



**HAL**  
open science

## Wafer-sized WS<sub>2</sub> monolayer deposition by sputtering

Michelle Marie S Villamayor, Sajid Husain, Reinier Oropesa-Nuñez, Fredrik O L Johansson, Rebecka Lindblad, Pedro Lourenço, Romain Bernard, Nadine Witkowski, Geoffroy Prévot, Nomi L a N Sorgenfrei, et al.

► **To cite this version:**

Michelle Marie S Villamayor, Sajid Husain, Reinier Oropesa-Nuñez, Fredrik O L Johansson, Rebecka Lindblad, et al.. Wafer-sized WS<sub>2</sub> monolayer deposition by sputtering. *Nanoscale*, 2022, 14 (17), pp.6331 - 6338. 10.1039/d1nr08375a . hal-03826871

**HAL Id: hal-03826871**

**<https://hal.science/hal-03826871v1>**

Submitted on 24 Oct 2022

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Cite this: DOI: 10.1039/d1nr08375a

## Wafer-sized WS<sub>2</sub> monolayer deposition by sputtering

Michelle Marie S. Villamayor,<sup>a</sup> Sajid Husain,<sup>b,c</sup> Reinier Oropesa-Nuñez,<sup>id b</sup>  
 Fredrik O. L. Johansson,<sup>id d</sup> Rebecka Lindblad,<sup>id e</sup> Pedro Lourenço,<sup>f</sup>  
 Romain Bernard,<sup>f</sup> Nadine Witkowski,<sup>f</sup> Geoffroy Prévot,<sup>id f</sup>  
 Nomi L. A. N. Sorgenfrei,<sup>id g,h</sup> Erika Giangrisostomi,<sup>g</sup> Alexander Föhlisch,<sup>id g,h</sup>  
 Peter Svedlindh,<sup>b</sup> Andreas Lindblad<sup>id \*d</sup> and Tomas Nyberg<sup>a</sup>

We demonstrate that tungsten disulphide (WS<sub>2</sub>) with thicknesses ranging from monolayer (ML) to several monolayers can be grown on SiO<sub>2</sub>/Si, Si, and Al<sub>2</sub>O<sub>3</sub> by pulsed direct current-sputtering. The presence of high quality monolayer and multilayered WS<sub>2</sub> on the substrates is confirmed by Raman spectroscopy since the peak separations between the A<sub>1g</sub>-E<sub>2g</sub> and A<sub>1g</sub>-2LA vibration modes exhibit a gradual increase depending on the number of layers. X-ray diffraction confirms a textured (001) growth of WS<sub>2</sub> films. The surface roughness measured with atomic force microscopy is between 1.5 and 3 Å for the ML films. The chemical composition WS<sub>x</sub> (x = 2.03 ± 0.05) was determined from X-ray Photoelectron Spectroscopy. Transmission electron microscopy was performed on a multilayer film to show the 2D layered structure. A unique method for growing 2D layers directly by sputtering opens up the way for designing 2D materials and batch production of high-uniformity and high-quality (stoichiometric, large grain sizes, flatness) WS<sub>2</sub> films, which will advance their practical applications in various fields.

Received 21st December 2021,

Accepted 10th March 2022

DOI: 10.1039/d1nr08375a

rsc.li/nanoscale

### 1. Introduction

Monolayer two dimensional (2D) transition metal dichalcogenides (TMDCs) recently gained attention due to their excellent electrical, optical and magnetic properties.<sup>1,2</sup> Because of their semiconducting characteristics, TMDCs provide the possibility to overcome the shortcomings of zero-bandgap materials, like graphene. Tungsten disulfide (WS<sub>2</sub>) is one of the most studied 2D-TMDCs, and is a layered material similar to graphene. A

layer of a TMDC is typically 6–8 Å thick and consists of one plane of metal atoms sandwiched between two planes of chalcogen atoms – in the planes, the atoms are arranged in hexagonal patterns. Consecutive layers are held together by weak van der Waals forces. Whereas bulk WS<sub>2</sub> has an indirect band gap of 1.3 eV, a monolayer has a direct band gap reported to be slightly lower than 2.05 eV since the direct electronic transitions in WS<sub>2</sub> originate from excitonic radiative relaxation.<sup>3,4</sup> FET devices based on monolayer WS<sub>2</sub> exhibit an excellent ON/OFF current ratio of 10<sup>8</sup> and carrier mobility greater than 200 cm<sup>2</sup> V<sup>-1</sup> (s<sup>-1</sup>).<sup>5</sup> The strong photoluminescence of WS<sub>2</sub> makes it a possible component for future electronic and optoelectronic devices. Its potential applications include transistors, lithium-ion batteries, solid lubricants, chemical sensors, membranes, heterogeneous catalysis especially for the hydrogen evolution reaction (HER) in photocatalytic water splitting, and spintronics.<sup>6,7</sup>

Several methods can be used to grow WS<sub>2</sub> films on various substrates. Chemical vapor deposition (CVD) is the most common process to grow TMDCs.<sup>8–15</sup> However related methods, including atomic layer deposition (ALD)<sup>6,16</sup> and metal-organic CVD (MOCVD)<sup>7,17,18</sup> have been used. Also exfoliation of monolayer, or few layers of a dichalcogenide have been achieved.<sup>10,19</sup>

The biggest issue of these methods is that they are unsuitable for the growth of large area films. They produce small areas, or even flake sizes in the case of exfoliation methods.<sup>20</sup>

<sup>a</sup>Division of Solid State Electronics, Department of Electrical Engineering, Uppsala University, Box 65, SE-751 03 Uppsala, Sweden

<sup>b</sup>Division of Solid State Physics, Department of Materials Science and Engineering, Uppsala University, Box 35, SE-751 03 Uppsala, Sweden

<sup>c</sup>Unité Mixte de Physique, CNRS, Thales, Université Paris-Saclay, 91767 Palaiseau, France

<sup>d</sup>Division of X-ray Photon Science, Department of Physics & Astronomy, Uppsala University, Box 516, SE-751 20 Uppsala, Sweden.  
E-mail: andreas.lindblad@physics.uu.se

<sup>e</sup>Division of Inorganic Chemistry, Department of Chemistry-Ångström, Uppsala University, Box 521, SE-751 20 Uppsala, Sweden

<sup>f</sup>Sorbonne Université, CNRS, Institut des NanoSciences de Paris, INSP, F-75005 Paris, France

<sup>g</sup>Institute for Methods and Instrumentation for Synchrotron Radiation Research, Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Albert-Einstein-Straße 15, 12489 Berlin, Germany

<sup>h</sup>Institut für Physik und Astronomie, Universität Potsdam, Karl-Liebknecht-Straße 24/25, 14476 Potsdam, Germany



Xu *et al.*, have reported large-scale deposition of monolayer WS<sub>2</sub> on SiO<sub>2</sub>/Si substrate that resulted in triangular flakes with 12.7 μm sides.<sup>12</sup> Another approach is to sputter from a W target and then post-anneal the metal film in sulfur atmosphere.<sup>14</sup>

A two-stage process has been developed to prepare high quality bilayer TMDC stacking using reverse-flow chemical vapor epitaxy.<sup>21</sup> Recently, Zhang and co-workers<sup>22</sup> succeeded in 6-inch wafer size growth of TMDCs *e.g.* MoS<sub>2</sub>. Monolayers of MoS<sub>2</sub> were grown using a low pressure face-to-face precursor CVD method where the Mo sheet is kept in front of a soda-lime glass substrate. This process allows large-scale wafer size TMDC production. However, during transfer of the TMDCs onto a different substrate, large strain and cracks develop – a shortcoming of this indirect growth method. High quality TMDCs were also successfully deposited on SiO<sub>2</sub> substrates using a two-step process where a metal film is deposited on a substrate followed by sulfurization.<sup>23,24</sup>

Monolayer TMDC films can be produced by CVD, MOCVD and ALD as outlined above. For instance, wafer-sized specimens synthesised by these techniques are available commercially.

Several attempts have been made to grow TMDCs using sputtering, including MoS<sub>2</sub><sup>25</sup> and WS<sub>2</sub><sup>26</sup> on various substrates such as sapphire Al<sub>2</sub>O<sub>3</sub>, glass, and Si/SiO<sub>2</sub>, but issues relating to film quality when grown on Si/SiO<sub>2</sub> substrates have been reported. To grow WS<sub>2</sub> films, Regula *et al.* have used a sintered WS<sub>2</sub> target in Ar/H<sub>2</sub>S atmosphere (H<sub>2</sub>S 0–10%), where the substrate was electrically grounded, and heated at 600 °C at a process pressure between 7.5–9 mTorr.<sup>27</sup> The group of Ellmer explored the effect of different process parameters (substrate temperature, amount of reactive gas, sputtering pressure, substrate material, process gas) using a W target for sputter depositing WS<sub>2</sub>.<sup>28,29</sup> Process parameters for growth of multilayer WS<sub>2</sub> films by sputtering from a WS<sub>2</sub> have been reported earlier by our group.<sup>30</sup>

The sputtering technique is a versatile and promising method for cost-efficient large scale industrial production of TMDCs – a scope unavailable to, *e.g.* the resource intensive CVD-technique.

Synthesizing TMDC monolayers over large areas (wafer-scale) using sputtering techniques would thus be a route providing industrially viable application of these materials. Tao *et al.*, deposited MoS<sub>2</sub> monolayers by sputtering of Mo together with evaporated sulphur.<sup>25</sup> To our knowledge, no one has produced a large scale monolayer TMDC by sputtering from a TMDC target without co-evaporation or post-processing (*e.g.* sulphurization or annealing).

In this paper we report on high quality WS<sub>2</sub> large area monolayers directly grown on 500 nm SiO<sub>2</sub> on Si, Si, and sapphire substrates. We have used a WS<sub>2</sub> target together with H<sub>2</sub>S atmosphere as described below. The quality of the films has been verified by several methods: Raman spectroscopy, atomic force microscopy (AFM), photoluminescence (PL), cross sectional transmission electron microscopy (TEM), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS).

## 2. Methods

### 2.1. Film preparation

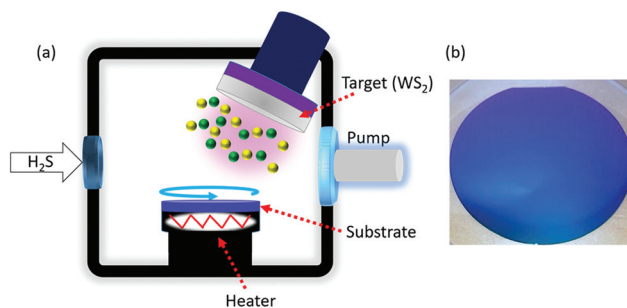
WS<sub>2</sub> films were deposited using a CS 600 von Ardenne high vacuum magnetron sputtering system. The magnetron was located on the top lid of the deposition chamber with a 45° angle towards the substrate table at the center of the chamber bottom shown as shown in Fig. 1(a). The target-substrate distance was fixed to 16 cm. Substrates (SiO<sub>2</sub>/Si, Si and Al<sub>2</sub>O<sub>3</sub>) were located in front of the target and heated to 700 °C during deposition.

The base pressure was 10<sup>-7</sup> Torr for all depositions. A 100 mm WS<sub>2</sub> target (99.9% purity, K. Lesker, Inc.) was powered with a 200 W pulsed-DC at 20 kHz frequency. The working pressure was kept constant at 50 mTorr with H<sub>2</sub>S flow rate of 20 sccm. The deposition time for one monolayer WS<sub>2</sub> was around 2 minutes resulting in a film covering a whole 4 inch wafer as shown in Fig. 1(b).

### 2.2. Characterization

**2.2.1. Raman spectroscopy and photoluminescence.** Raman spectra were recorded with a micro Raman spectrometer in-Via Renishaw Raman microscope using 532 nm laser wavelength. Measurements were performed with 10% of 20 mW max power to avoid damaging the sample due to laser heating. In order to determine the quality of the grown film, peak separation Raman mapping was taken from the A<sub>1g</sub> and E<sub>2g</sub> peak positions. The Raman signal was calibrated using the signal from substrate Si. We do not observe features from SiO<sub>2</sub> owing to the low intensity of from the amorphous phase.<sup>36</sup> Further, the same laser wavelength with 5% power was used to record the photoluminescence (PL) spectra on the monolayer and bilayer samples. The spot size for the measurements was 1 μm (using a 50×/0.75 objective).

**2.2.2. X-ray photoelectron spectroscopy (XPS).** XPS measurements were performed using a PHI Quantera II scanning XPS microprobe equipped with monochromatic Al K<sub>α</sub> radiation (1486.7 eV). A spot size of 100 μm, and a photoelectron take-off angle of 45° were used. The setup is regularly calibrated using reference samples of Ag, Au and Cu according to the ISO standard 15472.<sup>37</sup> Chemical compositions were



**Fig. 1** (a) Schematic diagram of the sputter source used to deposit a monolayer and few layers of WS<sub>2</sub>. (b) A 4-inch diameter wafer with 1 monolayer WS<sub>2</sub> on SiO<sub>2</sub> substrate.



obtained by fitting the W 4f and S 2p core level spectra using Voigt functions after removing a Tougaard background, and by using setup-specific sensitivity factors to account for *e.g.*, photoionization cross sections.

**2.2.3. Atomic force microscopy (AFM).** The AFM images were acquired using a Bruker Dimension Icon atomic force microscope (Bruker Dimension IconTM, Billerica, MA, USA). Silicon RTESPA-300 cantilevers (Bruker, Billerica, MA, USA) having a nominal tip diameter of 8 nm were used to perform the AFM measurements. Intermittent contact mode AFM images ( $1024 \times 1024$  data points) of  $1 \mu\text{m} \times 1 \mu\text{m}$  by keeping the working set point above 70% of the free oscillation amplitude was employed. A scan rate of 0.5 Hz was used for the acquisition of the images. The Gwyddion 2.54 software was used to process the images and characterize the roughness of WS<sub>2</sub> coatings on three different substrates (SiO<sub>2</sub>/Si, Si, and Al<sub>2</sub>O<sub>3</sub>).

**2.2.4. X-Ray diffraction (XRD).** The X-ray diffraction patterns of films consisting of 8 monolayers (8 ML) deposited on SiO<sub>2</sub>/Si, Si and Al<sub>2</sub>O<sub>3</sub> substrates were recorded with a Phillips X'pert MRD diffractometer using Cu K $\alpha$  radiation (spot size  $1.4 \text{ mm} \times 10 \text{ mm}$ ). These were measured in  $\theta$ - $2\theta$  mode. Further, the in-plane measurements were performed on a Rigaku SmartLab diffractometer with a 9 kW rotating Cu anode with a  $5 \text{ mm} \times 5.7 \text{ mm}$  spot size.

## 3. Results and discussion

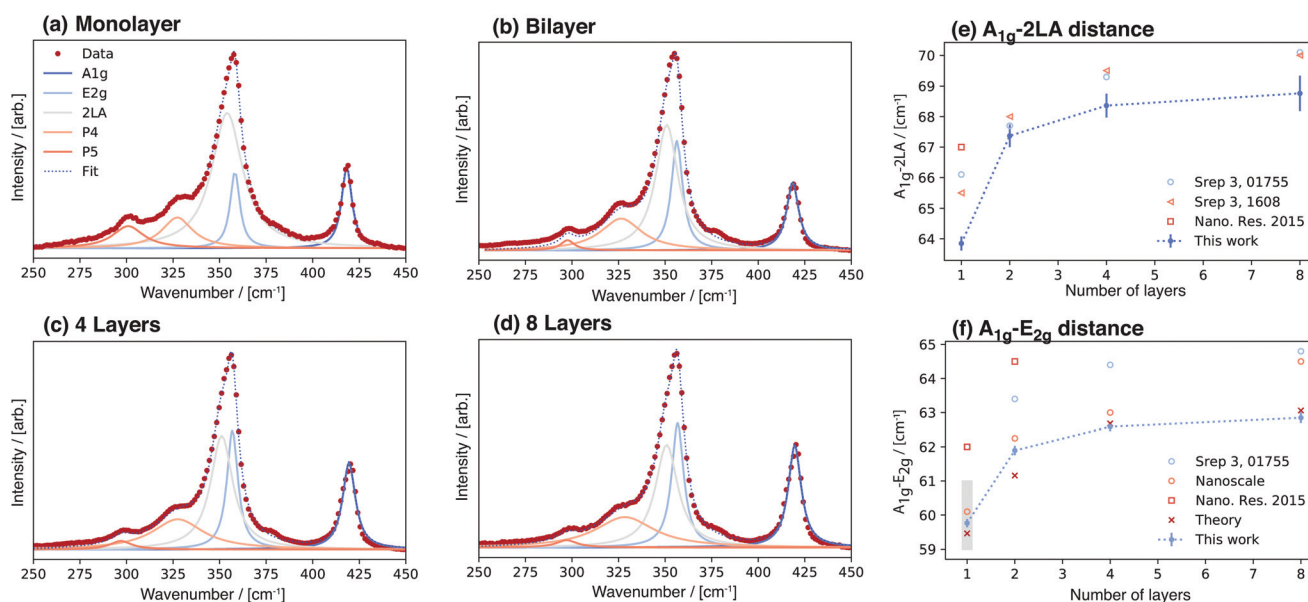
### 3.1. Raman spectroscopy

In WS<sub>2</sub> the first order phonon modes that occur at the Brillouin zone centre ( $\Gamma$ ) are: A<sub>1g</sub>, 2A<sub>2u</sub>, 2B<sub>2g</sub>, B<sub>1u</sub>, E<sub>1g</sub>, 2E<sub>1u</sub>,

2E<sub>2g</sub>, and, E<sub>2u</sub>. A<sub>2u</sub> and E<sub>1u</sub> are acoustic modes and infrared active. A<sub>1g</sub>, E<sub>1g</sub>, and E<sub>2g</sub>, are Raman active. B<sub>2g</sub>, B<sub>1u</sub>, and E<sub>2u</sub> are undetected optically. In addition to these, a longitudinal acoustic (LA) mode at the (M) symmetry point of the Brillouin zone exists in these TMDCs due to the collective in-plane movement of the atoms in the lattice.<sup>38</sup> Note that the 2LA is the second harmonic mode<sup>39</sup> appear due to the laser excitation and it can reduce with laser wavelength.<sup>38</sup> Moreover, the 2LA intensity is suppressed in more than one layer of WS<sub>2</sub>, which confirmed the higher layer numbers of WS<sub>2</sub> (discussed later). The LA mode overlaps at the  $\Gamma$  point with the E<sub>2g</sub> mode.

Fig. 2 shows the Raman spectra recorded on monolayer and few layers WS<sub>2</sub>. The peak positions are extracted by multi-peak least squares fit of Lorentzian peaks to the data. These Raman spectra mainly show A<sub>1g</sub> at  $418.27 \pm 0.06 \text{ cm}^{-1}$ , E<sub>2g</sub> at  $358.50 \pm 0.11 \text{ cm}^{-1}$ , and 2LA at  $354.42 \pm 0.42 \text{ cm}^{-1}$ . The uncertainty in the peak position is the standard error obtained from the least squares multi-peak fit. These peak positions are representative of monolayer of WS<sub>2</sub> at 300 K.<sup>40</sup> Notice that low intensity peaks observed at low wavenumber around 300 and 325  $\text{cm}^{-1}$  correspond to the out-of-plane acoustic phonon modes ascribed to the edge of the M-point in the Brillouin zone.<sup>41</sup>

When we increase the number of WS<sub>2</sub> layers, the peak positions are shifted with growing peak separation. For bilayer WS<sub>2</sub>, peak positions for A<sub>1g</sub>, E<sub>2g</sub>, and 2LA are observed at  $418.27 \pm 0.06 \text{ cm}^{-1}$ ,  $356.37 \pm 0.13 \text{ cm}^{-1}$ , and  $350.9 \pm 0.37 \text{ cm}^{-1}$ , respectively. Further increasing the number of WS<sub>2</sub> layers increases the peak separation as shown in Fig. 2(e) and (f) for A<sub>1g</sub>-2LA and A<sub>1g</sub>-E<sub>2g</sub>, respectively. This peak separation indicates the formation of one, two, and so on layers towards bulk WS<sub>2</sub>. Comparably, our results agree with those of Shi *et al.*,<sup>40</sup>



**Fig. 2** Raman spectra as a function of number of layers recorded on: (a) a monolayer (1ML), (b) bilayer (2ML), (c) four layer (4ML), and (d) eight layer (8ML), sample. (e) Peak separation A<sub>1g</sub>-2LA, and (f) A<sub>1g</sub>-E<sub>2g</sub>. The theory data points are from ref. 31, experimental data: blue circles,<sup>32</sup> red circles,<sup>33</sup> red squares,<sup>34</sup> red triangles,<sup>35</sup> The grey rectangle in (f) indicate the observed peak separations in the Raman mapping discussed in the text and shown in Fig. 4.



and theoretical predictions<sup>31</sup> rather than earlier experimental reports of peak separations of WS<sub>2</sub> on monolayer to bulk samples.<sup>34,35,38,42</sup> The peak intensity ratio is calculated as shown in Fig. 3. Relative intensity ratios of the 2LA and A<sub>1g</sub> phonon modes for mono- and bi-layer samples agrees with reported results.<sup>38</sup> An intensity ratio close to 2 indicates the presence of a monolayer.<sup>41</sup>

In order to determine the film uniformity, Raman mapping was performed on a 60 × 60 mm<sup>2</sup> area of a 4-inch SiO<sub>2</sub>/Si wafer. Fig. 4 shows the map of the separation between the two peak positions of A<sub>1g</sub>–E<sub>2g</sub>. The map indicate that the thickness is uniform over the whole 4-inch wafer. Raman mapping shows a narrow spread of the spacing around the value expected for a monolayer (59.9 cm<sup>-1</sup>). The peak separation is within the spread indicated with a grey rectangle in Fig. 2(f).

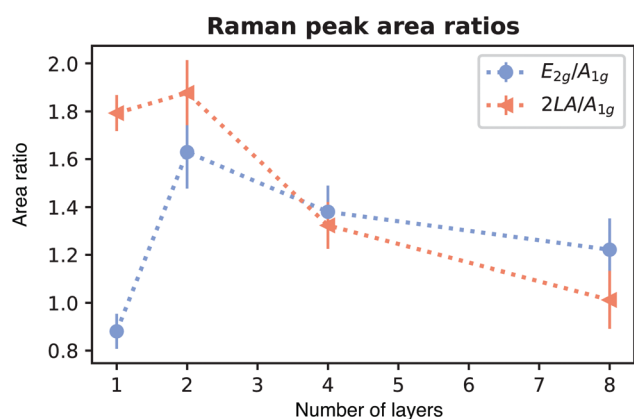


Fig. 3 Peak intensity ratio of E<sub>2g</sub>, A<sub>1g</sub>, and 2LA as function of number of layers.

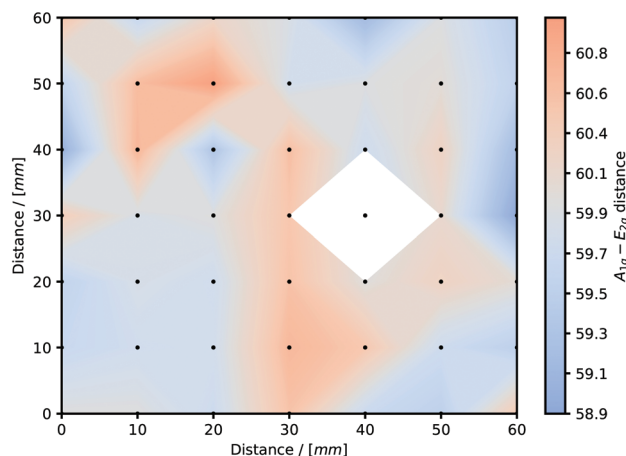


Fig. 4 (a) Raman mapping showing peak separation of A<sub>1g</sub>–E<sub>2g</sub> on very large area monolayer WS<sub>2</sub> sample on SiO<sub>2</sub>/Si. The peak separations were measured every 10 mm over area of 60 × 60 mm<sup>2</sup> here presented with the points linearly interpolated. The black dots indicate where the peak separations have been measured. The white area is centered on a position where no data was acquired. The range is represented by the gray rectangle in Fig. 2(f).

The mapping thus exhibits a high quality monolayer growth on a large area substrate. This demonstrates the industrial compatibility of WS<sub>2</sub> directly grown on SiO<sub>2</sub> substrates.

### 3.2. Photoluminescence (PL) spectroscopy

Fig. 5 shows the photoluminescence spectra of monolayer and bilayer WS<sub>2</sub> grown on SiO<sub>2</sub> substrate. The main peak is centered at 2.03 eV for the monolayer sample. The small peaks at 2.17 eV to 2.20 eV are Raman modes. There was significantly smaller photoluminescence signal observed for the bilayer sample. These observations agree with previous computations and experimental results.<sup>3,4,35,43–48</sup>

### 3.3. X-Ray photoelectron spectroscopy (XPS)

The core level photoelectron spectra recorded on WS<sub>2</sub> monolayer grown on SiO<sub>2</sub> substrates are shown in Fig. 6. A survey spectrum is shown in the bottom panel where we identify signatures at binding energies from: overlayer W, S (corresponding to WS<sub>2</sub> binding energies<sup>49</sup>); substrate Si and O (at SiO<sub>2</sub> binding energy positions<sup>50</sup>) and C species adsorbed on the surface<sup>51</sup> – we also find trace amounts of Ag.<sup>52</sup> The horizontal lines indicate the distance from the main peak to the plasmon excitation.<sup>53,54</sup> The C 1s core level (at binding energy 284 eV) do not have a plasmon which indicate that this element is weakly adsorbed on the surface.

The recorded spectra have been fitted with spin-orbit components for the W 4f and S 2p-core levels. The peaks corresponding to the W 5p<sub>3/2</sub>, W 4f<sub>5/2</sub>, and W 4f<sub>7/2</sub> orbitals are observed at 37.9, 34.6 and 32.5 eV, respectively. The peak position of W 4f<sub>7/2</sub> (32.5 eV) is at larger binding energy compared to metallic W 4f<sub>7/2</sub> (31.6 eV). For sulfur, the 2p<sub>1/2</sub> and 2p<sub>3/2</sub> binding energies are at 163.3 eV 162.1 eV respectively. The binding energies indicate the valence state of the material, and are consistent with a 4<sup>+</sup> valence state of tungsten, corresponding to a S:W ratio of 2, *i.e.* stoichiometric WS<sub>2</sub>.<sup>15</sup> The chemical composition WS<sub>x</sub> (x = 2.03 ± 0.05) was obtained from

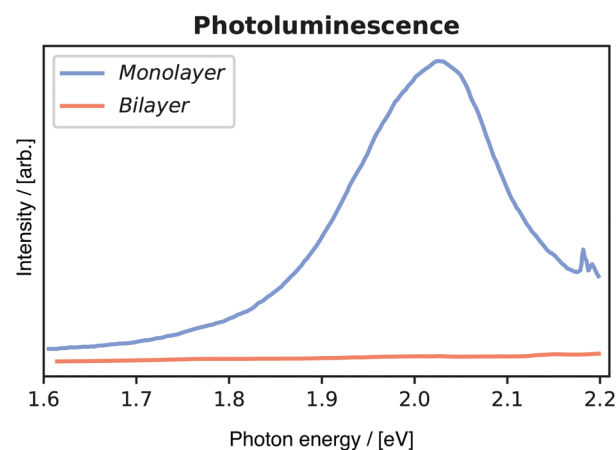
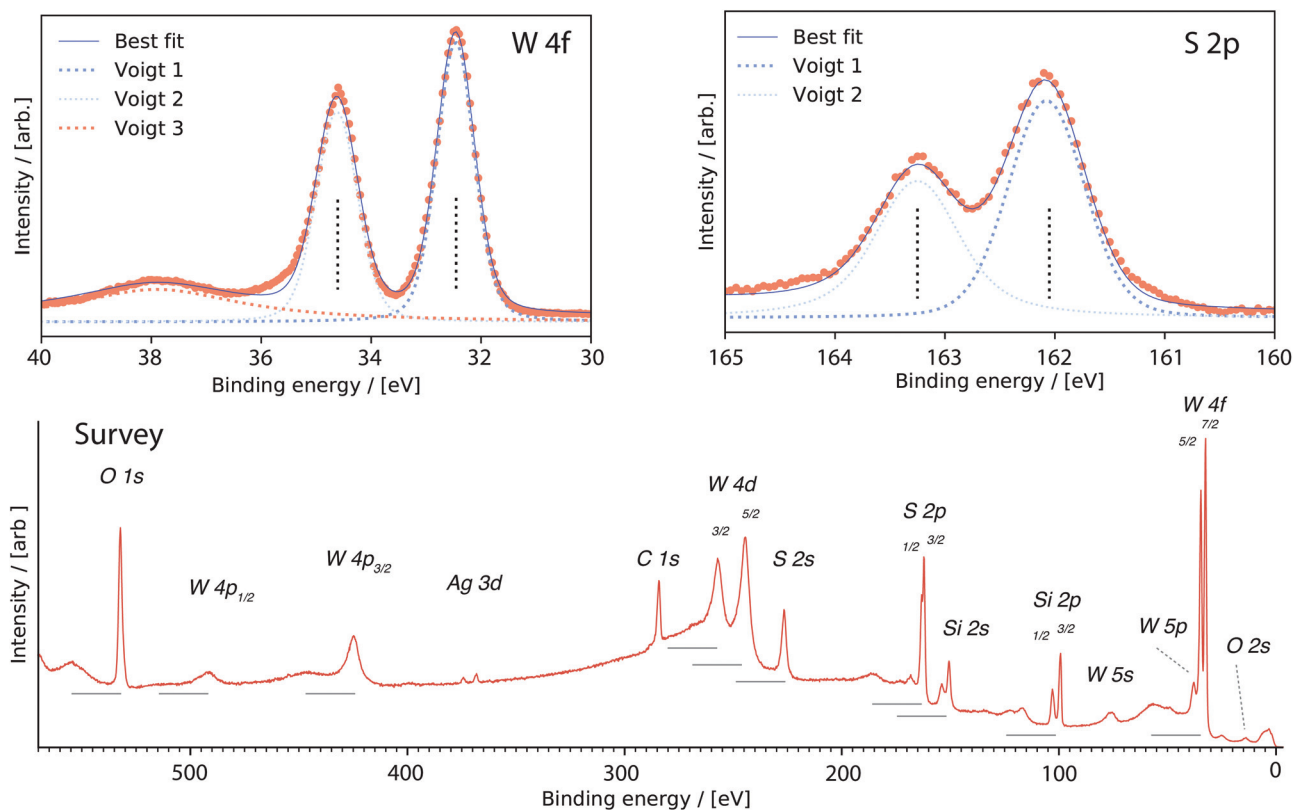


Fig. 5 The PL spectrum of the WS<sub>2</sub> monolayer (black) has its peak intensity at 2.03 eV. No significant PL peak was observed for the bilayer sample (red).



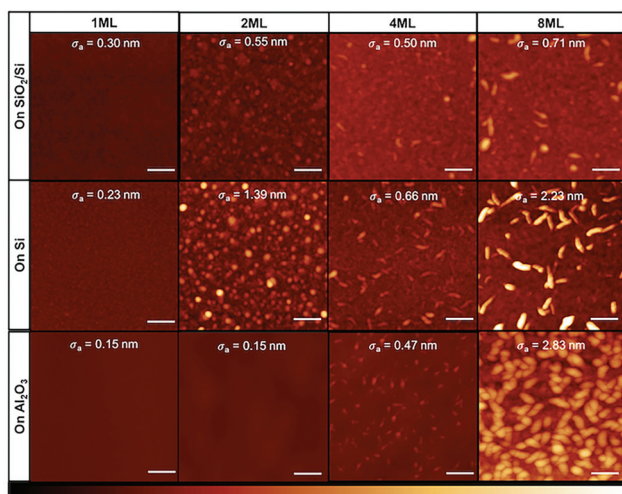


**Fig. 6** X-ray photoelectron spectra of sputter-deposited WS<sub>2</sub> monolayer (orange circles). The W 4f-core level spectrum is to the left and the S 2p-core level spectrum to the right. The components from a least squares fit to the data are also included. The positions of the spin orbit components are indicated with vertical lines. A survey spectrum is presented at the bottom with assignment of the core levels. Horizontal lines indicate the distance in energy from a main line to the plasmon peaks discussed in the text.

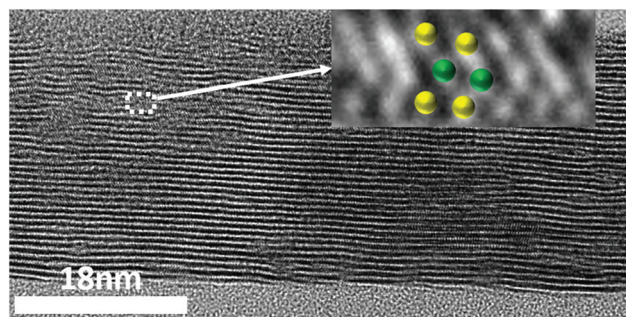
a least squares fit to the data (Fig. 6). Compared with thicker films obtained using the same deposition parameters for which the S/W ratio was found equal to 1.86,<sup>30</sup> monolayer films are thus found to be stoichiometric.

### 3.4. Atomic force microscopy (AFM)

Fig. 7 displays the topography of the WS<sub>2</sub> films on the SiO<sub>2</sub>/Si, Si, Al<sub>2</sub>O<sub>3</sub> substrates using AFM. The measured surface roughness  $\sigma_a$  is also indicated on each sample. On the SiO<sub>2</sub>/Si substrate, monolayer films present an atomically smooth surface (surface roughness, 3 Å). The roughness increases slightly with increasing number of layers (1 to 8 layers) – for a 8 layer film, we measured a surface roughness of 7 Å. Monolayers with small roughness are also found in the case of Si and Al<sub>2</sub>O<sub>3</sub> sub-

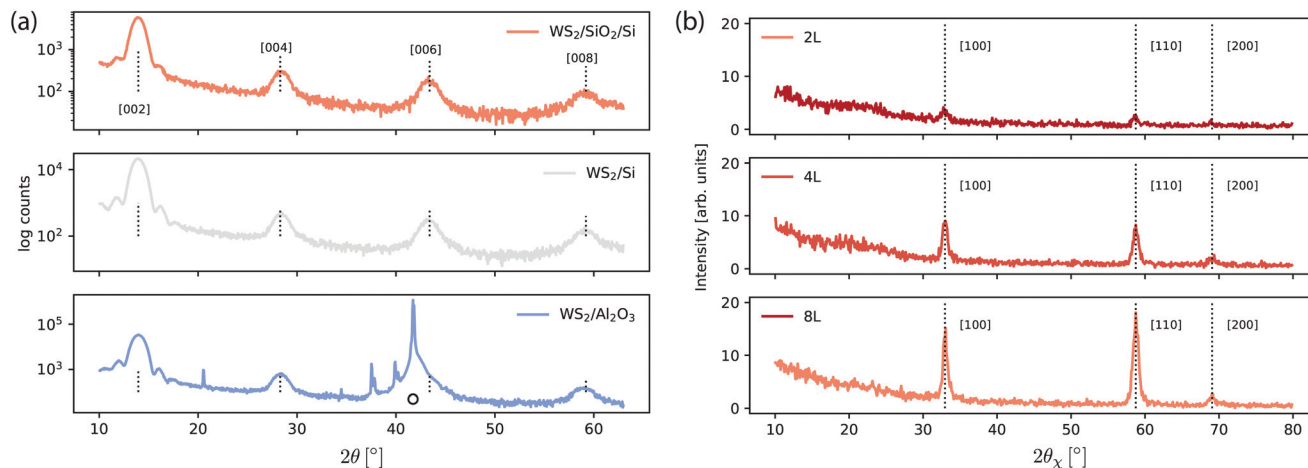


**Fig. 7** Topographical analysis from AFM of WS<sub>2</sub> deposited on SiO<sub>2</sub>/Si, Si, and Al<sub>2</sub>O<sub>3</sub> substrates and the measured surface roughness  $\sigma_a$ . (Scale bar: 200 nm; Z scale: 25 nm.)



**Fig. 8** High resolution cross-sectional TEM image of several layers of WS<sub>2</sub>. Inset is zoomed area of one monolayer WS<sub>2</sub> marked by spheres of different colors: green (W) and yellow (S).





**Fig. 9** (a) X-ray diffraction patterns of 8 monolayers of WS<sub>2</sub> deposited on different substrates. The main substrate peak is indicated by a solid circle (peaks at 20, 35, 38 and 40 degrees are also from the substrate). (b) In-plane X-ray diffraction patterns of 2, 4 and 8 monolayers of WS<sub>2</sub>/SiO<sub>2</sub>/Si.

strates. However, increasing the number of WS<sub>2</sub> layers leads to a significant increase in the surface roughness on Si and Al<sub>2</sub>O<sub>3</sub> substrates. On those substrates, layers grow rougher than those grown on SiO<sub>2</sub>/Si (top row in Fig. 7). Note that on the Al<sub>2</sub>O<sub>3</sub> substrate the bi-layer have a small surface roughness compared to the other bilayers. For bulk thicknesses, grain-like features that add to the to the larger surface roughness are observed.

From this analysis, we can understand that the growth is highly substrate dependent. It is visible that W and S atoms easily bond together when deposited on SiO<sub>2</sub> substrate which follow layer by layer growth even in the bulk regime, Fig. 7 (top panel 8ML). Layer by layer growth also occur on Al<sub>2</sub>O<sub>3</sub> substrate up to three layers, but island formation starts after four layers as shown in Fig. 7 (bottom panel 8ML). In case of Si, the growth is mixed, where the small flakes are formed in high number layers with layer-like growth. Thus it is clear that the TMDC growth is substrate dependent which was also observed previously,<sup>55</sup> and also depends on deposition conditions.<sup>30</sup>

### 3.5. Transmission electron microscopy (TEM)

To further verify the layer-by-layer growth and thickness of WS<sub>2</sub> layers, high resolution cross-sectional TEM imaging was performed on a thick film shown in Fig. 8. The total thickness of this film is 26 nm. The thickness of each layer of WS<sub>2</sub> was found to 7 Å. A zoomed cross section is shown in the inset with atomic positions marked with colored spheres, green for W and yellow for S.

### 3.6. X-Ray diffraction

Fig. 9(a) shows the XRD spectra for 8 monolayer WS<sub>2</sub> film deposited on SiO<sub>2</sub>/Si, Si and Al<sub>2</sub>O<sub>3</sub> substrates. All the films exhibit a strong orientation along the (001) direction which indicate the crystalline nature of WS<sub>2</sub> growth on all different substrates. The intensity of the [002] peak is highest for the Al<sub>2</sub>O<sub>3</sub>, followed by that on the Si, and then the SiO<sub>2</sub>/Si sub-

strate. The peak positions are identically matched with the commercially available high quality single crystal.<sup>56</sup> Fig. 9(b) shows the in-plane XRD pattern for 2, 4 and 8 monolayers of WS<sub>2</sub> film deposited on SiO<sub>2</sub>/Si. The in-plane lattice constant evolves from 0.3151 nm for the 2 ML thick film to 0.3140 nm for the 8 ML thick film.

The in plane measurements indicate the presence of polycrystalline flakes with domain sizes of the order of 10–20 nm – estimated from using the Scherrer equation and the FWHM of the [100] peak with shape factor 0.9.<sup>57</sup>

## 4. Conclusions

We have successfully grown stoichiometric monolayer (and multilayer) films of WS<sub>2</sub> on wafer-size substrates of SiO<sub>2</sub>/Si, Si and Al<sub>2</sub>O<sub>3</sub>. The stoichiometry of the film was verified by XPS and the uniformity by Raman mapping. The (001) texture of the WS<sub>2</sub> films is confirmed using X-ray diffraction analysis for all substrates. Raman spectroscopy and Photoluminescence measurements discriminate between the deposition of monolayer and few layers WS<sub>2</sub>. Atomic Force Microscopy shows the uniform growth and the atomic smoothness of the layers. The growth of WS<sub>2</sub> is substrate dependent, where monolayer and few layers are formed with layer-by-layer growth. However, islands are formed for large WS<sub>2</sub> film thickness when grown on Al<sub>2</sub>O<sub>3</sub> substrate.

Previous attempts to sputter stoichiometric 2D WS<sub>2</sub> films have resulted in slightly substoichiometric films.<sup>27–30</sup> Stoichiometric films, as produced here, are the result of post-deposition sulfurization caused by H<sub>2</sub>S in the chamber during cooling of the substrate. Complete sulfurization is possible since the deposited films are extremely thin in this study.

To summarise: large area monolayer WS<sub>2</sub> films have been grown with a scalable industrially compatible sputter process. This is proof-of-principle of a new route that is complementary to exfoliated and CVD-grown WS<sub>2</sub> (and other TMDC) films.



## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

The authors would like to acknowledge Lars Riekehr for the TEM images, Tomas Edvinsson for conducting the preliminary PL measurements, and Yunlin Zheng for XRD measurements. This work was supported by the FLAG-ERA grant for the Layered Metal Sulfides (LaMeS) project by the Swedish Research Council (VR Grant 2017-06816); by the French National Research Agency grant ANR-17-GRF1-0001-03 and by the Carl Tryggers Foundation contract CTS 19:258. A. L. acknowledges the support from the Swedish Research Council (Grants No. 2014-6463 and 2018-05336) and Marie Skłodowska Curie Actions (Cofund, Project INCA 600398). A. F. acknowledges funding by FLAG-ERA Graphene Basic Research 2 2017 in project LaMeS DFG project number 400335214. S. H. and P. S. acknowledges Carl Tryggers Stiftelse for Vetenskaplig Forskning (grant no: CTS 17:450) for the financial support. Reinier Oropesa-Nuñez acknowledges Olle Engkvist (project number: 194-0644) for the financial support.

## References

- 1 S. Manzeli, D. Ovchinnikov, D. Pasquier, O. V. Yazyev and A. Kis, *Nat. Rev. Mater.*, 2017, **2**, 17033.
- 2 S. Husain, R. Gupta, A. Kumar, P. Kumar, N. Behera, R. Brucas, S. Chaudhary and P. Svedlindh, *Appl. Phys. Rev.*, 2020, **7**, 041312.
- 3 H. R. Gutiérrez, N. Perea-López, A. L. Elías, A. Berkdemir, B. Wang, R. Lv, F. López-Urías, V. H. Crespi, H. Terrones and M. Terrones, *Nano Lett.*, 2013, **13**, 3447–3454.
- 4 S. Y. Choi, C. T. Yip, G. C. Li, D. Y. Lei, K. H. Fung, S. F. Yu and J. Hao, *AIP Adv.*, 2015, **5**, 067148.
- 5 A. Rawat, N. Jena, S. Dimple and A. De Sarkar, *J. Mater. Chem. A*, 2018, **6**, 8693–8704.
- 6 S. Yeo, D. K. Nandi, R. Rahul, T. H. Kim, B. Shong, Y. Jang, J.-S. Bae, J. W. Han, S.-H. Kim and H. Kim, *Appl. Surf. Sci.*, 2018, **459**, 596–605.
- 7 S. Cwik, D. Mitoraj, O. Mendoza Reyes, D. Rogalla, D. Peeters, J. Kim, H. M. Schütz, C. Bock, R. Beranek and A. Devi, *Adv. Mater. Interfaces*, 2018, **5**, 1–11.
- 8 Y.-H. Lee, X.-Q. Zhang, W. Zhang, M.-T. Chang, C.-T. Lin, K.-D. Chang, Y.-C. Yu, J. T.-W. Wang, C.-S. Chang, L.-J. Li, *et al.*, *Adv. Mater.*, 2012, **24**, 2320–2325.
- 9 A. Alharbi and D. Shahrjerdi, *Appl. Phys. Lett.*, 2016, **109**, 193502.
- 10 Q. Fu and B. Xiang, *Prog. Nat. Sci.: Mater. Int.*, 2016, **26**, 221–231.
- 11 G. V. Bianco, M. Losurdo, M. M. Giangregorio, A. Sacchetti, P. Prete, N. Lovergine, P. Capezzuto and G. Bruno, *RSC Adv.*, 2015, **5**, 98700–98708.
- 12 Z. Xu, Y. Lv, J. Li, F. Huang, P. Nie, S. Zhang, S. Zhao, S. Zhao and G. Wei, *RSC Adv.*, 2019, **9**, 29628–29635.
- 13 B. Groven, D. Claes, A. Nalin Mehta, H. Bender, W. Vandervorst, M. Heyns, M. Caymax, I. Radu and A. Delabie, *J. Chem. Phys.*, 2019, **150**, 104703.
- 14 J. Park, M. S. Kim, E. Cha, J. Kim and W. Choi, *Sci. Rep.*, 2017, **7**, 1–8.
- 15 K. M. McCreary, A. T. Hanbicki, G. G. Jernigan, J. C. Culbertson and B. T. Jonker, *Sci. Rep.*, 2016, **6**, 19159.
- 16 B. Groven, A. N. Mehta, H. Bender, Q. Smets, J. Meersschaut, A. Franquet, T. Conard, T. Nuytten, P. Verdonck, W. Vandervorst, M. Heyns, I. Radu, M. Caymax and A. Delabie, *J. Vac. Sci. Technol., A*, 2018, **36**, 01A105.
- 17 K. Kang, S. Xie, L. Huang, Y. Han, P. Y. Huang, K. F. Mak, C.-J. Kim, D. Muller and J. Park, *Nature*, 2015, **520**, 656–660.
- 18 G. Piccinini, S. Forti, L. Martini, S. Pezzini, V. Miseikis, U. Starke, F. Fabbri and C. Coletti, *2D Mater.*, 2019, **7**, 014002.
- 19 A. O. Tanoh, J. Alexander-Webber, J. Xiao, G. Delpont, C. A. Williams, H. Bretscher, N. Gauriot, J. Allardice, R. Pandya, Y. Fan, Z. Li, S. Vignolini, S. D. Stranks, S. Hofmann and A. Rao, *Nano Lett.*, 2019, **19**, 6299–6307.
- 20 F. Wang, S. Li, M. A. Bissett, I. A. Kinloch, Z. Li and R. J. Young, *2D Mater.*, 2020, **7**, 045022.
- 21 X. Zhang, H. Nan, S. Xiao, X. Wan, X. Gu, A. Du, Z. Ni and K. K. Ostrikov, *Nat. Commun.*, 2019, **10**, 598.
- 22 P. Yang, X. Zou, Z. Zhang, M. Hong, J. Shi, S. Chen, J. Shu, L. Zhao, S. Jiang, X. Zhou, Y. Huan, C. Xie, P. Gao, Q. Chen, Q. Zhang, Z. Liu and Y. Zhang, *Nat. Commun.*, 2018, **9**, 979.
- 23 S. Husain, A. Kumar, P. Kumar, A. Kumar, V. Barwal, N. Behera, S. Choudhary, P. Svedlindh and S. Chaudhary, *Phys. Rev. B*, 2018, **98**, 180404(R).
- 24 S. Husain, X. Chen, R. Gupta, N. Behera, P. Kumar, T. Edvinsson, F. García-Sánchez, R. Brucas, S. Chaudhary, B. Sanyal, P. Svedlindh and A. Kumar, *Nano Lett.*, 2020, **20**, 6372–6380.
- 25 J. Tao, J. Chai, X. Lu, L. M. Wong, T. I. Wong, J. Pan, Q. Xiong, D. Chi and S. Wang, *Nanoscale*, 2015, **7**, 2497–2503.
- 26 Y. Koçak and E. Gür, *ACS Appl. Mater. Interfaces*, 2020, **13**, 15785–15792.
- 27 M. Regula, C. Ballif, J. Moser and F. Lévy, *Thin Solid Films*, 1996, **280**, 67–75.
- 28 K. Ellmer, C. Stock, K. Diesner and I. Sieber, *J. Cryst. Growth*, 1997, **182**, 389–393.
- 29 K. Ellmer, S. Seeger, I. Sieber, W. Bohne, J. Röhrich, E. Strub and R. Mientus, *Phys. Status Solidi A*, 2006, **203**, 497–503.
- 30 M. M. S. Villamayor, A. Lindblad, F. O. Johansson, T. Tran, N. H. Pham, D. Primetzhofer, N. L. Sorgenfrei, E. Giangrisotomi, A. Föhlisch, P. Lourenço, R. Bernard, N. Witkowski, G. Prévot and T. Nyberg, *Vacuum*, 2021, **188**, 110205.





- 31 H. Terrones, E. Del Corro, S. Feng, J. Poumirol, D. Rhodes, D. Smirnov, N. Pradhan, Z. Lin, M. Nguyen, A. Elias, *et al.*, *Sci. Rep.*, 2014, **4**, 4215.
- 32 A. Berkdemir, H. R. Gutiérrez, A. R. Botello-Méndez, N. Perea-López, A. L. Elías, C.-I. Chia, B. Wang, V. H. Crespi, F. López-Urías, J.-C. Charlier, *et al.*, *Sci. Rep.*, 2013, **3**, 1–8.
- 33 W. Zhao, Z. Ghorannevis, K. K. Amara, J. R. Pang, M. Toh, X. Zhang, C. Kloc, P. H. Tan and G. Eda, *Nanoscale*, 2013, **5**, 9677–9683.
- 34 N. Peimyoo, J. Shang, W. Yang, Y. Wang, C. Cong and T. Yu, *Nano Res.*, 2015, **8**, 1210–1221.
- 35 H. Zeng, G.-B. Liu, J. Dai, Y. Yan, B. Zhu, R. He, L. Xie, S. Xu, X. Chen, W. Yao, *et al.*, *Sci. Rep.*, 2013, **3**, 1–5.
- 36 D. M. Popovic, V. Milosavljevic, A. Zekic, N. Romcevic and S. Daniels, *Appl. Phys. Lett.*, 2011, **98**, 051503.
- 37 M. P. Seah, *Surf. Interface Anal.*, 2001, **31**, 721–723.
- 38 A. Berkdemir, H. R. Gutiérrez, A. R. Botello-Méndez, N. Perea-López, A. L. Elías, C. I. Chia, B. Wang, V. H. Crespi, F. López-Urías, J. C. Charlier, H. Terrones and M. Terrones, *Sci. Rep.*, 2013, **3**, 1–8.
- 39 A. A. Mitioglu, P. Plochocka, G. Deligeorgis, S. Anghel, L. Kulyuk and D. K. Maude, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2014, **89**, 245442.
- 40 W. Shi, M.-L. Lin, Q.-H. Tan, X.-F. Qiao, J. Zhang and P.-H. Tan, *2D Mater.*, 2016, **3**, 025016.
- 41 M. R. Molas, K. Nogajewski, M. Potemski and A. Babiński, *Sci. Rep.*, 2017, **7**, 1–8.
- 42 M. O'Brien, N. McEvoy, D. Hanlon, T. Hallam, J. N. Coleman and G. S. Duesberg, *Sci. Rep.*, 2016, **6**, 19476.
- 43 Z. He, X. Wang, W. Xu, Y. Zhou, Y. Sheng, Y. Rong, J. M. Smith and J. H. Warner, *ACS Nano*, 2016, **10**, 5847–5855.
- 44 F. Zhang, Y. Lu, D. S. Schulman, T. Zhang, K. Fujisawa, Z. Lin, Y. Lei, A. L. Elias, S. Das, S. B. Sinnott, *et al.*, *Sci. Adv.*, 2019, **5**, eaav5003.
- 45 L. Yuan and L. Huang, *Nanoscale*, 2015, **7**, 7402–7408.
- 46 Z. He, Y. Sheng, Y. Rong, G.-D. Lee, J. Li and J. H. Warner, *ACS Nano*, 2015, **9**, 2740–2748.
- 47 D. Thakur, P. Kumar, M. Sabarigresan, R. Ramadurai and V. Balakrishnan, *Surf. Interfaces*, 2021, **26**, 101308.
- 48 X. Xu, L. Li, X. Li, X. Hu, M. Yang, Q. Guo, Y. Wang, X. Zhuang and B. Liang, *Optik*, 2022, **251**, 168374.
- 49 J. Sundberg, R. Lindblad, M. Gorgoi, H. Rensmo, U. Jansson and A. Lindblad, *Appl. Surf. Sci.*, 2014, **305**, 203–213.
- 50 D. S. Jensen, S. S. Kanyal, N. Madaan, M. A. Vail, A. E. Dadson, M. H. Engelhard and M. R. Linford, *Surf. Sci. Spectra*, 2013, **20**, 36–42.
- 51 G. Greczynski and L. Hultman, *Sci. Rep.*, 2021, **11**, 1–5.
- 52 J. C. Fuggle and N. Mårtensson, *J. Electron Spectrosc. Relat. Phenom.*, 1980, **21**, 275–281.
- 53 J.-J. Pireaux, J. Ghijsen, J. W. McGowan, J. Verbist and R. Caudano, *Surf. Sci.*, 1979, **80**, 488–502.
- 54 D. David, C. Godet, F. O. Johansson and A. Lindblad, *Appl. Surf. Sci.*, 2020, **505**, 144385.
- 55 J. You, M. D. Hossain and Z. Luo, *Nano Convergence*, 2018, **5**, 26.
- 56 2H Tungsten Disulfide, <http://www.hqgraphene.com/WS2.php>.
- 57 A. J. Ying, C. E. Murray and I. Noyan, *J. Appl. Crystallogr.*, 2009, **42**, 401–410.

