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Graphene-Based Junction Devices for Hydrogen Sensors

Sukumar Basu and Surajit Kumar Hazra

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Abstract

Graphene is quite a robust material for sensing hydrogen and other gases at room temperature as well as at elevated temperatures with high efficiency. This chapter deals with different junction devices based on graphene for hydrogen sensing. Graphene has excellent electronic attributes that make it suitable for gas sensor devices. However, till date, the research on graphene-based junction devices is not many. In this chapter, we present different types of graphene junction devices suitable for hydrogen sensing. Hydrogen sensor response of these junctions is analyzed, and the sensing mechanism is presented. The temperature- and atmosphere-dependent inversion of n-type to p-type conductivity in graphene is highlighted for hydrogen sensing. Moreover, the two dimensional nature of graphene makes it very convenient for device miniaturization. This chapter provides relevant information on the growth of graphene, the fabrication of different graphene junction devices, and hydrogen sensor applications. Also, the sensor-related concerns such as cross-sensitivity, signal drift, stability, and interference of humidity during hydrogen sensing are thoroughly discussed in this chapter.

Keywords: Graphene, Junction devices, Hydrogen sensor, Wide temperature range, Selectivity

1. Introduction

The importance of hydrogen sensor both domestically and industrially does not need a fresh introduction. Hydrogen has the prime potential applications as fuel in domestic, nuclear installations, and space vehicles. The huge calorific value and non-polluting by-products of hydrogen combustion are two principal advantages of using hydrogen as a fuel. But the negative aspect is its extremely high inflammability at fairly low concentration (~4% and above) when mixed with air leading to disastrous explosions. So, the use of hydrogen gas for combustion or

for any other purpose invariably requires a monitoring and controlling device to detect the hydrogen leakage and to alleviate the serious explosion danger. There are continuous R & D efforts to develop hydrogen sensors in different dimensions and for use at different temperatures.

Of late, graphene has been shown to be the most suitable material for hydrogen sensor because of its superior mechanical, electrical, and chemical properties. The two dimensional (2D) structure of graphene is most desirable for the development of miniaturized and fast hydrogen sensor devices. Graphene is a good device material owing to its intrinsic properties. The favorable thermal conductivity (~ 5000 W/mK) and very high electrical mobility ($\sim 200,000$ cm²/Vs) are very special attributes for developing excellent electronic devices [1]. Because of very large surface-to-volume ratio graphene is an interesting gas/vapor sensing material that can allow fast and high gas adsorption. The high hydrogen intake ability of graphene and other carbon nanostructures has been reported in the literature [2–4]. It is also reported with experimental evidences that the high hydrogen intake ability of graphene is mainly due to the intercalation phenomenon [5–7]. The basic concept of hydrogen intercalation in graphene is the attachment of hydrogen with the graphene layer at the graphene–substrate interface. For multilayer structures, the intercalation phenomenon also happens between the graphene layers, and hence, large amount of hydrogen interaction is possible [8–10].

The intercalation occurs between graphene and atomic hydrogen. So, the important concern for hydrogen sensor devices based on graphene is the generation of atomic hydrogen. This is due to the important fact that the percolation of molecular hydrogen through graphene is impossible because of the dimensions of hydrogen molecule and graphene network. The C–C lattice parameter is 2.46 Å, and the size (diameter) of hydrogen molecule is 2.89 Å [7]. Hence, hydrogen molecule cannot possibly percolate through the graphene layer. On the other hand, the Bohr radius of hydrogen atom is only 0.5 Å, which will easily allow the hydrogen atom to pass through the graphene layer, and subsequently getting attached with the graphene layer between the substrate and graphene. This attachment will temporarily isolate the graphene layer from the substrate, resulting in the intercalation phenomenon. The attachment of hydrogen atoms with the carbon atoms is via van der Waals forces, and hence, the hydrogen atoms can easily desorb upon the reduction of hydrogen partial pressure at a particular temperature during the recovery of the sensor signal. The generation of atomic hydrogen in graphene-based sensor devices depends on the activity of the graphene surface. For instance, the presence of functional groups can initiate reaction with hydrogen, or the presence of catalytic metal can trap hydrogen and break the molecules into atomic hydrogen. Sometimes, junctions with another semiconductor can also bring interesting sensing attributes.

In this chapter, we shall highlight the graphene-based devices that have potential for developing hydrogen sensors, with appreciably fast response and recovery characteristics at different temperature regimes. Since graphene is a high-temperature material, it can be used for sensing hydrogen and other gases at room temperature as well as at elevated temperature with high efficiency. Again, graphene is a 2D material and so it is convenient to fabricate miniaturized sensor devices for commercial applications. Another unique property of graphene is the reversible inversion of electrical conductivity from p-type to n-type and vice versa with temperature in both oxidizing and reducing atmospheres. The sensing nature can

be inverted with equal efficiency with the variation of temperature and environment. This versatile characteristic is rarely found in other sensing materials leading to the innovation of the new kind of junction devices. Graphene can enable smaller and lighter sensors with endless design possibilities. They are more sensitive, can detect smaller changes in matter, work faster, and eventually less expensive than the traditional sensors. Some graphene-based sensor designs contain a field effect transistor (FET) with a graphene channel. Upon detection of the targeted analyte the current through the transistor changes and sends a signal that can be analyzed to determine several variables.

The potential applications of different forms of graphene (including pristine, B- or N-doped and defective graphene) as gas sensors to detect small gas molecules (CO, NO, NO₂, NH₃, and H₂) have been investigated and confirmed theoretically by using density functional computations. The structural and electronic properties of the graphene–gas molecule adsorption adducts principally depend on the structure of graphene and the molecular gas adsorption configuration. The doped or defective graphene exhibits much stronger attraction than the pristine graphene for the above five gas molecules. While the defective graphene shows the highest adsorption energy for H₂, CO, NO, and NO₂ molecules, the B-doped graphene shows the tightest binding with NH₃. Also, the strong interactions between the adsorbed gas molecules and modified graphene can bring dramatic changes in the electronic properties of graphene. Both theoretical and practical evidences support that the sensitivity of a gas sensor using B-doped graphene is almost two orders of magnitude higher compared to pristine graphene. So, the performance of the graphene-based chemical gas sensors can be largely improved using the appropriately doped or defective graphene [11].

2. Graphene synthesis for device fabrication

Graphene can be synthesized by employing different methods. Exfoliation is an easy method, in which graphene layer is isolated from *highly ordered pyrolytic graphite* (HOPG). The exfoliated graphene layer can be transferred to a substrate for device fabrication. However, the size of the exfoliated layer is not suitable enough to cover the whole substrate wafer for large-scale device production [12].

Single-crystalline silicon carbide wafers can be heated at elevated temperatures to generate the graphene layer [13]. In this case, the silicon atoms escape the wafer leaving the hexagonal carbon network. But the transfer of thermally generated films is a major problem by this method [14].

Chemical vapor deposition (CVD) is a convenient technique to grow graphene films for sensor applications. For CVD growth, the substrates are coated with a metal (say copper), which acts as the catalytic layer [15]. Apart from copper, other metals such as nickel, silver, gold, platinum, and cobalt can be used for graphene growth [16]. Due to the high solubility of carbon in copper, it is often preferred for graphene growth by CVD.

For CVD growth of graphene films, normally thermally oxidized silicon substrate is the obvious choice [17]. Plasma-Enhanced Chemical Vapor Deposition (PECVD) grown SiO₂/Si

substrates can also be used. However, the surface quality of thermally oxidized silicon substrates is relatively better in comparison with PECVD substrates. A thin film of copper is deposited on the substrate by e-beam or thermal evaporation technique. The copper layer mainly acts as the catalytic layer which initiates the growth. The precursor is normally a mixture of a carbon containing gas (like CH_4), a reducing gas (like H_2), and an inert/neutral gas (like Ar/N_2) [18]. The important parameters of growth are deposition time, flow ratio of the gases, and the temperature of the substrate. All these parameters need to be optimized to have good device quality graphene films. It is reported that the CH_4 molecules decompose on the catalytic copper surface in the temperature range $900\text{--}1000^\circ\text{C}$ [19]. This temperature range can be modulated by suitable choice of the catalytic metal. The flow ratio is regulated very precisely with the help of mass flow controllers, owing to the important fact that if too much carbon containing gases are allowed to flow over the heated substrates, secondary nucleation can initiate haphazard growth, leading to poor film quality, which is not desirable for good device performance. Sometimes, oxygen groups need to be attached to the hexagonal carbon network for some specific applications. In that case, very small amount of oxygen can be incorporated into the flow stream during growth. The number of deposited graphene layers depends on the time of deposition and the activity of the catalytic layer. The thickness of the catalytic layer is another important parameter of growth. This is due to the fact that at elevated temperatures during growth, the fresh copper atoms from underneath diffuses through the bulk copper layer up to the surface for fresh reactions. Hence, optimization of the catalyst layer thickness is also an important priority for graphene growth. Owing to the fact that pristine graphene is insensitive to hydrogen and other gases functionalization of the grown graphene layer is often necessary for sensor application. Hence, oxygen functionalized graphene, for example, graphene oxide (GO) and reduced graphene oxide (rGO) are equally important for developing sensor devices. Functionalization with other groups can impart special device properties. Such functionalized layers are especially useful to develop resistive gas sensors. Apart from oxygen and other organic groups, the catalytic metals (Pd, Pt, etc.) are also useful for metal-decorated graphene gas sensors. The catalytic metal nanoparticles (NPs) can simply be dispersed on graphene surface to improve its gas sensing property. By this process, the response parameters such as sensitivity, selectivity, and time of response/recovery can be modulated. Another technique to improve the gas sensing activity of graphene is to disperse graphene layers (obtained by either exfoliation or CVD) in a polymer base [20, 21]. Such mixed composition can give special material properties suitable for gas sensing and other applications.

3. Sensor device characteristics

The characteristics of the graphene-based sensor device depend on both electronic and catalytic properties of the active layer (s). For instance, if the layer is electronically active but insensitive to detecting gases (like pristine graphene), it is not suitable as sensor material. In that case, the sensitivity is to be developed by functionalization or surface modification. Sometimes, both electronic and sensing properties can be achieved by simple surface modification techniques. In fact, the generated charge carriers during sensing need to flow through the device circuit

in order to show appreciable sensor response. But just after generation, if the carriers are annihilated or trapped by defects the response, even though happening, will not be observed. Surface modification technique takes care of the defect treatment and restores good electronic attributes, in many cases. Such surface modified layers can be used to develop good resistive sensors, where the important factor is how effective is the surface in capturing the analyte gas molecules, and how efficient the material is in transferring the generated charge to the electrode. The time of response gets prolonged if the solid–gas interaction is slow. However, the recovery of the sensor solely depends on how good is the material electronically. Whether the charge carrier annihilation is minimum or negligible the recovery characteristics are likely to be good.

Apart from the catalytic properties of the sensing material the I–V characteristics and junction bias are important for the junction devices. Generally, the forward barrier is low compared to the reverse one. However, for the defective active sensing layers, the reverse characteristic of the junction is far from the nature of the ideal diode. Therefore, the sensor performance may differ for the junction devices with forward and reverse biased cases, and hence needs optimization. The junction ideality factor is also an important parameter for hydrogen sensor applications, and it is necessary to improve the ideality factor to obtain the good device characteristics and superior gas sensor characteristics, respectively.

The operational characteristic of a junction device with respect to the junction barrier needs a close attention. The charge carriers generated due to solid–gas interaction reach the junction interface and modulate the junction capacitance. The magnitude of this capacitance is affected by the variation of the junction bias, which regulates the device barrier both in the forward and in the reverse bias operations. Hence, both forward and reverse bias studies are necessary for finding the optimum device characteristics.

Optical devices can operate at room temperature or below, which is good for hydrogen safety. Reflectance, transmittance, absorption, refractive index, etc. are the parameters that can be monitored in an optical sensor device. Palladium-based optical hydrogen sensors adsorb hydrogen and forms non-stoichiometric PdH_x , which changes the optical properties, mentioned above. Upon hydrogen desorption, the original properties of Pd are restored.

Surface acoustic wave (SAW) devices are also popular for gas sensors and are used for hydrogen detection. A transformation of acoustic signal to electrical and vice versa is done in SAW devices with the help of the piezoelectric materials. So, any change in the properties of these piezoelectric materials will modulate the acoustic signal that travels from the input to the output end. An important parameter that is considered for quantification is mass. So, if a gas sensitive material is coated on a piezoelectric substrate, the mass of this material changes upon gas adsorption and affects the traversing of the acoustic signal from the input to the output end. Hence, the synchronous frequency of the signal, which is inserted at the input end, is liable to change upon gas adsorption.

In all the above devices, the material platform is most important, and the device properties are majorly determined by the properties of the sensing material. For sensor devices, the contamination from moisture and other pollutants can alter the device characteristics with prolonged

usage. Such deterioration can be prevented by proper device packaging and temperature treatment of the sensing platform in a cyclic manner (low to high and vice versa) to eliminate volatile contaminants.

4. Hydrogen response of different types of graphene-based sensor devices

The traditional semiconductor devices which are used to fabricate the electronic gadgets can be effectively utilized to design and develop the graphene chemical sensors. Different physical and chemical characteristics of the sensing materials and/or the junctions are modified in presence of trace amounts of gases or chemicals. The sensor response is registered as the change of electrical, optical, and chemical properties. The following graphene-based devices are generally used for sensing hydrogen and other trace amount of chemicals, gases, and vapors.

4.1. Resistive devices

The surface sensitivity of materials is normally harnessed by fabricating a simple resistive-type sensor with interdigitated electrodes or with two parallel electrodes (**Figure 1**). Interdigitated electrodes are preferred when the material conductivity is not uniform throughout the exposed surface.

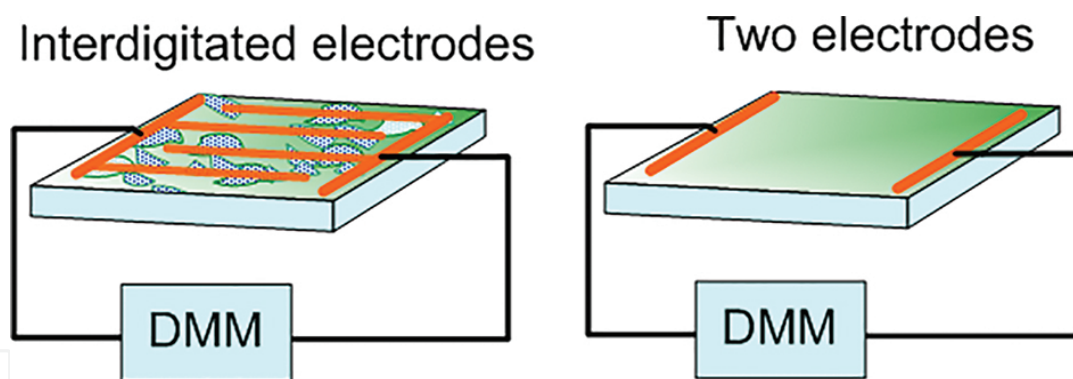


Figure 1. Resistive devices with different electrode configurations.

In case of graphene, pure pristine graphene surface may not be very lucrative to develop simple resistive sensors. However, other forms such as reduced rGO, or surface functionalized graphene, or catalytic NP dispersed on graphene, etc. are useful to develop resistive sensor devices. Zhou et al. [22] reported room temperature operation of resistive sensor devices based on rGO. The flow rates of the test gases influence the adsorption of gases on the active surface, and hence the sensitivity of the resistive device. Also, the rGO thickness is an important parameter for obtaining optimum response characteristics.

Pure platinum (Pt) and bimetallic platinum–iron (Pt₃Fe) NP were used to decorate nitrogen-doped graphene to develop resistive hydrogen sensors [23]. Polyol technique was used to synthesize the NPs and subsequent decoration. The sensors were responsive to 4 vol%

hydrogen and could be used for room temperature sensing. Pure Pt decoration yielded 47% response, while bimetallic Pt₃Fe yielded 35% response in 4% H₂ gas ambient. Pt NP decoration on rGO was also done to develop hydrogen sensors by Ghosh et al. [24]. The response of the devices in H₂/air ambient varied from 19% (200 ppm) to 57% (5000 ppm), and the response time of the devices in air was ~65 s [24]. Similar hydrogen sensor studies with bimetallic-graphene composites are reported [25]. The electrical resistance was measured in 2% H₂/Ar ambient in the temperature range -100 to 100°C. The reported response at room temperature is 4.3%. Optimum response was obtained at 40°C with the response time of 2 s.

Graphene flakes of nanoscale dimension- and spherical-shaped nanoporous palladium particles were combined to make the sensitive platform to fabricate resistive sensors [26]. The sensors were sensitive to hydrogen (10,000–1 ppm) at room temperature. The resistive devices showed repeatable response, recovery and a very high hydrogen selectivity during operation near room temperature. The appreciably good selective response to hydrogen is due to the high affinity of palladium to hydrogen relative to other gases. Also, the relatively lower activation energy for hydrogen adsorption is due to the porous nature of nanosize palladium. As a result, the resistive devices can operate even at room temperature.

Graphene nanoribbons (GNRs) have recently shown the novel physical, electronic, and spin transport properties for the wide range of device applications. Graphene nanoribbon in combination with Pd NPs can also be used for hydrogen sensing [27]. The graphene nanoribbon was fabricated by laser-assisted lithography. The nanoribbon of 200 nm width was patterned at a separation of 1 μm. In an atmosphere of 1000 ppm hydrogen in nitrogen, 90% response was obtained with a response time of 60 s. Almost 80% recovery could be achieved in a time span of 90 s. The devices were also sensitive to other gases. The incorporation of NPs in GNR-based gas sensors can be a novel approach to develop the high-performance gas sensors.

An interesting work on Pd-graphene resistive hydrogen sensor operating with and without bending strain was reported by Yi et al. [28]. A graphene mesh was developed by CVD technique using flexible PET as the substrate. The variation of the resistance of the simple Pd-graphene and the Pd-graphene mesh with bending/unbending cycle was investigated. It was revealed that the simple Pd-graphene showed relatively higher resistance change during bending in air compared to Pd-graphene mesh. The Pd-graphene mesh sensors are more stable to stress for the real field installations with a curvature. At room temperature, the hydrogen response of the Pd-graphene mesh sensor was 1.25 times higher than the simple Pd-graphene in the concentration range 2–15 ppm. Probably, the edges of the graphene mesh provided an additional surface for enhanced hydrogen adsorption and response for hydrogen. The use of flexible substrates was also reported by Chung et al. [29].

4.2. Catalytic dot contact device

The important concern for sensor devices is to attain good response parameters. This can be achieved by reducing the geometrical device area significantly. The geometrical contact area of the catalytic dot contact devices can be made very small. Both planar and vertical configurations (**Figure 2**) are used in this case. The vertical devices are sometimes advantageous

because the total vertical transport path of the generated charge carriers is short, which ensures minimum carrier loss due to annihilation and trapping. For transferable graphene films (like those obtained by exfoliation), both planar and vertical devices can be conveniently fabricated. However, for graphene films obtained by CVD on SiO_2/Si substrates (with undoped silicon), the planar device fabrication is more suitable because the insulating SiO_2 is the hindrance for vertical device fabrication. However, if the silicon wafer is highly doped and the barrier SiO_2 layer is very thin, the vertical configurations can be possible to fabricate a catalytic dot contact device for hydrogen sensing.

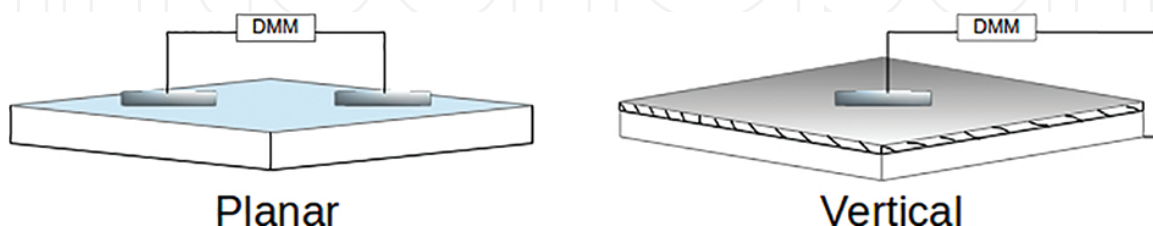


Figure 2. Planar and vertical device configurations.

The reduction in the geometrical area makes the sensor device saturate quickly during response and recover fast due to less adsorption. Hence, the response parameters such as time of response and time of recovery are faster, the essential criteria of an efficient gas sensor. However, the magnitude of % response is relatively less but it is not a big issue in today's sensor research due to advanced electronic circuitry that can amplify signal electronically to get higher electrical output. If the sensing platform is defective in nature, the number of active sites for gas adsorption is higher compared to the defect free matrices. The graphene film grown by CVD is usually defective but it is suitable for gas sensor applications [18, 19]. As reported by Dutta et al. [19], multilayer graphene films on SiO_2/Si substrates showed good response characteristics for hydrogen, with fast response (~ 12 s). The defective nature of the films was estimated from Raman studies. The nonuniformity of the films was corroborated by Field Emission Scanning Electron Microscope (FESEM) and Atomic-Force Microscopy (AFM) studies. So, considering the defective nature and the uneven surface topography of the CVD grown films, it can be inferred that any catalytic contact on the surface of CVD grown graphene should have large number of active sites for gas adsorption leading to high gas sensitivity. Dutta et al. [19] fabricated Pd/graphene/Pd planar devices using the graphene samples, grown by CVD for 15 min at 1000°C , and obtained good hydrogen sensitivity in the temperature range 110 – 150°C . The planar device was found to be insensitive to another reducing gas, methane, possibly due to insufficient thermal activation energy to dissociate the large methane molecule. The interesting observation reported by Dutta et al. [19] was the change in the surface morphology after hydrogen exposure. The reorientation of the graphene surface after exposure to hydrogen gas was probably due to the hydrogen passivation of the surface defects. In another study by the same research group using planar Pd/graphene/Pd junctions with graphene grown by CVD for 8 min at 1000°C , hydrogen was detected from room temperature to 150°C [30]. The junctions showed a change in the conductivity from n- to p-type at around 100°C and above, eventually due to hydrogen intercalation that has already been discussed in

the introduction part. If current increases upon exposure to hydrogen, it is referred to as n-type sensitivity due to n-type conductivity of the device matrix. And it is p-type response if the current decreases in the presence of hydrogen. At 150°C, the p-type response was reported to be very fast (1–2 s) for the same junction devices, which were very stable in the temperature range 25–150°C. The above discussion supports in favor of using defective graphene thin films as the catalytic contact devices for efficient hydrogen sensing.

Reports are available on the vertical devices with Pt contacts on the surface of graphene grown on SiC substrates [31]. Typical multilayer vertical device geometry is shown in **Figure 3**. Normally, the bottom metal contacts ensure good ohmic metallization, while the top metallic contact is catalytic in nature to accelerate the sensor performance. As reported by Shafiei et al., titanium and platinum multilayer bottom contacts, that is, metal-1 and metal-2 shown in **Figure 3** were used in this study. The graphene films of thickness ~10 nm or less were obtained by the reduction of spray-coated graphitic oxide film. The catalytic metal (Pt) dot (metal-3 in **Figure 3**) accelerated the dissociation of hydrogen molecules during sensing. The devices were operated at 100°C, in an ambient of 1% hydrogen mixed with air. The response was recorded in terms of voltage shift in the dynamic response patterns. At 100°C and in 1% H₂ in air, a 100 mV voltage shift was reported under a current bias of 1 mA.

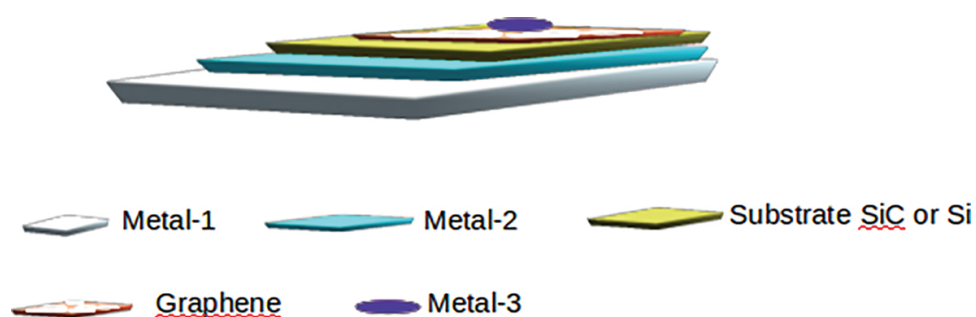


Figure 3. A simple multilayer vertical geometry for graphene-based sensor.

An important condition for both planar and vertical dot contact devices is that the contacts must be ohmic with low contact resistance. Different metal contacts to graphene layers have been studied and reported [32]. The metals selected and reported in this study are Al, Ti, Ni, Cu, Pt, and Pd. The bilayer of either of these metals (10 nm) and gold (50 nm) was deposited on graphene, and the contact resistance was measured. The contact resistance was almost similar in all the cases, and it was improved by different pretreatment. For instance, oxygen plasma treatment of the graphene surface prior to metal deposition gave lower contact resistance when compared with the untreated surfaces or post-processed contacts. The masking is necessary to ensure selected area plasma treatment; otherwise, the graphene surface properties are likely to change. However, Robinson et al. [32] did not report any surface degradation. Post-plasma treatments like thermal annealing at the temperature >450°C, showed a further decrease in contact resistance. A very low value of contact resistance ($4.5 \times 10^{-8} \Omega \text{ cm}^2$) was obtained when annealed in the temperature range 450–475°C for 15 min. There is a chance of reduction of the surface carrier concentration upon annealing; however, the

carrier mobility is preserved or further improved. Due to removal of volatile impurities from the graphene surface during annealing, the doping level is eventually decreased, thereby reducing the surface concentrations and increasing the purity. So the mobility remains intact or is improved to certain extent. Sometimes, ohmic contacts are used in the vertical devices for hydrogen sensing by displaying the change in the contact resistance. Zhang et al. [33] reported on the transfer of graphene nanoribbon (GNR) onto doped Si substrates with a native oxide layer and decorated with Pd NPs for hydrogen sensor applications. Carbon nanotube (CNTs) unzipped by a simple chemical reduction process was the source of graphene. Also, the synthesis of metal NPs and their incorporation in the unzipped CNTs were done during the chemical reduction. In the vertical structure, silver contact was made on top of the graphene surface and indium at the bottom of silicon substrate. The device sensitivity for 100 ppm H₂ in air was appreciably high to 94% at room temperature. In fact, this vertical structure showed better hydrogen response than the bare and simple resistive Pd-graphene nanoribbon in the identical condition.

A Flow chart for the vertical device fabrication is shown in **Figure 4** below.

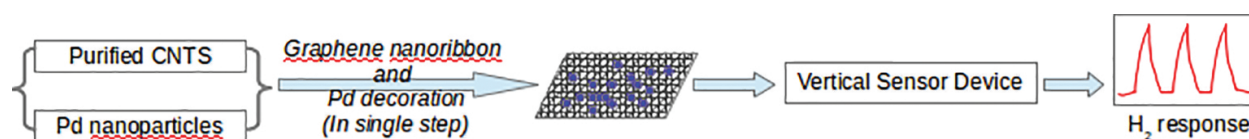


Figure 4. A schematic process flow for the fabrication of Pd-decorated graphene hydrogen sensors.

The improvement in response can be attributed to the concept of enhanced junction sensitivity relative to the simple devices. The vertical junction, (Pd-GNR)/(thin SiO₂ barrier)/(doped p-Si), acts as a simple p-n junction device with the Pd-GNR acting as the n-layer. The junction sensitivity in terms of barrier modulation has been discussed in Section 3 of this chapter. The planar Pd-GNR acts as a simple resistive device, whose surface interactions are similar to the vertical device, but the device speed is low and has relatively higher chances of carrier annihilation due to the planar configuration (also discussed in the beginning of this section). A similar vertical catalytic dot contact Schottky device with rGO (Pd-rGO-SiO₂-Si) was reported by Du et al. [34] with high sensitivity for hydrogen at room temperature.

4.3. Heterojunction device

Junction devices are fabricated with a goal to harness the high-charge carrier mobility of graphene (first layer) in coordination with other attributes of the second layer (either conventional semiconductor like silicon or oxides). Graphene-metal oxide heterostructures are suitable for versatile applications [18, 35–37]. The main advantage of graphene-based heterojunction is the tunable interface barrier, which makes these devices suitable for different applications including chemical sensing as the major area [38]. A basic schematic of a heterojunction device is shown in **Figure 5a**.

Sometimes, both the pristine graphene layer and the conventional semiconductor of the heterojunction are insensitive to a test gas. In that case, the catalytic metals are to be used to

initiate the gas sensor performance. Surface functionalization of the graphene layer can also be an alternative step to improve the sensitivity of the graphene based heterojunction. Normally, graphene-based heterojunction with other gas sensitive materials (like metal oxides, etc.) is likely to show improved sensor performance due to good electronic transport properties of graphene and excellent surface property of the oxide (in terms of gas adsorption/desorption), and scope of interface barrier modulation. The heterojunction can be fabricated by either transferring the graphene layers onto an oxide substrate or CVD grown graphene can be used as a substrate to deposit the oxide film.

A graphene/silicon heterojunction can be biased with pre-optimized bias voltage (either in forward or in reverse bias mode) to perform the sensor studies in a desired gas ambient. Uddin et al. [39] performed hydrogen sensor studies in reverse bias mode with palladium- and platinum-functionalized graphene/silicon heterojunction. The sensitivity of the junction is dependent on the junction bias, which ensures high band bending in the presence of test gas. The graphene/Si heterojunction showed high sensitivity to sub-ppm hydrogen. Liu et al. [40] used CVD grown graphene as substrates to grow ZnO nanowires in order to develop ZnO/graphene nanojunction. These junctions showed hydrogen sensitivity at relatively lower temperatures (<100°C).

A typical hydrogen response behavior of the p-TiO₂/n-graphene heterojunction at different hydrogen gas concentrations and temperatures has been reported by Dutta et al. [18]. The hydrogen response of the p-TiO₂/n-graphene heterojunction in the temperature range 75–150°C, revealed efficient, selective, and stable performance at 100°C. The selective performance was checked by using another reducing gas like methane. Also, an interesting study regarding the device recovery was reported in this work. As shown in **Figure 5b**, the p-TiO₂/n-graphene heterojunction could easily recover back to its baseline value after cutting off H₂ in air and the recovery was incomplete when H₂ was cut off in N₂ ambient. However, the response was similar in both the cases. Hence, it is evident that oxygen plays an important role in the signal recovery process by releasing hydrogen atoms via water formation as shown in Eq. (1) below [18]:

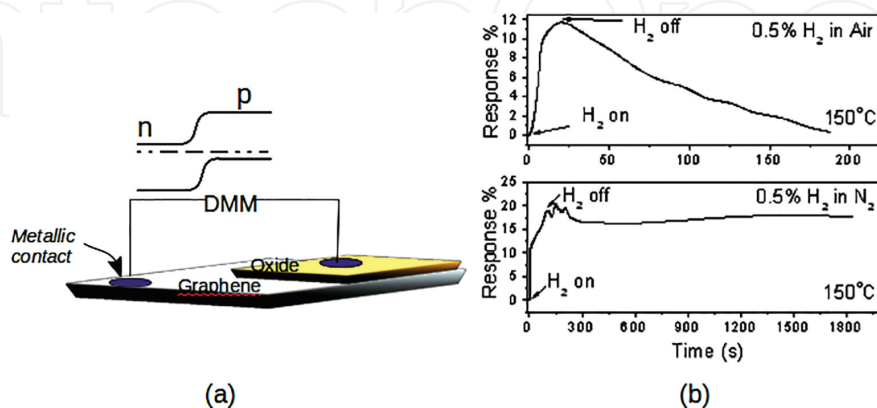
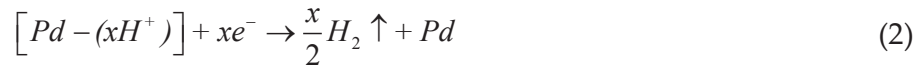
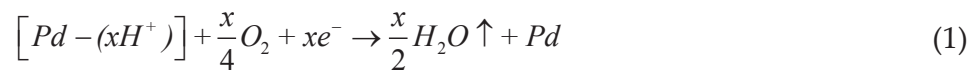


Figure 5. (a) Schematic of a heterojunction device. (b) Comparative sensor recovery in air and nitrogen ambient [18].



Sometimes, the heterojunction configuration also helps in improving the recovery characteristics. While pristine rGO (before and after annealing and with/without UV light exposure) as reported by Kang et al. [41] showed relatively poor recovery characteristics to NO₂, the nano-heterojunction sensor based on rGO and functionalized with tin dioxide nanocluster showed good recovery upon annealing and exposure to UV light. In fact for an optimized tin dioxide functionalization time of 55 min, the nano-heterojunction showed 100% recovery. The good recovery could be attributed to the modulation of the heterobarrier at the nanocontacts between tin dioxide and graphene under UV illumination, which enhanced the rate of surface reactions.

Similar type of nanoscale composite junctions was fabricated with Pd–WO₃ nanostructures and partially rGO by employing a hydrothermal process [42]. This composite material was sensitive to a wide concentration range of hydrogen (20–10,000 ppm) in the temperature range 25–250°C. Simply adding GO to Pd–WO₃ nanostructure showed nearly half the response shown by the nano-heterocomposite between Pd–WO₃ and partially rGO. This could be attributed to the difference in surface area and unsaturated oxygen functional groups between the two, which modulated the surface adsorption. Pd and Pt NPs are sometimes used to decorate heterostructures. As reported by Esfandiar et al. [43], TiO₂/rGO was decorated by Pd and Pt NPs. The reported hydrogen sensitivity of such decorated heterostructures was 92% in 500 ppm hydrogen in air, and the device response time was <20 s at 180°C.

Another type of heterostructures is graphene/Si-nanowire (Si-NW) array for molecular sensing. Such heterostructures are fabricated by using single-layer graphene vertically contacted with high-density Si NWs. Silicon nanowires produced by metal-assisted chemical etching of Si wafer are vertically aligned on CVD grown graphene. Si NWs stand on Si wafer detached from each other under graphene. The uniform Schottky-type junction between Si NWs and graphene thus produced act as the molecular sensors and respond very sensitively to hydrogen gas molecules in air with 1280% resistance change with 0.15 s response/recovery times, the highest performance so far reported. The surface-transfer doping mechanism was suggested based on the results together with the sensor response in vacuum [44].

4.4. Optical device

The response of optical sensors is normally monitored in terms of the parameters such as reflectance, absorbance, refractive index, and photoluminescence [45]. The configuration of a typical optical sensor assembly is shown in **Figure 6**.

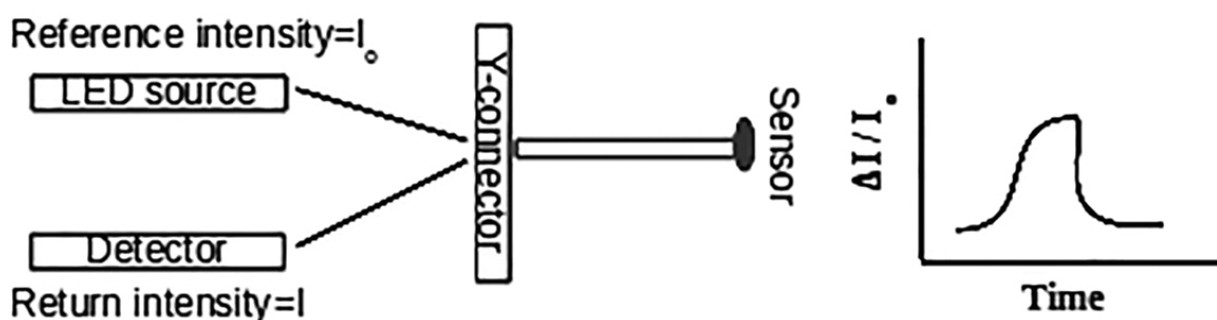


Figure 6. Optical fiber sensor assembly.

The increasing concern of safety demands the room temperature operation of non-electrical gas sensor devices. Hence, the use of optical gas sensors is important. Graphene can be used to develop optical gas sensors for the detection of hydrogen and other gases such as CH_4 , NH_3 [46, 47]. For the development of optical gas sensors, graphene has the preference. The chemical stability, affinity to inorganic and organic molecules, scope of surface functionalization and synthesis of composites with catalytic metals and/or other materials make graphene a suitable choice in the field of optical gas sensors [48].

The important step for the development of optical sensors is the transfer of the films from opaque substrates or from substrates with different optical properties. The exfoliated graphene films can be transferred onto any substrate as per the requirement, but for the CVD grown graphene films, the transfer process is complex. Moreover, the substrates must be able to withstand high temperatures because CVD is generally a high-temperature deposition process. Only low-temperature CVD (using good catalytic metals to initiate graphene deposition) is preferred. Lee and coworkers [49] reported on the deposition of graphene films on glass substrates at 450°C using nickel catalytic layer. Although Lee et al. used such low-temperature grown CVD films for humidity sensing, it can also be suitable for hydrogen and other gas sensing. The possibility of surface functionalization can improve the sensing performance. Furthermore, CVD grown films adhere well to the substrates in addition to its stable nature. Quartz substrates can be used instead of glass, if the optical transmission properties of the substrates are to be modulated for gas sensing. So, graphene can also be an appropriate material for the development of optical gas sensor devices.

4.5. Surface acoustic wave (SAW) device

The basic ideas regarding the operation of SAW devices have been discussed in the earlier section of this chapter. SAW is a well-known sensor device, and many sensor studies have been reported. The main concern here is the growth or transfer of graphene films on a piezoelectric substrate. The rest of device fabrication steps, like patterning of electrodes, are simple. SAW resonating platforms based on LiTaO_3 have been used for different gas sensing purposes [50]. A typical SAW platform is shown in Figure 7 below:

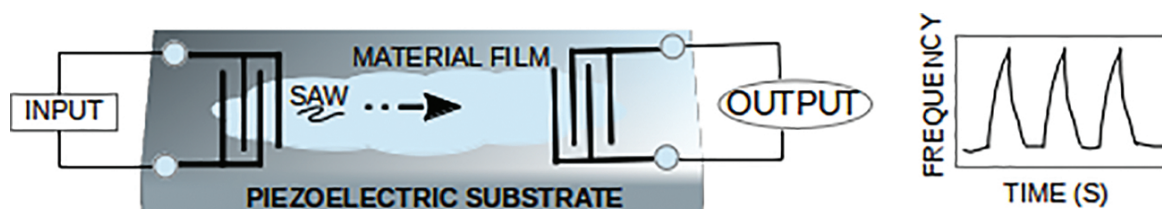


Figure 7. Surface acoustic wave (SAW) device.

The use of graphene-based LiTaO_3 SAW device has been reported for hydrogen sensing [51]. The graphene nanosheets were deposited on the LiTaO_3 substrate and exposed to hydrogen (0.06–1.0%) in air at room temperature. A typical frequency vs time response pattern was obtained upon hydrogen exposure, from which the response and recovery times were calculated. While the response time decreased with increase in gas concentration, the recovery time increased with increase in gas concentration. Probably, room temperature is not sufficiently enough to ensure complete desorption from the high adsorbing graphene surfaces and therefore, the recovery time is prolonged. Similar devices like graphene-based Rayleigh SAW Resonators fabricated on quartz were used for sensing oxidizing gas like NO_2 . The response was good, and the high sensitivity to NO_2 gas was attributed to the defects in the material responsible for the increased gas adsorption [52]. There are also other reports on the use of graphene-based SAW devices for sensing gases like dimethyl-methylphosphonate (DMMP) and dipropylene glycol monomethyl ether (DPGME) are available [53].

4.6. Prospective graphene-based devices

Two graphene-based prospective devices for hydrogen sensing.

4.6.1. Graphene p–n homojunction

Since 2D graphene can be doped n- or p-type like other semiconductors the graphene p/n homojunction can in principle be designed and fabricated using the traditional semiconductor processing technology. Although quite a few reports on the doping of graphene are available in the literature [54, 55], reports on the use of graphene p/n homojunction as hydrogen sensor is not yet available. The main technical problem during the formation of such junction is eventually the extremely thin dimension of the graphene geometry. Therefore, the technology must be very advanced and sophisticated to realize a successful and sustainable graphene p–n junction. Once succeeded, the graphene p–n homojunction can develop the most efficient hydrogen sensors with miniaturized dimension.

4.6.2. Metal-decorated 2D graphene/ MoS_2 flexible wearable gas sensors

The investigation on the gas-sensing properties of a metal-decorated device comprising two-dimensional (2D) flakes of molybdenum disulfide (MoS_2) and graphene electrodes has been reported. This hybrid structure was used to sense ~ 1 ppm NO_2 gas and ~ 10 ppm NH_3 . Such metal-decorated sensors operate with the mechanism of chemical as well as electronic

sensitization. The metal NPs could harness the electronic properties of the 2D graphene/MoS₂ device and enhance the sensitivity for a specific gas molecule.

This work cited an example of NH₃ sensing by graphene/MoS₂ using palladium NPs via accumulation of hole carriers and NO₂ detection using aluminum NPs through depletion of hole carriers. The synergistic combination of metal NPs and the 2D hybrid layers of both graphene and MoS₂ could be utilized for application of this sensor structure as a flexible gas sensor. It was also demonstrated that this hybrid sensor structure did not show any sign of degradation in sensing before/after 5000 times bending cycles. So, this highly sensitive and durable gas sensor could be used as the wearable electronic sensing device. It was also demonstrated that the metal-decorated 2D graphene/MoS₂ hybrid structure could be effectively used as a selective gas sensor. So, the hybridization of metal NPs and 2D materials could develop a highly sensitive, selective, reliable, and flexible gas sensor by appropriate selection of the metal NP for decoration [56]. The same device configuration could be strategically employed to develop a selective hydrogen sensor.

5. Device concerns of graphene-based gas sensors

5.1. Signal drift and device calibration

An important issue with gas sensor devices is the signal drift with time, and it is a matter of concern for the reliable operation of the sensors. The baseline parameter (either resistance or current) can vary with time, and this is not good for device compatibility with the control electronic circuit. There is also high chance of generating a false alarm. Such drifting can solely be attributed to the material interaction with the atmosphere. Normally, sensing surfaces are very active, and hence can have constant adsorptive/desorptive interaction with the operating atmosphere, which is normally oxidative air ambient (with some humidity concentration). And if the sensing material is defective, which is sometimes an added advantage for gas sensors, such interactions are pronounced. This can lead to change in the baseline resistance with time. Of course, a saturation of the drift is likely with time. However, the process is very slow, and hence, the change is sometimes unpredictable. Moreover, the ambient temperature, if it varies, can change the adsorption/desorption eventually. As a result, the device needs proper calibration both to counter the drift and to have operation in the linear regime of the device characteristics. The calibration is reported for hydrogen sensors [57]. In reality for any device, the linear operational regime is found by plotting the measured parameter (either resistance or current or voltage) with gas concentration. If the plot is throughout linear, the device will have excellent operation at all gas concentrations. However, if the plot is nonlinear, the device needs to be operated in the concentration range where it has linear characteristics.

5.2. Humidity

Humidity is an important concern, and the interference of humidity during sensing other gases is very crucial for all the chemical sensor devices including the graphene sensors. The interference of moisture in the operation of graphene-based sensor devices can be realized and

explained in the following manner. The water molecules coming in contact with the graphene surface can interact in two different ways at two different regions of the sensor surface. First, the exposed pure graphene surface (devoid of any catalytic material) attracts polar water molecules and makes hydrogen bonds (one or more hydrogen bonds). During sensing such graphene-adsorbed water complexes transfer very little charge to the active region of the surface, that is, the junction. As an example, the magnitude of charge transfer can be realized from the reported data, that for single walled CNTs (with tube-water separation of 2.69 Å), the charge transfer is of the order of $0.035e$, where “ e ” is the electronic charge [58]. So, the device sensitivity might not be influenced much due to this interaction. However, if the charge exchange is of higher magnitude, the device sensitivity may increase and this is possible if the surface is modified with the functional groups. And for most of the resistive sensors, pristine graphene needs to be modified in some way or other.

The second type of interaction with moisture can happen on the portion of the surface where catalytic materials (like palladium, etc.) are present. On the catalytic surface, water can ionize into H^+ and OH^- and H^+ is likely to be preferentially adsorbed due to the high affinity of catalytic materials (like palladium) to hydrogen. Eventually, the adsorbed H^+ species can increase the concentration of hydrogen at the interface. On the other hand, if the operating temperature is not very high, the OH^- species can occupy/block some of the active sites of the catalytic surface, and the device sensitivity is likely to be affected. Also the sites blocked by OH^- species can prevent further adsorption of the incoming H_2 molecules followed by its dissociation and release of electrons. As a result, the device sensitivity can be affected. So, the presence of moisture can initiate either or both of the above two mechanisms and influence the response characteristics.

An important aspect is the operating temperature during sensor measurements. If the temperature is high ($\geq 100^\circ C$), the moisture molecules will easily desorb, while at low temperatures, the interference is likely to be predominant. Therefore, considering all the factors discussed above, the relevant studies are necessary by varying the relative humidity from low ($\sim 30\%$) to high ($\sim 90\%$) to evaluate the moisture interference at the optimum temperature of sensing, for developing a reliable sensor in the commercial scale.

5.3. Stability and selectivity

The reliability and the robustness of the graphene-based gas sensors can be established from the stability studies. The devices are kept under a constant bias for a very long period either in the ambient of a mixture of test gas in air or in simply aerial atmosphere, and the magnitude of the signal (either resistance or current or voltage) is monitored with time. This study can be made continuously for a number of days, and the cumulative data are analyzed. Normally, the stable signal value recorded in the presence of the test gas for a period of one week or so can ensure the stability criteria of an activated sensor. Of course, the background signal without the test gas needs to be checked and calibrated from time to time. The stability study can also be conducted in a discontinuous manner by switching off the sensor device after each day operation and reactivating (by setting in the proper temperature and bias) the next day. Such

studies are necessary for the commercial deployment of a reliable sensor device. Dutta and coworkers [18, 19] have reported such studies for graphene-based hydrogen sensors (**Figure 8**).

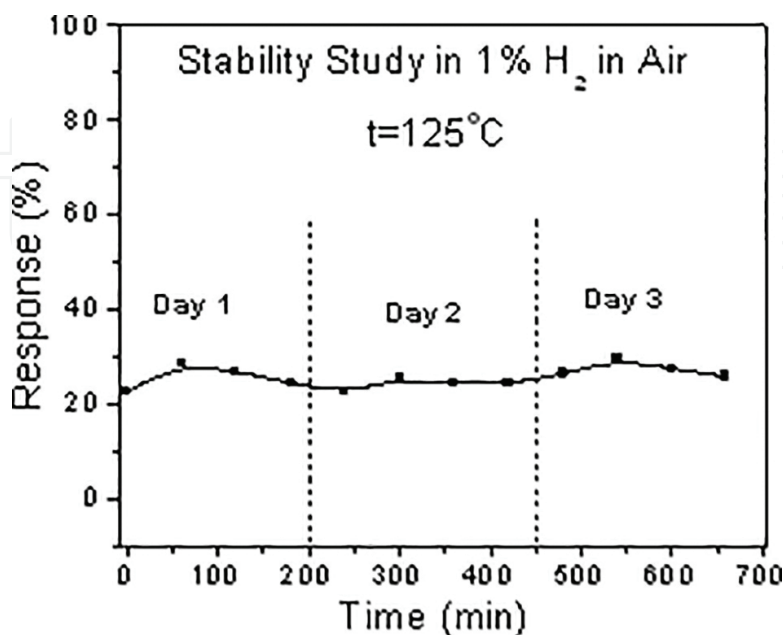


Figure 8. A typical stability study with graphene-based sensor [18].

The selectivity is a pertinent sensor parameter and a matter of concern for gas sensor devices. Almost all the renowned laboratories of the world working on the gas sensor devices consider the selectivity problem a major hurdle against the development of a complete gas sensor. Various methodologies are tried to sort out the problem of cross-sensitivity. Like the well-established oxide-based gas sensors graphene-based gas sensors also face cross-sensitivity problem.

Normally, the problem of cross-sensitivity is tackled by the following sensor operation factors:

1. Operating temperature
2. Gas concentration
3. Material characteristics and catalytic activity.

The operating temperature is a convenient way to eliminate the cross-sensitivity of other gases. For instance, in the case of sensing hydrogen in a mixture with another reducing gas like methane, the lighter gas like hydrogen can be detected at relatively lower temperature compared with methane, a heavier gas, because the heavier molecules require relatively higher activation energy for dissociation and sensing. Hence, some devices can be selective to hydrogen at relatively lower temperature. In the studies performed by Dutta et al. [18, 19, 30] with Pd/graphene and graphene-based heterojunction (**Figure 9**) for hydrogen sensing, it was shown that the devices were sensitive to H_2 but insensitive to CH_4 in the temperature range 75–150°C. This establishes the fact that hydrogen sensing operating temperature does not provide the required activation energy to dissociate heavy molecules like CH_4 .

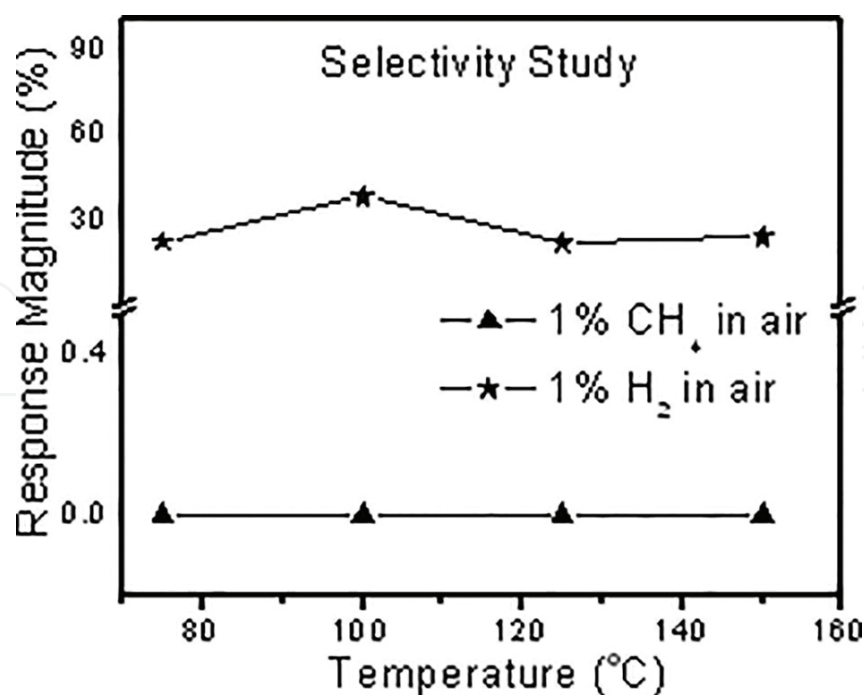


Figure 9. The selective response of TiO₂/graphene heterojunction sensor toward hydrogen gas [18].

The concentration of the sensing gas can determine the device selectivity. Basically, the sensitivity (or % response) is proportional to the gas concentration or the partial pressure of the test gas during sensing. If the partial pressure of the gas is high, the response magnitude becomes high. In the presence of two or more gases, it is likely that the gas component with higher concentration will have relatively higher response at the optimum temperature. In other words, if the gas concentration of the interfering gas (es) is lowered the response magnitude becomes negligible. Then, the device will have dominant sensitivity to the particular gas of interest showing the maximum response. The third important factor is the nature of the sensor surface and its catalytic potential. For example, pristine graphene surface may not be effective for sensing all kinds of gases. So, the surface activity can be improved by functionalization using the catalytic metals, such as palladium, platinum, or by physical/chemical treatment. For instance, studies with pure graphene and Pd-graphene nanocomposite were carried out for sensing hydrogen (1%), moisture, and NO₂ (38 ppm) in a mixture [59]. The response magnitude to 38 ppm NO₂ was excellent with pure graphene but poor with Pd-graphene nanocomposite. On the other hand, the response to 1% H₂ was excellent with Pd-graphene and poor with pure graphene. Moreover, the response was relatively faster for Pd-graphene device due to the catalytic influence of Pd. Furthermore, the presence of moisture influenced the response of Pd-graphene more in comparison with pure graphene. The obvious conclusion from the above study is that palladium-containing graphene sensors will be very good for hydrogen detection; pristine graphene (or functionalized with oxygen species) will be very useful for detecting oxidizing gases, like NO₂. In case, other reducing gases are to be detected, suitable choice of catalytic metal and operating temperature are necessary. The influence of moisture has to be carefully estimated by separate studies in order to have more assuring results.

6. Conclusions and future outlook

Graphene has very high potential for chemical gas sensor applications due to its excellent transport properties, superior mechanical properties and immense scope for the modulation of its surface property by functionalization [60]. Since the surface catalytic property influences the solid–gas interaction, surface functionalization is a convenient technique to improve the response characteristics of graphene-based sensors. The use of catalytic metals such as palladium, platinum, nickel can emphasize the manifold response characteristics and the selectivity. The graphene synthesis methods also play a vital role to increase the device compatibility, and the growth of good quality graphene films requires careful studies with the growth parameters in order to be useful for practical hydrogen and other gas sensors. The various types of graphene-based sensor devices and their sensing mechanisms, particularly for hydrogen sensing, have been discussed in this chapter. The discussions are directed toward understanding the potentiality of the graphene-based devices and their huge promise as a gas sensing platform. The gas detection limit of graphene hydrogen sensors may vary from low to high, which is again a device-dependent characteristic. Normally, catalytic surfaces can detect very low concentration of gases at relatively low temperatures. The importance of defects is quite important for chemical gas sensing, and it is evident from the studies reported so far that the defective surface has high capacity for adsorption, the first step of gas sensing. However, recovery of the sensor signal can be perturbed to some extent due to the gas trapping in the defective sites and it needs relatively higher temperature to remove the adsorbed gases. The multilayer graphene (MLG) hydrogen sensors have normally high response and fast response time at room temperature/moderately high temperature, but the recovery is delayed. However, high-temperature sensing registers faster recovery.

Issues like drift, calibration, stability, selectivity, and the interference of humidity of the graphene-based sensor devices have been thoroughly discussed. These concerns are elaborately considered with special emphasis on the techniques to avert the problems with a simple solution. Sometimes, very simple and judicious choice of some parameters (like temperature) can solve complicated cases of device selectivity in mixed gas ambient. Till date, cross-sensitivity has been an evergreen and challenging problem of the gas sensors in general and the graphene-based devices for hydrogen sensors in particular.

Due to progress in graphene-based research, it is likely that new synthesis techniques may allow the growth of complex device structures, suitable for developing ultra fast sensor devices with selective response characteristics. The problems of suitable ohmic metallization can be addressed if low-temperature CVD techniques are successfully devised. And this will simplify the process steps to fabricate vertical and planar category devices. Also, the quality of the graphene layer can be improved via innovative growth methodologies. These will eventually solve recovery related issues of the graphene-based gas sensor devices. Moreover, it is of utmost importance to understand the operational mechanism of the graphene device at the basic level in order to improvise the ways to improve the performance of the graphene-based sensor devices.

Author details

Sukumar Basu^{1*} and Surajit Kumar Hazra²

*Address all correspondence to: sukumarbasu@gmail.com.

1 IC Design and Fabrication Centre, Department of Electronics and Telecommunication Engineering, Jadavpur University, Kolkata, India

2 Department of Physics and Materials Science, Jaypee University of Information Technology, Waknaghat, Himachal Pradesh, India

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