Facile Synthesis of 2D-HfS₂ Flakes for μ -IDE-Based Methanol Sensor: Fast Detection at Room Temperature

Subhashis Das¹⁰, Member, IEEE, Shivani Sharma, and Satinder Kumar Sharma¹⁰

Abstract—A new and astonishing resistive gas sensor based on Al_{µ–IDE}/HfS₂, synthesized by chemical route, has been developed for precise detection of methanol vapor at room temperature. A high sensitivity of 1.29 has been found at room temperature with the exposure of 500 ppm of methanol vapor at an operating bias of 1 V. Sensitivity has been obtained from transient response analysis. Most importantly, very fast response/recovery characteristics with good baseline restoration have been witnessed. The response time and recovery time have been recorded in the range of ~12.12 s to ~21.14 s and ~23.72 s to ~39 s. Cross-sensitivity with other interfering species has also been studied. A comprehensive justification, including Langmuir adsorption-desorption isotherm for appreciable sensing response, has also been delineated.

Index Terms—Fast response, methanol sensor, HfS_2 flakes, resistive device.

I. INTRODUCTION

NPRECEDENTED material attributes of twodimensional transition metal dichalcogenides (TMDs) have usher in their utilization in the fields of electronics, optoelectronics and sensors [1]–[6]. Of late, it is well known that, TMD based materials have been developed for sensor applications with various surface morphologies, topology, geometry and structures because of their inherent versatile material and structural properties including ultra-large surface to volume ratio, high surface activities, etc. The improved electrical conductivity is well suited for sensing of analyte molecules and the sensor systems; of course, accords a very low signal-to-noise ratio [7]–[9]. Among these materials, MoS₂ has widely been explored for gas sensing. The sensing performance of monolayer MoS₂ has been investigated theoretically by Shokri and Salami [10]. MoS₂-graphene hybrid sensor has been studied by Long et al. and He et al. [11], whereas Kuru et al. [12], Cho et al. [13] and Sarkar et al. [14] have utilized functionalized MoS₂ for enhanced sensing of NO_X, NH₃,

The authors are with the School of Computing and Electrical Engineering, Indian Institute of Technology Mandi, Mandi 175005, India (e-mail: satinder@iitmandi.ac.in).

Digital Object Identifier 10.1109/JSEN.2019.2925027

CO etc. Monolayer WS₂ has been investigated for the sensing of NO_X and NH₃ by Zhou *et al.* [15]. Sajjad and Feng [16] have employed h-BN nanosheets for methane sensing.

On the contrary, HfS₂, a group IVB-TMD belonging to D_{3d} point group, has theoretically been predicted to better performance due to its superior electronic property [17]. Nonetheless, very sparse work has emerged based on this material may be due to the ample interlayer interaction between HfS₂ layers compared to its group VIB counterpart such as well-explored MoS₂ [18]. Of late, HfS₂ has been employed in transistor by Xu *et al.* [19] and Kanazawa *et al.* [3], whereas Xu *et al.* [2] and Wang *et al.* [20] have shown the phototransistor and photodetector applications, respectively. It has also been applied as a photocatalyst in water splitting by Sing *et al.* [21]. But, no such extensive report on HfS₂ based chemical sensor has been found to the best of authors' knowledge.

Furthermore, the wide-spread dominant usage of microinterdigitated electrode (μ -IDE) based sensor has coined recently owing to cumulative demand of high sensitivity and reliability of chemical sensors [22]. The controllability of output signal strongly depends on the careful design of micro electrode fingers [23].

Trace level of methanol (methyl alcohol), widely used as a chemical agent for food fermentation, biomedicines, manufacturing of colours, perfumes, dyes etc. [24] requires to be monitored because of its lethal effect to the environment. The wide use of methanol in automotive industries, as well as in brewing is also worth mentioning [25]. Besides, it is widely used for wastewater de-nitrification and biodiesel preparation [24]. However, its highly toxic nature is often fatal to human health and warrants online controlling with effective sensing systems. Low concentration (<300 ppm) methanol sensors are required outside the process line of the industries involving CO₂ to methanol conversion, whereas high concentration (>300) methanol sensors are useful during the methanol separation from other gases [26]. Lately, the growing anxiety on the safety in industry production and laboratory has spawned the aspiration for fast, efficient and cost effective room temperature detection of methanol [24].

In this present endeavor, we are introducing a new type of resistive sensor, $Al_{\mu-IDE}/HfS_2$ interdigitated structure, synthesized by facile chemical route for fast detection of methanol. Transient response has been recorded as a function of methanol concentration ranging from 100 to 500 ppm at room temperature. The newly designed and developed sensor device

1558-1748 © 2019 IEEE. Personal use is permitted, but republication/redistribution requires IEEE permission. See http://www.ieee.org/publications_standards/publications/rights/index.html for more information.

Manuscript received May 28, 2019; accepted June 19, 2019. Date of publication June 26, 2019; date of current version September 18, 2019. This work was supported in part by the Science and Engineering Research Board, Government of India, through the National Post Doctoral Fellow (N-PDF) Scheme under Grant PDF/2016/003135, and in part by the Ministry of Human Resource Development, Government of India. The associate editor coordinating the review of this paper and approving it for publication was Dr. Camilla Baratto. (*Corresponding author: Satinder Kumar Sharma.*)



Fig. 1. Schematic diagram of HfS_2 synthesis process and preparation of stock solution.

has shown striking methanol sensing properties with the apparent response time/recovery time of 12.12 s / 23.72 s at room temperature. The marked sensing response is for 100 ppm methanol vapor at an operating bias of 1 V. These sensing outcomes are far better than the present state of the art which suggests the response/recovery time of ~ 4.5 m / 1.5 m at room temperature as surveyed by Acharyya and Bhattacharyya [27].

II. EXPERIMENTAL

A. Materials and Instruments

Hafnium (IV) Chloride (0.23 g, 0.73 mmol) was mixed with oleylamine (3.0 g, 11.2 mmol) in a round bottom flask. CS₂ (0.30 ml, 5.0 mmol) was injected into the flask at 350 °C. The detailed process is explained elsewhere [28]. Then the solution is stirred vigorously for 9 hrs. The resulting solution was mixed with a solution prepared by mixing hexane and butanol (1:1) to make a stock solution. Further, the solution was sonicated for 5 hrs. The solution was centrifuged for 1 hr in 11000 rpm, followed by the addition of 20 μ l of centrifuged stock solution with 2 ml butanol. The schematic diagram of the synthesis process of HfS₂ and preparation of stock solution has been illustrated in fig. 1.

The surface morphology of HfS_2 flakes were examined by using atomic force microscopy (atomic force microscopy (AFM); Dimension Icon from Bruker) in tapping mode with a scan rate of ~0.5 Hz at room temperature. The high aspect ratio TESPA-HAR, AFM probe with resonant frequency of 320-369 kHz and spring constant (k) of 20–80 N/m was used for AFM measurements.

Structural analysis of the grown sample has been performed by confocal micro-Raman spectroscopy with the excitation wavelength of 532 nm. X-ray Photoelectron Spectroscopy (XPS) was performed to confirm the formation of HfS₂. Electrical measurements for the study of developed sensors have been performed by Keithley 4200 SCS. A fixed volume of methanol was kept in a bubbler throughout the measurement. Different amount of nitrogen gas was



Fig. 2. Schematic diagram of $Al_{\mu-IDE}/HfS_2$ sensor device with step-wise fabrication process flow (not to the scale).

flowed to change the concentration of evaporated vapor. The details of the sensor measurement set up described by Bhowmik *et al.* [29]. The desired concentration of testing vapor was calculated using the following relation C(ppm) as shown at the bottom of this page.

B. Fabrication of μ -IDE-Based Sensor Structure

Initially, SiO₂ substrate is cleaned by sonication in Acetone, ethanol and DI water for 15 minutes each. Then, the substrate was heated for 20 min. at 200 °C. A thin film of Al \sim 50 nm was deposited onto the substrate by thermal evaporation at an ultimate pressure of $\sim 1 \times 10^{-6}$ torr. After that the SU-8 (2002, Micro-Chem) photoresist was spin coated on the Al/SiO₂ samples. The samples were then subjected to pre-exposure bake (PB) from room temperature (RT) to 95 °C for 10 min and after PB, the samples were cool down to RT. After the PB process, the samples were exposed using Maskless Optical Lithography (Intelligent Micro Patterning-SF100) to pattern μ -IDE structure and the samples were then subjected to post exposure bake (PEB) from RT to 105 °C for 10 min. Subsequent process of developing, etching and photoresist removal to achieve the desired μ -IDE was performed [30]. The length of the fingers is 100 μ m and the finger spacings, and width is 15 μ m. Thereafter, 0.25 ml supernatant part of the centrifuged stock solution was drop casted upon the fabricated μ -IDE structure. The schematic of sensor structure fabrication has been illustrated in fig. 2.

III. RESULTS AND DISCUSSION

A. Structural Characterizations

Fig. 3 shows the Atomic Force Microscopy image of the HfS_2 flakes. The thickness measured from the image clearly indicates that 3-5 layers HfS_2 has been formed.

The room temperature micro Raman spectrum of the thin HfS_2 layers (<5 nm) on the Si substrate with the excitation wavelength of 532 nm is shown in fig. 4. The primary peak appeared at the Raman shift of approximately 340 cm⁻¹, and

 $C(ppm) = \frac{Evaporated \ volume \ of \ methanol(\mu l) \ in \ a \ fixed \ time}{Total \ volume \ of \ N_2 \ in \ that \ time + vacant \ volume \ of \ the \ bubbler}$



Fig. 3. Atomic force microscopy image of the HfS_2 flake: (a) multiple flakes and (b) single flake.



Fig. 4. Confocal Raman spectroscopy of HfS_2 at room temperature: (a) primary A_{1g} peak and (b) satellite E_g peak.



Fig. 5. XPS analysis: high-resolution a) Hf 4f scan and b) S 2p scan spectra of HfS_2 .

it was consistent with the previous experimental report of bulk HfS_2 that showed a first-order A_{1g} peak. Satellite peak at $\sim 325 \text{ cm}^{-1}$ were also considered as E_g mode [3], [31]–[34]. These results indicate the existence of single-crystal layers with well-aligned atoms. The peaks are obtained from different flakes.

X-ray photoelectron spectroscopy (XPS) was used to determine the elemental composition and bonding types in the HfS_2 layers. Hf 4f scan and S 2p scan were performed. Peaks are observed at 14.38 eV and 13.91 eV for Hf and 163.4 eV and 164.51 for S, as represented in fig. 5. The results are in accordance with the standard spectra for HfS_2 crystal.

B. Sensor Study

Current-voltage (I-V) characteristics have been shown in fig. 6 (a). A strong non-rectifying nature of the I-V has been observed as the current increases linearly with the increment of applied bias. The curve is showing symmetricity for both



Fig. 6. a) Current-voltage characteristics of the sensor device at room temperature in presence of air and b) Electrical responsiveness with 100 ppm methanol vapor.

polarities of bias. Therefore, all the successive calculations and studies have been carried out for one polarity of bias only. The current value of 127.8 μ A has been recorded at an applied bias of -1 V, due to higher carrier concentration in the HfS₂ layer.

However, all the transient responses have been investigated at the operating bias of 1 V as depicted in fig. 7. When the device has been exposed to 100 ppm of methanol vapor at the temperature of 300 K, the sensor response has been recorded as 0.46, as represented in fig. 6 (b). As it is evident from fig. 6 (b), the current of the HfS_2 layer increases with applied bias. It is expected that, this trend preserves until Va exceeds E_G/q , where V_a , q and E_G are the applied bias, electronic charge and the band gap of the sensing layers, respectively. After the afore-mentioned bias, the current will be higher than that of the linear regime. So, the prudent analysis of current-voltage characteristic of the sensing system will be useful in the linear regime to discreetly monitor the resistance changes as a sensor response due to the adsorption [10]. At room temperature, the transient responses with different concentrations of methanol have also been observed at a low bias of 1 V and illustrated in fig. 7. The sensitivity values are 0.46, 0.64, 0.94, 1.07, 1.14, 1.22 and 1.29 for the exposure to the methanol concentration of 100 ppm, 150 ppm, 200 ppm, 250 ppm, 300 ppm, 400 ppm, and 500 ppm, respectively at a fixed temperature of 300 K. It has also been observed that the sensor recovers its baseline very efficiently when the gas flow is withdrawn.

The sensing parameters such as sensitivity, response time, and recovery time have been extracted from the transient response curves and graphically represented as a function of methanol concentration in fig. 8.



Fig. 7. Transient response curve of the sensor device towards different concentrations of methanol at room temperature.



Fig. 8. (a) Sensitivity, (b) response time and (c) recovery time as a function of methanol concentrations.

Methanol detection sensitivity of $Al_{\mu-IDE}/HfS_2$ resistive sensor as a function of methanol concentration has been plotted at room temperature and operating voltage of 1 V as shown in fig. 8(a). *Sensitivity* can be mathematically defined as follows [35]:

$$Sensitivity = \frac{I_{me} - I_{air}}{I_{air}} \tag{1}$$

where I_{me} and I_{air} represent the current levels of the sensor in presence of methanol vapor and in presence of air respectively. *Sensitivity* has been found to be increase from 0.46 to 1.29 with the increase of methanol concentration from 100 ppm to 500 ppm. The sensitivity of the device is gradually increasing with the increase in vapor concentration which is a typical behavior of this kind of sensor. Once all the adsorption sites are occupied, the sensitivity saturates.

To qualify a sensor to be efficient, response time and recovery time are very important to be determined. The time required by the sensor to achieve 67 % of its saturated response value on exposure to methanol is calculated as response time whereas the time required by the sensor to achieve 67 % of its baseline value after methanol flow has been cut off [36], [37]–[39]. In the present report, response time and recovery time have been plotted as a function of methanol concentration as illustrated in fig. 8(b) and fig. 8(c), respectively. As revealed from the abovementioned figures (8(b) and 8(c)), the investigated sensor has shown fast response time ranges from ~ 12.12 s to \sim 21.14 s, whereas recovery time has been found to be in the range of ~ 23.72 s to ~ 39 s. The response time is decreasing with the increase in the concentration of methanol vapors. This variation in the response time is attributed to the adsorption of a greater number of methanol molecules at the same time. But, after a particular level of concentration, the response time gets saturated due to the maximum coverage of available free adsorption sites for chemical kinetics. On the contrary, the recovery time is increasing with the increase in concentration of methanol vapor. This variation of recovery time occurs because larger time is required to desorb the extra methanol molecules for higher concentration. This kind of rapid response-recovery behavior of the μ -IDE based sensors for detecting methanol at room temperature at a concentration range from 100 ppm to 500 ppm is reported for the first time as evident from the surveys by Hazra et al. [25] and Banerjee et al. [26]. The adsorption of polar molecules (gases/vapors) on the sulphide surfaces follows Langmuir adsorption-desorption isotherm [40]. Fast response than recovery has possibly been attributed to effect of fast adsorption as well as diffusion of the methanol molecules on the HfS₂ sensing layer. The rate of adsorption is firmly correlated by (i) sticking probability (S) of the methanol molecules on the HfS₂ surface and (ii) flux (F) developed by methanol molecules on the HfS₂ surface. Such adsorption and diffusion follows Langmuir adsorption-desorption isotherm as shown in (2) [41].

$$R_{ads} = S \times F = f(\theta) \exp\left(\frac{-E_a}{K_B T}\right) \times \frac{p}{\left(2\pi K_B m T\right)^{\frac{1}{2}}}$$
(2)

where R_{ads} is the rate of absorption, S = sticking co-efficient, F = flux, developed by the methanol molecules on the sensing surface, $f(\theta) = \text{methanol surface coverage}$, $E_a = \text{activation energy supplied by the operating temperature}$, $K_B = \text{Boltzmann constant}$, p = methanol partial pressure, m = mass of methanol molecule, T = absolute temperature. A comparative table (Table I) with proper references has

been prepared as represented at the beginning of next page:

The cross-sensitivity study of the $Al_{\mu-IDE}/HfS_2$ resistive device was tested in other interfering species like acetone, ethanol and 2-propanol at room temperature as shown in fig. 9. As revealed from the fig. 9, acetone was found to be the maximum response magnitude next to methanol. A maximum response magnitude difference of ~45%, ~53% and ~69% were found in the case of methanol-acetone, methanol-ethanol, and methanol-2-propanol, respectively. These responses corroborate the methanol selectivity of the sensing device. The higher rate of adsorption of methanol and its lower molecular size than that of acetone, ethanol, 2-propanol result in the substantial selectivity of the device towards methanol [48], [49]. However, the selectivity towards methanol can be enhanced further by covalently or non-covalently functionalizing HfS₂ with appropriate polymers [50].

TABLE I A COMPARATIVE STUDY OF RECENT WORKS ON METHANOL DETECTION

Material	Sensitivity	Response time	Recovery time	References
$Al_{\mu\text{-IDE}}/HfS_2$	1.29@500 ppm	12.12 s	39 s	This work
ZnO NTs	0.51@700 ppm	2.24 min	1.03	[27]
TiO ₂ NTs	0.6@1000 ppm	3.1 min	3.7 min	[42]
SnO ₂ /CNT nanocompos ite	0.96@200 ppm	1 min	1 min	[43]
TiO2 disperse in PVDF	0.23@350 ppm	120 s	360 s	[44]
Fe ₃ O ₄ -RGO	1.25@1000 ppm	140 s	120 s	[45]
TiO ₂ NT- RGO	0.96@800 ppm	18 s	61 s	[46]
RGO-Co ₃ O ₄ nanoparticle	0.08@800	90 s	60 s	[47]



Fig. 9. Selectivity study at room temperature with different inferring species such as methanol, acetone, ethanol and 2-propanol.

C. Methanol Sensing Mechanism of $Al_{\mu-IDE}/HfS_2$ Sensor Devices

When reducing vapor (such as methanol) comes to the contact of sensing surface, charge transfer takes place between the sensing material and targeted species. Consequently, the resistance of the sensing material changes due to the donation of electron to sensor surface. When the flow of vapor goes off, material resistance regains its initial value by the desorption of gas molecules [51], [15].

Initially, methanol gets adsorbed to the surface and forms methoxy (CH_3O) species by partial oxidation (3).

$$CH_3OH_{(gas)} \Leftrightarrow CH_3OH_{(ads)} \Leftrightarrow CH_3O_{(ads)}$$
 (3)

Adsorbed CH_3O species then forms CH_2O and CHO species and finally CO by C-H bond scission (4)

$$CH_3O_{(ads)} \rightarrow CH_2O \rightarrow CHO \rightarrow CO(C-H \text{ bond scission})$$

(4)

On the other hand, CH_3O species also forms carbon species by C-O bond scission with complete dehydrogenation (5).

$$CH_3O_{(ads)}$$

 $\rightarrow CH_X \rightarrow C(C-O \text{ bond scission and dehydrogenation})$ (5)

Generated CO and C species also get oxidized and form CO_2 that also enhance the sensitivity of the sensor with low operating temperature (6)-(7).

$$C + O_{(ads)}^{-} + h^{+} \to CO_{(gas)} \tag{6}$$

$$CO_{(gas)} + O_{(ads)}^{-} + h^{+} \rightarrow CO_{2(gas)}$$
(7)

IV. CONCLUSION

In summary, a new and interesting methanol sensor based on HfS_2 flake has been grown by chemical route and studied for fast response methanol sensing at low temperature of 300 K. The micro-interdigitated electrode (μ -IDE) sensor structure has been introduced for HfS_2 flake based volatile organic compound (VOC) sensor. The Raman spectroscopy result suggests that good quality single crystalline HfS_2 has been synthesized. Fast response transient characteristics have been obtained at 300 K for different concentrations of methanol. Response time and recovery time ranges from 12.12 s to 21.14 s and 23.72 s to 39 s have been found respectively in the methanol concentration range of 100-500 ppm. A possible explanation for the fast response has been furnished with proper references. Therefore, the sensor shows a great promise for methanol sensing applications.

ACKNOWLEDGMENT

The authors would like to thank the Centre for Design and Fabrication of Electronic Devices (C4DFED) and Advanced Materials Research Centre (AMRC) IIT Mandi, for the use of various state-of-the-art device fabrication and characterization facilities for this paper.

REFERENCES

- Z. Binjie *et al.*, "Vertically oriented few-layered HfS₂ nanosheets: Growth mechanism and optical properties," *2D Mater.*, vol. 3, no. 3, Sep. 2016, Art. no. 035024.
- [2] K. Xu et al., "Ultrasensitive phototransistors based on few-layered HfS₂," Adv. Mater., vol. 27, no. 47, pp. 7881–7887, Dec. 2015.
- [3] T. Kanazawa et al., "Few-layer HfS₂ transistors," Sci. Rep., vol. 6, Mar. 2016, Art. no. 22277.
- [4] F. K. Perkins, A. L. Friedman, E. Cobas, P. M. Campbell, G. G. Jernigan, and B. T. Jonker, "Chemical vapor sensing with monolayer MoS₂," *Nano Lett.*, vol. 13, no. 2, pp. 668–673, Jan. 2013.
- [5] S. Cui, Z. Wen, X. Huang, J. Chang, and J. Chen, "Stabilizing MoS₂ nanosheets through SnO₂ nanocrystal decoration for high-performance gas sensing in air," *Small*, vol. 11, no. 19, pp. 2305–2313, May 2015.
- [6] S. Zhang, T. H. Nguyen, W. Zhang, Y. Park, and W. Yang, "Correlation between lateral size and gas sensing performance of MoSe₂ nanosheets," *Appl. Phys. Lett.*, vol. 111, no. 16, Sep. 2017, Art. no. 161603.
- [7] W. Yang, L. Gan, H. Li, and T. Zhai, "Two-dimensional layered nanomaterials for gas-sensing applications," *Inorganic Chem. Frontiers*, vol. 3, no. 4, pp. 433–451, 2016.
- [8] B. Liu, L. Chen, G. Liu, A. N. Abbas, M. Fathi, and C. Zhou, "Highperformance chemical sensing using Schottky-contacted chemical vapor deposition grown monolayer MoS₂ transistors," *ACS Nano*, vol. 8, no. 5, pp. 5304–5314, Apr. 2014.
- [9] K. Xu et al., "Interface bonds determined gas-sensing of SnO₂-SnS₂ hybrids to ammonia at room temperature," ACS Appl. Mater. Interfaces, vol. 7, no. 21, pp. 11359–11368, May 2015.

- [10] A. A. Shokri and N. Salami, "Gas sensor based on MoS₂ monolayer," *Elsevier Sens. Actuators B, Chem.*, vol. 236, pp. 378–385, Nov. 2016.
- [11] Q. He *et al.*, "Fabrication of flexible MoS₂ thin-film transistor arrays for practical gas-sensing applications," *Small*, vol. 8, no. 19, pp. 2994–2999, Oct. 2012.
- [12] C. Kuru *et al.*, "MoS₂ nanosheet-pd nanoparticle composite for highly sensitive room temperature detection of hydrogen," *Adv. Sci.*, vol. 2, no. 4, Mar. 2015, Art. no. 1500004.
- [13] B. Cho *et al.*, "Bifunctional sensing characteristics of chemical vapor deposition synthesized atomic-layered MoS₂," *ACS Appl. Mater. Interfaces*, vol. 7, no. 4, pp. 2952–2959, Jan. 2015.
- [14] D. Sarkar *et al.*, "Functionalization of transition metal dichalcogenides with metallic nanoparticles: Implications for doping and gas-sensing," *Nano Lett.*, vol. 15, no. 5, pp. 2852–2862, 2015.
- [15] C. Zhou, W. Yang, and H. Zhu, "Mechanism of charge transfer and its impacts on Fermi-level pinning for gas molecules adsorbed on monolayer WS₂," *J. Chem. Phys.*, vol. 142, no. 21, May 2015, Art. no. 214704.
- [16] M. Sajjad and P. Feng, "Study the gas sensing properties of boron nitride nanosheets," *Mater. Res. Bull.*, vol. 49, pp. 35–38, Jan. 2014.
- [17] W. Zhang, Z. Huang, W. Zhang, and Y. Li, "Two-dimensional semiconductors with possible high room temperature mobility," *Nano Res.*, vol. 7, no. 12, pp. 1731–1737, Dec. 2014.
- [18] S. H. Chae *et al.*, "Oxidation effect in octahedral hafnium disulfide thin film," *ACS Nano*, vol. 10, no. 1, pp. 1309–1316, Jan. 2016.
- [19] K. Xu *et al.*, "Toward high-performance top-gate ultrathin HfS₂ fieldeffect transistors by interface engineering," *Small*, vol. 12, no. 23, pp. 3106–3111, Jun. 2016.
- [20] D. Wang *et al.*, "Epitaxial growth of HfS₂ on sapphire by chemical vapor deposition and application for photodetectors," 2D Mater., vol. 4, Jul. 2017, Art. no. 031012.
- [21] D. Singh, S. K. Gupta, Y. Sonvane, A. Kumar, and R. Ahuja, "2D-HfS₂ as an efficient photocatalyst for water splitting," *Catal. Sci. Technol.*, vol. 6, no. 17, pp. 6605–6614, 2016.
- [22] H. Wang et al., "Electrochemical biosensor based on interdigitated electrodes for determination of thyroid stimulating hormone," Int. J. Electrochem. Sci., vol. 9, pp. 12–21, Jan. 2014.
- [23] M. Soni, P. Kumar, A. Soni, and S. K. Sharma, "Selective detection of F⁻ using Al microarrays integrated graphene oxide," *Sens. Actuators B, Chem.*, vol. 247, pp. 224–227, Aug. 2017.
- [24] M. Babaei and N. Alizadeh, "Methanol selective gas sensor based on nano-structured conducting polypyrrole prepared by electrochemically on interdigital electrodes for biodiesel analysis," *Sens. Actuators B, Chem.*, vol. 183, pp. 617–626, Jul. 2013.
- [25] A. Hazra, B. Bhowmik, K. Dutta, V. Manjuladevi, R. K. Gupta, and P. Bhattacharyya, "Low temperature methanol sensing by p-type nanotitania: Correlation with defects states and Schottky barrier model," *IEEE Trans. Nanotechnol.*, vol. 14, no. 1, pp. 187–195, Jan. 2015.
- [26] N. Banerjee, S. Roy, C. K. Sarkar, and P. Bhattacharyya, "High dynamic range methanol sensor based on aligned ZnO nanorods," *IEEE Sensors J.*, vol. 13, no. 5, pp. 1669–1676, May 2013.
- [27] D. Acharyya and P. Bhattacharyya, "Alcohol sensing performance of ZnO hexagonal nanotubes at low temperatures: A qualitative understanding," *Sens. Actuators B, Chem.*, vol. 228, pp. 373–386, Jun. 2016.
- [28] S. Jeong, D. Yoo, J.-T. Jang, M. Kim, and J. Cheon, "Well-defined colloidal 2-D layered transition-metal chalcogenide nanocrystals via generalized synthetic protocols," *J. Amer. Chem. Soc.*, vol. 134, pp. 18233–18236, Oct. 2012.
- [29] B. Bhowmik, K. Dutta, A. Hazra, and P. Bhattacharyya, "Low temperature acetone detection by p-type nano-titania thin film: Equivalent circuit model and sensing mechanism," *Solid-State Electron.*, vol. 99, pp. 84–92, Sep. 2014.
- [30] M. Soni, T. Arora, R. Khosla, P. Kumar, A. Soni, and S. K. Sharma, "Integration of highly sensitive oxygenated graphene with aluminum micro-interdigitated electrode array based molecular sensor for detection of aqueous fluoride anions," *IEEE Sensors J.*, vol. 16, no. 6, pp. 1524–1531, Mar. 2016.
- [31] S. Deobrat, "2D-HfS₂ as an efficient photocatalyst for water splitting," *Catal. Sci. Technol.*, vol. 6, pp. 6605–6614, 2016.
- [32] X. Zhang, Q.-H. Tan, J.-B. Wu, W. Shi, and P.-H. Tan, "Review on the Raman spectroscopy of different types of layered materials," *Nanoscale*, vol. 8, no. 12, pp. 6435–6450, 2016.
- [33] S. Lai *et al.*, "HfO₂/HfS₂ hybrid heterostructure fabricated via controllable chemical conversion of two-dimensional HfS₂," *Nanoscale*, vol. 10, no. 39, pp. 18758–18766, 2018.

- [34] L. Roubi and C. Carlone, "Resonance Raman spectrum of HfS₂ and ZrS₂," *Phys. Rev. B, Condens. Matter*, vol. 37, no. 12, pp. 6808–6912, Apr. 1988.
- [35] T.-Y. Chen *et al.*, "On an ammonia gas sensor based on a Pt/AlGaN heterostructure field-effect transistor," *IEEE Electron Device Lett.*, vol. 33, no. 4, pp. 612–614, Apr. 2012.
- [36] A. Hazra, S. Das, J. Kanungo, C. K. Sarkar, and S. Basu, "Studies on a resistive gas sensor based on sol-gel grown nanocrystalline p-TiO₂ thin film for fast hydrogen detection," *Sens. Actuators B, Chem.*, vol. 183, pp. 87–95, Jul. 2013.
- [37] S. Das, S. Ghosh, R. Kumar, A. Bag, and D. Biswas, "Highly sensitive acetone sensor based on Pd/AlGaN/GaN resistive device grown by plasma-assisted molecular beam epitaxy," *IEEE Trans. Electron Devices*, vol. 64, no. 11, pp. 4650–4656, Nov. 2017.
- [38] S. Das, A. Bag, R. Kumar, and D. Biswas, "Fast response (7.6s) acetone sensing by InGaN/GaN on Si (111) at 373 K," *IEEE Electron Device Lett.*, vol. 38, no. 3, pp. 383–386, Mar. 2017.
- [39] S. Das, S. Majumdar, R. Kumar, S. Ghosh, and D. Biswas, "Thermodynamic analysis of acetone sensing in Pd/AlGaN/GaN heterostructure Schottky diodes at low temperatures," *Scripta Mater.*, vol. 113, pp. 39–42, Mar. 2016.
- [40] M. Johansson, O. Lytken, and I. Chorkendorff, "The sticking probability of hydrogen on Ni, Pd and Pt at a hydrogen pressure of 1 bar," *Topics Catal.*, vol. 46, nos. 1–2, pp. 175–187, Sep. 2007.
- [41] P. Bhattacharyya, B. Bhowmik, and H.-J. Fecht, "Operating temperature, repeatability, and selectivity of TiO₂ nanotube-based acetone sensor: Influence of Pd and Ni nanoparticle modifications," *IEEE Trans. Device Mater. Rel.*, vol. 15, no. 3, pp. 376–383, Sep. 2015.
- [42] A. Hazra, K. Dutta, B. Bhowmik, P. P. Chattopadhyay, and P. Bhattacharyya, "Room temperature alcohol sensing by oxygen vacancy controlled TiO₂ nanotube array," *Appl. Phys. Lett.*, vol. 105, Art. no. 081604, Aug. 2014.
- [43] F. Mendoza, D. M. Hernández, V. Makarov, E. Febus, B. R. Weiner, and G. Morell, "Room temperature gas sensor based on tin dioxidecarbon nanotubes composite films," *Sens. Actuators B, Chem.*, vol. 190, pp. 227–233, Jan. 2014.
- [44] M. Mabrook and P. Hawkins, "A rapidly-responding sensor for benzene, methanol and ethanol vapours based on films of titanium dioxide dispersed in a polymer operating at room temperature," *Sens. Actuators B, Chem.*, vol. 75, no. 3, pp. 197–202, May 2001.
- [45] T. T. Tung, M. Castro, I. Pillin, T. Y. Kim, K. S. Suh, and J. -F. Feller, "Graphene–Fe₃O₄/PIL–PEDOT for the design of sensitive and stable quantum chemo-resistive VOC sensors," *Carbon*, vol. 74, pp. 104–112, Aug. 2014.
- [46] D. Acharyya and P. Bhattacharyya, "Highly efficient room-temperature gas sensor based on TiO₂ nanotube-reduced graphene-oxide hybrid device," *IEEE Electron Device Lett.*, vol. 37, no. 5, pp. 656–659, May 2016.
- [47] N. Chen *et al.*, "Enhanced room temperature sensing of Co₃ O₄intercalated reduced graphene oxide based gas sensors," *Sens. Actuators B, Chem.*, vol. 188, pp. 902–908, Nov. 2013.
- [48] D. Acharyya, K. Y. Huang, P. P. Chattopadhyay, M. S. Ho, H.-J. Fecht, and P. Bhattacharyya, "Hybrid 3D structures of ZnO nanoflowers and PdO nanoparticles as a highly selective methanol sensor," *Analyst*, vol. 141, pp. 2977–2989, Mar. 2016.
- [49] S. Ghosal and P. Bhattacharyya, "A potential gas sensor device based on Pd/RGO/TiO₂ nanotube ternary hybrid junction," *Microelectron. Rel.*, vol. 78, no. 2, pp. 299–306, Nov. 2017.
- [50] S. C. Hernández, C. M. Hangarter, A. Mulchandani, and N. V. Myung, "Selective recognition of xylene isomers using ZnO-SWNTs hybrid gas sensors," *Analyst*, vol. 137, no. 11, pp. 2549–2552, Jun. 2012.
- [51] S. Yang, C. Jiang, and S.-H. Wei, "Gas sensing in 2D materials," Appl. Phys. Rev., vol. 4, Apr. 2017, Art. no. 021304.



Subhashis Das (M'17) received the master's degree in nano science and technology from Jadavpur University, Kolkata, India, in 2012, and the Ph.D. degree from in semiconductor device and solid-state gas sensor from IIT Kharagpur, India, in 2016.

He is currently a National Post-Doctoral Fellow with IIT Mandi, India. His current research interests include the development of chemical sensors and optoelectronic devices based on epitaxial compound semiconductors and 2D materials.



Shivani Sharma received the B.Tech. degree in electronics and communication engineering from Eternal University, India, in 2012, and the M.Tech. degree in VLSI technology from Graphic Era University, Dehradun, India, in 2014. She is currently pursuing the Ph.D. degree with the School of Computing and Electrical Engineering, Indian Institute of Technology (IIT) Mandi, India.

Her research interests include 2D materials, organic electronics, and photodetectors.



Satinder Kumar Sharma received the M.Sc. degree in physics (electronics science) from Himachal Pradesh University, Shimla, India, in 2002, and the Ph.D. degree from the Department of Electronics Science, on "Silicon based gate dielectric materials for VLSI/ULSI Technology," Kurukshetra University, Kurukshetra, India, in 2007.

From 2007 to 2010, he was a Post-Doctoral Fellow with the DST-Unit on Nanosciences and Nanotechnology, Department of CHE, Indian Institute of Technology (IIT) Kanpur, India. He was a Faculty

Member of the Electronics and Microelectronics Division, Indian Institute of Information Technology (IIIT) Allahabad, India, from 2010 to 2012. He is currently an Associate Professor with the School of Computing and Electrical Engineering (SCEE), Indian Institute of Technology (IIT) Mandi, India. His current research interests include microelectronics circuits and system, CMOS device, fabrication and characterization, nano/micro fabrication and design, polymer nano composite, sensors, and photovoltaic and self-assembly.