Device-relevant SiO₂ transfer of WS₂ from the growth substrate in the IC production process because of the high growth temperatures affecting the band alignment at the WS₂/SiO₂ interface and the electron tunnelling rate across the interface. These challenges are encountered in terms of high sensitivity of the interface properties to the processing details. For example, the electron band alignment of 2D layers with oxide substrates, e.g. SiO₂, may vary by ≈ 0.5 eV for different synthesis methods of few-ML thin MoS₂ as revealed by the valence band (VB) top energy shift. More recently, we have observed that the growth method affects the band alignment at the WS₂/SiO₂ interface even to a considerably lesser extent than in the case of MoS₂/SiO₂ structures. Furthermore, not only the TMD synthesis method affects the band alignment: The post-growth transfer of TMD layers from a growth substrate (SiO₂/Si or sapphire) to the target SiO₂/Si wafer has been found to cause a ≈ 0.5–1 eV VB shift ascribed to violation of the MoS₂/SiO₂ interface electroneutrality. This transfer process becomes unavoidable when implementing MoS₂ and WS₂ in the IC production process because of the high growth temperatures (>800 °C in the presence of H₂S) needed to obtain a larger grain size and less grain boundaries severely degrade insulating properties of SiO₂. At the same time, the band alignment represents a crucial factor directly influencing the built-in electric fields and the electron tunnelling rate across the interface and its knowledge and tight control are needed to ensure reproducibility of the devices.

In this work, we addressed the critical issue of stability of 1 ML WS₂ films grown by metal-organic CVD (MOCVD) on SiO₂ as affected by storage in air and by layer transfer from the growth sapphire substrate to the device-relevant SiO₂/Si wafers. As in the earlier studies we used internal photoemission of electrons...
(IPE) from the VB of the TMD film into the SiO₂ conduction band (CB) to monitor evolution of the band alignment. In addition to the good reproducibility of the VB top energy position of 1ML WS₂ films directly grown on SiO₂/Si substrates we found that storage in air over extended period of time (up to 9-14 months) has no significant effect on the density of states in the TMD VB and their energy distribution. This result is significantly different from the previously reported instability of the 2- and 4-ML WS₂ films synthesized by annealing (sulfurization) of metallic W layers in H₂S [20]. Furthermore, contrary to the MoS₂ case [15], the band alignment of MOCVD-grown 1ML WS₂ is not significantly impacted by layer transfer processing. Taken together, these results indicate MOCVD-grown WS₂ as a superior candidate for wafer-scale device fabrication.

2. Experimental details

The 1 ML-thin WS₂ films were grown from W(CO)₆ and H₂S precursors using similar approach as previously used for the MoS₂ synthesis [10] on top of a-SiO₂(50nm)/p-Si(100) 300 mm wafers. Two sets of samples were fabricated under a different base pressure of the MOCVD reactor: A high one, with possible presence of oxygen (referred to as sample set 1) and the lower one, supposed to be ‘purer’ (sample set 2). To investigate the possible impact of the TMD layer transfer on the band alignment, two additional 1 ML WS₂ films were grown on top of sapphire wafers, using the same MOCVD approach as set 1 and subsequently transferred on top of identical a-SiO₂(50 nm)/Si substrates. One WS₂ film was transferred using the widely used technique of water intercalation-based Poly(methyl methacrylate) (PMMA) assisted transfer [15,21] (the ‘wet transfer’ process). The other WS₂ film was first covered by a temporary adhesive/laser release layer on a glass carrier, then debonded from the growth wafer and permanently bonded in vacuum to the target a-SiO₂(50 nm)/Si wafer; after which the temporary glass stack was released by laser heating [22,23] (the ‘dry transfer’ process). On top all WS₂ films a combination of optically non-transparent small area contact pads (100 nm thick, 0.01 mm²) and large area semi-transparent electrodes (15 nm thick, 0.5 mm²) of Al, Au, and Cu were thermorestitively evaporated to minimize possible damage to the ML-thin films [24,25]. A photograph of a sample from set 1 with Al and Au contacts can be found in figure 1(a). A blanket Al layer was used as the backside contact to the Si substrate wafer. 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 hν range from 2 to 6 eV. In the biased 1 ML WS₂/SiO₂/Si capacitors (schematic cross section is shown in figure 1(b)), currents were measured under illumination and in darkness using a Keithley 6517a electrometer. Then the photocurrent was calculated as the difference between these currents and, by normalizing the photocurrent to the calibrated incident photon flux of the xenon lamp at given hν, the quantum yield Y(hν) was determined. To minimize transient effects a time delay between the start of illumination and the current readout was implemented, in combination with extensive averaging (>60 per current readout) in order to improve the signal-to-noise ratio. Powell’s model [26] was used to analyse spectral dependencies of the quantum yield. In order to determine the IPE spectral threshold energy Φₓ, the quantum yield in the region above Φₓ can be approximated as a power function of the photon energy hν [26]:

\[
Y(h\nu) = A(h\nu)(h\nu - \Phi_x)^p,
\]

where A(hν) depends on the optical properties of the illuminated sample, including the possible optical interference effects and variations of optical properties of the constituent materials. It is usually assumed that this constant does not vary significantly within the narrow spectral range above the spectral threshold since no abrupt variations of the optical behaviour is expected [26]. The exponent p is determined by the emitter type, in this case electrons are emitted from the VB of WS₂ into the CB of SiO₂ and p is expected to be equal to 3, corresponding to a linear increase of the states with energy below the VB top edge [26]. Indeed, this linear increase has been directly observed in x-ray photoelectron spectroscopy VB spectra of 1ML WS₂ within approximately 1 eV range below the VB top [27]. Therefore, the IPE spectral threshold energy Φₓ corresponding to the minimal energy required for an electron to be excited from the WS₂ VB top edge into the CB of the underlying SiO₂ insulator can be found by linear fitting the quantum yield spectral curve in \(Y^{1/3} - h\nu\) coordinates, also known as Powell coordinates. Finally, to account for the image-force barrier lowering effect [26], spectral thresholds determined at various externally applied gate bias voltages \(V_g\) are plotted in \(\Phi_x - \sqrt{F}\) 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 [24]. The built-in potential value related to the effective work function difference between Si and top electrode and possible presence of oxide charges was estimated from the voltage onset of the IPE current from WS₂ and subtracted from \(V_g\).
3. Results

The IPE spectra from 1 ML WS$_2$ directly grown on SiO$_2$ can serve as a reference in order to trace the possible influences of the processing factors, e.g., the type of layer transfer, on band alignment at the WS$_2$/SiO$_2$ interface. Figure 1 shows an example of IPE spectra (in Powell coordinates) for a sample from the set 1 using semi-transparent Cu contacts to WS$_2$. It has already been established that electrons photoexcited inside the top metal layer provide an insignificant contribution to the photocurrent [12], i.e. the observed spectra are due to electron photoexcitation within the WS$_2$ layer. The (quantum yield) to the IPE from WS$_2$ is seen to increase linearly with photon energy above $h\nu \approx 3.5$ eV allowing for the extraction of field dependent thresholds through linear fitting. The Schottky plot shown in figure 2 exhibits the IPE thresholds values obtained at different fields as well as the thresholds inferred from IPE measurements at 2 different locations within the wafer using a non-transparent Al contact. The results of two different contact schemes/contact metals are perfectly consistent yielding, by linear extrapolation of thresholds to a zero electric field, the zero field threshold of 3.7 ± 0.1 eV corresponding to the energy barrier between the 1 ML WS$_2$ VB top and the SiO$_2$ CB bottom edge. The same threshold values obtained from different places within the growth wafer indicate good homogeneity of the MOCVD deposited WS$_2$ in terms of the VB top energy.

To further examine the reproducibility of the MOCVD growth, IPE measurements were carried out on sample set 2 of 1 ML WS$_2$ also directly grown on SiO$_2$. Figure 3 compares two spectra of this particular sample with Al semi- and non-transparent contact pads to the spectrum of sample set 1. Spectra measured with non-transparent contact pads are normalized to match the spectra with semi-transparent contacts because the illuminated area of WS$_2$ photoemitter is expected to be smaller for the former case. This normalization is performed by aligning the maximum quantum yield for IPE from the Si backside photoemitter, used as the reference, at a +5 V gate bias. In the relevant spectral range $\approx 1$ eV above $\Phi_e$ the IPE spectra for sample set 2 are practically identical to those observed in sample set 1 indicating good reproducibility of the used MOCVD process. However, as the sample set 1 was grown at a higher base pressure suggesting a small air leak, presence of oxygen and nitrogen during WS$_2$ synthesis is expected. Nevertheless, the observed reproducibility of IPE spectra within the 1 eV region above the spectral threshold indicates that the presence of oxygen and nitrogen is not significantly impairing the band structure of the WS$_2$/SiO$_2$ interface for the H$_2$S pressure used (see Ref. [10] for details). Thus, the applied MOCVD process appears to be sufficiently “tolerant” to a limited presence of oxygen and nitrogen, with insignificant variations in the band structures below the valence band top edge. We suggest that, in the H$_2$S reactive ambient, W oxides and nitrides are converted into the desirable WS$_2$ compound resulting in a kind of ‘self-cleaning’ process during layer synthesis. For example, thermal sulfurization in H$_2$S at 900 °C is shown to convert MoO$_x$ and WO$_x$ layers deposited from nitrogen-containing precursors into stoichiometric MoS$_2$ and WS$_2$, respectively [28].

Additionally, the origin of the ‘diverging’ spectral curves at $h\nu > 4.5$ eV for the sample from batch 2 can be found in the aluminium contact, as the spectral curves are measured on the same chip with the thickness of top Al contact (100 or 15 nm) being the only physical difference. The optical excitation of electrons at the top
Al/WS₂ interface in the sample with thin semitransparent Al electrode represents the most probable source of the additional IPE current observed in this sample at $h\nu > 4.5$ eV as opposed to the case of non-transparent 100 nm thick electrode. This hypothesis is supported by the fact that, if plotted in the Fowler coordinates $(Y^{1/2} - h\nu)$, the ‘extra’ yield has spectral threshold of 4.2–4.3 eV which is close to the work function of metallic Al [29]. If not coincidental, this observation suggests that electron IPE from Al into SiO₂ across 2D material WS₂ becomes possible when the energy of electrons becomes sufficient to be ballistically transported across the Van der Waals (vacuum) gap. For comparison, electron IPE from Al evaporated directly on SiO₂ has a spectral threshold (at zero field) of 3.2–3.3 eV [30].

The good reproducibility of the MOCVD process is further supported by the results shown in the Schottky plot (figure 2), where the extracted field dependent thresholds of set 2 are presented for comparison with linear extrapolation yielding the same zero field barrier of 3.7 ± 0.1 eV. Therefore, we may conclude that the VB top edge of the MOCVD-grown 1 ML WS₂ is reproducibly found at 3.7 eV below the CB bottom edge of SiO₂ irrespectively of the used contacting scheme. The impact of different metals (Al, Cu, Au) used as a contact pad on the WS₂/SiO₂ interface band alignment has been previously explored [12]. These results show marginal sensitivity of the VB top position in WS₂ to the contact metal indicating that electron IPE predominantly occurs from the un-metallized WS₂ area surrounding the contact pad. Furthermore, the results of this present work
reveal that even in the case of electron IPE from the WS$_2$ covered by a continuous layer of semi-transparent Al (15 nm thick) the spectral threshold remains unchanged (cf figure 3). This suggests that the used gentle thermoresistive evaporation of metal contacts leaves electron states in WS$_2$ intact. Furthermore, the field dependence of thresholds in figure 2 does not change significantly between different samples indicating similar electrostatics of the WS$_2$/SiO$_2$ interface. These consistent results regarding band alignment at the WS$_2$/SiO$_2$ interface can now be used as a benchmark to evaluate the possible transfer-induced changes to the band alignment or the effects of the sample storage.

First we addressed the samples prepared using the dry transfer method as this minimizes the WS$_2$/SiO$_2$ interface exposure to water which was seen as the primary suspect responsible for the formation of interface dipoles and charges [15]. Figure 4(a) shows the typical IPE spectra of dry transferred MOCVD-grown 1ML WS$_2$ which appears to be surprisingly similar to those observed for the directly-grown 1 ML WS$_2$ (cf figure 1) suggesting that the transfer process has no significant impact on the IPE. Both the transferred and directly grown samples have similar maximum quantum yield values indicating that the photoexcited volume of WS$_2$ is barely affected by the transfer. The inferred field dependent thresholds are compiled in the Schottky plot (figure 5) together with the thresholds obtained from a different contact pad (original spectra not shown). Linear extrapolation to zero electric field yields the barrier height of 3.7 ± 0.1 eV, i.e. exactly the same as the value found for the WS$_2$ directly grown on SiO$_2$. Furthermore, the field dependence of the IPE thresholds remains essentially constant.

Figure 4. Powell plot of the IPE quantum yield spectra of MOCVD-grown 1 ML WS$_2$/SiO$_2$ samples with a non-transparent Al contact pad for (a) WS$_2$ transferred using the dry transfer process for gate bias voltages ranging from $-3$ V to $-15$ V. (b) WS$_2$ transferred using the wet transfer process for gate bias voltages ranging from $-1$ V to $-6$ V. Red lines illustrate the linear fit used to obtain the field dependent IPE threshold. As a comparison in both figures an IPE spectral curve of as grown material is plotted at the highest measured applied gate bias.

Figure 5. The Schottky plot of the IPE electron threshold values for as grown and transferred (dry or wet) 1 ML WS$_2$. Dashed lines indicate the linear fit used to obtain the zero field threshold value.
unchanged indicating an insignificant variation of the interface electrostatics, i.e. the absence of additional electric fields. These results indicate the stability of the band alignment after 2D layer transfer through the dry transfer process.

Next, it is still worth examining the widely adopted wet transfer method. Figure 4(b) shows IPE spectra for 1 ML WS$_2$ after wet transfer onto SiO$_2$ which exhibit behaviour similar to that observed for the already discussed directly grown layers. A somewhat reduced maximum quantum yield does not imply a large change in photoexcited WS$_2$ volume and might be related to the slight barrier transparency change. Obviously, there are no effects observed in the case of sulfurization-grown MoS$_2$ layers transferred onto SiO$_2$ [15]. The inferred field dependent thresholds are compiled in the Schottky plot (figure 5) with linear extrapolation resulting in the same value of the zero field threshold of 3.7 ± 0.1 eV as in the directly-grown WS$_2$/SiO$_2$ entities. As compared to the dry transferred WS$_2$ layers there is a small change in threshold field dependence slope which, however, falls within the range of variations observed in the case of directly grown films (figure 2). Furthermore, this field dependence change is marginal when compared to the field dependent IPE threshold changes observed for the transferred 2 ML MoS$_2$ using the same wet transfer process [15]. Thus, the MOCVD-grown 1ML WS$_2$ appears to be by far more stable (than MoS$_2$) in terms of the electronic structure, the band alignment at the interface with underlying SiO$_2$, and the electrostatics of this interface after been subjected to the critically important technological step of the layer transfer (both wet and dry). These results combined with the improved characteristics of electron transport make WS$_2$ a more attractive candidate for the device implementation on a wafer scale than MoS$_2$.

Finally, based on the revealed reproducibility of the MOCVD WS$_2$ growth process, we addressed the resistance of these MLs against oxidation in air because the previous study conducted on the sulfurization-grown WS$_2$ films revealed their inferior stability as compared to MoS$_2$ films synthesized in the same way [20, 25]. In general, the thin 2D TMD layers are well known to suffer from oxidation in air leading to significant degradation of their electronic properties [31–33]. In particular, CVD-grown WS$_2$ films have been found to show signs of oxidation within mere days/months [34] or a year [31] of storage. Therefore, we repeated the IPE spectral measurements on samples stored in ambient conditions which could reveal signs of film degradation. The WS$_2$ films investigated here were stored in room ambient, i.e. without any drying desiccant, which has been found to worsen the effect of oxidation [31]. Figure 6 shows a comparison of the IPE spectra of both sets of MOCVD 1ML WS$_2$ directly synthesized on top of SiO$_2$: the initial measurements were conducted right after the growth and metallization processing (<1 day) while the final measurements were performed 9–14 months after film synthesis. Would any significant oxidation of the film occur the IPE quantum yield would be reduced and accompanied by a shift of the IPE energy onset towards higher photon energies as observed for 2 ML WS$_2$ grown through sulfurization of metallic tungsten [20, 25]. However, no such shift is observed (figure 6), both the initial and the ‘aged’ sample spectra are essentially identical within ≈1eV wide spectral range above photoemission threshold. Furthermore, the maximum quantum yield values remain comparable in both cases indicating an insignificant change in photoexcited volume which would indicate ‘disappearance’ of WS$_2$ due to formation of the oxygen-containing bonds. These results suggest that the studied MOCVD-grown WS$_2$
films are sufficiently resistant to air exposure in order to allow one to process them under conventional clean-room conditions.

The available results on oxidation of WS\textsubscript{2} and MoS\textsubscript{2} under ambient conditions indicate that the initial oxygen reactions occur at the edges of 2D islands and grain boundaries suggesting crucial role of defects in the oxidation chemistry. A similar conclusion can be made on the basis of oxide nucleation analysis during atomic layer deposition of oxide overlayers on top of 2D TMD semiconductors. In this spirit, the possible explanation for the increased resistance of this MOCVD grown material to air exposure compared to the sulfidization grown WS\textsubscript{2} could be the difference in the structure of point defects. In the case of similarly grown MoS\textsubscript{2} layers, i.e. metal sulfidization in H\textsubscript{2}S versus MOCVD from Mo(CO)\textsubscript{5} and H\textsubscript{2}S at the same temperatures as used in the present work, electron spin resonance (ESR) measurements revealed structurally different defects: Sulfur vacancies are the most abundant defects in MoS\textsubscript{2} grown through sulfidization of metallic Mo\textsuperscript{35}; such defects are known to accelerate oxidation\textsuperscript{36}. By contrast, ESR measurements on MoS\textsubscript{2} layers grown by similar MOCVD process as used here for the WS\textsubscript{2} samples reveal Mo vacancies as the dominant defect\textsuperscript{18}. As both the investigated MoS\textsubscript{2} and WS\textsubscript{2} were grown according to the same procedure in the same reactors one may expect the defects to be the same in both Mo and W disulfides. This suggestion is supported by ESR observation of signal closely resembling LM1 signal in MoS\textsubscript{2} (see Ref.\textsuperscript{7}) in the similarly sulfidization-grown 2ML thick WS\textsubscript{2}\textsuperscript{37}. This difference in the nature of the growth-induced defects will obviously affect chemical reactivity of the surfaces and might explain the increased stability against oxidation of MOCVD grown WS\textsubscript{2}.

4. Conclusion

In conclusion, using internal photoemission spectroscopy we demonstrated that the MOCVD-grown 1 ML WS\textsubscript{2} films are sufficiently robust to withstand two most important technological factors critical for their implementation in the wafer-scale semiconductor processing. First, in sharp contrast to MoS\textsubscript{2}, transfer (both ‘dry’ and ‘wet’) has no significant impact the band alignment at the 1 ML WS\textsubscript{2}/SiO\textsubscript{2} interface with no indications of interface charges/dipoles introduced in the barrier region. Second, the MOCVD-grown 1 ML WS\textsubscript{2} films appear to be remarkably resistant against oxidation in air promising great simplification in their post-synthesis handling. Summarizing these findings, we conclude that MOCVD-grown WS\textsubscript{2} represents the ‘processing-friendly’ material with good potential for practical implementation in the IC technology.

Acknowledgments

This work was financially supported by the Flanders Innovation & Entrepreneurship [2Dfun (2D functional MX\textsubscript{2}/graphene heterostructures), an ERA-NET project in the framework of the EU Graphene Flagship] and by a KU Leuven Internal Fund (project C14/16/061).

Data statement availability

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

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