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Facile method of preparation of PbS films for NO₂ detection

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Abstract

Simple and inexpensive chemical bath deposition method was employed for the preparation of lead sulfide (PbS) thin films. Thin films of PbS were characterized using XRD, SEM, TEM, SAED, contact angle and two probe techniques. The gas sensing properties of PbS thin films ($t = 0.443 \mu\text{m}$) have been investigated for H₂S, NH₃, C₂H₅OH, CH₃OH, Cl₂ and NO₂. PbS thin films have been found to be highly sensitive and selective towards oxidizing NO₂ gas than the other test gases. The PbS sensor exhibits the maximum response of 74% towards 100 ppm of NO₂ gas with response time of 20 sec. PbS thin films are able to detect up low 5 ppm NO₂ concentration at room temperature with excellent reproducibility and stability. The sensing mechanism of PbS thin films towards NO₂ gas is also discussed. The interaction of NO₂ gas with PbS film was also investigated using impedance spectroscopy.

Keywords: Electronic materials; Chemical synthesis; Impedance spectroscopy;

Electrical properties; Sensors;

1. Introduction

In recent years, a tremendous amount of studies have been carried out on various materials as gas sensors due to the increasing concerns of environmental and health protection as well as accidental leakages of explosive gases. Now a day's, current research in the field of gas sensors has been focused on the development of low cost and highly sensitive efficient sensor devices for monitoring of hazardous, corrosive, toxic and flammable gases. Nitrogen dioxide, NO_2 , is one of the toxic, harmful and foul-smelling gases and is created during the several processes such as the high temperature combustion of coal, combustion of gasoline in internal combustion engines, home heaters, natural gas or oil in power plants, exhaust of furnaces, chemical production and also by the automobile engines [1-3]. Nitrogen dioxide is a main cause of acid rain and formation of photochemical smog as well as NO_2 is involved in the depletion of ozone in the stratosphere [2, 4]. Therefore, it is necessary to develop efficient devices which can sense toxic and corrosive NO_2 gas at low level (\sim ppm). Over the past few years, use of nanostructured inorganic semiconductors in a sensing material has attracted much attention of researchers because of their unique electrical and optical properties. Furthermore their low cost, ease of production, simplicity and capability of detecting large number of toxic as well as flammable gases under different conditions makes them suitable candidate in gas sensor field [5,6]. It is well known that, inorganic semiconductor based gas sensors involve a catalytic reaction (reduction or oxidation) of the target gas on the surface of the sensor.

Lead sulfide (PbS) is a typical direct narrow band gap IV–VI compound semiconductor, which possess special optoelectronic properties and found wide applications in optical communication apparatus, radioactivity detector and optical information storage [7-9]. Furthermore, PbS consists of large excitation Bohr radius (18 nm), which results in good quantum confinement of both

holes and electrons in nanosized structure. Therefore, according to the effective mass model the value of the band gap can be easily controlled by modifying the particle shape as well as the size. Therefore, the preparation of PbS thin film interests is growing in developing new processing routes. Currently, different techniques are in use for the fabrication of desirably shaped and structured thin films including chemical and physical methods. Chemical methods are economic and inexpensive as well as beautiful thin film structures can be obtained with them. Furthermore, physical methods are suitable for the fabrication of uniform and high quality thin films. But, these methods are expensive and highly energy consuming [10]. In recent years, various techniques have been used to deposit PbS thin films including microwave assisted chemical bath deposition [11], successive ionic layer adsorption and reaction (SILAR) technique [12], hydro chemical deposition [13], atomic layer epitaxial process [14], pulse electrodeposition [15], chemical bath deposition [16] and solid-vapor deposition [17].

Among these various techniques, chemical bath deposition method also called as chemical solution deposition technique have a several advantages and is widely used for thin film deposition because of its low temperature operating condition, low cost, no requirement of sophisticated instruments, freedom to deposit materials on a variety of substances suitability for large scale deposition areas, ability of tuning thin film properties easily by adjusting and controlling the deposition experimental parameters and non-polluting properties [18-20]. Normally, lead sulfide is used as an optical and a semiconductor material as well as photoconductive devices as detectors [21]. Very few reports are available on the application of semiconducting lead sulfide as a gas sensor. Shimizu et al [22] reported SO₂ gas sensing properties of Pb_{1-x}Cd_xS ($x = 0.1, 0.2$) system and the metal-mono sulfide based (NiS, CdS, SnS and PbS) solid electrolyte sensor elements operating in between 300°– 400°C. Fu [23] reported,

the NO₂ and NH₃ gas sensing properties of lead sulfide prepared by precipitation method at various operating temperatures with 5V operating voltage. Markov et al [24] reported the NO and NO₂ gas sensing properties of iodide doped lead sulfide films by chemical deposition method. While, Karami et al [25] reported the ammonia sensing properties of lead sulfide nanostructures prepared by chemical precipitation method. However, so far there is no report available on the preparation of lead sulfide by chemical bath deposition method and their room temperature NO₂ gas sensing properties at low concentration (5-100 ppm).

In the present paper, we demonstrate gas sensing properties of nanocrystalline PbS thin films prepared by simple and low cost chemical bath deposition method to develop a reliable, sensitive and low cost chemical sensor for monitoring nitrogen dioxide. Thin films of PbS have been characterized using XRD, FESEM, TEM, SAED and two probe techniques. Various reducing and oxidizing gases such as NH₃, H₂S, CH₃OH, C₂H₅OH, NO₂ and Cl₂ were used as target gases. The systematic gas sensing performance of PbS thin films was carried out at room temperature and explored. Also the plausible sensing mechanism between PbS thin film and NO₂ gas is discussed using impedance spectroscopy.

2. Experimental details

2.1 Materials

Lead acetate (AR grade, Sd Fine Chem. Ltd., India), Thiourea (AR grade, Sd Fine Chem. Ltd., India), ammonia (30% AR grade, Sd Fine Chem. Ltd., India), hydrochloric acid (AR grade, Sd Fine Chem. Ltd., India).

2.2 Preparation of nanocrystalline PbS thin films

Thin films of lead sulfide were deposited on commercially available glass slides of the dimensions of 7.5cm × 2.5cm by inexpensive chemical bath deposition method. For the thin film

formation, 0.005M of lead acetate was complexed with 0.15M of thiourea [CS (NH₂)₂] with vigorous stirring. The glass substrates were vertically immersed in magnetically stirred bath solution. The pH of the solution was maintained at 10-11 by adding ammonia as a complexing agent. The deposition was carried out at temperature of 60°C for 40 min. After a 40 min. deposition time, the glass substrates were removed from bath and washed thoroughly with distilled water and dried in air. It was observed that, chemical bath deposited PbS thin films are uniform, dark brown colored and well adherent to the glass substrate.

2.3 Characterization techniques

The structural properties of the prepared PbS thin films were carried out using X-ray diffractometer (Model: PW-3710, Holland) at step width of 0.02°/min. in 2θ range of 10°–80° with CuK_α radiation (λ = 1.5406 Å). The surface morphology of the prepared samples were analyzed using scanning electron microscopy (SEM, Model: Model: JEOL JSM 6360) operating at 20 kV. The Transmission electron microscopy and selected area electron diffraction of PbS film was carried out using Hitachi Model H-800 transmission electron microscopy. DC electrical conductivity and thermoelectric power measurement was carried out using two-point probe technique. The thickness of the as deposited films was measured using an Ambious XP-1 surface profilometer and it is found to be 0.449 μm.

Gas sensing characteristics of the prepared films was measured using custom fabricated room temperature gas sensing measurement unit described elsewhere [6]. The electrical resistance of a sensor films was measured in gas and in air atmosphere. In order to measure resistance of the films two silver electrodes separated by 10 mm each other were deposited on PbS thin film using silver paint and dried in air atmosphere. Various reducing viz. H₂S, NH₃, CH₃OH, C₂H₅OH, and oxidizing gases as NO₂ and Cl₂ were used as test gases. All these test gases were commercially

procured from Space Cryogases Pvt. Ltd. Mumbai, India. For the measurements of gas sensing properties, sensor films were mounted in an airtight stainless steel chamber having volume of 250 cm³. Desired concentration of a various test gases in the airtight stainless steel chamber was attained by introducing a measured quantity of known gas using a syringe. The change in resistance value of the sensor films were recorded using a Keithley 6514 System Electrometer controlled by a computer. Once resistance stability was achieved, sensor recovery was measured by opening the lid of the chamber to air atmosphere. All the gas sensing measurements on PbS thin films were carried out at room temperature. It was observed that, on exposure to oxidizing gases (NO₂ and Cl₂) the sample resistance was found to be decreasing ,while on exposure to reducing gases (NH₃,CH₃OH, C₂H₅OH and H₂S) the sample resistance increases, as expected for p-type nature of as synthesized PbS.

The response (S) was calculated using the relation,

$$S (\%) = |R_a - R_g| / R_a * 100 \quad \dots (1)$$

where, 'R_g' is resistance of the sensor in test gas and 'R_a' is resistance of the sensor in air atmosphere.

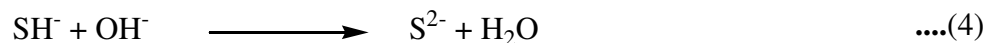
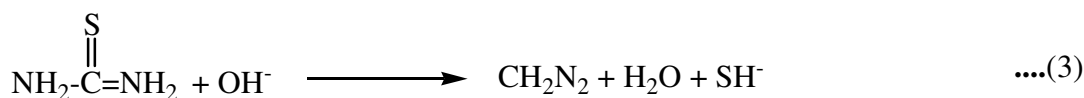
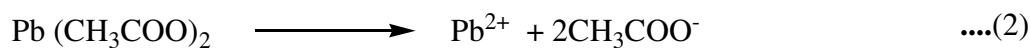
Impedance studies on PbS thin film in air and in gas environment was carried out using Wayne Kerr make precision impedance analyzer (Model: 6500-B) in the frequency range of 20 Hz to 10 MHz. All the measurements were carried out at room temperature (311K).

3. Results and discussion

3.1 PbS thin film formation mechanism

It is well known that, in chemical bath deposition method film formation takes place when the product of concentrations of cations and anions exceeds the solubility product. In other words, when solution supersaturates then ionic product of cation and anion is greater than the solubility

product [26]. Here, lead sulfide is formed when the ionic product of Pb^{2+} and S^{2-} ions exceeds the solubility product of PbS. Therefore, the concentration of lead and sulphur ions controlled very carefully during the growth. The formation of PbS may involve sequential reactions at the substrate surface and is enlightened in the following steps. When lead acetate [$\text{Pb}(\text{CH}_3\text{COO})_2$] dissolved in aqueous solution then releases Pb^{2+} ions. Dissociations of thiourea [$\text{CS}(\text{NH}_2)_2$] occur due to the addition of ammonia resulting into formation of SH^- ions, which then reacts with hydroxide species to give S^{2-} anions. Finally, PbS thin film is formed when Pb^{2+} cations are adsorbed on the substrate and combines with S^{2-} anions. The overall growth occurs by ion-by-ion process on the substrate and the corresponding reaction mechanism is as follows [27]:



3.2 X-ray diffraction analysis

X-ray diffraction pattern of PbS thin film deposited on glass substrate by chemical bath deposition method is shown in Fig 1 (a). In the XRD pattern of PbS, the observed broad hump is due to amorphous glass substrate [26]. Nanocrystalline PbS thin film shows prominent diffraction peaks at $2\theta = 26.60^\circ$, 30.70° , 43.62° , 51.42° , 53.90° , 62.85° , 69.15° , 71.30° and 79.30° are assigned to the scattering from (111), (200), (220), (311), (222), (400), (311), (420) and (422) planes of the cubic PbS structure respectively, which are well matched with the reported values for PbS [JCPDS card no. 78-1899]. The calculated lattice constant is found to be 5.88 \AA and which is close to the JCPDS file [$a=b=c=5.92 \text{ \AA}$]. A preferred orientation of the deposited PbS

thin film is observed along (1 1 1) direction. Therefore, the crystallite size for PbS thin film was estimated using the full width at half maximum (FWHM) towards (1 1 1) peak from the well known Debye-Scherrer's formula [Eqⁿ-(6)] and it was found to be 38 nm.

$$D = K\lambda/\beta \cos\theta \quad \dots(6)$$

where, 'D' is the crystallite size, 'β' is the full width at half maximum of X-ray peak in radians, 'K' is the correction factor taken as 0.90 in the calculation and 'λ' is the wavelength of CuK_α (1.54Å) source used [28]. Similar type of XRD results for chemical bath deposited PbS thin films have been reported [16, 20, 25, 27].

3.3 SEM analysis

The surface morphology of the nanocrystalline PbS thin film was analyzed using scanning electron microscopy (SEM) and displayed in Fig1(b). The deposited film under the optimized conditions was uniformly covered the substrate surface with good adherence. The micrograph of PbS thin film revealed that, a large number of tiny spherical type nanograins are interconnected each other with some pores are available between them.

The thickness of chemically deposited PbS thin film also determined by SEM cross section.

Fig 1 (c) shows SEM cross section of PbS film and thickness of PbS is 0.441μm. It is well match with thickness obtained from thickness profiler.

3.4 TEM and SAED analysis

Transmission electron micrograph (TEM) and selected area electron diffraction (SAED) pattern of PbS film is shown in Fig 2. The TEM image of PbS film in Fig 2(a) shows that, interconnected spherical nanoparticles with an average particle size of 41 nm. Selected area electron diffraction pattern of the PbS thin film in Fig 2(b) showed five clear diffraction rings, which corresponded to the (111), (200), (220) (331) and (222) planes of the cubic PbS

respectively. This is in good agreement with the XRD analysis results and indicated that, the PbS nanoparticles are well crystallized.

3.5. Surface wettability study

The as deposited PbS thin film was used in wettability study (water contact angle measurement). When the air is the surrounding medium, the wettability of PbS with water is dependent on the relationship with the interfacial tensions (water/air, water/ solid and solid/air). The ratio between these tensions determines the contact angle ' θ ' between a water droplet on a PbS surface. If the water contact angle is 0° indicate that the surface is completely wet (super hydrophilic) , and if the water contact angle is 180° means that the surface is not completely wet(super hydrophobic).The both super-hydrophilic and super-hydrophobic surfaces plays important role in gas sensing applications. Prior to contact angle measurements or treatment, film was rinsed with acetone and de-ionized water. The average contact angle was obtained by measuring for at least five separate drops on each sample surface by delivering de-ionized water with a microsyringe. Measurement of surface water contact angle is inversely proportional to the wettability and can be determined by Young's relation. Fig 2(c) shows the water contact measurements for PbS thin film.

From Fig 2 (c) it is observed that, the PbS thin films are hydrophilic as water contact angle is 75° (less than 90°) means high wettability. This may be due to the strong cohesive force between the water droplet and hydroxide present in the lead sulfide. Due to which the water is attracted rather repelled by the PbS film. This specific property is useful for making intimate contact with electrode surface in gas sensing application. We believed this specific property will tentatively demonstrate the feasibility of PbS film surface useful in material /electrode contact for better performances.

3.6 Electrical transport studies

3.6.1 DC electrical conductivity

Temperature dependent dc electrical conductivity of PbS thin films have been measured by using two probe technique in the 303 - 473 K temperature range and it was observed that as temperature decreases, the electrical resistance of PbS thin film increases indicating the semiconducting behavior of as synthesized PbS thin films [27, 28]. By using the temperature dependence of electrical conductivity data, the activation energy (E_a) for PbS thin films was estimated using the relation:

$$\sigma = \sigma_0 (-E_a/K_b T) \quad \dots(7)$$

where, ' σ_0 ' is a constant, ' K_b ' is the Boltzmann's constant and ' T ' is absolute temperature.

Fig 3(a) shows the plot of logarithmic conductivity as a function of inverse temperature and from the slope of this curve activation energy was calculated. The activation energy represents the location of trap states below the conduction band and it is 0.7 eV.

3.6.2 Thermoelectric power (TEP) measurement

The p-type semiconducting nature of chemical bath deposited PbS thin films was confirmed using thermoelectric power (TEP) measurement analysis. In case of TEP measurement, the temperature difference (ΔT) causes the transport of carriers from the hot to cold end, which creates an electric field and gives thermo-emf across the two ends (ΔV). Generated thermo-emf is directly proportional to the temperature gradient across the semiconductor. The plot of thermo-emf as a function of temperature is shown in Fig 3(b). The plot clearly shows linear increase in thermo-emf with increase in temperature. Type of conductivity was decided from the sign of thermo-emf generated across the ends. In the present case polarity of thermally generated voltage for PbS thin film is negative towards hot end with respect to cold end confirming the p-type

conductivity of the film. The similar type of results was reported for PbS and NiO films deposited by chemical bath deposition and sol-gel spin coating method respectively [27, 29].

3.7 Gas sensing measurement

3.7.1 Selectivity

Room temperature gas sensing properties of PbS thin films were investigated using two probe resistance measurement set up. The ability of a sensor to respond to a certain gas in presence of other gases is called as selectivity and it is a very critical factor for commercial gas sensors. Therefore for selectivity study, initially the sensing performance of PbS thin films towards fixed 100 ppm concentration of various oxidizing (Cl_2 and NO_2) and reducing gases (NH_3 , H_2S , CH_4OH and $\text{C}_2\text{H}_5\text{OH}$) were studied and the corresponding results are displayed in Fig4(a). It was observed that, PbS thin films shows a maximum response of 74% towards oxidizing NO_2 gas at room temperature compared to other test gases confirming the selectivity to NO_2 . Very less response is observed to Cl_2 , CH_3OH and $\text{C}_2\text{H}_5\text{OH}$ gases. It may be noted that on exposure to oxidizing NO_2 and Cl_2 gases the sample resistance decreases, whereas it increases for reducing gases such as NH_3 , H_2S , CH_4OH and $\text{C}_2\text{H}_5\text{OH}$ indicating p-type conduction in nanocrystalline PbS thin films. Furthermore, the selectivity coefficient (Q) is calculated using the relation,

$$Q = S_A / S_B \quad \dots(8)$$

where, S_A is the response of film to target gas (herein NO_2) and S_B is the response of film to other gas. The estimated Q values are tabulated in Table1. Larger the Q value for a specific gas demonstrates the sensor has a better competency to differentiate the target gas from the mixture gases [4]. Commonly, the selectivity coefficient (Q) of sensors should be more than 5 [30]. It is noted that, chemical bath deposited PbS thin films reach the criterion of selectivity coefficient. Results of selectivity study clearly revealed that, the PbS thin films are highly sensitive and

selective towards oxidizing NO₂ gas at room temperature. Therefore, the further investigations are also carried out for different concentrations of NO₂ gas.

3.7.2 Effect of film thickness and operating temperature on the NO₂ sensing

Fig. 4(b) shows the gas response transients of PbS films of different thicknesses upon exposure to 100 ppm of NO₂ at 311 K. It is evident that the film having thickness of 0.441 μm exhibited the highest response (74%), due to its uniform spherical nanocrystalline structure (about 35–41 nm, see TEM), which offered more efficient surface area for interaction with NO₂ molecules on the surface as well as inside porous structure. The lower response for thickness 0.351 μm is due to non uniform deposition of PbS film. At higher thicknesses 0.724 μm and 0.956 μm the film response was found to be decreased due to non porous morphology.

The inset of Fig.4 (b) shows the variation of gas response (100 ppm NO₂) of PbS film for different temperature. Before exposing to NO₂ gas, the film with thickness 0.441 μm was allowed to be stable for electrical resistance for 30 min and the stabilized resistance was taken as R_a . Initially, the gas response to 100 ppm of NO₂ was measured as a function of operating temperature for film. The sensor response reached maximum at 311K (gas response = 74%) and then decreased at 323K (gas response = 67%). The NO₂ gas molecules possess sufficient thermal excitation energy to react with adsorbed oxygen species at around 311 K. Therefore at that temperature PbS sensor reaches its maximum response as compared to other operating temperature.

3.7.3 Response study to different NO₂ concentrations

Typical response characteristics for PbS thin film exposed to different concentrations (5-100 ppm) of NO₂ gas is shown in Fig 4 (c).

From figure 4 (c) it is observed that, the response value of PbS thin film sensor increases with increasing concentration of NO₂ gas from 5 to 100 ppm at room temperature (311K). Response of the PbS thin films was found to be linear in 5–100 ppm NO₂ range. The responses of PbS thin film on exposure to 5-100 ppm NO₂ gas are 31%, 49%, 54%, 67%, 70% and 74% respectively. Lower NO₂ gas concentration covers the lower surface of PbS film hence lowers the interactions between NO₂ gas and film surface which results into lower response. On the other hand at higher NO₂ concentration increases the interactions between NO₂ and film surface, due to the higher surface coverage and resulting into higher response. The PbS thin film shows the decrease in resistance value on exposure to oxidizing NO₂ gas, which is due to the fact that, electrons of NO₂ act as the acceptor to the p-type PbS, thus causing a increase in hole concentration in PbS and film resistance decreases. PbS thin film exhibits the maximum response of 74% towards 100 ppm of NO₂ gas with very fast response time of 20 second. Such a higher response value is believed to be due to the response of the inorganic semiconductor sensors mainly governed by the interactions between the target gas (herein NO₂) and the surface of the sensors. Furthermore, chemical bath deposited PbS thin films are able to detect up low 5 ppm concentration of NO₂ gas with very high response of 31%, suggesting their suitability to be used as NO₂ sensor. The electrical response of PbS thin film towards different concentrations of NO₂ is shown in Fig4 (d).

3.7.4 Response and recovery times

The response and recovery time is an important consideration for characterizing a sensor. The response and recovery times for PbS thin films to different concentrations of NO₂ were depicted from the electrical response curve (Fig 4 (d)) and presented in Fig 5 (a). It was observed that as the concentration of NO₂ increases from 5-100 ppm, response times decreases from 35 sec. to 20

sec. and recovery times increases from 314 sec. to 1477 sec. The decrease in response time may be due to the availability of vacant sites on thin films for adsorption of gas. However, the observed behavior of increasing recovery time with increasing NO₂ concentration is similar to that of our previous report on α -Fe₂O₃ [6] and SnO₂ [31]. This may be probably due to, the reaction product's not leaving the lead sulfide surface immediately after the reaction and therefore the re-adsorption of oxygen is delayed, resulting in a longer recovery time.

3.7.5 Reproducibility and stability study

Reproducibility and stability of the sensor material is also an important consideration in the practical use of chemical sensors. Fig 5(b) shows the repetitive electrical response for PbS thin film upon periodic exposure of 100 ppm NO₂ gas. For reproducibility study, repeating the response measurement for three times. It was observed that, PbS thin film exhibits the same response upon repeating the 100 ppm NO₂ concentration and which confirms the excellent repeatability of the sensor material.

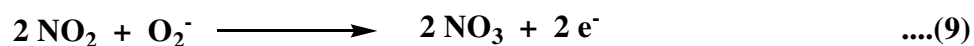
Stability performance of PbS thin films were studied for fixed 100ppm NO₂ concentration over the period of 40 days and corresponding results are displayed in Fig 5(c). Initially PbS thin film exhibits the response of 74%, but it drops (74% to 66%) with time and stable response was attained after 15 days with 89% stability.

Finally, the present work demonstrates competitive results on the highly sensitive and selective room temperature (311 K) NO₂ gas sensing properties of PbS thin films prepared by simple and inexpensive chemical bath deposition method. The sensor shows linear variation in response between 5-100 ppm NO₂ concentrations with very fast response time and long term stability. Most important, our PbS thin films are strongly adherent to the glass substrate and exhibits

excellent reproducibility in response. Such a material with excellent gas sensing properties is suitable for detecting lower concentrations of NO₂ at room temperature (311k).

3.7.6 Sensing mechanism

It is observed that, chemical bath deposited PbS thin films produced the sudden decrease in the value of resistance on exposure to oxidizing NO₂ gas molecules. Such an observed change in the resistance value is mainly due to the adsorption of NO₂ gas on the surface of PbS thin film. Based on the gas sensing results, we made an attempt to propose the following mechanism of NO₂ gas detection. Generally, inorganic materials can adsorb oxygen from the air such as the O²⁻, O₂⁻ and O⁻ species and relative changes occurs due to adsorption of oxygen. Oxygen can be adsorbed into following three manners depending upon the temperature [32]. Oxygen has O₂⁻ character in the temperature range <100°C. In the temperature range 100-300°C, oxygen has O⁻ character and for temperature >300°C, oxygen has O²⁻ character [32]. In the present study, operating temperature is room temperature (<100°C) therefore, the adsorbed oxygen is in the O₂⁻ form. It is well-known that, PbS is a P-type semiconductor with holes as majority carriers [24, 25, 27]. In air atmosphere (before exposing to NO₂), PbS grains adsorbs oxygen (O₂⁻) from the air ambient and creates the surface states. This created surface state allows the electrons to be excited from the valance band and which results in the more holes are induced in the p-type PbS grains. Due to the adsorbed oxygen species an accumulation layer is formed around the surface of PbS grain and this procedure is explained via a schematic, displayed in Fig 6(a). When the NO₂ gas molecules are exposed towards PbS grains then it reacts with a adsorbed O₂⁻ species via a reaction:



The released electrons from surface states are recombine with the holes in the valance band and therefore film resistance decreases due to the oxidizing nature (electron accepting) of NO_2 . If PbS thin film is exposed to fresh air atmosphere and NO_2 is removed then the recovery process of sensor is achieved. During this reaction, the thickness of accumulation layer decreases (Fig.6 (b)) and which leads to an increase in conductance of the material. The attractive feature of the PbS thin film sensor is its room temperature (311 K) operation, fast response time and the reproducible response characteristics. This may increase shelf life of sensor and makes it reusable.

3.8 Impedance spectroscopy studies

Impedance spectroscopy is a useful technique that has been widely used to distinguish different contributions to sensor response [33]. In the present study, in order to understand the better response of PbS thin films towards NO_2 gas, we have carried out impedance spectroscopy study, before and after exposure of 100 ppm NO_2 gas at room temperature (311 K) and the corresponding results are shown in Fig7(a) in the form of cole-cole plot. The impedance spectra clearly show a single semicircle arc from low frequency to high frequency region. The impedance spectrum was analyzed by using the equivalent circuit shown in Fig 7(b). It consists of two RC networks, in which R_0 is frequency independent resistance, R_b is bulk resistance, C_b is bulk capacitance, R_g is grain boundary resistance and C_g is grain boundary capacitance. Values of various parameters obtained from impedance spectra are given in Table 2.

From Fig 7(a) it is also seen that, there is very good agreement between the simulated data (shown by solid lines) and experimental data.

On exposure to 100 ppm NO_2 , both R_b and R_g were seen to decrease while C_b and C_g were found to increase. Based on the obtained results sensing mechanism can be proposed as follows;

PbS grains contains significant fraction of O_2^- adsorbates at grain boundaries which trap electrons from the grains of PbS results in increasing carrier density and conductivity of intergrain region. On the interaction of PbS film with oxidizing NO_2 gas, adsorbed oxygen on the grain boundary of the PbS film is replaced by gaseous species. Due to electron accepting nature of NO_2 the resistance of PbS film decreases. Such decreases in resistance on NO_2 exposure is mainly contributed by the grain boundaries of the PbS films.

4. Conclusions

The present paper demonstrates room temperature (311K) gas sensing performance of PbS thin films for different gases viz, Cl_2 , NH_3 , H_2S , NO_2 , CH_3OH and C_2H_5OH . The gas sensing studies shows that, the chemical bath deposited PbS thin films are highly sensitive and selective towards NO_2 gas with 74% (towards 100 ppm) response. However, PbS sensor exhibits reasonably fast response time of 20 sec. A noteworthy feature of the present work is that, the prepared PbS thin film sensors operate at room temperature and are able to detect up low 5 ppm NO_2 concentration with reasonable response of 37%. Furthermore, PbS thin films exhibit excellent repeatability with 89% stability. The reliable detection of NO_2 gas in low ppm level using PbS thin film makes them attractive candidate for high performance selective NO_2 gas sensors.

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Table captions:

Table1: Q values of PbS thin film sensor for NO₂ as a target gas.

Table2: Parameters obtained by fitting experimental curve to equivalent circuit.

Figure captions:

Fig.1. (a) X-ray diffraction pattern of PbS thin film, (b) SEM micrograph of PbS thin film,
(c) SEM Cross section of PbS thin film.

Fig.2. (a) TEM image of PbS thin film, (b) SAED pattern of PbS film,
(c) Contact angle of PbS thin film.

Fig.3. (a) Inverse temperature dependence of logarithmic conductivity for PbS thin film,
(b) Variation of thermo-emf with temperature for PbS thin film.

Fig.4. (a) Selectivity study for PbS thin film towards 100 ppm of various gases,
(b) The response transients of PbS films of different thickness with time 38 °C for the exposure of 100ppm NO₂. Inset: The variation of NO₂ response with PbS films of different temperature.
(c) Response of PbS thin film towards different concentrations of NO₂, (d) Change in resistance of PbS thin film as a function of time towards various concentrations of NO₂

Fig.5. (a) Response and recovery times for PbS thin film towards 5-100ppm NO₂,
(b) Repetitive response of PbS thin film as function of time towards 100 ppm NO₂.
(c) Stability study of PbS thin film towards 100 ppm NO₂.

Fig.6. Schematic showing (a) interaction between oxygen and PbS grain and corresponding energy band diagram (E_{SS} = surface states); (b) interaction between NO₂ and PbS grain and corresponding energy band diagram.

Fig.7. (a) Impedance spectra of PbS film before and after exposure to NO₂,
(b) Equivalent circuit used to interpret the impedance spectroscopy data obtained for PbS.

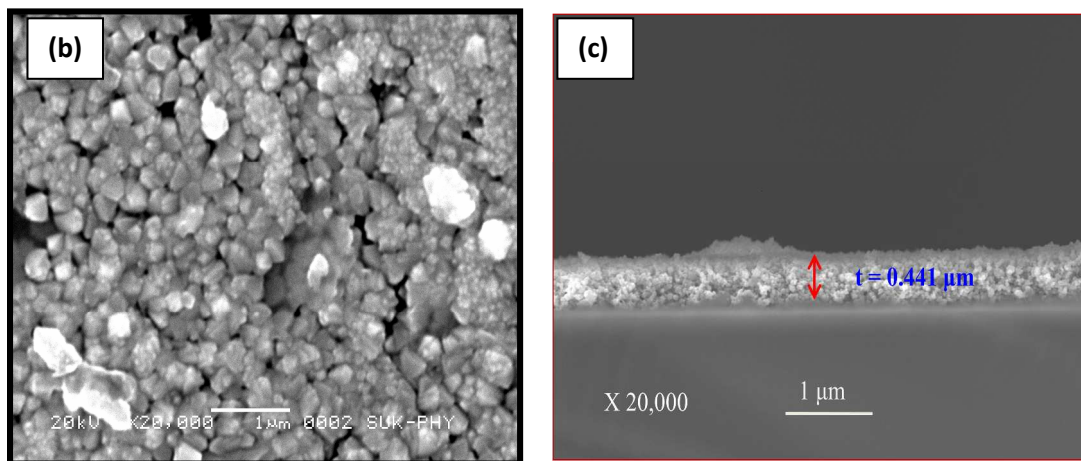
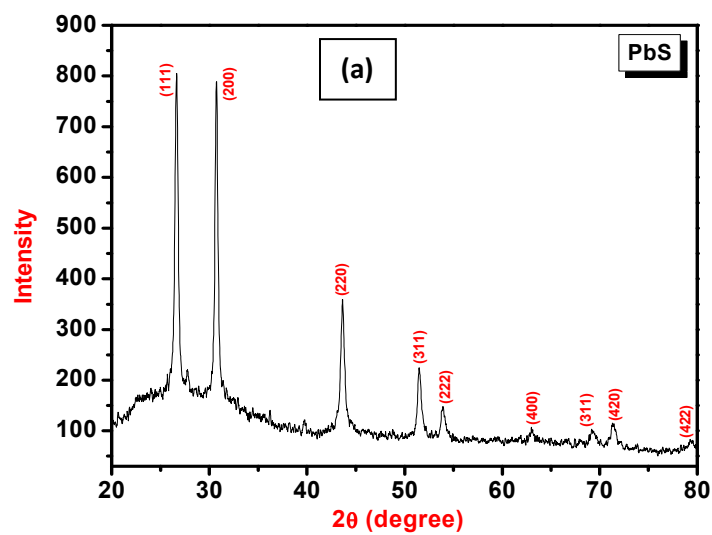


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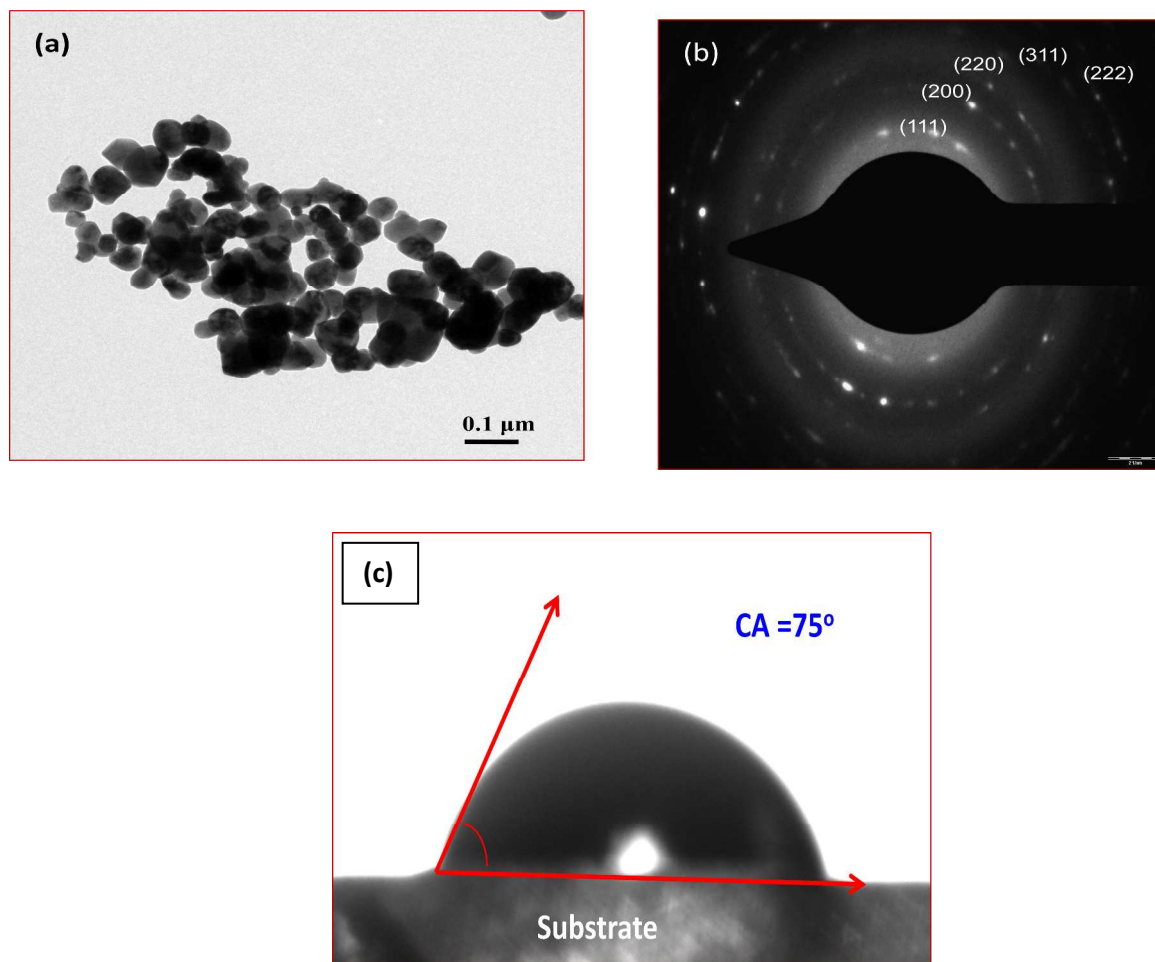


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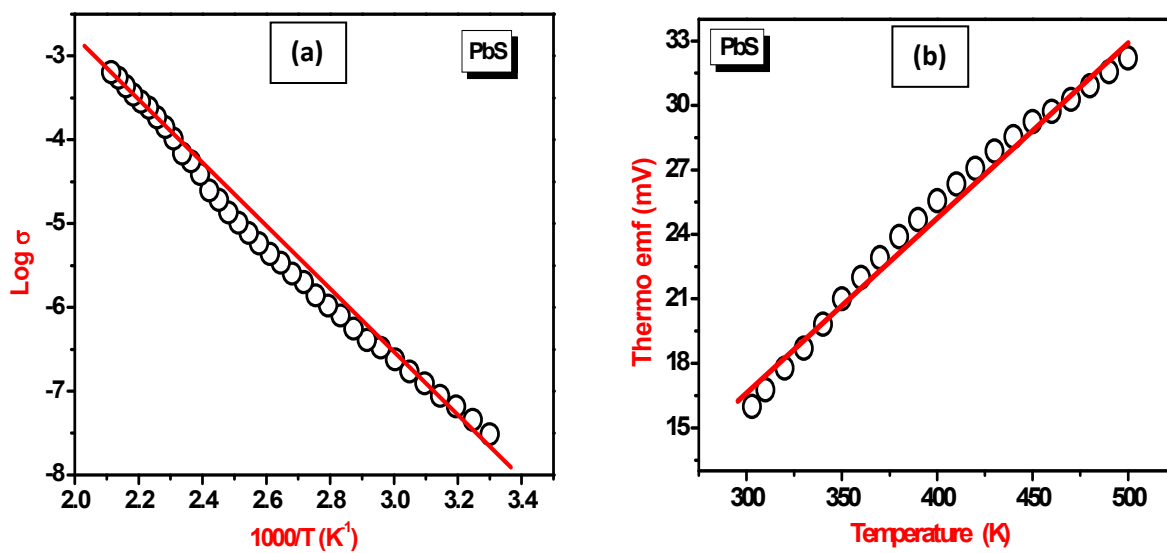


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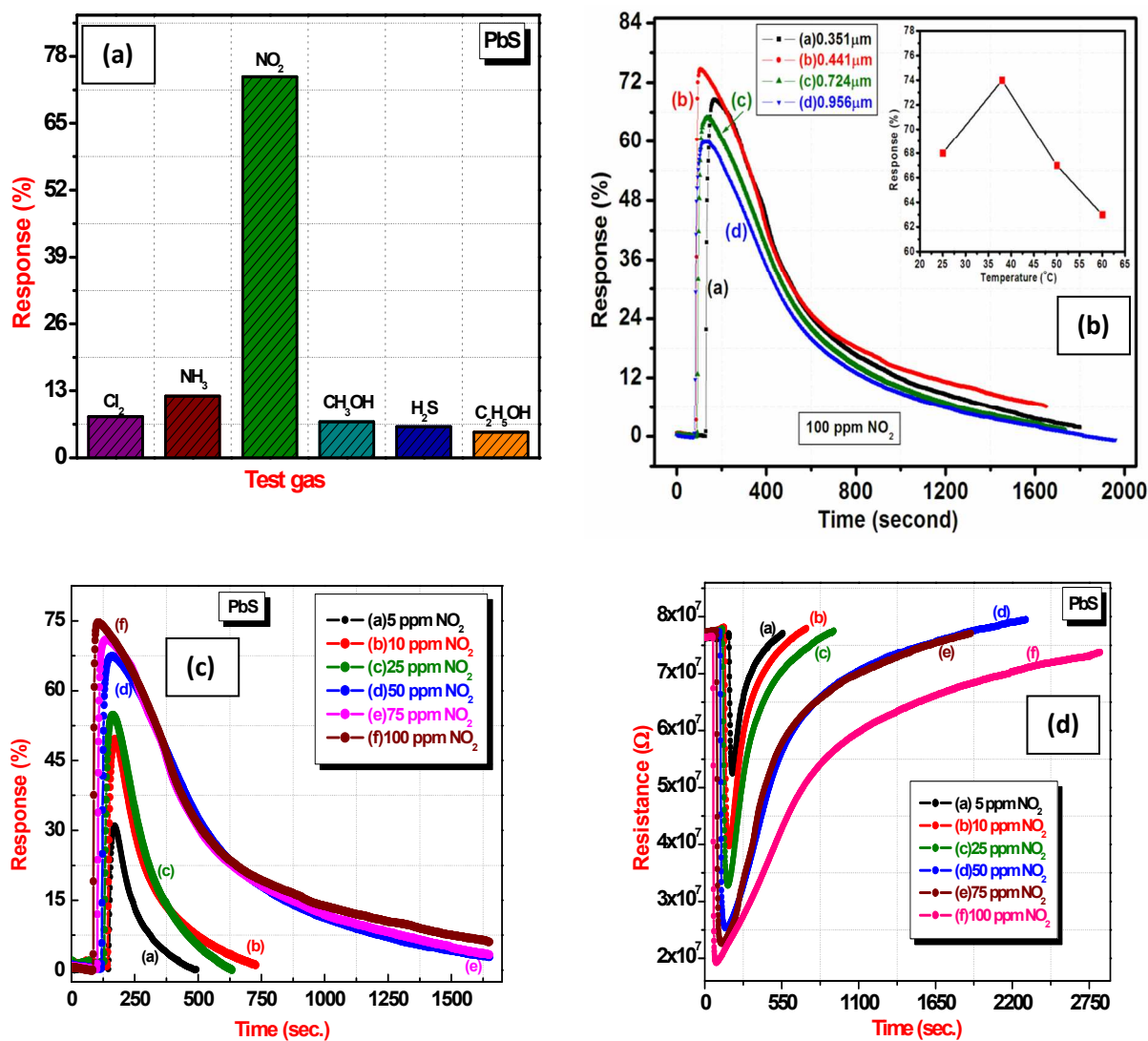


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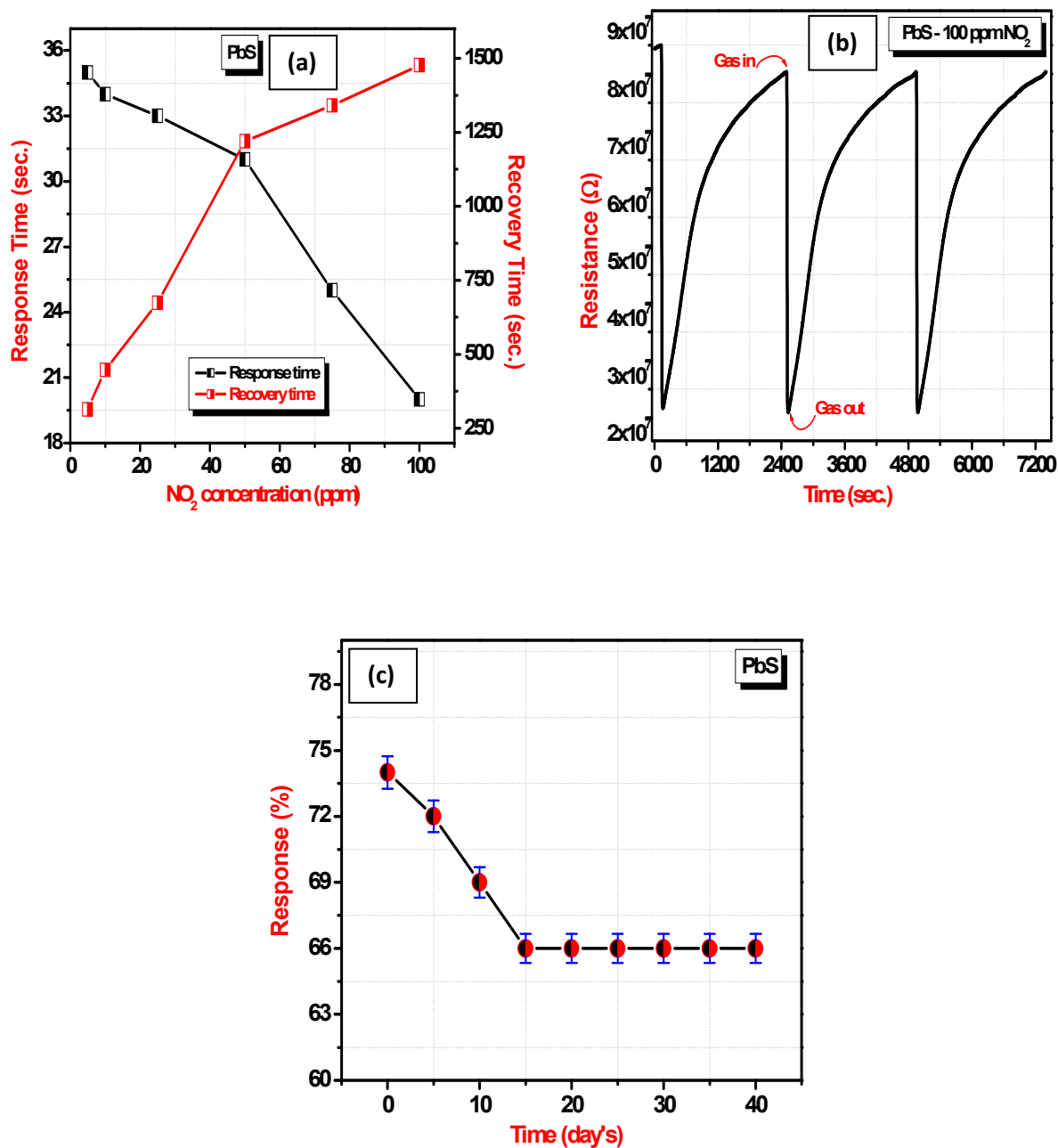


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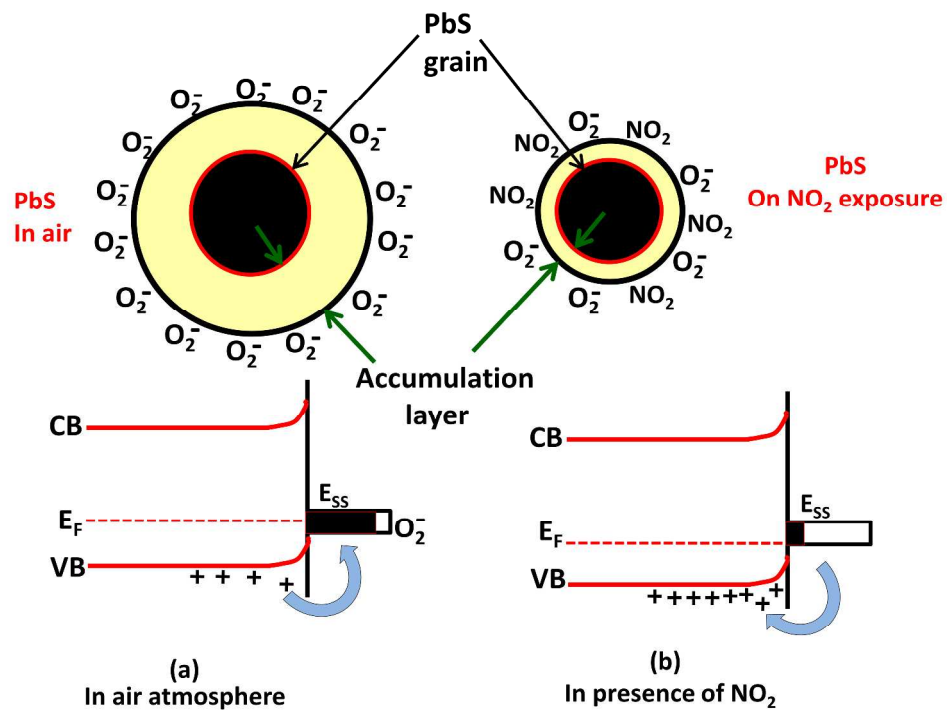


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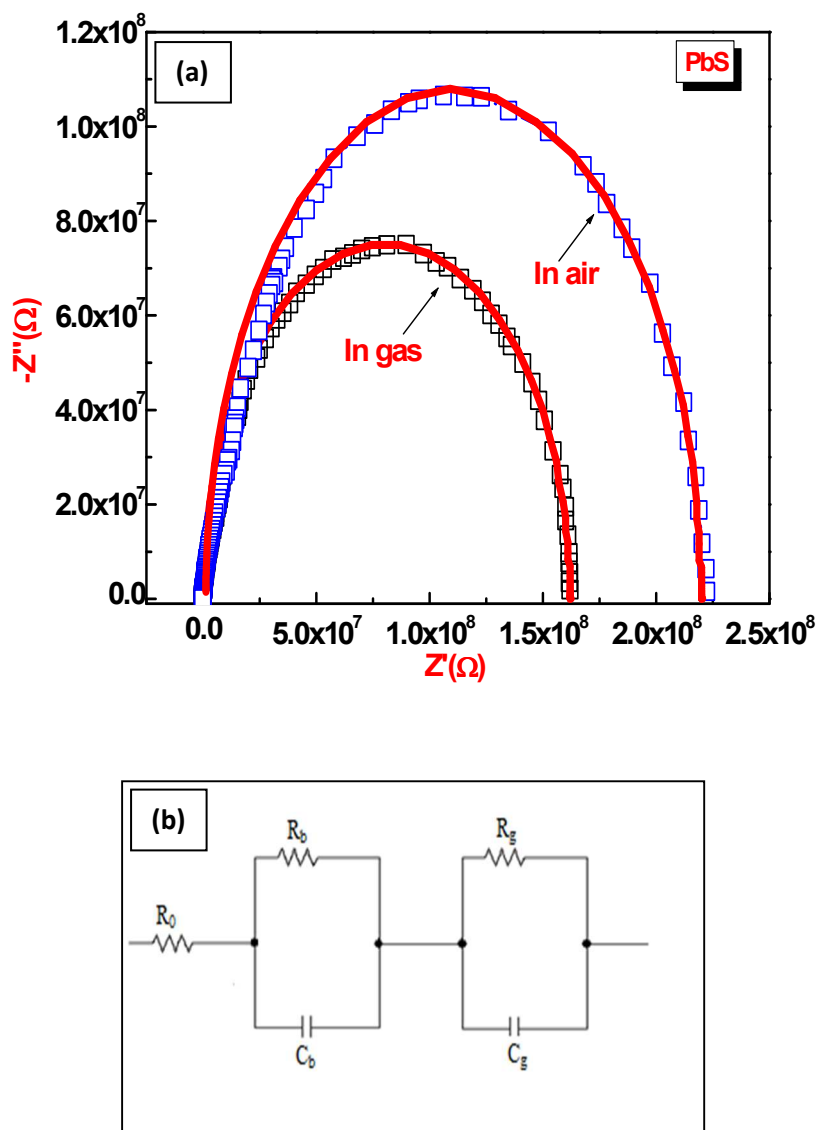


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Table1: Q values of PbS thin film sensor for NO₂ as a target gas.

Test gas	NH ₃	H ₂ S	C ₂ H ₅ OH	Cl ₂	CH ₃ OH
'Q' value	6.16	12.33	14.8	9.25	10.57

Table2: Parameters obtained by fitting experimental curve to equivalent circuit.

Parameter →		R₀	R_b	C_b	R_g	C_g (pF)
Condition	Unexposed	1 MΩ	94 MΩ	2.2pF	124MΩ	2 pF
	Exposed to 100 ppm NO₂	1 MΩ	79 MΩ	299nF	82 MΩ	132nF