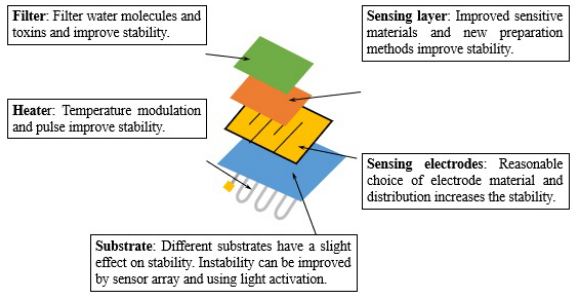
Stability of Metal Oxide Semiconductor Gas Sensors: A Review

Hongfeng Chai, Zichen Zheng, Kewei Liu, Jinyong Xu, Kaidi Wu, Yifan Luo, Hanlin Liao, Marc Debliquy, and Chao Zhang

***Abstract*—Sensor stability is defined as the ability to maintain a relatively stable and repeatable signal over a sufficient period. Long-term stability for gas sensors is an essential capability for carrying out long-term data collection of human exhaled breath, environmental monitoring and other gas detection in the modern electronic information age. This article reviews the research advances on the stability of metal oxide semiconductor gas sensors in the past five years. The impact of structure, environment, toxicity and sensor array on the sensor stability are discussed. Then, the improvement schemes of existing materials and structure design are summarized. The achievements of structure doping, humidity, anti-poisoning and photoactivation are overviewed. Finally, the great significance of elucidating the sensing mechanism and carrying out the life acceleration test for future research and development is pointed out.**



***Index Terms*—Semiconductor, metal oxide, gas sensor, stability.**

I. Introduction

CONVENTIONAL gas analyzers, such as mass spectrometry, energy spectrometry and chromatography, are limited by the high cost of the devices [1]. Compared with the analyzers, gas sensors based on metal oxide semiconductors are widely used due to their small size, easy operation, low cost and other benefits. Among the main characteristics of gas sensors, sensitivity and selectivity are the main objects of research. However, as one of the indicators which the costumers are concerned about, stability is not often discussed. In general, commercial sensors should have a life span of at least 2-3 years (17,000-26,000 hours). During this period, a stable and repeatable signal should be maintained [2]. Stability tests need to be measured and recorded in the long term, limiting the study of stability. At the same time, data about the sensor stability are often retained due to business secrets. In addition, until now, there is no specific index for sensor stability in the world [3].

Unlike other semiconductors, which undergo irreversible chemical reactions to form stable oxides when exposed to air at high temperatures, metal oxides usually remain stable when their surfaces interact with oxygen. The target gas molecules in the environment will interact with the adsorbed oxygen species on the surface, crystal planes and grain boundaries of metal oxide semiconductors, which will lead to the transfer of electrons at the interface, thus making the resistance change accordingly. Metal oxide semiconductor gas sensors are classified into two categories. One is the resistive type, which can be subdivided into surface resistance control and bulk resistance control. Surface control is divided into sintering, thick coating and film. The second is non-resistive type, which consists of solid electrolyte, diode and field-effect transistors (FET), etc.

According to the perspective of preparation technology and detection mechanism, the sensor performance is mainly determined by the gas-sensitive element, heating system and substrate, among which the gas-sensitive element is the core, and the gas-sensitive element determines the selectivity,

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sensitivity, stability and other aspects of the sensor. The heating system provides energy for the activation of gas sensors. The heating mode also affects the sensor stability. Continuous high-temperature heating may cause an unexpected crystal growth of sensing materials. Meanwhile, some external factors also affect the sensor stability, such as humidity, operating temperature, target gas, etc. [4].

Sensor life depends on several factors: 1. The material stability; 2. Environmental conditions (humidity, temperature, etc.); 3. Target gas (reducing or oxidizing gas, gas concentration, etc.) [5]. To assess sensor stability, the following two indexes must be tested: (1) Stability of the conductivity, which is also known as the sensor's baseline; (2) Stability of the response. Therefore, from metal oxide sensing materials to advanced devices, the operating stability of gas sensors should be a necessary evaluation index. Korotcenkov *et al.* summarized the factors which affect the stability of semiconductor gas sensors and the improvement strategies in 2014 [6]. The research advance on sensor stability in the last five years is reviewed in this article. Five factors determine the stability of semiconductor metal oxide sensors: sensitive materials, element doping, ambient humidity, poisoning and component composition of gas sensors, which will be discussed in Section II. In view of these five factors, according to the literature in recent years, several schemes to deal with sensitive materials, environment, poisoning and circuit are summarized, including photoactivation and advanced manufacturing methods, which will be discussed in Section III.

II. Key Factors of Stability

For metal oxide semiconductor gas sensors, the exchange of charge carriers in the gas adsorption and desorption is the cause of the electrical signal change. When the gas-sensitive layer reacts with gas, the conductivity of the film varies. The rate of change in conductivity is related to the concentration of the test gas. Subsequently, the electrical signal is transmitted. The material microstructure needs to be stabilized to maintain a stable sensing performance. Sensitive materials, element doping, ambient humidity and component composition of gas sensors are the key factors impacting stability, as shown in Fig 1.

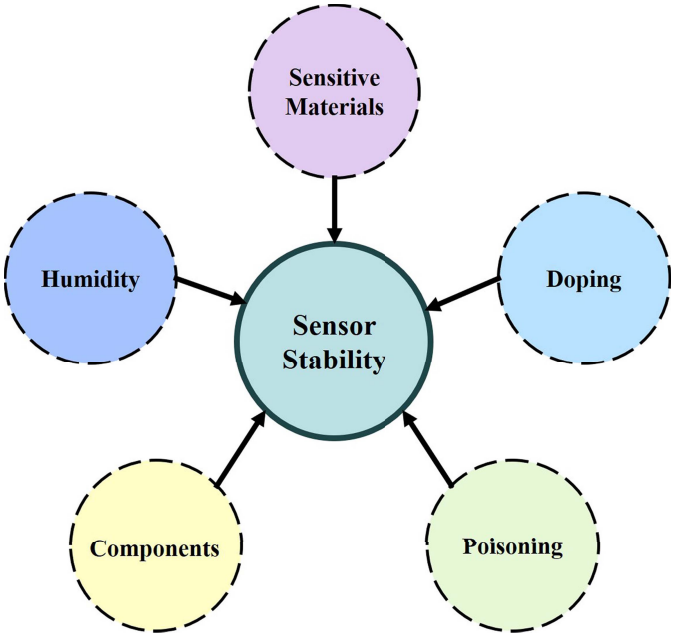

Fig. 1. Main influencing factors of stability.

A. Sensitive Materials

Nanomaterials used in gas sensors at a high temperature must have high thermal stability. The material thermal stability is related to the temperature at which the chemical sensor using the material can operate. This is evident in the atmosphere of reducing gas [4], [7].

Generally, the grain size of metal oxide gas-sensitive layer is less than 100 nm. The smaller the grain size is, the better the gas sensing performance of the sensor can be obtained. The grain size should be similar to twice the Debye length. Because the variation of grain size is inversely proportional to the specific surface area, the grain boundary decreases with the reduction of grain size, resulting in the noteworthy change of resistance. Because the nanoparticles are basically in a non-equilibrium state, the heat made the grains grow and homogenize, and sintering and even melting occurred [4]. When the sensor is in a high-temperature environment or the heating temperature rises, the grain size grows, which affects the sensing performance [8]. Formula (1) is the critical temperature of grain growth, in which T_{st} and t are the grain size and operating temperature, respectively. The length unit is nm.

$$T_{st} = 420(logt)^{3/4}\ (^{\circ}\mathrm{C}) \tag{1}$$

When the particle size decreases, the surface volume ratio increases. The decrease of melting temperature is mainly due to the increase of surface free energy of particles. The decrease of melting temperature nanoparticles is inversely proportional to the particle diameter [9].

For example, Motaung *et al.* found that ZnO grain growth resulted in long-term baseline drift under high-temperature conditions [10]. In a network composed of particles, the size variation of particles forms a gas-sensitive matrix. When the particles grow, the contact area among particles becomes more prominent, and the necking among grains is easy to form. Yin *et al.* evaporated WO_3 onto a tungsten substrate. The study showed that different temperatures of the substrate in the evaporating process would affect the structure and morphology of the material as well as the number of preferred orientations and grain size, as shown in TABLE I [11]. Similarly, in the high-frequency chemical vapor deposition technology, the variation of substrate temperature could change the grain size, and apparent agglomeration occurs [12].

In the nanometer size range, it is well known that the specific surface area is positively correlated with the sensitivity of the material. However, according to studies, there are other factors besides specific surface area that determine sensitivity. For example, some specific exposed crystal surfaces can provide better reaction control [13]. For the deposited metal oxide clusters, the change in size is generally followed by

TABLE I
GRAIN SIZES AT DIFFERENT TEMPERATURES

Growth temperature (°C)	FWHM(2θ)	Grain size (Å)
300	0.27	33
400	0.21	46
500	0.18	68
600	0.16	70

a significant change in cluster structure, which further varies as the metal oxide clusters are deposited on the substrate [14]. It is the smallest particle that is easy to grow that determines the stability of the gas-sensitive layer.

B. Doping

Element doping can significantly influence the material structure, adsorption ability, visual, electrical and other properties. Crystal boundary migration dynamics generally control the sintering rate of metal oxide material. The presence of additional grain boundaries between adjacent metal oxide particles inhibits cationic diffusion and microcrystalline growth. It means that changing the properties of grain boundaries by introducing a second phase can provide a method for controlling the sintering mechanism, kinetics and final properties of gas-sensitive materials, and this mechanism is mainly related to the structure of dopants and the selection of metal oxides [15].

Although the addition of noble metal additives can effectively improve the response of semiconductor metal oxides, the complex mechanisms of these additives have not been fully discussed. For example, SnO_2 suffers from excessive crystallization in sintering. Generally speaking, it reduces the porosity and specific surface area, which means the decrease of the adsorption sites for gas molecules and the adsorption capacity, leading to the decrease of sensor response. After the calcination of SnO_2 doped with the elements In^{3+} and Si^{4+}, crystallization inhibition can be seen [16]. However, different doping elements do not inhibit grain growth. According to Abbas *et al.*, the concentration of doped Ag is inversely proportional to the grain size [17]. Ran *et al.* also found that doping with Sm can affect the average particle size of SnO_2 nanoparticles [18]. G. Korotcenkov confirmed that dopants could change the crystal lattice of the material and cause instability of grain size [19]. In the review of Motaung *et al.*, it is concluded that recent studies have found that when ZnO is doped with manganese, the change of crystal lattice morphology is brought by Mn^{2+} [10]. Doping elements also cause the electron recombination of oxides, leading to a decrease in the concentration of the charge carriers. This effect is called the neutralization effect [20]. This means that the control of the doping content and the suitability of the doped element for the material may change the final stability of the gas-sensitive layer material.

C. Poisoning

In addition to the crystal size and the concentration of charge carriers, the metal oxide can react with some unwanted molecules, which leads to instability. A gas or chemical substance other than the target gas is generally called a disturbance as it causes a reversible reaction, while it is considered toxic if it produces an irreversible reaction. The sensing mechanism is the adsorption and decomposition reaction between surface and gas. Generally, the surface activity of metal oxide is relatively high, so it is easy to have an irreversible reaction with active elements, which leads to the decline of the long-term stability of semiconductors.

There are three main poisoning mechanisms: toxicant adsorption, toxicant-induced surface reconstruction, and compound formation with toxicant and catalyst [21]. The electron configuration of the reactants influences the interaction between the potential poison and the dopant. The configuration determines the final form of bond between the poison and the catalyst. Hexamethyldisiloxy (HMDS) can take the place of the reaction sites of Pt and Pd in the catalytic oxidation of methane, propane, carbon monoxide and hydrogen [22]. Palmisano *et al.* reported that H_2 sensors were affected by a variety of toxic gases [23]. TiO_2 is widely used in oxygen sensors because of its high sensitivity, fast response and good chemical stability. TiO_2 gas sensors could be poisoned by methylcyclopentadienyl manganese tricarbonyl (MMT) when detecting automobile exhaust. Mn mainly exists on the grain boundary of TiO_2 in the form of MnO_2, resulting in low resistance [24].

The adsorption of poisons is mainly through competitive adsorption with reactive substances, which can be understood through the classical adsorption isotherm Formula (2) established by Langmuir [25].

$$\theta = P/[P + (k_{des}/k_{ads})\exp(-\Delta H_{PHY}/RT)] \quad (2)$$

The electron density may also explain the sequence of increased sulfide poisoning activity, as the H_2S effect is stronger than that of SO_2. Catalytic poisoning of noble metals mainly incorporates the adsorption of poisons and the formation of compounds. Palmisano *et al.*'s experiments showed that Pd was more susceptible to sulfur poisoning than Pt, and the magnitude of the effect depended on the degree to which the metal atom's d orbital was involved in metal bonding (Pt < Pd) [23].

The compound formation between catalysts refers to the formation of a compound from a toxic precursor and a catalyst, which is similar to the principle of poison adsorption [26], [27].

D. Humidity

The relative humidity (RH) in the atmosphere can be close to 100%. Metal oxide semiconductor sensors are sensitive to water vapor and their stability is affected by ambient humidity. Water vapor is an unavoidable vital interfering gas in metal oxide semiconductor gas sensors [8], [28], [29], [30], [31], [32]. Firstly, the concentration of H_2O in the atmosphere

is high (for example, a RH value in the range 20-80% corresponds to 1200-4800 ppm at 0°C, but to 14000-56000 ppm at 38°C), while the concentration of the gas to be detected is in the tens of ppm or ppb level. Secondly, changes in climate, weather, night and day, temperature and latitude/longitude positions also impact the environment. The H_2O molecules can occupy the adsorption sites on the sensor surface [33]. Surfactant substances associated with H_2O are known as $-$OH [33], [34], [35]. Changes in humidity in the environment not only cause long-term shifts in the baseline resistance, but also in the calibration curve of the conductance and partial conductance. Studies have shown that the surface of SnO_2 adsorbs more water than oxygen [36]. Degler *et al.* [33] discussed three different water adsorption methods based on the interaction between SnO_2 and water vapor. The composition of the surface, the sensor resistance, and the gas sensing properties can be affected by different routes of water adsorption. The adsorption of water molecules is the cause of surface modification, which affects the adsorption of other gases [2], [37]. Yan *et al.* studied the sensing characteristics of four metal oxides for VOCs in different humidity environments, and the data showed that they were all affected by humidity [38]. A typical chemisorption reaction equation for water vapor is shown in Formula (3). Here the M_m is the metal sites on the surface, O_{ads} is the adsorbed oxygen and S is the site for chemically adsorbed oxygen.

$$H_2O + 2M_m + O^-_{ads} \leftrightarrow 2(M^+_m - OH) + e^- + S \qquad (3)$$

Humidity can also have an impact on the aging of the sensor. It is reported that the aging phenomenon of the SnO_2 sensor can be attributed to the change of water molecule adsorption [36]. The H_2O interacts with oxygen ions in the inner lattice of SnO_2 to produce free holes or electrons, which explains the decrease in resistance over time as the sensor ages or humidity increases rapidly [39], [40], [41], [42].

E. Sensor Components

In addition to the gas-sensitive layer and the external environment, the sensor components also impact its stability.

Metal oxide semiconductor gas sensors generally operate in the range of 150 to 450°C and are equipped with integrated heaters. The response of the gas sensor relies mainly on the operating temperature, so temperature control is the key component of the whole gas sensor system [9]. In recent years, to reduce heating power and energy consumption, the heater miniaturization strategy has been generally adopted [43], [44]. When the heaters get smaller, the accuracy in the fabrication becomes challenging to control. This may lead to a controlling issue of the working temperature. In addition, to improve selectivity, a temperature-pulse operating mode is used, in which temperatures are unevenly distributed and vary rapidly, which can cause severe thermal stress, thus shortening the life of the sensor and leading to film rupture [45].

Traditional metal-oxide semiconductor sensors need microheaters to control the temperature distribution, as well as interdigital electrodes to measure the in-situ resistance or in-situ current of the target material [44]. With the emergence of wearable flexible devices, sensors with good flexibility and high stability are urgently needed. The way to design and arrange electrodes has a significant impact on sensor stability. For example, electrode materials commonly used in semiconductor metal oxides have different disadvantages. Au electrode has good long-term stability, but it can quickly diffuse into the substrate at relatively low temperatures. Although Pt electrode is the most stable material, it is also prone to instability due to its poor adhesion [46]. In addition, the commonly used sensor temperature modulation (modulated by a temperature switch to enhance sensor selectivity) can lead to repeated expansion and contraction of wires and contacts, which can reduce sensor stability and even lead to sensor failure.

To sum up, the factors that determine the stability of semiconductor metal oxide sensor are not only affected by their own material structure, but also restricted by external conditions. How to control the nature of the material itself and reduce the influence of the surrounding environment will be discussed in the next Section.

III. Improvement Methods of Stability

The lack of stability leads to the failure of the data model obtained in the initial calculation in a relatively short time. The sensors responded differently to the same gas during the aging process so that the devices had poor repeatability [25], [47]. In this section, the instability factors mentioned in Section II are addressed through improved sensing materials, environmental impact reduction, circuit design, poisoning solutions, light activation and advanced manufacturing methods.

A. Sensing Materials

The methods to control the grain size are the key to improve the thermal stability of the material structure [48].

1) Nano-Phase Materials: Nano-phase materials have broader thermal stability than nanocrystalline materials, which is due to the higher activation energy of grain growth of nanomaterials. At the same time, the activation energy of micron particles with nanometer phase is more significant so that the growth of micron particles is difficult, and the thermal stability is good. Inhibiting interfacial migration can also prevent grain growth and improve thermal stability. Excessive energy at the interface and significant energy differences between adjacent interfaces will likely lead to interface migration. Therefore, when the crystal grains are selected as equiaxed grains with uniform particle size and narrow distribution, and remain isotropic, the interface energy will be significantly reduced and the growth of grains will not be easy to occur [4]. During the heating process, the grain boundary will first undergo a structural relaxation phenomenon, resulting in the rearrangement of atoms, which tends to be ordered, to reduce the grain boundary free energy. The energy of grain boundary relaxation is generally smaller than that of grain boundary migration. During the heating process, the energy is first consumed on the grain boundary relaxation, so the grains of nano-phase materials are not easy to grow up in a wide range [49], [50]. As a result, using nano-phase materials or even micron materials as the sensing material can

effectively improve the stability of metal oxide semiconductor gas sensors.

2) Pinning Effect: A stabilizer can be added to nano-phase material to make it segregate at the grain boundary, reducing the electrostatic energy and distortion energy of grain boundary. It also plays a role in pinning grain boundary, making grain boundary migration difficult, and finally realizes the control of grain growth. This effect is known as the pinning effect. In gas sensing materials, the pinning effect can be used to stabilize the grain growth in the life span of the sensing layer. Wu *et al.* found that Mn decreased grain boundary surface energy, and its influence on grain boundary energy was particularly significant, which was due to the segregation of Mn [51]. Tobaldi *et al.* reported that the addition of Cu element could cover the surface of nano TiO_2, which limited the further changes of its crystal lattice [52]. Doped zirconate particles in common metal oxides can effectively prevent grain growth, which has high stability and low diffusion kinetics, and can limit the movement of grain boundaries. A similar pinning effect is known as Zener pinning. Wildfire *et al.* prepared a sensing material composed of Y-GZO ($Gd_{1.8}Y_{0.2}Zr_2O_7$) and SnO_2, of which the stability and sensitivity were improved compared with pure SnO_2 [53].

3) Preheating Treatment: It is an effective method to improve the sensor stability by aging the sensor before testing at a higher temperature than the working temperature. Preheating sensors have several functions. It can somehow clean the surface contamination of the sensor and remove the possible organic compounds left from the fabrication period. Furthermore, it can limit the grain growth in the working period and eliminate the defects which can cause the sensor instability. In the study of Zhang *et al.*, since the heat treatment can effectively transform WO_{3-x} into WO_3 under 24 hours, the sensor performance can be stabilized [54].

In addition to processing on the integrity of materials and the structure of grains, it is also mentioned in Section 2.1 that the minimum grain size determines the activation energy of grain growth, so controlling the grain size at the beginning of deposition is considered to be the best way to improve stability [12]. According to Nanda's study, the morphology and grain size of CuO were controlled by chemical vapor deposition to obtain appropriate gas sensing properties and good stability [55]. In the experiment of Amarnath *et al.*, V_2O_5 and WO_3 coatings with controllable size were developed by in-situ chemical oxidation polymerization [56].

B. Testing Environment

In this section, the methods from the previous work about how to reduce interference from the service environment are summarized.

1) Temperature: Recently, temperature switches [57] or temperature-modulation [58] in metal oxide semiconductor gas sensors have become a prevalent technology. Compared with organic sensors, a heating device is equipped in metal oxide sensors. With the progress of micromechanics, the heater becomes smaller and the overall heat capacity is reduced simultaneously.

Since the temperature has a significant influence on the baseline resistance and the sensor response, the sensing characteristics can be optimized and the stability can be improved by adjusting the actual temperature of the heater itself through using a dedicated temperature sensor or heating resistance. In the experiment of Shaposhnik *et al.*, the chemical and physical properties and a good selection of temperature modulation parameters made the sensor obtain a good response and excellent stability [59].

Although sensors with temperature modulation introduce additional circuit complexity and increase cost, they have high reliability, especially when combined with pulse drives, but this method can effectively improve the recovery rate and the sensor stability [60], [61]. Wu *et al.* improved the recovery stability of the gas sensor at room temperature. 10 s pulse heating was used to reduce the time needed to reach the initial resistance [60].

By temperature modulation, the target gas can be accurately distinguished and the stability can be improved [62], [63]. Di Giuseppe *et al.* optimized the modulation system and realized drift compensation and fault identification [64].

2) Humidity: To obtain moisture-resistant sensors that can work in atmospheric conditions, it is essential to minimize the effects of −OH [65]. Generally, there are two methods to address the instability in a high humidity environment (especially when detecting human exhaled breath). Firstly, in terms of sensing materials and hardware, the response to humidity sensitivity can be weakened by improving the technology and preparation method. Suematsu *et al.* overcomed −OH poisoning by loading V_2O_5 on the surface of SnO_2 and prevented degradation of sensor response caused by −OH poisoning [66].

Similarly, Pawar *et al.* prepared a 3D porous In_2O_3 microcube, and the response changed little when the relative humidity varied [67]. Metal oxide sensors decorated with graphene showed long-term stability under various environments with varying humidity and oxygen conditions [68]. The effect of water vapor can be reduced by coating the surface of the metal oxide with some specific metal-organic frameworks (MOF). For example, MIL-160 can act as a filter for the selective adsorption of H_2O [31]. SiO_2 shows powerful water absorption properties. Using the commercial atmospheric pressure plasma spraying method to prepare an ultra-thin SiO_2 layer on the cover of ZnO columnar film can effectively reduce the influence of water vapor [69]. SnO_2 composited with g-C_3N_4 has excellent moisture resistance, since g-C_3N_4 is an ideal layered material that can overlie the cover of SnO_2 like a film, limiting the hydrolysis of SnO_2[70]. Lou *et al.* synthesized three-dimensional porous ZrO_2 film through a template method, and SnO_2 was deposited onto the substrates by Atomic Layer Deposition (ALD) technology. Since porous zirconia formed a hydrophobic layer, the influence of humidity on SnO_2 was significantly reduced [71]. Except for the addition of a protecting layer, some other methods can also be used to design humidity-independent sensors. Suematsu *et al.* aged the gas-sensitive material in the wet air at 580°C, and the oxygen adsorption equilibrium constant increased no matter in dry or wet environments. The increased oxygen

adsorption inhibited the adsorption of −OH [72]. Oxidation of −OH can also be achieved by doping elements. Kwak *et al.* found that Tb^{4+} and Tb^{3+} can react with −OH to update the SnO_2 cover and reduce the influence of vaporous water [35]. The latest research showed that adding appropriate desiccant can decrease the impact of water vapor and hydrophobic agents on the target gas at the same time. Mahdavi *et al.* reduced the impact of vaporous water on the gas sensor by using $CaCl_2$. Fig. 2 shows the influence of desiccant on the sensor [73].

Humidity drift compensation can depend on the development of software. In order to reduce or avoid resistance drift resulted from environmental fluctuations, Vafaei and Amini developed a compensation mechanism in which the sensor model was made with temperature, humidity, and response as inputs and concentration values as outputs. The sensor consisted of a built-in light source, a thermo-electric pile detector and two reflective walls. The cavity-free structure reduced the diffusion time and increased the linearity of the response [74]. The principle is to use the actual operation of the data processing to get a neural network, then direct output gas concentration through the introduction of humidity. Several reports in recent years have taken similar approaches [75], [76], [77], [78], [79]. Yan *et al.* realized the humidity model according to a power-law response, using absolute humidity to compensate relative humidity and temperature, and the final error was within 0.5-10% [38].

C. Sensor Design

The long-term drift of the sensor signal can be controlled in two ways. The first is to reduce or avoid the aging of the device, in which the electrode is the most critical, and the second is to offset the drift, such as pattern recognition [80].

1) Electrode Design: The electrode is responsible for transferring power or receiving current to the outside of the semiconductor gas sensor, which significantly influences the stability of the semiconductor gas sensor. The electrode must also have high-temperature resistance under extreme conditions [46].

In terms of the interdigital electrode, Pt is generally used as an electrode material, but its adhesion is poor. In order to solve the problem, adhesive can be added to the Pt material. Capone used a Ti/Au structure to reduce the dissolution of the gold electrode and pointed out that the Ti/Pt structure provides better stability [81].

At the same time, due to the heating and electricity, the sensing material will be subjected to mechanical stress, such as the nanowire structure, which will make the electrode and the material lose contact, resulting in sensor instability. The problem can be effectively solved by the reasonable arrangement of electrode gap. In Vallejos *et al.*'s study, a 5 μm electrode gap was found to have the best sensor stability [82].

2) Calibration Design of Sensor Array: The intrinsic changeability of gas sensors can degrade the ability to calibrate models, especially when the system changes [80]. Therefore, even if the conditions of the detection sensors are the same, each system needs to be calibrated separately. Fonollosa *et al.* built five dual-sensing units, each containing eight mixed-oxide gas

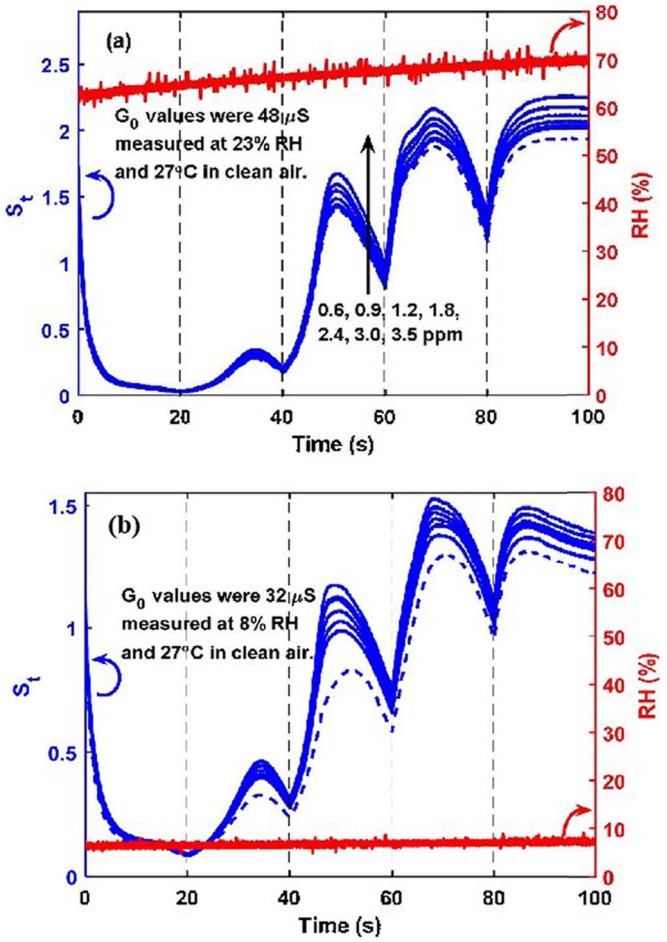

Fig. 2. Responses to different concentrations of acetone without any desiccant (a) and $CaCl_2$ (b) [73].

sensors, using a calibrated transfer strategy to offset drift [80]. Tian *et al.* adopted the method of classifier integration to cope with the sensor drift well [83]. Rehman *et al.* proposed an innovative classification strategy for reconfigurable sensor arrays. This approach allows sensors/individual classifiers to be added or removed from the model without recalibrating the entire system, while it also offsets the degradation in classification performance due to the occurrence of drift or sensor failure [84].

D. Sensor Poisoning Solutions

Octamethylcyclotetrasiloxane (OMCTS) is usually found indoors, and it can easily poison semiconductor gas sensors based on SnO_2. Organic compounds containing silicon can be toxic to semiconductor sensors as well. DSR (differential surface reduction) method can be used for further study of the effect of siloxane treatment on the dynamic performance of MOS sensors. DSR method focuses on the surface reaction rate, and can determine the sensor toxicity according to the application [85]. Schüler *et al.* showed that impedance-based detection of HMDSO (hexamethyldisiloxane) toxicity could be used to further improve the reliability of metal oxide gas sensor measurements by monitoring the time the sensor is exposed to the toxic gas of the sensor [86]. In the presence

of sulfur, cerium oxide is easily converted to cerium sulfate, resulting in a significant decrease in activity. Kim *et al.* developed a method to form an octahedral nanoceria on the crystal face of $CeO_2(111)$ after hydrothermal treatment of nano cerium oxide loaded on activated γ -Al_2O_3, and then loading Pt. The low basicity defect sites of Ce^{3+} are reduced, showing good sulfur resistance [87]. Suchorsk *et al.* studied CO poisoning and found that the higher CO tolerance at the nano-level around the metal-oxide interface made the whole micron-size Pd particles more resistant to CO poisoning [88], which provided a theoretical basis for improving the resistance of sensors to CO. In recent years, carbon nanotubes, as a stable material with support structure, have been widely used in combination with nano-metal or metal oxide as sensors. Due to the internal limitation of carbon nanotubes, it can effectively prevent the contamination of nano-metal elements like doped or loaded by external substances, such as CO. However, the uncontrollable formation process of carbon nanotubes leads to certain defects and vacancies, which also affects the stability of the composite with the sensor material [45].

In addition to improving the stability of baseline resistance, the detection of sensor poisoning can also reduce drift. Song *et al.* proposed a method for sensor array management, which can effectively evaluate the system status and achieve a maintenance recommendation accuracy of 98.25% [89].

E. Light Activation

Baseline drift is one of the most critical problems of metal oxide sensors, which must be reduced to improve the long-term stability [90]. As in sensor materials, excessive heating temperature always affects the stability of the material. To alleviate this problem, new activation methods other than heating can be used [91].

Adsorption begins when a semiconductor surface comes into contact with a gas, and light affects the adsorption rate [92]. Because ultraviolet (UV) light can activate metal oxides, it is considered to be utilized for sensor activation at room temperature [93], [94], [95]. Unfortunately, according to the equation $E = h\nu$, the higher the frequency of UV, the higher the energy of the photon, which can harm the electronics or the sensing layers in long-term service, leading to poor stability. So to obtain better stability, people are trying to use visible light to activate metal oxide sensors [96], [97]. Fig. 3 shows the effect of visible light on the sensing coating resistance. A combination of UV and temperature-activated ZnO nanostructures improves sensor dynamics, reduces response and recovery times, and decreases baseline drift [98]. To acquire good performance at room temperature, Choi *et al.* employed UV emitters (365 nm) as photoactivation, and used the photon energy of UV light to replace the heating energy [91]. The photon energy can increase the number of charge carriers in the conduction band, improve the surface chemical activity, and provide more active regions on the surface.

The advantage of light activation is that performing the test at room temperature reduces the damage from heating at a high temperature, while the disadvantage is that it can lead to relatively low gas response and a slow response/recovery rate [98]. Modifying the oxide bandgap to the absorption range of visible light can extend the optical response range [99]–[101]. Geng *et al.* prepared a CdS-ZnO sensitive layer by liquid plasma spraying technology, which can be activated by visible light and respond to NO_2 [102].

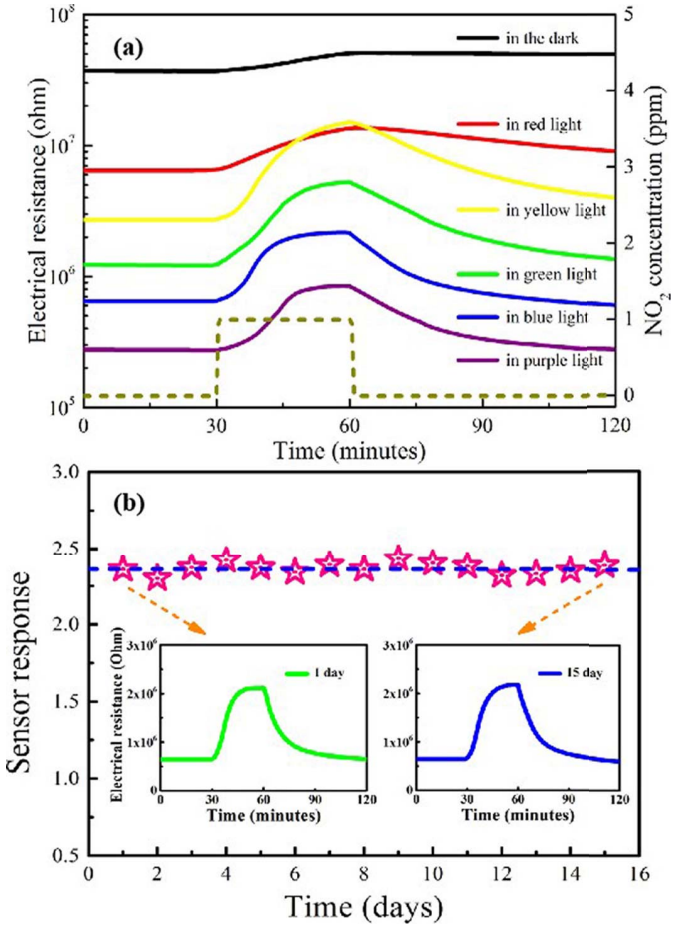

Fig. 3. (a) Response curve of SPPS sensor coating to 1.0 ppm NO_2 under different visible light at room temperature; (b) the stability test results of the SPPS coatings to 1.0 ppm NO_2 under blue light illumination at room temperature [93].

F. Advanced Preparation Methods

The sensor stability can be enhanced by improving the synthesis/deposition method.

Ink-jet printing is a simple and effective method to prepare coatings of metal oxide sensing materials by dipping the droplets onto the substrate by a printer. The In_2O_3 prepared by Jan *et al.* remained stable under an inert gas atmosphere without baseline drift, but the baseline had a significant drift when exposed to air [103]. Thermal spraying can obtain a unique gas-sensitive layer [104]. Zhang *et al.* deposited WO_3 gas-sensitive layer by atmospheric plasma spraying (APS), solution precursor plasma spraying (SPPS) and APS combined with SPPS (APS+SPPS). The coatings prepared by all three methods obtained good stability. Fig. 4 shows the combination of plasma spraying and gas-sensitive coating deposition [105]. Liu *et al.* used the method of APS to deposit the ZnO_{1-x} gas-sensitive coating to obtain the room temperature gas sensor,

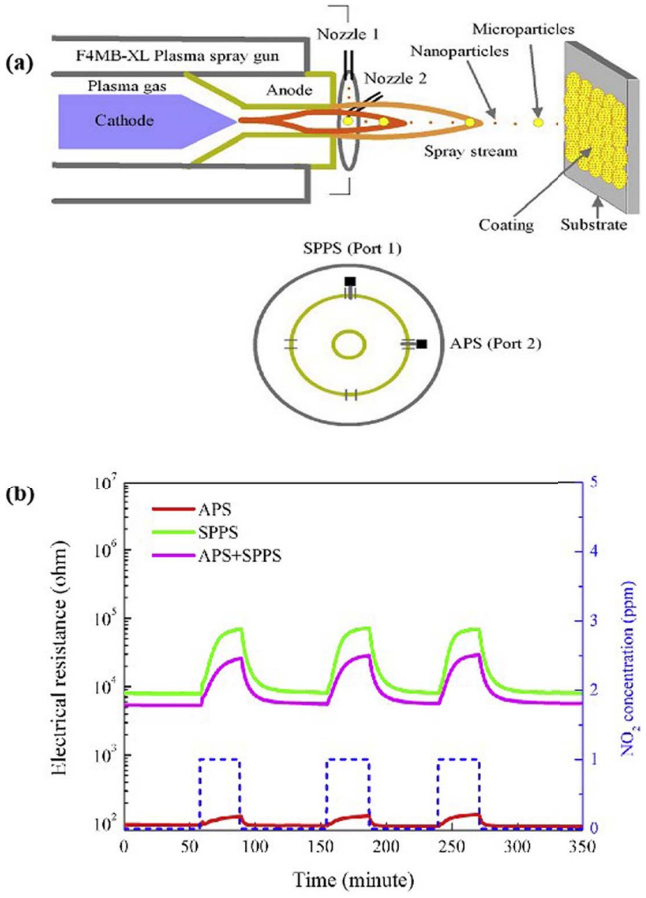

Fig. 4. (a) Plasma spray setup with micro-nano-structure coating schematic; (b) electrical resistances-time curves of the APS, SPPS and APS+SPPS coatings deposited at 24.5 kW exposed to 1 ppm NO_2 at 200°C with a relative humidity of 50% [105].

which slowed down the aging of components and improved sensor stability [106].

The micro-nano structure can improve the sensing performance and increase the sensor stability [107]–[109]. The preparation of spherical shell model can not only improve sensitivity, but also promote stability. The yolk-shell $ZnFe_2O_4$ synthesized by Zhou *et al.* using the template-free solution method had good long-term stability and improved sensing performance at the operating temperature of 200 °C [110]. Wang *et al.* synthesized a series of polyphase composites with multi-shell structure, high specific surface area and crystalline mesoporous skeleton, including binary (Fe-Co, Ni-Zn and Ni-Co oxide), ternary (Ni-Co, Mn-Ni-Co and Ni-Co ZnO) and five-element (Ni-Co, Fe-Cu-Zn oxide) polyphase composites with good stability [111].

Spray pyrolysis can form stable metal oxide nanocomposites with high porosity [82]. In the study of Song *et al.*, an easy method to synthesize $ZnO/ZnFe_2O_4$ three-shell hollow microspheres (ZZFO TSHMSS) by annealing and calcination of $Zn_3[Fe(CN)_6]_2 \cdot xH_2O$ precursors was proposed, which showed excellent long-term stability [112].

The stability of the sensor can be effectively increased by improving the material, optimizing the synthesis scheme and designing the sensor components reasonably. However, some parts, such as doping elements and material poisoning, need further research due to the lack of mechanism.

IV. Prospect

The stabilization of metal oxide semiconductor gas sensors is a very intricate problem, influenced by numerous factors, including physical and chemical properties of materials, environment, sensor design, etc. For materials, the main factors that affect the stability are the uncontrolled grain growth during the service period and the irreversible reactions between the surface and some molecules in the environment or target gases. For the electronic parts, the most crucial problem comes from the aging of the components such as the connection or the measuring elements, i.e., a regulator and a resistance. When it comes to the improvement of the stability, it can be divided into two general parts: improve the material stability, such as inhibiting the growth of grains, avoiding the effect of humidity and poison molecules, and improving the design of the sensing device, such as the circuit for correcting the errors or using new data treatment methods. Combining multiple methods can be an effective way. For example, fixing the response to humidity and sensing temperature reduction at the same time can effectively improve sensor stability. The electrical, UV and gas sensing properties evaluated by Postica *et al.* in the different situations over 203 days showed that SiO_2-covered ZnO/TiO_2 had higher immunity to water vapor and higher long-term stability [113].

Nevertheless, not all superpositions are good, because the sensing mechanisms involved are not fully understood. It is of great significance to clarify the sensing mechanism for improving sensor stability. For example, the grain size of metal oxide increases at high temperatures, leading to the change of gas-sensitive performance, which makes the sensing performance unstable. In terms of design, compensating and calibrating drift is still the focus of research. In addition, to facilitate research on sensor stability, rapid and effective life-accelerating tests are urgently needed to be developed. With the development of flexible equipment and long-term monitoring equipment becoming the mainstream, the direction of future sensors will be miniaturization and energy saving. Maintaining the sensor stability under this development trend is still the focus of future research.

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