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# Stabilization of Chemical-Vapor-Deposition-Grown WS<sub>2</sub> Monolayers at Elevated Temperature with Hexagonal Boron Nitride **Encapsulation**

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forming gas, during cooling below  $\sim$  323 K; the trion has an estimated binding energy of ~28 meV. It might occur because of doping level changes caused by charge defect generation by  $H_2$  molecules diffusing between the *h*-BN and the SiO<sub>2</sub>/Si substrate. The decomposition of uncovered WS<sub>2</sub> flakes in air suggests a dissociation and chemisorption energy barrier of  $O_2$  on the WS<sub>2</sub> surface of ~1.6

eV. Fitting the high-temperature PL intensities in air gives a binding energy of a free exciton of  $\sim$ 229 meV. KEYWORDS: WS<sub>2</sub>, monolayer, transition-metal dichalcogenide (TMD) monolayers, photoluminescence, h-BN encapsulation,

# INTRODUCTION

elevated temperature, excitons, trions

Layered transition-metal dichalcogenides (TMDs) have attracted much attention because of their electronic and optical properties.<sup>1</sup> One of the distinctive properties of several TMDs is the appearance of a direct band gap transition in the monolayer, rather than the indirect gap in the bulk material, and this can provide strong luminescence in the visible.<sup>2,3</sup> This can lead to several important applications in optoelectronic devices,<sup>4,5</sup> including photodetectors,<sup>6,7</sup> and light-emitting diodes (LEDs).8

One of the major obstacles in using TMDs to realize these applications at elevated temperature is their stability. Bulk TMDs are known to be relatively unstable at higher temperatures, in oxygen-containing media, in the presence of inert gases, and under vacuum.<sup>9,10</sup> Some recent work shows the limited stability of few-layer TMDs at elevated temperatures,<sup>11–15</sup> but less is known about the stability of monolayer TMDs under various environmental conditions at high temperature. It is known that potential microscopic structural transitions, defect formation, and substrate absorption resulting in trap states and undesirable doping can occur at higher temperatures, as well as decomposition.<sup>11-14</sup> The existence of imperfections can significantly degrade luminescence quantum yields and the on/off ratios of field-effect transistors (FETs).<sup>16</sup> Therefore, understanding TMD stability and developing effective passivation methods of TMDs are essential for highperformance applications at elevated temperatures.

h-BN (hexagonal boron nitride) is known to be thermally stable up to  $\sim 1800$  K.<sup>17</sup> *h*-BN encapsulation is now widely used for the passivation of graphene and 2D semiconductors, such as for improving luminescence efficiency and achieving high electronic quality.<sup>18,19</sup> In this study, we learn that WS<sub>2</sub> monolayers can be stabilized at high temperatures by using h-BN encapsulation. We investigated the stability and resulting quality of h-BN encapsulated and uncovered regions of WS<sub>2</sub> monolayers, grown by chemical vapor deposition (CVD), by using in situ optical photoluminescence (PL) and other optical

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#### **ACS Applied Materials & Interfaces Research Article** www.acsami.org b a с Objective lens h-BN Viewing window WS<sub>2</sub> WS, gas in SiO<sub>2</sub>/Si SiO<sub>2</sub>/Si gas out Water cooling system f d e 2.5 1500 cts) 2 (st) 1000 ntensity (10<sup>4</sup> 1.5 ntensity 1 500 0.5 30 µm 0 1.8 1.9 2 2.1 300 400 600 500 Energy (eV) Raman Shift (cm<sup>-1</sup>)

**Figure 1.** (a) Schematic depiction of a sample placed in a Linkam cell where the temperature and environment are controlled and materials processing is monitored in real time. (b) Crystal structure of CVD-grown monolayer WS<sub>2</sub> on a SiO<sub>2</sub>/Si substrate. (c) Crystal structure of a van der Waals stacked sample that is composed of monolayer WS<sub>2</sub> encapsulated with *h*-BN on a SiO<sub>2</sub>/Si substrate. (d) Optical image showing monolayer CVD-grown WS<sub>2</sub> on a SiO<sub>2</sub>/Si substrate, with a few of the flakes encapsulated by *h*-BN (and are not seen). Monolayer WS<sub>2</sub> is characterized in air by (e) PL measurement and (f) Raman scattering (with the 520 cm<sup>-1</sup> peak due to Si), at 300 K.



Figure 2. (a) In situ PL spectra of CVD-grown WS<sub>2</sub> flakes (a) covered, during heating, and (b) uncovered by *h*-BN, during the heating/cooling cycle in ambient air, at different temperatures in real time. (c) Positions, (d) fwhms, and (e) peak intensities of the PL peak of the *h*-BN-covered WS<sub>2</sub> flakes and uncovered flakes versus temperature (with symbols defined in (e)).

measurements at different stages of the heating/cooling cycles and in the presence of different gas environments.

# EXPERIMENTAL SECTION

The monolayer WS<sub>2</sub> was grown on a 285 nm SiO<sub>2</sub>/Si substrate by CVD,<sup>20</sup> and then characterized by optical microscopy, which showed resulting equilateral triangle flakes. The length of the side of the flake was ~5–30  $\mu$ m. *h*-BN flakes of near quadrilateral shape with a longest

side length of 50–100  $\mu$ m, and much larger than the corresponding WS<sub>2</sub> flake dimensions, were then exfoliated onto a SiO<sub>2</sub>/Si substrate, and their thickness and uniformity were determined by atomic force microscopy (AFM). Standard transfer methods were used to transfer *h*-BN flakes to the top of the WS<sub>2</sub>/SiO<sub>2</sub>/Si, by first picking up the *h*-BN layers with a PPC/PDMS slide (poly(propylene) carbonate (PPC), polydimethylsiloxane (PDMS))<sup>21</sup> and then transferring them on top of the monolayer WS<sub>2</sub>. Then the chips were put in acetone



**Figure 3.** (a) Optical image of triangular monolayer CVD-grown  $WS_2$  flakes on a SiO<sub>2</sub>/Si substrate, with several of the flakes covered by *h*-BN (light blue). These covered flakes are barely visible here, and the two of them that are clearly seen to have bluish spots in (b) and (d) are encircled in each image. (b) Optical image of the same sample after heating to 773 K in ambient air and cooling to room temperature. (c) and (d) are dark-field microscope images showing the same samples as in (a) and (b), and the outline of the *h*-BN is also seen in both. After heating, the uncovered  $WS_2$  flakes are seen to have decomposed, whereas the covered ones remain. The optical image exposure in (d) is longer than that in (c) to enable seeing the bluish centers in the center of covered  $WS_2$ . All images are at room temperature.

overnight and the remaining PPC residue was cleaned with isopropyl alcohol.

Optical analysis of the  $WS_2$  occurred with *in situ* control of the temperature and environment in a Linkam cell (LINKAM THMS 600) (Figure S1 in the Supporting Information). A schematic view of the *in situ* optical measurements with control of the temperature and gas environment is given in Figure 1a. Two regions on the chip were probed in the optical measurements: the CVD-grown monolayer  $WS_2$  with *h*-BN encapsulation, called the covered regions, and the bare monolayer  $WS_2$  on the substrate, called the uncovered regions. Schematic views of the crystal structure in the regions are shown in Figure 1b,c. The optical image of the entire sample is shown in Figure 1d.

In situ PL measurements using a continuous-wave argon ion laser (S14.5 nm) were performed over a range of temperatures in real time first in ambient air. The temperature was increased from room temperature to 773 K (and no higher because the uncovered sample decomposed at this temperature), with a heating rate of 50 K/min to a given target temperature, at which PL was measured after waiting 10 min to ensure thermal equilibrium, before further heating continued; the same procedure was followed during cooling. Signals were captured by a cryogenically cooled silicon CCD detector (Princeton Instruments Spec-10:400B). For confirmation that the WS<sub>2</sub> flakes did not macroscopically degrade and were well preserved after sample fabrication, the monolayer WS<sub>2</sub> flakes were characterized by room-temperature Raman scattering and PL before the start of each run, as seen in Figure 1e,f for ambient air, in Figure S2 for flowing N<sub>2</sub>, and in Figure S3 for flowing forming gas in the Supporting Information.

Figure 2a,b shows the temperature-dependent PL spectra of  $WS_2$  respectively in a covered and an uncovered region. The sample was heated in ambient air from room temperature to 773 K and then cooled down to room temperature, monitored by *in situ* PL at each targeted temperature. The PL evolved in covered and uncovered regions similarly from room temperature to 673 K. Above 673 K, the uncovered regions of the sample started to decompose and totally disappeared when the temperature approached 773 K, as seen by optical microscopy (Figure 3a,b). (This is why 673 K is the highest temperature with measurable PL in the uncovered regions.) In

contrast, in covered regions  $WS_2$  was still observable and still showed strong PL emission. However, the PL signals of the covered sample did not return to their initial values after cooling to room temperature (Figure 2e); the integrated PL intensities were ~63% lower than those at the beginning. This could be associated with the spot features that formed at the center of the covered  $WS_2$  triangles, as observed by optical microscopy in Figure 3c,d, that indicates some degradation.

In the *h*-BN-covered region, the PL peak position of monolayer WS<sub>2</sub> follows similar trends in the heating and in the cooling cycles, but they are not identical (Figure 2c). The peak is located at 1.954 eV at room temperature at the beginning of the run and at 1.942 eV after it. This small red shift of 12 meV could be caused by an increase in the biaxial in-plane tensile strain by ~0.12% (see below).<sup>22–25</sup> As seen in Figure 2d, the fwhm peak width was 51.3 meV before the heating cycle and 59.1 meV after cooling to room temperature. This broadening, along with the PL intensity decrease, might mean the exciton lifetime has decreased. Peak width broadening might result from impurity or defect formation leading to faster nonradiative recombination or from increased local inhomogeneity during heating.

The optical images of the sample in ambient air before and after the heating/cooling to 773 K are compared in Figure 3. Figure 3a,c shows the bright and dark field optical images at room temperature before the cycle. The triangles are monolayer  $\mathsf{WS}_2$  grown by CVD and the big blue quadrilateral-shaped flake is the several-layer h-BN on top of the WS2. The micrograph of the same sample region after the heating/cooling cycle in Figure 3b shows three things. First, all monolayer WS<sub>2</sub> in the uncovered region has totally decomposed, which is consistent with the in situ PL measurements presented in Figure 2b. Second, the shape and area of the monolayer WS<sub>2</sub> flakes in the covered region remain unchanged, indicating that the WS<sub>2</sub> flakes did not apparently decompose at 773 K because of the protection by h-BN encapsulation. Third, when the dark-field optical images in parts (c) and (d) of Figure 3 are compared, a blueish spot appears at the center of each triangular, a WS<sub>2</sub> flake in the covered region after the heating/cooling cycle in air; the two flakes where this spot is seen clearest are encircled. As noted, these spots might be one of the reasons why the PL intensity decreases in Figure 2e. These spots also appear in the bright-field image in Figure 3b.

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Figure 4. (a) PL exciton peak intensity of *h*-BN-covered WS<sub>2</sub> flakes and uncovered flakes versus temperature for (a) ambient air, (b) flowing N<sub>2</sub> at 1 atm, and (c) forming gas flowing (95% N<sub>2</sub>, 5% H<sub>2</sub>) at 1 atm. In (c) the PL trion peak intensity is also plotted, for the trion peak that is seen near the end of the cooling phase of the heating/cooling cycle, as resolved in (d) (where the trion peak is blue and exciton peak is red). In forming gas, uncovered WS<sub>2</sub> survives above 673 K and still shows strong PL and starts to decompose above 773 K.

Covering monolayer WS<sub>2</sub> with *h*-BN provides some passivation of monolayer WS<sub>2</sub> in air to ~773 K, but it is not perfect, as seen by the decrease of the PL intensity. Therefore, such PL measurements were repeated during heating/cooling cycles, during which 20 sccm N<sub>2</sub> (at 1 atm) flowed in the chamber (Figure 4b) and then repeated again with forming gas (95% N<sub>2</sub>, 5% H<sub>2</sub>) (Figure 4c), but now with heating to 873 K; for reference, the PL data for ambient air are shown in Figure 4a. For flowing N<sub>2</sub>, the PL from covered and uncovered regions were similar from room temperature until 673 K. The uncovered sample began to disappear when the temperature was above 673 K and disappeared totally at 773 K. Covered WS<sub>2</sub> still showed strong PL emission to 873 K. After this entire heating/cooling cycle, the integrated PL intensities of the covered region were ~47% lower than those at the beginning and there was a PL blue shift of ~11 meV.

Then the measurement was repeated with flowing forming gas and heating to 873 K. The temperature-dependent PL intensity is shown in Figure 4c. Interestingly, the uncovered WS<sub>2</sub> then started to decompose at 773 K, and totally disappeared when the temperature approached 873 K. The uncovered WS<sub>2</sub> survives to a higher temperature in a forming gas environment than in air or N<sub>2</sub>, perhaps because WS<sub>2</sub> decomposition is related to the oxygen and water vapor in the surrounding area, and forming gas helps reduce oxidation. With WS<sub>2</sub> covered by *h*-BN, the sample and the observed PL remain to the high temperature of 873 K. Trion peaks appear only for these covered samples and only with flowing forming gas, during cooling starting at

323 K, and they are strong at room temperature. This suggests unintentional charges are induced at high temperature and the doping level of the covered WS<sub>2</sub> changes. Finally, after the entire heating/ cooling cycle, the integrated PL signals of the covered region are  $\sim$ 96% lower than those at the beginning of the cycle. (Including only excitonic (and not trion) emission, the decrease in the integrated PL signal is 98%.) This suggests that covered WS<sub>2</sub> becomes more damaged than that with heating in air (to 773 K) or flowing  $N_2$  (to 873 K). Therefore, h-BN encapsulation passivates the covered WS<sub>2</sub> the least with forming gas present. The PL peak was blue-shifted by 67 meV, which also suggests damage (see below). The Raman spectra in Figure S4 show no evidence of sulfur-terminated surfaces after heating in forming gas, with the formation of thiols, which could be one route toward passivation; this route also appears to be unlikely because there is no excess sulfur for this to occur.<sup>26,27</sup> They also show no evidence of the partial reduction of the  $SiO_2$  (due to the  $H_2$  in forming gas), which could lead to the charges needed for trion formation-but these levels may be too small to be seen by Raman scattering.

Therefore, the best passivation occurred for covered samples with flowing  $N_{22}$  and the best for uncovered samples was with flowing forming gas.

Because heating caused the least damage in covered  $WS_2$  with flowing  $N_2$ , bright-field micrographs of the sample before and after heating were retaken for flowing  $N_2$  up to 873 K, as with that for air in Figure 3a,b with heating to 773 K, as shown in Figure S5 in the

Supporting Information. Unlike for air, no spots in the center of the  $WS_2$  were seen after heating, which also indicates less damage.

### RESULTS AND DISCUSSION

Gao et al. used XPS analysis to show that sulfur oxide does not form when WS<sub>2</sub> is in air, and therefore WS<sub>2</sub> oxidation starts with the breaking of the W–S bond, which is then followed by oxygen atoms displacing sulfur atoms at the surface.<sup>28</sup> The oxidized region has been identified as WO<sub>3</sub>.<sup>29</sup> Oxygen and water molecules present would induce degradation.<sup>30</sup>

Often the degradation and decomposition of TMDs can be attributed to exposure to oxygen. Oxygen dissociates into individual atoms and adsorbs on the surface of the TMD flakes. This degradation is limited at room temperature by the energy barrier for O<sub>2</sub> dissociation and chemisorption; therefore, TMDs are stable in an ambient environment.<sup>31</sup> In Figure 2 we see that the decomposition of uncovered WS<sub>2</sub> occurred at ~673 K and higher in air. Using this, the energy barrier for O<sub>2</sub> combined dissociation and chemisorption ( $E_a$ ) can be roughly estimated by setting  $10^{-12} e^{-E_a/k_BT} \sim 1$  at 673 K,<sup>32</sup> using the pre-exponential factor in the transition-state theory by Nan et al.<sup>32</sup> for the physical and chemical adsorption of oxygen molecules on MoS<sub>2</sub>. This gives ~1.6 eV, which is the same as that calculated by DFT.<sup>31</sup>

Because WS<sub>2</sub> is largely unchanged at 673 K in air when it is covered by *h*-BN, it is largely stabilized by *h*-BN encapsulation at high temperature (though the postcycle PL is still affected). The effectiveness of the *h*-BN encapsulation is not related to *h*-BN thickness (15–40 nm here) because the energy barrier for an O2 molecule across a monolayer van der Waals layer by quantum tunneling is very high, 5 eV.<sup>33</sup> Instead, the imperfect passivation of h-BN covering the TMD is attributed to  $O_2$ molecule penetration between the h-BN overlayer and the SiO<sub>2</sub> substrate surface, as in a previous study of van der Waals layer covering and passivating nanoparticle monolayers from oxidant gases,<sup>34</sup> which found an effective diffusion coefficient for 2D transport of O<sub>2</sub> underneath the van der Waals layer of  $\sim 10^{-10}$  cm<sup>2</sup>/s.<sup>34</sup> This might be due to the roughness and dangling bonds on the SiO<sub>2</sub> substrate surface, which would allow some molecules, such as O2 and H2O, to move here between the *h*-BN layer and SiO<sub>2</sub> substrate surface. Therefore, even if the covered sample is not seen to decompose, the transport of oxygen underneath the h-BN overlayer can degrade the PL measured after the heating cycle, and even more so for higher temperatures, longer heating cycles, and smaller area *h*-BN overlayers.

This mechanism could also help explain why covered WS<sub>2</sub> shows the lowest postcycle PL signal after heating in forming gas. The H<sub>2</sub> in forming gas likely moves faster across the *h*-BN/SiO<sub>2</sub> interface than these other, larger molecules used in the studies and apparently leads to defects in the covered monolayer WS<sub>2</sub>. The trion peaks originate from doping level changes caused by charge defects generated by H<sub>2</sub> molecules. In contrast, forming gas leads to the least macroscopic decomposition of uncovered WS<sub>2</sub> of the gas environments examined.

As noted above, after the heating/cooling cycle to 773 K in air, the peak position of PL of *h*-BN-covered WS<sub>2</sub> showed a small red shift of 12 meV, which corresponds to an increase in the biaxial in-plane tensile strain of ~0.12% if all due to strain.<sup>25</sup> Because WS<sub>2</sub> monolayers have a larger thermal expansion coefficient than does either Si or *h*-BN, an increase in this strain during the cooling cycle is expected (with

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adhesion between either WS<sub>2</sub> and the substrate (of ~0.21– 0.35%) or between WS<sub>2</sub> and *h*-BN (~0–0.13%), with the range due to the uncertainty in the WS<sub>2</sub> ML thermal expansion coefficient).<sup>35–37</sup> The integrated PL at room temperature decreases after this cycle in air by ~63%. This large amount of decrease cannot be attributed to this strain change. Lloyd et al. measured the integrated PL intensity change as a function of biaxial in-plane tensile strain and found that an ~0.12% increase in biaxial in-plane tensile strain corresponds to a decrease in PL integrated intensity of ~9%.<sup>38</sup> Thermal damage could be important for PL quenching, including some of it possibly being linked to the spots seen in Figure 3.

The overall PL blue shift with flowing  $N_2$  and forming gas would indicate additional factors beyond strain, such as changes in doping and the lattice parameters. This would be expected with electron concentration increases<sup>39</sup> and molecular bonding to sulfur vacancies.<sup>40</sup> This could indicate thermal damage in both cases, the more so with forming gas, which had the much larger PL blue shift and decrease in PL intensity.

The temperature dependence of the integrated PL intensity and the fwhm in ambient air are fit in parts (a) and (b), respectively, of Figure 5. The fwhm line width of the PL, due



**Figure 5.** (a) Integrated PL intensity and (b) fwhm of *h*-BN-covered  $WS_2$  flakes versus *T* under ambient air. The blue spots are the experimental data from the heating cycle run in Figure 2d. The red solid red line in (a) is a fitted curve and in (b) the peak fwhm fit with eq 1.

to exciton recombination in monolayer WS2, depends on T as  $^{41-44}$ 

$$\Gamma(T) = \sigma T + \gamma N + \Gamma_0 \tag{1}$$

The first term comes from the acoustic phonon–exciton interaction, with the acoustic phonon coupling strength  $\sigma$  typically having an order of magnitude of a few  $\mu$ eV/K. The second term arises from the exciton–optical phonon interaction, and above 100 K its contribution is much larger than that of the first term. This second term is proportional to the number of phonons, as given by the Bose–Einstein distribution function:

$$N = \frac{1}{\exp\left(\frac{E}{k_{\rm B}T}\right) - 1} \tag{2}$$

Here, *E* is the (weighted average) energy of the relevant phonons.  $\gamma$  is the optical phonon coupling strength. *E*,  $\gamma$ , and  $\Gamma_0$  parameters are obtained by fitting the curve for PL fwhm in Figure 2d for heating of covered *h*-BN in ambient air. The "average" phonon energy is *E* = 25 meV, the exciton phonon

coupling strength is  $\gamma = 67.6$  meV, and the temperatureindependent broadening  $\Gamma_0 = 2$  meV. These parameters are quite similar to those for MoS<sub>2</sub> in ref 43.

The dependence of the integrated PL signal on T is usually described by the following equation, which includes the quenching by two nonradiative recombination centers:<sup>45–48</sup>

$$I(T) = \frac{I_0}{1 + A \exp\left(-\frac{E_1}{k_{\rm B}T}\right) + B \exp\left(-\frac{E_2}{k_{\rm B}T}\right)}$$
(3)

(Supporting Information, Section S5). Parameters A and B represent the ratio of the nonradiative recombination rate to the radiative recombination rate for the two nonradiative recombination centers, and  $E_1$  and  $E_2$  represent the thermal activation energies for PL quenching for each one. For the PL intensity in Figure 2a of covered h-BN in ambient air, the activation energies are  $E_1 = 51.2$  meV and  $E_2 = 229$  meV, and A = 54 and B = 10160. Because the binding energy of free excitons in monolayer WS<sub>2</sub> is 320 meV,<sup>42</sup> the larger energy  $E_2$ is thought to be the energy needed to unbind bound excitons in WS<sub>2</sub>. The lower energy  $E_1$  represents the activation energy of exciton diffusion to the vicinity of local nonradiative recombination centers.<sup>48</sup> Nonradiative recombination dominates radiative decay at all studied T and does so increasingly at higher T. In the lower T range studied, exciton diffusion is more important than exciton unbinding, whereas in the higher temperature range, exciton unbinding dominates.

The PL intensity during the heating of covered  $WS_2$  in  $N_2$  of Figure 4b is also fit; similar parameters are obtained as those for air, as seen in the Supporting Information (Figure S6). It is not fit for covered  $WS_2$  heated in forming gas because of the noted PL damage in that case.

A trion peak is seen in the PL during the cooling of covered *h*-BN with flowing forming gas at and below 323 K (Figure 4c). The trion binding energy is very roughly estimated to be  $k_{\rm B}T$  at the temperature it first appears (323 K), which is approximately 28 meV. This corresponds well to the findings of a previous PL study of WS<sub>2</sub>, which was conducted down to 4 K, 20–30 meV.<sup>42</sup>

# CONCLUSIONS

CVD-grown triangular-shape high-quality monolayers of WS<sub>2</sub> can be well stabilized at elevated temperatures by encapsulation with several-layer h-BN, but to different degrees in the presence of ambient air, flowing N2, or flowing forming gas (95%  $N_2$ , 5%  $H_2$ ). The best passivation occurs for *h*-BNcovered samples with flowing N<sub>2</sub>, as judged by the PL intensity after the cycle, which decreases the least with that gas. Furthermore, no degradation of the covered WS<sub>2</sub> flakes is seen visually in N2 up to the highest tested examined temperature, 873 K. This might be due to "minimal"  $O_2$  and  $H_2O$  molecules. Spots are seen to form in the middle of the flakes after heating in ambient air, but not after heating in N2. Postcycle PL is weakest for forming gas, presumably due to the damage by the rapid H<sub>2</sub> diffusion between the *h*-BN and SiO<sub>2</sub> substrate surface. For forming gas only, trion PL peaks are seen, and they are seen near the end of the cooldown cycle. Also, macroscopic degeneration of the covered WS<sub>2</sub> is seen in forming gas at high temperatures. In contrast, flowing forming gas leads to the least macroscopic degeneration of uncovered WS<sub>2</sub> at elevated temperature. One would expect WS<sub>2</sub> flakes would be passivated even better with h-BN encapsulation on the top and bottom, and in the presence of  $N_2$ .

## ASSOCIATED CONTENT

### **Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.1c06348.

More details of the experimental setup; room-temperature Raman scattering and photoluminescence in flowing nitrogen and forming gas; Raman scattering before and after heating in flowing forming gas; optical micrographs before and after heating in flowing nitrogen; temperature dependence of photoluminescence; fitting the temperature dependence of photoluminescence in flowing nitrogen (PDF)

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#### Author Contributions

The paper was written through the contributions of all the authors. All authors have given approval to the final version of the paper.

#### Notes

The authors declare no competing financial interest.

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