

Effect of calcium deposition on the surfaces of WSe₂ and WS₂

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Functionalization of 2D materials and of transition metal dichalcogenides (TMDs) in particular is central for next generation devices and other applications. Here we study the effect of calcium dosing on the surfaces of clean WSe₂ and WS₂ in ultrahigh vacuum by x-ray photoelectron spectroscopy, low energy electron diffraction, and scanning electron microscopy. We find that Ca reacts with the chalcogens to CaSe_x or CaS_x and reduces the remaining tungsten. Ca forms an overlayer on top and causes an outdiffusion of the chalcogen. The overlayer oxidizes easily. We obtained detailed understanding of the interactions of archetypal TMD with an abundant alkali-earth element, which expands our knowledge of metal-surface interactions and of surface manipulation of 2D materials.

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I. INTRODUCTION

With the rise of 2D materials, transition metal dichalcogenides (TMD) received intense renewed interest in the last ≈15 years and are exceptionally well studied by now. This is especially true for its most prominent members, MoS₂ and WSe₂. Current scientific effort focuses on implementation into heterostructures and devices and, broadly speaking, on property engineering [1,2].

A central subject in this regard is doping, which is generally more difficult than in conventional semiconductors. A well-known method is surface charge transfer doping by depositing, e.g., alkali metals, on top [3–5], which act as electron donors, but many other elements and molecules have been tried [6–8]. Alkali metals are monovalent. The divalent alkali earth metals, on the other hand, may ideally contribute two electrons per ion and induce larger charge densities, a possibility that has received far less attention so far. In addition, the remaining positive ions exert strong, symmetry breaking electric fields at the surface, an effect that may also be enhanced [3,5].

Because of the layered crystal structure of TMDs, metal evaporation may also lead to intercalation, e.g., with the lighter alkali metals, which tend to diffuse toward the bulk. This changes bulk properties, and may induce insulator-metal transitions [9,10] and superconductivity [11]. It is unclear how the alkali earth metals behave in this respect.

In another threat of research metal deposition on TMD has been thoroughly scrutinized in the context of contact formation for device applications. Often the TMD—metal

interactions—are subject to adverse interface reactions, environmental instability and large Schottky barriers [6,12–14].

Here we study the effects of calcium evaporated on the surface of WSe₂ and WS₂. Studies dedicated to the investigation of the interplay of Ca, an abundant alkali earth element, and TMD are clearly underrepresented. Here we fill this gap by investigating tungsten-based TMDs. We prepare a clean surface of WSe₂ and WS₂ under ultrahigh vacuum (UHV) and study the effect of Ca evaporation by x-ray photoelectron spectroscopy (XPS). We find that under the given experimental conditions, Ca forms an overlayer on top and the dominant process at the interface is a chemical reaction between Ca and the chalcogenides including outdiffusion of the latter. These findings align well with the systematics implied by previous investigations of other metals.

II. METHODS

Single crystals of WSe₂ and WS₂ were purchased from 2D semiconductors. XPS measurements have been conducted at room temperature using a laboratory based system with a monochromatized Al-K α x-ray source ($h\nu = 1486.6$ eV) and a Scienta R8000 analyzer. Samples were cleaved *in situ* by the Scotch tape method before measurements under a base pressure of $p = 2 \times 10^{-10}$ mbar. Calcium evaporation was performed utilizing a home-built evaporator using granular Ca with 99.5% purity obtained from Alfa Aesar. A quartz balance was used to monitor the thickness of the evaporated film. The band structure calculations were performed using the full potential local-orbital code (FPLO) [15] employing the Perdew-Wang 92 exchange-correlation functional [16]. For bulk WSe₂, a $(12 \times 12 \times 12)$ k -point mesh was used. All calculations were performed in fully relativistic mode.

The Auger electron spectroscopy (AES) analysis was performed using a JEOL JAMP 9500 F Auger microprobe, which also has a scanning electron microscope (SEM) integrated. The measurements were conducted at a sample tilt of 30°. A

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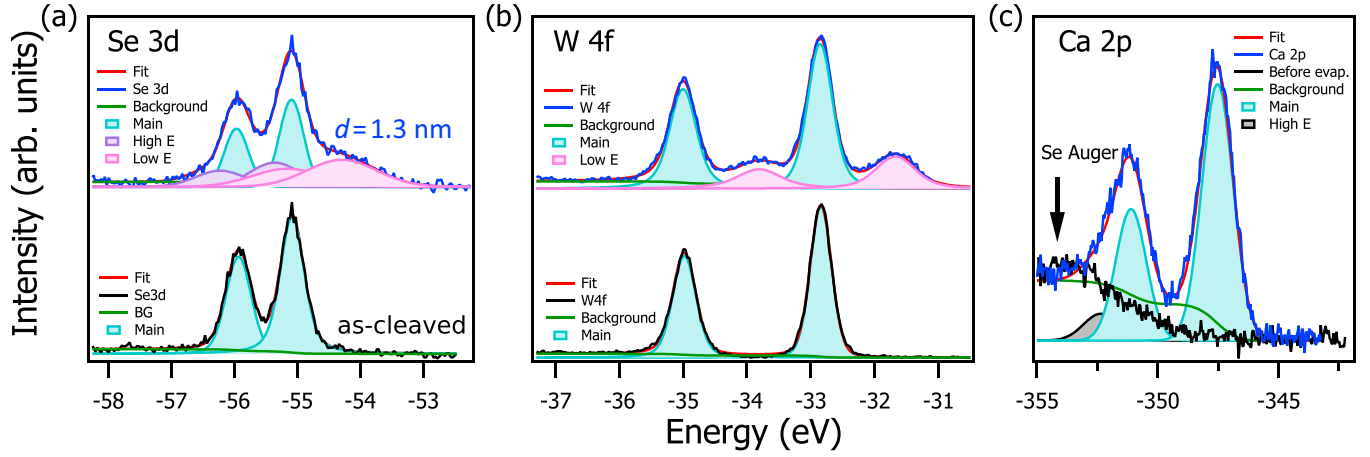


FIG. 1. Se 3d (a) and W 4f (b) XPS core levels before (as-cleaved) and after calcium deposition. The overlayer thickness of $d = 1.3$ nm is obtained from a quartz microbalance. (c) Ca 2p before and after evaporation. Before evaporation (black line) no Ca is present but the shape of the background is influenced by a Se Auger peak (arrow). All spectra are fitted with Voigt functions and Shirley background. The intensity ratios and the energy separations of the spin-orbit components were fixed to the expected values.

Schottky field emission electron gun was operated at 10 kV voltage and 10 nA electric current. The Auger electrons were collected with a constant retard ratio of 0.32. The chemical composition of the analyzed areas was calculated by applying standard single element sensitivity factors in the program MultiPak.

III. RESULTS

Figure 1 compares the most important XPS core levels of WSe_2 , namely Se 3d, W 4f, and Ca 2p before and after Ca deposition. The as-cleaved surface shows W and Se lines that are split by the spin-orbit coupling but can be otherwise fitted by a single component Voigt peak. This indicates that the elements are in their expected chemical state and no oxidation or other foreign phases are present. The binding energies of the W $4f_{7/2}$ ($E = -32.83$ eV) and Se $3d_{5/2}$ ($E = -55.08$ eV) lines fit to literature values of WSe_2 [13]. Significant changes are observed after evaporation of Ca, resulting in a more complex lineshape. Apparently, for both lines, low energy components develop. For the fitting this was taken into account by introducing an additional low energy doublet [pink peaks in Figs. 1(a) and 1(b)]. Closer inspection reveals that the high energy side of the Se 3d line experiences extra broadening. Therefore, an additional high energy doublet was considered for the Se 3d fit [purple peaks in Fig. 1(a)]. The quality of the fits is excellent.

A clear Ca 2p signal is observed as well. It overlaps at the high energy side with a Se Auger line [see Fig. 1(c)]. It can be well fitted by a p type doublet plus a small high energy peak, the latter probably accounting for the asymmetric broadening of the $2p_{1/2}$ component by the nonmonotonic background. The energy position of the Ca $2p_{3/2}$ line is $E = -347.53$ eV, a bit higher than what is expected for bulk Ca, CaO, or CaSe. The position of the W 4f low energy feature at $E = -31.67$ eV points to metallic W^0 . This means that the W-Se bond is broken and a fraction of tungsten is chemically separated from the surrounding chalcogen lattice. The most likely interpretation of the Se low energy component is then

the formation of CaSe_x . The high energy Se doublet can be associated with oxide formation. In fact, very similar observations were made, and an equivalent scenario was proposed, for scandium deposition on WSe_2 [14]. Sc is the immediate neighbor of Ca in the periodic table.

Figure 2 provides additional information by monitoring the valence band and the O 1s spectra. Figure 2(a) compares the XPS valence band before and after Ca deposition and density of states (DOS) of the pristine compound. The orbitals that contribute mainly to the valence band are W $5d$ and Se $4p$. The photoemission cross section of these orbitals is in the same range. The overall agreement between theory and experiment is satisfactory. After Ca evaporation, distinct changes are observed. While the high energy region above $E \approx -2$ eV remains constant, the low energy region is characterized by a transfer of spectral weight from the peak at $E \approx -2$ eV toward lower energy, stretching inside the gap. While the high energy side of the valence band is, according to the orbital resolved PDOS, dominated by Se $4p$, the low energy side, including the peak at $E \approx -2$ eV, consists mainly of W $5d$. We interpret the Ca induced changes in analogy to the W 4f core level as a signature of W^0 formation, which tends to have lower binding energy than the generic component. Although the experiments have been conducted in UHV, the formation of oxides is expected when dealing with highly reactive elements such as calcium. Figure 2(b) shows the O 1s line after Ca evaporation. There are two main components at $E = -530.1$ eV and $E = -532.6$ eV. The former fits to CaO whereas the latter can be assigned to the presence of $-\text{OH}$ groups.

Further insight can be obtained from the angle dependence of the spectra. Figure 3(a) provides the W 4f line again after Ca deposition but this time in an extended energy range encompassing the nearby Ca $3p$ line at $E \approx -26$ eV. We show the spectra for emission angles of 0° (normal emission) and 50° . Surface sensitivity increases with increasing emission angle, a well-known effect and routinely exploited in XPS studies. The two spectra in Fig. 3(a) are normalized to the Ca $3p$ intensity. Under this normalization a large intensity

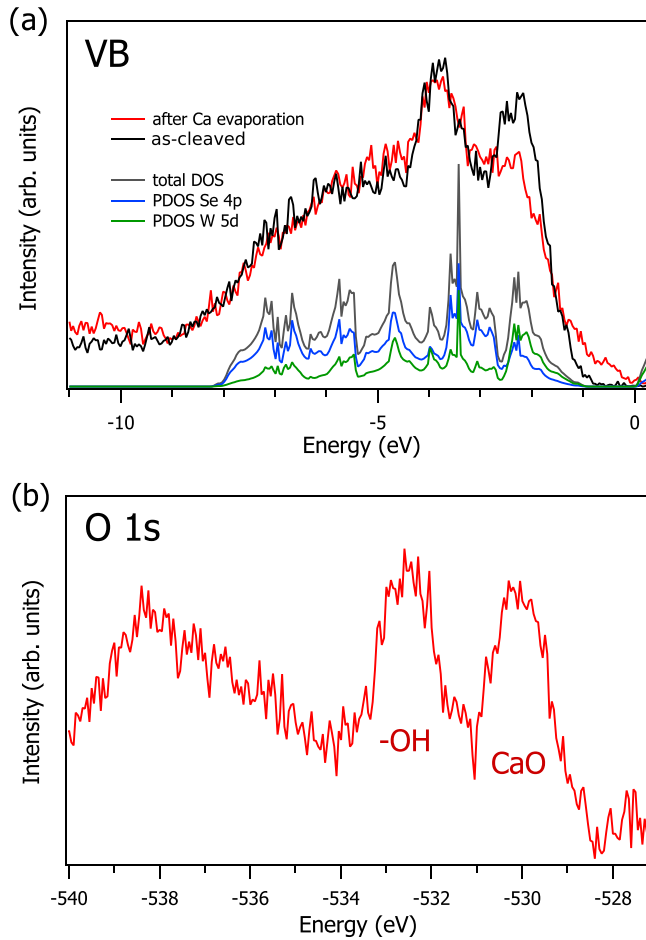


FIG. 2. (a) XPS valence band before and after Ca evaporation. Density of states data refer to the pristine compound. (b) O 1s core level after Ca evaporation.

difference is found for the W 4f line. In particular, the 50° becomes much lower, which means that, not surprisingly, tungsten must be situated below Ca. Figure 3(b) shows the Se 3d line maintaining exactly the same normalization. The overall effect is the same, and the 50° spectrum goes down in intensity. However, there is a subtle, yet important, difference with respect to the W 4f spectrum. Whereas for the W 4f line both components fall equally below the normal emission intensity, this is not the case for Se 3d, where only the main component at $E \approx -55$ eV is reduced. The low energy shoulder at $E \approx -54$ eV remains constant. This indicates that the main Se component originating from the WSe₂ surface is below the Ca overlayer as expected, but the second component, related most probably to CaSe_x, is intermixed with the Ca overlayer. Apparently, the Ca overlayer causes an out-diffusion of Se driven by chemical energy gains. Figure 3(c) completes the angle dependence by normalizing the W 4f line to the low energy component. This shows a clear decrease of the main line with increasing emission angle, confirming that the W⁰ related concentration is located above the generic WSe₂ part.

Overall, these results show that Ca reacts with Se at the surface, thereby dissolving its chemical bond with W. In addition,

part of the Se is physically removed from its original site by outdiffusion toward the Ca overlayer. Subsequently, both elements undergo oxidation at the surface.

Now we study the effect of *in situ* heating to $T = 260^\circ\text{C}$. The motivation to apply heat is to test the stability of the Ca overlayer with respect to diffusion toward the bulk and formation of an intercalation type of compound and with respect to back evaporation. The expectation would be that heat promotes diffusion and oxidation processes. Figure 4(a) shows the Se 3d line before and after heating. The low energy shoulder associated to CaSe_x formation increases upon heating, which is consistent with increased surface reactions and outdiffusion of Se from the WSe₂ lattice. The low energy shoulders of the W 4f lines, on the other hand, decrease upon heating [Fig. 4(b)]. At the same time the main W 4f_{5/2} line broadens at the high energy side. A natural explanation in this case is the oxidation of the W⁰ component by the residual UHV background.

Figure 5 presents the results of scanning electron microscopy and Auger spectroscopy of the same sample measured above. The sample had been subject to repeated Ca dosing and heating. The total Ca thickness amounts to 4 nm according to the thickness monitor. After the XPS measurements, the sample had been taken out of the UHV chamber and transported to the AES chamber in air which took about ten minutes. The image panels in Figs. 5(a) and 5(b) correspond to different spots of the same sample. Panel (a) shows a uniform surface region, homogeneously covered with Ca. The Ca overlayer is thick enough to attenuate almost completely the W and Se emission. A large oxygen component is found instead indicative of the formation of CaO. Interestingly, there are some other spots on the surface, which look different. Panel (b) shows clear inhomogeneity. There are elongated regions with a length scale of $\approx 50\mu\text{m}$ with almost no Ca on top. Also the oxygen content is much lower there, confirming that Ca oxidizes easily, whereas the original WSe₂ surface is more resilient to oxidation and adsorbates. Note that this lateral inhomogeneity may affect the angle-dependent measurements in Fig. 3 in a quantitative manner, since the uncovered spots cannot give rise to emission angle dependence with respect to Ca. However, the qualitative conclusions, especially concerning the vertical order of the spectral components, remain valid. The atomic concentration ratio of W and Se is approximately 1:2 as expected from the stoichiometry. The W⁰ component seen in the XPS spectra in Fig. 1 is expected to reside below the Ca overlayer and above the generic WSe₂ surface. Possible clustering effects are difficult to resolve by SEM.

The overlayer inhomogeneity is unexpected from a smooth evaporation source. It points to heating induced morphology changes. More investigations involving imaging techniques at earlier stages of the Ca evaporation are needed to clarify this point. Earlier investigations found initial islands like Volmer-Weber growth for Au evaporated on WSe₂ [13].

We have also investigated the surface by low energy electron diffraction (not shown). The pristine sample exhibits the expected hexagonal pattern and sharp spots. After Ca dosing, the pattern remains the same but becomes weaker and somewhat blurred. No additional spots, indicative of superstructures, are observed.

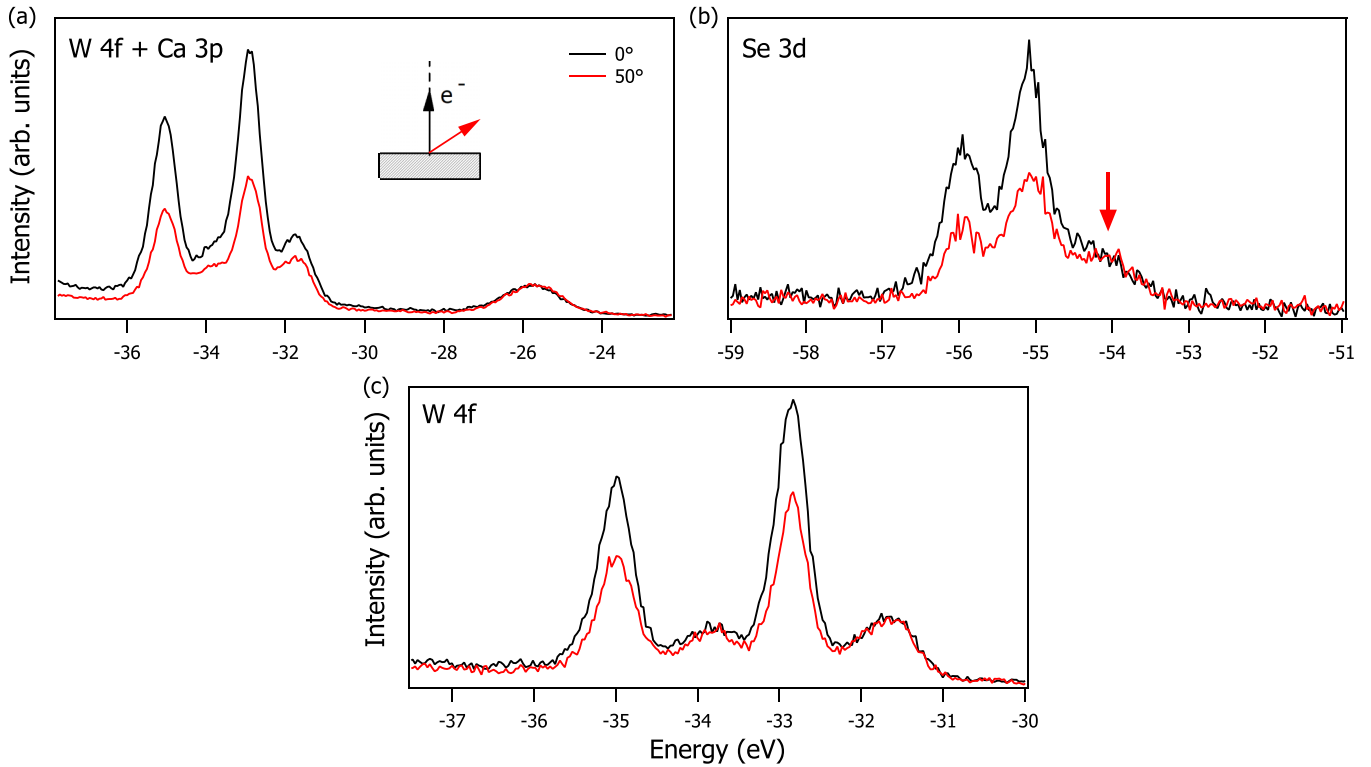


FIG. 3. (a) W 4*f* and (b) Se 3*d* XPS core levels as a function of emission angle normalized to Ca 3*p* at $E = -25.7$ eV. (c) W 4*f* normalized to the low energy component.

Figure 6 repeats the Ca evaporation for WS₂ instead of WSe₂. The results are very similar. The S 2*p* line develops a clear low-energy component and broadens significantly [Fig. 6(a)] upon Ca dosing. Fitting requires an additional low energy doublet [pink peaks in Fig. 6(a)] and a smaller high energy doublet (purple peaks) for a satisfactory result. The pristine surface can be well fitted by a single sharp doublet. The latter is also true for the W 4*f* emission. After Ca evaporation, the W 4*f* lineshape becomes more complex. A low energy component at $E = -31.54$ eV appears [pink peaks in

Fig. 6(b)], which is similar to WSe₂ and indicative of metallic W⁰. Also the Ca 2*p* line resembles the WSe₂ case in shape and position ($E_{3/2} = -347.5$ eV). The interpretation of these results is analogous to WSe₂: Ca reacts with S to CaS_x and leaves behind unbound W⁰. Also, a small oxidic component could be present. A significant difference is that a low energy shift is observed for the core levels upon Ca evaporation.

The valence band spectra and O 1*s* are also similar to WSe₂ (Fig. 7). After Ca evaporation the low energy part of the valence band broadens and shifts to lower energy, consistent

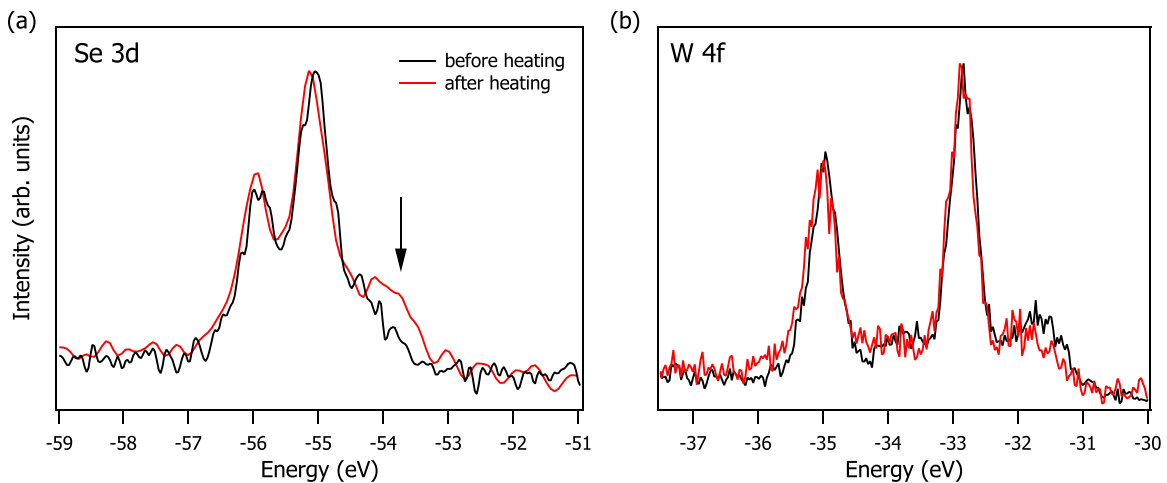


FIG. 4. (a) Se 3*d* core level before and after heating normalized to the main peak. The arrow highlights the low energy increase after heating. Moderate smoothing has been applied to improve the data presentation. (b) W 4*f* line before and after heating normalized to maximum intensity.

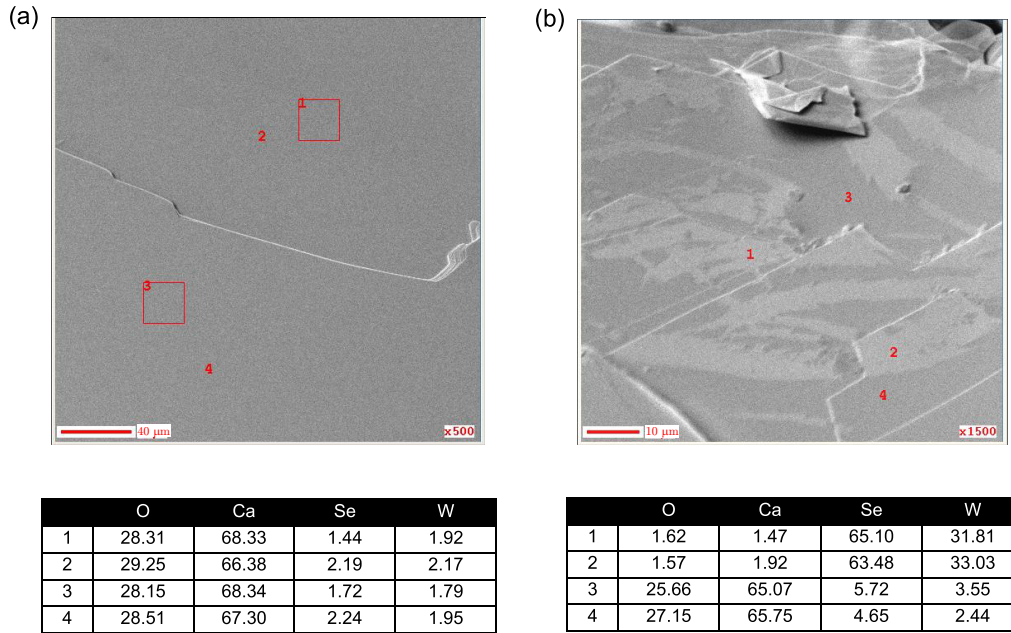


FIG. 5. Surface of the WSe_2 sample with Ca overlayer measured by SEM and AES. (a) and (b) correspond to different spots of the same sample. The red numbers indicate points where the atomic concentration has been evaluated by AES. The results of the latter are collected in the tables below the images.

with the core levels. The O $1s$ line has again two main features related to Ca oxide (≈ -530 eV) and, probably, a hydroxyl component (≈ -533 eV).

IV. DISCUSSION

Ca is located between K and Sc in the periodic table. Both elements are of some relevance in the field of 2D materials but for different reasons. Potassium is well known and often used as an electron donor for surface doping but also as intercalant facilitating the synthesis of staging compounds with properties markedly different from their parents and

relevant for battery applications [17,18]. Scandium, on the other hand, is of interest as a contact material. Low contact resistance values have been achieved using Sc, which roots in its low work function [19,20]. On the other hand, Sc is very reactive and interacts aggressively with the surface of, e.g., WSe_2 [14].

Our results regarding Ca evaporation on WSe_2 and WS_2 resemble rather Sc than K. Interface reactions dominate over charge transfer and doping effects. Ca remains concentrated at the surface and forms an overlayer rather than diffusing toward the bulk. It reacts with the substrate in a way similar to Sc: calcium selenides or sulfides are formed and the

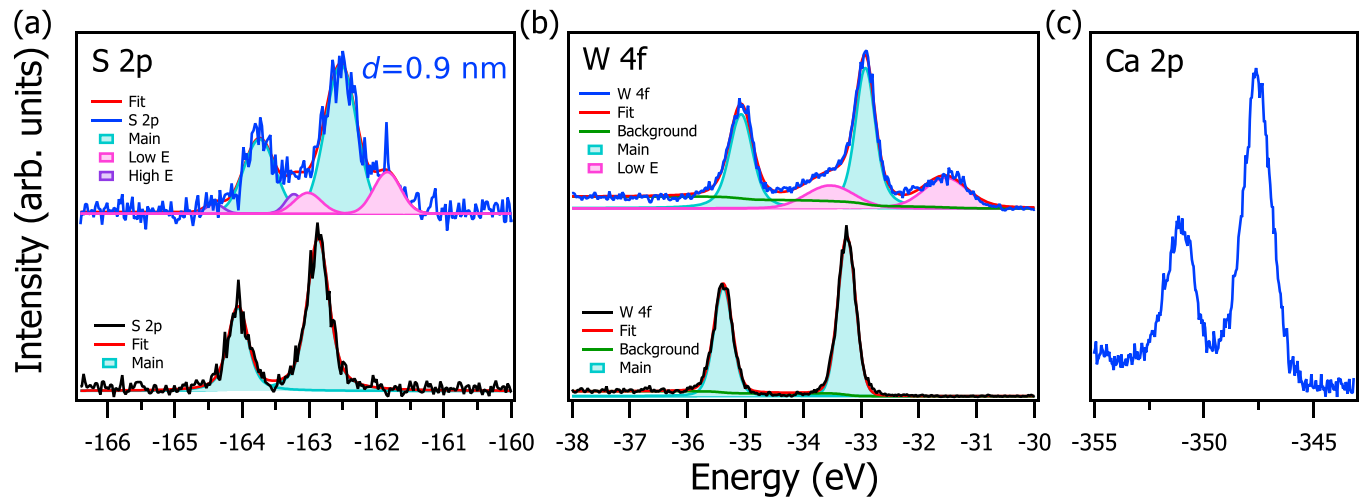


FIG. 6. S $2p$ (a) and W $4f$ (b) XPS core levels before (as-cleaved) and after calcium deposition. Spectra are fitted with Voigt functions and Shirley background. The intensity ratios and energy separations of the spin-orbit components were fixed to the expected values. (c) Ca $2p$ after evaporation.

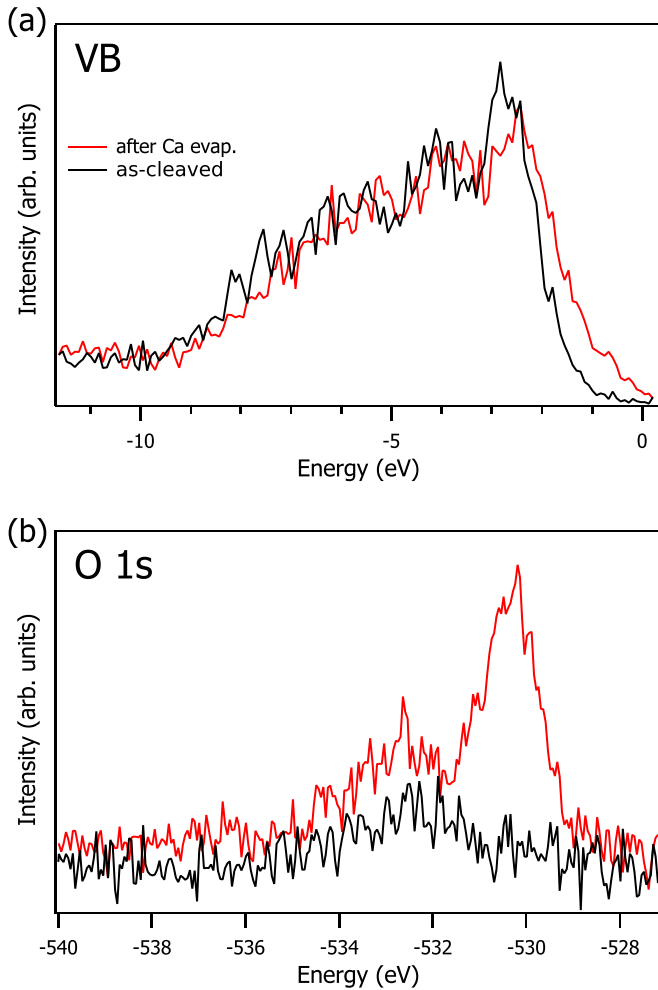


FIG. 7. (a) XPS valence band before and after Ca evaporation. (b) O 1s core level after Ca evaporation.

tungsten is strongly reduced to metallic W^0 . In addition, the Ca overlayer oxidizes easily.

Comparing Figs. 1 and 6, i.e., the dependence of the relevant core levels of WSe_2 and WS_2 on Ca deposition, the similarity of the two materials is apparent. This originates from the close chemical relationship of the two chalcogens S and Se, mirrored for instance in almost identical

electronegativities ($S = 2.58$, $Se = 2.55$). Still, a clear downshift of the WS_2 core levels upon Ca deposition is present in Fig. 6 but not for the WSe_2 spectra in Fig. 1. We note that we observed small shifts (0.1–0.2 eV) of either sign for different experimental runs of WSe_2 —Ca deposition. Smyth *et al.* observed a thickness dependence of the core level shift of WSe_2 upon Sc deposition. First, a downshift, followed by an upshift for thicker layers. This was interpreted as the result of two processes: initially the $ScSe_x$ interface shifts the Fermi energy toward the valence band in a *p* type manner, while a metallic Sc layer has the opposite effect [14]. We believe this is a plausible scenario also in the present case of Ca deposition: the effective E_F position being determined by competing influences of $CaSe_x/CaS_x$ and Ca or CaO_x .

V. CONCLUSION

We have studied the effect of Ca deposition on key representatives of the TMD family, carried out by *in situ* evaporation onto the surfaces of cleaved WSe_2 and WS_2 by XPS, LEED, AES, and SEM. Ca reacts with the chalcogen atoms to form selenides or sulfides leaving behind reduced, metalli-like tungsten, which has a tendency of being oxidized itself. Ca forms an overlayer, which attracts the chalcogen atoms and causes outdiffusion of the latter. A 4 nm thick overlayer on top of WSe_2 was found to be not completely homogeneous after mild annealing. The results for the chemical changes at the surface are very similar for WSe_2 and WS_2 .

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DATA AVAILABILITY

The data that support the findings of this article are not publicly available upon publication because it is not technically feasible and/or the cost of preparing, depositing, and hosting the data would be prohibitive within the terms of this research project. The data are available from the authors upon reasonable request.

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