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H$_2$S gas sensing performance and mechanisms using CuO-Al$_2$O$_3$ composite films based on both surface acoustic wave and chemiresistor techniques

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Abstract:
Surface acoustic wave and chemiresistor based gas sensors integrated with a sensing layer of sol-gel CuO-Al₂O₃ composite film were fabricated and their performance and mechanisms for H₂S sensing were characterized and compared. In the composite film, CuO nanoparticles provide active sites for adsorption and reaction of H₂S molecules while Al₂O₃ nanoparticles help to form a uniform and mesoporous film structure, both of which enhance the sensitivity of the sensors by providing numerous active CuO surfaces. Through the comparative studies, the SAW based H₂S sensor operated at room temperature showed a lower detection limit, higher sensitivity, better linearity and good selectivity to H₂S gas with its concentration ranging from 5 ppb to 100 ppm, compared with those of the chemiresistor sensor, which are mainly attributed to the effective mass sensing properties of the SAW sensor, because a minor change in the mass of the film caused by adsorbed H₂S molecules would lead to a significant and monotonous change of the resonant frequency of the SAW devices.

Key words: surface acoustic wave (SAW); chemiresistor; H₂S gas sensor; CuO-Al₂O₃; mass sensing
1. Introduction

H₂S is an acidic, highly toxic and flammable gas, which is often produced from petroleum and mining industries [1-5]. Each year more than 3 million tons of man-made H₂S gas is released to the ambient environment, leading to an elevated level of H₂S gas concentrations around factories and some areas of cities [6-8], which could potentially cause acute poisoning and even death of human beings and animals when the concentration is higher than 500 ppm [8,9]. Even at a low concentration level, people may still feel it uncomfortable because of its strong irritating and rotten egg type of smell [10-13]. However, when exposed to H₂S gas in a relatively high concentration for a short time, a person’s olfaction could quickly fail to operate properly [4]. Therefore, it is critical to develop gas sensors which can in-situ monitoring the concentration of the H₂S for the safety and environment issues.

Chemiresistor sensors are one of the most commonly used ones for the detection of H₂S [14-21]. Sensing performance of the chemiresistor sensors is highly dependent on the sensing materials, which are used to effectively capture and further react with H₂S gas molecules. The reaction would lead to a change of the resistance of the sensing material, resulting in the responses of the sensor [14-16]. Among various sensing materials available (ZnO [17], WO₃ [18], SnO₂ [19]), CuO, a p-type semiconductor, is regarded as one of the best candidates because of its high reactivity with H₂S. For example, Chen et al. reported a chemiresistor H₂S sensor based on CuO nanowire array, which can detect H₂S with a concentration of 500 ppb [20]. Ramgir et al. used CuO films as the sensing layer of the chemiresistor H₂S sensor, which can detect 100
However, despite their high sensitivity, these CuO based chemiresistor sensors suffer from poor linearity of the sensing data because responses of these sensors are increased non-monotonically with the increase of the H$_2$S concentration owing to the different reaction mechanisms between CuO and H$_2$S at different H$_2$S concentrations [20-26].

In order to achieve both good linearity and high sensitivity simultaneously, it is possible to develop surface acoustic wave (SAW) sensors using CuO material as the sensitive layer. CuO has a superior affinity to the H$_2$S molecules and can effectively adsorb these molecules [27,28]. For the SAW sensor with CuO sensing layer, apart from the previously mentioned sensing mechanisms from the changes of the resistance of the film, the adsorbed H$_2$S molecules can also lead to an increase of the mass of the sensing layer. It was commonly reported that a slight increase of the mass of sensitive film would result in a significant decrease of the working frequency of the SAW sensors, i.e., increasing the responses [29,30]. In addition, the decrease of the working frequency is positively correlated with the increase of the mass [29-31], which is monotonically correlated with the concentration of the gas. For example, Raj et al. reported that the decrease of working frequency of the SAW sensor coated with a ZnO layer is linearly proportional to the amounts of analytes adsorbed on the surface of the sensor with the increase of film mass [31]. Therefore, the SAW sensor with CuO layer may show both good sensitivity and linearity for H$_2$S gas simultaneously.

It has been well-reported that applying porous structures of the sensing material
can significantly enhance the sensing performance of gas sensors by providing more reactive surfaces for adsorption and reaction with gas molecules [32,33]. Porous CuO structures can be easily formed by loading CuO nanoparticles directly onto a porous supporting structure, for examples, SiO$_2$, Al$_2$O$_3$, TiO$_2$. Among these, Al$_2$O$_3$ nanostructures have the advantage of large volumes of specific surface areas and strong adsorption capabilities [34-36]. Based on this idea, in this research, we proposed a sensing layer using mesoporous CuO-Al$_2$O$_3$ nanocomposites, which will inherit mesoporous structures of Al$_2$O$_3$ and also significantly enhance the interactions and reactions between the CuO nanostructures and H$_2$S gas molecules. Accordingly, this film design will significantly increase the sensing performance of H$_2$S gas sensors.

Using this porous CuO-Al$_2$O$_3$ nanocomposite layer, in this study, we fabricated both the chemiresistor and SAW sensors for H$_2$S gases and their performance and mechanisms were compared. Results showed that the SAW sensor with the composite layer has a lower detection limit, higher sensitivity, better linearity, selectivity in the concentration range from 5 ppb to 100 ppm compared with those of the chemiresistor sensor at room temperature.
2. Experimental details

Commercial ST-Cut quartz substrate (CETC 26) was used for fabrication of SAW devices. Aluminum interdigital transducers (IDTs, 30 pairs) and reflecting gratings (100 pairs) with a thickness of 200 nm were deposited on the quartz substrate using standard photolithography and lift-off processes to fabricate the SAW resonator. The IDTs and reflecting gratings had a periodicity of 16 μm. The center-to-center distance between the IDTs was ~3 mm. The resonant frequency of the resonator was measured using a network analyzer (Agilent Technologies, E8363B) and the reading is 200.33 MHz. Its insertion loss is -10.2 dB, and the Q factor is 7210.23, as listed in Table 1.

Table 1 Measured parameters of SAW resonators with and without coated with sensing layers.

<table>
<thead>
<tr>
<th>Material Coated</th>
<th>Pristine</th>
<th>CuO</th>
<th>Al₂O₃</th>
<th>CuO-Al₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Operating frequency</td>
<td>200.33 MHz</td>
<td>201.29 MHz</td>
<td>199.91 MHz</td>
<td>199.75 MHz</td>
</tr>
<tr>
<td>Insertion loss</td>
<td>-10.2 dB</td>
<td>-19.86 dB</td>
<td>-18.75 dB</td>
<td>-14.44 dB</td>
</tr>
<tr>
<td>Q factor</td>
<td>7210.23</td>
<td>2677.18</td>
<td>4670.55</td>
<td>5705.63</td>
</tr>
</tbody>
</table>

For the preparation of sensing films on the SAW resonator, CuO, Al₂O₃ and mixed CuO/Al₂O₃ colloidal sols were firstly prepared. Copper (II) nitrate trihydrate (Cu(NO₃)₂·3H₂O, analytic pure, Kelong) was dissolved into 2-Methoxyethanol (analytic pure, Kelong) and deionized water (with a volume ratio of 2-Methoxyethanol to deionized water of 4:1) solution with the Cu concentration of ~0.3 mol/L. The resultant solution was stirred at room temperature for 10 minutes to
obtain a transparent and uniform solution, which was then aged at room temperature for 24 hrs to obtain the CuO colloidal sol. For the preparation of Al₂O₃ colloidal sol, aluminum tri-sec-butoxide (analytic pure, Kelong) was mixed with ethanol (analytic pure, Kelong) in a beaker under continually magnetic stirring at room temperature for 2 hrs to obtain a homogeneous solution. A moderate amount of water was added into the solution to promote the hydrolysis of aluminum tri-sec-butoxide, after which a creamy white sol was formed. Finally, nitric acid (analytic pure, Kelong) was added inside this creamy white sol to obtain a clear Al₂O₃ colloid sol with a concentration of 0.3 mol/L. The two colloidal sols were finally mixed in a beaker with a molar ratio of Cu:Al = 1:1 under magnetic stirring, and the obtained precursor solution was aged at room temperature for 24 hrs to obtain CuO/Al₂O₃ composite colloidal sols.

The obtained CuO, Al₂O₃ and CuO/Al₂O₃ colloidal sols were deposited onto the surfaces of SAW resonators using a spin-coating process with a spin rate of 6000 r/min for 20 s for 2 cycles. The coated SAW resonators were immediately put into an oven at 60 °C for about 5 min, and then were calcinated in air at a temperature of 450 °C for 2 hrs to obtain CuO, Al₂O₃ and CuO-Al₂O₃ sensing layers. Compared with the pristine resonator, the resonant frequencies and Q factors of SAW resonators coated with sensing layers of CuO, Al₂O₃ and CuO-Al₂O₃ are all decreased, whereas the insertion losses are increased, as listed in Table 1. The resonators with sensing layers were connected to their corresponding amplifying and phase-shift circuits to fabricate the SAW sensors.

In addition, the metallic IDTs on these resonators were used as the electrodes for
the chemiresistor sensors. The SAW sensor and chemiresistor sensor in our work were integrated into one simple sensing device and had the same sensing film, as shown in Fig. 1(a).

The experimental set-up for gas sensing measurement is illustrated in Fig. 1(b). The sensing device was put into a testing chamber with a volume of 20 L. It was then connected to a frequency counter (Agilent 53132A) and a source meter (Keithley 2400) to record the dynamic changes of the resonant frequency of SAW sensor and the resistance of the sensitive film. Heaters made of Ni-Cr ribbon were mounted right below the sensing device and were used to heat the devices for assisting the recovery of the sensors. The humidity and temperature in the chamber during the tests were kept at 55% and 20 °C to eliminate the influences of humidity and temperature, unless otherwise specified. To measure the gas responses of the sensors, a highly precision syringe was used to inject the testing gases (H₂S, H₂, NH₃, SO₂, NO₂, CO, NO gases diluted to 2 vol% in dry air purchased from the National Institute of Measurement and Testing Technology, China) into the testing chamber, and the gas concentration in the chamber was controlled by adjusting the injecting volume. The response of the SAW sensor was defined as \( \Delta f = f_s - f_0 \), where \( f_s \) is the oscillating frequency of the sensor in the test gas mixed in air, and \( f_0 \) is the oscillating frequency of the sensor in the air, respectively. Dynamic change of the sensitive film’s resistance was recorded as the response curve of the chemiresistor sensor. After the responses were recorded, the test gas was pumped out and pure air was immediately filled into the chamber to allow the recovery of the sensors.
Fig. 1 (a) The schematic diagram of a sensing device and (b) experimental setup for gas sensing measurement.

Electrical measurement of the sensing films was conducted using a source meter (Keithley 2400). X-ray diffraction (XRD) were tested using Bruker AXS D8 ADVANCE X-ray diffractometer with a Cu Kα (λ = 1.5418 Å) radiation source, operated at 40 kV and 40 mA. Diffraction patterns were collected at a scanning rate of 2°/min and with a step size of 0.02°. Surface morphology and elemental compositions of the films were obtained using a field-emission scanning electron microscope (SEM, FEI Inspect F), attached with an energy dispersive X-ray Spectroscopy (EDS). Chemical states of the films were analyzed using an X-ray photoelectron spectroscopy (XPS, Quantum 2000 Scanning ESCA Microprobe instrument) with a monochromatic Al Kα source (1486.6 eV). The Cu 2p spectra were deconvoluted using a commercially available data fitting program (XPS Peak fit software). The surface area was evaluated based on the Brunauer–Emmett–Teller (BET) method using the instrument of ASAP-2020, with the adsorption branch in a relative pressure range from 0.01 to 1. The pore size distribution was derived from the adsorption branches of the isotherms using the Barrett–Joyner–Halenda (BJH) model [37].
3. Results and discussion

3.1. Characterization of the prepared films

Fig. 2 shows XRD patterns of CuO, Al$_2$O$_3$ and CuO-Al$_2$O$_3$ films. The diffraction peaks appear at two theta values of 32.4°, 35.5°, 38.7°, 48.7°, 53.5°, 58.2°, 61.5°, 66.2°, 68°, 72.4° and 75.1° in the XRD spectra of the pristine CuO, which are corresponding to (110), (-111)/(002), (111)/(200), (-202), (020), (202), (-113), (-202)/(311), (220), (311), (004) planes of the CuO (JCPDS No. 45-0937). No significant impurity peaks are found, indicating that the CuO film consists of a single phase of monoclinic CuO crystals. Two peaks appear at two theta values of 46° and 66.2°, and they are corresponding to the (400) and (440) planes of the pristine Al$_2$O$_3$ (γ-alumina, JCPDS No. 10-425). The CuO and Al$_2$O$_3$ crystalline grain sizes calculated by Scherrer’s equation are ~25 nm and ~4 nm, respectively.

Both the characteristic peaks of CuO and Al$_2$O$_3$ are presented in the XRD pattern of the CuO-Al$_2$O$_3$ composite, which demonstrates that monoclinic CuO and γ-alumina are co-existed in the composite film. Besides, compared with those of the pristine CuO, the wider CuO diffraction peaks of the CuO-Al$_2$O$_3$ film indicate that the average size of CuO crystalline grain in the CuO-Al$_2$O$_3$ film is smaller than that in the pristine CuO film.
Fig. 2 XRD patterns of the CuO, Al₂O₃ and CuO-Al₂O₃ composite films.

SEM images of CuO, Al₂O₃ and CuO-Al₂O₃ composite films are shown in Fig. 3. From these images, the average particulate sizes in CuO, Al₂O₃ and CuO-Al₂O₃ films are ~20 nm, ~30 nm and ~30 nm, respectively. Apparently, the surfaces of Al₂O₃ and CuO-Al₂O₃ films are rough, and have pores with an average diameter of tens of nanometers. Whereas the CuO film has a smooth and uniform surface without apparent pores. The porous surfaces of films may allow gas molecules entering deeply inside the films, which is beneficial for the adsorption and reaction of the gases. The embedded images indicate that the thicknesses of CuO, Al₂O₃ and CuO-Al₂O₃ films are all ~100 nm.
Fig. 3 SEM images of (a) CuO, (b) Al₂O₃ and (c) CuO-Al₂O₃ films. Embedded images are the sectional views of the films.

EDS spectra of CuO, Al₂O₃ and CuO-Al₂O₃ films after exposed to H₂S gas are presented in Figs. 4(a) to 5(c). As shown in these figures, signals of S element appear in the spectra of CuO and CuO-Al₂O₃ films, whereas no signal of S element is presented in the Al₂O₃ spectrum, which clearly indicates that the CuO in the films reacted with H₂S gas molecules while Al₂O₃ did not. Fig. 4(d) shows the EDS spectrum of H₂S-exposed CuO-Al₂O₃ film after heat-treatment at 300°C for 3 min in
air. The disappearance of the signals of S element in this spectrum indicates that the adsorbed S element on the CuO-Al$_2$O$_3$ film is released after the heat-treatment.

Fig. 4 EDS spectra of (a) CuO, (b) Al$_2$O$_3$ (c) CuO-Al$_2$O$_3$ films after exposed with H$_2$S gas and (d) H$_2$S-exposed CuO-Al$_2$O$_3$ films after heat-treatment.

Figs. 5(a) to 5(c) exhibit the XPS spectra of CuO, Al$_2$O$_3$ and CuO-Al$_2$O$_3$ samples before and after exposed with H$_2$S. Peaks of Cu, Al, O, S and C are identified. Due to surface contamination of carbon compounds (CO and hydrocarbons, etc.), the C 1s peak also appears in the XPS spectra. The peaks of S appear in the XPS spectra of both CuO and CuO-Al$_2$O$_3$ films exposed with H$_2$S, whereas they do not appear in the XPS spectrum of Al$_2$O$_3$. This result is same with that from the EDS analysis, demonstrating that CuO reacts with H$_2$S gas molecules while Al$_2$O$_3$ doesn’t.

Figs. 5(d) and 5(e) show Cu 2p and S 2p spectra of the CuO-Al$_2$O$_3$ sample before and after tested with H$_2$S gas. Before exposure to the H$_2$S, the Cu 2p$_{3/2}$ spectrum shows a main peak located at 930.6 eV along with its satellite peaks, which are all attributed to different chemical states of the CuO. After exposure to H$_2$S, the main
peak can be deconvoluted into two peaks located at 930.6 eV and 929.2 eV which are linked with those of CuO and CuS, respectively [21]. For S 2p spectra, two peaks can be seen at 160.2 eV and 159.1 eV after exposed with H$_2$S gas, which are attributed to S 2p$_{1/2}$ and S 2p$_{3/2}$ states, respectively [38]. These results clearly confirm that the formation of CuS in the CuO and CuO-Al$_2$O$_3$ composite films after they are exposed with H$_2$S. In addition, after heating the H$_2$S-exposed CuO and CuO-Al$_2$O$_3$ composite films at 300 °C for 3 min in air, the XPS spectra appear to be the same as those before exposure to the H$_2$S, indicating the release of S after the heat-treatment.
Fig. 5 XPS spectra of CuO (a), Al₂O₃ (b) and CuO-Al₂O₃ (c) samples before and after tested with H₂S gas and XPS spectra of Cu 2p₃/₂ (d) and S 2p (e) of the CuO-Al₂O₃ samples before and after tested with H₂S gas.

Fig. 6 shows the N₂ adsorption and desorption isotherms and pore distribution of CuO, Al₂O₃ and CuO-Al₂O₃ samples before and after exposed to the H₂S gas. The measured BET surface areas, total pore volumes and average pore diameters are listed.
in Table 2. The BET surface areas of CuO, Al₂O₃ and CuO-Al₂O₃ samples are 3 m²/g, 271.8 m²/g and 98.3 m²/g, respectively, revealing the formation of porous structure of Al₂O₃ and CuO-Al₂O₃ samples, but not CuO sample. The pore sizes of Al₂O₃ and CuO-Al₂O₃ samples are in the ranges of 2-15 nm and 2-24 nm, respectively. The total pore volumes are 0.42 cm³/g and 0.26 cm³/g for Al₂O₃ and CuO-Al₂O₃ materials, and the average pore diameters are ~4.9 nm and ~8.8 nm, respectively. These mesopore structures are beneficial for the gas sensing applications because they can act as the efficient paths for gas molecules to diffuse into the materials and provide more effective surfaces for adsorption and reaction of gas molecules. After exposed to the H₂S gas, the BET surface areas, total pore volume and average pore diameter of CuO-Al₂O₃ sample were measured again and the data clearly show that they were decreased to 91.3 m²/g, 0.14 cm³/g and 5.1 nm, respectively, as listed in Table 2. These results confirm that the H₂S gas molecules have truly been adsorbed within the pores of the sensing layer.

Fig. 6 (a) N₂ adsorption and desorption isotherms and (b) pore distributions of the CuO, Al₂O₃ and CuO-Al₂O₃ samples before and after tested with H₂S gas.
Table 2 Surface areas, pore volumes and average pore diameters of CuO, Al₂O₃ and CuO-Al₂O₃ powders before and after exposed with H₂S gas.

<table>
<thead>
<tr>
<th>Material</th>
<th>BET surface area (m²/g)</th>
<th>Total pore volume (cm³/g)</th>
<th>Average pore diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuO</td>
<td>3</td>
<td>0.01</td>
<td>26.7</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>271.8</td>
<td>0.42</td>
<td>4.9</td>
</tr>
<tr>
<td>CuO-Al₂O₃</td>
<td>98.3</td>
<td>0.26</td>
<td>8.8</td>
</tr>
<tr>
<td>H₂S-exposed</td>
<td>91.3</td>
<td>0.14</td>
<td>5.1</td>
</tr>
<tr>
<td>CuO-Al₂O₃</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

3.2. Gas sensing performance of the sensors

The dynamic resistance responses of the chemiresistor sensor with CuO-Al₂O₃ film when exposed to different H₂S concentrations ranging from 1 ppm to 100 ppm are shown in Figs. 7(a). The chemiresistor sensor has no response when the H₂S concentration is lower than 1 ppm. When the H₂S concentration is higher than 1 ppm, the sensor exhibits a response curve which is similar to those reported in Ref. [20,21]. The response curve can be divided into two regions according to the concentration of H₂S gas: at lower concentrations (e.g., 1 ppm and 5 ppm), the film shows an increased resistance with the H₂S gas; whereas at higher concentrations (e.g., 10 ppm, 50 ppm and 100 ppm), a decreased resistance following the initial increased resistance can be observed. Clearly, the resistance responses of the chemiresistor sensor are not monotonously increased with the concentration of H₂S. The recovery curves of the
resistance are not presented in Fig. 7(a) since the recovery of the sensor operated at room temperature is very slow, and the sensor can’t fully recover to its initial state after 1 hour, as shown in Fig. 7(b). Therefore, a heat-treatment (300 °C) of the film in air was applied to assist the full recovery of the sensor and reduce the recovery time less than 10 min.

Fig. 7 (a) Dynamic resistance responses of the chemiresistor sensor with CuO-Al$_2$O$_3$ film to H$_2$S gas with the concentrations ranging from 1 ppm to 100 ppm; (b) Typical response and recovery curve of the chemiresistor sensor toward 50 ppm H$_2$S, which indicates the slow recovery of the sensor at room temperature.

Fig. 8(a) shows dynamic responses of the SAW sensors with composite CuO-Al$_2$O$_3$ films recorded at room temperature with H$_2$S concentrations increased from 5 ppb to 100 ppm. As shown in the figure, the SAW sensor exhibits a negative shift of $\Delta f$ when exposed to H$_2$S gas. Compared with the resistance responses of the chemiresistor sensor, the SAW sensor shows better responses toward H$_2$S at all different concentrations from 5 ppb to 100 ppm, and also exhibits a monotonous increase of negative responses with the increase of the H$_2$S concentration as shown in
Fig. 8(a). Fig. 8(b) also indicates that the response is linearly increased with the concentration of H$_2$S in both lower (5 ppb-1 ppm) and higher (5 ppm-100 ppm) concentration ranges. In addition, Figs. 7 and 8 show that the noise of the SAW sensor is much lower than that of the chemiresistor one, indicating that the sensitivity of the SAW sensor is much higher. It should be noted that heat-treatment ($300 \, ^\circ\text{C}$) was also applied to assist the recovery of the SAW sensor because of the very slow recovery of the sensor at room temperature as shown in Fig. 8(c).

Fig. 8 (a) Frequency response of the SAW sensor with CuO-Al$_2$O$_3$ film to H$_2$S gas with the concentration ranging from 5 ppb to 100 ppm; (b) Response of the sensor as a function of the H$_2$S gas concentration; (c) Typical response and recovery curve of the sensor toward 50 ppm H$_2$S, which indicates the slow recovery of the sensor at...
room temperature.

With the above results, it can be concluded that the room temperature operated SAW sensor with the CuO-Al₂O₃ sensitive layer has a lower detection limit, higher sensitivity and better linearity for H₂S in the concentration region of 5 ppb–100 ppm, if compared with those of the chemiresistor sensor. In addition, this SAW sensor also shows a good selectivity for H₂S. The responses for different gases i.e. 5 ppm H₂S, NH₃, SO₂, NO₂, CO, H₂, NO, are presented in Fig. 9(b). The sensor has no apparent responses to H₂, CO, NO, NO₂ gases, while it shows slight positive responses to NH₃ and SO₂ gases, which are much weaker than that to H₂S. This result indicates that the SAW sensor has a good selectivity to H₂S gas. In the case of the chemiresistor sensor, it also shows no apparent responses to H₂, CO, NO, NO₂ gases, however resistance responses to SO₂ and NH₃ gases can be clearly observed, along with the strong response to H₂S, as shown in Fig. 9(a). The reason for the resistance responses to SO₂ and NH₃ gases may be due to the H₂O adsorbed on the film. Owing to the high solubility of SO₂ and NH₃ in H₂O, H₂O can capture SO₂ and NH₃ to form H₂SO₃ and NH₄OH, respectively, which lead to the decrease of the resistance of the film through ionization mechanism [39]. This result indicates the good selectivity of the SAW sensor.

Stability is another critical parameter for a practical gas sensor. Therefore, the stability of the SAW sensor was further investigated by conducting the sensing test every 15 days within a 60-day period. As shown in Fig. 9(c), the sensor shows the similar responses to 50 ppb, 0.5 ppm and 5 ppm H₂S, respectively, in the four
different tests within 60 days, indicating its good stability. Humidity resistance is also important for a good gas sensor. Fig. 9(d) shows that the baseline of the SAW sensor has negative shifts of -4.1 kHz and -8.5 kHz, when the RH increases from 20% to 55% and 80%, respectively. This result indicates that this sensor may also be used as a sensitive humidity sensor. Fig. 9(d) also presents that the sensor’s response to 1 ppm \( \text{H}_2\text{S} \) has a change from -16.3 kHz to -11.4 kHz with the increase of the relative humidity from 20% to 80%. Therefore, it can be confirmed that this SAW sensor can be used for \( \text{H}_2\text{S} \) detection at different environments with RH value ranging from 20% to 80%. Results clearly show that the SAW sensor has a much better sensing performance for \( \text{H}_2\text{S} \) gas compared with that of the chemiresistor sensor because of its lower detection limit, higher sensitivity, better linearity, selectivity, good stability and humidity resistance.
Fig. 9 Dynamic responses of (a) chemiresistor and (b) SAW sensors toward 5 ppm H₂S, NH₃, SO₂, NO₂, CO, H₂, NO gases; (c) Responses of the SAW sensor toward 50 ppb, 0.5 ppm and 5 ppm H₂S gases in 60 days; (d) Dynamic responses of the SAW sensor to 1 ppm H₂S gas under environments with different RH. The shifts of baseline can be observed when RH changes.

3.3. Sensing mechanisms of the sensors

To fully understand the sensing mechanism and explain why the SAW sensor based on CuO-Al₂O₃ has a better sensing performance, the sensing performances of SAW and chemiresistor sensors with pristine CuO and Al₂O₃ films were investigated and compared. Fig. 10 shows that both these two-type sensors coated with only Al₂O₃ film have no apparent responses to H₂S gas, whereas the two-type sensors coated with
CuO film exhibit similar responses and recovery curves compared with the sensors based on CuO-Al₂O₃ film (Fig. 7(d) and Fig. 8(c)), however, much lower sensitivities toward 50 ppm H₂S gas has been found. These results clearly indicate that: (1) no apparent interactions occurred between pristine Al₂O₃ and H₂S, whereas the reactions between H₂S and CuO could be the key reason for the good responses of the sensors; and (2) the existence of Al₂O₃ component in the composite enhanced the interactions between CuO and H₂S significantly, thus leading to much stronger responses.

Fig. 10 Dynamic responses of (a) chemiresistor; and (b) SAW sensors with pristine Al₂O₃ and CuO films toward 50 ppm H₂S.

CuO is a p-type semiconductor, and its surface adsorbs O₂ from air and creates surface oxygen states (O⁻) by getting electrons from valence band because of the strong oxidizability of O₂ according equation (1). As a result, holes are induced in the valence band of the CuO (Fig. 11(a)) [40,41].

\[ \text{O}_2^{(ads)} + 2e^- \rightarrow 2\text{O}^-_{\text{ads}} \]  

(1)

The created surface oxygen states (O⁻) are highly reactive. At lower H₂S concentrations, H₂S reacts with the adsorbed oxygen (O⁻) on the surface of CuO according equation (2). This reaction releases electrons from the surface states, and...
then the electrons recombine with the holes (charge carriers) in the valence bands, thus resulting in increased resistances of the chemiresistor sensors with CuO and CuO-Al$_2$O$_3$ films (Fig. 11(b)) [20-26].

\[ H_2S_{\text{ads}} + 3O^-_{\text{ads}} \rightarrow H_2O + SO_2 + 3e^- \] \hspace{1cm} (2)

At higher H$_2$S concentrations, in addition to the reaction (2) as described above, the following chemical reaction may also take place [20-26], e.g.:

\[ H_2S_{\text{ads}} + CuO \rightarrow CuS + H_2O \] \hspace{1cm} (3)

This reaction results in the formation of a layer of CuS, which covers the surfaces of CuO grains (Fig. 11(c)). This result has been confirmed by the EDS, XPS and N$_2$ adsorption and desorption results as discussed in Section 3.1 and shown in Figs. 4 to 6. CuS is metallic and thus enhances the conductivity among the neighboring CuO grains, which results in a significantly decreased resistance of CuO. Therefore, the initial increase in the resistance in the sensing process is mainly due to the domination of the reaction (1), and the reaction of (2) i.e. CuS formation, will cause an apparent decrease in the resistance of the sensor film. Due to this sensing mechanism, the chemiresistor sensor should not have any good linearity performance, which might have problems in monitoring during its sensing applications. The slow recovery of the chemiresistor sensor at room temperature can be also attributed to this sensing mechanism, since the reverse reactions of equations (1) and (2) are all very slow [20-23]. However, an increased temperature would accelerate these reactions significantly [20,21,38], therefore, heat-treatment is applied for accelerating the recovery of the sensor, as illustrated in the Section 3.1.
Fig. 11 Schematics and band diagrams showing different stages before and after the CuO and CuO-Al2O3 films are exposed to H2S gas of different concentrations. (a) In air, the CuO grains in films adsorb oxygen from air and obtain electrons from valence band to form surface states (O\(^{-}\)); (b) at low H2S concentration, H2S reacts with O\(^{-}\) and then releases electrons, which recombine with the holes in the valence band; (c) At high H2S concentration, H2S reacts with the CuO and forms CuS layers.

Similarly, the change of the resistance of the sensitive CuO and CuO-Al2O3 upon reactions with H2S will cause the frequency responses of the SAW sensors based on the following equation: [42]

\[
\Delta f = -f_0 \times \frac{K^2}{2} \times \Delta \left( \frac{1}{1 + \left( \frac{V_0 C_s}{\sigma S} \right)^2} \right)
\] (3)

where \(f_0\) (= ~200 MHz) is the resonant working frequency of the ST-cut quartz SAW resonator, \(V_0\) (= 3158 m/s) is the unperturbed SAW velocity on the SAW resonator, and \(K^2\) (= 0.0011) is the electromechanical coupling coefficient for ST-cut quartz substrate, \(C_s\) (= ~0.5 pF/cm) is the capacitance of the SAW resonator per unit length,
and $\sigma_s$ is the sheet conductivity of the sensing film. However, based on the measured $\sigma_s$ values in H$_2$S and air, the calculated values of frequency change ($\Delta f_c$) due to the changes of the conductivity, are far less than the measured frequency responses ($\Delta f$) of the sensors, as summarized in Table 3. Therefore, there should have other major sensing mechanism for these measured frequency responses of the SAW sensors.

### Table 3

Comparison between calculated values of frequency response ($\Delta f_c$) due to the changes of the conductivity and the measured frequency responses ($\Delta f$) of the SAW sensor based on the CuO-Al$_2$O$_3$ film.

<table>
<thead>
<tr>
<th>Concentration of H$_2$S (ppm)</th>
<th>Calculated $\Delta f_c$ (Hz)</th>
<th>Measured $\Delta f$ (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>-1</td>
<td>-49600</td>
</tr>
<tr>
<td>50</td>
<td>-0.8</td>
<td>-37980</td>
</tr>
<tr>
<td>10</td>
<td>0.6</td>
<td>-25820</td>
</tr>
<tr>
<td>5</td>
<td>0.24</td>
<td>-23640</td>
</tr>
<tr>
<td>1</td>
<td>0.1</td>
<td>-14700</td>
</tr>
</tbody>
</table>

It has been well established that CuO has a superior affinity for H$_2$S gas, and can be used as a desulfurizer [28,43-45]. CuO nanoparticles in the CuO and CuO-Al$_2$O$_3$ films can effectively adsorb both low and high concentrated H$_2$S gas molecules, which then react with CuO, based on the equations (1) and (2). Except for the previously mentioned changes of the conductivity of the film caused by the reactions, the adsorbed H$_2$S molecules can also lead to an increase of the mass of films, which
causes a frequency response of the SAW sensors following the equation:

\[ \Delta f = (k_1 + k_2) \times f_0^2 \times \Delta \rho, \]  

(4)

where \( k_1 = -8.7 \times 10^{-8} \text{m}^2\text{skg}^{-1} \) and \( k_2 = -3.9 \times 10^{-8} \text{m}^2\text{skg}^{-1} \) are substrate material constants of ST-cut quartz, \( \Delta \rho \) is the variation of areal density of the layer. Based on the equation (4), it is clear that increased mass of films caused by the adsorbed gas molecules would result in negative frequency responses of SAW sensors since \( k_1 \) and \( k_2 \) are negative signs. Therefore, the mass loading could be the key reason for the responses of the SAW sensors based on CuO and CuO-Al\(_2\)O\(_3\) films. This sensing mechanism can well explain the high sensitivity and good linearity of the SAW sensor, since \( \Delta f \) is linearly related to the variation of the areal density of the sensitive film as shown in equation (4). In addition, the calculated value of \((k_1 + k_2) \times f_0^2\) in equation (4) is \(-5 \text{cm}^2\text{ng}^{-1}\text{kHz}\), which indicates that a trace variation of the areal density \( \Delta \rho \) of the film would lead to a significant change of frequency, e.g., \( \Delta f \).

Although the SAW sensors based on CuO and CuO-Al\(_2\)O\(_3\) films are based on the same sensing mechanism (mass loading effect) as discussed above, Figs. 8 and 10 reveal that the sensors based on CuO-Al\(_2\)O\(_3\) have shown higher sensitivity. The differences between the sensing performances of these two sensors could be attributed to the different microstructures of the sensing layer materials. Based on the results from SEM and N\(_2\) sorption analysis (Figs. 3 and 6), the presence of Al\(_2\)O\(_3\) leads to the formation of a mesoporous structure of the CuO-Al\(_2\)O\(_3\) layer, whereas the pristine CuO layer is relatively dense. Therefore, when the CuO-Al\(_2\)O\(_3\) film is exposed to the
H$_2$S gas molecules, a large amount of H$_2$S molecules can diffuse quickly and much
deeper inside the CuO-Al$_2$O$_3$ through the porous structures created by Al$_2$O$_3$ and then
can be efficiently adsorbed onto the CuO layer as shown in Fig. 12 (bottom panel).
Whereas when the dense CuO layer is exposed to H$_2$S gas, these H$_2$S molecules will
adsorb mainly on the CuO particles on the surface layer of the film as shown in Fig.
12 (upper panel). Hence, compared with the pristine CuO film, CuO-Al$_2$O$_3$ film can
adsorb much more H$_2$S molecules owing to its mesoporous structure created by Al$_2$O$_3$
at the same H$_2$S concentration level, and these adsorbed H$_2$S molecules thus lead to
much stronger mass loading effect and negative responses of the SAW sensor.

Fig. 12 Proposed H$_2$S sensing mechanism of the sensors coated with the CuO layer
and CuO-Al$_2$O$_3$ layer, respectively.
Conclusions

In this study, both the SAW and chemiresistor H$_2$S gas sensors with sol-gel CuO, Al$_2$O$_3$ and CuO-Al$_2$O$_3$ composite as the sensing layer were fabricated. Compared with the chemiresistor sensors, the SAW sensors were found to have a better sensing performance, e.g., good sensitivity, selectivity and linearity toward H$_2$S gas with concentration ranging from 5 ppb-100 ppm. These properties are mainly due to the sensing mechanism of the SAW sensor, which are based on the increased mass (mass loading effect), along with the changes in resistance of the CuO and CuO-Al$_2$O$_3$ films caused by the adsorption of H$_2$S on CuO nanoparticles. In addition, the SAW sensor with CuO-Al$_2$O$_3$ film was found to be much more sensitive than the sensor with pristine CuO film. This result is due to the presence of the Al$_2$O$_3$ in the composite film, which leads to a mesoporous structure of the composite film. This mesoporous structure enhances the sensitivity of the sensors significantly by affording more reactive surface for the adsorption and reaction with H$_2$S.
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Declaration of interests

The authors declare no conflicts of interests.
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