPs are clearly the best choice for optimizing the CO_2 sensitivity.
The different influence of the ligands on the CO_2 and HC_{mix} reponse is not understood yet: Organic residuals due to insufficient thermal degradation of the ligands at 300 °C operation might be responsible for this behavior by hampering the interaction of gas molecules with the Au-NPs and the Cu_xO surface. We expect that citrate is already dissociated at 300 °C. This would explain the high response for CO_2 for the citrate stabilized Au-NPs, but not the equally increased response towards HC_{mix} for all three types of ligands. Further investigations e.g. carefully increasing the operating temperature without decomposing the Au-NPs are necessary to reveal the influence of the ligand chemistry. From our results we conclude that metallic NP-systems have to be very carefully designed in order to fully utilize the potential of NP-functionalization for performance optimization.

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