Effect of La doping on the structural and gas sensing properties of PbS thin films deposited by spray pyrolysis

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Abstract. Phase pure PbS and lanthanum doped PbS thin films have been deposited by the spray pyrolysis technique. All the deposited films were gray to black, pin hole free and strongly adherent to the ITO glass substrates. The substrate temperature was varied between 450 and 500 °C, with doping concentration ratios of 1, 5 and 10% for La. The doping performed at 450 °C, showed phase segregation whereas successful incorporation of La in the PbS lattice was achieved at 500 °C. The films were characterized by x-ray diffraction (p-XRD), scanning electron microscope (SEM), transmission electron microscope (TEM), Energy-dispersive X-ray spectroscopy (EDX), and ultraviolet visible spectroscopy (UV). The sensitivity of the as deposited thin films was also tested against hydrogen gas. The sensor material was exposed to a low concentration of 200 ppm of the target gas to determine the sensitivity performance of the sensor, at different temperatures while measuring the variation in the resistance. The doping of lanthanum significantly enhances the sensitivity of the PbS thin films against the target gas. The gas sensor exhibited n-type conductivity as confirmed by the decrease in resistance on exposure to hydrogen. The as prepared catalysts show good sensing behavior near room temperature and at low concentration of hydrogen at 200 ppm without the need to apply an external voltage.

1. Introduction
Hydrogen detection has gained considerable interest as it is the main product in fuel cells, monitoring faults and combustion engines. Hubert et al. indicated that more than 1000 articles have been published in gas sensing between the period of 1975 and 2010 [1]. The physical and chemical properties of the hydrogen gas, i.e. colorless, odorless, tasteless, and flammable gas, makes its detection by human senses almost impossible and highly dangerous [2]. It is well known that a mixture of oxygen and hydrogen causes explosions and degradation of steels [3]. At a higher concentration of more than 4%, hydrogen becomes flammable and explosive. Extensive research has been carried out to use hydrogen as an alternate fuel, to meet the upsurge in energy demand. Hence, there is an urgent need to fabricate high performance hydrogen sensors, for safe use of hydrogen as a fuel [4].

Different techniques have been employed for the detection of hydrogen, these include, use of catalyst, mechanical methods, thermal conductivity, electrochemical, resistance, and optical processes [2]. The electrochemical and resistance-based techniques are most distinctive because of their selectivity and capability for detection even at much lower concentrations [2].
It is well established that the surface absorption or desorption of a gas by metal oxides or sulfides, results in change in the conductivity of these materials. The phenomenon was first investigated on ZnO thin films [5,6]. The sensitivity of a catalyst surface to the gas can be as low as parts per billion (ppb). Moreover, it was noticed that some of the catalysts showed higher selectivity towards a certain gas even in a mixture of different gases. The selectivity of a catalyst is at a maximum at a definite temperature, also known as the optimum working temperature, where the gas adsorption to the catalyst surface is at a maximum. However, the optimum temperature may vary considerably from one catalyst to the other and from gas to gas. Hence, a catalyst can show selective behavior towards different gases at different optimum temperatures. It is also known that the higher surface area of the catalyst, can lead to enhanced adsorption of a target analyte, resulting in a stronger and prominent response (specifically at the ppm concentration level). The interaction of the target gas with the surface of the metal sulfides nanoparticulate film (generally through surface adsorbed oxygen ions), results in a sudden and quick alteration in the charge carrier concentration of the catalyst. As a consequence, the conductivity (or resistivity) of the material also changes significantly [5].

Palladium based materials and metal-oxide semiconductors, such as, SnO₂, TiO₂, and NiO are considered good sensing materials because of their capability to detect hydrogen at lower concentrations and the ability to work near room temperature. Although these sensors display good sensitivity towards hydrogen, the high costs and inherent defects in some are limitations, e.g. Pd shows hysteresis behavior in electrical resistance as a result of the adsorption of hydrogen on its surface [7].

Metal sulfides are versatile materials with vital applications in diverse fields such as, solar cells, gas sensing, remote sensing and photoresists [8–13]. Lead sulfide (PbS) is an important member of the IV–VI class of the semiconductors with a band gap of 0.38 eV, and a relatively large excitonic Bohr radius (20 nm) [14]. Narrow band gap, large Bohr radius and quantum size effects are the prime features of PbS making it suitable for optoelectronics applications, such as, infrared detectors [15]. Different methods have been used successfully for the fabrication of PbS nanostructures, such include colloidal routes, spray pyrolysis, photo chemical deposition, chemical bath deposition, aerosol assisted chemical vapor deposition (AACVD), electro deposition and successive ionic layer adsorption and reaction (SILAR) methods [16–19]. Although, the synthesis of shape and size controlled PbS has been achieved by different routes, the drawback in some cases are the synthetic protocols which are tedious requiring high reaction temperatures, and toxic or expensive capping agents.

As compared to the other deposition techniques, spray pyrolysis is relatively facile, quick, cost effective and potentially suitable for the deposition of a relatively larger area. The films quality can be precisely controlled by altering the deposition parameters, such as, precursor concentration, substrate temperature, gas flow rate, irradiation time, volume of the solution sprayed and doping (type of metal and its ratio) [20].

The fabrication of reliable and sensitivity enhanced sensors, at relatively low cost, is highly desirable. The ability of the metal sulfides to be produced easily on a bulk scale with simple controllable process makes them potentially suitable materials for device fabrication. There is only limited literature available on the contribution of lead sulfide thin films in hydrogen sensing devices. In the current work, phase pure PbS and La doped PbS nano-particulate thin films have been deposited using the spray pyrolysis technique. The effect of doping on the structure has been investigated. Finally, the performance of the deposited thin films for 200 ppm hydrogen gas sensing has been recorded at different temperatures in the range of 50 to 150 °C.

2. Materials and methods

2.1. Materials
Lead acetate (Pb(CH₃COO)₂ (99%)), thiourea (CS(NH₂)₂, (99%)), lanthanum (III) acetate (La(Ac)₃.xH₂O), (99%)), and methanol (CH₃OH, (98%)) were obtained from (Sd fine-Chem limited – India) and used as such.
2.2 Samples preparation
The spray pyrolysis setup consists of a substrate heater with an iron–constant thermocouple, a solution reservoir, air compressor, spray gun, and a gas exhaust unit. The optically cleaned Indium doped tin oxide (ITO) substrates were heated to the desired temperature by placing them over the hot plate with a temperature probe. The aqueous solution containing a mixture of desired metal salt(s) and thiourea, was then sprayed on the pre-heated substrates, at different temperatures (450 °C or 500 °C) to obtain homogeneous thin films.

To prepare pure PbS thin films, lead acetate (0.05 M) and thiourea (0.051 M) were added in 100 mL of water and stirred for half an hour. A slightly higher molarity of thiourea over lead acetate ensures the completion of the reaction. After half an hour, the solution was ready to be sprayed by addition of an equal volume of methanol in the reaction mixture. The distance between the substrate and the spray gun nozzle was fixed at 40 cm and compressed air was used as a carrier gas. The flow rate of carrier gas was kept constant during the whole experiments. The solution containing the reaction mixture (5.0 mL) was sprayed as fine droplets on the substrate and allowed to be decomposed thermally over pre-heated ITO glass substrates. To avoid excess cooling of the substrate and to maintain the desired deposition temperature (450 °C or 500 °C), the solution was sprayed slowly (one mL of the sprayed solution pulsed every 5 mins.). The spraying processes continued for 30 min. As a result, continuous lead sulfide films were obtained with the substrates allowed to cool to room temperature naturally.

The same experimental conditions were used to prepare La doped lead sulfide thin films by adding the calculated amount of lanthanum salt, for 1, 5 and 10% doping ratio, the films were deposited at temperatures of 450 °C and 500 °C. The reactions involved in the formation of lead sulfide films are as follows:

\[
Pb(CH_3COO)_2 \rightarrow Pb^{2+} + 2CH_3COO^- \quad (1)
\]

\[
CS(NH_2)_2 + OH^- \rightarrow CH_3N_2 + H_2O + SH^- \quad (2)
\]

\[
SH^+ + OH^- \rightarrow S^2 + H_2O \quad (3)
\]

\[
Pb^{2+} + S^2 \rightarrow PbS \quad (4)
\]

2.3. Characterization of the prepared films
X-ray diffraction analysis of the films was performed on a PANalytical (Empyrean) X-ray diffractometer, with Cu Kα radiation (λ=1.54045 Å) and accelerating voltage of 40 kV, current of 35 mA, scan angle 20 - 70° range and scan step of 0.02°. The average crystallite size of the prepared nanocrystallites was determined by Scherrer’s equation (Eq. 5) [21–23].

\[
D = 0.94\lambda/\beta\cos\theta \quad (5)
\]

Where D represents average crystallite size, λ is the radiation wavelength, β shows the corrected full width at half maximum (FWHM) and 0 is the diffraction angle. The morphology of the films was analyzed by FE-SEM, Quanta FEG 250. TEM micrographs were captured using the JEOL JEM 1010 transmission electron microscope, which operates at 100 kV. The diffused reflectance spectra of all the deposited films were obtained from the double beam UV-Vis-NIR Shimadzu spectrophotometer model type UV-3600.

2.4. Sensing measurements
Ingenious gas sensing unit has been used to measure the change in thin film resistance upon exposure to the target gas, with variable concentrations mixed with a certain amount of dried air, in order to obtain the maximum sensitivity at 9% of hydrogen. Thin film was placed between two metallic crocodile forceps connected by Teflon bars to estimate the film resistivity. A coating of silver paste was introduced on the film surface to provide electrical contact with the external electrodes. The system was placed inside a digital horizontal furnace with a temperature controller unit to adjust the temperature to the...
desired values. The films have been tested at temperatures of 50, 80, 120 and 150 °C and the variation in the resistance recorded using a computerized digital multimeter (Avometer) of type Protex506.

Firstly, a continuous flow of dried air was allowed to pass over the as prepared thin films, and the resistance of the film was recorded for few minutes before the introduction of the target gas (hydrogen) flow, to obtain a baseline value. A known amount of hydrogen gas was introduced in the air stream and the change in the resistance recorded. The target gas could pass for 5 mins, after which the gas flow was stopped, the resistance was continuously recorded until it reached its original value. This process was repeated several times to confirm the reproducibility and stability.

3. Results and discussion

The phase determination and purity of deposited thin films was analyzed by p-XRD analysis. The X-ray diffraction patterns of the pure and the La-doped PbS films deposited at a substrate temperature of 450 °C are shown in figure 1. All films were found to be black in color, pin hole free and in good adhesion with the substrate. The diffraction planes recorded are (111), (200), (220), (311),(222), (400), (331) and (420) which correspond to pure PbS and matches well with the standard pattern (ICDD # 00-005-0592) [24]. In pure PbS films the (200) plane has the maximum intensity, indicating the preferred orientation of crystallites along this plane. However, upon doping of lanthanum, the intensity of the (111) reflection starts to change as a function of concentration. It may indicate that the La-doping changes the preferred orientation of the deposited lead sulfide films. At La doping concentration of 1 and 10 %, two new peaks, marked as (*), were observed at 2-θ value = 22.99 and 24.96°, which matches with the (200) and (111) diffraction peaks of the α-La2S3 phase (ICDD# 22-645) [25]. The intensities of diffraction peaks of the PbS phase were also found to increase at La concentration of 10 %. This is attributed to the formation of the La2S3 phase which consumes the lanthanum in the separated phase instead of getting it incorporated into the PbS lattice. In all deposited films a slight shift in the 2-θ value was observed as the La-content increases, as shown in figure 1 and table 1. No impurity peaks were observed for La concentration of 5%, which may indicate a good incorporation of La into the PbS lattice.

![Figure 1](image_url)

**Figure 1.** (a) p-XRD of the pure PbS and La-doped PbS films deposited at a substrate temperature of 450°C and (b) an extended part of the diffraction pattern.
Figure 2. (a) p-XRD of pure PbS and La-doped PbS films deposited at a substrate temperature of 500 °C, and (b) extended part indicating a slight shift due to doping.

Figure 2(a) shows the diffraction patterns for pure and La-doped PbS films deposited at 500 °C. The diffraction planes are indexed as (111), (200), (220) and (400), which correspond to the cubic PbS phase [23]. The PbS films seem to be highly textural as the (200) peak appears as the only main high intensity peak. By incorporation of La, the intensity of the (111) peak and other planes i.e. (311), (222), (311) and (420) also started to appear, with respect to the (200) plane [24]. Unlike films prepared at 450 °C, no phase segregation was observed as peaks belonging to La2S3 or another impurity were absent. It indicates the successful incorporation of La in the PbS lattice by increasing the temperature from 450 to 500 °C. The intensity of the diffraction peaks changes as the La- content increases in all the films and a slight shift in the 2-θ value was also observed as the La-content increased (figure 2(b)).

The grain size of all the films was estimated using both Scherrer’s equation and the Williamson-Hall equation [23,26]. The average crystallite size was obtained by the Scherrer’s equation (Eq. 5) as mentioned in the experimental section.

Figure 3. Change in grain size with respect to doping ratio and reaction temperature.

Figure 3 presents the variation of the grain size values with respect to the dopant concentration at the deposition temperatures of 450 and 500 °C. As observed for pure PbS, the size changes from 35.3 to 37.8 nm by changing the deposition temperature from 450 to 500 °C. Such results could be attributed to the increase in the deposition temperature which indicates agglomeration of the particles and improved crystallinity. Introducing dopants such as La has a significant effect on the grain size. Although not
regular, but generally a reduction in the grain size is observed at both temperatures and different dopant concentrations. The irregular behavior of size reduction was comparatively prominent in films deposited at 450 °C [27].

The overall reduction in the crystallite size may be attributed to the substitution of the divalent Pb$^{2+}$ ions with ionic radii equal to 119 (pm), by a smaller trivalent metal ion (for e.g. La$^{3+}$ with ionic radii 103 pm), respectively. As a result, the sulfur vacancy formed, and the crystal lattice reduced. The reduction in lattice parameters was also observed by a slight shift of diffraction peaks towards the higher 2-theta values, in the p-XRD pattern [28]. The lattice reduction reduces the particle size and could be explained by an increase in the point defects concentrations [29,30].

The strain induced in the crystal lattice, due to the presence of the defects can also contribute to peak broadness. As substitution of a divalent atom by trivalent atoms introduces defects in the lattice, hence the Williamson-Hall method was used to determine the effect of strain on the peak broadening and determination of the crystallite size by excluding the strain factor. The difference between crystallite size induced broadening and the strain induced broadening can be calculated by the Williamson–Hall plot using Eq. (6) as shown:

$$\beta \cos \theta = \frac{m \lambda}{D} + 2 \varepsilon \sin \theta$$

(6)

where $\beta$ is FWHM in radians, $\lambda$ is CuKα wavelength (0.154186 nm), $\theta$ is the Braggs diffraction angle, $D$ is the crystallite size in nm, $\varepsilon$ is the strain and $m$ is a correction factor which is considered to be 1.

Figure 4, shows a linear fit plot, obtained by plotting $\beta \cos \theta$ vs $\sin \theta$ at which the crystallite size and strain could be determined plotting the intercept with y-axis and the slope, respectively. The plot indicates that positive strain values were obtained for all prepared samples [31]. The strain values and a comparison of the size calculated from both the Scherrer and Williamson-Hall equation is shown in table 1.

![Figure 4. Williamson-Hall effect on the grain size of PbS thin films.](image)

**Table 1.** Grain size and strain values calculated for all prepared samples.

| Material          | Grain size by Scherrer's equation (nm) | Grain size by Williamson-hall method (nm) | Strain     |
|-------------------|----------------------------------------|------------------------------------------|------------|
| Pure PbS at 450 °C| 35.3                                    | 105.4                                    | 0.00307    |
| 1% La at 450 °C   | 32.8                                    | 85.7                                     | 0.00316    |
| 5% La at 450 °C   | 23.2                                    | 32                                       | 0.00135    |
| 10% La at 450 °C  | 30.9                                    | 44.9                                     | 0.00019    |
| Pure PbS at 500 °C| 38.7                                    | 127.8                                    | 0.00285    |
| 1% La at 500 °C   | 30                                      | 126.8                                    | 0.00448    |
| 5% La at 500 °C   | 22                                      | 30.3                                     | 0.00134    |
| 10% La at 500 °C  | 22.2                                    | 43.2                                     | 0.00362    |
Figure 5. SEM images of (a) pure PbS, (b) 1% La doped PbS and (c) 5% La doped PbS thin films prepared at 400 °C, whereas, (d) pure PbS, (e) 1% La doped PbS and (f) 5% La doped PbS thin films prepared at 500 °C.

3.1. Scanning electron microscopy
The morphology of the samples was observed using SEM analysis. Figure 5 (a-c) shows SEM images of pure lead sulfide, 1 and 5% La doped lead sulfide films deposited at 450 °C, whereas figure 4 (d-f) shows pure lead sulfide, 1 and 5% La doped PbS films deposited at 500 °C, respectively. The SEM images for pure PbS (figure 5(a)) prepared at 450 °C reveals that, highly condensed and agglomerated particles with stripes and rod-like structures were formed. While the SEM images of the La doped lead sulfide shows the formation of small dense particles which aggregate to form a porous surface, however, there are still some rod-like structures present in the sample with a small amount of La. By increasing the doping ratio from 1 to 5% the elongated particles began to evolve into particles that are smaller in size (figure 5(b, c)). Figure 4(d) shows the SEM image of a nanostructured PbS film prepared at a higher
temperature of 500 °C, it is clearly observed that the morphology is significantly affected because of raising deposition temperature. Slightly elongated, irregularly shaped, and agglomerated particles form a highly compact film. The higher reaction temperature may enable early formation of a metal sulfide with larger crystallite size before substrate adhesion and higher rate of diffusion on the substrate can lead to the bulky structures. The SEM images of La doped lead sulfide showed that small dense particles with porous surfaces were formed. By increasing the doping ratio from 1 to 5% the elongated structured particles disappeared but the particles were still agglomerated. The higher temperature may result in the formation of the product just before the interaction of the solution mixture with the substrate, which may cause increased agglomeration.

3.2. Transmission electron microscopy
The transmission electron microscopy (TEM) image of pure lead sulfide and the particle-size distribution histogram after scratching the powder over the film, which shows the size range for the width of particles for a count of over 100 particles, have been obtained and shown in figure 6. The morphology of the nanoparticles showed some anisotropic morphology with slight agglomeration. These obtained morphologies are comparable to those reported [16]. The estimated average particle diameters were found to be 40.32 nm.

![TEM image of pure PbS with its respective particle size distribution histogram deposited at 500 °C.](image1)

**Figure 6.** TEM image of pure PbS with its respective particle size distribution histogram deposited at 500 °C.

![EDX images of pure PbS sprayed at 400°C and 10% La doped PbS at 500°C.](image2)

**Figure 7.** EDX images of pure PbS sprayed at 400°C and 10% La doped PbS at 500°C.

Energy dispersive X-ray (EDX) analysis was performed on pure lead sulfide film and films doped with 1 and 10% of La at both temperatures and the representative spectra are shown in figure 7. The obtained results confirm the presence of La in the doped samples. The spectrum exhibits signals
corresponding to lead, sulfur, and lanthanum. All the films were slightly sulfur enriched. The atomic % of La was found nearly like what was expected, as calculated for feed ratio and is shown in table 2.

| Material                  | Elements | Atom % of expected feed | Atom %     |
|---------------------------|----------|--------------------------|------------|
| Pure PbS at 450 °C        | Pb       | 39.044                   | 39.62      |
|                           | S        | 59.504                   | 60.38      |
| 1% La at 450 °C           | Pb       | 39.93                    | 43.00      |
|                           | S        | 52.64                    | 56.69      |
|                           | La       | 0.29                     | 0.31       |
| 10% La at 450 °C          | Pb       | 37.9                     | 41.34      |
|                           | S        | 49.7                     | 54.29      |
|                           | La       | 3.12                     | 4.37       |
| Pure PbS at 500 °C        | Pb       | 38.8                     | 39.65      |
|                           | S        | 59.05                    | 60.35      |
| 1% La at 500 °C           | Pb       | 39.4                     | 40.79      |
|                           | S        | 56.97                    | 59.06      |
|                           | La       | 0.136                    | 0.14       |
| 10% La at 500 °C          | Pb       | 38.5                     | 44.08      |
|                           | S        | 44.6                     | 51.05      |
|                           | La       | 4.22                     | 4.87       |

**Table 2.** Mass and atomic percent of the as prepared samples.

### 3.3. Optical properties

The incorporation of La in PbS films was better in films deposited at 500 °C, no phase segregation was observed, hence, the optical properties of these films were studied by using double beam UV-Vis-NIR spectroscopy. The optical absorbance spectra were studied in the range of 200-1200 nm wavelength for pure and La doped lead sulfide deposited on ITO glass substrates at 500 °C (figure 8(a)). It is clearly seen that the strong peak belongs to pure lead sulfide film at 380 nm absorbed in the UV region and a small broad peak above 700 nm in the region of near-IR. For La-doped films, a strong peak for all doping ratio also appears in the UV region but shifted to the left, indicating the reduction of crystallite size as observed by p-XRD analysis.

![Figure 8. UV-Vis-NIR spectra of pure PbS and La-doped PbS films.](image-url)
Also, a broad peak appears in all the doped samples at 580 nm in the visible range. This absorbance increases with the increase of the doping ratio of lanthanum in the pure phase from 1 to 10%. The new absorption in the visible region played a good role to enhance the activity of the prepared catalysts. Based up on the type of direct allowed transition, the optical band gap values were estimated using Tauc’s equation (Eq.7), for all thin films prepared at 500 °C [32].

\[ \alpha = A \left( \frac{(h \nu - E_g)}{h \nu} \right)^{1/2} \]  

where \( \alpha \) is the absorption coefficient, \( A \) is the samples absorbance, \( \nu \) is reciprocal of the wavelength, \( E_g \) is the optical band gap and \( h \) is the Planck constant. As the calculations did not consider the reflected light so, for better accuracy, it is important to calculate reflected light first. As the light is either absorbed or transmitted or reflected, the absorption coefficient \( \alpha \) can be estimated by calculating first the reflected radiations according to the following equations (8-10).

\[ A = 1 - R - T \]  

\[ R + T = e^{-\alpha d} \]  

\[ \alpha = \frac{-1}{d} \ln \left( \frac{T}{(1-R)^2} \right) \]

where \( d \) is the thickness of the sample. The band gap values were measured by extrapolating \((\alpha h \nu)^2\) versus \(h \nu\) and the band gap energy can be obtained at the intersection between the photon energy axis and the steep part of the curve (figure 9). Pure lead sulfide, 1, 5 and 10% lanthanum doped lead sulfide showed band gap values of 1.62, 1.52, 1.5 and 1.48, eV, respectively. The values are strongly blue shifted as compared to the bulk value of 0.38 eV, for PbS [14]. This type of blue shift in absorption spectra has been reported due to the well-known quantum confinement effect for the lead sulfide nanoparticles as compared to the bulk. The reduction in the band gap can be related to the small doping ratios, which might create ground and excited f-energy states in the band gap of lead sulfide, these energy states of lanthanum take up many excited electrons coming from O 2P level [1], in addition, the concentration of Pb2+ in the lattice boundary was limited by doping. For these two reasons the band gap decreased.

![figure 9](image-url)

**Figure 9.** Estimated band gap of (a) pure PbS, (b) 1% La doped PbS and (c) 5% La doped PbS thin films prepared at 500 °C.
3.4. Gas sensing properties

The sensing performance of all the deposited films was measured based on their resistance variation upon absorption and desorption of H$_2$ gas. The baseline value was obtained by measuring resistance of the samples in the absence of hydrogen. Figure 10 shows the sensitivity of pure lead sulfide thin films on exposure to hydrogen gas (H$_2$) at different reaction temperatures. With increase in the reaction temperature, up to 150 °C, the sensitivity of the pure lead sulfide films increased, which means that the optimum operating temperature is probably at 150 °C or above. The temperature dependent sensitivity can be explained based on the kinetics and adsorption/desorption mechanism of the gas to the materials surface. The sensitivity is affected by the speed of the chemical reaction and the diffusion rate of the gas molecules to the surface of material. At low temperatures, the sluggish rate of the chemical reaction and reduced surface adsorption of the gas is responsible for a low response, whereas the rate of reaction and adsorption at surface is much efficient at higher temperature, therefore increasing the sensitivity at elevated temperatures.

Similarly, figure 11 shows sensitivity of La doped PbS thin films, with different concentrations of La at different temperatures, the figures are arranged in increasing order of concentration from left to right at a temperature. Increase in temperature for a doping concentration is depicted from top to bottom. As clearly observed the resistance of all samples decreased by the introduction of the gas to the reaction chamber. Such reduction in resistance, as indicated by the literature, ensures the n-type behavior of lead sulfide by exposure to a reducing gas [33]. In n-type semiconducting materials, electrons are the majority charge carriers, and such materials upon interaction with the reducing gas, results in an increase in the conductivity (decrease in the resistivity), whereas, the oxidizing gas decreases the overall conductivity (increase in the resistivity) by diminishing the sensing layer of the charge carrying electrons from the surface. Likewise, a p-type semiconductor is a material that conducts through the movement of positive holes, as a result reverse effects are observed with the material. Therefore, the conductivity of p-type semiconductor will be increased in the presence of an oxidizing gas (whereby the gas increases the number of positive holes) [34], and the reducing gas will result in decrease in conductivity (high
resistivity), by providing the negatively charged electrons into the material, thereby decreasing the overall positive (hole) charge carrier concentration.

Figure 11. Gas sensing response of La-doped PbS thin films at different temperatures.

Figure 12 shows the sensitivity performance of the samples at different temperatures (50-150 °C). The sensitivity was measured by using the following eq. 11 [35];

\[ S = \frac{R_g - R_o}{R_o} \times 100 \]  

(11)

Where \( R_g \) is the resistance of the target gas and \( R_o \) is the resistance under \( \text{N}_2 \) atmosphere. It is clearly observed that doping increases the sensitivity of the PbS thin film. By increasing the doping ratio of lanthanum from 1 to 10%, the optimum working temperature is shifted from 150 °C to 50 °C. For gas sensing phenomena the surface interaction must not be neglected, considering what happens when \( \text{H}_2 \) gas interacts. Firstly, the presence of lanthanum plays an important role for hydrogen sensing, as it helps in the ionization of \( (\text{H}_2 \text{ to } 2\text{H} + \text{e}^-) \) [36]. The lanthanum on the surface of the lead sulfide thin film forms Schottky junctions and take electrons from lead sulfide, resulting in an increase in widths of the interfacial electron depletion regions. Hence, the lead sulfide thin film become more sensitive to adsorb the gas on the surface on picking electrons. Therefore, it can be suggested that lanthanum can help in the dissociation-ionization mechanism of \( \text{H}_2 \) gas. Also, when lead sulfide thin films interact with the target gas, it directly diffuses to the interior part filling the lattice vacancies. This removes the holes formed and increases the charge carrier concentration. These effects accompanied with the reduction in the particle size causes an increase in the sensitivity of doped thin films.
Figure 12. Sensors sensitivity behavior of pure and La-doped PbS thin films at different temperatures.

4. Conclusion
Pure PbS and lanthanum doped PbS thin films have been fabricated by the spray pyrolysis technique at temperatures of 450 and 500 °C, with a doping concentration ratio of 1, 5 and 10% for La. The sensor materials have been exposed to the target gases with concentration of (200 ppm) mixed with certain amount of dried air. The sensing performance of the films have been tested at temperatures of 50, 80, 120 and 150 °C where it was found that doping increases the sensitivity of the PbS thin film. The synthesized materials showed comparable activity to other sensing materials prepared by different synthetic ways. All films have large surface area and good sensing behavior near room temperature without the need to apply external voltage to enhance the electrons movement.

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