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H₂S Sensing in Dry and Humid H₂ Environment with p-type CuO Thick Film Gas Sensors

Barbara Urasinska-Wojcik, Julian W. Gardner, *Senior Member, IEEE*

Abstract—In this study we report for the first time detailed analysis of a *p*-type copper oxide based MEMS gas sensor to low ppm levels of hydrogen sulfide in a pure hydrogen environment and under various operating temperatures and humidity conditions. The *p*-type metal oxide sensing response to hydrogen sulfide seems to be reasonably stable and reversible under both dry and humid hydrogen ambiances. The response was sensitive to significant changes in ambient humidity, but was found to have no cross-sensitivity to carbon monoxide in dry and humid hydrogen. We believe that these copper oxide gas sensors could be exploited in harsh applications, i.e. in a gas contamination detector for testing the quality of hydrogen fuel.

Index Terms— gas sensor, hydrogen environment, hydrogen sulfide

I. INTRODUCTION

METAL OXIDE (MOX) based gas sensors have attracted considerable attention due to their potential application in monitoring poisonous gases in air [1]. *n*-type semiconducting metal oxide materials - such as WO₃, SnO₂, and ZnO - have been intensely studied and are exploited in commercial gas sensors [2]. In contrast, the chemiresistors fabricated using *p*-type oxide semiconductors - such as NiO, Co₃O₄ and CuO - have received relatively little attention to date and further studies are required to understand the properties of these materials and their combinations for sensing applications [3]. It is also well known that surface reactions that control detection of target gases by semiconducting metal oxides operating at temperatures below 500 °C generally involve changes in the concentration of surface oxygen species such as O₂⁻, O⁻ or O²⁻, which are stable over a different temperature range [4-6]. Only a few reports have been published on the mechanism of the response of MOX sensors in the absence or at trace levels of oxygen concentrations and these sensors employ mainly *n*-type metal oxides, such as WO₃ and SnO₂ [7-11]. Among *p*-type MOX semiconductors, CuO has received some attention for hydrogen sulfide (H₂S) detection in air [12-16]. This gas is one of the highly toxic and flammable gases and is widely needed in industrial processes. Exposure to it affects our

nervous system and causes loss of consciousness [17]. It is also a common impurity along with carbon monoxide and ammonia, in hydrogen fuel that typically feeds a polymer electrolyte membrane (PEM) fuel cell stack for automotive and stationary power generation applications [18-20]. These applications of H₂S detection require sensors to operate under harsh conditions, such as absence or low oxygen content and elevated humidity and temperature environments.

In a previous study we showed that CuO, a *p*-type semiconductor, is a good candidate for detecting of H₂S at low concentration under harsh conditions such as a pure hydrogen environment and high relative humidity (RH) levels [21]. This has been achieved using thermally modulated CuO based low-power MEMS gas sensors [22]. In this paper, we present the results from direct current (DC) measurements. We show for the first time the response to H₂S in dry and humid pure hydrogen environment over wide range of operating temperature.

II. EXPERIMENTAL METHODS

A. DC Measurements

The typical sensing method for semiconducting metal oxide gas sensors is the measurement of DC resistance or conductance. In this study, a low power MEMS based micro-hotplate gas sensor was used, and the operating temperature was controlled by an adjustable constant current circuit. The micro-hotplate is shown in Figure 1(a) (CCS09C, Cambridge CMOS Sensors Ltd, now ams Sensors UK Ltd). The MEMS structure was fabricated in a commercial foundry and is based on silicon on insulator (SOI) technology [23]. In the membrane structure, a tungsten resistive micro-heater is embedded within a 5 µm thick metal/oxide stack ensuring a low DC power consumption (e.g. 65 mW at 600 °C). The membrane was fabricated via a post CMOS deep reactive ion etch (DRIE) and both mechanically supports and thermally isolates the heater from the sidewalls. The MEMS micro-hotplate can reach temperatures well in excess of 500 °C and has a sub-5 V controlled temperature ramp capability of 30 ms heating time and 60 ms cooling time from ambient to 500 °C.

B. Sensor Fabrication

In this work, CuO powder (New Metals and Chemicals Ltd) was mixed with an organic dispersant ESL 400 to obtain a paste. The weight ratio of the powder and the organic

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dispersant was 1:2. The paste was drop cast onto the 1 mm × 1 mm silicon die, which consisted of gold interdigitated electrodes on top of the membrane as a single-chip solution (Figure 1(a) and 1(b)). After deposition of the CuO paste, the substrate was left to dry in air at room temperature for ~12 h followed by annealing at 450 °C using the sensor's heater for 2 h under ambient air. This annealing process was optimized to obtain the required sensor element consisting of *p*-type CuO. Figure 2 shows a scanning electron microscopy (SEM) (The Zeiss, Model: SUPRA 55VP) image of the annealed paste. The film exhibited large numbers microparticles having average grain size <1 μm.

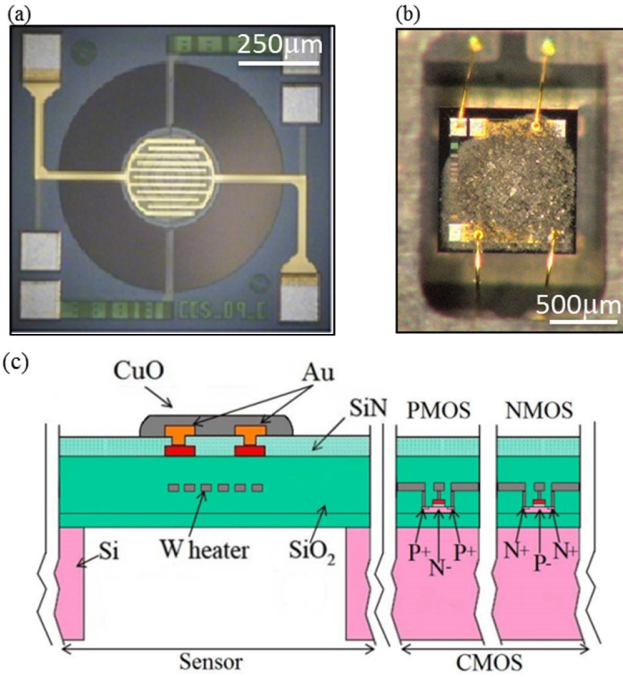


Fig. 1. (a) Optical microscopy image of a bare micro-hotplate (CCS09C, CCS Ltd, now ams Sensors Ltd). (b) Optical microscopy image of a device after deposition of CuO layer. (c) Schematic cross-section of a CuO resistor on an SOI CMOS micro-hotplate with adjacent CMOS electronic cells, which was exposed to impurities in H₂.

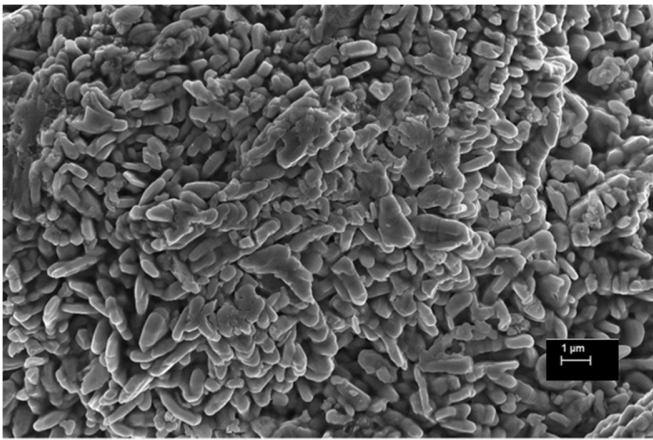


Fig. 2. (a) SEM image of the surface of the deposited *p*-type CuO material.

C. Gas sensing measurements

The gas sensing measurements were performed at the Microsensors and Bioelectronics Laboratory at the University of Warwick using a fully-automated custom rig as illustrated earlier in [11, 24]. The CMOS microhotplate substrates were connected to a custom made printed circuit board. Both the micro-0.3heater and chemiresistor were driven/measured using National Instruments data acquisition (DAQ) module (NI-6343) hardware and software. The gas sensing properties of the sensor element were characterized using a flow type sensing measurements apparatus. The gas sensor was placed inside an aluminium sample chamber equipped with standard Swagelock™ gas inlet and outlet connectors. The devices were tested in a static (isothermal) mode where H₂S in H₂ (Research Grade N5.5 containing trace O₂ concentration <1 ppm) and pure H₂ (Zero Grade N4.5 containing trace O₂ level ≤5 ppm) were introduced alternately into the sample chamber for 4 min in steps of varying concentrations of 1, 2, 4, 6, 8, and 10 ppm. The total gas flow rate was 300 ml/min and the measurements were performed using different sensor operating temperatures (150-400 °C) in dry conditions and then at 25 %, 50 %, 60%, and 75% relative humidity (RH) controlled using a commercial sensor (Bosh, BME280). The average temperature inside the test chamber was 23.0 ± 0.5 °C. LabView (NI, version 13.0) interface allowed fully automated control of the digital mass flow controllers of the gas testing system. The response (*S*) from this *p*-type sensor was calculated using the following relation for reducing gases:

$$S = \frac{R_g}{R_0} \quad (1)$$

where R_g and R_0 correspond to the electrical resistance of sensing material (copper oxide) in test (H₂S) and reference (H₂) gases, respectively, and will be indicated further as R_{H_2S}/R_{H_2} . Response (t_{90}) and recovery (t_{10}) times were calculated as the time required by the sensor to reach 90 % and 10 % of its saturation and original values, respectively.

III. RESULTS AND DISCUSSIONS

The goal of this work is to demonstrate for the first time detailed analysis of *p*-type CuO based CMOS gas sensors exposed to low ppm levels of H₂S in pure hydrogen environment and high RH levels.

In order to determine the optimum conditions of the H₂S detection in H₂, a systematic investigation of operating temperature and humidity effects on gas sensing properties of CuO were performed. When these *p*-type sensors were exposed to H₂S gas, the resistance of the CuO sensor element increased with increasing concentration of the gas. This is a typical response of a *p*-type oxide towards a reducing gas, leading to $R_g > R_0$.

A. Detection of H₂S impurities in dry H₂ environment

Initially the CuO based sensors were exposed to H₂S in dry H₂. Figure 3(a) presents an example time-dependent resistance

change of CuO sensors to H₂S pulses in dry H₂ at 350 °C which was the highest obtained in dry environment, and the average values of sensors response at 1 ppm and 10 ppm are calculated to be 1.19 ± 0.06 and 1.27 ± 0.05 , respectively. The average responses of the sensors to the target gas in dry H₂ environment at the operating temperature ranging from 150 °C to 400 °C are shown in Figure 3(b). Sensors response was almost unchanged for lower heater temperatures between 150 °C and 250 °C and gradually increased with further increases in temperature. The highest response in these conditions was obtained at 350 °C. The response of semiconductor metal oxide gas sensor is empirically represented by the following power law [25]:

$$S = 1 + A_g \cdot C_g^\beta \quad (2)$$

where A_g is a prefactor that depends upon the type of the sensing material, the operating temperature, and the type of gas interacting with the sensor. C_g is the gas concentration and β is the exponent factor, and its ideal value of 0.5 or 1 depends on the charge state of surface oxygen species and the stoichiometry of the elementary reactions on the surface [26]. According to the above power law Eq. (2), the value of β from the experimentally measured response versus concentration plot (Figure 3(b)) was 0.822 ± 0.003 for measurements performed at 150 °C suggesting that the chemisorbed surface oxygen species are nearly all in the O_2^- state. The values of β factor for measurements performed between 200 °C and 400 °C are nearer to the fractional value of 0.5 suggesting that the chemisorbed oxygen species are in O^- state. These power law exponents β deviates from the fractional values of 0.5 and 1, respectively, and this can be due to several factors. Primarily, it is very difficult to obtain an ideal homogenous packing of the crystal grains throughout the whole sensing layer. This depends on the conditions used during preparation and operation of sensors having direct impact on sensors microstructures such as pore size and distributions. As a result of this, there are some domains present within the layer which are gas-insensitive and are located between gas sensitive junctions obeying the power law response characteristics. Therefore, the ratio of gas sensitive and insensitive parts within the sensing layer may vary considerably and has impact on the value of the response exponent. Our gas response values increase with the gas concentration (Figure 3(b)). However, in the temperature range from 350 °C to 400 °C these values are mainly dependent on the gas concentration below 6 ppm before sensors reach the saturation stage gradually at higher H₂S levels (> 6 ppm). The available surface area of the CuO film is enough to let gas molecules interact at low H₂S concentrations, and at higher temperature range we can assume that there are insufficient adsorption sites for higher gas concentrations and H₂S gas molecules have to compete for these adsorption sites.

TABLE I
AVERAGE RESPONSE AND RECOVERY TIMES TO H₂S IN DRY H₂ WITH STANDARD DEVIATION (STD) FROM 3 SENSORS

Concentration [PPM]	t_{90} [s]						t_{10} [s]							
	[°C]	150	200	250	300	350	400	[°C]	150	200	250	300	350	400
2		58, 75, 73, 54, 24, 91							140, 149, 93, 125, 51, 89					
		STD 4, 19, 10, 14, 3, 2							STD 4, 15, 17, 18, 1, 15					
4		90, 76, 65, 45, 15, 76							119, 157, 80, 101, 46, 67					
		STD 15, 19, 10, 11, 1, 15							STD 14, 8, 8, 3, 1, 14					
6		92, 70, 46, 46, 11, 42							116, 118, 85, 110, 42, 95					
		STD 21, 15, 3, 12, 2, 3							STD 11, 8, 9, 11, 8, 1					
8		57, 88, 48, 38, 10, 44							138, 136, 85, 120, 37, 68					
		STD 14, 11, 6, 12, 3, 14							STD 4, 20, 12, 13, 12, 26					
10		70, 76, 36, 39, 8, 45							129, 158, 82, 123, 47, 69					
		STD 15, 5, 8, 1, 2, 7							STD 8, 20, 1, 3, 9, 29					

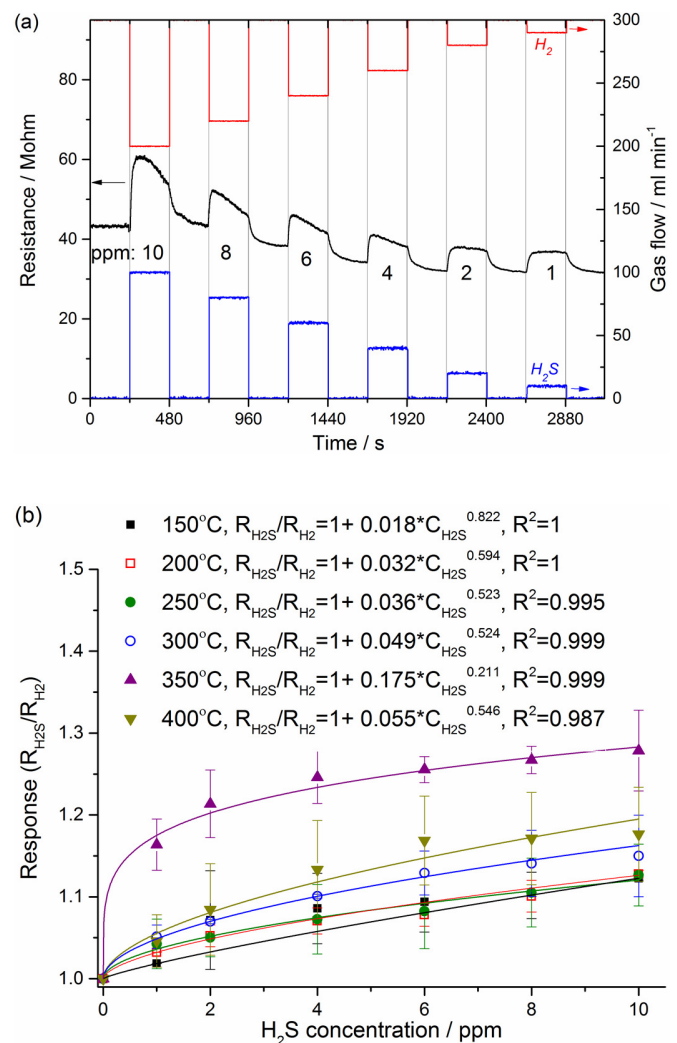
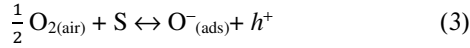


Fig. 3. (a) Typical dynamic response of CuO based gas sensor in presence of H₂S (10-1 ppm) in dry H₂ at 350 °C. (b) Response of the sensors tested at temperature ranging from 150 °C to 400 °C in presence of H₂S in dry H₂ as a function of concentration plot. Solid lines represent the power law fitted through the experimental points. The error bars represent the standard deviation of three measurements performed on separate sensors.

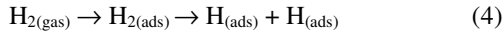
Response and recovery times at different concentrations of H₂S in dry H₂ are presented in Table 1. It was observed that

both the response and recovery times do not depend significantly on the H_2S concentration. Films performing under the operating temperature of 350°C showed the fastest response (16.9 ± 2.2 s) and recovery (49.4 ± 7.4 s) times. These values increased in experiments performed at other heater temperatures and ranged between 40-90 s (t_{90}) and 70-150 s (t_{10}).

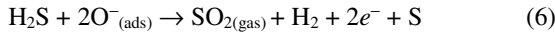
During annealing process at high temperatures oxygen adsorbed from an atmosphere of air acts as a surface acceptor state of the sensors [27]. The ionosorption of oxygen can be described as:



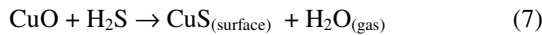
where $\text{O}_{2(\text{air})}$ presents the oxygen in the atmosphere, S an adsorption site, $\text{O}^-_{(\text{ads})}$ describes ionosorbed oxygen species, and h^+ the hole generated by electron transfer to the surface acceptor level. When the sensors are exposed to hydrogen environment, a quick increase of resistance of the sensing layer is attributed to the adsorption of hydrogen and this fast reaction of H_2 at the surface layer can be represented as [28]:



The effect of exposure to reducing gases, like H_2S is the reduction of the negative charge trapped at the surface of the metal oxide $\text{O}^-_{(\text{ads})}$ [13, 29]:



Analogously, the same reaction can take place with chemisorbed oxygen O_2^- at 150°C when the sensor is exposed to the target gas. These reactions compete with a second type of reaction that is probably less dominant for the temperature range used in our experiments and could be described as [13]:



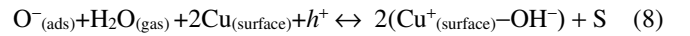
In the above reaction H_2S directly reacts with copper oxide to form metallic copper sulfide (CuS). It has been shown before that this sulfuration process is dominant at low temperatures whereas at higher temperatures ($> 200^\circ\text{C}$) desulfuration (re-oxidation) process is dominating [12]. The above processes shown in both reactions can be recovered if H_2S is removed and CuO sensing film is exposed to the ambient conditions.

During recovery process, the adsorption of reactive oxygen species at trace levels easily rejuvenates the CuO surface. It has been observed that both response and recovery processes are spontaneous and their times are independent of concentration, as experimentally showed.

B. Influence of humid H_2 environment on detection of H_2S impurities

The *p*-type CuO based sensors were also tested in presence of H_2S at dry H_2 , 25 % RH, 50 % RH, 60 % RH and 75 % RH H_2 to see the humidity effect on sensing as shown in Figure 4.

The sensor response did not significantly change when exposed to H_2S at 25 % RH H_2 compare to the sensor output in dry gas, but there was more effect at higher humidity levels. The effect of H_2S exposure in humid environment is increased sensor resistance as a result of competitive reaction between water vapours with H_2S on the sensing layer. We also assume that an interaction between pre-adsorbed oxygen and water may take place at the surface which may result in the formation of terminal hydroxyl groups and this was proposed earlier by Hubner *et al.* [27]:



where $\text{Cu}_{(\text{surface})}$ presents a Cu site on the surface, h^+ the consumed hole, $\text{Cu}^+_{(\text{surface})} - \text{OH}^-$ the formed terminal hydroxyl groups, and S an available site on the surface.

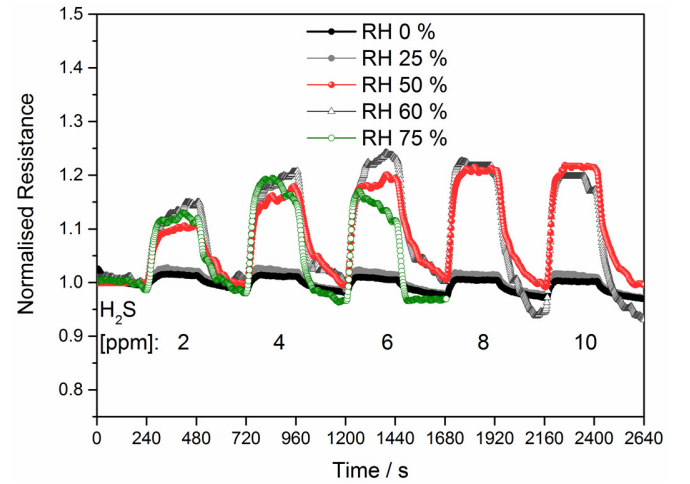
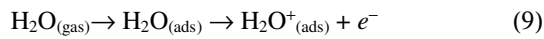
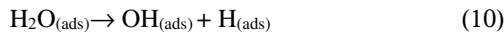


Fig. 4. Normalised dynamic response as R/R_{H_2} of CuO based gas sensor to H_2S (2-10 ppm) in dry and humid H_2 at 350°C .

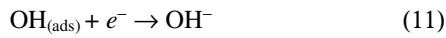
The response to H₂S at 350 °C in humid H₂ varied from 1.03-1.04, 1.10-1.22, and 1.14-1.28 as the target gas concentration was changing from 2-10 ppm at 25 %, 50 %, and 60 % RH H₂, respectively. The response at 75 % RH H₂ varied from 1.13-1.22 for H₂S concentration changing from 2-6 ppm. At 6 ppm the response increased by 16.5 %, 18.7 % and 19.3 % for 50 %, 60 % and 75 % RH, respectively. When humidity was introduced inside the chamber, we observed that the resistance of CuO decreased sharply and after few seconds increased slowly to its original value. This is not shown in Figure 4 as the sensors were stabilized for several minutes before sensing experiment was started and sensor signal recorded. This fast change in resistance has also been observed earlier by Illyaskutty *et al.* on molybdenum oxide and can be due to the adsorption process of water molecules that generates free electrons to the CuO sensitive layer [28]:



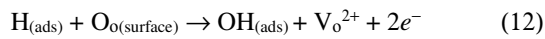
Such a slow increase of resistance can be attributed to the dissociation of the adsorbed water molecules and formation of hydrogen and hydroxyl groups on the CuO layer [28]:



The adsorption of OH groups on copper ion may be associated with an acceptor effect according to the chemical reaction:

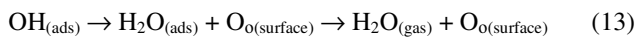


Additionally, the hydrogen formed during the dissociation of water (Eq. 10) may react with the lattice oxygen according to the following reactions [30]:



where O_o represents the lattice oxygen and V_o is the vacancy created at the oxygen site.

As the water vapour injection is withdrawn desorption process is expected to occur at the surface which can be described as [28]:



Temperature is also important factor for metal oxide gas sensors. Typical curves of gas response at operating temperature ranging from 150 °C to 400 °C in humid environment are presented in Figure 5 (a-d). The responses reach their maximum values at a certain temperature and e.g. for 6 ppm of H₂S in 25 % RH H₂ the maximum response (1.25 ± 0.02) was obtained at 150 °C, and a maximum response in RH H₂ 50 %, 60 %, and 75 % (1.27 ± 0.03, 1.31 ± 0.05, and 1.25 ± 0.01) was at 200 °C. These results for humid H₂ are in contrast with the sensor response obtained in dry H₂ were the maximum value (1.26 ± 0.02) was at much higher temperature of 350 °C. We have also found that the response of sensors to

TABLE 2
AVERAGE RESPONSE AND RECOVERY TIMES TO H₂S IN 25 % RH H₂ WITH STANDARD DEVIATION (STD) FROM 3 SENSORS

Concentration [PPM]	t_{90} [s]					t_{10} [s]				
	[°C]	150	200	250	300, 350, 400	[°C]	150	200	250	300, 350, 400
2		65, 70, 44, 75, 74, 39				108, 137, 73, 98, 100, 79				
		STD 3, 17, 2, 10, 25, 2				STD 26, 29, 23, 33, 32, 2				
4		68, 52, 48, 50, 54, 26				93, 121, 66, 103, 92, 79				
		STD 7, 5, 24, 5, 21, 16				STD 15, 22, 25, 32, 38, 15				
6		63, 50, 52, 60, 38, 40				125, 115, 58, 136, 98, 79				
		STD 7, 15, 4, 14, 20, 4				STD 12, 26, 6, 32, 41, 4				
8		52, 65, 52, 51, 47, 24				112, 150, 72, 137, 98, 81				
		STD 12, 15, 15, 7, 10, 14				STD 6, 21, 24, 31, 44, 14				
10		53, 60, 52, 38, 45, 36				139, 142, 80, 147, 120, 90				
		STD 7, 15, 16, 4, 12, 7				STD 6, 27, 7, 30, 11, 7				

TABLE 3
AVERAGE RESPONSE AND RECOVERY TIMES TO H₂S IN 50 % RH H₂ WITH STANDARD DEVIATION (STD) FROM 3 SENSORS

Concentration [PPM]	t_{90} [s]					t_{10} [s]				
	[°C]	150	200	250	300, 350, 400	[°C]	150	200	250	300, 350, 400
2		69, 96, 94, 92, 72, 51				151, 140, 117, 126, 119, 112				
		STD 12, 16, 11, 17, 4, 5				STD 5, 33, 31, 12, 15, 5				
4		72, 83, 80, 78, 46, 55				143, 125, 132, 128, 129, 97				
		STD 37, 26, 22, 25, 8, 23				STD 11, 17, 3, 14, 5, 1				
6		73, 66, 73, 59, 43, 38				133, 115, 106, 125, 127, 95				
		STD 28, 35, 3, 16, 8, 9				STD 11, 20, 1, 2, 2, 10				
8		66, 75, 80, 51, 35, 39				142, 126, 142, 121, 112, 95				
		STD 19, 26, 5, 16, 4, 5				STD 9, 36, 21, 10, 7, 26				
10		50, 76, 91, 39, 50, 22				131, 143, 146, 120, 95, 103				
		STD 12, 17, 9, 7, 9, 5				STD 11, 35, 22, 17, 23, 10				

TABLE 4
AVERAGE RESPONSE AND RECOVERY TIMES TO H₂S IN 60 % RH H₂ WITH STANDARD DEVIATION (STD) FROM 3 SENSORS

Concentration [PPM]	t_{90} [s]					t_{10} [s]				
	[°C]	150	200	250	300, 350, 400	[°C]	150	200	250	300, 350, 400
2		68, 73, 76, 103, 78, 70				103, 129, 115, 122, 84, 108				
		STD 32, 12, 5, 1, 26, 24				STD 15, 7, 18, 3, 18, 13				
4		50, 76, 76, 66, 67, 47				102, 122, 109, 136, 110, 110				
		STD 16, 23, 11, 6, 4, 1				STD 23, 21, 24, 6, 16, 3				
6		54, 62, 70, 60, 76, 39				91, 142, 120, 145, 111, 105				
		STD 18, 22, 6, 1, 27, 11				STD 5, 8, 13, 6, 20, 1				
8		40, 66, 69, 56, 46, 47				102, 127, 113, 126, 102, 99				
		STD 23, 27, 20, 6, 9, 20				STD 5, 23, 18, 16, 1, 24				
10		37, 67, 58, 50, 57, 35				78, 155, 119, 82, 101, 110				
		STD 15, 7, 24, 4, 22, 6				STD 2, 23, 8, 12, 5, 29				

TABLE 5
AVERAGE RESPONSE AND RECOVERY TIMES TO H₂S IN 75 % RH H₂ WITH STANDARD DEVIATION (STD) FROM 3 SENSORS

Concentration [PPM]	t_{90} [s]					t_{10} [s]				
	[°C]	150	200	250	300, 350, 400	[°C]	150	200	250	300, 350, 400
2		51, 49, 68, 54, 35, 44				105, 100, 106, 98, 80, 84				
		STD 4, 7, 11, 1, 18, 5				STD 26, 3, 17, 20, 8, 5				
4		53, 57, 40, 52, 40, 42				104, 102, 111, 117, 88, 89				
		STD 4, 2, 5, 3, 3, 1				STD 1, 28, 18, 16, 25, 1				
6		39, 56, 48, 39, 40, 37				125, 110, 131, 98, 120, 73				
		STD 8, 4, 3, 7, 3, 10				STD 3, 22, 1, 25, 12, 10				

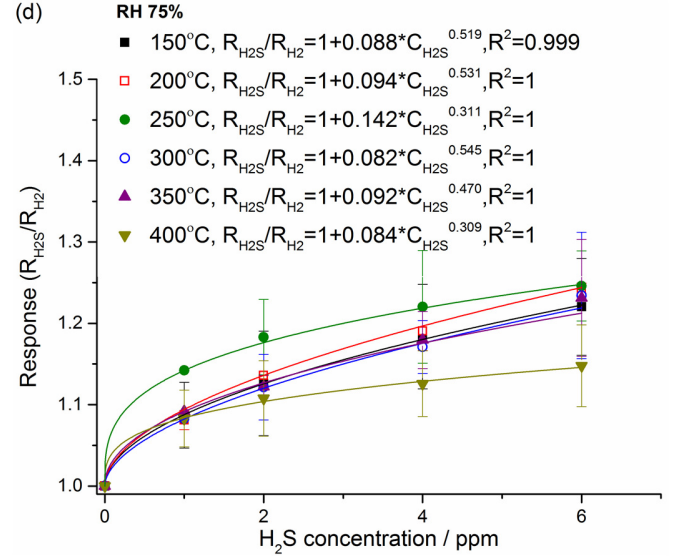
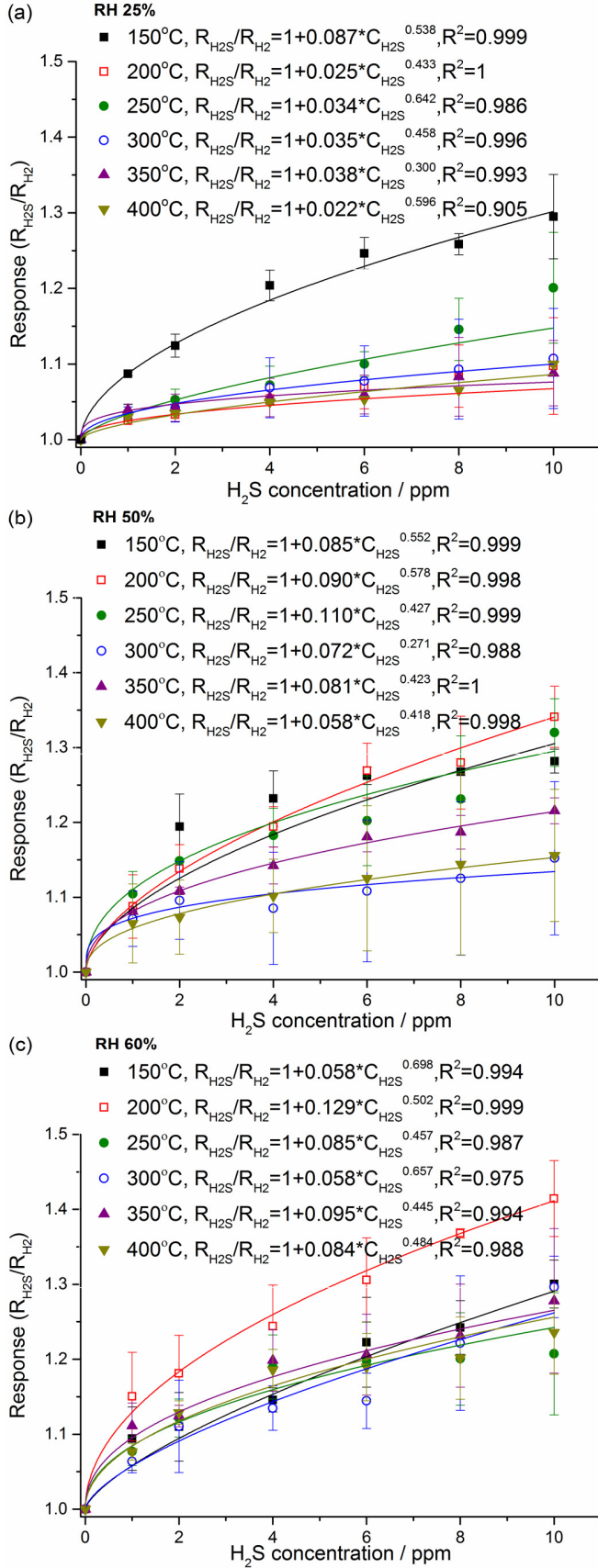


Fig. 5. Response of the sensors tested at temperature ranging from 150 °C to 400 °C in presence of H₂S in 25 % (a), 50 % (b), 60 % (c) and 75 % (d) RH H₂ as a function of concentration plot. Solid lines represent the power law fitted through the experimental points. The error bars represent the standard deviation of three measurements performed on separate sensors.

the target gas at 75 % RH was slightly suppressed across the range of temperatures tested compared with the results obtained at 60 % RH. Although this is not very prominent, it can be a result of increased concentration of blocking hydroxyl groups adsorbed on the grain surface. The values of power law β exponent for measurements performed in humid H₂ environment do not depend on operating temperature and are all near to 0.5 suggesting that the chemisorbed oxygen species are in O⁻ state.

Response and recovery times at different concentrations of H₂S in humid H₂ are presented in Tables 2 to 5. Response times ranged from 30 to 90 s and recovery times ranged from 70 to 150 s for operating temperatures between 150 °C and 400 °C and both times did not significantly change with H₂S concentration for humidity levels between 25 % and 75 %. We observed that in the humid environment and higher temperatures (350-400 °C), response and recovery times were faster and average values ranged between 30-50 s and 70-120 s for t_{90} and t_{10} , respectively. These faster response and recovery times could result due to desorption of surface hydroxyls at these temperatures which was experimentally confirmed earlier by Wang *et al.* [6].

C. Reference and cross-sensitivity measurements

We also tested our laboratory sensors along with a commercial sensor (TGS 2602 supplied by Figaro Inc, Japan) in the same static (isothermal) mode where H₂S in H₂ and pure H₂ were introduced alternately for 4 min. In case of metal oxide commercial sensor, during exposure to H₂ the signal was not stable, thus the device was unsuitable for application in reducing environment. Our sensor devices were also tested for cross-sensitivity in the presence of CO from 1 to 400 ppm in dry and humid H₂ and no signal changes were observed

during the exposure to the tested gas.

IV. CONCLUSION

In this study we report for the first time detailed analysis of a *p*-type copper oxide based MEMS gas sensor to a low ppm levels of hydrogen sulfide in a pure hydrogen environment and under various operating conditions. Hydrogen sulfide sensing behaviours of CuO micro-structured thick films at dry and humid H₂ environment give various characteristic response features which have been discussed in context with common reaction models available in literature. The sensors responses to H₂S impurities in H₂ were reproducible and, may indicate that for these gases there are two interaction paths: firstly a direct interaction with metal oxides, which does not involve lattice oxygen, and secondly a reaction with pre-adsorbed oxygen. The operating temperature has significant influence on sensing performance of CuO layer towards the target gas and humidity. The optimal operating temperature was determined to be 350 °C for H₂S detection in the absence of humidity and similar sensor response in humid environment was obtained at much lower temperature range 150-200 °C. The presence of higher concentration of water vapours increased sensors response on average by 18 % indicating less prominent blocking nature of hydroxyl groups, which is usually observed in atmospheric air. The CuO sensing response to hydrogen sulfide seems to be reasonably stable and reversible under both dry and humid hydrogen ambiances. Response and recovery times did not significantly change with the H₂S concentration and RH levels but they showed minor temperature dependence. In conclusion, we believe that this MEMS based semiconducting gas sensor can be used to detect low ppm H₂S levels under the harsh conditions of hydrogen ambience and high RH levels and could be exploited further in a gas sensing module for testing the quality of hydrogen fuel.

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