WS$_2$ and MoS$_2$ thin film gas sensors with high response to NH$_3$ in air at low temperature

Topias Järvinen$^{1}$, Gabriela S Lorite$^{1}$, Jani Peräntie$^{1}$, Geza Toth$^{2}$, Simo Saarakkala$^{3}$, Vesa K Virtanen$^{3}$ and Krisztian Kordas$^{1,4}$

$^1$Microelectronics Research Unit, Faculty of Information Technology and Electrical Engineering, University of Oulu, PO Box 4500, FI-90014 University of Oulu, Finland
$^2$VTT Technical Research Center of Finland, PO Box 1100, FI-90571, Oulu, Finland
$^3$Research Unit of Medical Imaging, Physics and Technology, Faculty of Medicine, University of Oulu, PO Box 5000, FI-90014 University of Oulu, Finland

E-mail: krisztian.kordas@oulu.fi

Received 16 April 2019, revised 12 June 2019
Accepted for publication 27 June 2019
Published 18 July 2019

Abstract
Transition metal dichalcogenides (TMDs) have received immense research interest in particular for their outstanding electrochemical and optoelectrical properties. Lately, chemical gas sensor applications of TMDs have been recognized as well owing to the low operating temperatures of devices, which is a great advantage over conventional metal oxide based sensors. In this work, we elaborate on the gas sensing properties of WS$_2$ and MoS$_2$ thin films made by simple and straightforward thermal sulfurization of sputter deposited metal films on silicon chips. The sensor response to H$_2$, H$_2$S, CO and NH$_3$ analytes in air at 30 $^\circ$C has been assessed and both MoS$_2$ and WS$_2$ were found to have an excellent selectivity to NH$_3$ with a particularly high sensitivity of 0.10 ± 0.02 ppm$^{-1}$ at sub-ppm concentrations in the case of WS$_2$. The sensing behavior is explained on the bases of gas adsorption energies as well as carrier (hole) localization induced by the surface adsorbed moieties having reductive nature.

Supplementary material for this article is available online

Keywords: 2D materials, gas sensors, WS$_2$, MoS$_2$, room temperature sensing, NH$_3$

(Some figures may appear in colour only in the online journal)

Introduction
Continuous and reliable detection of different gases is essential in industrial process monitoring, vehicle emission control, in and outdoor air quality safety and environment protection [1]. In these applications, traditionally metal oxide semiconductors such as SnO$_2$, WO$_3$, CeO$_2$, Nb$_2$O$_5$ and ZnO as well as their metal or metal oxide decorated derivatives have been most commonly utilized as sensing materials [2–5]. While these sensors and their arrays offer excellent and reliable discrimination and even quantification of analytes, their operation is only possible at high temperatures that requires considerable power sourcing. Nowadays, with the spread of internet-of-things and dispersed networks that involve complex sensing systems with small but large number of devices, power consumption becomes a significant factor. Powering such devices is even more cumbersome in the case of remote and autonomous off-grid systems [6–8] running on batteries and/or energy scavenging units with limited power output [9]. Accordingly, new materials that would allow for low temperature operation could inevitably alleviate power related
challenges and contribute to better and more robust sensor networks.

2D layered transition metal dichalcogenides (TMDs) have recently been found very attractive for a wide range of applications such as energy storage, photodetectors and switches, electrocatalysis, photocatalysis as well as for chemoresistive sensors [10–14]. TMDs (MX$_2$, where M is a transition metal and X is a chalcogen) have a layered structure, in which the coordination of metal atoms can be trigonal or octahedral resulting in either hexagonal or rhombohedral structure symmetry [15–17]. These materials have not only high specific surface area but as the covalent layers are hold together with weak van der Waals forces, and thus have large interplanar spacing, intercalation of small moieties in between the layers is also possible making such structures suitable for multitude interactions with the environment. Recent studies of WS$_2$ and MoS$_2$ as well as their hybrid structures (functionalized nanofibers [18, 19], quantum dots [20] and metal doped nanoflower structures [21]) in gas sensing applications indicate substantial response at low operating temperatures with particular selectivity to certain gases such as H$_2$S and NH$_3$ [18, 22–24]. The lowered operation temperature of transition metal chalcogenide-based sensors, in reference to the oxides of the corresponding metals, is due to their typically lower bandgap and better conductivity. Furthermore, similar to semiconducting metal oxide sensors, the gas selectivity of TMDs is in many instances is associated to the affinity of surfaces for adsorbing different analytes and related surface charging/polarization effects [18, 24]. In addition, it has been identified that apart from surface charging/polarization, reversible doping of the chalcogenide lattice with heteroatoms can significantly contribute to sensing [18].

The aim of the present work is to elaborate on the low temperature gas sensing properties of TMDs produced by sulfurizing sputter deposited tungsten and molybdenum films. As we show, the direct synthesis of WS$_2$ and MoS$_2$ thin films on Si chips is robust and offer a route which is up and down-scaleable without necessitating any transfer steps of 2D materials [24]. Thin films of crystalline WS$_2$ grown on Si chips display distinct selectivity towards NH$_3$ with a sensitivity of 0.10 ± 0.02 ppm$^{-1}$, even at 30 °C. Interestingly, the surfaces remain practically irresponsive to other analytes (CO, H$_2$, and H$_2$S), which is unexpected in the light of our previous studies on WS$_2$ nanowire-nanoflake hybrids that showed unprecedented selectivity and sensitivity to H$_2$S.

**Experimental**

**Materials and sensor fabrication**

A 4″ p-type Si wafer with 1500 nm thermal oxide layer was pre-cut to 7 × 7 mm$^2$ size chips using a pulsed laser (LPKF ProtoLaser U3). The chips were then coated with metal films (W or Mo) of 20 nm thickness by sputtering (Torr International PVD System) and sulfurized subsequently. The sulfurization was carried out in a tube furnace (Thermo Scientific Thermolyne having a quartz tube of 2″ in diameter) in which four identical chips at a time were inserted together with 1.0 g of sulfur powder (Sigma-Aldrich 215236). Before heating up the furnace, the reactor was evacuated to a base pressure of about 5 Torr and purged with N$_2$. After repeating the pumping and purging steps three times, the reactor was heated to 800 °C and a flow of 400 sccm N$_2$ was set and maintained throughout the process. (Note: experiments using Ti and Cr metal thin films were also carried out but as turned out, the sulfurized films were not electrically conductive.)

Contact electrodes were deposited on the chips by sputtering films of Ti (25 nm) and then Pt (220 nm) through a shadow mask (laser patterned polycrystalline alumina with a thickness of 250 μm) mounted on the chips. The mask pattern was designed to house two pairs of electrodes, each with a gap of 500 μm.

**Materials characterization**

Atomic force microscopy (AFM, MultiMode 8, Nanoscope V, Bruker) was used to evaluate the surface topology and root mean square roughness of the sulfurized films using conical Si probes (NSC18/Al BS MikroMash, Tallin, Estonia) in PeakForce mode. Each film was scanned over 10 × 10 μm$^2$ and 1 × 1 μm$^2$ areas. All AFM images were processed and analyzed using Gwydion software. Particle size distribution curves were compiled by counting at least 150 particles of each film in the AFM topology maps.

The chemical composition and crystal structure of the sulfurized films were characterized using energy-dispersive x-ray spectroscopy (EDS, Zeiss ULTRA Plus with multiple point analysis and averaging), Raman spectroscopy (Thermo Scientific DXR2xi Raman imaging microscope, 532 nm wavelength and 10 mW power) and grazing incidence x-ray diffraction (GIXRD, Bruker D8 Discovery, Cu K$_\alpha$, 2θ sweep from 10° to 80° at a fixed grazing incidence angle of 4.5°).

**Electrical and gas sensing measurements**

The conductance of the films was assessed with current–voltage (I–V) measurements by probing the Ti/Pt contact electrode pads with a Wentworth Labs probe station connected to a Keithley 2636A SYSTEM SourceMeter®. Voltage sweeps between −5 and 6 V were applied in each measurement. Because of the poor conductivity of sulfurized Ti and Cr, only the MoS$_2$ and WS$_2$ films were considered for further analyses.

Gas sensitivity measurements were performed in a temperature controlled chamber (Linkam TMS 94) connected to mass flow controllers (MKS Instruments 1179A Mass-Flo®). The analyte gases we used were H$_2$ (AGA, 99% N$_2$, 1% H$_2$), CO (AGA, 50 ppm CO in N$_2$), NH$_3$ (AGA, 50 ppm NH$_3$ in N$_2$), and H$_2$S (AGA, 200 ppm H$_2$S in N$_2$), all buffered in synthetic air (AGA, 80% N$_2$, 20% O$_2$) at total flow rates from 500 sccm to 1000 sccm (depending on the analyte gas and its desired concentration range). The measurement profile had a 60 min stabilizing period in the beginning, which was followed by analyte pulses of 30 min duration with increasing concentrations. Between each pulse,
Figure 1. AFM surface topologies of sputter deposited (a) Mo and (b) W thin films as well as their sulfurized derivatives displayed in panels (c) and (d), respectively. Scale bars indicate 200 nm. Insets show the evolution of particle size in the films before and after sulfurization. Raman spectra of sulfurized (e) Mo and (f) W confirming the corresponding phases in the thin films are MoS$_2$ and WS$_2$. Panels (g) and (h) are the respective x-ray diffraction patterns acquired using grazing incidence setup including the original and sulfurized W and Mo films.
Results and discussion

AFM images of large scans areas (10 × 10 μm²) revealed the sulfurized Mo films were uniform, whereas the sulfurized W layers had some small pinholes of 0.5–2 μm in diameter (not shown here). Apart from the surface defects in the sulfurized W layer, both products were found homogeneous with grain-like morphology. The original particle size of the metal films increased from 23 ± 4 nm (Mo) and 21 ± 4 nm (W) to 37 ± 9 nm and 36 ± 8 nm, respectively. The particle size distributions (inset panels) seem to follow a log-normal curve rather than Gaussian. The increased particle diameters are likely caused by the formation of the corresponding sulfides, having lower density than that of the corresponding metals (figures 1(a)–(d)).

Raman spectra of the films displayed in figures 1(e) and (f) indicate the materials are crystalline MoS₂ and WS₂, respectively [25, 26]. Two strong peaks are observed for MoS₂ at 378 and 405 cm⁻¹ that correspond to the in-plane (E₂₉) and out-of-plane (A₁₉) vibration modes [27]. According to the difference of Raman shifts and also to the intensity ratio of these two peaks, MoS₂ is multi-layered [28]. Likewise, the WS₂ film has two intensive peaks at 349 and 415 cm⁻¹ that can be assigned to in-plane (E₂₉) and out-of-plane (A₁₉) vibration modes, evidencing that the structure is multi-layered [29, 30]. The presence of the longitudinal acoustic mode vibrations (LA) and their higher-order harmonics (2LA and 4LA) are also visible in the spectra. The low intensity of the 2LA peaks confirms the chalcogenides are multi-layered [26].

Note, that in each spectrum, the relatively intensive peak at around 520 cm⁻¹ is due to the Si substrate.

Grazing incidence x-ray diffraction patterns of the original and sulfurized metal films are displayed in figures 1(g) and (h). The metal films pattern fits well the reference patterns PDF 42-1120 and PDF 01-1204 for Mo and W, respectively. In addition, the metallic tungsten film shows some W₅O which is indexed according to PDF 02-1138. The pattern of MoS₂ shows two strong reflections at 33.2° and 59.5°, which may be indexed as the (110) plane and superposed reflections from the (110) and (008) planes of the hexagonal form of the crystal (PDF 75-1539). However, the strong reflections of the (002) and (102) planes at 14.1° and 36.0° of layered structure that should be also present in the pattern are missing from our diffractogram suggesting the lack of long-range order in stacking of the layers in the material. Another explanation might be a specific crystal orientation on the substrate with basal planes being perpendicular to the surface. However, this latter option is unlikely, since the AFM images show spherical particles on the surfaces that do not resemble oriented crystals. On the other hand, in the case of the WS₂ film, the pattern can be assigned to the planes of the hexagonal lattice (PDF 02-0131). The reflection at 14.1° corresponds to the (002) plane, the broad peak at 33.1° is due to the superposed intensities of the (100) and (101), whereas the broad reflection centered at 59.0° can be assigned to the unresolved (110), (008) and (112) planes [29]. It is also worth noting here, that the broad reflection at around 20.0° is due to amorphous SiO₂ of the substrate.

The composition of the films was analyzed with EDS (table 1). The aforementioned pinhole defects seen in WS₂ films comprise only silicon and oxygen confirming that the defects are indeed voids in the film. Since the thickness of TMD films is ~20 nm, both Si and O of the Si/SiO₂ substrate are visible in the energy-dispersive x-ray spectra even at locations without pinholes. The ratio of sulfur and metal is very close to 2:1 for both TMD films, which implies the films are at least nearly stoichiometric. In the case of WS₂ there is a notable amount of C contamination present, which was not observed in MoS₂ films.

Before the actual sensor measurements, the electrical conductivity of each film was assessed with I–V measurements. Both MoS₂ and WS₂ films were sufficiently conductive (with resistances of several tens of megaohms and hundreds of megaohms, respectively) to perform sensor measurements on those. The I–V curves were found linear for MoS₂, whereas WS₂ showed slight nonlinearity (figures 2(a) and (d), respectively), suggesting a barrier between the semiconductor film and the Ti/Pt electrodes [31]. Although the primary direct contact with the chalcogenide films was meant to be Ti, some Pt also deposited on the films around the perimeter of the Ti under-metallization due to the imperfect contact between the shadow mask and the substrate. Considering the typical bandgap, electron affinity and the work function values of bulk MoS₂ (E₀ ≈ 1.3 eV, χ ≈ 4.0 eV and φ ≈ 5.25 eV) [32, 33] and WS₂ (1.4, 4.0 and 5.1 eV) [34] as well as the work function values of Ti (φₜ ≈ 4.3 eV) and Pt (φₚt ≈ 5.3 eV), we find that the contact between Ti and the chalcogenide films is Schottky-type (figures 2(b) and (e)), whereas it is quasi-ohmic with Pt (figures 2(c) and (f)). Furthermore, because of the better alignment of the Fermi level of Pt with the valence band of MoS₂ in reference to WS₂, the ohmic character is also expected to be better, which explains the good linearity of the I–V slopes and higher conductivity for the MoS₂ based devices and slight nonlinearity measured for the WS₂ based ones.

In general, WS₂ based devices were electrically less conductive but had considerably higher response to the
analytes, although with higher device-to-device variation (average of six devices for each gas) in reference to MoS2 sensors (figures 3 and 4(c)). The films show a small response to H2 (0.00005 ± 0.00003 ppm⁻¹ and 0.00016 ± 0.00017 ppm⁻¹ for MoS2 and WS2, respectively). This is comparable to previous results with WS2 nanowire/nanoflake hybrid structures [18]. For H2S and CO the responses were either nonexistent or inconsistent. Regardless of the variance of the response to other analytes, for NH3 the devices display a consistent and very good response (0.0026 ± 0.0022 ppm⁻¹ and 0.0586 ± 0.0305 ppm⁻¹ for MoS2 and WS2, respectively).

Since the response to NH3 with both sensors was very distinct at 1 ppm gas concentration, additional measurements were performed in the sub-ppm NH3 concentrations. Significant responses to 200 ppb of the analyte could be measured with average sensitivities of 0.0315 ± 0.00282 ppm⁻¹ and 0.104 ± 0.0243 ppm⁻¹, respectively (figure 4). According to the signal to the base noise ratio, the limit of detection (LOD) is under 100 ppb for both materials. The response time of the MoS2 based sensors to the analytes were found to be rather short for NH3 (5–6 min) and slightly longer for other gases (10–30 min). The sensor recovery time constants were long (30–60 min) and varied greatly among the gases. On the other hand, sensors made of the WS2 films showed a consistent and quick (5–6 min) response and recovery for each gas, which is excellent considering that the measurements were carried out at near room temperature.

According to the reducing nature of all the analyte gases and the response of the sensors, it can be concluded that both WS2 and MoS2 exhibit p-type semiconducting behavior, and the resistance of the sensors increase with the concentration of the analytes. This is usually explained by surface adsorption and subsequent charge transfer based mechanisms; the reducing gases donate electrons (or localize holes) in the materials, thus reducing the concentration of charge carriers, and consequently reduce the conductivity of the material [18, 20]. A number of other studies show selectivity to NH3 for both WS2 [22, 23, 31, 35] and MoS2 [20, 36, 37]. In the case of MoS2, the LOD of 100 ppb is similar to other results (300 ppb measured and 50 ppb predicted) [24]. In the case of WS2, the reported LODs are about a decade worse (~1 ppm)[38, 23] than our data. (In table S2, we list a more detailed comparison of the results with other reported values for MoS2 and WS2 based devices and commercial NH3 sensors.)

As the sensing behavior of the thin films presented in the manuscript is similar to or better than those reported for other MX2 based devices regarding NH3, we may assume that the
sensing mechanism is also similar, i.e. associated with surface adsorption and consequent partial charge transfer. Calculated (local-density approximation, LDA) surface adsorption energies of H₂, NH₃ and CO on MoS₂ with corresponding values of $-82$ meV, $-250$ meV and $-128$ meV, respectively, also seem to support the high response to NH₃ on MoS₂ films [20, 39]. Similarly, on WS₂, the calculated energies [18] are $-57.4$ meV (H₂), $-171.7$ meV (NH₃) and $-84.7$ meV (CO) indicating that the response to NH₃ is expected to be the highest. Here, we have to point out another effect regarding H₂S. Namely, considering the high adsorption energy of H₂S ($-181$ meV) on WS₂ nanosheets, we shall also expect to see

**Figure 3.** Baseline corrected responses to MoS₂ ((a), (c), (e), (g)) for H₂, H₂S, Co and NH₃) and WS₂ films ((b), (d), (f), (h), respectively). Note: the responses represent the best performing sample of the material for the particular analyte.
good response to H2S. However, this is not the case with our thin films. The reason is that competitive lattice doping with O and S is responsible for the detection of H2S as we have concluded in our earlier work \[18\] based on XPS analysis of WS2 nanowire-nanoflake hybrid structures, in which nanosheets of \(\sim 5\) nm thickness were sticking out from the surface of the nanowires. The structure is different now, since both WS2 and MoS2 films are comprising nanoparticles of 20–30 nm in their diameter with limited diffusion of O and S in the lattices, thus despite the large adsorption energy of H2S, the sensor response is insignificant to this analyte.

To analyze the cross-sensitivity of the sensors, we performed two sets of measurements for two samples of each material (figure 5). In the first set, we applied gas pulses with concentrations of 1 ppm, 200 ppm, 10 ppm and 5 ppm for NH3, H2, CO and H2S, respectively. In the other set, the respective concentrations were 10, 100, 5 and 5 ppm. The sensitivity to NH3 remained high for all samples throughout the measurements (the first three pulses in each plot), which proves the repeatability and reproducibility of the devices. During the long 4th pulse of NH3 (starting at 300 min) we introduced also H2, then CO and H2S for short intervals (30 min each starting at 330 min, 390 min and 460 min, respectively) to see the influence of the secondary analytes. The MoS2 film was affected only by H2 but only when its concentration was high relative to the concentration of NH3 (figure 5(a)). The influence of secondary analytes on the response to NH3 introduced at similar concentrations was insignificant (figure 5(c)). However, in the case of the WS2 based device, we observe a decreased response to low
Concentration NH₃, when introducing the other gases at high concentrations (figure 5(b)). The effect is lower, when the analyze concentrations were adjusted to be similar (figure 5(d)). The results measured with WS₂ sensors indicate, that the secondary gas pulses clan flush away the surface adsorbed NH₃ thus influencing the sensor performance.

Furthermore, it is worth pointing out that all sensors were operating in a rather reliable and repeatable manner throughout a period of more than nine month testing in various experimental conditions, which indicates that the thin film WS₂ and MoS₂ structures are very robust and practical.

Conclusions

A method to produce MoS₂ and WS₂ thin films by simply annealing sputtered Mo and W films in S vapor is proposed, and the gas response of the as-synthesized films are examined in the classical resistive sensor arrangement. Both materials showed excellent selectivity for NH₃ with very high corresponding sensitivity values (0.03 ± 0.0 ppm⁻¹ and 0.10 ± 0.02 ppm⁻¹, respectively) at 30 °C. Despite the low operation temperature, the WS₂ based sensors responded to the stimuli and then recovered after each gas pulse quite fast (5–6 min). The results obtained with our robust TMD films compete with other exfoliated or CVD grown single or few-layer chalcogenides and outperforms metal oxides. Since the process steps involved apply standard techniques, up and down-scalable, and the films produced are easy to process further (e.g. coating with other materials) the results presented in this paper may pave the road for sensor applications of TMD thin films.

Acknowledgments

Support received from the Väisälä Foundation, Riitta and Jorma J. Takenan Foundation, Academy of Finland (298409), University of Oulu (Project: Entity) and European Union Interreg Nord – Lapin liitto (Project: Transparent, conducting and flexible films for electrodes) are acknowledged. Kai Metsäköivu (Center of Microscopy and Nanotechnology, University of Oulu) is acknowledged for the metal films deposition.

Conflicts of interest

The authors declare no conflicts interest.

ORCID iDs

Vesa K Virtanen https://orcid.org/0000-0002-5797-5365
Krisztian Kordas https://orcid.org/0000-0002-7331-1278

References

[1] Meixner H and Lampe U 1996 Metal oxide sensors Sensors Actuators B 33 198–202
[2] Neri G 2015 First fifty years of chemoresistive gas sensors Chemosensors 3 1–20
[3] Kukkola J et al 2012 Inkjet-printed gas sensors: metal decorated WO₃ nanoparticles and their gas sensing properties J. Mater. Chem. 22 17878
[4] Kukkola J, Mohi M, Leino A–R, Mäkkin J, Halonen N, Shchukarev A, Konya Z, Jantunen H and Kordas K 2013 Room temperature hydrogen sensors based on metal decorated WO₃ nanowires Sensors Actuators B 186 90–5
[5] Dey A 2018 Semiconductor metal oxide gas sensors: a review Mater. Sci. Eng. B 229 206–17
[6] Aponte-Luis J et al 2018 An efficient wireless sensor network for industrial monitoring and control Sensors 18 182
[7] Somov A, Baranov A, Savkin A, Spirjakin D, Spirjakin A and Passerone R 2011 Development of wireless sensor network for combustible gas monitoring Sensors Actuators 171 398–405
[8] Jarvinen T, Lorite G S, Rautio A–R, Koppany L J, Kukovecz A, Konya Z, Kordas K and Toth G 2017 Portable cyber-physical system for indoor and outdoor gas sensing Sensors Actuators B 252 983–90
[9] Akhtar F and Rehmani M H 2015 Energy replenishment using renewable and traditional energy resources for sustainable wireless sensor networks: a review Renew. Sustain. Energy Rev. 45 769–84
[10] Kuc A 2014 Low-dimensional transition-metal dichalcogenides Chemical Modelling vol 11 (London: Royal Society of Chemistry) pp 1–29
[11] Li B L, Wang J, Zou H L, Garaj S, Lim C T, Xie J, Li N B and Leong D T 2016 Low-dimensional transition metal dichalcogenide nanostructures based sensors Adv. Funct. Mater. 26 7034–56
[12] Kim T, Kim Y, Park S, Kim S, Jang H, Kim T H, Kim Y H, Park S Y, Kim S Y and Jang H W 2017 Two-dimensional transition metal sulfoxides for chemoresistive gas sensing: perspective and challenges Chemosensors 5 15
[13] Eftekhar A 2017 Tungsten dichalcogenides (WS₂, WSe₂, and WTe₂): materials chemistry and applications J. Mater. Chem. A 5 18299–325
[14] Hasani A, Tekalrne M, Van L Q, Jang H W and Kim S Y 2019 Two-dimensional materials as catalysts for solar fuels: hydrogen evolution reaction and CO₂ reduction J. Mater. Chem. A 7 430–54
[15] Andoshe D M, Jeon J-M, Kim S Y and Jang H W 2015 Two-dimensional transition metal dichalcogenide nanomaterials for solar water splitting Electron. Mater. Lett. 11 323–35
[16] Song I, Park C and Choi H C 2015 Synthesis and properties of molybdenum disulphide: from bulk to atomic layers RSC Adv. 5 7495–514
[17] Wang Q H, Kalantar-Zadeh K, Kis A, Coleman J N and Strano M S 2012 Electronics and optoelectronics of two-dimensional transition metal dichalcogenides Nat. Nanotechnol. 7 699–712
[18] Asrres G A et al 2018 Ultrasensitive H₂S gas sensors based on p-type WS₂ hybrid materials Nano Res. 11 4215–24
[19] Cha J-H, Choi S-J, Yu S and Kim I-D 2017 2D WS₂-edge functionalized multi-channel carbon nanofibers: effect of WS₂ edge-abundant structure on room temperature NO₂ sensing J. Mater. Chem. A 4 58725–32
[20] Yue N, Weicheng J, Rongguo W, Guomin D and Yifan H 2016 Hybrid nanostructures combining graphene–MoS₂ quantum dots for gas sensing J. Mater. Chem. A 4 8198–203
[21] Zhang D, Wu J, Li P and Cao Y 2017 Room-temperature SO₂ gas-sensing properties based on a metal-doped MoS₂
nanoflower: an experimental and density functional theory investigation. *J. Mater. Chem.* A **5** 20666–77

[22] Li X, Li X, Li Z, Wang J and Zhang J 2017 WS2 nanoflakes based selective ammonia sensors at room temperature *Sensors Actuators* B **240** 273–7

[23] O’Brien M, Lee K, Morrish R, Bern N C, McEvoy N, Wolden C A and Duesberg G S 2014 Plasma assisted synthesis of WS2 for gas sensing applications *Chem. Phys. Lett.* **615** 6–10

[24] Lee K, Gatesby R, McEvoy N, Hallam T and Duesberg G S 2013 High-performance sensors based on molybdenum disulfide thin films *Adv. Mater.* **25** 6699–702

[25] Gołasa K, Grzeszczyk M, Bożek R, Leszczyński P, Wysmolek A, Potemski M and Babiński A 2014 Resonant Raman scattering in MoS2—from bulk to monolayer *Solid State Commun.* **197** 53–6

[26] Berkdemir A et al 2013 Identification of individual and few layers of WS2 using raman spectroscopy *Sci. Rep.* **3** 1755

[27] Cwik S, Mitoraj D, Mendoza Reyes O, Rogalla D, Peeters D, Kim J, Schütz H M, Bock C, Beranek R and Devi A 2018 Direct growth of MoS2 and WS2 layers by metal organic chemical vapor deposition *Adv. Mater. Interfaces* **5** 1800140

[28] Li S-L, Miyazaki H, Song H, Kuramochi H, Nakaharai S and Tsukagoshi K 2012 Quantitative Raman scattering and reliable thickness identification for atomic layers on insulating substrates *ACS Nano* **6** 7381–8

[29] Asres G A et al 2016 A novel WS2 nanowire-nanoflake hybrid material synthesized from WO3 nanowires in sulfur vapor *Sci. Rep.* **6** 25610

[30] Viršek M, Jesih A, Milošević I, Damnjanović M and Remškar M 2007 Raman scattering of the MoS2 and WS2 single nanotubes *Surf. Sci.* **601** 2868–72

[31] Huo N, Yang S, Wei Z, Li S-S, Xia J-B and Li J 2015 Photoresponsive and gas sensing field-effect transistors based on multilayer WS2 nanoflakes *Sci. Rep.* **4** 5209

[32] Baik S S, Im S and Choi H J 2017 Work function tuning in two-dimensional MoS2 field-effect-transistors with graphene and titanium source-drain contacts *Sci. Rep.* **7** 45546

[33] Hao G, Huang Z, Liu Y, Qi X, Ren L, Peng X, Yang L, Wei X and Zhong J 2013 Electrostatic properties of few-layer MoS2 films *AIP Adv.* **3** 042125

[34] Asres G A et al 2018 High photoresponse of individual WS2 nanowire-nanoflake hybrid materials *Appl. Phys. Lett.* **112** 233103

[35] Qin Z, Zeng D, Zhang J, Wu C, Wen Y, Shan B and Xie C 2017 Effect of layer number on recovery rate of WS2 nanosheets for ammonia detection at room temperature *Appl. Surf. Sci.* **414** 244–50

[36] Late D J et al 2013 Sensing behavior of atomically thin-layered MoS2 transistors *ACS Nano* **7** 4879–91

[37] Yao Y, Tolentino L, Yang Z, Song X, Zhang W, Chen Y and Wong C 2013 High-concentration aqueous dispersions of MoS2 *Adv. Funct. Mater.* **23** 3577–83

[38] Perrozzi F, Emanjomeh S M, Paolucci V, Taglieri G, Ottaviano L and Cantalini C 2017 Thermal stability of WS2 flakes and gas sensing properties of WS2/VO3 composite to H2, NH3 and NO2 *Sensors Actuators* B **243** 812–22

[39] Wang X, Yang S, Yue Q, Wu F and Li J 2014 Response of MoS2 nanosheet field effect transistor under different gas environments and its long wavelength photoresponse characteristics *J. Alloys Compd.* **615** 989–93