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Variability of Band Alignment between WS_2 and SiO_2: Intrinsic *versus* Extrinsic Contributions

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Internal photoemission of electrons was used to determine the energy position of the top valence band of mono- and few-layer WS_2 on a SiO_2/Si substrate. It was found, contrary to density functional theory calculations, that the valence band top in WS_2 shifts up in energy with respect to the conduction band minimum of SiO_2 with decreasing number of monolayers. At the same time, the band alignment of WS_2 with SiO_2 appears to be less sensitive to the WS_2 synthesis route than in the previously studied case of the MoS_2/SiO_2 interface indicating less extrinsic WS_2 variability.

I. INTRODUCTION

Since demonstration of the first functional two dimensional (2D) transistor by Radisavljevic et al.[1] using MoS_2 as channel material, a lot of research has been done on semiconducting transition metal dichalcogenides (TMDs). Initially, mostly MoS_2 was explored, as it showed promising results[2345]. However, it has been found that synthetically grown MoS_2 suffers from significant intrinsic and extrinsic variability. The latter's origin can be correlated with synthesis and processing details of the 2D layers. It has been shown that there is a $\approx$ 0.6 eV difference in the band alignment between SiO_2 and MoS_2 grown by DC magnetron sputtering compared to high temperature sulfurization of metallic molybdenum in H_2S; tentatively ascribed to the influence of hydrogen present in the ambient in the last case[6]. Moreover, significant die-to-die threshold voltage (V_T) variability has been observed for metal-organic chemical vapor deposition (MOCVD) grown monolayer (ML) MoS_2[7], while, few-layer (FL) material seems to be less prone to the V_T variability. Furthermore, layer transfer from growth- to target-substrate of MoS_2 layers grown through high temperature sulfurization of metallic Mo also introduces a significant change in the band alignment with SiO_2, causing up to a $\approx$ 1 eV energy difference at edges of the transferred layers, while at the wafer centre the MoS_2 valence band (VB) top is shifted by $\approx$ 0.5 eV compared to as grown material[8].

These observations suggest the variability might be due to a combined action of intrinsic and extrinsic factors. For example, MoS_2 thickness variability has been shown to cause degradation of the subthreshold slope (SS). Statistical analysis of 60 devices with a 100 nm channel length show that a MOCVD grown monolayer MoS_2 containing islands of a second monolayer results in the SS degradation[7]. Upon further reduction of the channel length the SS degradation is expected to worsen. The thickness-dependent band gap width is a well-known intrinsic feature of ML/FL TMDs implying that the gap edges also shift when changing the ML number[9]. This behaviour may have a profound effect on electron transport, because synthetic TMD layers grown on a wafer scale often contain regions with thicker FL "islands" leading to a local gap narrowing[10]. As a result, trapping of charge carriers in these inhomogeneities may significantly impair their transport because the capture cross section becomes comparable to the island size. However, little experimental information is available regarding the VB shift and conduction band (CB) edges upon TMD film thickness change.

Recently, ML & FL WS_2 emerged as a more promising candidate for the use in ultrathin channel transistors since it exhibits a higher electron mobility[11] and provides a better on/off current ratio[12] compared to MoS_2-based devices. WS_2 also exhibits improved variability of the layer transfer process in terms of energy band alignment with industry standard insulator SiO_2[13]. Additionally, we previously noticed that sensitivity to the hydrogen presence during TMD synthesis might have less of an effect on the WS_2 band alignment[14]. Therefore, in this present study, we addressed the intrinsic band alignment variability by using internal photoemission (IPE) spectroscopy to determine the energy band alignment of ML and FL WS_2 grown though molecular beam epitaxy (MBE) on SiO_2. This is achieved by observing optically-excited electron transitions from the WS_2 VB into the CB of SiO_2 which allows one to determine the energy barrier between two bands. Unexpectedly, we found an opposite trend in the case of WS_2 compared to MoS_2[6]. The WS_2 VB top shifts upwards in energy relative to the SiO_2 CB when decreasing the film thickness from 7 to 1 ML. Additionally, the extrinsic effects were investigated by comparing the hydrogen free MBE synthesis to the WS_2 films grown by chemical vapor deposition or sulfurization of metallic tungsten in H_2S. By contrast to the earlier studied MoS_2 case, we found a negligible impact of hydrogen on the energy band alignment with SiO_2. This would point to

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WS_2 as a promising TMD for wafer-scale integration.

II. EXPERIMENTAL DETAILS

A set of 1, 3, 5 and 7 ML thin WS_2 films was grown by MBE on top of SiO_2(50 nm)/p-Si(100) substrates at 480 °C with a S to W flux ratio of ≈5000:1. After deposition the films were left at the growth temperature for 2 min and then allowed to cool down in a continuous S flux. These WS_2 layers were *in situ* capped with a ≈ 5 nm layer of amorphous Se to prevent oxidation in air. The number of MLs were calculated from the physical thickness (0.5, 1.9, 3.7 and 4.8 nm) determinated by post growth X-ray photoelectron spectroscopy (XPS) attenuation analysis of the Si 2p core level assuming a 0.7 nm WS_2 ML thickness found in literature[15][16]. The ML sample 0.5 nm thickness has to be interpreted as partial coverage of the substrate. An effective attenuation length (EAL) for the Si $2p_{3/2}$ core level in the WS_2 overlayer was calculated to be 2.30 nm using the NIST electron EAL database[17]. More details of the system used for the MBE growth of WS_2 can be found elsewhere[18]. The set of studied samples was complemented by 1 ML WS_2 films synthesized on top of similar SiO_2/Si substrates by metal-organic chemical vapor deposition (MOCVD) from $W(CO)_6$ and H_2S precursors at 800 °C using the same approach as described in Ref.[10] as for MoS_2. On top all the WS_2 films large area optically semi-transparent Al and Au electrodes (15 nm thick, 0.5 mm^2) were thermoresistively evaporated to minimize possible damage to the 2D films[19][20]. For the backside contact to the Si substrate wafer a blanket Al layer was used.

IPE measurements were carried out at room temperature using a 150 W xenon arc lamp as light source in combination with a monochromator (spectral resolution of 2 nm) providing photons in the energy $h\nu$ range from 2 to 6 eV. In the biased WS_2/SiO_2/Si capacitors, currents were measured under illumination and in darkness using a Keithley 6517a electrometer. The photocurrent was then determined as the difference between these currents and, by normalizing it to the xenon lamp's calibrated incident photon flux at given photon energy $h\nu$, the quantum yield $Y(h\nu)$ was determined. By implementing a time delay between the start of illumination and the current readout, transient effects were minimized. Extensive averaging (> 60 per current readout) was applied in order to improve the signal-to-noise ratio. Powell's model[21] was used to analyse spectral dependencies of the quantum yield. In order to determine the IPE spectral threshold energy Φ_e, the quantum yield in the region above Φ_e can be approximated as a power function of the photon energy $h\nu$[21]:

$$Y(h\nu) = A(h\nu)(h\nu - \Phi_e)^p \quad (1)$$

where $A(h\nu)$ depends on the optical properties of the illuminated sample, including the possible optical interference effects and variations of optical properties of the constituent materials. This factor is usually assumed not to vary significantly within the narrow spectral range above the spectral threshold since no abrupt variations of the optical behaviour is expected for the materials in the stack[21]. The exponent p is determined by the excited electron energy distribution in the emitter. As in this case the VB of WS_2 is the emitter and the CB of SiO_2 the collector, p is expected to be close to 3, corresponding to a linear increase of the density of states with energy below the semiconductor VB top edge[21]. Indeed, such linear increase has been directly observed in X-ray photoelectron spectroscopy VB spectra of 1 ML WS_2 within approximately 1 eV range below the VB top[22]. Therefore, the IPE spectral threshold energy Φ_e corresponding to the minimal energy required for an electron to be excited from the WS_2 VB top edge into the CB of the underlying SiO_2 insulator can be found by linearly fitting the quantum yield spectral curve in $Y^{1/3}$-$h\nu$ coordinates, also known as Powell coordinates[21]. Finally, to account for the image-force barrier lowering effect[21], spectral thresholds determined at various externally applied gate bias voltages V_g are plotted in $\Phi_e - \sqrt{F}$ coordinates (the Schottky plot). These are then linearly extrapolated to a zero electric field F, determined by normalizing the V_g to the oxide thickness, to obtain the interface barrier height[19].

III. RESULTS AND DISCUSSION

First, we examined the die-to-die consistency of the results to ensure reproducibility of the MBE growth. Figure 1 compares the between yield spectra of two 7 ML WS_2 MBE grown samples from different growth runs. Both IPE spectra have an onset of photoemission after 3.5 eV, and behave similarly at higher energies. However, there is a slight deviation between both curves above $h\nu \approx 4.3$ eV, this can possibly be explained by the small difference in the growth runs. Namely, sample A was directly grown up to a 7 ML thickness, while sample B was initially grown to 1 ML thickness for *in situ* characterization and continued to 7 ML thickness a day later. As the second sample used a "seed" layer it might have induced some changes in the morphology, e.g., less/more island formations or grain size differences, in sample B compared to A. This might explain the small deviation at higher energies of the IPE spectra. Similarly, an apparent kink observed at ≈ 4.75 eV for the spectral curve of sample A, its origin can be found in a morphology difference. Given the observed IPE quantum yield spectrum is sensitive to the density of states below the VB top, changes in morphology might induce variations in the WS_2 density of states. Nevertheless, the IPE threshold values inferred from the Schottky plot, shown in the inset of figure 1 for both samples have a close zero field threshold values of 4.0 ± 0.1 eV with the SiO_2 CB. The thresholds were inferred through linear fitting of the spectral curves at various gate biases over an ≈ 1 eV region above the spectral threshold according to XPS valence band emission spectra indicating 1 eV linear increase in the occupied electron state density below the VB top[22]. The difference between the two slopes of the Schottky plots for two samples suggests a difference in built-in electric

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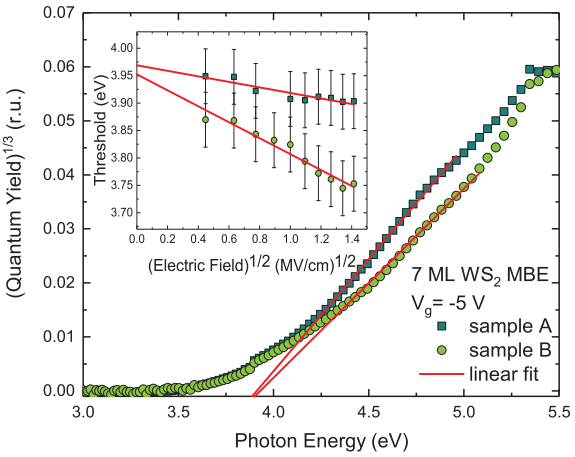

FIG. 1: Powell plots of the IPE quantum yield spectra for two MBE grown 7 ML WS_2 samples for a gate bias of -5 V. Red lines indicate the linear fit used to obtain the field dependent threshold value. The inset shows Schottky plots of the obtained threshold values for both samples, with red lines indicating the linear fit used to obtain the zero field threshold corresponding to the barrier height between the WS_2 VB and the SiO_2 CB. Where r.u. is used as an abbreviation for relative units.

fields at the WS_2/SiO_2 interface. Nevertheless, the zero field threshold values remain consistent and can be used to trace the potential sources of the band alignment variations.

Given that MBE synthesis delivers a consistent die-to-die band alignment of WS_2 with SiO_2, it allows for the direct comparison between ML & FL WS_2. Figure 2 shows Powell plots for samples with 7, 5, 3 and 1 ML WS_2 films for a range of gate biases. An obvious difference between the spectra is the decreased quantum yield for a decreasing number of layers, a direct result of the difference in the photoexcited WS_2 volume. This is a straightforward indication that the observed IPE spectra are the result of electron photoemission from the WS_2 films. The intensity difference between 3 and 7 ML is similar to the earlier reported IPE intensity difference between 3 and 6 ML WSe_2[14], while the intensity difference between 1 and 3 ML is larger than the 5 to 7 ML transition, it is not unexpected as the transition from ML to FL leads to the larger relative difference in the film thickness. It needs to be pointed out that the Se cap has no influence on the IPE spectra as the photoemission onset of 5 nm Se occurs at a higher energy than observed for these WS_2 films[14]. It was already proven that the metal contact (Al *versus* Au) have no significant influence on the IPE spectra[14], suggesting that the observed IPE spectra in figure 2 originate from the WS_2 films.

While the IPE spectra in figure 2 have a similar shape, the photoemission onset in 7 ML WS_2 sample is somewhat different than observed for the other WS_2 film thicknesses. We already reported a similar difference in onset of photoemission shape for 3 and 6 ML WSe_2 (cf. figure 6 in Ref.[14]). This similarity between two WX_2 (X=S, Se) films probably indicates an intrinsic property of the valence band top edge in the transition from a 2D layer to more bulk-like material. Nevertheless, the energy onset of photoemission appear to be similar in energy for all FL WS_2 films as indicated by the red lines in figure 2. All the inferred field dependent spectral threshold values are combined in the Schottky plot shown in figure 3. Linear extrapolation to zero field of the FL WS_2 spectral threshold results in a zero field threshold of 4.0 ± 0.1 eV for 5 and 7 ML. Meanwhile the 3 ML sample has a slightly higher threshold but it falls within the margin of error as compared to other FL films. These results are consistent with the band structure evolution of WS_2 which is not expected to change significantly with the film thickness between 3 and 7 MLs[9]. By contrast, the noticeable IPE threshold shift is observed upon transition from FL to ML WS_2 indicating a change in the band alignment between WS_2 and SiO_2. The zero field threshold obtained for 1 ML WS_2 is 3.8 ± 0.1 eV, which is approximately 0.2-0.3 eV lower in energy compared to FL WS_2, indicates an up-shift of the VB top for the FL to ML transition as schematically illustrated in figure 4. This up-shift trend is opposite to what has been observed for the band alignment of MoS_2 with SiO_2[6]. Not only is the trend for WS_2 opposite to that of MoS_2, it is also opposite to density functional theory (DFT) calculations of WS_2 films[23,24,25]. These predict that with increasing number of layers the valence band moves up in energy. It needs to be pointed out, however, that these calculations are based on free-standing films, while these experimental results are obtained from films on Si/SiO_2 substrates. Earlier we reported on the failure of DFT to correctly predict the band alignment of WS_2 versus WSe_2 with SiO_2[14]. So, while DFT calculations might be correctly predicting the band structure evolution over different thicknesses, there are some discrepancies when the film is supported by a substrate. Knowing that experimental results on WS_2 band alignment with SiO_2 have been different in terms of predicted relative positions for two separate experiments compared to DFT calculations, there is a possible, e.g. electrostatic, interaction of WS_2 with the SiO_2 substrate which has not been observed for MoS_2. The latter trend for MoS_2 thickness dependent VB positions follows well the trend predicted by DFT calculations. The unexpected result for WS_2 suggests that care has to be taken when assessing the origins of devices variability such as island formations causing SS degradation as observed for MoS_2[7] might not be the same for other semiconductors from the TMD group.

Keeping in mind that the extrinsic synthesis variability observed for MoS_2[6] is possibly caused by hydrogen presence during TMD film growth, a similar investigation was performed on WS_2 layers. We compared these MBE (intrinsically hydrogen free process) grown films to earlier reported band alignment values for 4 ML WS_2 synthesized on SiO_2 by sulfurization of metallic W in H_2S at 800 °C[26]. Figure 5 compares the IPE spectra for 5 ML WS_2 grown by MBE with

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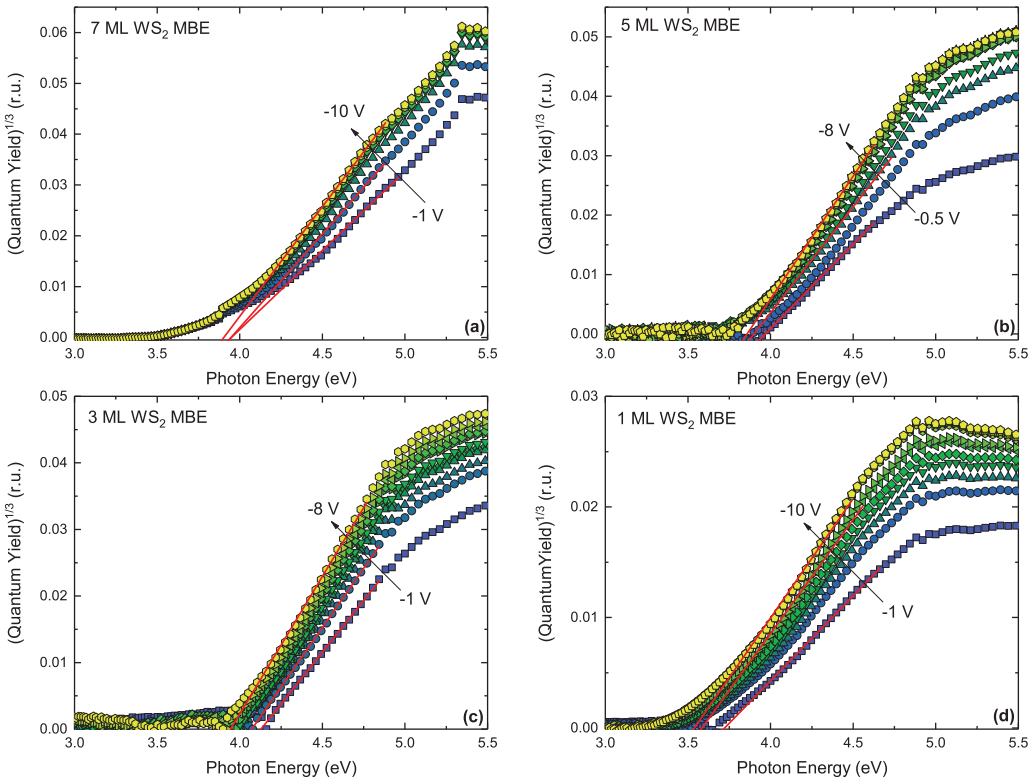

FIG. 2: Powell plots of the IPE quantum yield spectra for MBE grown (a) 7 ML (b) 5 ML (c) 3 ML (d) 1 ML WS_2 films for gate biases ranging between -0.5 V and -10 V. Red lines illustrate the linear fit used to obtain the field dependent threshold values.

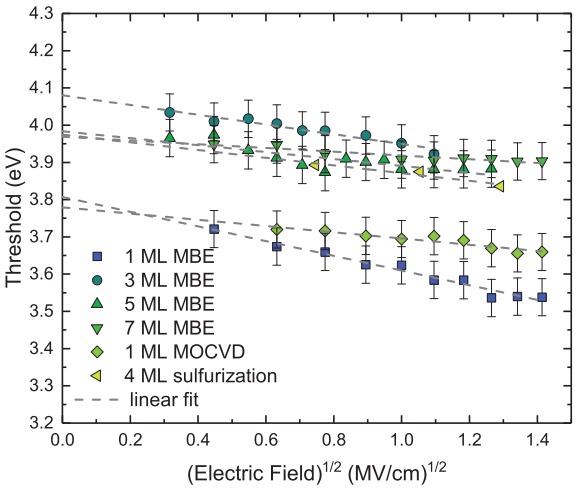

FIG. 3: Schottky plot of the inferred spectral thresholds for MBE grown ML & FL, MOCVD grown ML and sulfurization grown FL WS_2. Dashed grey lines indicate the linear fit used to determine the zero field threshold.

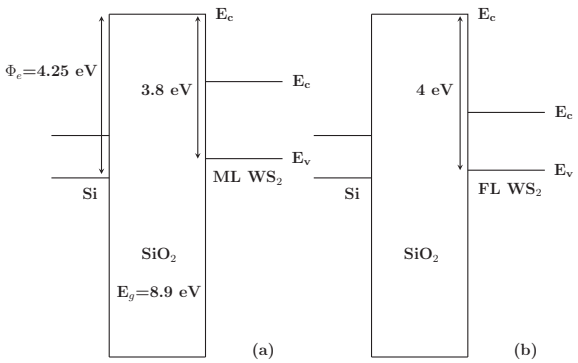

FIG. 4: Schematic representation of the energy band alignment of (a) ML (b) FL $WS_2/SiO_2/Si$ heterostructures.

4 ML film grown by W sulfurization taken at the WS_2 gate bias of -5 V. These spectra are in remarkable agreement with each other, both in terms of intensity and the energy onset of photoemission. Nevertheless, a slight decrease of intensity is observed for the 4 ML sample, but that is to be expected for a decreased number of layers. This resemblance is also

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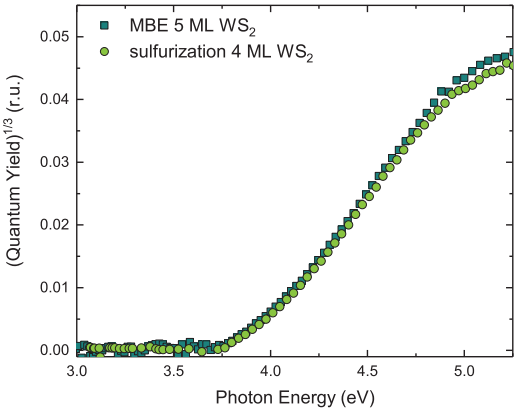

FIG. 5: A comparison between IPE spectra of WS_2 grown through MBE (5 ML) and sulfurization (4 ML) with a gate bias of -5 V.

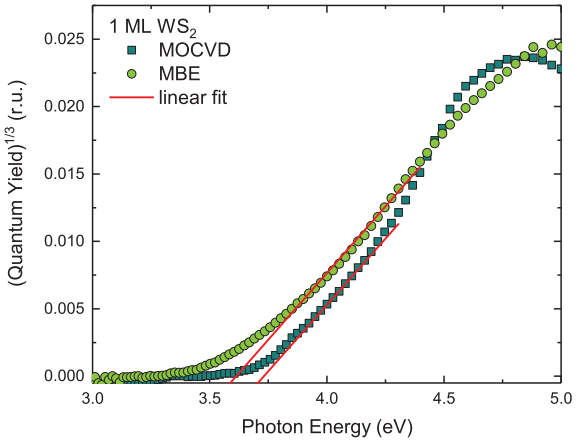

FIG. 6: Comparison between IPE spectra obtained from 1 ML WS_2 layers grown through MOCVD and MBE with a gate bias of -5 V. Red lines indicate the linear fit used to determine the spectral threshold values.

reflected in the zero field threshold of 4.0 $\pm$ 0.1 eV obtained from the Schottky plot shown in figure 3. This result is a first indication of a limited extrinsic variability of the band alignment of WS_2 caused by the change of synthesis method. On the other hand, comparing IPE yield spectra for MBE- and MOCVD- grown 1 ML WS_2 in figure 6 reveals a slight increase of the spectral threshold for the latter. However, the Schottky plots shown in figure 3 yield close zero field threshold values for both synthesis methods of ML WS_2 at 3.8 $\pm$ 0.1 eV. The change in the Schottky plot slope for the MOCVD grown film suggests introduction of charges to the interface probably associated with the presence of hydrogen in the synthesis ambient. Earlier we already demonstrated the initial indications of good reproducibility of the MOCVD process for 1 ML materials in terms of band alignment with the Si/SiO_2 substrate[13]. However, as the band alignment for all three synthesis methods discussed above falls within the margin of error of one another, it suggests that the presence of hydrogen during WS_2 synthesis might have by far lesser impact on the interface band alignment than in the case of MoS_2/SiO_2. Together with the earlier reported reduced variability due to the film transfer process[13], WS_2 seems to be less prone to extrinsic variability compared to its MoS_2 counterpart. The similarity in threshold values between ML MBE- & MOCVD- grown and FL MBE- & sulfurization-grown allows for the indirect comparison between the MOCVD and sulfurization synthesis. As the same band alignment evolution trend is observed for those synthesis methods, the opposite trend to theoretical calculations seems to be an intrinsic property of synthetic WS_2. Band alignment characterization of exfoliated WS_2 materials on SiO_2 could reveal if the apparent intrinsic trend is caused by the use of synthetic material, although to our knowledge none has been performed up to the date. This is probably related to typically small size of the exfoliated flakes precluding reliable measurements of the IPE current.

Summarizing the above results one may point to several significant differences in the evolution of WS_2/SiO_2 band alignment to the earlier studied seemingly similar MoS_2/SiO_2 systems. First, the intrinsic VB shift with increasing ML number occurs in the opposite direction, i.e., the VB of ML WS_2 is energetically positioned above that of multilayer's as shown in figure 4. The effect of the substrate-related artifacts can be considered as insignificant since the VB position appears to be the same in the 7 ML samples (A and B). Second, the extrinsic factors related to the WS_2 synthesis route appear to have by far less impact on the band alignment with SiO_2 than in the case of MoS_2.

IV. CONCLUSION

In conclusion, a reduced WS_2 extrinsic variability and a consistent band alignment with SiO_2 were found for three different synthesis routes, showing less sensitivity to hydrogen presence during synthesis than in the previously studied case of MoS_2/SiO_2 interface. At the same time, for intrinsic WS_2 variability an unexpected trend was found as the valence band top in WS_2 shifts up in energy with decreasing number of monolayers as measured with respect to the conduction band minimum of SiO_2. This would make localization of holes in the islands of larger thickness energetically unfavourable and deliver a higher hole mobility in the inhomogeneous layers. Therefore, WS_2 might be a more suitable material for p-channel devices than MoS_2. Taken together with a higher electron mobility, WS_2 seems to be the TMD of choice for complementary MOS device integration.

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DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

[1]B. Radisavljevic, A. Radenovic, J. Brivio, V. Giacometti, and A. Kis, Nat. Nanotechnol. **6**, 147–150 (2011).
[2]H. Wang, L. Yu, Y.-H. Lee, Y. Shi, A. Hsu, M. L. Chin, L.-J. Li, M. Dubey, J. Kong, and T. Palacios, Nano Lett. **12**, 4674–4680 (2012).
[3]S. Das, H.-Y. Chen, A. V. Penumatcha, and J. Appenzeller, Nano Lett. **13**, 100–105 (2013).
[4]S. B. Desai, S. R. Madhvapathy, A. B. Sachid, J. P. Llinas, Q. Wang, G. H. Ahn, G. Pitner, M. J. Kim, J. Bokor, C. Hu, *et al.*, Science **354**, 99–102 (2016).
[5]J. Wang, Q. Yao, C.-W. Huang, X. Zou, L. Liao, S. Chen, Z. Fan, K. Zhang, W. Wu, X. Xiao, *et al.*, Adv. Mater. **28**, 8302–8308 (2016).
[6]I. Shlyakhov, J. Chai, M. Yang, S. Wang, V. V. Afanas' ev, M. Houssa, and A. Stesmans, Apl. Mater. **6**, 026801 (2018).
[7]Q. Smets, D. Verreck, Y. Shi, G. Arutchelvan, B. Groven, X. Wu, S. Sutar, S. Banerjee, A. N. Mehta, D. Lin, *et al.*, in *2020 IEEE International Electron Devices Meeting* (IEEE, 2020) pp. 3–1.
[8]V. Afanas'ev, D. Chiappe, M. Perucchini, M. Houssa, C. Huyghebaert, I. Radu, and A. Stesmans, Nanotechnology **30**, 055702 (2018).
[9]I. Tanabe, M. Gomez, W. C. Coley, D. Le, E. M. Echeverria, G. Stecklein, V. Kandyba, S. K. Balijepalli, V. Klee, A. E. Nguyen, *et al.*, Appl. Phys. Lett. **108**, 252103 (2016).
[10]D. Chiappe, J. Ludwig, A. Leonhardt, S. El Kazzi, A. N. Mehta, T. Nuytten, U. Celano, S. Sutar, G. Pourtois, M. Caymax, *et al.*, Nanotechnology **29**, 425602 (2018).
[11]A. Rawat, N. Jena, A. De Sarkar, *et al.*, J. Mater. Chem. A **6**, 8693–8704 (2018).
[12]T. Georgiou, R. Jalil, B. D. Belle, L. Britnell, R. V. Gorbachev, S. V. Morozov, Y.-J. Kim, A. Gholinia, S. J. Haigh, O. Makarovsky, *et al.*, Nat. Nanotechnol. **8**, 100–103 (2013).
[13]G. Delie, D. Chiappe, I. Asselberghs, C. Huyghebaert, I. Radu, S. Banerjee, B. Groven, S. Brems, and V. V. Afanas'ev, Nano Express **2**, 024004 (2021).
[14]G. Delie, P. M. Litwin, S. J. McDonnell, D. Chiappe, M. Houssa, and V. V. Afanas'ev, ECS J. Solid. State Sc. **9**, 093009 (2020).
[15]K. Tian, K. Baskaran, and A. Tiwari, "Growth of two-dimensional ws_2 thin films by pulsed laser deposition technique," Thin Solid Films **668**, 69–73 (2018).
[16]Y. Yoo, Z. P. Degregorio, and J. E. Johns, J. Am. Chem. Soc. **137**, 14281–14287 (2015).
[17]C. J. Powell *et al.*, "Nist database for the simulation of electron spectra for surface analysis (sessa), version 2.1. 1," (2018).
[18]K. M. Freedy, P. M. Litwin, and S. J. McDonnell, ECS Transactions **77**, 11 (2017).
[19]V. V. Afanas'ev, D. Chiappe, C. Huyghebaert, I. Radu, S. De Gendt, M. Houssa, and A. Stesmans, Microelectron. Eng. **147**, 294–297 (2015).
[20]V. V. Afanas'ev, G. Delie, M. Houssa, I. Shlyakhov, A. Stesmans, and V. Trepalin, J. Phys.-Condens. Mat. **32**, 413002 (2020).
[21]R. Powell, J. Appl. Phys. **41**, 2424–2432 (1970).
[22]H. Zhu, C. Zhou, B. Tang, W. Yang, J. Chai, W. Tay, H. Gong, J. Pan, W. Zou, S. Wang, *et al.*, Appl. Phys. Lett. **112**, 171604 (2018).
[23]J. Kang, S. Tongay, J. Zhou, J. Li, and J. Wu, Appl. Phys. Lett. **102**, 012111 (2013).
[24]D. Bocharov, S. Piskunov, Y. F. Zhukovskii, and R. A. Evarestov, Phys. Status Solidi-R **13**, 1800253 (2019).
[25]H.-g. Kim and H. J. Choi, Phys. Rev. B **103**, 085404 (2021).
[26]V. V. Afanas'ev, D. Chiappe, A. Leonhardt, M. Houssa, C. Huyghebaert, I. Radu, and A. Stesmans, ECS Transactions **80**, 191 (2017).
[27]V. V. Afanas'ev, *Internal photoemission spectroscopy: principles and applications* (Elsevier, 2010).

V. FIGURE CAPTIONS

1. Powell plots of the IPE quantum yield spectra for two MBE grown 7 ML WS_2 samples for a gate bias of -5 V. Red lines indicate the linear fit used to obtain the field dependent threshold value. The inset shows Schottky plots of the obtained threshold values for both samples, with red lines indicating the linear fit used to obtain the zero field threshold corresponding to the barrier height between the WS_2 VB and the SiO_2 CB. Where r.u. is used as an abbreviation for relative units.

2. Powell plots of the IPE quantum yield spectra for MBE grown (a) 7 ML (b) 5 ML (c) 3 ML (d) 1 ML WS_2 films for gate biases ranging between -0.5 V and -10 V. Red lines illustrate the linear fit used to obtain the field dependent threshold values.

3. Schottky plot of the inferred spectral thresholds for MBE grown ML & FL, MOCVD grown ML and sulfurization grown FL WS_2. Dashed grey lines indicate the linear fit used to determine the zero field threshold.

4. Schematic representation of the energy band alignment of (a) ML (b) FL $WS_2/SiO_2/Si$ heterostructures.

5. A comparison between IPE spectra of WS_2 grown through MBE (5 ML) and sulfurization (4 ML) with a gate bias of -5 V.

6. Comparison between IPE spectra obtained from 1 ML WS_2 layers grown through MOCVD and MBE with a gate bias of -5 V. Red lines indicate the linear fit used to determine the spectral threshold values.