Advances in sensing mechanisms and micro/nanostructured sensing layers for surface acoustic wave based gas sensors

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Surface acoustic wave (SAW) technology has been extensively used in communications and sensing applications. For SAW based gas sensing applications, the sensitive material or sensing layer which is coated onto the SAW sensors is vital for its sensitivity, selectivity, limit of detection, and repeatability, as changes of sensing signals (including frequency, amplitude, and phase angle) are strongly linked to variations of mass loading, electrical conductivity and elastic modulus (or elastic loading) of this sensing layer. There are rapid development in this field recently but great challenges are still remained in choices of suitable sensing materials, structures and mechanisms of these sensing layers. This paper reviews recent advances of micro and nanostructured sensing materials and selections, their sensing mechanisms and designs towards enhancing the gas sensing performance of SAW devices. We firstly discuss different sensing mechanisms based on SAW principles, along with the key sensing influencing parameters. We then highlighted and categorized recently reported gas sensing materials into semiconductor metal oxides, carbon-based materials and polymers. We further then focused the discussions on relationships among micro/nanostructures, compositions, and structure-sensing performance for the SAW based sensors. Finally, we highlighted key challenges and potential solutions as well as future directions of sensing materials for SAW based gas sensors.

1. Introduction

With the rapid development of economics worldwide, there are great concerns about environmental issues, public safety, and human health conditions, as various hazardous gases and numerous volatile organic compounds (VOCs) are released into atmosphere, and pose great threats to cause severe diseases, damage of living environment, and potential fires/explosions. For example, hydrogen sulfide (H$_2$S) is colorless but harmful and toxic, and often causes adverse effects for people, even at a low concentration of 2 parts-per-million (ppm). It could be mortal if there is an exposure to a level of H$_2$S up to 100 ppm. Ammonia (NH$_3$) is another toxic gas which is commonly released from the combustion of the chemicals in industrial processes. Excessive NH$_3$ is pernicious to animals and plants. Hydrogen (H$_2$) has also commonly been used in industry but is very dangerous and explosive. Therefore, there are huge demands for rapid and accurate detection of these gases.

Currently, many types of sensors have been explored to detect various gases such as impendence gas sensors, electrocatalytic gas sensors and optical gas sensors. Many impedance gas sensors are based on resistance or capacitance changes of semiconductors (such as conducting oxides) in the forms of either thick films, porous pellets, or thin films. Nevertheless, they have many drawbacks such as slow recovery characteristics and poor sensitivity, especially at room temperature or low operating temperatures. The principle of electrocatalytic gas sensor is to use catalytic materials as the sensing layer to monitor changes of carrier concentrations, mainly due to the variations of the concentration of the measured gas in the test environment. However, the disadvantage of this type of gas sensor is its limited sensitivity and accuracy. Optical gas sensor is based on the principle that when the sensitive layer of the sensor adsors the gas molecules, the optical absorption spectrum of the sensor is changed which is associated with the type and concentration of the gas. However, test equipment of this sensor is often bulky and high cost. Therefore, significant attention has been paid to enhance the sensitivity, and selectivity of gas sensors, recovery characteristics, and/or wireless passive capabilities.

Acoustic wave based sensors, especially surface acoustic wave (SAW) ones, are often used to detect various physical and chemical parameters such as temperature, pressure, mass percentage of solution, electric field, ion concentration, gas flow, gas and vapor concentration. They generally have high sensitivity, high selectivity and good stability. The first generation acoustic wave based resonators were developed in nineteen sixties. Later, ultra-high frequency SAW resonators up to GHz devices have been developed. These SAW sensors have found wide applications in RF filters or couplers, and other types of electronic devices, wireless communication tools, and smart miniaturized sensors. By integrating with sensing layer materials, they show remarkably high sensitivity, small size, and fast response speed. The ability to integrate with different receptors or sensing layer materials are the distinct characteristics of SAW
devices. These features make it highly suitable for detecting a variety of gases such as VOCs, toxic gases, chemical warfare agents, explosive gases and bi-analyses. With the continuously increased demands, SAW devices are becoming widely used in the detection of toxic and harmful gases.

![Figure 1] Schematic diagram of various sensing material nanostructures used for SAW gas sensors.

To date, different nanostructured sensing materials such as supramolecular coatings, semiconductor metal oxides, carbon-based materials, self-assembled monolayers, and polymers have been synthesized and coated on a SAW device to detect various gases. Among them, semiconductor metal oxides, carbon-based materials, and polymers (Figure 1) are the most commonly reported ones. Semiconductor metal oxides have high carrier concentrations and good chemical and thermal stabilities. Carbon-based materials have many potentially good characteristics such as high sensitivity, structure diversity, good conductivity and low cost. Whereas polymer based materials have potentially excellent electromagnetic and microwave absorption performance, good electrochemical performance, high conductivity, good environmental stability, easy availability of raw materials and other characteristics make it considered as the potential material to be applied in practice.

Generally, an ideal sensing material deposited on SAW device should have the features of high efficiency, good stability, and excellent sensing performance under variable environmental conditions. However, in reality many sensing materials have issues of low sensitivity, poor long-term stability, or poor environmental intolerance. Therefore, exploring/designing new sensing materials and their sensing mechanisms for a targeted gas are an urgently needed to improve the sensing efficiency of the SAW sensors. So far, there are not many review papers which were focused on the sensing layer materials on SAW devices and the influences of these materials’ characteristics on the sensing performance. A few of them are focused more on applications of wireless sensor networks in precision agriculture, or basic principles and physical applications of SAW gas sensors, and/or the applications of biosensing and microfluidic integration into the SAW sensor. Moreover, with the continuous improvement and development of SAW gas sensor devices, enormous progress has been made recently in the design and preparation of significantly improved or new generation sensing layer materials. Therefore, this review aims to review the intrinsic relationships among sensing materials (or sensing layer), their characteristic designs of micro/nanostructures, and SAW gas sensing performances, shedding light on the rational design and synthesis of advanced gas sensing materials.

In this review, we firstly discussed the basic sensing mechanisms of SAW gas sensors, along with of the key sensing parameters. Recent advances of gas sensing materials are then highlighted and categorized into semiconductor metal oxide nanostructures, carbon-based materials and polymers from the aspects of the microstructures, composition, and structure-sensing performance relationships. Finally, we highlighted current challenges along with solutions and potential trends of sensing materials for SAW gas sensors.

2. Fundamentals of SAW gas sensing principles and mechanisms

SAW technology is attractive for sensor industry because it conforms to requirement of system miniaturization, digitization, intelligence, integration and high precision. SAW gas sensors are commonly consisted of SAW device (such as those based on quartz, LiNbO$_3$ or thin films), sensitive adsorption materials and external circuit. To improve the sensor performance, a clearly understanding of the sensing mechanisms and specifications is necessary.

2.1 Mechanisms of SAW based gas sensing

If a piezoelectric substrate is excited by the electric field, surface vibrations will be generated due to the piezoelectric effects. The vibration of the surrounding dielectric atoms or particles, forming the mechanical waves. The commonly used piezoelectric substrate materials to generate SAWs include bulk substrates of quartz, LiNbO$_3$ and LiTaO$_3$, PbZr,Ti$_{11-x}$O$_3$ (PZT), or the films of AlN, ZnO, and GaN. SAWs are mechanical waves rather than electromagnetic waves, and their propagation speeds are much lower than those of electromagnetic waves (e.g., speed of light), and they propagate along the surface of the material. The most common wave modes are Rayleigh wave, Lamb wave, Love wave, and shear-horizontal wave.

Acoustic waves are commonly generated on SAW devices by using a periodic comb-shaped electrode, called interdigital transducers (IDTs), which are a group of thin metal strips periodically arranged at the surface of a piezoelectric substrate and fabricated using the conventional
Among all the effects, the most significant one is that absorption of gas molecules results in the changes of mass loading, which leads to the shift of the resonant frequencies. By comparing the degrees of frequency shifts or phase angle changes, we can detect the gas molecules absorption using the SAW sensor. Equation (1) reveals the relationship between the frequency shift and mass loading changed:

$$\frac{\Delta f}{f} = -\frac{k\Delta m f_0^2}{A}$$

where $\Delta f$ represents the frequency shift caused by mass changed, $f_0$ is the central frequency of SAW resonators, $K$ is on behalf of the material constant, $\Delta m$ is the mass loading and $A$ is the sensing areas.

Elastic loading is associated with the changes of the surface viscosity of the sensing layer under the gas atmosphere, resulting in the change of the wave speed. It is another parameter to cause the frequency shift/response, which can be described using the following equation:

$$\frac{\Delta f}{f} = C_e h f_0^2 \left( \frac{4v}{v_0^2} \right) \left( \frac{\mu+\lambda}{\mu+2\lambda} \right)$$

where $C_e$ is the sensitivity coefficients for elasticity, $h$ represents the thickness of the sensing material film, $f_0$ represents the fundamental resonance frequency, $v_0$ is the original SAW propagation speed ($3158$ m s$^{-1}$), $\lambda$ and $\mu$ are the bulk and shear modulus of elasticity, respectively.

Electric loading is related to the changes in the electrical characteristics (such as conductivity and permittivity) of the sensitive layer after adsorbing gas, which causes the center frequency of the resonator to shift. It can be expressed by the following equation:

$$\frac{\Delta V}{V_0} = -\frac{k^2}{2} \left( \frac{1}{1+\left(\frac{\rho_{\text{gas}}}{\rho_0}\right)} \right)$$

where $k^2$ is the electromechanical coupling coefficient, $V_0$ is the original SAW propagation speed ($3158$ m s$^{-1}$), $\rho_0$ is the initial conductivity of the sensing film, and $C_e$ represents the capacitance per unit length of the device.

Mass loading, elastic loading and electric effect could have totally different influences for the frequency changes (i.e., increase or decrease), as revealed by the equations (1) to (3). These three effects affect sensing response characteristics of SAW gas sensors. We should address that the mass loading and others loading have the opposite changes of the frequency.

There are two common designs of SAW devices, i.e., delay line type (DL type) and resonator type (R type). The former one is shown in Figure 2a, in which the SAWs are generated from one of the IDTs, and then propagate along a delay line region to the opposite IDT2. For the R type one shown in Figure 2b, the sensing layer is set in the middle, with two IDTs and reflectors at both ends, and the wave is reflected by metal strips or grooves in the wave propagation path. The key working mechanism of the DL type-based SAW devices can be explained as follows. When the sensor receives the sinusoidal excitation signal through the antenna and transmits it to the IDTs, the SAW propagates on the piezoelectric substrate and reaches the reflection grid after a period of delay. The reflection grating reflects part of the sound wave, which is converted into a sinusoidal excitation signal through the IDT based on the piezoelectric effect, thereby realizing electro-acoustic conversion. Due to the changes of properties at the delay line region (such as mechanical, physical or chemical properties), the frequency or phase angles of the waves will be changed, which can be used to predict the changes of sensing parameters.
values of the SAW sensor after the target vapors and molecules are absorbed onto the SAW device.\textsuperscript{34,62,64}

2.2 Performance indicators of SAW gas sensor

To evaluate the performance of a SAW gas sensor, several key indicators need to be considered, e.g., selectivity, sensitivity and stability.

Selectivity refers to the ability of SAW gas sensing to the specific gas among various other types of gases. It is one of the basic requirements of the sensing material, and is commonly determined by comparing the signal changes which are generated by absorption of a certain concentration of tested gas and those of interfering gases.\textsuperscript{65} For different types of gases, different sensing layers might be needed to use for selective detections, and sensing layers with an excellent selectivity will absorb the specific gas to be measured among mixed gases. Therefore, the selectivity for the specific gas is the most basic requirement of the sensor material, and it is also the ultimate goal for the SAW gas sensor.

Sensitivity refers to the minimum concentration of the target gas that can be detected. It is also usually defined as the ratio of relative frequency shift to concentration ($\Delta f/\Delta c$, where $\Delta f$ is the shift of the vibration frequency and $\Delta c$ is the change in the concentration of the detected gas).\textsuperscript{65} In the experimental process, there are many factors that can affect the sensitivity of the SAW sensor, such as temperature, humidity, surface area and conductivity of the sensing material. For example, Fan et al.\textsuperscript{56,67} discussed the effect of conductivity on SAW sensor sensitivity and reported that changes in mass loading and conductivity shifted the central frequency of the sensor in the opposite directions. If the conductivity of the sensitive layer is increased due to the absorption of the gases, the combined effects will cause the increase of the sensitivity. Through simulation, they found that the sensitivity of the SAW gas sensors can be improved by optimizing of the operating frequencies, structural parameters and properties of the multilayered materials in the sensors.\textsuperscript{68}

Stability means that the sensor can continue to work stably without attenuation under various conditions such as high temperature, high pressure and corrosive environment.\textsuperscript{65,69} Whether designed for the commercial market applications or in experimental testing, SAW gas sensors must guarantee the stability of their sensing performance. They should display stable and repeatable signals over a period of time or after many cycles of testing. Here the stability includes both chemical and physical ones, such as chemical's structure and composition, thermal stability and functional (such as optical) properties of sensing material.

3. Micro and nanosstructuring of sensing layers for SAW gas sensor

Considerable efforts have been made to study the influence of the structures and morphologies of the sensing layer materials on SAW gas sensors’ performance. Amongst the sensitive materials employed for SAW gas sensing, nanostructured materials have drawn increased considerations in the last a few years. Recently, nanostructured sensing layers with various morphologies, including porous structure, hollow structure, and one-dimensional nanoscale structure, have been considered as exceptional approaches for optimizing sensing performance and sparked intensive research interests.

It is generally accepted that the morphology of the sensitive layer, especially the porosity, plays a critical role in the performance of the SAW gas sensor. The porous structure ensures a large-area contact between gas molecules and the sensing material, which provides excellent responses of the sensors.\textsuperscript{70} The gas detection capability of the SAW sensor is also affected by the uniformity and compactness of the film. For examples, Han et al.\textsuperscript{71} and Chen et al.\textsuperscript{72} prepared hierarchical WO\textsubscript{3} flower-like spheres and single-crystal WO\textsubscript{3} nanosheets to detect triethanolamine. The former study showed excellent performance and a low theoretical limit of detection of 83 ppb for triethanolamine, which was better than the latter one. The reason for the former’s apparent outstanding sensing performance was that this unique nanostructure facilitated the activities of surface reactions and accelerated the diffusion of triethanolamine molecules into the sensing layers. Particularly, hierarchical structures with large surface-to-volume ratios and porous features provide abundant active sites, and the loosely connected WO\textsubscript{3} nanosheets facilitate the gas transportation and thus promote the response and recovery speeds.

Compared to one or two-dimensional nanomaterials, three-dimensional structures possess much larger effectively specific surface areas and porosities, which are beneficial to gas molecules to diffuse and electrons/holes to transport.\textsuperscript{73} For example, Wang et al.\textsuperscript{74} synthesized four different WO\textsubscript{3} structures (nanorods, spheres, sea urchins and flowers respectively) as sensing materials to detected VOCs. Among these, three-dimensional sea urchin morphology exhibited the best sensitivity in a low concentration. This can be explained by the fact that the large area exposure of the crystal surfaces affected the pre-adsorption of negative oxygen ions and also provided more channels for the faster gas diffusion, thus enhancing the gas sensing performance. Morphologies of different types of sensing materials can be easily optimized using various types of synthesis methods, reaction conditions and solution concentrations. For example, Xu et al.\textsuperscript{75} adjusted the concentration of the raw materials to change the shape of WO\textsubscript{3}. With a suitable concentration of NaHSO\textsubscript{4}, three-dimensional flower-like WO\textsubscript{3} was produced and possessed large specific areas and hierarchically porous structures, which provided more channels for fast gas diffusion and increased active sites for adsorbing target gases easily. This unique structure showed the highest sensing response compared with the other types of morphologies and the responsive value was at $\sim$ 96 at the ethanol concentration of 35 ppm. In addition, Wang et al.\textsuperscript{76} found that Sb-doping changed the morphology of
SnO$_2$ from nanowires to nanosheets. The structural features of nanosheets increased the number of surface active sites and defects, thereby greatly improving the responses and sensitivity of gas sensors. It should also be pointed that the introduction of foreign ions in SnO$_2$ leads to changes in the growth state of SnO$_2$. Particularly, if Sb$^{3+}$ replace Sn$^{4+}$, the electrons provided by Sb$^{5+}$ are easily captured by NO$_2$, causing the SnO$_2$ to enter a depleted state which improves gas responses. If Sb$^{3+}$ is replaced with Sn$^{4+}$, a certain concentration of O vacancy is induced by Sb-doping, which can be ionized into second-order ionized oxygen vacancy V$_{O}$. More free electrons can be produced which can be captured by NO$_2$ to further enhance performance of the gas sensor. Therefore, doping has become a good methodology to improve the gas sensing performance of SAW sensors.

For constructing well-organized micro- and nanoscale morphologies, strategies using various advanced synthetic methods have been applied for preparing high-performance SAW gas sensor materials. For example, pulse laser deposition is often used in the preparation of sensor materials because of its multiple tunable parameters such as atmospheric pressure, laser power, substrate temperature, and flexible geometry. Recently, Miu et al.$^{73}$ used pulsed laser deposition to synthesize ZnO films with different porosities by controlling various parameters such as the gas pressure inside the deposition chamber, the number of pulses and pulse duration and the substrate temperature. The ZnO films deposited using the optimal parameters show a larger density of porous and a better sensing response. This is because the higher deposition pressure leads to the increase plasma density and the increased collisions among the ablated species, thus resulting in the formation of relatively smaller nanoparticles in the target-substrate region. Liu et al.$^{74}$ designed and successfully prepared aperture-controllable three-dimensional mesoporous ZnO nanostructures to detect acetone and methanol. These unique structures with the large macropores demonstrated a much better gas sensing performance than ZnO nanoparticles, because largest cavity pores provide numerous spaces for gas diffusion and a synergistic effect of electron transportation and electron density of gas molecules.$^{79}$ Specifically, mesoporous ZnO structures provide excellent transportation channels and surface accessibility for gas molecules to diffuse into the inner part of nanostructures whereas the absence of these macropores in those nanoparticles significantly slows down the gas responses due to the existence of long and tortuous pathways for gas permeation and diffusion. Shu et al.$^{80}$ explored the relationships and mechanisms between the frequency shift of the SAW gas sensor and the surface morphology of ZnO thin film. They found that grain size was dependent on the grain diffusion rate and the deposition rate of ZnO crystals, which were determined by the deposition temperature. Their experimental results showed that the deposited porous ZnO films possess a large frequency response (310 KHz) to a concentration of 40% O$_2$ and a good stability for a long period under a high temperature at the deposition conditions (850 °C). Therefore, selecting suitable methods and process parameters is necessary for synthesizing porous materials to further improve the sensing performance of the SAW device. Other synthetic methods such as electrospinning, magnetron sputtering and hydrothermal growth have also been applied to deposit dense or porous structures and control the distributions of incorporated crystals or nanoparticles. In the next section, we will focus on several types of nanostructured sensing materials such as semiconductor metal oxides, carbon-based and polymer-based materials, and discuss in detail the influences of their structural morphologies and different modifications on their sensing performance.

4. Sensing materials for SAW gas sensor

In SAW sensing technology, development and integration of new sensing materials have been a focused research area. These nanostructured SAW sensors can be used for a large range of applications, such as the detection of VOCs, poisonous gases, or explosive gases. The commonly used sensing materials have been listed in the following categories.

4.1 Semiconductor metal oxides

An important category of sensing layer materials for SAW sensors is semiconductor metal oxides, which are applied into many fields such as luminescent materials and gas sensing materials. Many nanostructured semiconductor metal oxides have a large surface area due to their ultrafine crystals or particles, which can adsorb more target analytes on their surfaces, providing stronger signals and causing more measurable responses. Besides, the abundant free electrons on their surface after triggered by external sources can effectively interact with reducing or oxidative gas molecules, which is beneficial to improving the sensing efficiency.$^{3,14,17,26,83-84}$ For SAW based gas sensors, the following metal oxides have been extensively applied.

4.1.1 ZnO-based sensing layer

ZnO is an important representative of such sensitive materials in the field of gas sensors. Its relatively simple synthesis process can control the morphology and generate of oxygen vacancies, which are advantageous in the field of sensors for gas molecule adsorption.$^{35,85,86}$ Meanwhile, ZnO is an n-type II-IV element, and a wide and direct band gap semiconductor with a bandgap of about 3.37 eV and a large excitation binding energy (60 meV)$^{35,87-89}$ Its high electron mobility makes it become the most favored materials in the field of optoelectronics and sensors.

Rai et al.$^{90}$ prepared a series of different metal oxides (ZnO, TeO$_2$, SnO$_2$ and TiO$_2$) with same thickness (40 nm) by using RF sputtering technique for the detection of NH$_3$. The deposited
ZnO thin film had the highest sensitivity to NH₃ compared with other oxides. This can be attributed to numerous native defects related to the zinc interstitials, zinc vacancies, oxygen interstitials, oxygen vacancies and antisite defects are existed in the ZnO thin film, which are beneficial for the better performance than the other oxide films. They sequentially studied the influences of the thickness of ZnO sensing layer (20-40 nm) on the SAW sensing characteristics, and found that with the increase in film thickness, both the crystallite size and the average roughness of films are decreased. Their results also showed that the number of adsorption sites for the targeted gas molecules increases with increasing in the thickness of sensing layer from 20 to 40 nm, and the best sensing performance was obtained with the thickness of 40 nm. Rana et al. successfully fabricated ZnO thin film based sensing layer on a quartz SAW device to detect NO₂ gas, and selectively detected trace NO₂ concentration (400 ppb to 16 ppm) due to the deposited ZnO thin films with small particle sizes, which led to larger specific surface areas and was favorable for efficient adsorption and desorption of target gas molecules on their surfaces.

Figure 3 (a) Schematic diagram of ammonia gas. (b) Top-view morphology image of ZnO nanorods. (c) Frequency shifts of SAW devices based on ZnO nanorods to various concentrations ammonia. (d) Frequency shifts of SAW devices based on ZnO nanorods at different concentrations of NH₃ gas for 60 days. Reproduced with permission from Ref. 96, © MDPI journals 2017.

The sensitivity of the sensor is strongly related to the ZnO deposited volume on the specific surface area, and also dependent on its morphology. Marcu et al. synthesized ZnO nanowires and ZnO thin films onto quartz substrates using a laser beam processing and measured the SAW device’s responses for various concentrations of hydrogen and deuterium gases. They designed and synthesized ZnO nanowires (300 nm and 600 nm-long) and thin films (100 nm and 200 nm-thick). High frequency responses and rapid responses for nanowires at a low concentration were found. In particular, the nanowire (600 nm) showed a higher sensitivity (0.015 Hz ppm⁻¹) and lower limit of detection (2117 ppm) for detection of hydrogen. Meanwhile, the response time (9-15 s, the time to reach 90% of the maximal signal) of the nanowire sensors was longer than that of thin films-based SAW sensors (2-3 s). The recovery time (i.e., the time required for the response signal to return to 90% of the original baseline signal when the target gas is removed) for the nanowire sensors (6-9 s) was shorter than that for the film sensor (7-11 s). Meanwhile, Marcu et al. also applied ZnO nanowires (888 nm long) prepared via a vapor-liquid-solid technique as the sensing layers also exhibited a higher sensitivity (0.062 Hz ppm⁻¹) for hydrogen detection than ZnO thin films (0.01 Hz ppm⁻¹).

ZnO nanorods have also been proved to have a better sensing performance than thin film when they are deposited onto the SAW devices. As reported by Li et al., the large specific surface area of the ZnO nanorods were synthesized by a seed layer-free hydrothermal method and showed excellent sensitivity, repeatability and stability in detection of NH₃. Figures 3a and b show schematic illustrations of the measurement system and the morphology of ZnO nanorods, respectively. Figure 3c shows that the frequency shifts of two morphologic materials were observed under different concentrations of ammonia gas. Notably, the one with nanorods showed a larger frequency shift at the same gas concentrations because ZnO nanorods possess large specific surface areas that can adsorb more oxygen species and react with more ammonia molecules than that of the ZnO film. The sensors based on ZnO nanorods also manifested stable responses in a certain range of NH₃ concentrations for 60 days (Figure 3d).

Metal doped ZnO has also been applied as the sensing layer in SAW devices. Platinum (Pt), as a noble metal, has attracted extensive attention in chemical and physical fields such as catalysis and sensing. Huang et al. used the Pt doped ZnO nanorods as the selective sensing layer for the SAW device in H₂ detection. The frequency shift for detecting a H₂ concentration variation of 6000 ppm was 26 KHz, which was superior to pure ZnO nanorods and ZnO thin films. Particularly, it took less than 15 s to reach about 90% of the steady state, and the recovery time was about 2-3 min. This remarkable sensing performance is mainly due to the doping of Pt, which acts as a catalyst to speed up the reaction rate.

 Palladium (Pd) has excellent hydrogen adsorption properties, the highest hydrogen solubility at atmospheric pressure as well as thermodynamically favored H₂ dissociation. Viespe et al. designed Pd/ZnO bilayer structure for H₂ detection based on a quartz SAW sensor operated at room temperature. The sensor structure has combined the hydrogen absorption and diffusion properties of Pd with the excellent diffusion properties of the nanoporous Pd film, which result in the increased amounts of hydrogen gas molecules to reach the Pd/ZnO interface. At this interface, the ZnO surface conductivity is highly sensitive to adsorbed species, thus improving the detection sensitivity for hydrogen. Therefore, this sensor showed a higher sensitivity (0.51 Hz ppm⁻¹) and a better limit of detection (59 ppm) than those of the single ZnO films and single Pd films.

As it is well known, oxygen vacancies, generated by element doping or chemical reduction, have a critical role in the gas sensing performance of semiconductor metal oxide materials due to the increased free carrier concentration.
For example, Ghosh et al.\textsuperscript{103} discovered that the performance of ZnO thin film coated langasite SAW sensor could be improved by calcium (Ca) doping of ZnO in CO\textsubscript{2} detection. There are two mechanisms of frequency responses for these Ca doped ZnO sensing. The first one is the mass loading effect produced by the reaction of CO\textsubscript{2} gas with O\textsuperscript{-} species to forms CO\textsubscript{3}\textsuperscript{2-}. The second one is the increased in conductivity owing to the catalytic effect of Ca, and the influence of the increase in conductivity is predominant. It is noteworthy that the SAW sensor is also sensitive to H\textsubscript{2} and CO gas. Shu et al.\textsuperscript{104} reported that the doping of Fe element could obviously change the morphology of the ZnO sensitive film and improve the gas sensing performance in O\textsubscript{2} detection. With the increasing of Fe content in the film, both the size and amount of the nanosheets are increased. The proportion of Fe\textsuperscript{3+} ions are increased, which results in an increased content of Fe\textsubscript{2+}. This will cause that the Fe\textsuperscript{3+} ions substitute Zn\textsuperscript{2+} ions, thus generating more free electrons.

Composites of ZnO and other materials have been recently explored for examining the dependence of the response of a composite SAW sensor to oxidizing or reducing gases. The improvement in sensing performance using these composites have been ascribed to many factors. These include: (1) electronic effects such as the separation of charge carrier\textsuperscript{105} and the manipulation of depletion layer;\textsuperscript{106} (2) chemical effects such as reduced activation energy\textsuperscript{107} and synergistic surface reactions;\textsuperscript{108} and (3) physical geometric effects such as grain shrinkage\textsuperscript{109} and surface area expansion.\textsuperscript{110} For example, Tang et al.\textsuperscript{111} synthesized ZnO-Al\textsubscript{2}O\textsubscript{3} nanocomposite coated on the quartz SAW device using a sol-gel method for H\textsubscript{2}S detection. The composite with porous structure had a good affinity with H\textsubscript{2}S, and thus could selectively adsorbed H\textsubscript{2}S, which led to an increase in the elastic modulus of bi-layer, and a positive frequency shift (15 KHz ppm\textsuperscript{-1}). The elastic loading is mainly due to the fact that the newly formed ZnS has a higher molar mass and a lower density compared with original ZnO nanoparticles. The key sensing mechanism is that as the ZnO-Al\textsubscript{2}O\textsubscript{3} layer has a mesoporous structure and a rough surface, a large amount of H\textsubscript{2}S molecules can enter deeply inside the layer diffusing through the porous structures and then react with ZnO nanoparticles. Tang et al.\textsuperscript{112} also reported that a ZnO/SiO\textsubscript{2} bi-layer nanofilm synthesized by a sol-gel process was much more sensitive than the single layer films due to their appropriate sheet conductivity. With the increase of the top thickness of ZnO layer in the bi-layer film structure, the sensitivity of the SAW sensor was significantly improved. Particularly, bi-layer nanofilms of ZnO had a better frequency response (a frequency shift of 2 KHz at the NH\textsubscript{3} concentration of 30 ppm), while the response time and recovery time were much higher than other thin films. The sensing mechanism can be explained as follows. Oxygen molecules are absorbed on the surface of the top ZnO layer owing to the van der waals force, and the absorbed oxygen molecules capture the free electrons on surface to form a depletion layer. When the film is exposed to NH\textsubscript{3} gas, some NH\textsubscript{3} molecules diffuse and even penetrate into the film because of the film’s porous structure. These molecules react with oxygen species causing lots of electrons\textsuperscript{113} to be released back to the depletion layer. These electrons will recombine with some of holes, thus changing the conductivity of ZnO layer. Consequently, this results in a negative shift in frequency. Wang et al.\textsuperscript{114} also reported ZnO/SiO\textsubscript{2} composite films with different molar ratios, which were synthesized using a sol-gel method. Experiments showed that when the ratio of ZnO to SiO\textsubscript{2} in the composite films is 1 : 2, the SAW sensor showed the best sensing performance. At an injected NH\textsubscript{3} concentration of 10 ppm, the response of SAW sensor was 1.132 KHz, which was much higher than that of the sensor based on a pure ZnO film. The excellent performance for this device is attributed to the enhanced absorption of NH\textsubscript{3} molecules and unique surface reactions due to the existence of silica on the surface of the composite film.

There are also studies using a composite layer by combining ZnO with InO\textsubscript{x} for the SAW gas sensor. The oxygen vacancies in the InO\textsubscript{x} film serve as donors and the sample’s conductivity is changed by controlling the concentration of oxygen deficiencies.\textsuperscript{115} InO\textsubscript{x} layers deposited on XZ cut LiNbO\textsubscript{3} with a 1.2 μm ZnO guiding layer were also reported,\textsuperscript{116} and a large frequency shift of positive 91 KHz for 2 ppm of NO\textsubscript{2} and negative 319 KHz for 1% H\textsubscript{2} in synthetic air were observed for the 40 nm InO\textsubscript{x} layer. Nieuwenhuizen et al.\textsuperscript{117} used a quartz SAW sensor coated with ZnO-SiO\textsubscript{2}-Si layers and a dual delay-line oscillator system to detect the NO\textsubscript{2} gas. Results clearly showed that the sensing performance of an NO\textsubscript{2} SAW sensor of this type using copper phthalocyanine (CuPC) as the chemical interface was excellent.

\textbf{4.1.2 SnO\textsubscript{2}-based sensing layer}

SnO\textsubscript{2} is one of the most stable oxides among n-type oxides widely used for semiconductor gas sensors. It has a higher mobility of electrons and higher stability compared with those of ZnO, and thus SnO\textsubscript{2} has been explored as a good semiconductor for gas sensors.\textsuperscript{117,118} In 2015, Luo et al.\textsuperscript{119} applied SnO\textsubscript{2} films synthesized by an aqueous sol-gel technique as an efficient H\textsubscript{2}S sensing layer in a quartz SAW device. They examined the gas sensing properties of the SAW sensors under different concentrations of H\textsubscript{2}S and different temperatures using a testing system as shown in Figure 4a. Their experimental results showed that SnO\textsubscript{2} thin layer had a maximum frequency response of 112.232 KHz (Figure 4b) at the H\textsubscript{2}S concentration of 68.5 ppm and the minimal low of detection limitation was 1.7 ppm. Figure 4c shows the responses of gas sensors with different SnO\textsubscript{2} film thickness towards 68.5 ppm of H\textsubscript{2}S at 120 °C were compared. It clearly shows that the sensor with a film thickness of 275 nm exhibited the highest sensitivity (1.6384 KHz ppm\textsuperscript{-1}). Moreover, the authors also found the electric effect was dominant in the sensing mechanism of this SAW sensor.
4d shows three-dimensional relationships between the relative frequency shift and the sheet conductivity of the SnO$_2$ films with different thicknesses before and after contacting H$_2$S gas. When the sheet conductivities of the film with a thickness of 275 nm (operated at 120 °C) were increased, the frequency shift caused became significantly increased. They also used SnO$_2$ as the sensitive film of SAW gas sensor to detect H$_2$S. Raj et al. used SnO$_2$ thin film served as the sensing layer, which was coated on quartz SAW oscillator to detect NO$_2$ gas. They reported that the film thickness is the most important factor affecting the sensor performance. This is because with the increase of its thickness, the average roughness of the SnO$_2$ thin films was increased and the average porosity of the sensing film was also increased, which causes absorption of more targeted molecules on the SnO$_2$ thin films. Therefore, with increasing the film thickness, the frequency of SAW sensor was increased leading to the enhanced the sensing responses with a fast response time (~ 2 s) and a recovery time (~ 45 s).

![Figure 4](https://example.com/figure4.png)

**Figure 4** (a) Manufacturing process of the SAW gas sensors. (b) Morphology images of the SnO$_2$ films on quartz. (c) Sensor response towards 48.5 ppm of H$_2$S for samples with different film thickness at 120 °C. Three-dimensional plots of the relations among the relative frequency shift, the sheet conductivity of the films and (d) film thickness. Reproduced with permission from Ref. 119, ©Elsevier 2015.

Nevertheless, SAW sensors using the pure SnO$_2$ sensing layer often suffer from the poor selectivity, and the operation temperature is also quite high. Therefore, researchers have been exploring various methods to enhance its performance, such as doping with other elements, modifying microstructures, and using composite structures. As described earlier, noble metals can be efficiently used to improve the performance of gas sensors. For instance, Yang et al. prepared SnO$_2$ thin film using a sol-gel method with doped Pd nanoparticles. Pd catalytic nanoparticles increased the quantity of O$_2$ species and the adsorption capacity of H$_2$ gas on the surface of SnO$_2$, resulting in a decrease of initial electrical conductivity and an increase of electrical conductivity in H$_2$ gas. This bi-layer structure enhanced the H$_2$ gas sensing properties of composite thin films with a frequency shift of 115.9 KHz at the H$_2$ concentration of 2000 ppm. Furthermore, this SAW sensor displayed fast response (1 s) and recovery time (512 s).

Constantinou et al. deposited p-type Co$_2$O$_4$ on n-type SnO$_2$ thin films to improve the SAW gas sensing performance of single SnO$_2$ thin films layer for detection of NH$_3$. Two different types of oxides form a heterojunction, which is the active areas to adsorb oxygen species, thus improving the sensitivity of the sensor. Apparently, compared with a single layer of Co$_2$O$_4$ or SnO$_2$ thin films layer, the sensitivity (3.33 Hz ppm$^{-1}$), limit of detection (9 ppm), response (100-120 s) and recovery time (30-50 s) of the sensor in the case of NH$_3$ detection were improved. Meanwhile, p-type CuO was also deposited on n-type SnO$_2$ thin films layer to enhance the performance of H$_2$S detection. The p-n junctions were modified by the CuS formation, which was formed by CuO particles and H$_2$S, and the conductivity of the films was increased drastically and then the operating frequency was decreased. Thus, high sensitivity (16.9 KHz ppm$^{-1}$), excellent selectivity, fast response time (55 s) and superior repeatability were obtained. The above examples show that the combination of other metal oxides or single noble metal layers with SnO$_2$ can effectively improve the SAW gas sensing performance.

### 4.1.3 WO$_3$-based sensing layer

WO$_3$ is another important and promising candidate to be used as sensing elements in gas analysis. Moreover, WO$_3$ film also shows electrochromic properties and is suitable for H$_2$ sensing in a photodetector device. Wen et al. developed a NO$_2$ gas sensor which was consisted of a dual track SAW device and the microporous network WO$_3$ film. They reported that there were lots of microporous networks in the WO$_3$ film since the polyaniline-pyrroldone was used in the preparation, and these porous structures effectively adsorbed NO$_2$ molecules at room temperature by means of the mass loading effects. When the SAW sensor was exposed to the NO$_2$ concentration of 3 ppm, the frequency response was up to 0.185 KHz with good reproducibility and stability. According to the previous theories, the sensor response was significantly increased with a decrease in the thickness of the WO$_3$ lamellae and was well-correlated with its thickness. Kida et al. fabricated lamellar-structured WO$_3$ particles by acidification of Na$_2$WO$_4$ and subsequent calcination of the resulting precipitates. The obtained material was spin-coated on quartz SAW device as a sensing layer to detect NO$_2$, and the device exhibited a good SAW sensing performance. The excellent performance was attributed to the use of smaller lamellae which decreased the electrical resistance of the device and allowed the detection of NO$_2$ in a wide concentration range.

As discussed above, noble metals such as Pd, Ag, Au, Pt, are the most common catalyst activators used on semiconductor metal oxide gas sensor, which can significantly strengthen the reactions between the target gas and oxides surface and reduce the response/recovery times. Ippolito et al. reported that WO$_3$ selective layer modified with Pt or Au exhibited a much higher sensitivity compared to a layered SAW sensor employed only a bare WO$_3$ selective layer. Particularly, they obtained the large frequency shifts of 705 and 118 KHz towards 1% H$_2$ in air for the Au-WO$_3$ and Pt-WO$_3$ SAW sensors,
respectively, and the bare WO$_3$ selective layer only showed a shift of 25.8 KHz. Jakubik et al.$^{132}$ also compared the SAW sensing performance of WO$_3$ and bilayer Pd-WO$_3$ in the detection of H$_2$. Their experimental results showed that adding a Pd thin layer onto the WO$_3$ layer greatly improved the sensor’s sensitivity to H$_2$ with a concentration from 0.5% to 4% in dry air. In addition, Miu et al.$^{131}$ deposited Pd modified WO$_3$ film onto ST-X cut quartz SAW sensor to detect H$_2$. Their experiments identified that the combination of nanoporous Pd (which was efficient in dissociating H$_2$) and WO$_3$ thin films of nanostructure made the SAW device with a good sensing performance.

### 4.1.4 TiO$_2$-based sensing layer

Among the known semiconducting metal oxides, nanostructured TiO$_2$ is one of the mostly investigated materials for gas sensor, pigments in coating, electrocatalysis, energy storage, photovoltaic and photocatalysis applications because of its low-cost, high band gap energy, excellent chemical stability, and environmental friendliness.$^{134-138}$ Rella et al.$^{139}$ synthesized TiO$_2$ nanoparticles thin film using a novel chemical route and deposited on Si and Al$_2$O$_3$ substrates by matrix assisted pulsed laser evaporation to detect acetone and ethanol solid-state gas using the quartz SAW device. A uniform distribution of TiO$_2$ nanoparticles layer with an average particle size of about 10 nm was obtained and this thin sensing layer has round-shaped clusters, with a high degree of roughness and porosity. As it is well-known that the single semiconductor metal oxide cannot achieve high sensitivity and selectivity due to the low chemical reactivity. Therefore functionalization of semiconductor metal oxides to improve both the precise selectivity and highly sensitivity of semiconductor metal oxide based gas sensor have been widely explored. For example, Tang et al.$^{140}$ prepared pure SiO$_2$, TiO$_2$ and SiO$_2$-TiO$_2$ bi-layer composite (Figure 5a) using a sol-gel and coated them on the quartz SAW resonator using a spin coating technique. The sensing performance and mechanisms of SAW NH$_3$ sensor were systematically investigated. They concluded that the bi-layer composite formed by these two oxides had a highly porous structure with more compact pores and micro cracks, and meanwhile the particle size was larger than that of pure SiO$_2$ and TiO$_2$. The compact pores and micro cracks served as the channels for target gas molecules to fast diffuse into the membrane structure, consequently, porous states were formed on the surface acted as the absorption sites for target gases, which is in favor of enhancing the sensitive performance. Figure 5b shows the responses or frequency shifts of the pure SiO$_2$, TiO$_2$ and bi-layer composite SiO$_2$-TiO$_2$ sensors, respectively, and the composite sensing layer showed a larger frequency response, which can be ascribed to the fact that the composite was more easier to adsorb NH$_3$ in the air. The sensing mechanisms on the sensing film surface for interacting with NH$_3$ are schematically illustrated in Figure 5c. The first mechanism is that this film is able to capture the water molecules in the surrounding environment. The second one is that the absorbed water can
serve as the active sites for trapping NH₃, as NH₃ can easily dissolve in water, thus increasing the mass of the bi-layer composite. The third one represents that the hydroxyl groups are formed by the catalytic condensation reaction of the adsorbed NH₃ on the surface of bi-layer film. The composite SiO₂-TiO₂ films had a much better sensitivity to NH₃ at a low concentration level (1 ppm) with a response of 2 KHz (Figure 5d and 5e), and also showed fast response and recovery times (Figure 5f), excellent selectivity, stability and reproducibility.

Constantinou et al.¹⁴³ deposited Pd/TiO₂ composite thin film onto the quartz SAW device to detect the concentration of H₂. They obtained the sensitive films with different morphologies by changing the O₂ and Ar pressures in the pulsed laser deposition chamber. With increase of Pd pressure, the composite films possessed a more porous structure, and more H₂ molecules were adsorbed and dissociated which results in the improved performance of Pd/TiO₂ composite thin films than the pure TiO₂ thin films. Therefore, Pd/TiO₂ thin films with a porous morphology had a larger frequency response (1.8 KHz at 2% H₂ concentration), a higher sensitivity (0.10 Hz ppm⁻¹) and a lower limit of detection (1210 ppm) than pure TiO₂ thin films. The experiment further confirmed that efficiency modifying can greatly improve the sensing performance of single semiconductor metal oxide.

4.1.5 Other types of sensing layer

Apart from the above discussed semiconductor metal oxides, other sensing layer materials also exhibit excellent sensing performance. For example, Li et al.¹⁴² explored nanoparticulate CuO films served as a sensing layer of a SAW sensor for the detection of H₂S (Figure 6a). The key mechanism is that CuO thin films (Figure 6b) are able to catch H₂S molecules in the surrounding environment and then react with these molecules to generate Cu₂S or CuS particles on its surface. Compared with original CuO particles, these newly formed phases by chemical reactions have changed both physical and chemical properties, such as the increases of mass and elastic modulus, and the decrease of electrical conductivity. The performance of CuO-based SAW sensor was tested with the H₂S concentration range from 0.5 to 10 ppm at room temperature and 75% relative humidity. The obtained results are displayed in Figure 6c. The information from Figure 6d shows that the response time and recovery time are positively correlated to H₂S concentration. The relations between concentration and frequency shifts are shown in Figure 6e. The data were highly fit with a a linear curve, confirming that relative humidity affects the response of SAW sensor (Figure 6f). Moreover, the excellent sensing performance in CuO film sensing layer was achieved, for instance, the frequency shift was -1.2 KHz when the H₂S concentration was 500 ppm.

Tang et al.¹⁴³ synthesized CuO-Al₂O₃ composite film through optimizing the single CuO thin film for the detection of H₂S gas. Among them, CuO nanoparticles served as active sites adsorbed more H₂S molecules, and meanwhile Al₂O₃ nanoparticles were easier to form the uniform and mesoporous structure. The synergistic effect of them enhanced the sensing performance of the SAW sensors. Compared with pure CuO nanoparticles, the composite film showed a lower detection limit (0.005 ppm), higher sensitivity (-16.3 KHz ppm⁻¹) to H₂S gas at the concentration from 5 ppb to 100 ppm. Kiriakidis et al.¹⁴⁴ prepared a crystalline InOₓ layer using a DC magnetron sputtering to detect the sensitivity of SAW sensor to ozone gases, and studied the sensing properties of different thicknesses of oxides to NOₓ, reducing gases H₂ and ozone. The 20 nm InOₓ coated on quartz SAW device showed a 73.562 KHz frequency shift for 510 ppb of NO₂ at an operating temperature of 168 °C, and the frequency responses towards H₂ gas concentrations of 600-10000 ppm were in the range of 78.5 KHz-319.4 KHz. H₂ as a reducing gas, increased the conductivity of InOₓ, thus the acoustic wave velocity was decreased, and this was the main reason why the observed decrease in the oscillation frequency in the presence of H₂. At an operation temperature of 123 °C, a frequency shift of 42.7 KHz for 50 ppb and 52.7 KHz for 100 ppb of ozone were detected.

Dewan et al.¹⁴⁵ reported that TeO₂ₓ(y=0-1) thin films were sensitive to the NOₓ gas. They studied the influence of the sensing layer thickness on the response characteristics and a thicker TeO₂ film was found to generate an enhanced sensitivity of a SAW device. Tang et al.¹⁴⁶ found that CoOₓ/SiO₂ composite layer could act as sensing films applied to SAW sensor for the detection of NH₃. Material characterization studies, such as using scanning electron microscope (SEM) and atomic force microscope (AFM), indicated that the films showed porous structures, which was beneficial to selectively adsorb and react with gas molecules. In addition, the existence of SiO₂ was also demonstrated to enhance the NH₃ sensing property of the composite sensor significantly due to the porous structure of pristine SiO₂ film. The loading of 50% CoOₓ produced the roughest surface morphology and displayed a positive frequency shift of 3.5 KHz to NH₃ at a concentration of 1 ppm and showed excellent selectivity, stability and reproducibility at room temperature. Wang et al.¹⁴⁷ also reported that porous Fe₂O₃-SiO₂ layer was coated on the surface of a quartz SAW device to detect H₂S. Porous structure facilitates the diffusion of gas into the sensing layer, thereby enabling the full interactions between the layer and gas molecules. In this experiment, Fe₂O₃ nanoparticles effectively adsorbed and reacted with H₂S molecules because the porous SiO₂ was served as a support to disperse nanoparticles, thus it manifested a fast response shift of -4.4 KHz at the H₂S concentration of 100 ppm.

In summary, different semiconductor metal oxide based sensing materials have different reactivities to the targeted gases. Structures and morphologies are the key point to affect the sensing performance of SAW sensors. Large surface area of semiconductor metal oxides can provide numerous reaction contact areas between gas sensing materials and target gases. Porous nanostructure, assembled by lots of small grains with nanoscale voids and pores, is useful to enhance the sensitivity.
Besides, modifying semiconductor metal oxides using doping is also an effective way to improve SAW sensor performance.

4.2 Carbon-based sensing materials

Carbon-based nanomaterials, including carbon nanotubes and graphene oxides, exhibit excellent performance in sensing application owing to their high surface area, mechanical properties and outstanding electrical conductivity.\textsuperscript{148,149} In this section, we will discuss two micro/nanostructure examples of carbon-based sensing materials acted as sensing layers applied to SAW sensor, including carbon nanotubes and graphene oxides.

4.2.1 Carbon nanotubes-based sensing layer

Carbon nanotubes have outstanding mechanical, physicochemical, thermal and electrical properties. Moreover, carbon nanotubes possess huge surface areas, which make them prospective candidates for sensing applications.\textsuperscript{150,151} For example, Sivaramakrishnan et al.\textsuperscript{152} applied carbon nanotube films coated on quartz SAW device (Figure 7a) to monitor the CO\textsubscript{2} gas concentration by detecting the change in acoustoelectric coupling between the piezoelectric SAW substrate and the carbon nanotube film deposited on the acoustic pathway. Their studies showed an alternative technology of SAW-based carbon nanotube sensors for carbon dioxide sensing in respiratory monitoring.

Single-walled carbon nanotubes (SWCNTs) are potential gas sensing materials with prominent properties such as hollow structure, high specific surface areas, one-dimensional tubular nanostructure, high electron mobility and high chemical reactivity.\textsuperscript{153,154} It was reported that multi-wall carbon nanotubes (MWNTs) made the sensing film more porous, increasing the contact areas between gas molecules and sensing material, thus enhanced the performance of traditional gas-sensitive materials in room temperature.\textsuperscript{155,156} Penza et al.\textsuperscript{157} fabricated quartz SAW sensors coated by either SWCNTs or MWNTs for chemical detection of volatile organic compounds, such as ethanol, ethylacetate and toluene. They reported that the sensitivity of SWCNTs-based sensor in the detection of ethanol (6.89 KHz ppm\textsuperscript{-1}) was higher than those of ethylacetate (3.32 KHz ppm\textsuperscript{-1}) and toluene (3.17 KHz ppm\textsuperscript{-1}). There are two reasons for this phenomenon.\textsuperscript{157} The first is that the SWCNTs exhibited more surface areas for gas detection than MWNTs. The second is the key role of the oxygen. When it comes into contact with carbon nanotubes at ambient conditions, oxygen is chemisorbed and serves as a chemical mediator between carbon nanotubes and the organic solvents used. Penza et al.\textsuperscript{158} also designed and synthesized SWCNT-based sensing layers and coated its onto 36° Y-cut X-propagation LiTaO\textsubscript{3} piezoelectric SAW substrate to detect various gas. In their study, SWCNT-based nanocomposite served as sensing layer was deposited on SAW oscillators (Figures 7b and 7c). The sensing of NO\textsubscript{2}, NH\textsubscript{3} and H\textsubscript{2} gases was monitored by the changes of SAW device’s phase velocities, because the mass-loading, elastic-loading and electric-loading caused by gas adsorption can lead to a change in the SAW phase velocity. Figures 7d-f show that when exposed to a certain concentration of gas, the layered SAW sensor adsorbed the gas molecules, and the phase velocity of the SAW...
sensor was decreased until the saturation occurred in the sensitive

layer. Therefore, the sensor signal was restored to its initial base line when the test gas was exposed to dry air.

Recent studies showed that SAW sensors' sensing performance of carbon nanotubes can be improved by using polymer coatings, carbon nanotubes-based nanocomposites, certain functional groups, and physical and chemical modifications using metal nanoclusters. For example, Asad et al. applied SWCNTs as a sensing layer decorated with Cu nanoparticles (denoted as Cu NP-SWCNTs) to detect H₂S gas. Cu nanoparticles have been reported to act as the modified layer materials which greatly enhanced the sensing performance of ZnO and WO₃. Cu NP-SWCNTs were reported to have good sensing results as its coated SAW device showed a larger frequency shift to H₂S (~260 kHz at the gas concentration of 10 ppm) compared with others at the optimum operating temperature (175 °C). Additionally, at this temperature and the H₂S concentration of 300 ppm, the response time and recovery time of the sensor were 7 and 9 s, respectively. Duan et al. also reported MWCNT decorated with phthalocyanine copper (CuPc) and ZnO showed good performance attributed to the unique heterojunction structures (Figures 7g and h), which increased the carriers’ lifetime. The electron depletion of the p-n heterojunction increased the ability of surface active sites to adsorb NO₂ molecules. The authors also tested the performance of SAW sensor at 100 ppm concentration of NO₂ and the response times at different concentration of NO₂. Their obtained results are shown in Figures 7i and j, respectively, and the composites displayed high sensitivity (0.0505 kHz ppm⁻¹), good linearity and fast response time. Furthermore, carbon nanotubes functionalized using polymers are promising candidates to obtain new sensitive layers for gas detection in order to improve sensitivity and selectivity of the gas sensors.

4.2.2 GO-based sensing layer

Graphene oxide (GO) is an important nanomaterial for SAW sensor applications because it combines 2D structural features of graphene with the presence of oxygen-containing functional groups (hydroxyl, epoxide and carbonyl groups) that interact with a great variety of analytes. Sayago et al. presented a Love-wave SAW sensor deposited with the GO layers to detect different concentrations for simulants of chemical warfare agents below the median lethal doses. When tested using various chemical warfare agents, the quartz SAW device with GO layers show a higher sensitivity (3.087 K ppm⁻¹) to dimethyl-methylphosphonate than to the others (the sensitivity of 1,2-dichloroethane, dipropylene glycol monomethyl ether, and dimethylacetamide were 0.0009, 0.0069, 0.76 K ppm⁻¹, respectively), with a limit of detection as low as 9 ppb detected. It was attributed that the multiple oxygen-containing functionalities, such as epoxy, hydroxyl and carbonyl groups on the surface of GO sheets, can be connected with P=O groups to form stronger hydrogen bonds. Tang et al. reported that GO spin-coated on ST-cut quartz Love mode SAW substrate to detect NH₃. The multifunctional groups such as hydroxyl and epoxy ones on the surface of GO film can adsorb more NH₃ molecules. The NH₃ molecules could be easily adsorbed and filled within the gaps between different GO atomic layers, and thus increasing the stiffness of the film, and finally leading to a

Figure 7 (a) CNT-coated SAW delay line; Reproduced with permission from Ref. 152, ©Elsevier 2008. (b) High magnification of Langmuir–Blodgett (LB) 75 wt.% nanocomposite film of SWCNTs-in-Cadmium arachidate (CDA). (c) Scheme of the experimental setup used for gas sensing testing of SAW devices. (d) SAW phase response of the uncoated reference ZnO/LTaO₂ device and the ZnO/LTaO₂ Love-mode sensor coated with 10 monolayers 75 wt.% SWCNT-in-CDA LB nanocomposite film towards NO₂ gas at room temperature. (e) SAW phase response of the uncoated reference ZnO/LTaO₂ device and the ZnO/LTaO₂ Love-mode sensor coated with 10 monolayers 75 wt.% SWCNT-in-CDA LB nanocomposite film towards NO₂ gas, at room temperature. (f) SAW phase response of the uncoated reference ZnO/LTaO₂ device and the ZnO/LTaO₂ Love-mode sensor coated with 10 monolayers 75 wt.% SWCNT-in-CDA LB nanocomposite film towards NH₃ gas, at room temperature. (g) SAW phase response of the uncoated reference ZnO/LTaO₂ device and the ZnO/LTaO₂ Love-mode sensor coated with 10 monolayers 75 wt.% SWCNT-in-CDA LB nanocomposite film towards H₂ gas, at room temperature. Reproduced with permission from Ref. 158, ©Elsevier 2007. (h) SEM image of the CuPc/ZnO film based on MWNTs framework. (i) Hetero-structure of ZnO and CuPc/MWNTs. (j) ZnO doped CuPc/MWNTs film SAW sensor response to 100 ppm NO₂. (k) ZnO doped CuPc/MWNTs film SAW sensor response to 1-80 ppm NO₂. Reproduced with permission from Ref. 167, ©IEEE Xplore 2015.
positive frequency shift of 620 Hz at a lower NH$_3$ concentration of 500 ppb.

As mentioned above, the catalytic properties of Pd and its sensitivity towards H$_2$ of the SAW devices can be improved by doping with Pd. Li et al. proposed a H$_2$ SAW sensor based on the decoration of GO by Pd nanoparticles on the AlN/Si layered structure. This H$_2$ SAW sensor showed a higher sensitivity (~9.5 times) and a lower cross-sensitivity towards NO$_2$ compared to those based on pure GO. Hydrogen molecules are dissociated into atoms on Pd surface and the resulting hydrogen atoms are dissolved into Pd/GO composite with a high solubility, and the composite film provided larger exposure areas and penetration depths for hydrogen molecules, which contributed to a good sensing performance. Arsat et al. reported that thin graphene-like nanosheets were deposited on quartz SAW interdigitated transducer to assess the sensing performance. However, GO that was incompletely reduced by hydrazine would be covered with hydroxyl, carbonyl epoxide and other functional groups on its surface. These functional groups not only passivated the GO surface, but also reduced the affinity of the surface with adsorbate molecules. It can be seen from that ideal GO-based SAW sensor may have better sensing characteristics than that incomplete reduced GO.

As discussed above, carbon-based materials due to their excellent thermal, electronic and optical properties as well as high electron mobilities have become key sensing nanomaterials for SAW gas sensor applications. It is worth noting that the hybrids of carbon materials and nanoparticles of noble metals and oxides are one of the main research directions of SAW gas sensor, owing to their superior sensing performance.

4.3 Polymers-based sensing materials

Polymers are frequently used as active layers in SAW sensor devices due to their large range of capabilities. Nowadays, polymers are readily available and easily tunable in terms of their functional groups in polymeric backbone, as a result, they are often used to detect different analyte vapors.

Amati et al. summarized various organic polymers which have been applied to SAW sensor with good sensitivities, selectivity and response times for several concentrations of toluene, acetone and dichloromethane. Rabus et al. described a SAW passive wireless sensor coated with a polymer thin film to monitor the presence of H$_2$S in the subsurface environment. The combination of SAW and ground penetrating radar was reported and thus the presence of gas below underground could be detected with the sensor, even at a depth of 1 meter. However, it has a disadvantage that the wireless detection signal to noise ratio is degraded by radiofrequency signal attenuation when propagating through soil leading to poorer detection limits than in the wired configuration. In following sections, we will discuss several typical polymer-based active sensing materials applied to SAW gas sensors.

4.3.1 PANI-based sensing layer

Polyaniline (PANI) exhibits a good sensing performance because of its large specific surface areas and interconnected network structures. Shen et al. investigated a SAW sensor coated with PANI film to monitor the presence of NH$_3$. The concentration of NH$_3$ was 20.45 ppm, the frequency shift was 1.79 KHz, and the response time was less than 150 s. The performance could be attributed to the fact that NH$_3$ molecules are easily adsorbed by H$_2$O molecules, and more NH$_3$ molecules are capable of diffusing into their films and reacting with active site of PANI chains. Specifically, the sensing film becomes deprotonated, and the
deprotonation rate depends on the concentration of NH₃, which in turn resulting in a change of the resistance.

The sensing performance of polymers-based SAW gas sensors can be improved by enhancing electrical and physical properties of polymers by means of the using of various dopants and the modification of its structures.¹⁸⁵ Nanofibers have a cylindrical morphology and will form porous structures when deposited as thin films. The synthesis of modified PANI nanofibers was found to have a remarkable influence on the SAW device sensitivity.¹⁸⁶ Hence, hydrochloric acid (HCl) and camphor sulfonic acid (CSA) as dopant acids were used in the synthesis processes to obtain PANI nanofibers with average diameter of 30- and 50-nm (Figures 8a and b, respectively) to detect the sensitivity of SAW sensor to H₂.¹⁸⁷ Figure 8c shows that the responses were 3 KHz and 14.6 KHz toward 1% of H₂ for HCl and CSA doped PANI nanofiber sensors, respectively. The dynamic responses of the CSA- and HCl-doped PANI nanofiber sensors to different H₂ concentrations are shown in Figures 8d and e. The HCl doped sensor had faster response and recovery times compared to the CSA doped sensor for all concentrations of H₂ (Figure 8f). Three possible reasons for these phenomena were reported: 1) the diameter of the nanofibers provided a different amount of surface area for H₂ interaction. 2) the differences in volatility and mobility of the dopants might cause variable speeds of reaction. 3) there might be variation in the doping level of the dried films.¹⁸⁷

Sadek et al.¹⁸⁸ reported a PANI/In₂O₃ nanofiber composite based SAW gas sensor to detect H₂. The activation of the hydrogen by In₂O₃ makes the composite to absorb more H₂, which enhanced the sensing performance. Besides, facilitated by In₂O₃, the hydrogen dissociates and interacts with the PANI backbone, leading to either a doping type response or chain alignment, which also contributes to a good sensing performance. 4.3.2 TEA-based sensing layer

Liu et al.¹⁸⁹ reported a quartz SAW device deposited with triethanolamine (TEA) to detect H₂S at room temperature, owing to the high efficiency adsorption of TEA and the existence of van der Waals’ interactions and hydrogen bonds with H₂S molecules. The sensing mechanism was attributed to that the adsorption of TEA towards H₂S modulated the propagation of SAW, and the corresponding phase changes were converted into voltage signals proportional to the concentration of H₂S which were collected as the sensor signals. The obtained experimental results showed that fast response time (7 s), high sensitivity (0.152 mV ppm⁻¹) and a lower detection limit (0.15 ppm) were achieved with the H₂S concentration of 4 ppm at room temperature. However, an undesirable coating loss caused by thermal evaporation of TEA at a high temperature and high flow rate was observed, thus affecting the sensing performance. Qin et al.¹⁹⁰ reported a SAW gas sensor coated with TEA modified with boric acid to detect SO₂. The SAW device with the modified TEA has a better performance than that using the pure TEA, which was attributed to that the reaction of boric acid and TEA derived the nitrogen atoms in the cage structure possessed a lone pair of electrons, making it more sensitive to SO₂.

4.3.3 PEO-based sensing layer

Methylene chains in polyethylene oxide (PEO) are of an antioxidant nature and increase the lifetime of the films, which not only enhances the mechanical properties of the polymeric film but also increases the elasticity of the suspension liquid during the spraying process. It is a good choice for the SAW gas sensor na matter if it is in the selection of materials or in the preparation of the spin coating solution. For example, Liu et al.¹⁹¹ reported a SAW sensing layer which was synthesized using ultrafine (100-300 nm) PEO fibers (Figure 8g). The nanofibrous film achieved a high surface area to volume ratio, which could not offer more adsorption sites for vapor molecules, but also shorten the diffusion length of vapor molecules into polymer materials, and these superiorities are favorable to enhance the performance of sensor. The electrospun nanofiber SAW sensor showed an excellent repeatability with variations lower than 5%. The frequency shifts of SAW sensor are shown in Figure 8h, and the test environment is shown in Figure 8i.

4.3.4 PPy-based sensing layer

Polypyrrole (PPy) is an attractive conducting polymer in SAW sensor design due to its easy polymerization into film, its relative stability and high electrical conductivity.¹⁹² Mashat et al.¹⁹³ previously presented a quartz SAW device deposited with PPy nanofibers for the detection of H₂ and NO₂ at room temperature. PPy nanofibers were prepared by a template-free chemical route and characterized with SEM, Fourier transform infrared spectroscopy (FT-IR) and transmission electron microscopy (TEM) techniques, respectively. The information from Figure 8j indicates that the length of the nanofibers was several microns and the average diameter was 18 nm. SAW gas sensing tests using the device with a PPy layer showed that when exposed to the gas concentration of 1% H₂ and 2.1 ppm NO₂, the frequency deviation was 20.194 KHz and 4.5 KHz, respectively, and meanwhile the SAW sensor had a good repeatability (Figure 8k).

Chen et al.¹⁹⁴ developed the SAW NH₃ gas sensors based on different layers of PPy and Pt doped PPy layers. The doping of Pt was conducted by immersing substrates with PPy film. Comparing with different layers of PPy, it was found that the device with two layers of PPy film showed the best performance among the devices with different layers of PPy films. The rough surface enabled the film to adsorb more NH₃ molecules, and meanwhile, Pt catalyst enhanced the reaction between the NH₃ and PPy, causing larger decrease of PPy’s resistance and thus leading to larger electrical loading effect. Furthermore, response and stability of device with two layers PPy could be further improved by doping of Pt. Chen et al.¹⁹⁴ showed that it could be possible to use the other noble metal, such as Au, Ag, and Pt for doping PPy films as the sensing materials for the SAW sensor.
Pasupuleti et al.\textsuperscript{195} reported that the quartz SAW device with a sensing layer of PPy modified poly (3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT-PSS) hybrid nanocomposite exhibited a high sensitivity of ~9.38 KHz with a positive frequency shift and a low detection limit (~231 ppb) towards CO (100 ppm) gas. The outstanding performance is attributed to the sensing layer's high porosity, large surface area, abundant OH and amine functionalizing groups. Moreover, the synergetic effect of the p-n hybrid heterojunction, which can act as active surface sites, further improved the effective absorption of CO gas molecules. The addition of PPys enhanced the conductivity of the composite and there was a strong interfacial charge interaction at the hybrid heterojunction interface, which is further beneficial to improve the gas reaction kinetics.\textsuperscript{195}

4.3.5 PVP-based sensing layer

Polyvinylpyrrolidone (PVP) has many extraordinary physical and chemical properties, such as good high thermal and chemical stability, non-toxicity and excellent solubility in water and many organic solvents, which make it suitable materials for gas detection.\textsuperscript{196} Besides, PVP, a nonconducting polymer, has also been reported to be sensitive to ammonia and aliphatic amines, since its carbonyl groups and nitrogen sites are considered as hydrogen bond acceptor.\textsuperscript{197} Recently, He et al.\textsuperscript{198} prepared PVP fibers by electrospinning and investigated the effects of the concentration of PVP solution and electrode-to-collector distance on the morphology of the electrospun PVP fibers. Electrospinning processes of such PVP layer can be varied by changing the electric field intensity and solution viscosity, thereby affecting its morphology and the SAW sensing performance.\textsuperscript{199} When the concentration of PVP solution was 58%, the smooth and uniform nanofibers were obtained, it possessed a larger surface-to-volume than using the other concentration of PVP. In the gas sensing test, the frequency shift was about 5.6 KHz at the H\textsubscript{2} concentration of 1% and it had a fast response time (120 s) and recovery time (200 s). This outstanding sensing performance can be attributed to the unique chemical and physical structures of the PVP. Particularly, the PVP can act as hydrogen bond acceptor due to the existence of both carbonyl groups (C=O) and nitrogen (N\textsubscript{2}) sites.\textsuperscript{200} H\textsubscript{2} acted as the hydrogen bond donors can be easily adsorbed by PVP fibers causing a significant mass loading. Chee et al.\textsuperscript{201} investigated the gas sensing performance of PVP/MWNTs composite based SAW sensor. The effect of the amount of PVP on morphologies of composite was investigated because the PVP is well known to prevent agglomeration of the particles and stabilize the particle sizes. Characterization results showed that the morphology with a large amount of PVP is nanofibers, while that with a small amount of PVP is nanoparticles dispersed in MWNTs. Meanwhile, experimental results also identified that the sensing performance of composite is mainly attributed to the hydrogen bond connection between PVP and H\textsubscript{2}. Therefore, PVP has a great potential for the detection of H\textsubscript{2}. Matatagu et al.\textsuperscript{199} also used PVP fibers prepared using an electrospinning technique as a sensitive layer of the SAW sensors to detect VOCs. The process voltages were changed to obtain a series of different diameters of PVP. With a higher voltage applied, the diameter of nanofiber was lower and possessed larger active surface which can adsorb more toluene molecules. The sensing sensitivity of PVP (3.25 Hz ppm\textsuperscript{-1}) to toluene was also reported to be superior to that reported of PEO (0.45 Hz ppm\textsuperscript{-1}).\textsuperscript{202}

To sum up, the unique tunable electrical properties, along with easy synthesis, structural diversity, facial functionalization as well as flexibility of these polymer sensing materials are suitable for gas sensing. Attention should be paid to their low sensitivity and poor stability, which hinder their practical sensing applications. As listed above, various strategies have been proposed to enhance the sensing performance, including increasing the active surface area, redox doping and surface functionalization. Therefore, it is crucial to continuously develop high-performance polymer materials for the application of SAW gas sensor.

4.4 Other types of common sensing materials

Apart from the sensing materials reported above, many other types of sensing layer materials also exhibit excellent sensing performance on SAW sensors.

4.4.1 Cellulose-based sensing layer

Cellulose has various exceptional characteristics such as large specific area (~250 m\textsuperscript{2} g\textsuperscript{-1}) and abundant surface hydroxyl groups, which are beneficial for gas sensing. In recent years, researchers have successively developed cellulose as a sensing layer coated on a quartz SAW device to detect the sensitivity to various gases. For instance, Tang et al.\textsuperscript{203} reported that cellulose nano-crystals (CNCs) could be used as a sensitive and selective layer in SAW sensors for HCl gas detection. The CNCs have been identified to possess abundant hydroxyl groups on their surfaces, which were acted as the perfect adsorption sites for H\textsubscript{2}O and also greatly promoted the adsorption of HCl gas. The sensor showed an ability to detect HCl at a low concentration of 1 ppm with a response of ~2 KHz, and the response could reach as high as ~80 KHz when the concentration of HCl gas was increased to 200 ppm.\textsuperscript{203} Wang et al.\textsuperscript{204} synthesized bi-layer composite film composed of bacterial cellulose and polyethyleneimine (PEI), which were deposited on a quartz SAW device to detect formaldehyde. The bacterial cellulose films possessed ultrafine fibrous and filamentous network structures, and the unique structure provided a large amount of adsorption sites for the PEI particles. Meanwhile, the hydrogen bonds formed between the hydroxyl group on the surface of bacterial cellulose and the amine group of PEI were found to prevent the aggregation of PEI particles, ensure the uniform distribution of PEI on the bacterial
cellulose films, and enhance the adsorption effect of formaldehyde gas. Therefore, the SAW sensor exhibited a good sensing performance such as a frequency response of 35.6 KHz with the formaldehyde concentration of 10 ppm.

Figure 9 (a) The SEM images of (a) F-1-150. (b) F-1-300. (c) F-1-450. (d) F-2-300. (e) F-3-300. (f) F-4-300. Film-spin coating cycles-temperature. Inset images are the cross-sectional views of films. (g) The proposed sensing mechanism of the SAW HCl sensor based on AlOxOH, films. (h) The dynamic responses of sensors based on F-1-300, F-2-300, F-3-300 and F-4-300 coated resonators to 0.5 ppm HCl. (i) The dynamic responses of the sensor based on F-4-300 to HCl of various concentrations. (j) The response, response time and recovery time as a function of the concentration of HCl (log scale). Reproduced with permission from Ref. 205, Elsevier 2020.

4.4.2 Hydroxylate-based sensing layer

Tang et al.205 synthesized hydroxyl-rich AlOxOH films onto a quartz SAW device using a sol-gel method with different spin coating cycles and temperatures (Figures 9a-f). The fabricated SAW sensors showed negative frequency shifts when exposure to HCl gas. The reason was attributed to the increased weight of sensitive films induced by the adsorption of HCl assisted by the hydroxyl groups and H2O captured on the films. The sensing mechanism of the SAW HCl sensor based on AlOxOH films is illustrated in Figure 11g. The sensor with a 198-nm-thick AlOxOH film annealed at 300 °C showed a response of ~1.4 KHz to HCl at a low concentration level (0.05 ppm) in an environment with a temperature of 25 °C (Figures 9h and 9i). The response and recovery times as a function of HCl gas concentration are shown in Figure 9j. As can be seen from that the recovery time was changed inconspicuously whereas the response time significantly increased when the concentration of HCl increased from 0.05 to 50 ppm.

4.4.3 Noble metal-based sensing layer

Noble metals are well known for their unique large surface area-to-volume ratio, optical and electronic properties, and high stability. Hence, they are widely used in various applications such as catalytic system, fuel cell and sensor. Take the noble metal Pd as an example, many studies reported that the dissociation of H2 on Pd is thermodynamically favorable because the combination of H2 into Pd easily causes the formation of PdH2. The formation of Pd-H is mainly through the following processes, e.g., physisorption, chemisorption and dissociation of H2 on the surface, introduction of hydrogen atoms on the Pd surface and diffusion of H atoms into the bulk, and finally the palladium hydride formation.98,99 Meanwhile, the absorption of H2 can cause strain formation in the lattices of Pd, and further change the electrical properties.121 Consequently, Pd can be applied as the sensing material for H2 gas detection. For example, Sil et al.206 reported that using Pd nanoparticles (5-20 nm) as the sensing layer coated on quartz SAW devices to detect H2. Experiments confirmed that exposure to H2 induces lattice expansion in Pd, which brought the nanoparticles together more tightly and enhanced sensing performance. Moreover, the decreased binding energy of the Pd lowered the miscibility gaps, and a set of surface adsorption sites for hydrogen adsorption appeared, which enhanced the hydrogen sensing property. Amico et al.207 deposited Pd thin films on quartz SAW device to detect the concentration of H2. The interparticle distance in the Pd nanoparticle films provided spaces for hydrogen to induce morphological changes. Pd nanoparticles also showed a higher specific surface area thus providing more adsorption active sites, enabling the hydrogen to diffuse in and out more readily, increasing the rate at which the sensor could respond to a change in hydrogen vapor concentration and reducing hysteresis. All of the aforementioned properties made Pd nanoparticles had a better excellent performance than Pd films.

Au thin film served as a sensing layer coated on the SAW device also exhibited excellent sensing performance, for example, to detect chloroform.208 Laser-deposited Au immobilization layers with different porosities was obtained which further improved the sensing performance. The results show that the porous Au layer showed a much larger frequency shift (26 KHz) in the same conditions compared with those of other morphologies. This excellent performance can be ascribed to high surface to volume, which is beneficial to the gas diffusion.

Figure 10 (a) TEM of the synthesized PbS CQDs. Inset was the size distribution of the sample. (b) Schematic diagrams on the gas sensing mechanism of the SAW gas sensors based on the untreated and Pb(NO3)2-treated PbS CQD films. (c) Transient response curves of the Pb(NO3)2-treated PbS CQD-based SAW sensor to 0.3-30 ppm NO2 gas at room temperature. (d) The selectivity of the sensor. Reproduced with permission from Ref 211, Elsevier 2019. (e) SEM of Bi2S3 nanobelts. (f) The dynamic sensing responses of the sensor to 1.2-10 ppm NO2 gas. (g) Response curves of the Bi2S3 nanobelts based SAW sensor to 6 ppm NO2 at room temperature. (h) The selectivity of the sensor towards diverse gases. Reproduced with permission from Ref. 215, IEEE Xplore 2021.

4.4.4 Sulfide-based sensing layer
Compared with metal oxides, metal sulfide has a wider forbidden band and better thermal stability, suitable for SAW sensors. For example, crystal structure of ZnS, with a wide band gap of 3.72 eV, is similar to that of ZnO and has abundant
**Table 1** Summary of sensing materials of SAW gas sensor.

<table>
<thead>
<tr>
<th>Material</th>
<th>Target gas</th>
<th>C(ppm)</th>
<th>Response (kHz)</th>
<th>T_{res}/T_{rec(s)}</th>
<th>LOD (ppm)</th>
<th>Ref.</th>
</tr>
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<td>ZnO films</td>
<td>NH₃</td>
<td>120000</td>
<td>376.9</td>
<td>/</td>
<td>/</td>
<td>90</td>
</tr>
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<td>/</td>
<td>/</td>
<td>21/180</td>
<td>/</td>
<td>91</td>
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<td>6</td>
<td>/</td>
<td>0.4</td>
<td>93</td>
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<td>94</td>
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<td>100</td>
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<td>/</td>
<td>2253</td>
<td>95</td>
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<td>151/568</td>
<td>/</td>
<td>96</td>
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<td>/</td>
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<td>/</td>
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<td>Zn₆Fe₂O₁₄ films</td>
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<td>/</td>
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<td>/</td>
<td>104</td>
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<tr>
<td>ZnO/Al₂O₃ films</td>
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<td>~0.5</td>
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<td>/</td>
<td>111</td>
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<td>2</td>
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<td>/</td>
<td>112</td>
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<td>~70/~60</td>
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<td>0.92</td>
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<td>~30</td>
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<td>/</td>
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<td>2000</td>
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<td>/</td>
<td>123</td>
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<td>/</td>
<td>/</td>
<td>100/30</td>
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<td>124</td>
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<td>55/45</td>
<td>~0.53</td>
<td>125</td>
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<td>/</td>
<td>3</td>
<td>129</td>
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<tr>
<td>WO₃ particles</td>
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<td>/</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>130</td>
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<tr>
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<td>H₂</td>
<td>10000</td>
<td>118</td>
<td>240/480</td>
<td>/</td>
<td>131</td>
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<tr>
<td>Au-WO₃ films</td>
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<td>10000</td>
<td>705</td>
<td>180/360</td>
<td>/</td>
<td>131</td>
</tr>
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<td>40000</td>
<td>2.4</td>
<td>~100/100</td>
<td>/</td>
<td>132</td>
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<tr>
<td>TiO₂ particles</td>
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<td>/</td>
<td>/</td>
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<td>/</td>
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<td>SiO₂-TiO₂ films</td>
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<td>InO₃ films</td>
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<td>/</td>
<td>/</td>
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<td>TeO₂⁺⁺ films</td>
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<td>/</td>
<td>/</td>
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<td>Co₂O₃/SiO₂ films</td>
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<td>Fe₂O₃-SiO₂ films</td>
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<td>/</td>
<td>/</td>
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<td>Cu NP-SWCNT</td>
<td>H₂S</td>
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<td>~300/1800</td>
<td>/</td>
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<td>420/420</td>
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<td>Toluene,Octane</td>
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<td>0.101,0.43</td>
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<td>9.2/1.7</td>
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<td>1,1</td>
<td>3.087,0.76</td>
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<td>6.2</td>
<td>250/700</td>
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<td>1000</td>
<td>2.07</td>
<td>7/7</td>
<td>/</td>
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<td>Graphene-like nano-sheets</td>
<td>H₂,CO</td>
<td>10000,1000</td>
<td>5.8,8.5</td>
<td>12/&lt;60,300/1200</td>
<td>/</td>
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<td>/</td>
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<td>PANI film</td>
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<td>1.79</td>
<td>20.45</td>
<td>&lt;150/-</td>
<td>25</td>
<td>184</td>
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<td>PANI</td>
<td>NH₃</td>
<td>1.79</td>
<td>20.45</td>
<td>&lt;150/-</td>
<td>25</td>
<td>187</td>
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<td>H₂</td>
<td>10000</td>
<td>11</td>
<td>30/40</td>
<td>/</td>
<td>188</td>
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<td>TEA</td>
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<td>/</td>
<td>/</td>
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<td>PPy nanofibers</td>
<td>H₂,NO₂</td>
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<td>39/219, (133/298)</td>
<td>/</td>
<td>193</td>
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<td>Pt/PPy</td>
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<td>/</td>
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<td>120/200</td>
<td>/</td>
<td>198</td>
</tr>
<tr>
<td>PVP fiber</td>
<td>toluene</td>
<td>10</td>
<td>30</td>
<td>/</td>
<td>10</td>
<td>199</td>
</tr>
<tr>
<td>Cellulose nano-crystals</td>
<td>HCl</td>
<td>1/5</td>
<td>-2/-10</td>
<td>~45/~500</td>
<td>/</td>
<td>203</td>
</tr>
<tr>
<td>Cellulose/polyethylene</td>
<td>Formaldehyde</td>
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<td>35.6</td>
<td>34/28</td>
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<td>204</td>
</tr>
<tr>
<td>AIOxHy films</td>
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<td>~0.0014</td>
<td>/60</td>
<td>0.05</td>
<td>205</td>
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<tr>
<td>Pd nanoparticle</td>
<td>H₂</td>
<td>1600</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>206</td>
</tr>
<tr>
<td>Pd films</td>
<td>H₂</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>50</td>
<td>207</td>
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<tr>
<td>ZnS films</td>
<td>NH₃</td>
<td>20</td>
<td>~3.8</td>
<td>45/148</td>
<td>/</td>
<td>210</td>
</tr>
<tr>
<td>PbS CQDs</td>
<td>NO₂</td>
<td>10</td>
<td>9.8</td>
<td>45/58</td>
<td>0.032</td>
<td>211</td>
</tr>
<tr>
<td>SnS CQDs</td>
<td>NO₂</td>
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<td>~1.8</td>
<td>180/446</td>
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<tr>
<td>Bi₂S₃ nanobelts</td>
<td>NO₂</td>
<td>10</td>
<td>2</td>
<td>/</td>
<td>0.017</td>
<td>215</td>
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sulfur vacancies on its surface. Long et al. developed mucosal-like ZnS nanostructures which was applied as a sensing layer for SAW NH$_3$ sensor. When the ZnS film was exposed to NH$_3$ atmosphere, the active O$^{2-}$ ions reacted with the NH$_3$ molecules are adsorbed on the surface of the film to release electrons, which leads to a decreased depletion layer and an increased of conductivity in the film. The good sensing performance is mainly attributed to its large specific surface areas and increased active sites on their surface, which makes ZnS films adsorbing more NH$_3$ molecules. Li et al. deposited Pb(NO$_3$)$_2$-treated PbS colloidal quantum dots (CQDs, Figure 10a) onto a quartz SAW device to detect the sensing performance of NO$_2$. Compared with PbS CQDs, the Pb(NO$_3$)$_2$-treated PbS CQDs SAW sensor displayed faster response and recovery times (45 s and 58 s, respectively), as well as a larger positive frequency shift (9.8 KHz). It can be ascribed the excellent performance to the porous structure of Pb(NO$_3$)$_2$-treated PbS CQDs trapped more NO$_2$ molecules (Figure 10b). Meanwhile, the Pb(NO$_3$)$_2$-treated PbS CQD-based SAW sensor to 0.5-30 ppm NO$_2$ gas at room temperature was tested (Figure 10c) and it showed good stability and selectivity (Figure 10d). Effective combination of PbS and CQDs is the key reason for the improved performance because these CQDs have large specific surface areas that contribute to a large amount of active sites for adsorbing target gases. However, Pb has cost environmental and health problems which limits its widely use. Thus, it is necessary to explore SAW gas sensors based on the sensing materials with low toxicity but still having a high performance. Li et al. reported SnS CQDs as sensing layer deposited onto quartz SAW sensor to detect NO$_2$. The SnS CQDs, with their ultrafine particles (5 nm), large surface areas and numerous adsorbed active sites, were capable of detecting a low concentration of NO$_2$ gas (10 ppm) and showed good selectivity and repeatability.

Narrow band gap semiconductors such as Bi$_2$S$_3$ (1.3-1.7 eV) have been widely studied due to its application in optoelectronic devices, hydrogen storage materials, solar cells, gas sensors. Luo et al. deposited one-dimensional Bi$_2$S$_3$ nanobelts onto the sensing area of ST-cut quartz SAW device for NO$_2$ gas detection at room temperature. Figure 10e shows these Bi$_2$S$_3$ nanobelts with porous structures are beneficial to adsorb NO$_2$ gas molecules, thereby improving the sensing performance. The Bi$_2$S$_3$ nanobelts SAW sensor exhibited a positive frequency shift of 2 KHz toward 10 ppm NO$_2$ with good sensitivity, stability and selectivity (Figures 10f-h).

5. Conclusions and Future Perspectives

Design and application of novel sensing materials provides a valuable method for the development of SAW gas sensors. This review summarizes the advances of sensing materials towards gas sensing applications based on SAW technology in recent years. The basic sensing mechanism of SAW gas sensor and the evolution of sensing parameters have been discussed. A wide range of materials (including semiconductor metal oxides, carbon-based materials, and polymers) as efficient sensing layers used in the SAW based gas sensors are reviewed in Table 1. The synthesis strategy, composition and structure-activity relationship of these sensing materials are also discussed.

Despite considerable advances have been made in recent years towards sensing materials synthesis and improvements of SAW gas sensor, there are still many challenges to be tackled and various issues to be explored. Some of these future directions are listed below.

(i) One of the main challenges for SAW gas sensors is the ability to maintain a long-term stability of the under varying environment conditions, such as temperature and humidity. For the last few years, a great deal of studies have explored the effects of humidity and temperature on the sensitivity of SAW gas sensors. It should be pointed out that the sensing performance of SAW sensors in literature is based on the results obtained in the controlled laboratory conditions. However, in practical applications, the gas sensing performance of the SAW sensors would be changed significantly with the variations of the external environment. Therefore, the influences of external variables on the sensing performance need to be explored in order to establish a mathematical model, thereby enhancing the adaptability of the SAW gas sensors.

(ii) IDTs play an important role to generate, localize and transmit the frequency signals in SAW gas sensors. However, the main challenge is to find a reliable and effective combination of piezoelectric materials and suitable IDT structures to generate the efficient wave modes. Simulation and modelling have played a valuable role in analyzing and designing the SAW gas sensors. For instance, mathematical and physical methods such as piezoelectric equation, dispersion equation and wave equation are often used to analyze the propagation characteristics of SAWs in substrates or overlaid structures. Therefore, the period of IDT, the logarithm of IDT, and IDT spacing can be designed through software simulations to improve the quality factor of the SAW device and reduce the insertion loss.

(iii) Porous structured materials have attracted enormous interests in gas sensors due to their highly dispersed active sites at different length scales of pores, which can result in the shortened mass diffusion paths or minimized diffusion barriers, easier accessibility for gas molecules and improved mass transport. The internal volumes and the concentrations of monomers/additives can be rationally varied to tune the pore size, pore volume, and pore interconnectivity which will in turn affect mechanical stability, diffusivity, and response sensitivity of the SAW gas sensors. Therefore, the porous materials (such as Al$_2$O$_3$, SiO$_2$ and Fe$_3$O$_4$) or suitable preparation methods (such as surfactant templating, microporous polymer templating, freeze-drying and sol-gel controlling and post treatment) should be further studied using various explored as the modification methods to improve the sensor responses.

(iv) Many strategies for improving the SAW gas sensing performance have been proposed in literature and briefly discussed in this paper, such as doping and compositing. Doping can change the properties of the morphology and microstructure, electronic structure, activation energy, and generate oxygen vacancies. For example, oxygen vacancy can be served as the direct adsorption sites as well as electron donor sites and lower activation energy is more
beneficial to speed up the rate of the response of the SAW gas sensor. Heterojunctions can be formed at the interfaces of different materials, which can accelerate the transformation of electrons and enhance oxygen adsorption to improve the selectivity and response rates of SAW gas sensors. Therefore, suitable improvement methods should be explored as effective ways to enhance the SAW gas sensing performance.

(v) SAW sensors are developed rapidly for many new fields such as chemical gas detection, military applications and biological detection have great potential applications. For example, wearable SAW devices in the military could be used to detect chemical gases used in battlefields, or to monitor soldiers’ own biological parameters. Besides, a suitable application is the use of SAW gas sensor in smart food packaging to detect rotten or spoiled food. These sensors can accurately identify spoilage gases such as NH3 in meat and fruit products and can be read by smartphones. Therefore, in the future, intelligent flexible or wearable SAW sensor could be integrated into human production and daily life to provide more help for human being’s life and activities.

Conflicts of interest
There are no conflicts to declare.

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