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Optimization study for work function based CO\textsubscript{2} sensing using CuO-nanoparticles in respect to humidity and temperature

N.B. Tanvir\textsuperscript{a,b}, O. Yurchenko\textsuperscript{a,b,*}, G. Urban\textsuperscript{b}

\textsuperscript{a}University of Freiburg, FMF, Stefan Meier Str. 21, 79104 Freiburg, Germany
\textsuperscript{b}University of Freiburg, IMTEK, Georges-Koehler-Allee 103, 79110 Freiburg, Germany

Abstract

The detection of CO\textsubscript{2}, based on metal oxide nanoparticles has a lot of potential due to their higher surface area and easy implementation in microsystem devices. In this work, we investigated semiconducting copper oxide nanoparticles (CuO-NPs) with respect to different conditions affecting the stability and sensitivity of the CO\textsubscript{2} response. The adsorption induced changes have been recorded through work function (WF) based alterations using Kelvin probe measurements. It is shown that an optimized CO\textsubscript{2}-sensing behavior for CuO-NPs by using combined effect of humidity and temperature is achievable and can play a pivotal role towards the development of low cost CO\textsubscript{2} gas sensors.

Keywords: Work function; Gas sensor; Metal oxides; CO\textsubscript{2} sensors; Kelvin method

1. Introduction

CO\textsubscript{2} as a target gas has great relevance for both indoor and outdoor air quality monitoring. However the reversible interaction of CO\textsubscript{2} with sensing material is difficult to achieve and has many chemical and environmental challenges. In the modern era, the detection of CO\textsubscript{2}-concentration can be performed using optical and electrochemical sensors, however the optical sensors have been proved to be too expensive and the electrochemical sensors have shown serious reliability issues [1]. The gas sensors based on semiconducting metal oxide (MO\textsubscript{x}) layers have been the center of attraction in the last decade due to their high sensitivity to a number of gases and...
effective cost to performance ratio. However, the implementation of gas sensors based on MO\textsubscript{X} towards industrial applications has still a lot of challenges to overcome [2]. These challenges include signal stability over time, cross-sensitivity to different environmental factors and high power consumption. Thus moving towards energy conservation, work function readout is considered to be one of the most promising and challenging principle for gas sensing applications [3]. Furthermore, the principle of work function readout based gas sensing, can be directly deployed into sensor devices such as suspended-gate field effect transistor (SGFET) [4]. The principle of work function readout can be characterized using Kelvin probe measurements which detect the changes in the contact potential difference (CPD) between the reference electrode and the sensing material whose work function change needs to be characterized when exposed to certain gases. This concept of work function readout using kelvin probe measurements has already been utilized for many sensing materials in response to different target gases [5–7]. In this work we investigated \textit{p}-type semiconducting CuO-NPs as CO\textsubscript{2} gas sensitive material. CuO has already been reported to be sensitive for target gases such as CO, NO\textsubscript{2} and H\textsubscript{2}S and has been utilized in many other applications [8,9]. In our previous work, it was found that the sensitivity of CuO-NPs for CO\textsubscript{2}-sensing is highly dependent on the humidity level in the environment [10]. Thus in this work, the combined effect of humidity and temperature on CO\textsubscript{2}-sensing is investigated and optimized conditions to achieve the maximum signal response have been presented.

2. Experimental

The Kelvin probe samples were prepared using silicon substrates having a size of 4x4 mm. The silicon substrates were sputtered with smooth titanium nitride (TiN) layer having a thickness of 200 nm. The purpose of TiN-layers is to act as a backing electrode and is found out to be inert to CO\textsubscript{2}-exposure. The investigated CuO-NPs were prepared in an aqueous dispersion and were drop coated on top of TiN-back electrode. A schematic representation of kelvin probe sample along with gold (Au) reference electrode is presented in figure 1.

The Kelvin probe setup was procured from Besocke which is driven piezo electrically and uses the principle of lock-in amplifier for effective gas sensing measurements [11]. All the measurements were performed in synthetic air consisting of 20% oxygen and 80% nitrogen at a total flow of 1000 ml/min with controlled relative humidity (\textit{r.h.}).

3. Results and discussion

The change in work function response (\(\Delta\Phi\)) of CuO-NPs layer in dependence to CO\textsubscript{2}-concentration for varying temperature conditions (RT \(\leq T \leq 110 \, ^\circ C\)) and at two different relative humidity levels (\(r.\text{h.} = 45\%\) and 60\%) is depicted in figure 2. The CO\textsubscript{2}-concentrations are varied in the range of 400 to 4000 ppm with each bar graph representing an increment of 1000 ppm, except for the first step where the concentration is changed from 400 ppm (normal CO\textsubscript{2} background in the air) to 1000 ppm. In case of room temperature, the change in the work function response of CuO-NPs during CO\textsubscript{2}-exposure has been observed to be higher for the sample exposed to CO\textsubscript{2} in the presence of constant humidity level of 45\% (with the maximum signal height of \(\Delta\Phi_{\text{PCO}_2=4000} = 86\) mV) as compared

![Fig. 1. Kelvin probe sample along with Au-reference electrode (a) Actual image; (b) Cross-sectional sketch.](image-url)
Fig. 2. Kelvin probe measurements for work function response of CuO-NPs to changing CO\(_2\) exposures (400 to 4000 ppm) at varying temperature (room temperature to 110°C) for two different relative humidity levels (45% and 60%).

This decrease in work function for CuO-NPs at relatively higher humidity levels can be attributed to the formation of water film which decelerates the diffusion of CO\(_2\) towards gas active centers. As the temperature increases from room temperature, the change in the work function response at the beginning increases as well for the measurements at both relative humidity levels. This increase in temperature has a maximum at 50°C and starts decreasing as the temperature rises beyond 50°C (figure 3a). However it is interesting to notice that at \(T = 65°C\), the influence of humidity is negligible but the work...

Fig. 3. (a) Work function response of CuO-NPs as a function of temperature at two different humidity levels for a CO\(_2\) exposure of 400 to 4000 ppm; (b) Work function response times as a function of temperature.
function sensitivity ($\Delta \phi_{pCO_2=4000} = 95 \text{ mV}$) is still higher than it is observed at the room temperature ($\Delta \phi_{pCO_2=4000} = 86 \text{ mV}$). Thus it can be concluded that the increase in temperature acts as an opposing factor to humidity dependency and can be used to nullify the humidity induced variation of the work function response. Nevertheless, the increase in temperature beyond 65°C imposes a negative impact on the work function sensitivity and results in the lower signal response as compared to the one observed at room temperature.

The dependence of CuO-NPs response time on temperature when exposed to CO₂-concentration of 400 to 4000 ppm and at two different relative humidity levels ($r.h. = 45\%$ and $60\%$) is depicted in figure 3b. At room temperature, the response times of the sample treated at $r.h. = 45\%$ is detected to be faster than the one treated at $r.h. = 60\%$. This behavior can again be attributed to the formation of water film resulting in not only lower work function response but also slower response times. However it is interesting to notice that this response time dependency on humidity levels is negligible in case of very high temperature levels ($T \geq 95^\circ\text{C}$) and approximately no differentiation in the two signals can be detected.

4. Conclusions

In this work we have investigated the gas sensing behavior of CuO-NPs towards CO₂ by the means of work function readout based on Kelvin probe measurements. The sensitivity of CuO-NPs is found out to be dependent on both relative humidity level in the environment and the temperature. The measurements indicate that the highest CO₂ change in work function response is achievable at the temperature of 50°C; however the influence of humidity is still quite high on CO₂ sensing at this temperature. This optimized effect of combining temperature and humidity can be achieved at the temperature of 65°C, where the influence of humidity is negligible whereas the CO₂ sensitivity is found out to be higher than at the room temperature. In future, more detailed investigations on humidity and temperature influence, selectivity analysis of CuO-NPs for different gases along with the detailed study of the reaction mechanism for CO₂ sensing will be performed.

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References