Sensitive and Low-Power Metal Oxide Gas Sensors with a Low-Cost Microelectromechanical Heater

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ABSTRACT: In this study, a simple and cost-effective metal oxide semiconductor (MOS) gas sensor, which can be fabricated utilizing only two photolithography steps, was designed and developed through the planar microelectromechanical systems (MEMS) technique. Ball-milled porous tin dioxide nanoparticle clusters were precisely drop-coated onto the integrated microheater region and subsequently characterized using a helium ion microscope (HIM). The spatial suspension of the silicon nitride platform over the silicon substrate provides superior thermal isolation and thus dramatically reduces the power consumption of the microheater. The well-designed microheater exhibits excellent thermal uniformity, which was verified both computationally and experimentally. The as-fabricated sensors were tested for ethanol gas sensing at various operating temperatures with different concentrations. At the optimal work temperature of $\sim 400^\circ\text{C}$, our gas sensors demonstrated a respectable sensitivity to 1 ppm ethanol, which is the lower detection limit to most commercial products. Moreover, stable performance over repetitive testing was observed. The innovative sensor developed here is a promising candidate for portable gas sensing devices and various other commercial applications.

INTRODUCTION

A metal oxide semiconductor (MOS) gas sensor is a type of solid-state gaseous-atmosphere-dependent resistive gas sensor that has been extensively used in many practical applications, such as toxic and polluting gas alarms,¹ indoor air quality control,² environmental monitoring,³ medical diagnostics,⁴ domestic appliances, etc. There have been rapid developments of applications and great progress in the fundamental understandings of the MOS gas sensors since the first proposal by Seiyama et al.⁵ and Taguchi⁶ in the 1960s. There are numerous advantages of the MOS gas sensors, including simplicity, low cost, high gas sensitivity, miniature size, and thus compatibility with state-of-art electronic devices.⁷ MOS gas sensors typically utilize nanoscale polycrystalline n-type oxide particles, such as SnO_2 ,^{8,9} ZnO ,¹⁰ WO_3 ,¹¹ TiO_2 ,¹² and In_2O_3 ,¹³ or p-type oxides, such as NiO ,¹⁴ Cu_2O ,¹⁵ Cr_2O_3 ,¹⁶ and Co_3O_4 .¹⁷ When the oxide material is exposed to a volatile gas of a low concentration (e.g., a few ppm) in air, its electrical resistance may change accordingly, rendering it useful for gas sensitivity.¹⁸

The working principle of the MOS gas sensors can be briefly described as follows. The gas-sensitive resistor consists of a porous assembly of small grains of an n-type or p-type oxide.¹⁹ For the instance of n-type semiconductor, the oxygen (e.g., O_2^- , O^- , and O^{2-}) in air may be adsorbed on these grains, resulting in an electron depletion layer (EDL) as well as an increased surface potential.^{20–24} A double-Schottky barrier for

the migration of electrons is then formed across the interfaces (i.e., grain boundaries) connecting neighboring grains.²⁰ Such barriers predominantly control the electric resistance of the sensing material.¹⁹ For example, the oxygen adsorbates are consumed if a reducing gas is in contact, which causes a decrease in the potential barrier and resistance (or increase in current) of the sensing body as a function of the partial pressure of the reducing gas.²⁰

The MOS gas sensor typically consists of a sensing material layer that will react with the target gas, at least two electrodes to monitor the electrical resistance/current variations, and a microheater to increase the operating temperature.²⁵ There are four most important parameters, termed sensitivity, selectivity, response transients, and stability, which define the MOS gas sensor working behaviors.¹⁹ The sensitivity is the most commonly used characteristic, and it is defined as the ratio of the sensor electrical resistance in air (R_a) to a steady level upon exposure to the mixture of target gas and air (R_g).^{19,21} The gas response is strongly dependent on the working

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temperature.^{7,21} Also, the increasing operating temperature accelerates the response process, because it influences the oxygen adsorption and the reaction rate with the target gases.^{23,26} The selectivity is defined as the ratio of the sensitivity of gas to that of a different gas.²¹ Moreover, the response transients are the time required to attain the majority of the electrical resistance (or current) change upon switching the gas concentration.²¹ The selectivity and response transients were demonstrated to change as a function of the working temperature.²⁷ The stability and long service lifetime are usually required for practical applications, and they are pertinent to the operating temperature as well. Thermal stress usually accumulates during the repetitive heating/cooling cycles in the device, which may induce vertical deflection of the suspended membrane. To sum up, achieving an optimal operating temperature (typically between 200 and 400 °C²⁸) upon exposure to a target gas is of paramount importance for improving gas sensing performance.

To achieve gas sensing at an elevated temperature, a typical semiconductor gas sensor requires not only a microheater (e.g., a serpentine track of a metal resistor) for maintaining a good temperature distribution but also interdigital electrodes (IDEs) for measuring the *in situ* electrical resistance or current of the sensing material. According to the type of heating components, the MOS gas sensor products may be divided into three categories, termed ceramic tube heater, planar ceramic substrate heater, and microelectromechanical systems (MEMS) microheater. Both the ceramic tube and planar substrate exhibit high power consumption, and therefore, they may not be the optimal choices for lithium ion battery-powered sensor devices.²⁹ MEMS sensors recently attract increasingly more academic and industrial attentions due to their miniaturization (e.g., through microfabrications), excellent sensing performance, and dramatically lowered power consumption since the suspended heater design significantly reduces the heat loss of the substrate.²⁹ Currently, there are only a few planar substrate-type MEMS gas sensors available in the market.³⁰ The primary limitation for high-volume industrial and commercial applications of the MEMS technique is its high costs due to the complex fabrication process.³¹ Specifically, the fabrication usually involves four sequential lithography steps: (a) Mask one creates a layer of a patterned serpentine metal resistor for ohmic heating, (b) mask two produces a patterned SiN_x insulating layer where the bonding pads are exposed, (c) mask three defines the sensing electrode, and (d) mask four forms selective openings on the insulating membrane for the subsequent anisotropic wet etching. More recently, some researchers use a single photolithography step to define both the microheater and IDE structure on the suspension platform, where IDEs are enclosed by the serpentine microheater to minimize unwanted thermal diffusion.^{32,33} Therefore, the fabrication process can be reduced to three lithography steps. The remaining two steps aim to pattern an isolation layer between the microheater and the sensing film, and to make a mask to expose the silicon for wet etching, respectively.³² In general, more process steps usually lead to longer development time, lower yield and ultimately higher cost. Hence, to facilitate the high-volume adoption of MEMS-type gas sensors, a strategy to further simplify the fabrication process is highly desired.

In this work, we introduce the design, simplification, and fabrication of a low-cost MEMS microheater for MOS gas sensor applications. By optimizing the design of the layout and

etching processes for the two metal electrodes and the silicon nitride insulation layer, we successfully consolidate the fabrication process into only two photolithography steps. To demonstrate the excellent performance of our re-designed microheater for gas sensing, SnO₂ is used as the metal oxide sensing material for ethanol detection. This particular material is chosen because of its high mobility of electrons, high chemical and thermal stability under the sensor operating conditions.²¹ The properties of the fabricated novel gas sensors are characterized in detail. The results show that the optimal operating temperature of our device is ~400 °C at a power consumption of 39 mW, which is significantly lower than that of commercially available non-MEMS gas sensors. The microheater also exhibits excellent thermal uniformity with a small temperature gradient of ~0.03 °C/μm. In addition, the gas sensor yields a respectable sensitivity to gaseous ethanol. More specifically, the sensitivity was recorded to be 10.2 upon exposure to 1 ppm of ethanol, which is at least three times higher than most of the commercially available MEMS-type gas sensor. Overall, the fabricated sensor in this work demonstrated a high response to the target gas with relatively small power consumption, which can be a crucial step toward the high-volume manufacturing of low-cost, high-yield MEMS-based gas sensors.

EXPERIMENTAL PROCEDURES

Design and Fabrication of the Device. The schematics of the fabrication process are shown in Figure 1. As mentioned,

Figure 1. Schematic illustration of the fabrication process of an MHP: (a) an n-type (100) silicon substrate; (b) a thin layer of silicon nitride layer deposited by LPCVD, which provides thermal isolation between the microheater and the silicon substrate; (c) the serpentine platinum resistor, the IDEs, and the bonding pads were fabricated by double resist lift-off processes; (d) the silicon nitride insulating layer coated by PECVD; (e) wet etching windows, IDEs, and the bonding pads were uncovered through photolithography and dry etching; (f) the microheater and IDE structure was suspended by anisotropic wet etching.

we simplified the fabrication process to only two lithography steps where mask 1 patterned the platinum resistor, sensing electrode, and bonding pads, while mask 2 uncovered the metal electrodes, bonding pads, and the openings for wet etching. Notably, the platinum components which constructs the bonding pads and the IDEs were also utilized as a hard mask for protecting the underneath silicon nitride layer from dry etching. The fabrication of a micro-hot platform (MHP) started with growing ~1000 nm-thick low-stress silicon nitride

films on both sides of a 4 inch silicon (100) wafer through low-pressure chemical vapor deposition (LPCVD). Electron beam evaporation and a double layer lift-off processes were carried out to pattern the platinum serpentine resistor, the IDEs, and bonding pads with a thickness of ~ 200 nm on the front side (i.e., mask 1). The wafer was then coated with an ~ 500 nm-thick silicon nitride film (i.e., an isolation layer) by plasma-enhanced chemical vapor deposition (PECVD). Afterward, the silicon nitride membrane was selectively dry-etched by inductively coupled plasma (ICP) etching with gaseous CHF_3 and O_2 to uncover the releasing windows, bonding pads, and the contact areas of IDEs (i.e., mask 2). Lastly, the platinum heater and IDEs were suspended over a silicon cavity by four beams through anisotropic wet etching with a 40 wt % KOH at 60°C for 12.3 h.

Measurement of Thermal Properties. The temperature distribution of the MHP was measured using a thermal emission microscope (Optotherm Sentris, U.S.A.) with a spatial resolution of $\sim 5\ \mu\text{m}$ and a detection waveband of $7\text{--}14\ \mu\text{m}$. The device was heated to 45°C by placing it on a hot stage for ease of focusing. The 2D thermograph was constructed using Matlab from the outputting raw data. It is worth noting that some of the thermal image contrasts may result from different emissivity of various materials, since the surface emissivity was assumed to be one for all materials in the thermograph. In addition, a finite element tool of COMSOL was utilized to computationally investigate the thermal distribution. The boundary conditions here are as follows: (1) The silicon substrate was fixed without any displacement, and (2) the substrate was set as an ambient temperature. The parameters used in this simulation were extracted from the COMSOL material library.

In addition, the temperature coefficient of resistance (TCR) of the device was determined for accurate temperature calibration. The temperature of the MHP was raised from an ambient temperature to 295°C through immersing the device in silicone oil, while the temperature was maintained by a water bath heater. The temperature and the corresponding resistance were measured using a thermocouple and a resistance meter, respectively. Once the TCR is calibrated, the actual temperature of the device can be calculated by measuring the resistance at such temperature according to the following equation:

$$\text{TCR} = \frac{1}{T_2 - T_1} \cdot \frac{R_2 - R_1}{R_1} \quad (1)$$

where R_1 is the resistance of the MHP at temperature T_1 , and R_2 is the resistance at temperature T_2 , respectively. The temperature resistance method is an appropriate and convenient approach to estimate the working temperature of the device at a given applied voltage and power consumption.

Synthesis and Characterization of the Sensing Material. The synthesis approach utilized in this work basically follows ref 34. In a typical experiment, 500 g of as-received SnO_2 micropowders with particle sizes ranging from 2 to $5\ \mu\text{m}$ (Jinxin Advanced Materials, China) was added into 1425 g of deionized water with magnetic stirring, followed by mixing with 75 g of triethanolamine (Usof Chemical, China) as dispersant. The stirring and dispersing were continued for 10 min. Afterward, the mixture was ball-milled (WG-1 L, Vgreen Nanometer Technology, China) with a ball diameter of 0.3 mm for 2 h to create a uniform dispersion. At last, 1 g of tetraamminepalladium nitrate (Aladdin, China) was added into

12 g of the synthesized dispersion as a palladium dopant. Consequently, the stable nanodispersion with a solid content of 15% was acquired. The gas sensitive material was deposited on the MHP through drop coating.

The morphology characterization of the as-fabricated gas sensor and the sensing material was conducted via secondary electron detection using a helium ion microscope (HIM, Zeiss Orion Nanofab, Germany) at an accelerating voltage of 30 kV, a beam current of 0.6 pA, and a working distance of ~ 8.7 mm.

Gas Sensing Testing. The gas sensing performances for ethanol were studied using a homemade testing system. An 8 L chamber was initially filled with ambient air. A certain amount of liquid ethanol was then injected onto the evaporator (i.e., to facilitate diffusion) through the gas inlet. The fans mounted on the chamber sidewalls also assist the gaseous flow within the chamber. The sensing material which acts as a chemiresistor may interact with the injected gas, and the change of its current measured by IDEs with respect to a reference current was monitored as a function of time. The temperature of the microheater was carefully controlled through supplying a certain voltage by a source meter (Keithley 2602A, U.S.A.).

RESULTS AND DISCUSSION

The optical and HIM images of the as-fabricated gas sensor are shown in Figure 2. The separation distance between the

Figure 2. Optical images of (a, b) the as-fabricated gas sensor. The bonding pads and the sensing electrodes (i.e., the three white stripes in the middle) are exposed for wire bonding and chemiresistance bridging, respectively, whereas other regions are coated with silicon nitride for isolation. HIM images of (c) top and (d) 45° tilted views of the as-fabricated gas sensor. The IDEs are surrounded by the serpentine track of the heating resistor. Since the silicon nitride isolation layer is only 500 nm thick, He^+ ions may still interact with the platinum underneath it and exhibit similar secondary electron yields compared to that of exposed platinum regions, as shown in the HIM images.

coplanar platinum electrodes was designed to be $9.8\ \mu\text{m}$ allowing electrical bridging with the sensing material to form a chemiresistor. The three IDEs were surrounded by the serpentine microheater to provide necessary heating for gas sensing. The serpentine track of resistor yields analogous thermal uniformity compared to stack-type microheaters.³³ In order to reduce the thermal strain during operation and to improve the mechanical strength of the serpentine micro-

heaters, corner compensations were introduced via replacing sharp corners by rounded corners.^{35,36} In addition, only the platinum IDEs were exposed, while other regions were covered with a silicon nitride layer in the central active region (Figure 2a,b). Therefore, the circuitous heating resistor was electrically insulated in-plane from the platinum sensing electrodes. Furthermore, a silicon pit (i.e., for thermal isolation purposes) created via anisotropic etching under the membrane is visible in the tilted view image (Figure 2d).

The measured resistance of the resistor as a function of temperature is shown in Figure 3a. The TCR value of the

Figure 3. (a) Experimentally measured electrical resistance as a function of the actual temperature; the linear relationship is used to extrapolate the TCR. (b) Correlation between the applied voltage on the device and the resulting power consumption and the estimated temperature from the TCR method.

platinum resistor was experimentally determined to be $2.39 \times 10^{-3} \text{ }^{\circ}\text{C}^{-1}$. This is in good agreement with the literature values of the TCR of platinum, $2.70 \times 10^{-3} \text{ }^{\circ}\text{C}^{-1}$ ³⁶ and $2.19 \times 10^{-3} \text{ }^{\circ}\text{C}^{-1}$.³⁷ The relationship between the applied heating voltage and the corresponding power consumption was also measured, and the obtained results along with the estimated temperature via the TCR method were shown in Figure 3b. Consequently, the temperature of the microheater at various applied voltages can be estimated. In addition, the suspended MHP from the silicon substrate confines the heat within the platform. Thus, the device exhibits low power consumption. For example, the power consumption is approximately 39 mW for achieving a working temperature of $\sim 400 \text{ }^{\circ}\text{C}$, which is significantly lower compared to other commercially available non-MEMS microheaters for gas sensing applications (e.g., 400 mW for the SP series of Nissha FIS; 210 mW for Figara TGS2620).

In an MOS gas sensor, homogeneous temperature distribution in the active membrane enclosing the IDEs is vital for the optimal sensing performance.³⁸ Heat transfer usually occurs in three different pathways, termed heat conduction, heat convection, and thermal radiation. In an MHP with four supporting beams, the heat conduction occurs in the lateral plane, while heat convection and possible thermal radiation take place above and below the suspended membrane through neighboring air molecules and infrared photons. The temperature distribution of the fabricated microheater was simulated and experimentally investigated. Figure 4a shows the simulated temperature distribution using a COMSOL multiphysics simulator. The active area of the MHP is at $\sim 394 \text{ }^{\circ}\text{C}$ under 4.3 V, while the other area is approximately at an ambient temperature. In comparison, the temperature was estimated to be $400 \text{ }^{\circ}\text{C}$ under 4.3 V according to the TCR correlation. The good accordance between the simulated microheater temperature and the extrapolated temperature using the TCR approach corroborates the reliability of the simulation method. The thermal isolation and the consequent

Figure 4. (a) Temperature distribution of the microheater under 39 mW obtained by COMSOL simulation, and (b) the temperature profile along the dotted diagonal line in (a).

minimized power consumption may be attributed to the air gap between the microheater and the silicon substrate, as well as the four suspended slender beams where the temperature gradient is high, since the relatively small dimensions of the beam suppress significant heat flow from the heated membrane. The temperature profile along the diagonal line in Figure 4a is shown in Figure 4b. The temperature distribution within the membrane region yields good thermal homogeneity with a subtle temperature gradient of $\sim 0.03 \text{ }^{\circ}\text{C}/\mu\text{m}$ enclosing the active sensing area.

The emitted radiation distribution (Figure 5) measured using the infrared microscope shows, however, some deviations

Figure 5. Infrared photo of the microheater showing emitted radiation distribution on the suspended membrane with a supplied voltage of 1.57 V (i.e., estimated temperature of $\sim 150 \text{ }^{\circ}\text{C}$ from the TCR). The zoomed active area and the processed infrared photo with the emissivity compensation are shown in the inset. It is worth noting that the suspended MHP emits thermal radiation in all directions, while only the radiation emitted from the front side may be captured by the thermal microscope.

from the simulated temperature distribution, especially at the platinum IDEs. These measurement errors are possibly because of the material-dependent emissivity. That is, materials with lower emissivity emit less radiation and may appear to be cooler in an uncorrected infrared thermograph. Typically, the infrared thermal microscope detects the infrared radiation emitted from the material's surface, and the temperature or thermography is estimated through the well-known Stefan–Boltzmann law: $R = \epsilon \sigma T^4$, where R is the emitted radiation, ϵ is the material's emissivity, σ is the Stefan–Boltzmann constant, and T is the temperature. Hence, the measured infrared temperature is directly correlated to the emissivity of the material. In practice, most of the infrared thermal systems

assume the whole material is considered as a blackbody (i.e., emissivity is 1)³⁹ or it presumes emissivity normalization that the whole surface has a uniform emissivity ranging from 0 to 1.⁴⁰ Some researchers utilize a spin-coated paint⁴¹ or nanocomposite coating⁴⁰ with known emissivity to normalize various radiation emission sources. However, such additional layer induces heat loss and thermal redistribution, leading to reduction of spatial measurement accuracy and possible damage to the device.⁴¹ Other investigators place the device on a thermal stage while the temperature is precisely controlled; thus, an emissivity map can be created to acquire the actual thermography.⁴² Nevertheless, the exact one-to-one pixel correspondence between the emissivity map and the thermography is difficult to achieve.⁴⁰ In this work, we placed an as-wet etched wafer (e.g., prior to dicing) on a hot plate with a set temperature of 150 °C (the hot plate temperature may not exceed 150 °C or the thermal camera could be damaged) while measuring the thermography assuming emissivity is 1 for all materials. Therefore, the true emissivity for various materials can be extrapolated according to the Stefan–Boltzmann relationship. Here, the emissivity at 150 °C of the region where platinum IDEs were exposed was calculated to be 0.37, while the emissivity of the silicon nitride covered region was determined to be 0.73. Afterward, we performed an emissivity adjustment at the platinum IDEs and the silicon nitride areas using a customized Matlab code. The emissivity-corrected results (Figure 5 insert), which may more correctly present the actual temperature distribution, indicate that the true temperature difference between the platinum and silicon nitride is only $0.3 \pm 0.2\%$ compared to that of the uncorrected temperature difference of $17.4 \pm 0.7\%$. The emissivity-adjusted results infer the temperature distribution in the active region is isothermal (e.g., $\frac{T_{\text{Pt}} - T_{\text{SiN}_x}}{T_{\text{Pt}}} = 0.3 \pm 0.2\%$), which is in good agreement with the COMSOL simulation result. Therefore, the microheater fabricated in the experiment exhibits a uniform thermal distribution, which facilitates the subsequent gas sensing performance.

An HIM is one of the ideal techniques to characterize small-scale structures, because the He^+ –sample interactions induce backscattered electrons with no high energy, therefore, reveals better secondary electron image and surface morphology fidelity.⁴³ The SnO_2 nanostructure imaged using an HIM is shown in Figure 6. The as-synthesized SnO_2 nanoparticles

Figure 6. HIM images of the (a) as-drop coated gas sensor; zoomed in images are shown in (b) and (c), respectively. The clusters of SnO_2 nanoparticle are separated with a large number of voids and channels.

seem homogeneous without additional phases. They are almost spherical with a tiny particle size of ~ 30 to 40 nm. The nanoparticles were aggregated tightly with their neighbors and form large aggregations or clusters of particles. The voids and channels between the aggregations not only facilitate the diffusion of the sensing gas but also increase the surface-to-

volume ratio of the sensing material. The observed aggregation effect might depend on the nanoparticle size, for example, the aggregation occurrence may intensify while the particle size is moving toward nanoscale.⁴⁴

The work temperature is vital and dictates the gas sensing performances. The desired temperature of the microheater can be obtained by adjusting the heater voltage. The gas sensitivity to 10 ppm ethanol of the fabricated gas sensor at stepped temperatures are shown in Figure 7a. The sensor response

Figure 7. Gas sensing performance: (a) the sensitivity (e.g., R_g/R_a or I_g/I_a) to 10 ppm ethanol under stepped temperatures, where I_g and I_a represents the sensor electrical current in the mixture of target gas and air and that of upon exposure to merely air, respectively. (b) Dynamic response of the sensor current for 1–25 ppm of ethanol at ~ 400 °C. (c) Sensitivity as a function of various concentrations of target gas; the insert shows their logarithmic correlation. (d) Repeated sensing test to 25 ppm ethanol confirms repeatability and reproducibility of the device. The sensor voltage was maintained at 5 V.

initially increases with temperature, then reaches a maximum sensitivity (e.g., 29.7 at ~ 400 °C), and decreases along the operation temperature. Such temperature dependence of the gas sensing sensitivity is in good accordance with the literature.²¹ The optimal work temperature with the best response signal to ethanol was determined to be ~ 400 °C. Furthermore, Figure 7b shows the sensitivity as the gas sensor is sequentially exposed to ethanol at different gaseous concentrations ranging from 1 to 25 ppm at ~ 400 °C. The current rise upon exposure to gaseous ethanol with a response time of 17.6 ± 1.2 s is clearly observed. The rapid recovery of the current with a transient of 16.7 ± 0.9 s after ethanol off also demonstrates good reversibility of the gas sensor. Figure 7c shows the gas sensor response increases with the increasing gaseous concentration, e.g., 10.2 to 57.4 from 1 to 25 ppm. Typically, the gas sensing sensitivity can be expressed as $\ln S = \ln a + b \ln C$,^{45,46} where S is the sensitivity, C is the gas concentration of ethanol, and a and b are the gas sensor/gas sensing material-dependent constants. The logarithmic relationship, which can be utilized to predict the target gas concentration, is shown in the inset of Figure 7c. If we presume a smallest acceptable sensitivity value of 3, the lowest detection limit for ethanol was calculated to be ~ 120 ppb according to the logarithmic correlation. Moreover, the response measure-

ment was repeated for 8 cycles to ethanol at 25 ppm (Figure 7d). The reproducible results with a small variation of approximately 0.5 μ A (i.e., $\sim$ 1% of the measuring currents upon injecting gaseous ethanol) suggest satisfied repeatability of the device.

The gas sensor fabricated in this work yields excellent and reliable gas sensing performances. For example, the gas sensor response to 1 and 10 ppm of ethanol was measured to be 10.2 and 29.7, respectively, which are superior compared with other commercially available MEMS gas sensors (Table 1).

Table 1. Comparison of Gas Sensing Performance to Ethanol with Other Commercially Available MEMS Gas Sensors. Gas Sensing Performances Were Extracted from the Product User Manuals

product name	sensitivity at 10 ppm	lower detection limit (ppm)	work power consumption (mW)
this work	29.7	1	39
SGX MiCS-5524	3.3	10	76
ams AS-MLV-P2	11.1	10	34
ams CCS801	4	10	33
FIS SM-30	3.3	1	20
Figaro TGS8100	4	1	15

CONCLUSIONS

An easily fabricated, low-cost, simple gas sensor was designed and developed by planar MEMS technology with only two photolithographic steps, whereas conventional MEMS-based gas sensors require at least three masks. Porous and uniformly distributed clusters of SnO₂ nanoparticles were carefully synthesized and loaded onto the suspended MHP. Gaseous ethanol was utilized to test the performance of the fabricated gas sensor. The optimal work temperature was determined to be $\sim$ 400 $^{\circ}$ C with a small microheater power consumption of 39 mW and a reliable gas sensing sensitivity to 1 ppm ethanol. In addition, the gas sensor exhibited excellent sensing repeatability and reproducibility. The sensor reported in this experiment reduces the fabrication cost in terms of minimized photolithography steps (e.g., higher total yield) compared to traditional gas sensors; therefore, the insights obtained here will be attractive and promising for large-scale industrial manufacturing of MEMS microheaters and gas sensors.

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Author Contributions

X.C., W.Y., and K.W.N. acquired funding for this study; Y.C. and M.L. designed the experiment; Y.C., M.L., W.Y., and X.Z. carried out the experimental procedure; M.L. analyzed the results and wrote the article; and M.L., K.W.N., and X.C. reviewed and edited the article.

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Notes

The authors declare no competing financial interest.

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REFERENCES

- (1) Tyagi, P.; Sharma, A.; Tomar, M.; Gupta, V. Metal oxide catalyst assisted SnO₂ thin film based SO₂ gas sensor. *Sens. Actuators, B* **2016**, 224, 282–289.
- (2) Wolfrum, E. J.; Meglen, R. M.; Peterson, D.; Sluiter, J. Metal oxide sensor arrays for the detection, differentiation, and quantification of volatile organic compounds at sub-parts-per-million concentration levels. *Sens. Actuators, B* **2006**, 115, 322–329.
- (3) Fine, G. F.; Cavanagh, L. M.; Afonja, A.; Binions, R. Metal oxide semi-conductor gas sensors in environmental monitoring. *Sensors* **2010**, 10, 5469–5502.
- (4) Gregis, G.; Sanchez, J.-B.; Bezverkhyy, I.; Weber, G.; Berger, F.; Fierro, V.; Bellat, J.-D.; Celzard, A. Detection and quantification of lung cancer biomarkers by a micro-analytical device using a single metal oxide-based gas sensor. *Sens. Actuators, B* **2018**, 255, 391–400.
- (5) Seiyama, T.; Kato, A.; Fujiishi, K.; Nagatani, M. A New Detector for Gaseous Components Using Semiconductive Thin Films. *Anal. Chem.* **1962**, 34, 1502–1503.
- (6) Taguchi, N. *Published patent application in Japan*; S37–47677 1962.
- (7) Liu, H.; Zhang, L.; Li, K. H. H.; Tan, O. K. Microhotplates for Metal Oxide Semiconductor Gas Sensor Applications—Towards the CMOS-MEMS Monolithic Approach. *Micromachines* **2018**, 9, 557.
- (8) Shin, J.; Choi, S.-J.; Lee, I.; Youn, D.-Y.; Park, C. O.; Lee, J.-H.; Tuller, H. L.; Kim, I.-D. Thin-Wall Assembled SnO₂ Fibers Functionalized by Catalytic Pt Nanoparticles and their Superior

Exhaled-Breath-Sensing Properties for the Diagnosis of Diabetes. *Adv. Funct. Mater.* **2013**, *23*, 2357–2367.

(9) Wang, L.; Dou, H.; Lou, Z.; Zhang, T. Encapsulated nanoreactors (Au@SnO₂): a new sensing material for chemical sensors. *Nanoscale* **2013**, *5*, 2686–2691.

(10) Park, S.; An, S.; Ko, H.; Jin, C.; Lee, C. Synthesis of Nanograined ZnO Nanowires and Their Enhanced Gas Sensing Properties. *ACS Appl. Mater. Interfaces* **2012**, *4*, 3650–3656.

(11) Shendage, S. S.; Patil, V. L.; Vanalakar, S. A.; Patil, S. P.; Harale, N. S.; Bhosale, J. L.; Kim, J. H.; Patil, P. S. Sensitive and selective NO₂ gas sensor based on WO₃ nanoplates. *Sens. Actuators, B* **2017**, *240*, 426–433.

(12) Bai, J.; Zhou, B. Titanium Dioxide Nanomaterials for Sensor Applications. *Chem. Rev.* **2014**, *114*, 10131–10176.

(13) Xu, X.; Fan, H.; Liu, Y.; Wang, L.; Zhang, T. Au-loaded In₂O₃ nanofibers-based ethanol micro gas sensor with low power consumption. *Sens. Actuators, B* **2011**, *160*, 713–719.

(14) Zhang, Y.; Zheng, W. New insight into gas sensing performance of nanoneedle-assembled and nanosheet-assembled hierarchical NiO nanoflowers. *Mater. Lett.* **2017**, *195*, 217–219.

(15) Li, T.; He, M.; Zeng, W. Polyhedral Cu₂O crystal: Morphology evolution from meshed nanocube to solid and gas-sensing performance. *J. Alloys Compd.* **2017**, *712*, 50–58.

(16) Kim, T.-H.; Yoon, J.-W.; Kang, Y. C.; Abdel-Hady, F.; Wazzan, A. A.; Lee, J.-H. A strategy for ultrasensitive and selective detection of methylamine using p-type Cr₂O₃: Morphological design of sensing materials, control of charge carrier concentrations, and configurational tuning of Au catalysts. *Sens. Actuators, B* **2017**, *240*, 1049–1057.

(17) Zhou, T.; Zhang, T.; Zhang, R.; Lou, Z.; Deng, J.; Wang, L. Ultrahigh-sensitive sensing platform based on p-type dumbbell-like Co₃O₄ network. *Appl. Surf. Sci.* **2017**, *426*, 951–956.

(18) Barsan, N.; Koziej, D.; Weimar, U. Metal oxide-based gas sensor research: How to? *Sens. Actuators, B* **2007**, *121*, 18–35.

(19) Gao, X.; Zhang, T. An overview: Facet-dependent metal oxide semiconductor gas sensors. *Sens. Actuators, B* **2018**, *277*, 604–633.

(20) Yamazoe, N.; Shimanoe, K. Theory of power laws for semiconductor gas sensors. *Sens. Actuators, B* **2008**, *128*, 566–573.

(21) Yamazoe, N.; Sakai, G.; Shimanoe, K. Oxide Semiconductor Gas Sensors. *Catal. Surv. Asia* **2003**, *7*, 63–75.

(22) Yamazoe, N.; Fuchigami, J.; Kishikawa, M.; Seiyama, T. Interactions of tin oxide surface with O₂, H₂O AND H₂. *Surf. Sci.* **1979**, *86*, 335–344.

(23) Barsan, N.; Weimar, U. Conduction Model of Metal Oxide Gas Sensors. *J. Electroceram.* **2001**, *7*, 143–167.

(24) Kim, H.-J.; Lee, J.-H. Highly sensitive and selective gas sensors using p-type oxide semiconductors: Overview. *Sens. Actuators, B* **2014**, *192*, 607–627.

(25) Gao, X.; Li, F.; Wang, R.; Zhang, T. A formaldehyde sensor: Significant role of p-n heterojunction in gas-sensitive core-shell nanofibers. *Sens. Actuators, B* **2018**, *258*, 1230–1241.

(26) Peterson, P. J. D.; Aujla, A.; Grant, K. H.; Brundle, A. G.; Thompson, M. R.; Hey, J. V.; Leigh, R. J. Practical Use of Metal Oxide Semiconductor Gas Sensors for Measuring Nitrogen Dioxide and Ozone in Urban Environments. *Sensors* **2017**, *17*, 1653.

(27) Heszler, P.; Ionescu, R.; Llobet, E.; Retes, L. F.; Smulko, J. M.; Kish, L. B.; Granqvist, C. G. On the selectivity of nanostructured semiconductor gas sensors. *Phys. Status Solidi B* **2007**, *244*, 4331–4335.

(28) Zhang, C.; Luo, Y.; Xu, J.; Debliquy, M. Room temperature conductive type metal oxide semiconductor gas sensors for NO₂ detection. *Sens. Actuators, A* **2019**, *289*, 118–133.

(29) Tanihira, T.; Yoshioka, K. I.; Shinnishi, K.; Izawa, K.; Kaneyasu, K. Development of CH₄ sensor using MEMS technology for battery operated town gas leak detector. *Sens. Lett.* **2011**, *9*, 414–417.

(30) Bhattacharyya, P. Technological journey towards reliable microheater development for MEMS gas sensors: A review. *IEEE Trans. Device Mater. Reliab.* **2014**, *14*, 589–599.

(31) Fitzgerald, A. M.; Jackson, K. M.; Chung, C. C.; White, C. D. Translational Engineering: Best Practices in Developing MEMS for Volume Manufacturing. *Sens. Mater.* **2018**, *30*, 779–789.

(32) Hsueh, T.-J.; Lu, C.-L. A hybrid YSZ/SnO₂/MEMS SO₂ gas sensor. *RSC Adv.* **2019**, *9*, 27800–27806.

(33) Behera, B.; Chandra, S. An innovative gas sensor incorporating ZnO–CuO nanoflakes in planar MEMS technology. *Sens. Actuators, B* **2016**, *229*, 414–424.

(34) Sun, S.; Liu, B.; Liu, X.; Yin, Z. Dispersion of antimony doped tin oxide nanopowders for preparing transparent thermal insulation water-based coatings. *J. Mater. Res.* **2017**, *32*, 2414.

(35) Ghaderi, M.; Ayerden, N. P.; de Graaf, G.; Wolffenbuttel, R. F. Minimizing stress in large-area surface micromachined perforated membranes with slits. *J. Micromech. Microeng.* **2015**, *25*, No. 074010.

(36) Xu, L.; Li, T.; Gao, X.; Wang, Y. Development of a Reliable Micro-Hotplate With Low Power Consumption. *IEEE Sens. J.* **2011**, *11*, 913–919.

(37) Prasad, M.; Dutta, P. S. Development of micro-hotplate and its reliability for gas sensing applications. *Appl. Phys. A: Mater. Sci. Process.* **2018**, *124*, 788.

(38) Briand, D.; Krauss, A.; van der Schoot, B.; Weimar, U.; Göpel, W.; De Rooji, N. F. Design and fabrication of high-temperature micro-hotplates for drop-coated gas sensors. *Sens. Actuators, B* **2000**, *68*, 223–233.

(39) Christofferson, J.; Maize, K.; Ezzahri, Y.; Shabani, J.; Wang, X.; Shakouri, A. Microscale and Nanoscale Thermal Characterization Techniques. *J. Electron. Packag.* **2008**, *130*, No. 041101.

(40) Wang, Y.; Cheng, P.; Liu, Q.; Sun, Y.; Zhang, X.; Chen, J.; Ding, G. A nanocomposite coating improving the accuracy in infrared temperature measurement for thermal micro-devices. *Sens. Actuators, A* **2019**, *293*, 29–36.

(41) Oxley, C. H.; Hopper, R. H.; Hill, G.; Evans, G. A. Improved infrared (IR) microscope measurements and theory for the micro-electronics industry. *Solid-State Electron.* **2010**, *54*, 63–66.

(42) Cheng, J.; Liang, S.; Wang, J.; Li, X. A Stepwise Refining Algorithm of Temperature and Emissivity Separation for Hyperspectral Thermal Infrared Data. *IEEE Trans. Geosci. Remote Sens.* **2010**, *48*, 1588–1597.

(43) Ohya, K.; Yamanaka, T.; Inai, K.; Ishitani, T. Comparison of secondary electron emission in helium ion microscope with gallium ion and electron microscopes. *Nucl. Instrum. Methods Phys. Res., Sect. B* **2009**, *267*, 584–589.

(44) Mayandi, J.; Marikkannan, M.; Ragavendran, V.; Jayabal, P. Hydrothermally synthesized Sb and Zn doped SnO₂ nanoparticles. *J. Nanosci. Nanotechnol.* **2014**, *2*, 707–710.

(45) Chen, Y.; Xu, P.; Li, X.; Ren, Y.; Deng, Y. High-performance H₂ sensors with selectively hydrophobic micro-plate for self-aligned upload of Pd nanodots modified mesoporous In₂O₃ sensing-material. *Sens. Actuators, B* **2018**, *267*, 83–92.

(46) Ma, L.; Fan, H.; Tian, H.; Fang, J.; Qian, X. The n-ZnO/n-In₂O₃ heterojunction formed by a surface-modification and their potential barrier-control in methanal gas sensing. *Sens. Actuators, B* **2016**, *222*, 508–516.