

# Density functional theory of influence of methane adsorption on the electronic properties of a PbS cluster

A MOSAHEBFARD<sup>1</sup>, R SAFAIEE<sup>2</sup> and M H SHEIKHI<sup>1,\*</sup>

<sup>1</sup>Research Laboratory for Fabrication of Advanced Semiconductor Devices, School of Electrical and Computer Engineering, Shiraz University, Shiraz, Iran

<sup>2</sup>Faculty of Advanced Technologies, Shiraz University, Shiraz, Iran

\*Corresponding author. E-mail: msheikhi@shirazu.ac.ir

MS received 20 July 2018; revised 23 November 2018; accepted 29 November 2018;  
published online 4 May 2019

**Abstract.** The effect of methane adsorption on the electronic properties of a lead sulphide (PbS) cluster is investigated using density functional theory (DFT) when an oxygen molecule was previously adsorbed to the cluster. This paper studies how the pre-adsorption of oxygen influences the tendency of PbS cluster to adsorb CH<sub>4</sub> and variations of its electronic properties due to CH<sub>4</sub> adsorption. Further investigation on how these variations occur was carried out by charge transfer calculations. The discussion based on the results of this study succeeded in explaining the previously reported experimental observations.

**Keywords.** Lead sulphide; methane gas sensing; room temperature; density functional theory.

**PACS Nos** 31.15.E–; 73.22.–f; 07.07.Df

## 1. Introduction

Monitoring of methane concentration is very important in petrochemical and oil refinery complexes, coal mines and so on, because methane can cause explosion or even suffocation in humans if the concentration level exceeds beyond 5% in air [1–3]. Moreover, methane detection in ppm levels is important in medical diagnostic tests [4,5]. There are, instantly, some applications of ppm-level detection of methane in medical diagnostic laboratory tests [4,5].

Among various methane gas sensors, the semiconductor gas sensors have certain advantages such as simplicity of application in gas monitoring and control systems, and cost-effective compared to other types of gas sensors. However, some drawbacks such as high operating temperature and non-reversibility of some materials limit their usage in some industrial applications [6–8]. Using nanofabricated sensing materials in many semiconductor gas sensors have improved their properties such as operating temperature, sensitivity, selectivity and so on [9–17]. Recent studies have revealed the capability of PbS in sensing some gases such as NH<sub>3</sub>, NO<sub>2</sub>, H<sub>2</sub>S and so on [18–24]. Fabrication of gas sensors, based on PbS in its nanocrystalline

form, has also revealed good sensing characteristics [25–27].

We have recently reported the fabrication of a methane gas sensor based on PbS nanocrystals (NCs) for the first time [28] and presented some modification methods for improving sensing ability in our further experimental studies [29,30]. In this study, the adsorption of methane to a PbS cluster and its effect on the electronic properties of the cluster have been investigated. Furthermore, the effect of oxygen in this interaction has been considered and the corresponding results are reported and discussed in this paper. The calculations have been done based on the density functional theory (DFT) as it is a common method in the first-principle study of material interactions [31–33] (especially the investigation of the adsorption of gas molecules on various materials [34,35]). We believe that the outcomes of this study – despite some limitations – will enlighten some cases regarding the methane sensing mechanism of PbS and make a basis for more detailed studies in the future. The details of the computational method, the software utilised and parameter definitions are given in §2. The obtained results and a comprehensive discussion are provided in §3.

## 2. Computational method

Calculations have been performed within the DFT using Quantum Espresso package [36] with projector augmented wave (PAW) pseudopotentials. Exchange correlation effects were treated by means of Perdew–Zunger functional. Spin–orbit coupling effects are also included in our calculations. The cluster has been cleaved from the rock salt (NaCl) crystal of PbS (face centred cubic (fcc) structure). The crystal structure of the bulk was fully relaxed before slicing out the NC, and its cut-off energy,  $k$ -points and lattice parameter were optimised.

The cut-off energy was set to 45 Ry and integration over the Brillouin zone for the bulk structure was performed using the Monkhorst and Pack [37] scheme with  $(10 \times 10 \times 10)$   $k$ -points. Full relaxation with respect to the atomic positions was performed for all configurations. All self-consistent calculations were continued until the difference between the two energies in the row becomes less than  $1 \times 10^{-6}$  eV. The adsorption (binding) energy is defined as the amount of energy released when a configuration is set. The adsorption energies of PbS/CH<sub>4</sub>, PbS/O<sub>2</sub> and PbS/O<sub>2</sub>/CH<sub>4</sub> configurations are obtained from the following equations:

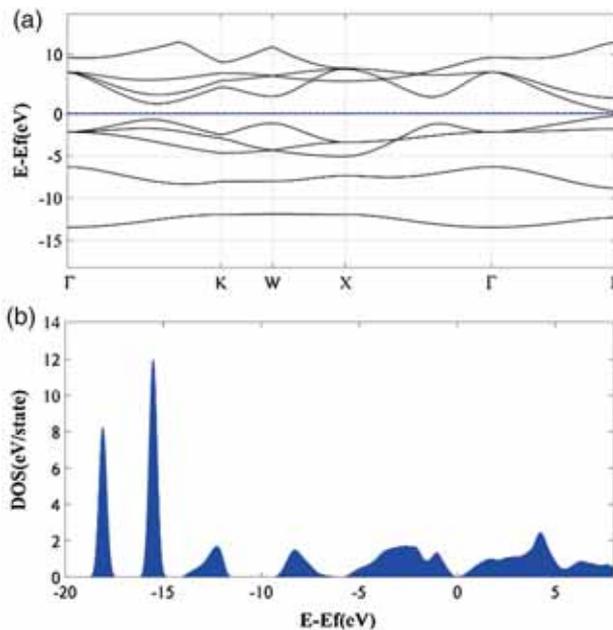
$$E_{\text{ad,CH}_4} = E_{\text{tot}}(\text{CH}_4) + E_{\text{tot}}(\text{PbS}) - E_{\text{tot}}(\text{PbS/CH}_4), \quad (1)$$

$$E_{\text{ad,O}_2} = E_{\text{tot}}(\text{O}_2) + E_{\text{tot}}(\text{PbS}) - E_{\text{tot}}(\text{PbS/O}_2), \quad (2)$$

$$E_{\text{ad,tot}} = E_{\text{tot}}(\text{CH}_4) + E_{\text{tot}}(\text{PbS/O}_2) - E_{\text{tot}}(\text{PbS/O}_2/\text{CH}_4). \quad (3)$$

The calculations of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of the cluster, before and after gas adsorption, have been performed using the  $\Delta$ SCF method. In this method, the electronic or quasiparticle band gap is determined as  $E_{\text{gap}}^{\text{qp}} = \text{IP} - \text{EA}$ , where  $\text{IP} = E_{N-1} - E_N$  and  $\text{EA} = E_N - E_{N+1}$  stand for ionisation potential and electron affinity, respectively [38]. Therefore, for each configuration, three total energies are needed to calculate  $E_N$ ,  $E_{N-1}$  and  $E_{N+1}$  for neutral, the system containing  $N - 1$  and the system containing  $N + 1$  electrons, respectively.

It is demonstrated in [38] that the best agreement between the DFT calculations and experimental measurements is achieved when the produced clusters are stoichiometric and spherically symmetric. On the basis of this approach, limited cluster structures are to be considered such as Pb<sub>4</sub>S<sub>4</sub>, Pb<sub>28</sub>S<sub>28</sub>, Pb<sub>44</sub>S<sub>44</sub> and so on. In this work, Pb<sub>4</sub>S<sub>4</sub> was chosen as the stoichiometric spherical cluster. In fact, a PbS cluster must have over 100 atoms of Pb and 100 atoms of S such that its size should be comparable with the smallest PbS NCs or PbS quantum dots (QDs). The simulation of such



**Figure 1.** (a) Band structure and (b) density of states of optimised rock salt bulk PbS crystal after relaxation.

a large molecule, especially including spin–orbit coupling effects, is not possible at the moment, because of the limitations in the available computers. However, the results (as discussed in §3) agree with the experimental observations.

## 3. Results and discussion

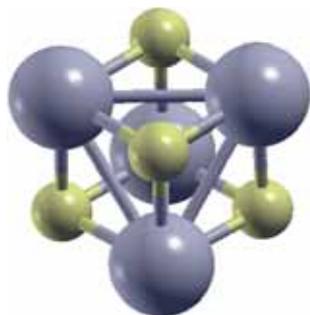
### 3.1 Crystal production

The rock salt crystalline bulk of PbS, from which the stoichiometric spherical cluster was cleaved, had been fully relaxed with optimised  $k$ -points and cut-off energy values. Figures 1a and 1b show the band structure and density of states of the relaxed bulk crystal. The band structure of the bulk shows a band-gap energy of 0.412 eV at the  $L$ -point. The band structure, lattice parameter (5.83 Å) and band-gap energy values are very close to the previous reports [39–41].

The cluster was produced by considering a section of the relaxed crystal of the PbS bulk, which contains four atoms of Pb and four atoms of S. The cluster was then fully relaxed before any further calculations such as  $\Delta$ SCF and adsorption energy. Figure 2 shows the obtained cluster after relaxation.

### 3.2 Gas adsorption simulation

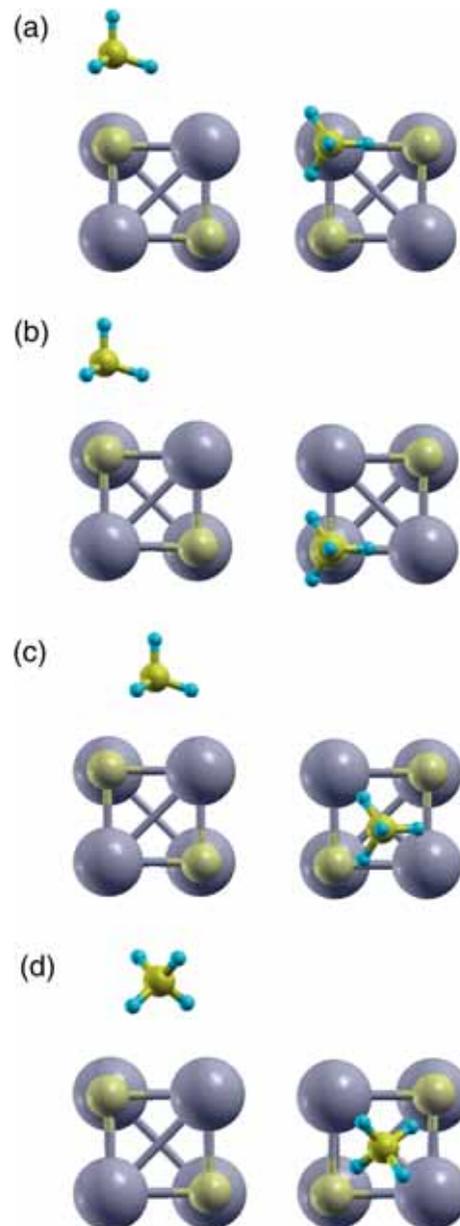
Methane adsorption on the PbS cluster was studied, both before and after the adsorption of the oxygen molecule.



**Figure 2.** The structure of the considered PbS cluster after relaxation.

In each system (PbS/CH<sub>4</sub>, PbS/O<sub>2</sub> and PbS/O<sub>2</sub>/CH<sub>4</sub>), the molecules had been fully relaxed prior to adsorption. Among different possible configurations in each system, the one having the most adsorption energy was selected as the most favourable configuration. For the PbS/CH<sub>4</sub> system, three different configurations were studied. Figures 3a–3d demonstrates the considered configurations and the relaxed system of the most favourable one. A similar approach was suggested to find the most favourable configuration for the PbS/O<sub>2</sub> system. For the PbS/O<sub>2</sub> system, eight configurations were studied and are shown in figures 4a–4h. The PbS/O<sub>2</sub>/CH<sub>4</sub> system was constructed by placing – previously relaxed – the CH<sub>4</sub> molecule into the PbS/O<sub>2</sub> system (figure 4i). The atomic positions of CH<sub>4</sub> were obtained from the relaxed PbS/CH<sub>4</sub> system. Figures 5a and 5b show the configuration of PbS/O<sub>2</sub>/CH<sub>4</sub> before and after relaxation, respectively. The adsorption energy of this system was obtained as 5.77 eV, whereas the adsorption of CH<sub>4</sub> to the PbS cluster and O<sub>2</sub> to the PbS cluster released 176 and 971 meV, respectively.

A comparison of the binding energies of the PbS/O<sub>2</sub>/CH<sub>4</sub> system (5.77 eV) and PbS/CH<sub>4</sub> system (0.176 eV) reveals that the adsorption of methane to the O<sub>2</sub>-adsorbed PbS cluster is much more probable than its adsorption to the pristine PbS cluster. In other words, it shows that oxygen facilitates methane adsorption to the PbS cluster. On the basis of these findings, it may be concluded that PbS-based methane sensors would be able to detect methane in the presence of oxygen (like ambient air) even better than O<sub>2</sub>-free atmospheres and vacuum circumstances. It can also be concluded that the response of PbS to methane, where there is no oxygen, would not be as good as its response in ambient air (where oxygen exists). This is due to the fact that the adsorption of CH<sub>4</sub> to the single PbS cluster has released 0.176 eV, whereas its adsorption to the PbS/O<sub>2</sub> system has released 5.77 eV. Moreover, considering the binding energy of O<sub>2</sub> to PbS cluster (971.4 meV), one can conclude that O<sub>2</sub> would be possibly present in methane

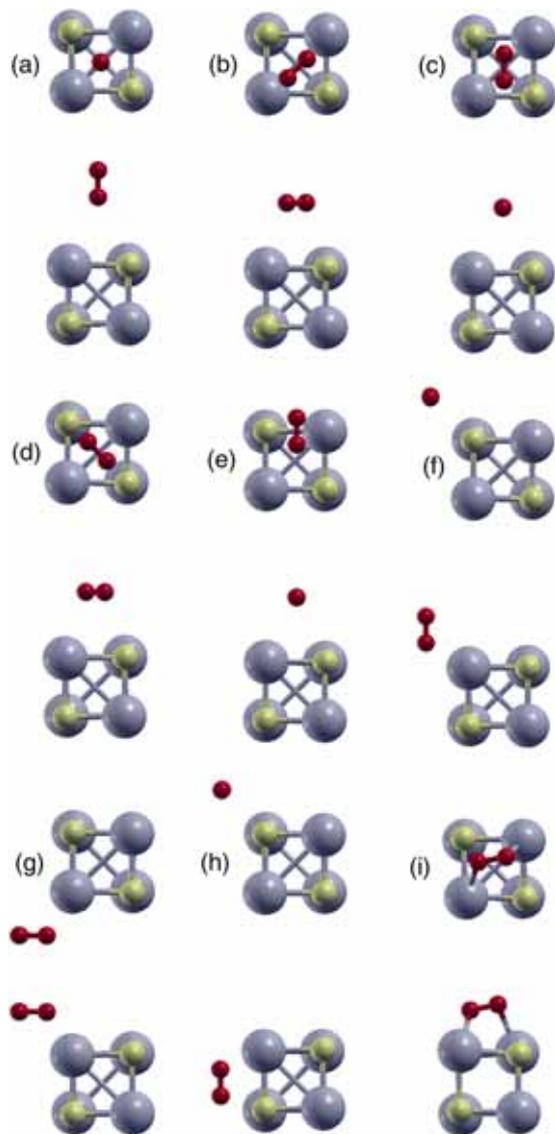


**Figure 3.** (a)–(c) Side and top views of the three proposed configurations of PbS/CH<sub>4</sub> and (d) the relaxed system of the most favourable configuration of PbS/CH<sub>4</sub>.

detection process of PbS in ambient air, as this energy is much larger than the energy released during the adsorption of CH<sub>4</sub> to the pristine PbS cluster.

### 3.3 Electronic properties

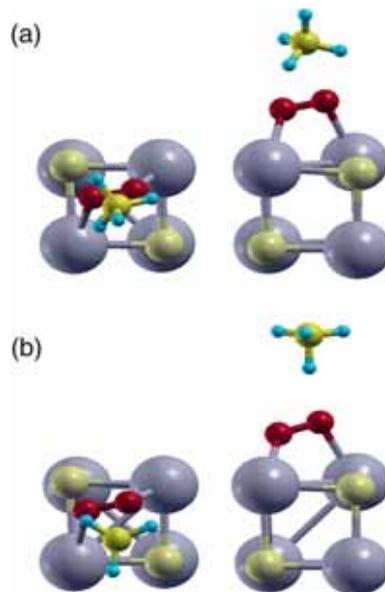
The results of HOMO–LUMO calculations of PbS cluster, PbS/CH<sub>4</sub>, PbS/O<sub>2</sub> and PbS/O<sub>2</sub>/CH<sub>4</sub> systems are shown in table 1. The comparison of PbS and PbS/CH<sub>4</sub> shows that the adsorption of methane to the cluster had made just a slight variation (5 meV) in the band gap of



**Figure 4.** (a)–(h) Top and side views of eight different PbS/O<sub>2</sub> configurations and (i) the relaxed system of the most favourable configuration of PbS/O<sub>2</sub>.

the cluster. Moreover, the decrease of the band gap – translating in conductivity improvement – is in contrast with the experimental observations. Previously reported experimental results demonstrate that the conductivity of PbS NCs is expected to decrease on exposure to methane [28].

On the other hand, the adsorption of methane to the PbS/O<sub>2</sub> system has increased  $E_g$  from 4.561 to 4.616 eV (an increase by about 55 meV). The increase of the band gap results in the decrease of the conductivity of the PbS cluster on exposure to methane, which is in complete agreement with the experimental observations. Moreover, this shows that without O<sub>2</sub>, the influence of CH<sub>4</sub> on the electronic properties of PbS molecules would not be



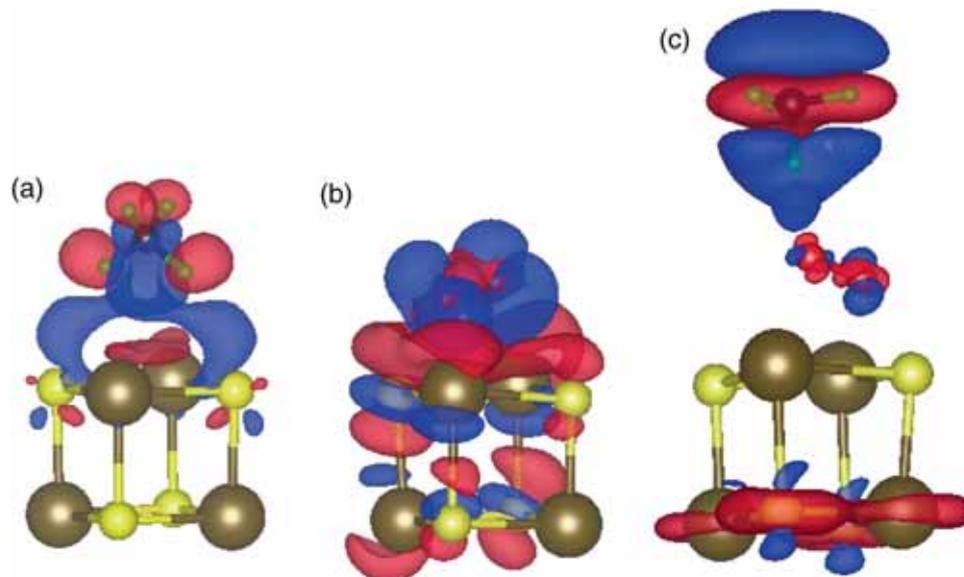
**Figure 5.** The configuration of PbS/O<sub>2</sub>/CH<sub>4</sub> before (a) and after (b) relaxation.

**Table 1.** Electronic structure parameters of PbS cluster in four situations (all values are in eV).

Structure	LUMO	HOMO	$E_g$	Binding energy
PbS cluster	− 1.856	− 7.397	5.540	–
PbS/CH <sub>4</sub>	− 1.803	− 7.338	5.535	0.176
PbS/O <sub>2</sub>	− 2.728	− 7.289	4.560	0.971
PbS/O <sub>2</sub> /CH <sub>4</sub>	− 2.559	− 7.175	4.616	5.77

significant. Therefore, oxygen would play an essential role in PbS-based methane sensors in methane detection.

Further insight into the effect of methane and oxygen adsorptions on the electronic characteristics of the PbS cluster would be possible by studying the results of charge transfer calculations. Our calculations show that the cluster donates  $0.36e^-$  to the adsorbed oxygen in the PbS/O<sub>2</sub> system. Figure 6b also shows this fact qualitatively. This charge transfer makes an electric dipole in the system, forming an electric field from the cluster towards O<sub>2</sub>. This electric field is responsible for the significant decrease of  $E_g$  after O<sub>2</sub> adsorption. However, methane, by accepting  $0.047e^-$  after its absorbance to the PbS/O<sub>2</sub> system, lowers the intensity of the electric field formed between the cluster and O<sub>2</sub> (figure 6c). As a consequence of the shrinkage of the electric field, the band gap increases after CH<sub>4</sub> adsorption to the system. On the other hand, the PbS cluster accepts  $0.0005e^-$  from methane in PbS/CH<sub>4</sub> system, which can explain the reverse and weak effects of CH<sub>4</sub> adsorption on the cluster band gap in the absence of O<sub>2</sub> (figure 6a). Therefore, charge transfer between



**Figure 6.** Difference in electron density of (a) PbS/CH<sub>4</sub>, (b) PbS/O<sub>2</sub> and (c) PbS/O<sub>2</sub>/CH<sub>4</sub> systems. The blue regions in the isosurfaces indicate the electron density accumulation and red regions indicate the electron density depletion due to the adsorption.

CH<sub>4</sub> and PbS cluster (in PbS/CH<sub>4</sub> system) and also between CH<sub>4</sub> and PbS/O<sub>2</sub> (in PbS/CH<sub>4</sub>/O<sub>2</sub> system) succeeds in explaining the band gap variations of each system.

The results of this work show good agreement with the reported experimental observation. However, calculations with larger cluster sizes (if there are sufficient resources and time to perform it) are recommended which would probably give more information about the methane sensing mechanism of PbS-based gas sensors.

#### 4. Conclusion

Adsorption energies and electronic properties of PbS/CH<sub>4</sub>, PbS/O<sub>2</sub> and PbS/O<sub>2</sub>/CH<sub>4</sub> systems were studied after identification and relaxation of the most favourable configuration for each system. On the basis of our results, the binding energy of the PbS/O<sub>2</sub>/CH<sub>4</sub> system is significantly more than the binding energy of the PbS/CH<sub>4</sub> system, indicating that the adsorption of O<sub>2</sub> on the PbS cluster facilitates the adsorption of methane. Moreover, the influence of CH<sub>4</sub> adsorption on the PbS cluster and its adsorption on the PbS/CH<sub>4</sub> system on  $E_g$  value of each system was investigated based on HOMO–LUMO calculations.  $E_g$  variations of the cluster caused by CH<sub>4</sub> adsorption could not explain the reported changes in electrical conductivity of PbS clusters due to exposure to methane, but  $E_g$  variations of the PbS/O<sub>2</sub> system by CH<sub>4</sub> adsorption agree with the previously reported observations. Charge transfer

calculations were done to understand the reasons for different interactions of CH<sub>4</sub> adsorption. The charge transfer calculations show that the adsorption of methane on the PbS/O<sub>2</sub> system lowers the intensity of the built-in electric field of the PbS/O<sub>2</sub> system by redistribution of the system's charge density, whereas it makes no significant change in the charge density of the individual PbS cluster. On the basis of the outcomes of this study, PbS-based methane sensors are expected to sense methane in O<sub>2</sub>-rich atmospheres much better than O<sub>2</sub>-free atmospheres.

#### References

- [1] W V B Street, *Methane, Material Safety Data Sheet*, pp. 1 (2013)
- [2] S Basu and P K Basu, *J. Sensors* **2009**, 1 (2009)
- [3] UNECE – United Nations Economic Commission for Europe (Methane to Markets Partnership) ECE Energy Ser. No. 31 86 (2010)
- [4] R Tormo, A Bertaccini, M Conde, D Infante and I Cura, *Early Hum. Dev.* **65**, S165 (2001)
- [5] K M Behall, D J Scholfield, A M C van der Sluijs and H Hallfrisch, *J. Nutr.* **128**, 79 (1998)
- [6] M T Humayun, R Divan, Y Liu, L Gundel, P A Solomon and I Paprotny, *J. Vac. Sci. Technol. A: Vac. Surf. Films* **34**, 01A131/1 (2016)
- [7] W Li, J Liang, J Liu, L Zhou, R Yang and M Hu, *Mater. Lett.* **173**, 199 (2016)
- [8] J Liang, W Li, J Liu and M Hu, *Mater. Lett.* **184**, 92 (2016)

- [9] Z Karami Horastani, S M Sayedi and M H Sheikhi, *Sens. Actuator B-Chem.* **202**, 461 (2014)
- [10] Z Karami Horastani, S M Sayedi, M H Sheikhi and E Rahimi, *Mater. Sci. Semicond. Process.* **35**, 38 (2015)
- [11] G Jiménez-Cadena, J Riu and F X Rius, *Analyst* **132**, 1083 (2007)
- [12] D Haridas and V Gupta, *Sens. Actuator B-Chem.* **166–167**, 156 (2012)
- [13] P Dhivya, A K Prasad and M Sridharan, *Sens. Actuator B-Chem.* **222**, 987 (2016)
- [14] A K Prasad, S Amirthapandian, S Dhara, S Dash, N Murali and A K Tyagi, *Sens. Actuator B-Chem.* **191**, 252 (2014)
- [15] A Tarat, R Majithia, R A Brown, M W Penny, K E Meissner and T G G Maffei, *Surf. Sci.* **606**, 715 (2012)
- [16] R Mota, S B Fagan and A Fazzio, *Surf. Sci.* **601**, 4102 (2007)
- [17] T G G Maffei, G T Owen, M W Penny, T K H Starke, S A Clark, H Ferkel and S P Wilks, *Surf. Sci.* **520**, 29 (2002)
- [18] S Kaci, A Keffous, S Hakoum and A Mansri, *Vacuum* **116**, 27 (2015)
- [19] N B Sonawane, K V Gurav, R R Ahire, J H Kim and B R Sankapal, *Sens. Actuator A-Phys.* **216**, 78 (2014)
- [20] S Kaci, A Keffous, S Hakoum, M Trari, O Mansri and H Menari, *Appl. Surf. Sci.* **305**, 740 (2014)
- [21] S V Patil, R N Bulakhe, P R Deshmukh, N M Shinde and C D Lokhande, *Sens. Actuator A-Phys.* **201**, 387 (2013)
- [22] H Karami, M Ghasemi and S Matini, *Int. J. Electrochem. Sci.* **8**, 11661 (2013)
- [23] S V. Patil, P R Deshmukh and C D Lokhande, *Sens. Actuator B-Chem.* **156**, 450 (2011)
- [24] T Fu, *Sens. Actuator B-Chem.* **140**, 116 (2009)
- [25] M Li, D Zhou, J Zhao, Z Zheng, J He, L Hu, Z Xia, J Tang and H Liu, *Sens. Actuator B-Chem.* **217**, 198 (2015)
- [26] H Liu, M Li, O Voznyy, L Hu, Q Fu, D Zhou, Z Xia, E H Sargent and J Tang, *Adv. Mater.* **26**, 2718 (2014)
- [27] H Liu, M Li, G Shao, W Zhang, W Wang, H Song, H Cao, W Ma and J Tang, *Sens. Actuator B-Chem.* **212**, 434 (2015)
- [28] A Mosahebfard, H Dehdashti Jahromi and M H Sheikhi, *IEEE Sens. J.* **16**, 4174 (2016)
- [29] H Roshan, A Mosahebfard and M H Sheikhi, *IEEE Sens. J.* **1748**, 1 (2017)
- [30] A Mosahebfard, H Roshan and M H Sheikhi, *IEEE Sens. J.* **17**, 3375 (2017)
- [31] R Bhattacharjee and A Datta, *J. Phys. Chem. C* **120**, 24449 (2016)
- [32] R Bhattacharjee and A Datta, *J. Phys. Chem. C* **121**, 20101 (2017)
- [33] S Karmakar, C Chowdhury and A Datta, *J. Phys. Chem. C* **122**, 14488 (2018)
- [34] R Azimirad, A H Bayani and S Safa, *Pramana – J. Phys.* **87**: 46 (2016)
- [35] F Shojaie, *Pramana – J. Phys.* **90**: 4 (2018)
- [36] P Giannozzi, S Baroni, N Bonini, M Calandra, R Car, C Cavazzoni, D Ceresoli, G L Chiarotti, M Cococcioni and I Dabo, *J. Phys. Condens. Matter* **21**, 395502 (2009)
- [37] H J Monkhorst and J D Pack, *Phys. Rev. B* **13**, 5188 (1976)
- [38] S Z Bisri, E Degoli, N Spallanzani, G Krishnan, B J Kooi, C Ghica, M Yarema, W Heiss, O Pulci, S Ossicini and M A Loi, *Adv. Mater.* **26**, 5639 (2014)
- [39] J M Skelton, S C Parker, A Togo, I Tanaka and A Walsh, *Phys. Rev. B* **89**, 205203 (2014)
- [40] H Overhof and U Rössler, *Phys. Status Solidi* **37**, 691 (1970)
- [41] G B Bhandari, *Synthesis and ab-initio simulations of colloidal PbS nanosheets* (Bowling Green State University, 2014)