Controlled Layer Thinning and p-Type Doping of WSe\textsubscript{2} by Vapor XeF\textsubscript{2}

Rui Zhang,* Daniel Drysdale, Vasileios Koutsos, and Rebecca Cheung*

This report presents a simple and efficient method of layer thinning and p-type doping of WSe\textsubscript{2} with vapor XeF\textsubscript{2}. With this approach, the surface roughness of thinned WSe\textsubscript{2} can be controlled to below 0.7 nm at an etched depth of 100 nm. By selecting appropriate vapor XeF\textsubscript{2} exposure times, 23-layer and 109-layer WSe\textsubscript{2} can be thinned down to monolayer and bilayer, respectively. In addition, the etching rate of WSe\textsubscript{2} exhibits a significant dependence on vapor XeF\textsubscript{2} exposure pressure and thus can be tuned easily for thinning or patterning applications. From Raman, photoluminescence, X-ray photoelectron spectroscopy (XPS), and electrical characterization, a p-doping effect of WSe\textsubscript{2} induced by vapor XeF\textsubscript{2} treatment is evident. Based on the surface composition analysis with XPS, the causes of the p-doping effect can be attributed to the presence of substoichiometric WO\textsubscript{x} (x < 3) overlayer, trapped reaction product of WF\textsubscript{6} and nonstoichiometric WSe\textsubscript{x} (x > 2). Furthermore, the p-doping level can be controlled by varying XeF\textsubscript{2} exposure time. The thinning and p-doping of WSe\textsubscript{2} with vapor XeF\textsubscript{2} have the advantages of easy scale-up, high etching selectivity, excellent controllability, and compatibility with conventional complementary metal-oxide-semiconductor fabrication processes, which is promising for applications of building WSe\textsubscript{2} devices with versatile functionalities.

1. Introduction

As the gate length of metal-oxide-semiconductor field-effect transistors (MOSFETs) rapidly approaches sub-10 nm scale, the short-channel effect is becoming a key factor for limiting the miniaturization of conventional Si-based electronics.[1] The layered transition metal dichalcogenides (TMDs), such as MoS\textsubscript{2} and WSe\textsubscript{2}, with promising carrier transport properties, high on/off ratio, and most importantly, scalable thickness down to monolayer, have triggered tremendous interest in the application of future scaled devices.[2] Also, the excellent mechanical properties of TMDs with breaking strain ≥ 6% suggest their great application prospects in flexible semiconducting electronics.[3] Furthermore, by utilizing the dependence of TMD-based FETs’ electrical performance on different operating conditions, TMD-based FETs have been demonstrated widely to be used for sensing applications, such as strain/pressure/motion sensor,[4] gas sensor,[5] and biosensor.[6] Particularly, the 2D WSe\textsubscript{2}, reported to own high optical quality, including strong photoluminescence intensity,[7] along with high electroluminescence and photo-conversion efficiency,[8] is a promising 2D material for applications in optoelectronic devices.

Since some reports have shown that TMDs exhibit thickness dependent electrical,[9] optical,[10] thermal,[11] mechanical,[12] and piezoelectrical properties,[13] the ability to produce different numbers of TMD layers controllably is highly desirable for various applications. So far, several methods have been developed to prepare 2D TMDs, which can be classified into top-down and bottom-up approaches generally. The top-down method mainly consists of mechanical and liquid-based exfoliation from bulk crystals,[14,15] while the bottom-up approach is implemented by chemical vapor deposition.[16] In principle, however, none of these methods can achieve a good control over the number of layers, which limits the application of 2D TMDs. Moreover, a simple, efficient, and selective patterning approach (complete removal) of TMDs for defining complex structures is desirable for TMD-based very-large-scale integration (VLSI) fabrication. To date, several methods of TMD thinning (removal of specified number of layers) and patterning have been reported to tune the number of TMD layers produced. High energy beams, including laser beam and focused ion beam (FIB), have been demonstrated for thinning/patterning of MoS\textsubscript{2}.[17] However, the low efficiency and limited lateral resolution of this approach bring a huge challenge for large-scale processing. Although thermal annealing assisted thinning can be scaled-up,[18] the extremely slow thinning rate and the requirement of high temperature (> 300 °C) to initiate the thinning make the approach incompatible with standard semiconductor fabrication process. Meanwhile, several kinds of plasma (e.g., Ar, O\textsubscript{2}, CHF\textsubscript{3}, CF\textsubscript{4}, and SF\textsubscript{6})[19] have been reported to be advantageous at efficient thinning/patterning and good compatibility.
with conventional complementary metal-oxide-semiconductor (CMOS) technologies. However, the physical crystal damage caused by the ion bombardment inevitably could enhance the possibility of carriers surface roughness scattering and hence degrade the electrical performance of the thinned TMDs. Furthermore, plasma etching with currently reported recipes also suffers from low selectivity to some of the commonly used dielectrics and metals (e.g., SiO₂, Al₂O₃, HfO₂, and Al) in TMD-based devices. Although Huang et al. [19] recently reported a novel method of MoS₂ etching with vapor XeF₂ which can overcome the disadvantages of the approaches above, the etching mechanism of MoS₂ is still not fully understood.

Moreover, in order to integrate the TMDs with CMOS logic circuits in future VLSI, both n- and p-type TMD-based FETs need to be fabricated. Therefore, the control of the carrier type and concentration achieved through doping is essential for applications of TMDs in CMOS technologies. Also, the type and height of Schottky barrier formed at the contact/TMDs interface, which determine the contact resistivity, can be tuned by doping TMDs [20]. Although a lot of research have been conducted on the doping of MoS₂ [21], the study of methods for doping WSe₂, especially with good air-stability, scalability, and controllability, is still quite limited.

In this work, we demonstrate a controllable layer thinning and p-doping of WSe₂ with vapor XeF₂. The thickness and the surface roughness variation of WSe₂ as a function of vapor XeF₂ exposure time and exposure pressure have been characterized using atomic force microscopy (AFM). The effects of vapor XeF₂ thinning on the surface modification, luminescence properties, and Fermi levels of WSe₂ have been investigated with a combination of Raman, photoluminescence (PL), and X-ray photoelectron spectroscopy (XPS). Additionally, the evolution of electrical properties of WSe₂ induced by vapor XeF₂ treatment, including threshold voltage, mobility, and doping concentration, has been studied systematically through the electrical characterization of WSe₂-based FETs. By simply adjusting the XeF₂ exposure time, the etched depth and p-doping level of WSe₂ can be controlled easily. The thinning and p-doping of WSe₂ with vapor XeF₂ not only benefits from air stability, easy scale-up, high selectivity, but also the compatibility with conventional CMOS fabrication technologies. The simplicity and applicability of the approach will pave the way for practical applications of WSe₂ in the future.

2. Results and Discussion

2.1. Vapor XeF₂ Thinning of WSe₂

During our experiments, 2D WSe₂ have been exfoliated mechanically from bulk WSe₂ crystals (supplied by 2D semiconductors) and transferred onto thermally grown 300 nm SiO₂ on highly p-doped Si substrates by the scotch tape method [14a]. Afterward, the samples have been immersed in acetone and rinsed with isopropyl alcohol and deionized water to remove tape residues. Then, the samples have been treated with XeF₂ (25 sccm)/N₂ (100 sccm) gas in a XeF₂ etcher at room temperature. In Figure 1a,b, we compare optical images of a WSe₂ flake before and after XeF₂ treatment under 1 Torr for 60 s. The color contrast of the WSe₂ flake, which represents the information of WSe₂ thickness [22], can be seen to change upon vapor XeF₂ treatment. The thicknesses of the WSe₂ flake before and after XeF₂ treatment (represented by $d'$ and $d$, respectively) have been determined through AFM analysis (insets of Figure 1a,b) and

Figure 1. Optical images of WSe₂ before a) and after XeF₂ treatment b) under 1 Torr for 60 s. Insets are corresponding AFM images of the WSe₂ flakes. Scale bars of insets are 10 µm. The etched depth ($h$, black curves) and the root-mean-square roughness ($R_{RMS}$, blue curves) of WSe₂ versus etching times $t$ under 1 Torr c) and etching pressure $P$ within 60 s d). Symbols are measured results, and the solid lines serve as a guide to the eye.
annotated in the corresponding optical images. As can be seen, after XeF₂ exposure for 60 s, the thickness of the WSe₂ flake has been reduced by 1.5 nm, which is equivalent to a bilayer of WSe₂. Figure 1c,d summarizes the etched depth \( h = d' - d \) and root-mean-square roughness \( R_{\text{RMS}} \) variation as a function of increasing etching time \( t \) and etching pressure \( P \). The AFM topography images of WSe₂ before and after vapor XeF₂ thinning can be found in Figure S1 (Supporting Information). As shown by the black curve of Figure 1c, before 90 s, not much thickness variation is observed, while the etching rate \( h/t \) starts to increase significantly after 90 s. In contrast to the change of etching rate, the \( R_{\text{RMS}} \) value (blue curve in Figure 1c) increases quickly before 90 s and is seen to flatten gradually after 90 s. The increase in roughness would result in an increased surface area and defect sites hence supplying more reaction sites, which can contribute to an accelerated etching rate as etching time increases. Figure 1d shows the effect of the exposure pressure on the etched depth and surface morphology during an etching time of 60 s. Both the etching rate and surface roughness show a rising trend when the exposure pressure increases, possibly caused by an increased amount of available etchant (F radicals) with increasing pressure. Notably, the etching rate is observed to increase by one order of magnitude when the exposure pressure is doubled. Therefore, by varying the exposure pressure, the controllability and efficiency of WSe₂ etching can be tuned for different applications, i.e., slow speed etching for thinning and fast speed etching for patterning. Moreover, distinct from thinning with thermal annealing methods, vapor XeF₂ thinning is more efficient than FIB, laser, and thermal annealing assisted thinning methods, and hence easier to scale-up for wafer-level processing. Meanwhile, a highly selective etching of WSe₂ over most dielectrics and metals (e.g., SiO₂, Si₃N₄, Al₂O₃, HfO₂, and Al) can be achieved by using vapor XeF₂.

Figure 2 shows an example of layer thinning of 23-layer and 109-layer WSe₂ into a monolayer (Figure 2a–c) and a bilayer (Figure 2d–f), respectively, by vapor XeF₂ with appropriate exposure times based on the results in Figure 1c. Note that the number of layers of WSe₂ films annotated in Figure 2b,e is confirmed further by Raman measurements, which will be explained later. The thicknesses of XeF₂ thinned WSe₂ (1.3 nm for monolayer and 2.1 nm for bilayer), as shown in Figure 2c,f, have been found to be larger than those of pristine monolayer (≈0.8 nm) and bilayer (≈1.5 nm) WSe₂. Moreover, distinct from thinning with thermal annealing methods, no etching pits and excellent uniformity in thickness have been observed on vapor XeF₂ thinned WSe₂ (the dots seen in Figure 2b,e originate from tape residues beneath the WSe₂ films introduced during the sample preparation process).

Raman scattering has been conducted to characterize the influence of vapor XeF₂ treatment on the crystal quality of the thinned WSe₂ and determine the number of WSe₂ layers. Figure 3a compares the Raman spectra of WSe₂ before (5- and 6-layer) and after vapor XeF₂ exposure (3- and 4-layer) under 1 Torr for 60 s. The Raman peaks located at around 249 and 258 cm⁻¹ are attributed to the in-plane vibrational mode \( (E_{12g}) \) and out-of-plane vibrational mode \( (A_{1g}) \), respectively. Another Raman peak at 308 cm⁻¹ is assigned to the \( B_{12g} \) mode arising from the presence of interlayer interaction, which can be used to distinguish monolayer and multilayer WSe₂. After XeF₂ treatment, blueshifts of the \( E_{12g} \) mode are observed, and the
Raman peak intensities of $E_{2g}^1$ and $A_{1g}$ modes show an increase compared to the spectra of pristine WSe$_2$, due to the reduction in number of layers, which have also been observed in previous reports. Figure 3b shows the Raman spectra of pristine WSe$_2$ (black curves) and vapor XeF$_2$ thinned WSe$_2$ (red curves) with the same number of layers. Note that the first two rows (from the top) Raman spectra of thinned WSe$_2$ in Figure 3b are obtained from the samples shown in Figure 2b, e, respectively. The thinned WSe$_2$ in Figure 2b is determined to be monolayer because of the absence of the $B_{2g}^1$ mode, as shown in the first row spectrum in Figure 3b. The appearance of the $B_{2g}^1$ mode in the second row Raman spectrum of thinned WSe$_2$ in Figure 3b indicates the presence of multilayer WSe$_2$ in Figure 2e. In addition, the thinned WSe$_2$ in Figure 2e is thicker than the thinned monolayer WSe$_2$ (Figure 2b) by 0.8 nm, which is equal to the interlayer distance of WSe$_2$ so the WSe$_2$ film in Figure 2e can be determined to be a bilayer WSe$_2$. In comparison with pristine WSe$_2$, all of the $E_{2g}^1$ modes of XeF$_2$ thinned WSe$_2$ in Figure 3b show a similar degree of blueshift ($\approx 1.1$ cm$^{-1}$), regardless of the number of WSe$_2$ layers, which is likely to be caused by a decrease in electron concentration (p-doping) after vapor XeF$_2$ treatment. Moreover, after XeF$_2$ exposure, no significant change but a slight broadening in the full width at half maximum (FWHM) of the $E_{2g}^1$ peaks (from 3.7 to 4.5 cm$^{-1}$ for monolayer, 3.8 to 4.6 cm$^{-1}$ for bilayer, 3.8 to 5.3 cm$^{-1}$ for 8-layer) together with the reduction of Raman peak intensities have been observed, which implies that the vapor XeF$_2$ thinning does not compromise the crystalline quality of WSe$_2$ at the macroscopic level but introduces some minor defects and/or crystal damage.

Photoluminescence (PL) spectroscopy has been performed on pristine and thinned monolayer WSe$_2$ in order to characterize the band-to-band emission arising from excitonic transitions. Figure 3c compares the normalized PL spectra of pristine monolayer WSe$_2$ and thinned monolayer WSe$_2$ achieved by XeF$_2$ exposure for 1 and 2 min. As shown in the first row spectrum, the pristine monolayer WSe$_2$ presents a prominent PL peak at 1.65 eV (the $A$ excitonic emission), corresponding to the direct band gap transition (K to K point of the Brillouin zone). The $A$ exciton PL peak can be deconvoluted further into neutral exciton emission at 1.65 eV ($A^0$) and trion emission at 1.63 eV ($A^*$). It can be seen that the neutral excitons ($A^0$) dominate the PL emission of pristine WSe$_2$. In contrast to pristine WSe$_2$, the thinned monolayer WSe$_2$ after 1 min (second row spectrum) and 2 min (third row spectrum) XeF$_2$ treatment exhibit a 7- and 21-fold decrease in the A peak intensities and broadening of the A emission peaks from 78 to 70 meV and 80 meV in FWHM, respectively. In addition, redshifts of the A emission peaks by 21 meV (1 min XeF$_2$ exposure) and 33 meV (2 min XeF$_2$ exposure) are observed in the thinned WSe$_2$. Moreover, the intensity ratios of trion ($A^*$) to neutral exciton ($A^0$) emissions are found to increase with extending XeF$_2$ thinning time, from 0.4 (0 min) to 0.8 (1 min) and 1.4 (2 min), which indicates the existence of enhanced concentrations of excess carriers, thus doping effects, caused by XeF$_2$ treatment, as suggested from Raman measurements. As trions ($A^*$) possess the features of lower PL efficiencies and lower PL emission energy compared to neutral excitons, the presence of the higher ratio of trions in XeF$_2$ thinned WSe$_2$ can give rise to the observed weakening, broadening, and redshifts of the A emission peaks. Note that the defects produced during vapor XeF$_2$ exposure could also contribute to the reduction of the PL peak intensity of the thinned WSe$_2$.

To investigate the evolution of the surface composition of WSe$_2$ before and after vapor XeF$_2$ treatment, XPS measurements have been carried out. Note that most of XPS experiments have been conducted on multilayer WSe$_2$ unless otherwise specified. The survey spectrum (Figure S2a, Supporting Information) of pristine WSe$_2$ consists of C, Si, O, W, and Se related peaks. An additional peak associated with F appears after vapor XeF$_2$ exposure. Figure 4a,b shows the high-resolution XPS spectra of W 4f and Se 3d core levels of WSe$_2$...
before and after XeF₂ treatment under 1 Torr for 2 and 5 min, respectively. Before XeF₂ exposure, the doublet observed at 32.6 and 34.8 eV (first row spectrum in Figure 4a) corresponds to W ⁴f⁷/₂ and W ⁴f⁵/₂ lines of W⁺⁺⁺⁺ contributed from pristine WSe₂ and the peak at 37.9 eV can be assigned to the W ⁵p₃/₂ core level of WSe₂.[35] The Se ³d core level spectrum of pristine WSe₂ (in the chemical state of Se⁻⁻⁻⁻) exhibits a ³d⁵/₂ and ³d³/₂ doublet at 54.9 and 55.7 eV, as shown in the first row spectrum in Figure 4b. After WSe₂ has been treated with vapor XeF₂ for 2 min, a weaker doublet peak appears at 35.5 and 37.7 eV (second row spectrum in Figure 4a) which can be associated with the W ⁵p₃/₂ core level of WSe₂.[36] The W ⁴f core level of W⁺⁺⁺⁺ shifts toward lower binding energy with 32.1 (⁴f⁷/₂) and 34.2 eV (⁴f⁵/₂). When the exposure time reaches 5 min as shown in the third row spectrum in Figure 4a, the W ⁴f core level of W⁺⁺⁺⁺ downshifts further by ~0.8 eV compared with the spectrum of pristine WSe₂. Meanwhile, similar shifts in binding energy are also found in Se ³d core level spectra of WSe₂ treated by vapor XeF₂ for the same time (Figure 4b). This observation indicates a Fermi level shift toward the valence band of the WSe₂ film, therefore confirming the presence of a p-doping effect caused by XeF₂ exposure, which is consistent with Raman and PL measurements. However, no additional doublet representing any other chemical state of Se is observed in the Se ³d core level spectra after XeF₂ exposure.

To determine the origin of chemical states of W⁺⁺⁺⁺ and W⁺⁺⁺⁺⁺, the high-resolution XPS spectra of F １s and O １s core levels of the samples have been acquired. After vapor XeF₂ treatment, a feature at 687.3 eV associated with W-F bond appears in Figure S2d (Supporting Information), which can be attributed to WF₆ physically trapped in the lattice of thinned WSe₂. Similar results have also been reported in tungsten etching with fluorine-based etchants.[37] Although another etching product
in the form of WF$_6$ has been observed in some of the previous reports on tungsten etching, represented by an XPS peak of F 1s core level at 684.0–685.0 eV.$^{[37c,38]}$ No sign of WF$_6$ is seen from our XeF$_2$ thinned WSe$_2$. The possible reason is that our etching process has operated in the F sufficient regime (see Section S3 in the Supporting Information for details), so the intermediate product WF$_4$ has reacted further with two fluorine atoms to form WF$_6$, and therefore the etching products are expected to be fully fluorinated species, i.e., WF$_6$ and SeF$_6$. Because of the greater volatility of SeF$_6$ (−46.6 °C in boiling point) than WF$_6$ (18 °C in boiling point), there is less chance for SeF$_6$ to be trapped inside of the WSe$_2$ lattice, which explains the observed absence of additional chemical states of Se. In addition, some W−O bonds are suspected to form on top of the thinned WSe$_2$ after the samples have been exposed to air, due to the presence of a weak O 1s feature observed at around 531 eV (buried by the strong O 1s peak at 533 eV contributed from SiO$_2$ substrate because of the smaller lateral dimension of WSe$_2$ than the X-ray spot) in the O 1s core level spectra of XeF$_2$ treated WSe$_2$ (Figure S2e Supporting Information), which can be assigned to WO$_x$ (x ≤ 3).$^{[29a,36c,37b]}$ Also, the fact that the monolayer and bilayer WSe$_2$ achieved by vapor XeF$_2$ thinning are detected to be thicker than pristine WSe$_2$ as presented in Figure 2c,f, together with previously reported observation of the presence of WO$_x$ from fluorine etched tungsten with no/low ion bombardment,$^{[39]}$ supports the existence of WO$_x$ overlayer on XeF$_2$ thinned WSe$_2$. Based on thermodynamic analysis (see Section S4 in the Supporting Information for details), the WO$_x$ could be the reaction product of trapped WF$_6$ and water in the air, while the possibility of the existence of WOF$_x$ is possibly due to the remaining nonstoichiometric WSe$_x$ before KOH solution immersion. At the same time, an upshift of W 4f$_{7/2}$ core level in binding energy has been observed, which indicates the formation of nonstoichiometric WSe$_2$ with larger lateral dimension (in millimeter scale) than the X-ray spot to eliminate the interference of the signals contributed from the SiO$_2$/Si substrates. As shown in Figure 4c-e, the F 1s, O 1s, and W 4f core level spectra of pristine WSe$_2$, as well as XeF$_2$ treated WSe$_2$ before and after KOH solution immersion have been investigated. Before XeF$_2$ treatment, no peak in F 1s spectrum (Figure 4c), one O 1s peak located at 532.8 eV attributed to adsorbed water on WSe$_2$ (Figure 4d)$^{[42]}$ and one doublet peak at 32.6 and 34.8 eV contributed from W$_4^+$ in WSe$_2$ (Figure 4e) have been observed. After vapor XeF$_2$ treatment of bulk WSe$_2$ for 5 min, an F 1s peak and an additional O 1s peak appear at 687.4 eV (Figure 4c) and 531.3 eV (Figure 4d), respectively, accompanied by the emergence of a weaker doublet peak corresponding to W$_6^+$ and W$_5^+$ chemical states in W 4f spectrum (Figure 4e), which indicates the existence of WF$_6$ and WO$_x$ after XeF$_2$ treatment and air exposure. Meanwhile, the W$_6^+$ core level presents a downshift in binding energy (Figure 4e), similar to the observation in Figure 4a, implying the p-doping of WSe$_2$. Subsequently, the XeF$_2$ treated bulk WSe$_2$ has been immersed in 1 mol L$^{-1}$ KOH solution for around 15 s, which is able to remove any existing WF$_6$ and WO$_x$. Then, the previously observed F 1s peak, the additional O 1s peak, and the weaker doublet peak of W$_6^+$ and W$_5^+$ disappear simultaneously, as shown in the third row spectra in Figure 4c-e, suggesting the removal of WF$_6$ and WO$_x$ by the KOH solution immersion. At the same time, an upshift of W$_6^+$ core level in binding energy has been observed, which indicates a degradation of the p-doping effect in WSe$_2$ after WF$_6$ and WO$_x$ are removed. This observation implies that WF$_6$ and WO$_x$ contribute to the p-doping effect. However, the W$_6^+$ core level of WSe$_2$ after KOH solution treatment does not shift back to the original binding energy of WSe$_2$ (first row spectrum in Figure 4e), the reason of which will be explained later.

In order to quantify the surface composition of WSe$_2$, the area of peaks attributed to different components (W$_6^+$ and Se$^-$ from WSe$_2$; W$_4^+$ and W$_5^+$ from WF$_6$ and WO$_x$) have been computed after subtraction of background by the Shirley method and normalization with empirical relative sensitivity factors ($2.75$ for W and 0.67 for Se).$^{[43]}$ The overall atomic ratio of Se to W in all chemical states is seen to reduce as etching time increases (not shown here), indicating the presence of a W-rich surface after XeF$_2$ treatment. Also, the ratio of (W$_6^+$ + W$_5^+$) to W$_4^+$ is seen to increase (shown in Figure 4f) as the exposure time is extended. Notably, despite the different etching times, the XeF$_2$ thinned monolayer and bilayer WSe$_2$ are thicker by the same amount (0.5–0.6 nm) than pristine WSe$_2$ with the same number of layers, as shown in Figure 2c,f. This observation indicates a fixed thickness of WO$_x$ overlayer regardless of etching time, due to the previously reported self-limiting growth mechanism of WO$_x$. Therefore, the observed atomic ratio change in (W$_6^+$ + W$_5^+$)/W$_4^+$ is likely to be the result of an increased amount of trapped WF$_6$ produced during the vapor XeF$_2$ exposure, which could be within several nanometers from the surface of XeF$_2$ thinned WSe$_2$. Additionally, the atomic ratio of Se$^-$ to W$_4^+$ goes beyond the standard stoichiometric ratio of WSe$_2$ (2:1) as the etching time increases, suggesting that the availability of W$_4^+$ bonded with Se$^-$ to form stoichiometric WSe$_2$ becomes less and less during the XeF$_2$ treatment, thus rendering the presence of nonstoichiometric WSe$_2$, i.e., WSe$_x$ with $x > 2$. In the case of the uniform layer thinning with surface roughness below 0.7 nm here, the WSe$_x$ is estimated to be 1–2 layer thick, mainly formed at the reaction interface of WSe$_4$ with vapor XeF$_2$. As mentioned before, the fact that removing WF$_6$ and WO$_x$ by KOH solution immersion does not shift the W$_6^+$ core level back to the binding energy of pristine WSe$_2$, as shown in third and first row spectra of Figure 4c, is possibly due to the remaining nonstoichiometric WSe$_x$ contributing to the p-doping effect.

To summarize the observed p-doping effect on WSe$_2$ induced by vapor XeF$_2$ treatment, three factors could play important roles as depicted in the schematic of Figure 5: (1) the large work function of WO$_x$ (≈6.7 eV)$^{[44]}$ enables electron transfer from the underlying thinned WSe$_2$ to the WO$_x$ overlayer, resulting in the electron carriers depletion in thinned WSe$_2$ (serving as hole-injection layer),$^{[29b]}$ (2) the presence of...
fluorine atoms within the WF$_6$ trapped in the lattice of thinned WSe$_2$, owing to a stronger electronegativity (3.9) than that of W (1.7) and Se (2.55),[45] attracts the excess electrons from WSe$_2$ making the thinned WSe$_2$ p-doped,[46] 3) the nonstoichiometric WSe$_{x}$ with W$^{4+}$ cation deficiency formed near the top surface of the XeF$_2$ treated WSe$_2$ could act as electron acceptor and lead to the increase in the hole density.[34a,47] It is noteworthy that the p-doping region, where electrons are depleted and holes are the major conductive carriers, can exist beyond the nonstoichiometric WSe$_x$ layers and F$^-$ resided layers through the surface charge transfer mechanism.[23b] Additionally, as shown in Figure 4g, the degree of binding energy downshift of W 4f$_{7/2}$ and Se 3d$_{5/2}$ core levels of WSe$_2$, extracted from high-resolution XPS spectra in Figure S2b,c (Supporting Information), increases as XeF$_2$ exposure time extends. This observation indicates the reduced energy difference between the Fermi level and the valence band of WSe$_2$ and hence increased p-doping level with longer XeF$_2$ treatment.

2.2. WSe$_2$ Field-Effect Transistor

To gain more insight into the doping effects introduced by vapor XeF$_2$ treatment, WSe$_2$ FETs have been fabricated and characterized electrically. For these devices, highly p-doped Si substrates serve as back gate electrodes with 300 nm SiO$_2$ as gate dielectrics, and E-beam evaporated Ti (30 nm)/Al (200 nm) metal stacks have been used as metal electrodes. The details of the device fabrication process can be found in the Experimental Section. Figure 6a,b displays the optical images and schematic illustrations of a WSe$_2$ FET before and after vapor XeF$_2$ treatment. In order to eliminate the impact of contact resistance on the device performance, four-terminal measurements have been performed. The transfer characteristics ($I_D$–$V_{GS}$) of the WSe$_2$ FET at $V_{DS} = 1$ V before and after XeF$_2$ treatment under 1 Torr for different etching times, plotted in linear c) and logarithmic d) scales. e) The threshold voltage on the p-side $V_{th(p)}$ and hole conductivity $\sigma$ at $V_{GS} - V_{th(p)} = -20$ V versus etched depth. f) Hole mobility $\mu_h$ and volume concentration $n_h$ when $V_{GS} - V_{th(p)} = -20$ V as a function of etched depth. The top axes of (e) and (f) indicate the remaining thickness of the WSe$_2$ channel after XeF$_2$ etching.
been employed (see Section S6 in the Supporting Information for details), unless otherwise specified. Figure 6c,d shows the linear and logarithmic plots of transfer curves ($I_{DS}-V_{GS}$) of the WSe$_2$ FET obtained at a fixed drain bias ($V_{DS} = 1$ V) before and after vapor XeF$_2$ exposure under 1 Torr for various times. The transfer characteristic of the WSe$_2$ FET exhibits an evolution from n-type dominant ambipolar into p-type dominant ambipolar behavior as the etching time and etched depth increase. Left axis of Figure 6e presents the relationship of the threshold voltage at the hole transport regime (p-side) $V_{th(p)}$ with respect to etching time and etched depth, which has been extracted by extrapolating the slopes of the linear plots of $I_{DS}-V_{GS}$ curves (Figure 6c) in the linear hole transport regime down to 0 A. A shift of the $V_{th(p)}$ toward higher voltage with increasing etching time and etched depth has been observed in Figure 6e, which can be attributed to the vapor XeF$_2$ induced p-doping effect and the reduced thickness of the WSe$_2$ channel. Notably, when the WSe$_2$ channel is etched to $\approx 20$ nm after 3.5 min XeF$_2$ treatment, the FET possesses a threshold voltage $V_{th(p)}$ of $\approx 0$ V (Figure 6e), and holes start to become the dominant carriers at $V_{GS} = 0$ V (Figure 6d) in the meantime. By using the equation $\sigma = \frac{I_{DS}}{V_{DS} \times L/W}$, where $L$ and $W$ are the length and width of the channel, respectively, the sheet conductivity $\sigma$ of WSe$_2$ can be extracted, and the volume conductivity $\sigma_V$ can be determined by $\sigma_V = \frac{\sigma}{d}$ subsequently. After 4 min vapor XeF$_2$ treatment, the volume conductivity at a constant gate voltage bias ($V_{GS} - V_{th(p)} = -20$ V) increases by more than one order of magnitude (from $3.2 \times 10^4$ to $4.8 \times 10^7$ $\mu$S cm$^{-1}$), as presented by the right axis of Figure 6e. The field-effect hole mobility can be calculated from linear region of the $\sigma_V$-$V_{GS}$ curves on the p-side with the expression of $\mu_h = \frac{(d\sigma_V/dV_{GS}) \times (1/\sigma_{ox})}{(L/W)}$, where $\sigma_{ox} = 11.5 \times 10^{-9}$ F cm$^{-2}$ is the capacitance between the WSe$_2$ channel and back gate per unit area ($\varepsilon_{ox}/d_{ox}$; $\varepsilon_{ox} = 3.9$; $d_{ox} = 300$ nm). Furthermore, the hole volume concentration $n_h$ can be derived from the relation $\sigma_V = n_h q \mu_h$, where $q$ is the elementary charge. As shown in Figure 6f, the hole mobility (left axis) first shows a positive then negative dependence on the increasing etching time and etched depth, while the hole volume concentration (right axis) only exhibits a rising trend as etching time extends. When WSe$_2$ is relatively thick, the current $I_{DS}$ injected from metal contacts on the top surface of WSe$_2$ needs to flow down to lower layers (bypass some interlayer resistors) before flowing across the WSe$_2$ channel, because the gate electric field only modulates the free carrier in the bottom layers as a result of charge screening. Therefore, the improvement of hole mobility with increasing etching time in the first stage is caused mainly by the decreasing series interlayer resistors resulting from the reduction of WSe$_2$ thickness. As the thickness of the WSe$_2$ channel is thinned to $\approx 30$ nm, the hole mobility enters a downtrend, while further reduction in the thickness of the thinned WSe$_2$ results in a significant enhancement in hole concentration. This observation suggests that for a thinned WSe$_2$ with thickness $\leq 30$ nm, the impact of the XeF$_2$ induced p-doping is much larger, and the hole carriers in the XeF$_2$ treated WSe$_2$ film are likely to experience more ionized impurity (F$^-$) and charge–charge scattering. In addition, the thinner WSe$_2$ films are more susceptible to carrier scattering induced by increased surface roughness and interfacial Coulomb impurities (including chemical residues on top of WSe$_2$ film and surface dangling bonds on the SiO$_2$/Si substrate), which can also be responsible for the observed degraded hole mobility.

As the thickness variation of WSe$_2$ can affect the electrical performance of the FET including electrical mobility, threshold voltage, and contact resistance, in order to study the p-doping effect of vapor XeF$_2$ treatment without the contribution of reduced thickness of WSe$_2$, two FETs were first fabricated from pristine WSe$_2$ (Figure 7a) and XeF$_2$ thinned WSe$_2$ (Figure 7b) with a similar number of layers ($\approx 7$-layer) have been characterized and their transfer properties have been compared, as shown in Figure 7c. The pristine WSe$_2$ FET exhibits an n-type dominant ambipolar behavior with a $V_{th(p)}$ of $\approx 45$ V, as reported previously,[3c,50] while the XeF$_2$ thinned WSe$_2$ FET shows an increased value of $V_{th(p)}$ with 18 V, which confirms the p-doping effect introduced by vapor XeF$_2$ treatment. Further calculation (see Section S7 in the Supporting Information for details) supports the conclusion of a degenerate p-type doping with the vapor XeF$_2$. However, distinct from some degenerate doping methods that lead to a near-metallic transport behavior of WSe$_2$,[50,51] the XeF$_2$ treated WSe$_2$ still possesses an apparent semiconducting behavior, which is critical for the fabrication of logic circuits and optoelectronic devices. Figure 7d depicts the contact resistance $R_{contact}$ between Ti electrodes and WSe$_2$ of the two kinds of FETs with respect to gate voltage, which has been extracted from two-terminal and four-terminal measurements (details can be found in Section S6 in the Supporting Information). As the gate voltage increases, the contact resistance of pristine WSe$_2$ FET shows a descending tendency while the contact resistance of the FET made from XeF$_2$ thinned WSe$_2$ ramps up and with values of more than one order of magnitude smaller. For the pristine WSe$_2$ FET, the Fermi level of Ti with a low work function of $\approx 4.3$ eV lies between the conduction band minimum (CBM, $\approx -4.0$ eV) and valence band maximum (VBM, $\approx -5.2$ eV) of WSe$_2$ but closer to the CBM,[35d] thus forming an n-type Schottky barrier at the interface. As the gate voltage increases, the width of Schottky barrier decreases due to the upshift of Fermi level of WSe$_2$, leading to the reduction of contact resistance. In the case of XeF$_2$ thinned WSe$_2$ FET, where an additional layer of WO$_x$ exists on the thinned WSe$_2$, the contact between Ti and thinned WSe$_2$ includes Ti/WO$_x$ and WO$_x$/thinned WSe$_2$ dual interfaces. Although WO$_3$ is an n-type semiconductor with a comparatively large band gap of 2.6–2.9 eV,[52] the oxygen vacancies in the WO$_x$ lattice can narrow the band gap greatly.[16c] Therefore, the substoichiometric WO$_x$ can be considered as a metal with a low density of states at the Fermi level and should form an Ohmic contact with Ti at the Ti/WO$_x$ junction.[53] Owing to a high work function of WO$_x$ ($\approx 6.7$ eV),[44] the Fermi level of WO$_x$ should lie below the VBM of thinned WSe$_2$, and one would expect an Ohmic hole contact at the WO$_x$/thinned WSe$_2$ junction when the interface Fermi-level pinning of WO$_x$ contacts can be neglected.[53] However, in reality, the WO$_x$ work function can be lowered by oxygen vacancies in the substoichiometric WO$_x$ and carbon contamination (e.g., resist residues) introduced from the device fabrication process, which has been observed in previous reports.[29,54] Therefore, the notable Schottky contact behavior of Ti/WO$_x$/thinned WSe$_2$ interfaces seen in Figure 7d can be attributed to the degraded work function of WO$_x$ which makes the Fermi level of WO$_x$ lie
between the CBM and VBM of WSe$_2$. Nevertheless, the WO$_x$ contact still forms a lower Schottky barrier with WSe$_2$ than Ti contact does, which allows more effective tunneling of charge carriers through the contact barriers.

Further test on the electrical performance of the XeF$_2$ thinned WSe$_2$ FET demonstrates that the p-doping effect can be degraded to a certain extent after exposure to ambient air for 10 d, due to the adsorption of water and contamination in the air on top surface of WO$_x$, but still presents far better air stability than some doping methods with unstable surface adsorption, e.g., NO$_2$, K vapor, and polyethyleneimine doping. More details about the air stability of vapor XeF$_2$ doping can be found in Section S8 of the Supporting Information. In the future, further improvement of the air stability of XeF$_2$ doping can be achieved by the deposition of an additional passivation layer on top of the devices. The doping of WSe$_2$ with vapor XeF$_2$ approach can be used to fabricate complementary inverters and lateral p--n junction on the same WSe$_2$ film for applications in logic circuits, p--n diodes, photovoltaics, and light-emitting diodes (LEDs).

3. Conclusion

In summary, we have demonstrated a controllable layer thinning and p-type doping of WSe$_2$ with vapor XeF$_2$. The surface roughness of XeF$_2$ thinned WSe$_2$ can be controlled to below 0.7 nm at an etched depth of 100 nm, which is smoother than general plasma thinning methods. The etching rate of WSe$_2$ shows a significant dependence on the exposure pressure of vapor XeF$_2$. Therefore, by tuning the exposure pressure, slow etching and fast etching can be achieved easily for different applications, i.e., thinning and patterning. The phenomena of blueshifts of the $E_{2g}$ mode, redshifts of the PL peaks, downshifts of W 4f and Se 3d core levels in binding energy, and upshifts of the threshold voltage toward higher voltage, observed from Raman, PL, XPS, and electrical characterization of XeF$_2$ treated WSe$_2$, respectively, indicate a p-doping effect introduced by vapor XeF$_2$ exposure. The p-doping effect could be the result of (1) the formation of a substoichiometric WO$_x$ ($x < 3$) overlayer on thinned WSe$_2$ when exposed to air, (2) the trapped reaction product of WF$_6$ within the thinned WSe$_2$ lattice, and (3) the nonstoichiometric WSe$_2$ ($x > 2$) formed at the reaction layer of WSe$_2$ with vapor XeF$_2$. By simply adjusting the XeF$_2$ exposure time, the p-doping level can be controlled easily. The XPS measurements show a Fermi level shift of 0.5–0.8 eV as a function of the vapor XeF$_2$ exposure time and the hole doping concentration extracted from electrical measurements can be up to $25.9 \times 10^{17}$ cm$^{-3}$ which lies in degenerate doping regime. The junction of Ti/WO$_x$/thinned WSe$_2$ exhibits a p-type Schottky contact behavior with a contact resistance of more than one order of magnitude lower than that of the Ti/pristine WSe$_2$ junction. The thinning and p-doping of WSe$_2$ with vapor XeF$_2$ have the combinatorial advantages of easy scale-up, excellent controllability, high etching selectivity, and compatibility with CMOS fabrication technologies, which is promising for future practical applications.

4. Experimental Section

Preparation and Thinning of WSe$_2$: WSe$_2$ flakes were exfoliated mechanically from bulk WSe$_2$ crystals (supplied by 2D semiconductors) and transferred onto to oxygen plasma cleaned 300 nm SiO$_2$ on highly p-doped Si substrates using adhesive Scotch tape. In order to remove tape residues, the samples were immersed in acetone for 2 h and rinsed with isopropyl alcohol and deionized water subsequently. Then, the transferred WSe$_2$ flakes were treated with XeF$_2$ gas (25 sccm) mixed with N$_2$ (100 sccm) as carrier gas in a XeF$_2$ etcher (ORBIS ALPHA, memsstar) at room temperature under various pressures for different times.

AFM Characterization of WSe$_2$: Tapping mode AFM (Bruker: MultiMode, Nanoscope IIIa) in the air was used to obtain the thickness and topography of WSe$_2$ flakes before and after vapor XeF$_2$ treatment. To maximize the imaging resolution of AFM, an AFM probe (NuNano: Scout 350 HAR) with a small half-cone angle and tip curvature radius was used. Prior to the characterization, the samples were scanned for 1 h under AFM to minimize the thermal drift of the piezoelectric scanner. The number of layers of the corresponding WSe$_2$ flakes was derived by dividing the measured thickness by the interlayer distance. An interlayer distance of 0.7 nm for WSe$_2$ was adopted for calculation.

Raman and PL Spectrum Characterization: The Raman and PL measurements were performed in a confocal Raman microscope (inVia Renishaw) in the backscattering configuration under the ambient air condition with a 514 nm laser excitation. A 100× magnification objective
Probe XPS system (Thermo Scientific) utilizing a monochromated Al Kα X-ray source (hν = 1486.7 eV) with a spot size of 20 μm in diameter. The incident laser power was kept at ≈100 μW, to avoid the sample heating effect. The Raman spectra were obtained with a 2400 lines mm⁻¹ grating, resulting in a spectral resolution of ≈1 cm⁻¹. Each spectrum acquisition was accumulated for 10 times with 20 s for per accumulation. Raman spectra were calibrated with the Raman band of Si substrate at 520 cm⁻¹. The PL spectra were collected using a 1200 lines mm⁻¹ grating with an integration time of 50 s. Lorentzian fitting was applied to deconvolute the PL spectra.

**XPS Characterization**

XPS spectra of WSe₂ were obtained from a Theta Probe XPS system from Thermo Scientific. The X-rays were from a monochromated Al Kα source (hν = 1486.7 eV) with a spot size of 20 μm in diameter. The X-ray source was placed at a fixed distance from the sample with an angle of incidence of 90° with respect to the sample surface normal. The incident X-ray and the analyzer were positioned at angles of 30° and 90° with respect to the sample surface normal, respectively. The sampling depth of the XPS measurements is estimated to be 7–8 nm by the relation of λL, where L is the inelastic mean free path of an electron in WSe₂, which can be found from NIST Standard Reference Database 71.[38] The Si 2p peak at 103.2 eV from the SiO₂ of the substrates and adventitious carbon C 1s peak at 284.8 eV were used for binding energy calibration of multilayer and bulk WSe₂, respectively. The high-resolution XPS core level spectra were analyzed by deconvolution with the least-squares fitting of spectra with Gaussian–Lorentzian functions, except for the C 1s peak. During the curve fitting, some constraints were applied: The spin–orbit splitting for the W 4f5/2 and W 4f7/2 components was fixed at 2.17 eV with an area ratio of 4:3 and same FWHM, while the 3d₅/₂–3d₃/₂ components separation for Se was set into 0.86 eV with an area ratio of 3:2.

**Device Fabrication and Electrical Characterization**

Conventional photolithography method with a mask aligner (Karl Suss MA/BAB) was used for WSe₂ transistor fabrication. After WSe₂ flakes had been transferred onto SiO₂/Si substrates, the random shaped WSe₂ flakes were patterned into the channels of transistors by vapor XeF₂. Then metal contacts of the devices were made through deposition of Ti (20 nm)/Al (200 nm) metal stacks with an E-beam evaporator and subsequent lift-off in acetone. More details of the device fabrication can be found in ref. [38]. Electrical measurements were carried out using a Keithley 4200-SCS semiconductor parameter analyzer at room temperature with a shielded probe station in ambient air.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

**Acknowledgements**

The authors would like to thank the financial support of UK Engineering and Physical Sciences Research Council (EPSRC) for this work. The authors genuinely acknowledge the assistance from Dr. Andrey Gromov and Dr. Ron Brown for Raman/PL spectroscopy and XPS measurements, respectively. The copyright line for this article was changed on November 3, 2017, after original online publication.

**Conflict of Interest**

The authors declare no conflict of interest.

**Keywords**

field-effect transistors (FET), layer thickness, p-type doping, vapor XeF₅, WSe₂
Phys. Lett. 2017, 110, 183501; c) J. Kwon, J. Y. Lee, Y. J. Yu, C. H. Lee, X. Cui, J. Honed, G. H. Lee, Nanoscale 2017, 9, 6151.

50] a) W. Liu, J. Kang, D. Sarkar, Y. Khatami, D. Jena, K. Banerjee, Nano Lett. 2013, 13, 1983; b) H. J. Chuang, X. B. Tan, N. J. Ghimire, M. M. Perera, B. Chamlangain, M. M. C. Cheng, J. Q. Yan, D. Mandrus, D. Tomanek, Z. X. Zhou, Nano Lett. 2014, 14, 3594.

51] P. Zhao, D. Kiriya, A. Azcatl, C. Zhang, M. Tosun, Y.-S. Liu, M. Hettick, J. S. Kang, S. McDonnell, K. C. Santosh, J. Guo, K. Cho, R. M. Wallace, A. Javey, ACS Nano 2014, 8, 10808.

52] a) H. Zheng, J. Z. Ou, M. S. Strano, R. B. Kaner, A. Mitchell, K. Kalantar-zadeh, Adv. Funct. Mater. 2011, 21, 2175; b) M.-T. Chang, L.-j. Chou, Y.-L. Chueh, Y.-C. Lee, C.-H. Hsieh, C.-D. Chen, Y.-W. Lan, L.-j. Chen, Small 2007, 3, 658.

53] S. Chuang, C. Battaglia, A. Azcatl, S. McDonnell, J. S. Kang, X. Yin, M. Tosun, R. Kapadia, H. Fang, R. M. Wallace, A. Javey, Nano Lett. 2014, 14, 1337.

54] a) M. T. Greiner, L. Chai, M. G. Helander, W.-M. Tang, Z.-H. Lu, Adv. Funct. Mater. 2013, 23, 215; b) M. T. Greiner, L. Chai, M. G. Helander, W.-M. Tang, Z.-H. Lu, Adv. Funct. Mater. 2012, 22, 4557.

55] a) M. Tosun, S. Chuang, H. Fang, A. B. Sachid, M. Hettick, Y. J. Lin, Y. P. Zeng, A. Javey, ACS Nano 2014, 8, 4948; b) Y. Du, H. Liu, A. T. Neal, M. Si, P. D. Ye, IEEE Electron Device Lett. 2013, 34, 1328; c) J. Yu, C.-H. Lee, D. Bouilly, M. Han, P. Kim, M. L. Steigerwald, X. Roy, C. Nuckolls, Nano Lett. 2016, 16, 3385.

56] J. J. Pei, X. Gai, J. Yang, X. B. Wang, Z. F. Yu, D. Y. Choi, B. Luther-Davies, Y. R. Lu, Nat. Commun. 2016, 7, 10450.

57] C. J. P. Powell, A. Jablonski, NIST Electron Inelastic-Mean-Free-Path Database—Version 1.2, National Institute of Standards and Technology, Gaithersburg, MD 2010.

58] R. Zhang, T. Chen, A. Bunting, R. Cheung, Microelectron. Eng. 2016, 154, 62.