Identification of Ubiquitously Present Polymeric Adlayers on 2D Transition Metal Dichalcogenides

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ABSTRACT: The interest in 2D materials continues to grow across numerous scientific disciplines as compounds with unique electrical, optical, chemical, and thermal characteristics are being discovered. All these properties are governed by an all-surface nature and nanoscale confinement, which can easily be altered by extrinsic influences, such as defects, dopants or strain, adsorbed molecules, and contaminants. Here, we report on the ubiquitous presence of polymeric adlayers on top of layered transition metal dichalcogenides (TMDs). The atomically thin layers, not evident from common analytic methods, such as Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), or scanning electron microscopy (SEM), could be identified



with highly resolved time-of-flight secondary ion mass spectrometry (TOF-SIMS). The layers consist of hydrocarbons, which preferentially adsorb to the hydrophobic van der Waals surfaces of TMDs, derived from the most common methods. Fingerprint fragmentation patterns enable us to identify certain polymers and link them to those used during preparation and storage of the TMDs. The ubiquitous presence of polymeric films on 2D materials has wide reaching implications for their investigation, processing, and applications. In this regard, we reveal the nature of polymeric residues after commonly used transfer procedures on MoS_2 films and investigate several annealing procedures for their removal.

KEYWORDS: 2D materials, transition metal dichalcogenides, time-of-flight secondary ion mass spectrometry, polymers, surface contaminations

INTRODUCTION

Beside graphene, transition metal dichalcogenides (TMDs) are the most studied two-dimensional (2D) materials. They offer extraordinary physical, optical, and chemical properties which stem from their reduced dimensionality and have therefore emerged as promising materials in numerous technological applications over the past decade, including optics, electronics, sensing, and catalysis.^{1–6}

Many prominent studies for high-performance device preparation rely on mechanical exfoliation, conducted within gloveboxes in clean, inert gas atmosphere environments.⁷ To ensure the environmental stability of the atomically thin structures, encapsulation between additional 2D layers, building heterostructures, is often required.⁸ As a result, the device performance often depends on artificially idealized experimental conditions and these processes are not currently scalable to the largest layers or high-throughput production. This has led to a large variation in measured 2D material properties in the literature, including electronic characteristics. For example, carrier mobilities of monolayer MoS_2 field-effect transistors (FETs) have been measured in the range of 0.5– 150 cm²/Vs,^{9–13} and the theoretically calculated value of 400 cm²/Vs¹⁴ has still not yet been achieved.¹⁵ A similar variability is seen for other properties, such as photoluminescence, which is strongly governed by the surface chemistry.^{16,17} Therefore, a major challenge is the preservation of the pristine surface of 2D materials, to ensure reproducible experiments and durable devices in typical environmental conditions. Due to the high surface to volume ratio, adsorbance of molecules can result in alteration of the materials' intrinsic properties.^{18,19} This becomes increasingly problematic with each additional processing step or simply storage, regardless if carried out on a laboratory or industrial scale, which involves being in the vicinity of polymers. This is even more so the case for processes which involve direct contact to polymers such as

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Figure 1. TOF-SIMS positive ion spectra (left) and chemical maps (right) of the combined isotopes of Mo⁺ and ion fragments of PDMS at m/z 43, 73, 147, and 207 for (a-c) a clean MoS₂ sample, extracted from the center of an in situ sputtered crystal, measured in bunched mode (high mass resolution, low lateral resolution), (d-f) freshly exfoliated flakes, and (g-i) MoS₂ flakes after storage in a Gel-Pak#0 for 1 month, measured in unbunched mode (high lateral resolution, lower mass resolution). Scale bar is 10 μ m in all images.

transfer and lithographic structuring of 2D materials. Many studies therefore focus on the optimization of fabrication processes and preservation of the materials' cleanliness.^{20–23} However, with the most common analytical methods thin contamination layers are highly difficult to identify.

In this study, we present a comprehensive time-of-flight secondary ion mass spectrometry (TOF-SIMS) study of commonly investigated TMD surfaces from different synthesis techniques and after different processing steps. TOF-SIMS is an extremely surface-sensitive technique with a sampling depth of approximately 1 nm, and is able to detect even trace elements down to ppm levels with a lateral resolution limited to $\sim 100 \text{ nm.}^{24}$ With this technique, we are able to show that thin adsorbent layers of organic and polymeric nature are omnipresent on nearly all measured 2D material surfaces. We identify thin polymeric films on chemical vapor deposition (CVD)-grown and mechanically exfoliated TMDs, such as MoS₂, WS₂, and WSe₂, and relate them to their storage and processing environments. We reveal that these molecular thin layers adsorb preferentially to the hydrophobic TMD surfaces from most likely airborne hydrocarbons. For MoS₂ layers that were in direct contact with polymers during standard transfer, we can identify distinct residues from the polymers used by fingerprint patterns in the mass spectrum. These, so far not described, sub-nanometer layers must be considered in all studies on 2D materials and are of particular significance where clean surfaces and interfaces are essential. Finally, we assess the efficiency of different annealing procedures to clean the MoS₂ surface from these ubiquitously present polymer contaminant adlayers.

RESULTS AND DISCUSSION

Mechanically Exfoliated MoS_2 —Influence of Storage Conditions. Mechanical exfoliation (ME) is the prime method to obtain many different high quality 2D layers from bulk single crystals. This approach nearly always involves some type of adhesive tape, and potentially additional polymeric stamps, to cleave the bulk crystals and deposit the material onto a clean substrate or other 2D layers. Three samples of MoS_2 flakes on SiO_2/Si were prepared by mechanical exfoliation, using adhesive tape (Nitto 150E-KL, TOF-SIMS

spectrum of the tape included in Figure S1). The MoS₂ TOF-SIMS spectra (Figure 1a,d,g) are normalized to the main Mo isotope signal at a mass to charge ratio (m/z) of 98. A "clean MoS₂" reference spectrum was obtained from a portion of a depth profile through a bulk crystal, excluding the surface region, presented in Figure 1a. The spectrum displays the pure Mo^+ isotope pattern, including signals at m/z 92, 94, 95, 96, 97, 98, and 100 in the relative ratios of their natural abundancy (pink marked area). An additional strong signal at m/z 72 originates from the SiO₂ substrate and a high background starting at higher m/z from the Cs⁺ sputter ion signal, which was cut off at m/z 133 for clear representation. The spectrum shown in Figure 1d is from a freshly exfoliated and soon after measured MoS₂ sample. It displays strong Mo⁺ isotope signals together with additional peaks for molybdenum hydride species at m/z 93, 99, and 101 (from ${}^{92}Mo + H$, ${}^{98}Mo + H$, and ¹⁰⁰Mo + H), here marked with red stars. The hydride compounds indicate the presence of some contamination on the TMD surface, which is not present in the "clean MoS₂" spectrum. Additionally signals of very weak intensity at m/z 73 and 147 are also visible.

The third sample, which was stored in a Gel-Pak#0 inside a N_2 flow box for 1 month, shows even higher intensity peaks for the molybdenum hydride species and, this time higher intensity signals at m/z 73 and 147, as shown in the spectrum (Figure 1g). Inspection of a wider mass range of the spectra also shows signals at m/z 43 and 207 for the freshly exfoliated and stored samples, as well as signals at m/z 221 and 281 with decreasing intensities toward higher masses for the stored sample (Figure S2).

The peaks at m/z 43, 73, 147, 207, 221, and 281 may be attributed to fragments of polydimethylsiloxane (PDMS). The fragmentation of polymers during bombardement in TOF-SIMS has been subject to numerous studies, with most signals in the low mass region up to 500 Da. The most intense and characteristic features stem from the discharged fragment ions of the polymer backbone, side chains and end groups and are often found in the fingerprint domain with $m/z \leq 150$.²⁵ TOF-SIMS has been previously applied to study the fragmentation mechanism of PDMS with regard to the effects of different molecular weight, terminal groups or functional groups on the

polymer main chain.^{26–28} The standard spectrum of PDMS is dominated by fragment ions at m/z 28 (Si⁺), 43 (CH₃Si⁺), 73 (C₃H₉Si⁺), 147 (C₃H₁₅Si₂O⁺), 207 (C₃H₁₅Si₃O₃⁺), 221 (C₇H₂₁Si₃O₂⁺), and 281 (C₇H₂₁Si₄O₄⁺) (chemical structures in Figure S3).^{27,29} Similar polymers like PHMS and PMPhS, deviating in only one of the functional groups in the repeating unit, show differences in the mass spectra as compared to PDMS.²⁶ Therefore, the specific set of fingerprint peaks found in the spectra of the freshly exfoliated and Gel-Pak stored samples identifies PDMS as a main contamination. Nevertheless, the presence of additional organic contaminations, which are poorly ionized and therefore do not produce secondary ions or only unspecific low-mass fragments in TOF-SIMS, cannot be ruled out completely.

This polymer is present in the tape used for exfoliation (Figure S1), as well as in the Gel-Pak used for storage in this experiment (according to the technical datasheet³⁰). The higher counts/intensities for hydride species and PDMS fragment peaks also indicate stronger contamination of the Gel-Pak stored sample as compared to the MoS_2 directly measured after exfoliation.

Figure 1b,e,h displays intensity maps of the summarized Mo^+ isotope signals. The Mo^+ signal represents the MoS_2 flake area for all samples (the weaker contrast in Figure 1b is due to the depth profiling mode and lower lateral resolution when compared to the other two measurements).

Figure 1c,f,i shows maps of the combined ion fragments of PDMS (summarized over the most intense and specific fragments at m/z 43, 73, 147, and 207). The "clean MoS₂" reference sample shows no signal, due to the absence of contaminants on the milled surface. The freshly exfoliated sample has a weak, but clearly visible, PDMS fingerprint, mainly in the flake region and largely reduced signal on the surrounding substrate region. The Gel-Pak stored MoS₂ flake (one month) clearly shows a high level of PDMS contamination located on the flake. The intensity variation over the flake can be explained by the primary ion impact angle, which results in stronger extraction of secondary ions and therefore higher measured signal intensity from the left edge of the flake. These PDMS intensity maps demonstrate that even a short exposure to adhesive tape, during the exfoliation process, results in a detectable selective deposition of a PDMS adlayer onto the flake surface. It should also be noted that the polymeric tape was never in direct contact with the investigated surfaces, due to the cleavage during repeated exfoliation before and during deposition. The higher intensity of PDMS on both contaminated flakes, compared to the SiO₂ substrates, clearly shows that the contaminants preferentially adsorb on the MoS₂ surface. An adsorption of PDMS on the flake/substrate interface is additionally possible but not detectable in this surface sensitive measurement. The PDMS contamination is more pronounced due to storage in, e.g., Gel-Pak over time, supporting the notion of the strong tendency of 2D material surfaces to adsorb hydrocarbons, in this case preferentially.

Investigation of Pristine CVD-Grown MoS₂. To investigate this polymeric deposition on TMDs produced by different synthetic methods, CVD-grown predominantly monolayer flakes on SiO₂/Si substrates were examined. It is generally accepted that CVD-grown TMDs offer a clean surface directly after growth;^{31,32} however, storage, shipping, and additional processing steps such as transfer or structuring can lead to contamination. After synthesis, the samples

examined here were shipped in standard polystyrene (PS) sample boxes (see TOF-SIMS reference spectrum of box material in Figure S4) in vacuum-sealed bags and stored in N_2 flow boxes without direct contact to any other material before examination.

The optical micrograph in Figure 2a shows the clear contrast between typical triangular shaped, CVD-grown MOS_2 flakes



Figure 2. (a) Optical image of CVD-grown MoS_2 flakes on SiO_2/Si . (b) Raman spectra of a MoS_2 flake. Inset: Raman intensity map. (c) TOF-SIMS elemental map of isotopes of Mo^+ visualizing the MoS_2 flakes. (d) TOF-SIMS elemental map of the summarized PDMS contamination fragments at m/z 43, 73, 147, and 207. Scale bar is 10 μ m in all images.

and the SiO₂/Si substrate studied here. The Raman spectrum in Figure 2b confirms the presence of a monolayer MoS₂ flake with characteristic ¹E_{2g} (in-plane) and A_{1g} (out-of-plane) vibrational modes located at 385 and 406 cm⁻¹ and the middle multilayer region showing a ~2 cm⁻¹ redshift and blueshift for the ¹E_{2g} and A_{1g} modes, respectively. No indication of polymeric contamination was found in the Raman or PL analysis for this material (Figure S5), as well as in SEM micrographs (Figure S6). The XPS analysis in Figure S7 shows a carbon signal in the C 1s core region, but the identification of the carbon source is not possible solely from this method. Additionally, a representative AFM height profile and topographic image of a typical CVD MoS₂ flake is included in Figure S8, confirming the typical monolayer height of less than 1 nm and a low roughness flake surface with no evidence of surface adlayers.

In contrast to this, TOF-SIMS inspection reveals the existence of hydrocarbons on top of the CVD grown flakes and identifies them as polymeric adlayers. The elemental TOF-SIMS map (Figure 2c) of the combined Mo⁺ isotopes shows triangular shaped MoS₂ flakes with a higher ion count seen in the middle of the flakes, where the multilayer regions are located. The corresponding TOF-SIMS spectrum of this measurement and the "clean MoS₂" reference, discussed above, are shown side by side in Figure S9. Alongside the expected Mo⁺ isotope pattern and substrate signals, the spectrum displays intense signals at mass to charge ratios of 43, 73, 147, and 207, corresponding to PDMS. The combined map of those fragment ions again shows the most intense



Figure 3. (a) Process flow of monolayer MoS_2 polymer supported transfer onto SiO_2/Si substrates. (b) TOF-SIMS spectra normalized to the total positive ion counts of the pristine and transferred MoS_2 with PS, PVA/PMMA, or PMMA, measured in bunched, high-mass-resolution mode. The insets depict enlarged spectra in specific m/z regions. The y-axis of all spectra is multiplied by a factor of 5, starting at m/z 103. Isotopic peak patterns of special interest (Mo^+ , MoC^+ , and MoS^+) are highlighted in the pink colored boxes. Peaks of special interest are labeled in red.

signal on the MoS_2 flakes, highlighting that most of the contamination is located on the TMD rather than on the substrate, as presented in Figure 2d (this is also confirmed by the region of interest (ROI) analysis in Figure S10). It must be emphasized that the 2D flakes have never been in direct contact with the polymers identified here. The contaminants form a thin adsorbed layer are therefore of a different nature than often reported particle like residues after transfer or etching processes.^{33–35} Furthermore, it is noteworthy that no signals for PDMS fragments can be found on the SiO₂ substrate. Analogous contamination layers were also found on CVD-grown WS₂ and WSe₂ monolayers. The TOF-SIMS spectra and elemental maps of these materials are presented in Figures S11–S13.

Investigation of Transferred CVD-Grown MoS₂. Although CVD allows the growth of TMDs directly on insulators, for many applications and device implementation additional process steps, such as transfer and etching, are often required. The transfer of any 2D material commonly involves coating the surface with a polymer, thus the 2D material surface being in direct contact with hydrocarbons. The removal of these polymers after transfer is done by etching/dissolution or mechanical release (dry transfer). It has been reported previously that this removal is incomplete, potentially leaving behind residues.³⁶ However, the nature of these residues has not been clarified yet nor has their complete removal been realized. Thus, three commonly used methods of polymer assisted transfer were examined in terms of their cleanliness by TOF-SIMS. Freshly CVD-grown MoS₂ was used for transfer, poly(methyl methacrylate) (PMMA)-assisted transfer (#1), a method based on a combined poly(vinyl alcohol) (PVA) with PMMA support layer (#2) and polystyrene (PS) transfer (#3) (Figure 3a). In #2, the water-soluble PVA layer is there to act as a protection layer against the PMMA support, avoiding the need for organic solvents in the polymer-removal step.³⁷ In #3, PS is claimed to provide more intimate contact to MoS₂

therefore being superior for the intact transfer of a monolayer TMD material. $^{\rm 38}$

TOF-SIMS surface analysis was performed on the pristine and transferred materials, over large 400 μ m \times 400 μ m acquisition areas in bunched, high mass-resolution mode (m/m) $\Delta m \geq 5000$ for all peaks). The spectra (Figures S14 and S15) as well as reference spectra (Figure S16) of all polymers used in these experiments on SiO₂/Si are displayed in the Supporting Information (SI) with detailed discussion. Figure 3b shows the positive ion spectra for the pristine and all three transferred films. The pristine film shows contamination from PDMS, represented by the typical fragment peaks at m/z 43, 73, as well as 147, 207 (see extended spectrum in the SI), which were identified before for the exfoliated and CVD-grown MoS₂ flakes. After transfer the PDMS signals vanish. Instead, the MoS₂ transferred by all three methods show clear fingerprints (Figure 3b, red peak labels) of contamination from the respective supporting polymer, which were identified from the positive or negative ion spectra (Figures S14 and S15) and discussed in detail in the SI.

The quantitative comparison of the cleanliness of these samples with different polymers is complicated by the different ionization rates of those fragments in positive and negative ion polarity. Further, strong isotopic patterns of the MoS_2 partially interfere with the more specific, but low intensity, high mass polymer fragments. Therefore, instead of comparing the abundance of polymer signals, we propose the comparison of isotopic patterns corresponding to MoS_2 .

In the positive ion mode, prominent isotope patterns of Mo^+ , MoC^+ , and MoS^+ can be identified (pink colored regions in Figure 3b). The further comparison is focused on the transferred samples only: The dominant Mo^+ isotopes are most intense in the PS transfer sample, followed by PMMA then PVA/PMMA.

In negative ion mode, the isotope patterns of MoC⁻, MoO⁻, MoS⁻, MoS⁻, MoS², and MoS₂O₂⁻ can be identified as shown in Figure S15. Again, the dominant MoS⁻ and MoS₂⁻ isotope patterns are most intense for the PS transferred sample, followed by the PMMA transferred, while in the PVA/PMMA transferred sample the relevant signals are extremely low in intensity. A detailed examination of the signal intensity ratios is provided in Figure S17.

The overall stronger peak intensities of MoS_2 related isotopes, in positive as well as negative polarity, for the PS transfer suggests a relatively clean and preserved surface. For the PVA/PMMA and PMMA assisted transfer samples, a larger amount of polymeric residue on the surface could be responsible for lower yields of MoS_2 related isotopes.

To determine a procedure for a more quantitative description of the contaminants on the MoS_2 samples, the abundance of molybdenum hydride (MoH⁺) species in comparison to Mo⁺ isotopes was measured. The MoH⁺ abundance can be taken as a measure of contamination present on a sample surface, as these are not present on pristine MoS₂ surfaces (see "clean MoS₂" reference sample spectrum in Figure 1a) and therefore the H⁺ must stem from adsorbed surface contaminants. To evaluate this, the most intense and relatively simplest isotope pattern of the molybdenum ion is evaluated in detail. The seven Mo⁺ isotope peaks with high abundance, namely, ⁹²Mo, ⁹⁴Mo, ⁹⁵Mo, ⁹⁶Mo, ⁹⁷Mo, ⁹⁸Mo, and ¹⁰⁰Mo, are located between *m/z* 92 and 100 in the positive ion spectrum. The peak analysis of MoH⁺ is more complex as the metal and metal hydride peaks may be

very close (for example, ⁹⁴MoH and ⁹⁵Mo differ by only 7.07 × 10^{-3} amu), which is not resolvable even with best mass resolution settings.³⁹ Overlapping occurs at nominal m/z 95, 96, 97, and 98, while peaks at m/z 92, 94, and 100 are purely from Mo⁺ and m/z 93, 99, and 101 are from MoH⁺ isotopes only.

Figure 4a depicts a histogram of the Mo^+/MoH^+ fragments in the positive ion spectra of the transferred MoS_2 films. Peak



Figure 4. (a) Mo isotope ratios extracted from the positive ion TOF-SIMS spectra of pristine MoS_2 (gray) and PS (blue), PVA/PMMA (green), and PMMA (red) transferred MoS_2 . The black curve represents the theoretical values for Mo^+ isotopes. (b) Raman spectra averaged over a large area ($100 \ \mu m \times 100 \ \mu m$ with 225 single spectra) on MoS_2 on SiO_2/Si substrate before (dashed lines) and after transfer (bold lines) with the different supporting polymers in the same region and (c) fitted ${}^{1}E_{2g}$ and A_{1g} Raman mode positions prior to (gray) and after transfer (red) with the respective polymer.

intensities for the MoS₂ films transferred with PS are depicted in blue, PVA/PMMA in green and PMMA in red. For comparison, data from the "clean MoS₂" on SiO₂/Si reference spectrum was added. All peaks in the range of m/z = 92-101were each fitted with a modified Lorentzian line shape to extract their intensities (for details on fitting, see SI). The theoretical ratios for pure Mo isotopes from literature⁴⁰ are depicted by the black curve.

As mentioned previously the overlapping of Mo⁺ and MoH⁺ species leads to an intermixing of peaks and their intensities. In a report from Gelb et al.,³⁹ the resulting intensities for the intermixed peaks at m/z 95, 96, 97, and 98 were described as

$$I(x) = I(^{x}Mo) + r \cdot I(^{x-1}Mo)$$
(1)

where $I(^{*}Mo)$ represents the theoretical intensity of an isotope of certain mass x, I(x) is the experimentally measured intensity, and r is the ratio factor between them (hydride to metal). From the ratio of the intensities at m/z 92 and 93, where the pure ${}^{92}Mo$ and the pure ${}^{92}Mo + H$ isotopes are located, the ratio factor r can be calculated. For the transferred films, r is 0.220 for PS, 0.309 for PVA/PMMA, and 0.276 for PMMA. All



Figure 5. (a) Schematic representation of CVD-grown MoS₂ flakes transferred with PMMA supporting polymer onto a Si/SiO₂ substrate with CVD-grown MoS₂ flakes and (b) optical microscopy image of the examined area. (c) TOF-SIMS elemental maps of ${}^{32}S^-$ visualizing the MoS₂ flakes. (d,e) TOF-SIMS elemental maps of ${}^{28}Si^-$, ${}^{16}O^-$, visualizing the SiO₂ substrate and (f) TOF-SIMS elemental maps of the summed PMMA fragments at m/z 31, 55, 85, 141, and 185, visualizing the polymeric contaminations, which are only visible on a faction of the flakes on the substrate—presumably the transferred ones. All TOF-SIMS maps were acquired in the unbunched mode. Scale bar is 10 μ m in all images.

of these ratio values by far exceed reported literature values of 0.145.³⁹ Though this previously reported value, from a bulk powder sample, may differ from a CVD-grown material, the marked increase in r values in the present materials still indicates a trend of increasing contaminant concentration going from PS to PMMA to PVA/PMMA, noting that the ideal ratio is zero for the theoretical Mo isotope ratio with no hydride species present. This is highlighted in the "clean MoS_2 " spectrum which results in the lowest experimental r value of 0.047 (Figure 4a, the ratio of m/z 92 to 93). Overall, for the transferred films, differences in the isotope ratios are present but the overall trend of abundances is in accordance with the theoretical data and the highest abundance peak is also located at m/z 98. The lowest r value of 0.220 for the PS transferred sample supports the previous suggestion, from the qualitative polymer isotope intensity analysis, of a cleaner sample surface and preserved chemistry, followed by PMMA and then PVA/PMMA transferred samples.

Raman analysis was performed to further analyze the effect of the different transfer methods on the CVD-grown monolayer MoS₂. Figure 4b displays the averaged Raman spectra on the films from before (dashed lines) to after transfer (solid lines) in the same location on the material, minimizing effects from differences in grain boundaries and crystallinity of the film in different areas. The fitted (Lorentzian line shape) A_{1g} to ${}^{1}E_{2g}$ peak positions from before (gray) to after transfer (red) are presented for each supporting polymer in Figure 4c. The peak positions of the A_{1g} to ${}^{1}E_{2g}$ modes, as well as their respective full width at half-maximum (fwhm) and splitting (Δ = $A_{1g} - {}^{1}E_{2g}$) values are displayed in Figure S18. The A_{1g} and ${}^{1}E_{2g}$ modes prior to transfer are located at ~384.9 and 404.3 cm^{-1} with fwhm ~3.2 and 5.1, respectively (values from fitting results). The peak splitting of 19.4 cm⁻¹ and intensity ratio ${}^{1}E_{2g}/A_{1g}$ of 0.58 is in good agreement with literature values for monolayer MoS_2 .^{41,42} After transfer, the ${}^{1}E_{2g}$ peak blueshifts in energy by 1.0-2.0 cm⁻¹, while the A_{1g} mode only slightly redshifts for PS and PVA/PMMA, ~0.5-1.0 cm⁻¹, staying unchanged for PMMA transferred MoS₂.

Previous reports state that the A_{1g} mode is influenced by surface charges, restraining of flakes and surface adhesion, while defects and strain mainly affect the ${}^{1}E_{2\alpha}$ mode position, which is the mode most influenced in this experiment.⁴³⁻⁴⁵ Increasing uniaxial strain on MoS_2 was shown to lead to a redshift and splitting of the ${}^{1}E_{2g}$ mode.^{46,47} Different thermal expansion coefficients of the substrate and TMD material can also lead to incorporation of intrinsic strain during the fastcooling step at the end of the CVD process. Hence, the blueshift for the transferred MoS₂ films can mainly be attributed to a strain release upon transfer of the MoS₂ film from the SiO₂/Si growth substrate, in agreement with previous reports.^{48–50} This effect also causes a decrease of the splitting between ¹E_{2g} and A_{1g} mode for all transferred films. Other possible influences on the changes of peak position, fwhm and ratio are discussed in the SI. The large blueshift of the ${}^{1}E_{2\alpha}$ mode for the PS transferred sample, as compared to PMMA and PVA/PMMA, indicates a stronger stress release after transfer to the new substrate, which would suggest the presence of less residue left on the surface of this film, as supported by TOF-SIMS analyses. Overall, the Raman analysis for all transfer methods demonstrates changes from before to after transfer, which indirectly points toward differences in residual contaminants on the MoS₂ surfaces after transfer.

To further observe the presence of residual contamination from the transfer process, CVD-grown MoS_2 was transferred, using PMMA, onto a substrate with uncoated, pristine CVDgrown MoS_2 . This enables a direct comparison between pristine and transferred MoS_2 flakes within the same elemental mapping acquisition (see schematic representation in Figure 5a).

The TOF-SIMS elemental mapping indeed shows two types of flakes present in the imaged area. The spatial map of the ${}^{28}\text{Si}^-$ signal, representing the SiO₂ substrate, clearly shows a high contrast between the MoS₂ flake covered and uncovered area. Interestingly the ${}^{16}\text{O}^-$ signal map does not exactly follow the ${}^{28}\text{Si}^-$ signal, which would be expected for a pristine sample where the oxygen signal can only originate from the substrate.

While the highest oxygen signal intensity (yellow) can be found on the SiO₂ substrate, lower intensities (red-orange) can be identified on some of the MoS₂ flakes, whereas the nontransferred material, distributed in the middle to right bottom corner of the imaged area, appear black with no ¹⁶O⁻ signal. Further, the transferred flakes which show oxygen intensity, have much lower or almost no ³²S⁻ signal in Figure 5c. The flakes, which are oxygen free in contrast, show high intensity sulfur signal, as expected for pristine MoS₂ flakes (Figure 5c,e). A striking difference is observed in the signal intensities at m/z 31, 55, 85, 141, and 185, corresponding to the PMMA polymer fragments CH₃O⁻, C₃H₃O⁻, C₄H₅O₂⁻, C₈H₁₃O₂⁻, and C₉H₁₃O₄⁻ in negative ion polarity respectively (see PMMA reference spectrum in Figure S16).

The transferred flakes can be clearly seen to have residual polymer on their surface, which masks their respective sulfur signals in the TOF-SIMS surface map completely, giving implications for further chemical analysis of transferred films in general. Figure 5f displays a combined map of the identified PMMA fragment ions.

Annealing Procedures for Cleaning of Transferred CVD-Grown MoS₂. Annealing procedures are often employed in an attempt to remove polymeric contaminants on 2D materials.^{51,52} Xie et al. reported on efficient removal of PDMS from transferred graphene through a high temperature annealing at 500 °C determined by TOF-SIMS.⁵¹ However, only few systematic studies with full analysis of the effect on the 2D materials exist. The removal of photoresist residues from lithographic processing by annealing at 400 $^\circ\rm C$ in Ar/H $_2$ atmosphere was reported to be efficient, 53 while Garcia et al. found it to be insufficient in the case of exfoliated h-BN and suggested instead treatment in Ar/O2 atmosphere.54 Also annealing at higher temperatures can be harmful to the TMDs or the substrates,⁵⁵ in particular, when residual oxygen or water is present. Thus, treatments have to be carried out in a HV/ UHV environment, which is time-consuming and costly. Further, higher temperature annealing is only possible on a number of TMDs, which do not thermally decompose and are deposited on temperature stable substrates.

Here we evaluate three previously reported annealing processes on their effectiveness on MoS₂ films transferred with three different polymer supports: PS, PVA/PMMA and PMMA. The procedures carried out were 2 h annealing in (1) N₂ atmosphere at 150 °C, (2) N₂ at 450 °C, and (3) forming gas (FG) at 300 °C; (1) is a mild annealing, below the decomposition temperature of MoS₂; higher temperatures, such as (2) at 450 °C in N₂, were previously reported to be necessary for removal of organic/polymeric contaminations on graphene;⁵¹ (3) at 300 °C and reducing forming gas (FG) atmosphere can help to eliminate organic residues but can also lead to decomposition of MoS₂ due to loss of sulfur, forming H₂S.⁵⁶

Figure 6 displays a bar graph of the relative intensities of the combined molybdenum hydride isotopes ($^{92}Mo + H$, $^{98}Mo + H$, $^{100}Mo + H$) in the positive ion spectra of the PS, PVA/PMMA, and PMMA transferred samples that were analyzed immediately after transfer (gray) and then after the three annealing treatments. The selected isotopes, $^{92}Mo + H$, $^{98}Mo + H$, and $^{100}Mo + H$, are all hydride species of the Mo isotopes, representing the contamination of the sample surfaces (as discussed above). The higher intensity of the isotope signal infers higher organic/polymeric contamination of the surface. In Figure 6, the effects of the three different treatments on the



Figure 6. Comparison of the relative intensities of the combined positive ${}^{92}Mo + H$, ${}^{98}Mo + H$, and ${}^{100}Mo + H$ ions of as-transferred (gray), and annealed at 150 °C in N₂ (orange), 450 °C in N₂ (green) and 300 °C in FG (violet) MoS₂, transferred with PS (left), PVA/PMMA (middle), and PMMA (right) onto SiO₂/Si.

PS transferred MoS_2 are examined and show the lowest contamination levels for the 300 °C, FG treatment, with little effect from 450 °C, N₂ and no improvement after the mild 150 °C, N₂ anneal. In contrast the PVA/PMMA and PMMA transferred materials show the highest reduction in hydride species, and therefore inferred contamination, for the 450 °C, N₂ anneal, followed by the 300 °C, FG and again showing no effect after the 150 °C, N₂ annealing. Overall, the lowest metal hydride levels were achieved for the PMMA transferred sample after 450 °C annealing in N₂. The complete positive and negative ion spectra and the detailed, relative isotope ratio comparison for Mo⁺, MoS⁻ and MoS₂⁻ fragments are shown in Figure S19, S20 and S21. Summarizing, we could achieve partial removal of the polymeric residues using the described procedures.

While heat treatments target the removal of surface contaminations, it is important to also consider the interfaces. Thin, uniform layers of contaminants were revealed at the interface of heterostructures formed by stacking of exfoliated 2D materials.⁵⁷ Other than topographically detectable blisters or bubbles, which are a common issue in the formation of heterostructures, these layers are not detectable with AFM or optical microcopy. Annealing procedures maybe inefficient as the layers are encapsulated, thus alternative procedures targeting these hard-to-reach surfaces need to be found. For example, "nanosqueegee" has been demonstrated for local cleaning of interfaces with an AFM tip and simultaneous chemical identification of the contamination via infrared spectroscopy. In conclusion, the detailed investigation of clean 2D material surfaces remains a challenging topic.

CONCLUSIONS

The ubiquitous presence of polymeric adlayers on top of TMDs has been revealed with highly resolved TOF-SIMS measurements. The atomically thin contamination layers are not detected with standard characterization methods such as Raman spectroscopy or XPS, and most likely stem from the adsorption of airborne hydrocarbons. The adsorption of PDMS during storage conditions was demonstrated for mechanically exfoliated MoS_2 flakes. In particular, the usage of Gel-Pak for storage was shown to lead to high levels of contamination on the TMD surface, due to the adsorption of the PDMS from the gel. Even though contamination levels can be decreased for mechanically exfoliated samples by more

elaborate exfoliation techniques, for example using metal adhesion layers instead of tape and polymeric stamps,⁵⁸ as well as transferring the whole process to an inert gas environment in a glovebox,⁷ this preparation route still lacks scalability and still involves the presence of polymer materials.

Polymeric adlayers were found to also be present on CVDgrown MoS_2 , WS_2 , and WSe_2 flakes on SiO_2/Si , which were stored in N_2 flow-boxes in the laboratory, with no direct contact to a contamination source. Laterally resolved TOF-SIMS images confirmed this contamination specifically on the flakes, when compared to the substrate, even though conventional analytical methods, such as Raman and PL spectroscopy, AFM, SEM, and XPS fail to show any specific indication of a contaminated TMD surface or identify the origin.

On MoS_2 films transferred with the polymer-assisted method using common transfer polymers, PMMA, PVA/PMMA, and PS, we identified the polymeric contaminants by their fingerprint pattern in the mass spectrum. The efficiency of different annealing treatments on the transferred films with these polymers could be determined. With these commonly applied annealing procedures we achieved partial removal of polymeric contamination, but the standard annealing procedures did not result in completely clean surfaces.

The omnipresence of organic/polymeric contaminants must be considered when dealing with 2D materials on all levels. The variation of significant material properties, such as photoluminescence or carrier densities and mobilities, may be linked not only to intrinsic defects or strain on the material but also to surface contamination.¹⁹ The affected surface chemistry will be strongly influenced by polymeric layers and must be considered in functionalization or catalytic reactions. Therefore, the impact on the end-application and processing of 2D materials must be considered during device integration. Performance variation in electronics, optics and sensing are not negligible and strategies for reliable processing must be developed.

EXPERIMENTAL SECTION

Mechanical Exfoliation of MoS₂. A bulk MoS₂ crystal (HQ Graphene, ≥99.995%) was mechanically exfoliated several times between adhesive tape (Nitto 150E-KL). The SiO₂ (300 nm)/Si substrates were cleaned by O₂/Ar plasma treatment at reduced pressure for 10 min (Oxford Instruments PlasmaPro 100 Cobra) prior to flake deposition to remove any organic surface contamination. The MoS₂ covered Nitto tape was then pressed onto the substrate and slowly peeled off with predominantly few-layered MoS₂ crystals remaining on the substrate.

CVD Growth of MoS₂, WS₂, and WSe₂ Flakes. MoS₂, WS₂, and WSe₂ flake samples were grown in a microcavity in a two-zone chemical vapor deposition furnace, directly on SiO₂ (300 nm)/Si substrates, as described previously^{59,60} and detailed in the SI. The growth resulted in randomly distributed, predominantly monolayer flakes $\leq 10 \ \mu$ m in lateral size.

CVD Growth of MoS₂ Films. MoS_2 monolayer films were grown as previously described by Luo et al.⁶¹ (details in the SI) in a quartz tube furnace directly on SiO₂ (300 nm)/Si substrates. The growth yielded near continuous, mostly monolayer MoS_2 films with micrometer-sized domains.

Transfer of CVD-Grown MoS₂ Monolayer Film onto SiO₂/Si Substrate Using PMMA. For transfer, PMMA solution (7-fold dilution, AR-PC-504 in AR 600–01, Allresist) was spin-coated on a 1 cm² sample of CVD-grown MoS₂ film on SiO₂(300 nm)/Si at 500 rpm for 10 s, followed by 4500 rpm for 60 s followed by a soft bake at 120 °C for 15 min in air. The underlying SiO₂ was then etched in 50 mL of KOH solution (2 M in deionized (DI) water, VWR Chemicals, 85.0–100.5% AnalaR NORMAPUR Reag. Ph. Eur.). The detached film was then transferred to DI water (18 M Ω cm) with a glass slide and allowed to soak for 30 min. This wash was repeated once after which the film was transferred onto a SiO₂(300 nm)/Si substrate and left to dry in air for ~15 min, then placed in a desiccator at 0.8 bar overnight. Following drying the sample was immersed in 30 mL acetone (Honeywell, ≥99.5%) for 30 min to dissolve the PMMA layer, which was repeated twice before rinsing (IPA, Honeywell, ≥99.5%) and drying under N₂.

Transfer of CVD-Grown MoS₂ **Monolayer Film onto SiO**₂/Si **Substrate Using PVA/PMMA.**³⁷ An aqueous poly(vinyl alcohol) (PVA) solution was prepared by dissolving 150 mg of PVA (Sigma-Aldrich, partially hydrolyzed, M.W. ~160 kmol/g) in 20 mL DI water and stirring at 120 °C for 2 h. The PVA solution was spin-coated on a 1 cm² sample of CVD-grown MoS₂ film on SiO₂(300 nm)/Si, at 1000 rpm for 10 s and 3000 rpm for 60 s, followed by a soft bake at 100 °C for 60 s in air. Following, a layer of PMMA (7-fold dilution, AR-PC-504 in AR 600–01, Allresist) was spin-coated on top, at 1000 rpm for 10 s and 3000 rpm for 60 s. The sample was then transferred using the same KOH etching procedure described above. For removal of the PVA/PMMA membrane, the sample was immersed in DI water, placed on a hot plate at 130 °C and stirred for ~30 min allowing the water-soluble PVA to be removed together with the PMMA film. The sample was then dried under N₂.

Transfer of CVD-Grown MoS₂ Monolayer Film onto SiO₂/Si Substrate by PS Method.³⁸ A polystyrene (PS) solution was prepared by dissolving 0.9 g of PS powder (Sigma-Aldrich, M.W. ~280 kmol/g) in 10 mL of toluene (Sigma-Aldrich, ≥99.0%) and stirring at room temperature (RT) for 30 min. The PS solution was then spin-coated on a 1 cm² sample of CVD-grown MoS₂ film on SiO₂(300 nm)/Si, at 3500 rpm for 60 s, followed by a soft bake at 80 °C for 15 min in air. Again, the film was transferred by etching the underlying SiO₂ using the KOH procedure above. After transfer, the assembly was heated on a hot plate at 80 °C for 1 h followed by 30 min at 150 °C, to dry the film and remove wrinkles. The PS was then removed by immersing the sample in toluene for 30 min, which was repeated twice before rinsing (IPA, Honeywell, ≥99.5%) and dried under N₂.

Transfer of CVD-Grown MoS₂ Flakes onto Samples with Pristine CVD-Grown MoS₂. The transfer process of CVD-grown MoS₂ monolayer flakes onto samples with pristine CVD-grown MoS₂ was analogous to the previously described transfer on SiO₂/Si by PMMA. The only deviation was in transferring the film onto a substrate with pristine, uncoated, CVD-grown MoS₂ on SiO₂/Si, instead of a bare SiO₂/Si substrate.

TOF-SIMS. TOF-SIMS analyses were performed on a PHI TRIFT V nanoTOF II instrument (Physical Electronics, Inc., USA). For surface measurements, the analysis beam (Ga⁺ 30 kV, 3 nA) was scanned over a predefined area together with a low energy electron flood and Ar^+ ion gun for charge compensation on the sample. For depth profiling, an additional sputter gun (Cs⁺ 0.5 kV, 30 nA) was used in interleaved dual-beam mode, eroding an area six times larger than the actual analysis area (located in the middle of the sputter crater to avoid edge effects). Spectra were obtained in negative or positive ion polarity. The elemental maps were produced from the spectral raw data files using the TOF-DR software (v 3.0.0.13, ULVAC-PHI, Inc., Japan). For detailed analysis of specific isotope patterns, the peaks were fitted with a modified asymmetric Lorentzian (LA) line shape (for details see SI) using the software CasaXPS⁶² (v 2.3.24PR1.0, CasaSoftware Ltd., U.K.) to extract their intensities.

Raman Spectroscopy. Raman spectroscopy was carried out with an WITec alpha300 R microscope (WITec GmbH, Germany), with a spectral resolution of ~0.5 cm⁻¹. Spectra were collected with acquisition times of 10 s and 0.5 mW laser power with a central wavelength of 532 nm, unless stated otherwise. Data analysis was conducted in the Project FIVE software (v 5.1.8.64, WITec GmbH, Germany). After background subtraction and removal of cosmic rays, the A_{1g} and ${}^{1}E_{2g}$ peaks were fitted with Lorentzian line shapes in the range of 355 to 420 cm⁻¹. **AFM.** AFM images were acquired using a Bruker NanoIR2 system (Bruker Inc., USA) with standard tapping probes (PR-EX-T125, 300 kHz, tip radius \sim 50 nm). The resulting topography images were extracted to Gwyddion software (v 2.52) for analysis and height profile measurements.

SEM. SEM images were acquired using a JEOL JSM-6700F instrument (JEOL Ltd., Japan) with 2 kV acceleration voltage and a working distance of 7 mm. Images were gathered with the secondary electron detector.

XPS. XPS measurements were performed on a PHI VersaProbe III system (Physical Electronics, Inc., USA), operated with SmartSoft-VersaProbe software (version 3.1.2.13, ULVAC-PHI, Inc., Japan). An Al K α X-ray line (1486.6 eV) was used as monochromated microfocused scanning X-ray source and a low energy electron flood and Ar⁺ ion gun for charge compensation on the sample. Survey and core-level spectra were collected with a pass energy of 224 and 26 eV, respectively. The spectra were shifted to a C 1s binding energy value of 284.8 eV in MultiPak software (version 9.8.0.19, ULVAC-PHI, Inc., Japan) and further analyzed with the software CasaXPS⁶² (version 2.3.24PR1.0, CasaSoftware Ltd., U.K.). A Shirley-type background was subtracted, and the core-level spectra were generally fitted with Gaussian–Lorentzian line shapes.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsnano.3c01649.

Additional experimental details, including materials, methods and data treatment. AFM topography and height scans, SEM images, XPS and Raman spectroscopy spectra, TOF-SIMS spectra and chemical maps of pristine and contaminated 2D materials and reference polymer/packaging materials (PDF)

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Notes

The authors declare no competing financial interest.

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ABBREVIATIONS

AFM, atomic force microscopy; SEM, scanning electron microscopy; TMD, transition metal dichalcogenide; TOF-SIMS, time-of-flight secondary ion mass spectrometry; XPS, Xray photoelectron spectroscopy

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