We are IntechOpen, the world’s leading publisher of Open Access books
Built by scientists, for scientists

4,500 Open access books available
119,000 International authors and editors
135M Downloads

154 Countries delivered to
TOP 1% Our authors are among the most cited scientists
12.2% Contributors from top 500 universities

WEB OF SCIENCE™
Selection of our books indexed in the Book Citation Index in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com
Chapter

Environmental Gas Sensors Based on Nanostructured Thin Films

Nithya Sureshkumar and Atanu Dutta

Abstract

Since the discovery of electron microscopes, nanomaterials and nanotechnology have been influencing academic and industrial research greatly for bringing out newer and better products with improved materials’ properties. In the field of environmental gas sensors too, the demonstration of nanomaterials for sensing various gases has become a common practice. Environmental gas pollution has turned out to be a huge concern in the society due to the progress of civilization. The awareness of health hazard for different toxic/polluting gases and rectification measure by imposing stricter norms has prompted extensive research to develop efficient gas sensors to detect trace level of pollution from various sources. Thin film, ultrathin film, and nanostructure materials of metal oxide semiconductor, polymer, metal, carbon nanotube, graphene, etc. with or without sensitizers have been investigated for sensing various toxic gases. New device structures have been fabricated to achieve high sensitivity, selectivity, fast response, etc. The microstructure and thickness of film are found to influence the performance greatly. Various methods of preparations and mechanism of sensing are being explored. All these aspects and the challenges were discussed in this chapter.

Keywords: gas sensor, nanostructure, thin film, carbon nanotube, metal oxide semiconductor

1. Introduction

Sensor as given in the Handbook of Modern Sensors by Fraden [1] is defined as “A device that receives a stimulus or signal such as chemical, physical or biological signal and responds or convert into an electrical signal.” Sensor is an essential tool for everyday life which is used to identify a specific task assigned to it. The best sensors are already there in human body, namely, eye to see, ear to hear, nose to smell, tongue to taste, and skin to feel the surrounding. However, there are several threats which need to be identified well in advance, and appropriate measures can be taken to prevent any accident or health hazard. Due to urbanization, development of industries, and requirements of society, we have invited several intimations to our society. Environmental gas pollution is one of them. The society is now concerned about how due to various reasons air pollution is harming our planet. It is impossible to find solutions for all these problems very quickly as civilization and its progress cannot be stalled. Therefore, efforts are being made to avoid and minimize environmental pollution and put safeguards for human health. Specifically, gases such as hydrocarbons (HCs), nitrogen oxides (NOx), carbon monoxide (CO), carbon dioxide (CO2), sulfur dioxide (SO2), ammonia (NH3), hydrogen sulfide (H2S),
volatile organic compounds (VOCs), etc., which are released or emitted in the environment, cause either directly or indirectly health problems and accidental situations. The sources of such accidental release vary with pollutant gas, and mostly industries and human amenities are responsible. Since the presence of such hazard gases in low concentrations cannot be smelled by human nose, improvised sensors or electronic noses are required to detect these gases efficiently. The detection of gas results in changing properties of the sensor which in turn activates an actuator circuit for alarm alert. Several governmental norms are published for health safety on exposure concentration and time of exposure [2]. Likewise, stringent norms have been imposed on each of the possible sources of all these pollutant gases.

The research of environmental gas sensors started since the 1960s with metal oxide films. In 1962, Seiyama et al. [3] reported thermally evaporated ZnO thin film sensor of thickness 1–100 nm for the detection of several volatile organics, hydrocarbon, and carbon dioxide at temperature above 400°C. Taguchi demonstrated SnO$_2$-based semiconductor sensor. He patented his work [4] and formed the famous company named Figaro Engineering Inc. Due to the strict environmental pollution norms imposed for emission of various toxic gases, research on gas sensors and materials expanded exponentially in the last 50 years. Several 10,000 research papers were published to claim suitable gas sensors. In 1980, Advani et al. proposed a SnO$_2$ thin film for H$_2$ gas sensor [5]. The device based on SnO$_2$ thick film gas sensor was reported by Heiland et al. [6] and thin film by Sberveglieri [7]. More efforts were given to develop sensors based on thin films to detect toxic gases mostly at room temperature. Several review articles on the progress of thin film sensors are available in the literature.

1.1 Importance of sensors in day-to-day life

The rapid growth of industrializations in modern life has enhanced the risk of pollution deteriorating the atmospheric environment around us. Thus it is necessary to control and monitor such pollutants to avoid health hazards. Table 1 depicts potential gas sensor applications for various reasons. Several commercial sensors are available for gas detection in different environments. However, the demand of compact, reliable, cheap, selective, and low power consuming sensors is still not yet met. Therefore, extensive research is going on to satisfy the specific need of the situation.

1.2 Thin film

There is no accurate definition of thin film but it is limited by thickness. The film below 1 μm is considered as thin film, and film above it is considered as thick film. But, normally when a solid material is coated on solid support, called substrate, by either physical or chemical process, it is called as a thin film. It should be highlighted here that it is not only a small thickness (<1 μm) that endows the great and special distinguished characteristics but also the microstructure which is equally important. Thin films characteristically have different properties from the thick films [8]. Many researchers are investigating thick and thin film gas sensors using different materials like metal oxides, ceramic and polymer materials, etc. But, the problems associated with these sensors are limited by the measurement accuracy and long-term stability [9]. To solve this problem, nanotechnology plays a major role to rectify and provide huge opportunity to establish the next-generation gas sensor devices with enhanced sensing performance in terms of fast response and recovery, good reversibility, low power consumption, and excellent sensitivity at extremely low gas concentration by using nanostructured sensing materials [10–12].
2. Nanostructure film materials for gas sensor application

From the literature it is seen that nanostructured materials have attracted keen attention for several applications including gas sensing. These include semiconductor metal oxide nanowires, nanoribbons, nanorods, carbon and other nanotubes, diamonds, graphene, and combination of these which make more interesting nanostructures. A major attraction of the nanomaterials in the gas sensor application is because of high surface area to volume ratio. This possibly deliberates high sensitivity due to the excellent adsorption of gas species on the available molecular binding site and thus often increases sensing capability [13]. Based on the materials, the following gas sensors can be considered for research and developments.

2.1 Semiconducting metal oxide nanostructure gas sensor

To fabricate the nanostructured gas sensors, semiconducting metal oxides are the most widely used material. The schematic diagram of semiconducting metal oxide thin film gas sensor is shown in Figure 1. The electrical conductivity of semiconductor gets modified once the surface is exposed to sensing gas. Nanostructure metal oxide thin film produces very high sensitivity due to high surface activity and unique microstructure. High adsorption of gas species on the surface and subsequent catalytic activity with the adsorbed species enhance sensing performance and thus reducing response time compared to the conventional microstructure gas sensor.
Semiconducting metal oxides in the form of nanowire, nanobelt, and nanoparticles are also widely used for detecting various gases. The majority of the sensor work reported in the literature so far are based on various metal oxide semiconductors. These materials can be doped easily or sensitized by appropriate metal to tailor-made sensitivity, selectivity, and also operating temperature. Very recently, a comprehensive review article was published by Li et al. to document all different types of such gas sensors for detecting several toxic gases [14]. The metal oxide gas sensors have an advantage of working in the lower-temperature range with high sensitivity. However, metal oxide nanosensors are more expensive than the thick film or bulk material gas sensors because of the deposition of nanothin film using highly sophisticated techniques and also the use of advanced microscopic analysis for characterizing the materials to improve its sensing characteristics [15].

2.2 Polymer-based nanosensors

In recent year, organic polymer-based nanosensors have been specially developed for detecting aromatic compounds, medicine, ionic species, amines, organic vapor, and gases [16]. Generally, the conducting polymers are coated on a substrate in the form of thin film. The sensor structures can either be with film with two electrodes or field-effect transistor with controlled electric field to monitor sensing current. Many such structures are also available in the literature. Figure 2 shows such structures. The sensitivity of the polymer-based gas sensor depends on the sensing area of the device and thickness of the film. Addition of metal oxides, carbon nanoparticles, or fibers in the polymer-based sensors leads to the increase of sensitivity. The deposition techniques of thin film are very simple and the process is cheap also. The main problems with polymer-based sensor are lower stability with temperature and time and their lack of selectivity. The studies have been carried out to improve the stability and selectivity of polymer-based sensors by adding the carbon nanoparticles and fibers, but still some problems are yet to be solved.

2.3 Metal and metal complex nanosensor

Nanosensor with metal or normally metal nanoparticles dispersed on the substrate surface is also proposed [18]. In this case, very high surface exposure with
Environmental Gas Sensors Based on Nanostructured Thin Films
DOI: http://dx.doi.org/10.5772/intechopen.89745

respect to volume results more adsorption of gases. When these nanoparticles interact with gas molecules, change of electronic properties including that of substrate takes place rapidly. Vaporizing metal precursor deposition method produces metal film or metal nanoparticles, and subsequent annealing treatment produces these kinds of nanosensor. Maximum studies reported so far use metal oxide as a substrate with metal nanoparticle dispersed for such nanosensor device surface. Some of these sensors work at low temperature. Metal complex nanosensors have their unique property, i.e., ability to create reversible interaction with other atoms. Many studies, reported as metal complex, mostly act as a receptor for various types of molecules. This activity can increase the sensitivity and selectivity of different sensors [19]. The advantage of using metal complex as a sensing layer creates reversible interaction between the gas molecules and the device. The changing chemical environment or increasing the temperature affects the bonding formation during the gas sensing process. This type of sensors, based on the receptors, is designed to interact with specific gases to increase selectivity. However, synthesizing metal complex sensing layers for nanosensors is generally expensive.

2.4 Carbon-based nanosensor

Among the nanostructured gas sensor, carbon-based materials are proven to be very promising gas sensors due to high surface area, excellent intrinsic electrical properties, and good thermal and chemical stability [20–22]. A typical carbon-based nanostructured (CNT-carbon nanotube) gas sensor is shown in Figure 3. In the twenty-first century, the carbon allotrope, graphene, has been found to be an extraordinary material for many applications due to its excellent electronic, optical, chemical, thermal, and mechanical properties [23]. Graphene is defined as one-atom-thick planar with sp$^2$ hybridized 2D honeycomb crystal lattice of carbon. The stack of few atomic layers of graphene considered as a graphene sheets exhibits the semimetallic electronic behavior with zero bandgap energy state [24]. Graphene is differentiated as pristine graphene (PG), graphene oxide (GO), and reduced graphene oxide (RGO).

In gas sensing application, graphene materials have unique sensing capability based on two-dimensional structural property of PG, GO, and RGO due to superior electron transport phenomena [25]. In 2007, the charge density of graphene was found to increase by the adsorbed gas molecules. Schedin developed the first graphene-based gas sensor [26]. The adsorption of gas molecules leads to the change
of the electrical conductivity, i.e., local carrier concentration of graphene that attributed to the electron acting as donor/acceptor. All the varieties of graphene have different surface functional group and unique electrical properties, which play vital role in the sensing mechanism. In pristine graphene (PG), the adsorption of gas molecules can induce even very few charge carriers, resulting in a notable change in electrical conductivity.

Graphene oxide (GO) is different from pristine graphene due to its physical and chemical properties. GO is considered as promising material for gas sensing application because of highly rich oxygen functional group [27]. Prezioso et al. [28] using GO sensor device studied NO\textsubscript{2} gas sensing performance by varying the gas concentration at different operating temperatures to optimize the sensing efficiency. The oxygen functional group on the surface is mainly attributed to the sensing activity, and also when the device tested in both oxidizing and reducing environment, a typical p-type sensing response is observed. GO-based gas sensors have been used to detect the low concentration of nitrogen dioxide, hydrogen, and other gases also. GO-based sensor device reveals the high and fast sensing performance as compared to the RGO-based device. However, reduced graphene oxide (RGO) is easily synthesized from graphene oxide. By removing oxygen-containing groups and without changing the conjugated structure from GO, reduced graphene oxide (RGO) sheet can be obtained. In gas sensing application, RGO has more advantages than pristine graphene (PG) like inexpensive to prepare, possible to modify structure, fine tuning of structure, etc. [29, 30]. Many reported as available on the use of RGO for detecting gas molecules like NH\textsubscript{3}, NO\textsubscript{2}, H\textsubscript{2}, etc. [31–33]. These sensors are tested in lower gas concentrations, and they exhibit high sensitivity response and reversibility at ambient temperature with low power consumptions. The limitation of RGO in practical application of low selectivity in gas sensor device is the same as the pristine graphene (PG). More detail of literature can be referred in the recent sensor review article based on carbon nanotube and graphene by Mao et al. [21].

3. Techniques used for thin film fabrications

The first gas sensor reported in the literature is based on thin film semiconductor. Since sensitivity, selectivity, and long-term stability are the main parameters for sensor for mass applications, various methods have been used to prepare sensor devices. Developing ultrathin film sensor with enhanced sensitivity at low
concentration is challenging. In the field of gas sensor applications based on semiconductor thin film, the morphology and thickness of film play a crucial role for sensing properties of the materials. Several standard techniques are available for the fabrication of thin film. Thermal evaporation, electron beam evaporation, laser-assisted evaporation and sputtering, molecular beam epitaxy, etc. are well-known physical deposition techniques.

On the other hand, many useful techniques such as hydrothermal, sol-gel, chemical vapor deposition (CVD), spray CVD, microwave, dip coating, spin coating, etc. are used for depositing ultrathin films. The steps of making thin films using the above techniques are either standardized or as per the requirements; some modifications are done to achieve good quality films. Standard methods can be referred from various handbooks of thin film preparation [34–36]. The surface of thin film should be very active for gas sensing. Therefore, each of the techniques has some advantages and limitations. Grain size, film thickness, surface roughness (surface area) porosity, etc. significantly transform the film for effective detection of gas molecules down to ppm or sub-ppm level at room temperature.

In most of the films, surface adsorption-desorption of gases modifies the electrical conductivity of the material. Very recently, using slow evaporation rate of 0.02–0.3 nm/s in thermal evaporation technique, copperphthalocyanine (CuPc) organic semiconductor was deposited with thickness 10–40 nm to fabricate organic thin film transistor for ppm level NH$_3$ detection in room temperature [37]. The structure is shown in Figure 4. Using RF sputtering method, a 30-nm NiO film was deposited over sapphire and subsequently 1-nm platinum film was deposited over it by thermal evaporation for the detection of ammonia efficiently at low concentration at elevated temperature [38]. Several such works with ultrathin film have been reported in the literature. Since the demonstration of graphene-based sensor for detection of individual gas molecule almost a decade ago, several graphene-based sensors have been reported in the literature following newer techniques to improve the performance of the sensors [39, 40].

Generally, CVD, exfoliation, and other methods are used to prepare graphene for sensing. Wu et al. have recently developed graphene-based thin film using microwave plasma-enhanced chemical vapor deposition (MPCVD) followed by deposition of the fragmented 3D structure on substrate to develop nanoporous graphene (Gr) thin film [41]. Both NH$_3$ and CO$_2$ were detected efficiently using this technique. Figure 4.

Figure 4. (a) Topography image of AFM of CuPc films with different thicknesses on PMMA dielectric. (b) Response curves for the four types of devices to NO$_2$ pulses (reproduced with Ref. [37]).
film as conductance channel. Tian et al. have reviewed graphene-based gas sensor material preparation and characteristics [42].

4. Basic properties and gas sensing principle for nanostructured thin film devices

The popular environmental gas sensors operate on the principle of chemisorption. The adsorption and desorption processes of gas molecules on the active surface play a crucial role for sensing. Change in resistance or electrical current under an applied voltage in the presence of sensing gas is considered as the sensing signal response. Therefore, stability of the surface for long-term operation and also for repeatability of performance, the microstructure, and film thickness play a major role.

For instance, in the case of CuPc ultrathin film [37] and SnO$_2$ [43], the variation of microstructures of materials greatly improves the sensing performance for NO$_2$ and formaldehyde (VOC), respectively. These microstructures and performance are shown in Figures 4 and 5.

4.1 Gas sensing principle for sensor device

The metal oxide gas sensor works on chemi-resistance principle. When the gas molecule interacts with metal oxide surface, it acts as either an acceptor or donor. This changes the resistivity or electrical conductivity of thin film. The resistivity of the metal oxide semiconducting thin film depends on the majority carrier in the film and also gas molecule nature, i.e., whether it is oxidized or reduced in the ambient temperature [44]. Surface adsorption sites ensure appropriate interaction of gas molecules with the material. In the case of n-type (electron being majority carrier), the surface is generally get depleted with electrons by the appearance of oxygen ion species (O$^-$, O$_2^-$, etc.), and upon exposure to sensing gas, these species react with gas molecules to revert back electron on the surface, thereby increasing conductivity. The creation of these oxygen species on the surface is material specific and broadly dependent of temperature. In the case of p-type (hole being majority carrier), similar situation arises. The sensing behavior of metal oxide thin film sensor is shown in Figure 6.

Among the various nano gas sensor materials particularly, carbon-based materials like carbon nanotube (CNT), graphene, graphene oxide, and reduced graphene oxide of nanosensors play an imperative role for sensing applications. A two-dimensional sp$^2$ bonded allotropy of carbon called as graphene. A characteristic of high surface area to volume of carbon-based materials leads to a great potential for gas sensor applications. Especially, graphene acts as good device material due to its intrinsic properties. The graphene-based thin film sensor is shown in Figure 7. It has very large surface to volume ratio that can enhance adsorption of gas molecules, and hence response becomes fast and high. The working principle of graphene-based gas sensor depends on the catalytic and electronic properties of the active layers. For example, in the case of pristine graphene layer, it is electronically active but not sensing to detecting gas. In that case, surface modification or functionalization techniques are used to attain both electronic and sensing properties of graphene layer. But, this kind of surface modification technique should enhance the surface activity to adsorb the detecting gas molecules and quickly transfer the generated charges to the electrode.
Furthermore, the electronic properties of graphene changed by metal nanoparticles influence the increase of selectivity and sensitivity in gas sensing characteristics. **Figure 8** shows graphene decorated with metal nanoparticle-based sensor devices with interdigitated electrodes. Graphene with suitable sensitizer can improve the sensing performance and rectify the selectivity issues. Graphene-based functional nanohybrids can also facilitate fabrication of the nanosensor device [46].
The demand of reliable sensors for toxic gases and VOCs is increasing rapidly for the safe life. A lot of progress has been made to produce sensor especially in the form of thin film or nanostructure materials to exploit effectively sensing properties. The challenging parts of the devices are uniform fabrication of nanostructure in terms of thickness, shape, and morphology. The process is expensive also. Sensitivity, effect of temperature, stability of detection, selectivity, response and recovery time, repeatability, and durability are the concern for all these sensors for gas detection. Sensors during operation suffer from multiple limitations which require several optimization procedures meticulously. Commercial production of these ultrathin film or nanostructure sensors in large scale will depend on how all these properties of sensor materials are achieved uniformly. However, on the positive note, because of so much sophistication in technologies and materials engineering it, it will be possible to achieve high-quality and cheap sensor devices to be available in the market very soon.

5. Challenges for nanothin film-based gas sensors

The importance of environmental sensors has been increasing exponentially due to the increase of toxic gas emission and at the same time imposition of several emission norms in the industries and permissible health hazard limits announced by health organizations. Looking at the historical aspects of the sensor development works, the chapter starts with the scope of various gas sensors to make environment risk free. Defining thin film, ultrathin film, and nanomaterials, efforts were made...
to categorize sensors and structures based on materials although there is always
an overlapping research prospect. Various standard methods of preparation were
mentioned. However, every sensor research based on nanotechnology is bring-
ing some improvised method to fabricate sensor structures modifying available
techniques. Sensing mechanisms were elaborated. Since to prepare nanostructure
is tricky and expensive, more efforts should be given to achieve sensor fabrication
viable, sustainable, and useful for mass production with acceptable quality.

Conflict of interest

The authors declare no conflict of interest.

Author details

Nithya Sureshkumar and Atanu Dutta*
Division of Physics, School of Advanced Sciences, Vellore Institute of Technology,
Chennai, India

*Address all correspondence to: atanudutta@vit.ac.in
References


Surface and Coatings Technology. 2005 Aug 1;198(1-3):36-39


of Electronic and Photonic Materials. Springer; 2017 Oct 4

[36] Mattox DM. Handbook of Physical Vapor Deposition (PVD) Processing, 2nd ed. 2010


