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Recent advances in thin film hydrogen sensors, materials and methods

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Hydrogen has become the center of attraction from the research point of view because of its renewable and pollution-free characteristics and its use in many fields. Hydrogen is now being used in various industrial areas in order to generate green energy and power for numerous purposes. It is used as fuel in aircraft and spacecraft because of its renewability and lightness. It is used in storage tanks, refueling stations, automotive vehicles, metal smelting, glassmaking, semiconductor processing, petroleum extraction, etc. Green hydrogen can be used to generate electricity at night. Due to the wide range of use of hydrogen, it is vital to make the technology safer for the people. Hence, in this paper we shall discuss the need for hydrogen sensors and how useful are they in industries as hydrogen usage is growing rapidly. The detailed overview about the bulk and thin film sensors like "Thin film bulk acoustic resonator sensors" and carbon nanotubes-based sensors, etc. and main materials used such as palladium as catalyst in hydrogen sensing was briefed. Further, the discussion about materials and methods of fabrication and future scopes in this technology was an important component of this paper. Finally, we will conclude this review with recent advancements and types of hydrogen sensors such as mechanical, electrical, optical sensors, etc.

Keywords: hydrogen sensors, thin films, palladium, electrical sensors

INTRODUCTION

Hydrogen is the lightest element and attracted a significant attention of researchers around the world from fundamental, as well as technological point of view. Earth has around 70% of water which is one of the biggest sources of hydrogen. The huge use of hydrogen in several applications has made it one of the hot topics of current research. The use of hydrogen specially for renewable green energy in automotive vehicles is the best green fuel for the future [1]. Hydrogen, because of its lightness and renewability nature, is one of the best fuels for spacecraft. Because of the broad range of use of hydrogen in several fields, it is vital to make the technology safer for everyone [1-5]. More than 156 countries revealed their new 'Hydrogen Policies' in Glasgow in 2021, and formulated strategies to alter their energy usage and infrastructure to become 'Carbon-Zero' by 2030 [1]. The realization of hydrogen policies depends on the production, storage, transportation, and extensive applications of hydrogen [6-10]. As we know, hydrogen is a very inflammable gas and has a very high flame propagation velocity. Since hydrogen molecule has a very small size, it can leak through many materials and can be the cause of explosive disasters. In the past there have been many disasters happened, as the FUKUSHIMA NUCLEAR DISASTER (loss of reactor cooling resulted in a nuclear meltdown and 3 hydrogen explosions which led to the release of radioactive contamination), the Kennedy space center disaster (large H_2 tank got ruptured causing the shuttle Challenger to explode and killing all 7 astronauts onboard) and many more. Therefore, the detection of hydrogen leakage and its concentration monitoring is very necessary to give the public confidence in using this technology.

Hydrogen monitoring is highly required for nuclear reactor safety, mines, industries, hospitals, households, storage tanks, pipelines, hydrogen production plants, refueling stations, spacecraft, etc. and for that reason, hydrogen sensors have been introduced. Hydrogen sensors that are preferred to be small for mass production, must work at room temperature to make it sustainable with respect to energy, and response and recovery time must be as low as possible, should be affordable by cost, reliability must be high for longevity. As we have seen above how dangerous hydrogen is if not used appropriately. There are several types of sensors that were reported in literature, e. g., palladium capped rare earth thin film hydrogen sensors, TFBAR, CNTs [11-16]. These sensors work great in room temperature ranges which is an essential desirable component for any device. The widespread

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applications and the increase in commercial interest for these sensors led to an exponential increase in related publications since the year 1970, as shown in Figure 1 (a). Some types of sensors are shown in Figure 1 (b). However, despite the significant importance of the present field, not much attention was given in hydrogen sensing field by the scientific community. This lack of knowledge base documentation makes the scope of the present paper. In this review paper, we shall discuss various aspects of types of sensors, methods of fabrication, bulk and thin film sensors, materials used, and future scope.

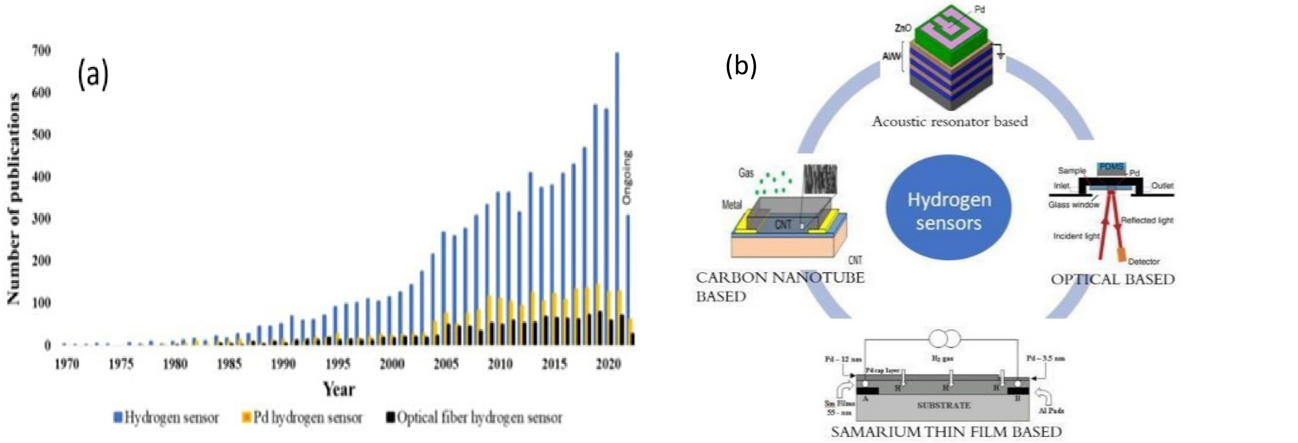
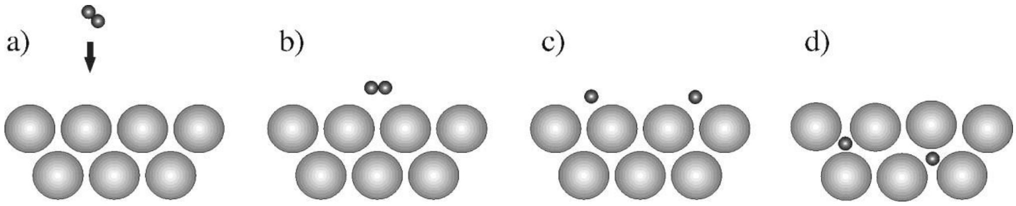


Figure 1. (a) Trends in increase in the publication on hydrogen sensors since 1970 as per SCOPUS (June 2022) [1]; **(b)** Different kinds of hydrogen sensors.



F igure 2. Reaction steps between hydrogen molecule and Pd [2].

Several types of hydrogen sensors

There are many types of hydrogen sensors that are used these days, e. g., thermal-based hydrogen sensors, work function-based hydrogen sensors, mechanical-based hydrogen sensors, electrical-based hydrogen sensors, optical-based hydrogen sensors. We shall mainly discuss electrical and optical based hydrogen gas sensors in this paper.

Electrical-based hydrogen sensors

These sensors work on the basis of electrical resistivity shift of the sensor material when exposed to hydrogen gas concentrations, the main material here is palladium that acts as a catalyst to dissociate hydrogen molecule into atomic hydrogen that further diffuses into underneath materials and results in the change of resistance. The advantage of these sensors is that based of substrate these can be modified for different working temperature ranges.

Optical based-hydrogen sensors

These sensors work on the basis of catalytic and absorption properties of palladium during hydrogenation that results in changes of reflectance, transmittance, absorbance and refractive index. The major advantage of these sensors is that they have good response time compared to other sensors and are very safe as they don't generate any sparks during the detection process. Further discussion shall be conducted in the following sections.

Pd NPs-based electrical H_2 sensors with different substrates

When Pd is placed in hydrogen-rich environment, the hydrogen gas gets absorbed by it exothermally. At the equilibrium state it is reversible in nature. Hydrogen reacts with Pd atoms through Van der Waals interactions. The absorbed gas molecule of hydrogen breaks down into hydrogen atoms and gets diffused in metal. The reaction can be written as:

$$Pd + (x/2)\, H_2 \leftrightarrow PdH_x$$

Figure 2 illustrates the process of hydrogen diffusion in Pd step by step. The structural change of Pd caused by its interaction with hydrogen results in alterations of its electrical, mechanical, and optical properties due to increase in lattice volume of Pd, as illustrated in Figure 3.

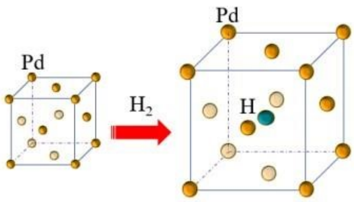


Figure 3. Hydrogen absorption results in expansion of the Pd lattice [2].

Building a hydrogen sensor frequently involves fabrication of either optical or electrical devices. The most universally found Pd NPs-based sensors for H_2 sensing are electrical. The system's modification in resistivity or work function upon exposure to H_2 takes place in these kinds of sensors [2]. The electrical and optical hydrogen sensors are normally based on Pd NPs. In one of the reports by Joshi *et al*. Pd nanoparticles and Pd thin films were exposed to hydrogen to study sensing properties. The experimental setup used for sensing is shown in Fig. 4 (a) where the green part in the measurement chamber is the sensing element. In general, an experiment involves cyclical switching from a carrier gas to an H_2 enriched atmosphere within a gas chamber containing a sensing sample, while measuring the resulting changes in the system's resistance or conductance. Here gas rates are controlled by mass flow controllers (MFC) [4].

The response time of the film was taken to the 90% of the maximum resistance attained by a film when exposed to the hydrogen environment. In this study by Joshi *et al*., the comparative hydrogen sensing of the film deposited on Si substrate by two methods, i.e, electrochemically and via sputtering has been reported. It was observed in this study that the electrochemically deposited films have shown better hydrogen response than the film deposited by sputtering. The response time observation can be seen in Fig. 4(b). Further it was also concluded that the grain size plays a significant role in hydrogen sensing response time. In Fig. 4(b), we can see that overall gas sensing response increases in smaller grain size that was attributed to the activation of surface states in nano size particles. It is also known that the smaller particle size has more active sites which leads to improved chemical sensitization phenomena. Electrical hydrogen sensors based on Pd NPs can be categorized as per the design of the setup used. In these types of systems, Pd NPs can be deposited on different types of substrates like silicon; oxide materials like ZnO, WO_3, etc.; sometimes they functionalize carbon materials like CNTs. Different types of substrates used are described here [2].

Pd NPs on silicon carbide (Ta_2O_5/SiC)

Silicon is a most abundant material on earth and extensively used as a substrate for semiconductor devices. Si has a very small band gap that restricts the maximum working temperature of Si to below 250 °C. Alternatively, silicon carbide (SiC) has a wide band gap, stability and chemical inertness that made SiC a better substrate candidate for high-temperature operations. Kim *et al*. reported the fabrication of Pd/Ta_2O_5/SiC-based hydrogen gas sensors. Here the thin layer tantalum oxide (Ta_2O_5) on SiC was used to improve the sensitivity due to its stability at higher temperature with high permeability for hydrogen gas. The schematic diagram of the sensing device is displayed in Fig. 5 (a) and the hydrogen sensing arrangement in Fig. 5(b). The I-V characteristics and capacitance response properties of the device were investigated on exposure to hydrogen concentration in the temperature range from room temperature to 500°C. In this study they have reported a good performance of device for hydrogen gas sensing at high temperatures [9].

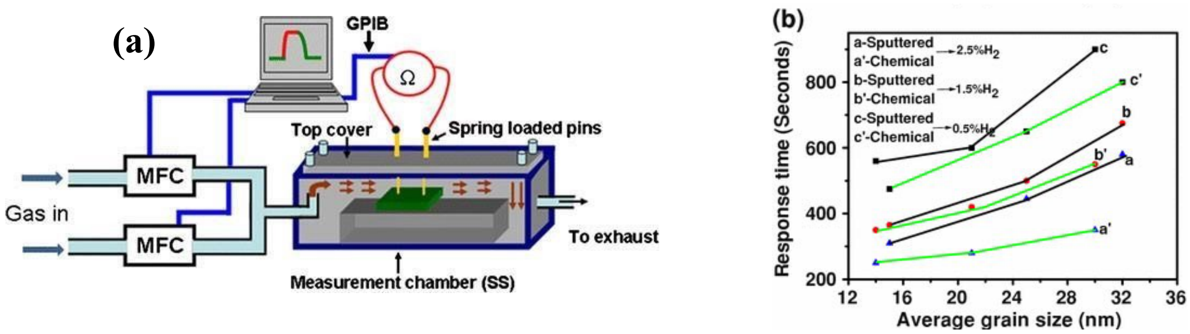


Figure 4 (a) Typical H_2 electrical sensing experiment setup; **(b)** Response time of Pd nanoparticles thin films prepared by electrochemical and sputtering technique of thickness 150 nm as function of grain size [4] open access source.

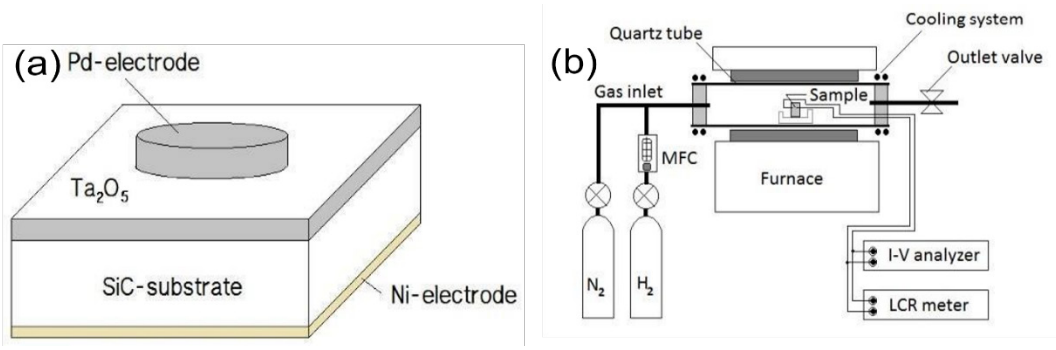


Figure 5 (a) Pd on SiC substrate with thin layer of Ta_2O_5; (b) complete setup for hydrogen sensing [9] open access source.

In Fig. 6, it can be seen that a drastic change in capacitance of the device was observed when exposed to the hydrogen concentration at the working temperature of 500 °C.

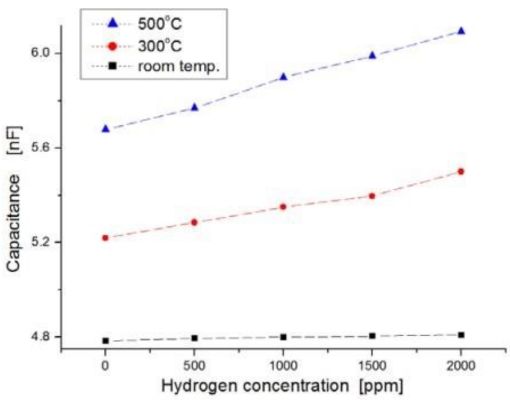


Figure 6. Change in capacitance as a function of hydrogen concentrations at different temperatures [9].

However, change in capacitance was almost consistent at room temperature when the device was subjected to hydrogen environment. Further it was also seen quantitatively that the capacitance was enhanced from 5.6 nF to 6.1 nF after the hydrogen concentration varied from zero to 2000 ppm at 500 °C. From the observation it was concluded in this paper that Ta_2O_5 dielectric thin layer provides great possibilities for hydrogen sensing application at high temperatures [9].

Pd NPs on carbon nanotubes

In one of the reports published by Sayago *et al.* [8], Pd has been integrated to CNTs to amend their hydrogen sensitivity. They prepared three different types of sensing materials: (1) SWNTs (single-walled nanotubes); (2) SWNTs functionalized with palladium; (3) SWNTs doped with palladium. These sensing materials were deposited on alumina substrate. Sensing concentrations of hydrogen varied from 0.5 to 4% and the carrier gas used was nitrogen with 99.99% purity with a constant flow of 200 ml/min. The response and recovery time was found to be 30 and 60 min respectively. The effect of temperature on the sensor with SWNTs was studied on Heraeus MSP 769 instrument in the temperature range of 100-250°C. After the complete study they found the results that only the sensors functionalized with Pd detect H_2 at room temperature and as the Pd content is increased, the sensor starts to give better response. Unfortunately, these sensors do not attain saturation throughout exposure time, but they provide good response time of 2 min. The sensor with SWNTs on alumina substrate (Heraeus MSP 769) only detects H_2 for temperatures higher than 200 °C and same condition was also observed with Pd-doped SWNTs. Because of random distribution of CNTs arrays, gas can be adsorbed at multiple active points (like tube ends, edges and valleys outside, inner and between) and that's the reason of longer exposure time. As a conclusion we can say that all these sensors show very low response, and their resistance doesn't vary much with H_2 concentration and hence the practical utility of such sensors needs more research to improve.

Pd-based optical H_2 sensors

A number of optical hydrogen sensors have been developed based on the permittivity fluctuation and catalytic characteristics of Pd during hydrogenation. Pd has a weaker optical sensitivity than other sensing materials like Mg and Y because hydrogenation only causes a minor change in its dielectric constant. For other hydrogen sensing materials, hydrogen absorption is quite typical as they have need of catalysts to dissociate hydrogen molecules into atoms which can enhance the expense of sensor. To prevent the hydrogen poisoning on Pd from other gases a kind of protection layer (e.g., PMMA, PTFE) can be applied on the sensing materials. Optical sensors are safer than other sensors because of the absence of any ignition source. Different measurement techniques, including reflectance, interferometry, surface plasmon resonance, and evanescent light, can be used for optical detection. Its adaptability for various sensing applications is further increased by fibre Bragg gratings and field interaction. In this section we will discuss various kinds of optical response-based sensors.

Pd-PMMA bilayer on a soft PDMS substrate (PPBE)

She *et al.* in his work on hydrogen sensor tried to make a sensor based on light scattering, a low price and high contrast hydrogen sensor that can produce enormously high reflectance variation due to the conversion of specular to diffusion reflection during surface wrinkling [10]. They studied the reflectance change of PPBE (Pd-PMMA bilayer on an elastomer like polydimethylsiloxane (PDMS)), with Pd and polymethyl methacrylate (PPMA) as protecting layer. They used PPBE because it is of low cost and simple to manufacture. In order to fabricate PPBE a thin Pd film was first deposited on it. The Pd film was then covered with a PMMA/PAA bilayer on a quartz substrate. Lastly, after polyacrylic acid (PAA) was mixed in water, the PMMA film coating on the Pd film was left behind. Here they chose PMMA because of its high selective filtration of H_2. The schematic diagram of same is shown in Fig. 7 for better understanding. In this work, they measured the reflectance spectra of the sensor in order to show the effect of PMMA on its performance. The thickness of Pd film and PMMA is 25 and 22 nm, respectively. The variation in reflectance spectra in the visible band and response time for Pd on PMMA at 0% and 4% exposure of H_2 gas mixed with N_2 and air are shown in Fig. 8. They further investigated the effect of thickness of Pd film on response time and it was found that the latter increases with increase in thickness. It was also seen that thinner the PMMA, more reflectance changes are in lesser time. When thickness of PPMA was taken of 16 nm the hydrogenation time decreased from 15 to 5 seconds, heading to quick response rate of the sensor. In practical application here the response time and reflectance change decreased with increase in temperature. The reflectance change was found more than 22.7% in the whole visible band with reflectance contrast over 370% in wrinkle surface. The response time can be 1 second if the alarm point is set at a 4% change in reflection at wavelength 600 nm. Hence the PPBE is extremely appropriate for real hydrogen sensing.

Sensor based on tunable laser diode spectroscopy (TDLAS)

Avetisov *et a*l. used tunable laser diode spectroscopy [TDLAS] as it can detect hydrogen gas without collecting gas samples (which is safer compared to other types of sensors) and has low maintenance cost and operational costs [14]. Cavity ring down spectroscopy (CRDS), intro cavity output spectroscopy (ICOS), etc. were not preferred because of contamination of reflective mirrors that were a major concern in industrial uses. The sensor consists of two units i.e., transmitter unit that contains diode laser, microprocessor board, input output electronics and receiver unit which contains photodetector, amplifier, mixer, etc. The sensor diagram is given in Fig. 9 for reference.

The absorption spectrum of hydrogen in the infrared region is very weak, the first band is located between 1100-1500 nm, this is also due to the low mass of the H_2 molecule. From HITRAN simulation they concluded that 3 transition bands were suitable for H_2 sensing, i.e., 2407 nm, 2223 nm, 2122 nm.

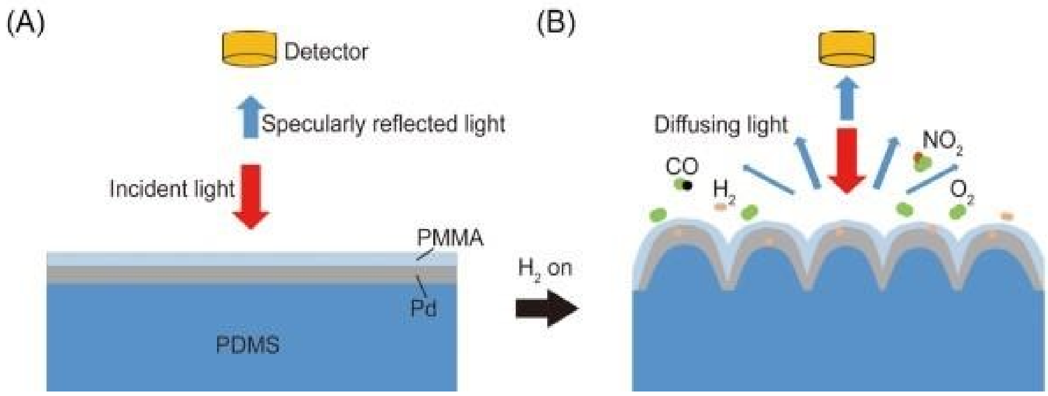


Figure 7. Schematic exhibiting the sensing mechanism of the PPBEs. (A) The specularly reflected light by the flat Pd/PMMA bilayer before hydrogenation and (B) diffused reflectance by the wrinkling surface generated by volume expansion of Pd thin film after hydrogenation [10]- open access source.

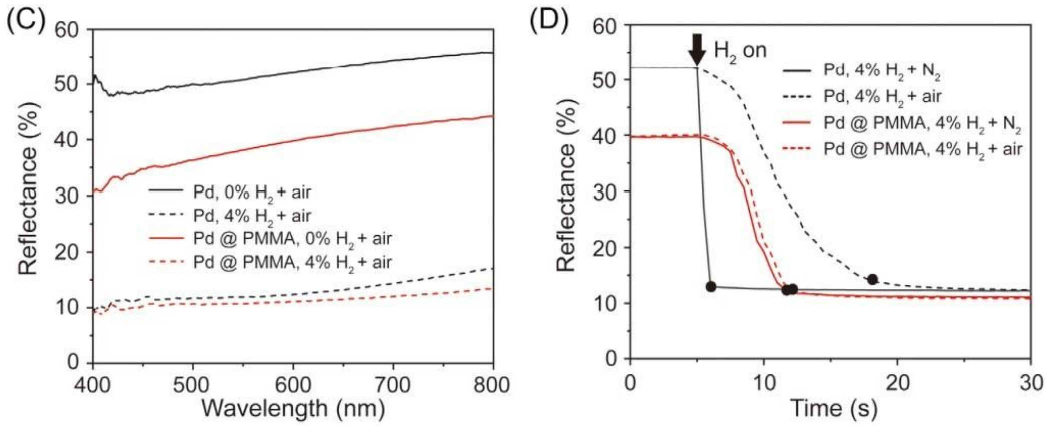


Figure 8. (C) Reflectance spectra as function of wavelength of the PPBE and a Pd film on PDMS when exposed to 0% and 4% H_2 mixed with dry air, respectively. (D) Reflectance change as function of time at a fixed wavelength of 600-nm of a PPBE (red line) and a Pd film on PDMS (black line) on exposure to 4% H_2 mixed with N_2 (solid line) and dry air (dash line), respectively [10] open access source.

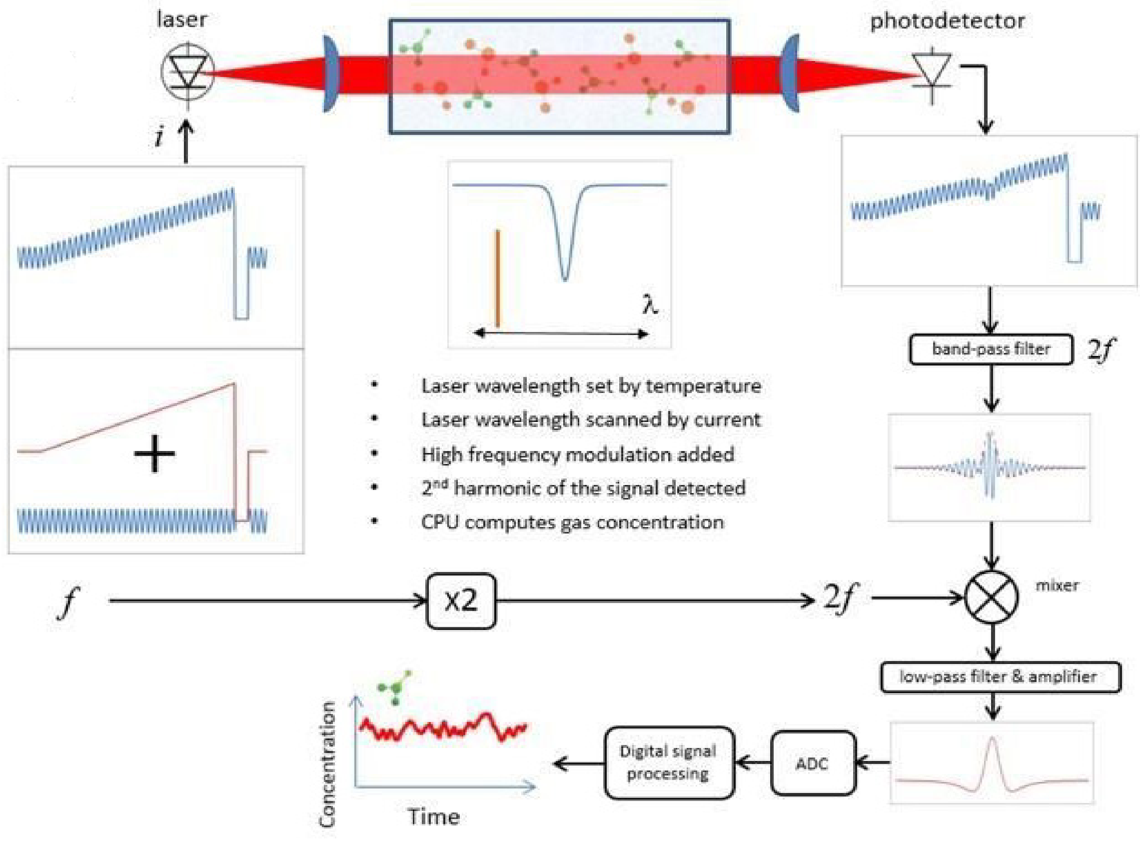


Figure 9. Typical arrangement for a spectroscopy-based H_2 gas sensor [14] open access source.

The best suitable line is the one that doesn't coincide with spectral lines of other gases such as CO_2, H_2O, CO, etc., as shown in Figure 10.

During the experimental session major issues faced with TDLAS sensors were optical fringe noise and coupling of stray light in the active laser area. These were solved by AR coating the surfaces and tilting them. For estimating the sensor performance, the transmitter and receiver unit were kept 1 m away and the cell was maintained at ambient temperature, also the sensor was calibrated with known values of H_2 and N_2, the H_2 concentration was reduced from 10-0.1 percent and the concentration set *vs*. measured result was plotted and shown in Fig. 11. Measurement precision of 0.02%v H_2 was found within 1s of integration time. As we increase the pathlength, the absorption also increases that results in the increase of sensor precision. Which indeed makes it more suitable for industry uses.

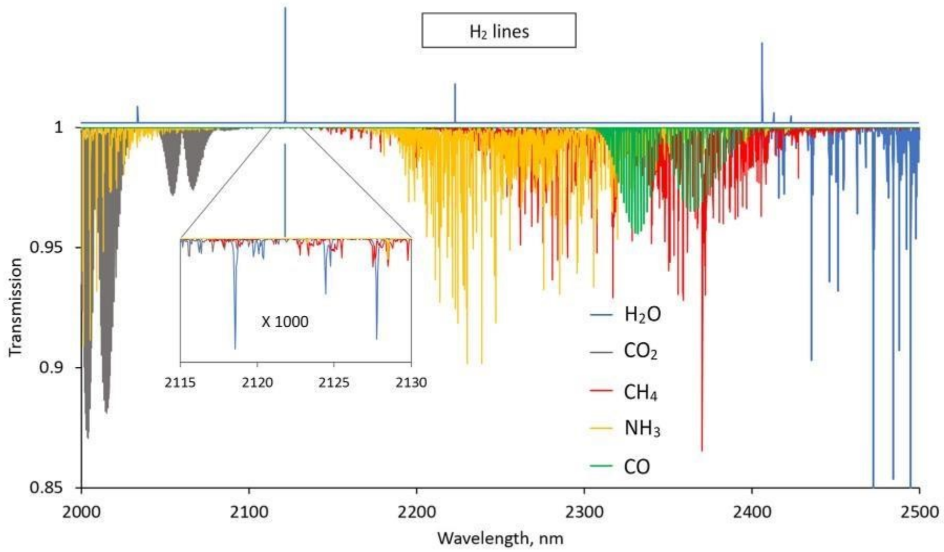


Figure 10. HITRAN simulation for the absorption spectrum of various gases and H_2 which might be present in typical usage environments of the sensor [14] open access source.

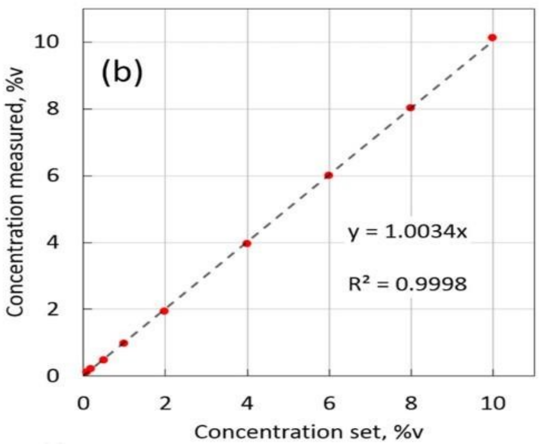


Figure 11. Graph of concentration of H_2 in chamber with detection precision [14].

Future scopes and applications

With its multiple uses in fertilizer factories, nuclear power plants, refineries, and other emerging technologies like eco-friendly fuels, hydrogen has a bright future. A hydrogen sensing system is necessary because the hydrogen has distinctive characteristics including strong flammability, low viscosity, low density, high escape rate, and the ability to burn with an unnoticeable flame. The sensitivity, reaction time, accuracy, detection range, durability, and dependability of gas sensors are the main determinants of their use. The current study focuses on the application of these sensors for a variety of businesses, including those that produce fertilizers, refineries, hydrogenating agents, and fuel cell-powered cars [1]. To monitor hydrogen concentrations and optimize process settings for optimal efficiency, hydrogen sensors can be used in hydrogen generation processes such steam methane reforming, electrolysis, and biomass gasification. In addition to the above hydrogen sensors can also be employed for safety monitoring, leak detection, and risk avoidance. In order to monitor hydrogen concentrations at various points throughout the operation of the fuel cell, including the hydrogen input, fuel cell stack, and exhaust gases, hydrogen sensors can be employed in hydrogen fuel cell systems. By guaranteeing enough hydrogen supply and averting any dangers, hydrogen sensors can aid in maximizing the efficiency of fuel cells. In chemical companies, early detection of hydrogen leaks using hydrogen sensors can assist to avoid accidents, reduce losses, and guarantee safety. The car industry and the US DOE have examined the need for H_2 safety sensors. The recommended range for sensors per vehicle is 2 to 6. The cost of sensors per vehicle will be reduced and operational costs will be better managed if one kind of sensor can function in all these diverse operating situations [2]. It may also be utilized inside automobiles to look for potential hydrogen leaks in the fueling system, hydrogen storage system, or other hydrogen infrastructure components. To ensure safety and avoid risks like explosions or fires, early identification of hydrogen leakage is essential. In order to ensure the safe storage of hydrogen in high-pressure tanks or other types of hydrogen storage systems used in cars, hydrogen sensors are essential. In the event of leaks or other safety issues, they can set off alarms or shut off the system. Vehicles using hydrogen internal combustion engines may monitor hydrogen concentrations during combustion using hydrogen sensors. They offer feedback for effective engine running and aid in ensuring safe hydrogen combustion. These car's hydrogen sensors generally gauge the amount of hydrogen present in the intake or exhaust gases. Hydrogen sensing might undergo a revolution if other technologies, such as the Internet of Things, artificial intelligence, and wireless communication, were integrated with hydrogen sensors. Algorithms powered by artificial intelligence can increase sensor selectivity, dependability, and calibration, resulting in better sensor performance and fewer false alarms. In the current paper, the electrical and optical hydrogen sensors based on different systems with their advantages and disadvantages were elaborated in detail. This information at one place will definitely help scientific society for future expansion in the field of hydrogen sensing.

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