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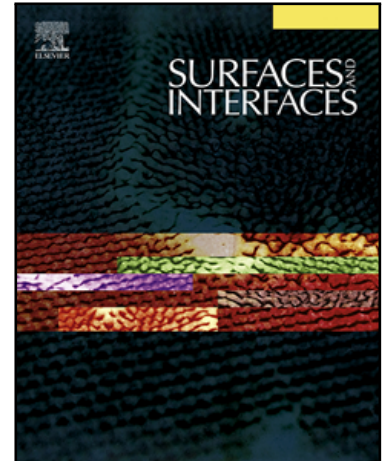
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Study of surface oxidation and recovery of clean MoTe₂ films

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Transporting the sample through different characterization units while maintaining its integrity is crucial if multiple surface sensitive probes are to be employed. In this context, the layered transition metal dichalcogenides (TMDs) are known to be extremely susceptible to ambient degradation, leading to the formation of protrusions and particles on the films. Compared to MoS₂ and MoSe₂, MoTe₂ is one of the most reactive surfaces to ambient conditions. Therefore, understanding its surface oxidation and how to recover a clean surface is very important. In this paper, we report the MBE synthesis of single phase of 2H-MoTe₂ with good stoichiometric films on graphene terminated 6H-SiC(0001) substrates and are able to recover the clean surface after exposure to air under properly protected conditions. Our films are analyzed in detail by reflection high energy electron diffraction (RHEED), X-ray photoemission spectroscopy (XPS), and scanning tunneling microscopy (STM).

I. INTRODUCTION

The layered quasi-two-dimensional transition metal dichalcogenides (TMDs) attract increasing research interest due to their particular electronic, optical, mechanical, chemical and thermal properties [1–6]. Unlike graphene (a unique two-dimensional system), their electrical properties can vary from superconducting to metallic and to semiconducting with tunable bandgaps that undergo transition from an indirect one in bulk crystals to a direct one in monolayer films. Like other TMD materials, MoTe₂ exists in multiple phases among which the most stable phases are hexagonal (2H) and monoclinic (1T'). The 2H phase is semiconducting while the 1T' is semi-metallic. Monolayer 2H-MoTe₂ has a direct bandgap about 1.1eV, the smallest among all semiconducting TMDs [7, 8], similar to the width of the indirect bandgap of Si. This makes it attractive for applications in electronics and optoelectronics. For the practical integration of MoTe₂ into devices, a thorough understanding of its surface and interfacial reactions is really needed.

A fundamental understanding of such reactions relies upon *in-situ* characterization methods conducted in ultra-high vacuum (UHV) in order to avoid contamination at the atomic level. In the present study, we have used molecular beam epitaxy (MBE) to grow high crystalline quality films with well controlled properties [9]. However, not all characterisation can be done in the same UHV unit and there is a need to move samples across characterization chambers.

A specific difficulty in surface science research and especially in the case of TMDs, is the transport of samples from one UHV system such as MBE to another system at a different location. TMDs are extremely susceptible to ambient degradation, displaying significant structural and morphological changes upon exposure to atmosphere [10]. Oxidation of the TMD thin films occurs preferentially at the grain edges inducing the formation of protrusions and

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particles on the films, leading to changes in the electronic properties of the films due to the formation of defect states [11, 12]. Besides the surface deformation, air exposure also results in an increase in the resistivity of the TMDs films and changes in the work function [13, 14]. This problem is more evident in the case of MoTe_2 , one of the most reactive surfaces to ambient conditions as effects of the oxidation are visible after a few minutes of exposure to air [15, 16]. This oxidation is inevitable as TMD tellurides are more prone to oxidation than their sulphide or selenide counterparts [17, 18]. Therefore, transporting the sample through different characterization units while maintaining its integrity is crucial if multiple surface sensitive probes are to be employed.

A possible method for moving samples between UHV chambers without breaking vacuum is to use a vacuum suitcase [19]. The available commercial vacuum suitcases are equipped with an ion pump to maintain UHV conditions as well as several battery packs for independent power supply. However, the ion pump and the battery packs make the vacuum suitcase heavy and difficult to handle. Moreover, the use of vacuum suitcase often necessitates modifications of the configuration of the UHV system [20]. Alternatively, a widely used method is to protect the sample surface with an *in-situ* capping layer deposited at room temperature (RT) thick enough to prevent oxidation to reach the actual sample surface. This method is effective if the capping layer can be removed by heating in UHV after the sample has been transferred through air. In general, Te and Se have been used for capping MBE synthesized TMDs. The high vapour pressure of these species under moderate temperatures makes them good candidates for capping layers and these can be easily removed by moderate annealing while maintaining the integrity of the surfaces [21–23]. However, not all analysis chambers possess the facility for thermal anneal or can pump out relatively high vapour pressure materials like Se and Te that otherwise contaminate adjoining systems. In addition, if the annealing is not precisely monitored during decapping process, there is a risk that the deposited films will be damaged or even carried off along with the oxidized Te layers. Effects of such capping layers on MoTe_2 for preventing oxidation during transfer through air has not been reported yet.

Through an understanding of the surface oxidation effect, one can stimulate the search for ways to preserve sample as long as possible for future applications. According to previous studies reported in literature, surface effects can significantly impact on the electrical transport properties [24–27]. Thus, it would be helpful for device fabrication if MoTe_2 TMD layers could present unaltered surface quality after exposure to ambient environment. Although it is highly desired, the studies of oxidation control have been rarely performed and characterized in details. In this work, we make a systematic study of surface oxidation on $2H$ - MoTe_2 as synthesized by MBE on graphene terminated $6H$ -SiC(0001) substrates [9] and are able to recover the clean surface after passing through unavoidable air exposure for *ex-situ* characterization. Under properly protected conditions, the sample can be reintroduced in the UHV chamber and a clean surface can be recovered with controlled annealing. Our films are analyzed in detail by reflection high energy electron diffraction (RHEED), X-ray photoemission spectroscopy (XPS), and scanning tunneling microscopy (STM).

II. EXPERIMENTAL DETAILS

We use a kinetically controlled multi-step MBE process to synthesize large scale single-layer $2H$ - MoTe_2 films on graphene as detailed in previous work [9]. Four sets of samples were produced with the same conditions (8-min deposition). Growth was monitored by reflection high energy electron diffraction (RHEED) (Riber). After growth,

samples were characterized by scanning tunneling microscopy (Park Autoprobe VP2 with an R9Plus controller from RHK Technology) and X-ray photoelectron spectroscopy (XPS) (K-Alpha spectrometer from Thermo Scientific with a monochromated Al $K\alpha$ X-ray source operating with an incident photon energy of 1486.6 eV). All measurements were made at room temperature. The scanning tunneling microscope is directly connected to the MBE chamber. Hence, STM images can be taken without exposing the samples to air. However, XPS is part of another UHV system, making transfer through air unavoidable. Before transfer of samples through air for XPS measurements, samples #2 and #4 are capped by a protective Te layer on top while samples #1 and #3 are not. Except for sample #1, other samples were placed in a clean dry box filled with nitrogen gas from a pressurized nitrogen gas cylinder ($\geq 99.9\%$ pure) whenever they were removed from a UHV system.

Although several sets of samples were prepared, we present our results here based on one representative sample from each of the four sets which are labelled and organized in order as follows:

Full exposure to air (~ 24 hours): sample #1 (MoTe₂ surface without Te cap), and reloaded in UHV-STM for recovery after XPS.

Preserved in nitrogen box (~ 24 hours): sample #2 (MoTe₂ surface with Te cap, decapped in XPS chamber and transferred back into UHV - STM to check surface topography and re-annealed to clean its surface), sample #3 (MoTe₂ surface without Te cap, and reloaded in UHV - STM after XPS for annealing to clean its surface), sample #4 (MoTe₂ with Te cap, preserved in nitrogen box for the same 24 hours as sample #2 for comparison, then reloaded and decapped in UHV - STM).

III. RESULTS AND DISCUSSION

Large STM image of pristine graphene and after formation of $2H$ -MoTe₂ films on graphene of sample #1 are shown in Figs. 1(a) and 1(b), respectively. Single layer of $2H$ -MoTe₂ can be observed together with a very small $2H$ -layer on top. RHEED pattern in the inset shows the diffraction streaks from the $2H$ -MoTe₂ deposited films and from the graphene substrate. The long streaks on RHEED pattern indicate a flat surface of the overgrown $2H$ -MoTe₂ films. Indeed, the flat domains are visible in Fig. 1(b), covering almost the underlying graphene substrate.

Thanks to the different contrast between two materials, the small parts of the exposed graphene can still be observed; they are marked by 'G'. The atomic resolution image is easily obtained by zooming on a small area as indicated on Fig. 1(b). This kind of structure is typical of a $2\sqrt{3}R30^\circ$ Moiré pattern of monolayer $2H$ -MoTe₂ on graphene which was already analyzed earlier [9] as shown in an inset of Fig. 1(b). It is evident that the as-grown layers are clean and of good crystalline quality. In order to investigate effects of air exposure on $2H$ -MoTe₂ films, the sample was removed from the UHV chamber and exposed to air for nearly one day (~ 24 hours). Exposure to air leads to changes in surface quality as seen on a STM image of sample #1 in Fig. 1(c). Root-mean-square surface roughness increases from 0.33 nm before exposure to air to about 0.42 nm after exposure. RHEED also confirms the loss of crystallinity (see inset of Fig. 1(c)). The corresponding XPS survey spectrum of this sample #1 is shown in Fig. 2 (a). Besides the peaks from Te and Mo (from the MoTe₂ layer) and Si and C (from the substrate), there is a significant amount of oxygen contamination. The formation of Te-O and Mo-O bonds in the films is confirmed by the higher resolution spectra of Te $3d$ (Fig. 2 (b)), and Mo $3d$ (Fig. 2 (c)).

The oxide peaks are clearly visible on Te $3d$ spectra (next to the Te- $3d_{5/2}$ and Te- $3d_{3/2}$ peaks) and Mo $3d$ spectra

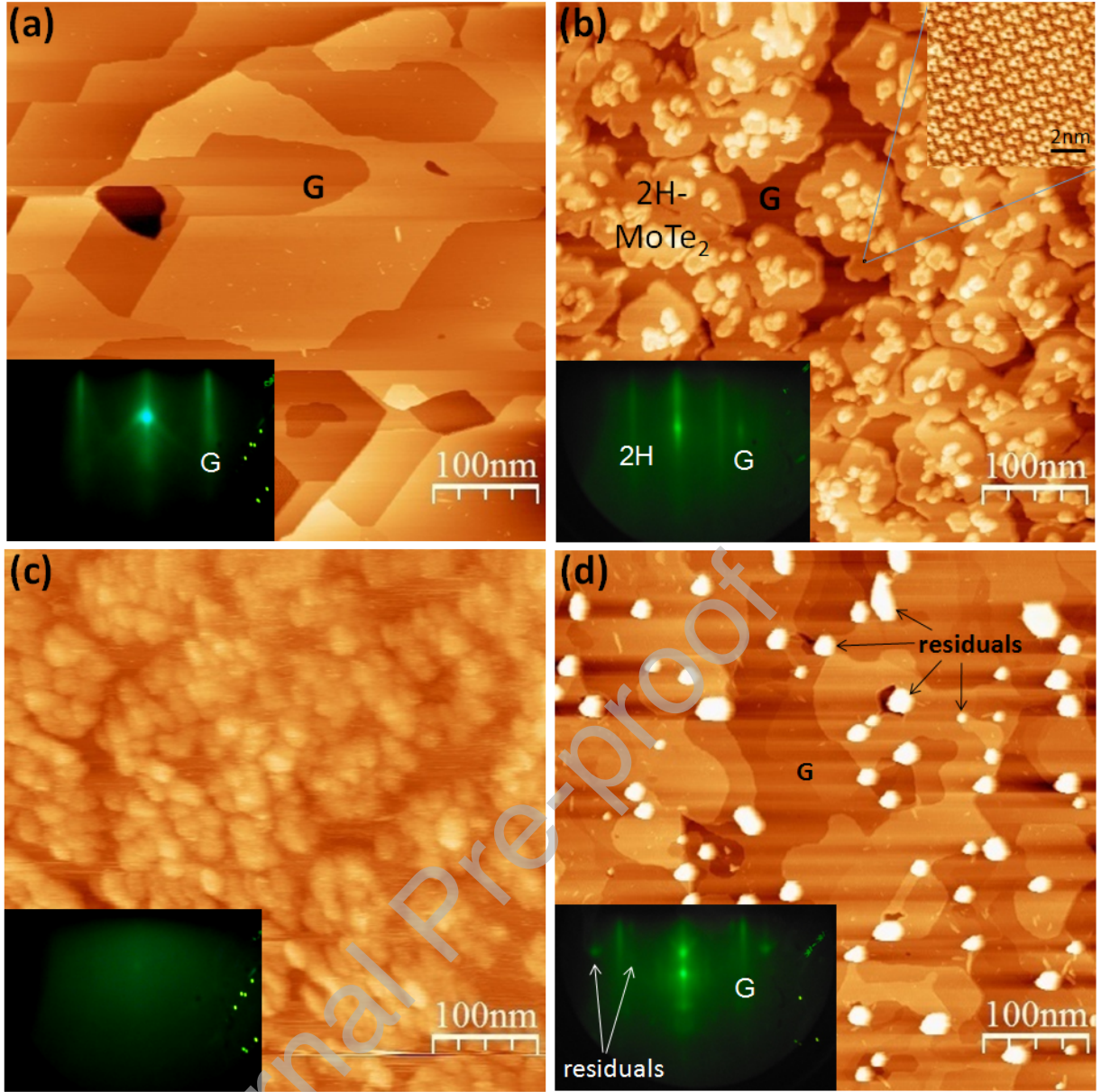


FIG. 1: $500 \times 500 \text{ nm}^2$ STM images of sample #1: (a) Pristine graphene on terminated $6H$ -SiC(0001) substrates ($V_{\text{Sample}} = +1 \text{ V}$, $I_{\text{Tunnel}} = 1000 \text{ pA}$) with the corresponding RHEED pattern from graphene. (b) after MoTe_2 growth with parts of the underlying graphene substrate as indicated by G ($V_{\text{Sample}} = -0.5 \text{ V}$, $I_{\text{Tunnel}} = 600 \text{ pA}$). The inset shows the RHEED image confirming the epitaxial growth of MoTe_2 on graphene together with an atomic resolution image in the inset showing a typical Moiré pattern of the $2\sqrt{3}R30^\circ$ monolayer $2H$ - MoTe_2 on graphene ($V_{\text{Sample}} = +0.2 \text{ V}$, $I_{\text{Tunnel}} = 1300 \text{ pA}$). (c) Surface topography of the MoTe_2 films after full exposure to air ($V_{\text{Sample}} = +1.3 \text{ V}$, $I_{\text{Tunnel}} = 500 \text{ pA}$) together with the RHEED pattern in the inset. (d) after annealing the sample in UHV - STM at $\sim 350^\circ\text{C}$ ($V_{\text{Sample}} = -0.5 \text{ V}$, $I_{\text{Tunnel}} = 200 \text{ pA}$).

(denoted as MoO_2 and MoO_3 by peak fittings), confirming oxidation of both Mo and Te in the MoTe_2 films.

The question is how to remove this oxide layer and recover the clean MoTe_2 films in a UHV chamber. Starting with sample #1, we gradually increased the sample temperature to 200°C while monitoring with RHEED, but the diffraction streaks of MoTe_2 did not appear (see Supporting Information Fig. S1). Thus, annealing was further continued up to 350°C . The substrate is maintained at this temperature for few minutes and RHEED pattern appears

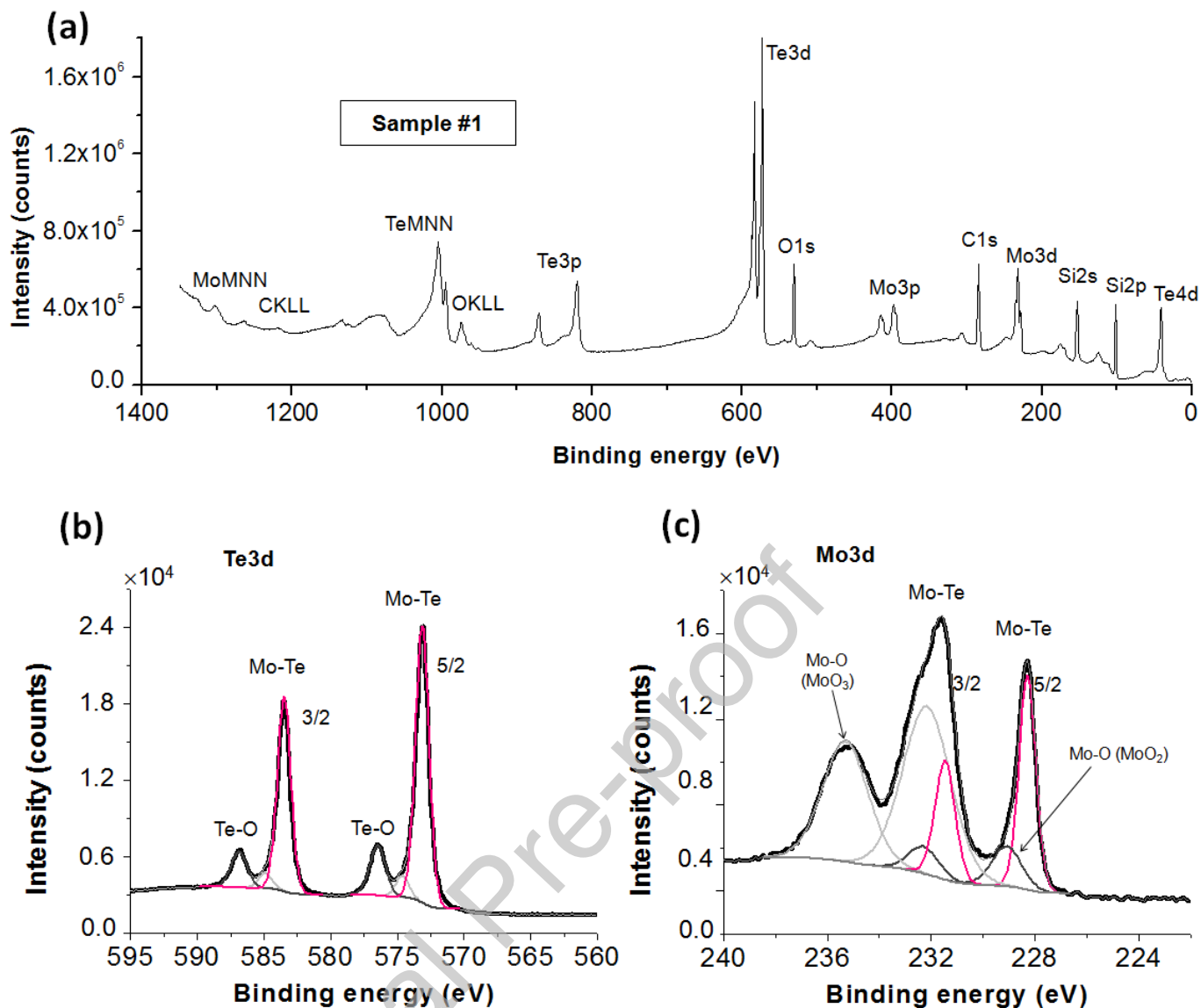


FIG. 2: XPS analyses of corresponding sample #1 after full exposure to air for handling XPS spectroscopy: (a) General survey showing quite high O 1s peak, indicating heavy surface oxidation. (b) a zoom-in of Te 3d, and (c) Mo 3d.

and then, allowed to cool it down to RT. STM topography image shows large areas of graphene and some remaining bright spots on the surface (Fig. 1 (d)) which could be from residual Mo bonded on the substrate (marked by black arrows). These contaminants are also visible in RHEED (see the inset) which shows some spots and very faint streaks near graphene. It is clear that graphene is recovered, but MoTe₂ is also removed by such heat treatment.

Actually, it is expected to see graphene instead of MoTe₂. Indeed, as MoTe₂ binds to graphene mainly through Van der Waals interaction, heating to a temperature that is sufficient to decompose MoO₃, MoO₂ and TeO₂ oxides will also lead to desorption of MoTe₂. Such behaviour has been observed on several samples, despite very accurate control of the sample temperature.

In order to protect the MoTe₂ films, a layer of pure Te was deposited before removing the samples from the UHV

system. The capping layer must be thick enough to prevent oxidation of the underlying MoTe_2 . However, they should not be unnecessarily thick because this would make their subsequent removal more difficult. Without a real-time monitoring technique like RHEED, there is a risk of damaging the MoTe_2 surface unless a precise calibration of removal process for each of the UHV chambers is done beforehand. **A few samples of MoTe_2 with such a coverage of the thin Te capping layer were produced and followed by the same air exposure as sample #1, then the annealing was also performed in the same UHV chamber, but the crystalline quality of the films could not be recovered (not shown here).** From this fact, one can conclude that a full exposure of MoTe_2 films with or without a coverage of protective Te layers to air always induces a heavy oxidation of the sample and degrades the crystalline quality of deposited MoTe_2 during annealing to recover the clean films.

To prevent surface oxidation due to air exposure during transportation as much as possible, we use a dry nitrogen box for the transfer process. From the MBE chamber, the samples with or without a protective layer can be transferred to the box. Details of transfer process are shown in supplementary information (Fig. S2). We compare the XPS spectra of two samples: sample #2 (MoTe_2 capped with Te and decapped in XPS chamber) and sample #3 (MoTe_2 preserved in nitrogen box without Te cap) to understand the surface behaviour.

In order to compare the Mo-Te peaks before and after decapping Te layers, we work with thin capping layers; otherwise only Te peak from protective Te layers would be detected. Another advantage of thin capping layers is that they need only short annealing at moderate temperatures for their removal. **In this work, the thickness of protective Te layer is estimated about 5nm.** The XPS spectra of sample #2 (capped with Te in MBE chamber and subsequently uncapped in the XPS at $\sim 200^\circ\text{C}$ for 10min under a base pressure $\sim 10^{-8}$ mbar) together with sample #3 without protective Te layer are shown in Fig. 3.

With a protective Te layer on the MoTe_2 surface, the XPS survey spectrum shows a very small Mo 3d peak located at ~ 228 eV which could be still visible while the Te 3d peak at ~ 573 eV is broad and quite strong (Fig. 3(a)). This signal is dominated by the Te capping layers rather than from the underlying MoTe_2 layers due to the thick protective Te films formed on top. Details in the formation of Te-Te and Mo-Te bonds will be examined later by focussing on the higher resolution spectra of Te 3d and Mo 3d in Fig. 4. When the sample is heated to desorb Te atoms, the surface composition is recovered (Fig. 3(b)). Comparison of spectra from MoTe_2 transferred under nitrogen atmosphere (Fig. 3(c)) and samples coated with Te and decapped after transfer through nitrogen atmosphere (Fig. 3(b)) show that both methods produce samples with similar surface composition. However, there is the small oxygen contamination after decapping which comes from outgassing during heating sample #2 in the XPS chamber, as this system is not optimized for heating under UHV conditions.

More information about surface chemistry is obtained from Mo 3d and Te 3d spectra as shown in Fig. 4 in combination with a summary of the stoichiometric determination from XPS spectra as given in Table I. We analyze spectra from sample #2 (MoTe_2 coated with Te and transferred through nitrogen box) before and after heating in the XPS system and those from sample #3 (MoTe_2 transferred through nitrogen box). For MoTe_2 coated with Te, Fig. 4(a) shows the $\text{Mo-}3d_{3/2}$ and $\text{Mo-}3d_{5/2}$ peaks corresponding to Mo-Te bonds at ~ 231.34 eV and ~ 228.15 eV respectively. These peaks are strongly attenuated by the Te capping layer. However, the peaks are enhanced after recovering the sample surface due to increased detection of the Mo-Te bonds in the MoTe_2 films (Fig. 4(b)) and are located at ~ 231.43 eV and ~ 228.24 eV respectively. These values are very close to those of sample #3, where $\text{Mo-}3d_{3/2}$ and $\text{Mo-}3d_{5/2}$ peaks corresponding to Mo-Te bonds occur at ~ 231.43 eV and ~ 228.28 eV respectively (Fig. 4(c)).

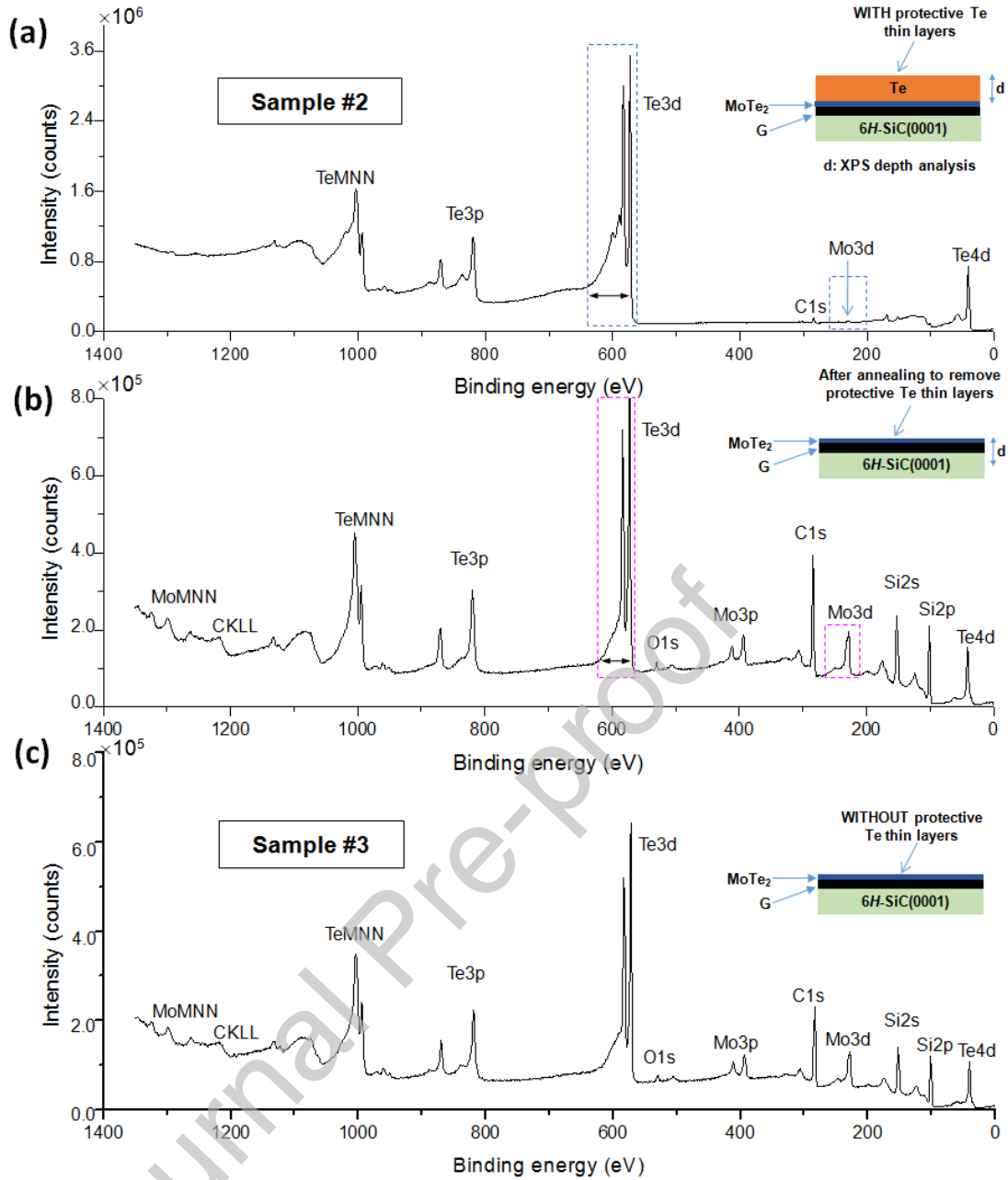


FIG. 3: Survey XPS spectra of samples #2 and #3: (a) Sample #2 capped with Te in UHV-STM, (b) After the removal of the capping layer in XPS chamber. The difference on the vertical intensity scale is highlighted. XPS depth analysis is indicated by d. (c) Sample #3 without protective Te layer for comparison with sample #2 after decapping.

$\text{Te-}3d_{3/2}$ and $\text{Te-}3d_{5/2}$ peaks corresponding to Mo-Te and Te-Te bonds for the capped sample are located at ~ 583.43 eV and ~ 573.04 eV respectively (Fig. 4(d)). The Te cap contributes strongly to the Te signal. A plasmon loss (marked by Te^* in the red box) at ~ 591 eV is attributed to elemental Te. Once annealed, the plasmon satellite peak disappears (Fig. 4(e)). The $\text{Te-}3d_{3/2}$ and $\text{Te-}3d_{5/2}$ peaks corresponding to only Mo-Te bonds occur at ~ 583.45 eV and ~ 573.06 eV respectively. After heating, the full width at half maximum (FWHM) of $\text{Te-}3d$ peaks increases from 0.85 eV to 0.93 eV. This is due to the fact that the Te signal comes from Te in MoTe_2 rather than elemental Te. For sample #3, the $\text{Te-}3d_{3/2}$ and $\text{Te-}3d_{5/2}$ peaks corresponding to Mo-Te bonds are located at ~ 583.47 eV and ~ 573.07

Mo3d spectra

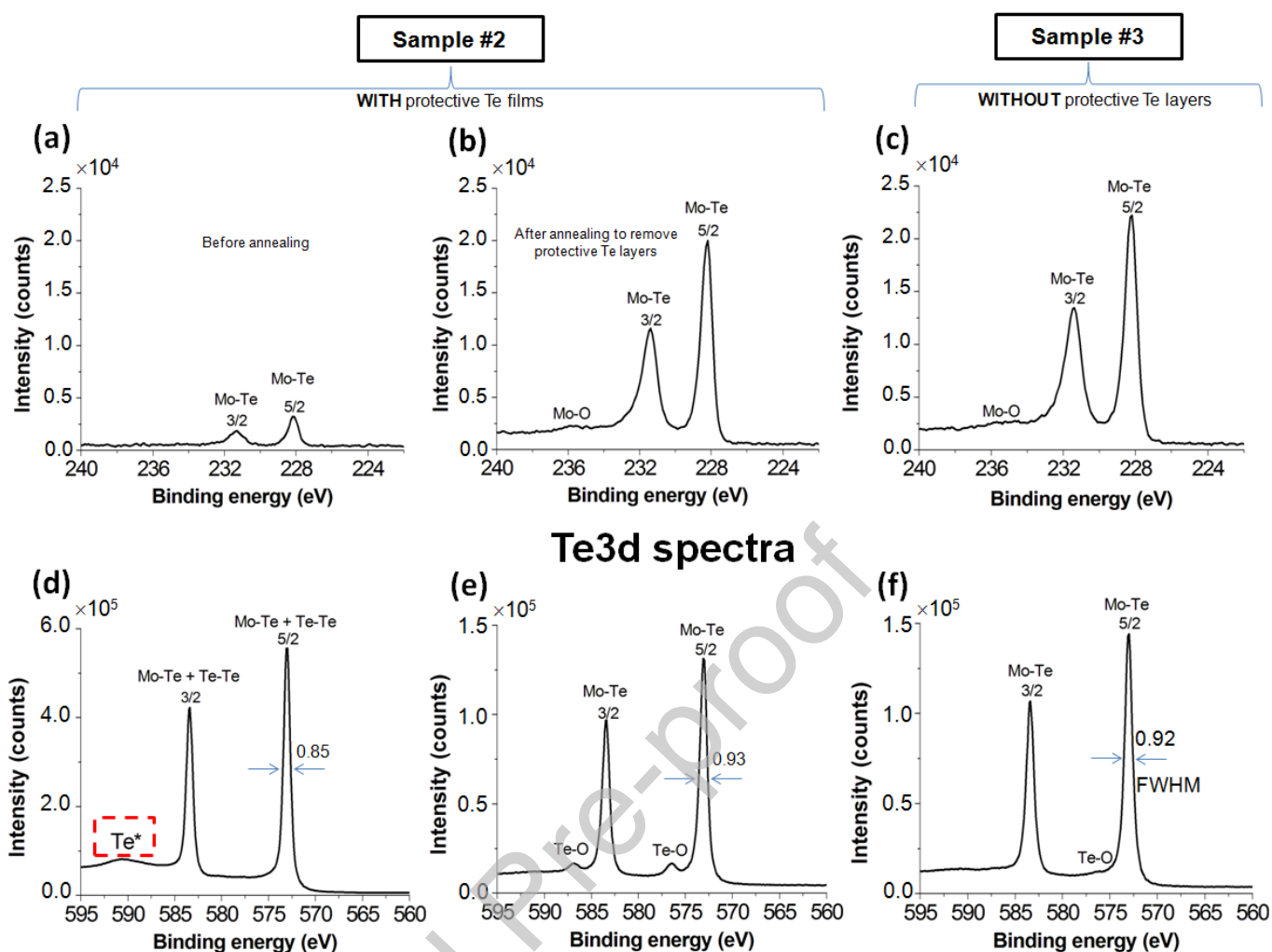


FIG. 4: Mo 3d and Te 3d spectra of samples #2 and #3: (a) and (b) Mo 3d spectra of sample #2 capped with Te and uncapped in XPS respectively. (c) Mo 3d spectra of sample #3 without protective Te layer. Corresponding (d) and (e) Te 3d spectra of sample #2 capped with Te and uncapped in XPS respectively. The boxed region in (d) corresponds to the plasmon loss due to metallic bonding of elemental Te. (f) Te3d spectrum of sample #3.

eV respectively (Fig. 4(f)). Their FWHM is ~ 0.92 eV, very similar with the one of sample #2 after removing the protective Te layer.

After thermally removing the Te cap layer, small oxide peaks appear at 236 eV (Mo-3d, Fig. 4(b)) and near 576 eV and 587 eV (Te-3d, Fig. 4(e)). They are due to the presence of MoO_3 and TeO_2 [28, 29]. As mentioned earlier, such surface oxidation is related to the annealing of the sample in the XPS chamber where the sample holder is not designed for heating samples under UHV conditions. Compared to sample #3, the intensity of Mo-Te peaks of sample #2 after annealing are very similar, confirming the successful removal of protective Te layers. In addition, sample #2 is re-annealed in the UHV-STM chamber (under a base pressure $\sim 10^{-11}$ mbar) to improve its surface quality and another XPS measurement was taken (see the numerical results in Table I).

One can see the relative upshift in Mo-Te peaks of Mo 3d and Te 3d of sample #1 with a full coverage

Sample No.	Sample status	Sample surface	Binding energy (eV)*				$\Delta E(eV)$ Mo-Te 3d _{5/2}	Atomic ratio (Te/Mo)	Ref.
			Mo3d		Te3d				
//	//	//	3d _{3/2}	3d _{5/2}	3d _{3/2}	3d _{5/2}	//	//	//
#1	full exposure to air	without protective Te layers	231.46	228.32	583.51	573.13	344.81	2.18	This work
#2	preserved in dry N ₂ box	with protective Te layers	231.34	228.15	583.43	573.04	344.89	77.62	This work
		after annealing in XPS to recover MoTe ₂	231.43	228.21	583.45	573.07	344.86	2.44	This work
		after re-annealing in UHV	231.40	228.30	583.47	573.07	344.77	1.98	This work
#3	preserved in dry N ₂ box	without protective Te layers	231.43	228.28	583.47	573.07	344.79	2.15	This work
Reference sample	CVD synthesis	single crystal	231	227.8	583	572.6	344.80	2.125	[29]

*Graphene: C1s ~284.6 eV.

TABLE I: XPS analyses of various samples

of oxide layers compared to samples #2 and #3 (preserved in dry N₂ box). This can be explained by the higher electronegativity of oxygen compared with Mo and Te atoms which results in a decrease of the electron density around Mo and Te leading to the increase in binding energy [6, 15]. The upshifting to higher binding energy of Mo-Te peaks after oxidation of MoTe₂ films by air-exposure is also reported by Diaz et al. [30]. The upshift in these cases is not due to the doping effects. However, it is worth noting that Refs. [16, 31] reported the downshift of the Mo-Te peaks in Mo 3d and Te 3d to lower binding energy after surface oxidation via O₃ exposure [16] or by O₂ plasma treatments [31] which are attributed to hole doping effects in MoTe₂ films. The possible explanation for the discrepancy between our results and literature in this aspect is derived from the different mechanisms of oxygen exposure. In our case, the MoTe₂ surface is gradually oxidized under the exposure of sample to air (sample #1 with full exposure) with the fact that MBE-grown MoTe₂ has the superclean surface with the chemical instability due to the weak Mo-Te bond energy as reflected in the small electronegativity difference between Mo and Te [32]. As a result, amorphous oxide layer is completely covered on the surface. The broadening and shifting in the Mo-3d_{3/2} peak (see Fig. 2 (c)) toward higher binding energy suggests that oxidation strongly occurred in the sample rather than doping effects. For less oxidized samples #2 & #3, the oxidation effect is very weak, the position of Mo-Te peaks is almost not shifted as expected.

By measuring the integrated peak area (I) and using sensitivity factors (SF) 5.4, 1.66 corresponding to the peaks Te-3d_{5/2}, Mo-3d_{5/2} respectively, the atomic ratio can be calculated by [33]

$$\frac{\text{Te}}{\text{Mo}} = \frac{I_{\text{Te}3d_{5/2}}/\text{SF}_{\text{Te}3d_{5/2}}}{I_{\text{Mo}3d_{5/2}}/\text{SF}_{\text{Mo}3d_{5/2}}}$$

Comparing the Te:Mo ratio with the single crystal of 2H-MoTe₂ as reported by Bernede et al. [29], it can be concluded that sample #2 (after annealing in UHV) and sample #3 present stoichiometric films.

Further characterization was focussed on the O 1s spectrum of all measured samples for comparison in Fig. 5. For better evaluation, the surface topography of corresponding samples is also shown together in the inset. With the same vertical scale for all the spectra, it is obvious that the amount of oxygen varies strongly among different samples. The highest intensity of the O 1s peak is observed on sample #1 (full exposure to air) in Fig. 5 (a) while there is little oxide on sample #3 (preserved in the dry N₂ box) in Fig. 5 (d). Some oxide appears in sample #2 after removing the Te cap layer in XPS chamber (see explanation above) in Fig. 5 (c). Compared to samples #1 and #2 (after decapping), the surface of sample #3 exhibits the lowest surface oxidation.

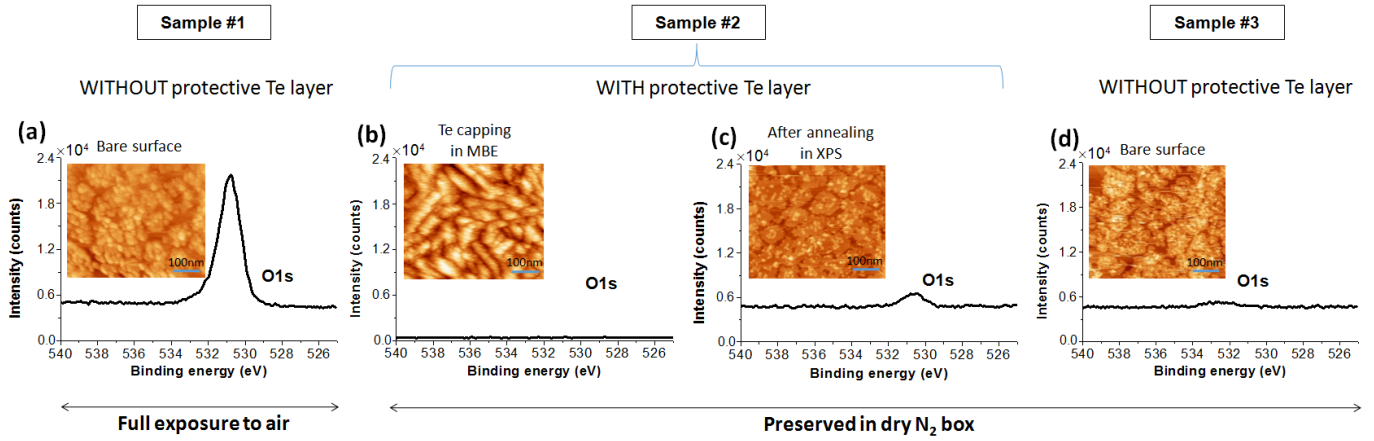


FIG. 5: The O 1s core level on corresponding samples showing different topographic images as seen in the inset, respectively: (a) #1, (b) #2 (with capped Te layer in MBE chamber) and (c) with decapped Te layer in XPS chamber, (d) #3 for comparison between different degrees of surface oxidation.

To confirm the surface structure, STM images are acquired for samples #2 and #3 as shown in Fig. 6. First, large scale STM images were taken on sample #2. The as-grown sample (Fig. 6(a)) reveals a uniformly distributed $2H$ -MoTe₂ domains on graphene.

The single-crystalline quality of $2H$ -MoTe₂ films is confirmed by bright RHEED diffraction streaks in the inset. After the deposition of the capping Te layer on the surface (Fig. 6(b)), the surface becomes quite rough, as expected for room temperature deposition, with a root mean square (RMS) roughness ~ 0.5 nm compared to ~ 0.28 nm for bare $2H$ -MoTe₂ films/graphene on this sample. The RHEED pattern in the inset shows only diffraction streaks from such a rough Te capping layer. $2H$ -MoTe₂ streaks are no longer observed, indicating that the surface is completely covered by Te. The sample is decapped in the XPS chamber as seen in Fig. 6(c). Although the surface topography shows a recovery, STM image indicates an unclear surface with non-ideal scanning conditions which could be due to the residual oxide formation as suggested by the XPS characterization (see Figs. 4(b) & (e)). Indeed, the corresponding RHEED pattern in the inset shows very faint streaks, suggesting that the surface is still contaminated. Annealing the film in UHV-STM chamber later cleans the sample surface as confirmed by STM image with its corresponding RHEED pattern in the inset of Fig. 6(d).

The as-grown sample #3 also shows flat domains of $2H$ -MoTe₂ with a nice RHEED pattern in the inset (Fig. 6(e)), similar to sample #2. After XPS measurement (the XPS analysis was performed on this sample without the annealing treatment), the sample is reloaded in the UHV - STM chamber and its surface is checked. Although STM image is not really sharp, the surface of sample #3 still shows domains of MoTe₂ (Fig. 6(f)), indicating that its surface is much less contaminated than that of sample #1 after full exposure to air (Fig. 1(c)). Then, the sample was annealed at $\sim 200^\circ\text{C}$ for 10min and the result is shown in Fig. 6(g). The crystalline quality of recovered films can be confirmed by corresponding RHEED pattern in the inset and its STM image in Fig. 6(h).

For practical applications, it may be necessary to store samples outside of UHV conditions for extended periods. In order to check the effect of such extended storage, we have removed sample #3 from the UHV chamber, kept it in the dry N₂ box for one week and then, reloaded into the UHV system. STM shows that the crystalline quality of MoTe₂ is preserved (supplementary information Fig. S3).

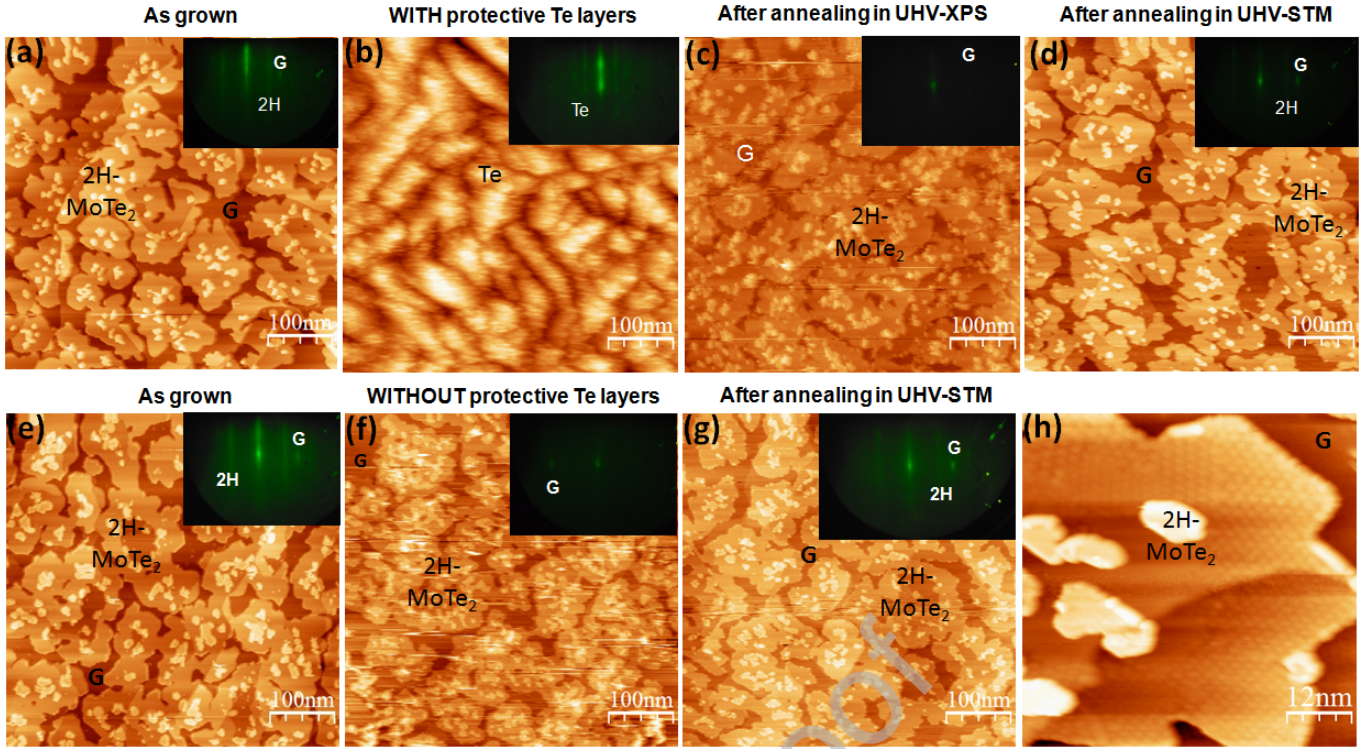


FIG. 6: STM images of sample #2: (a) As-grown surface ($V_{Sample} = -0.5$ V, $I_{Tunnel} = 700$ pA), (b) STM image after the deposition of Te capping layer ($V_{Sample} = +2.5$ V, $I_{Tunnel} = 1000$ pA), (c) The sample after desorbing the Te layer in XPS chamber ($V_{Sample} = -1.6$ V, $I_{Tunnel} = 1000$ pA), (d) Recovered sample after re-annealing in the UHV-STM ($V_{Sample} = -0.6$ V, $I_{Tunnel} = 1400$ pA); STM images of sample #3: (e) As-grown surface ($V_{Sample} = -0.5$ V, $I_{Tunnel} = 1000$ pA), (f) The surface topography after XPS measurement ($V_{Sample} = 0.7$ V, $I_{Tunnel} = 1300$ pA), (g) The recovered surface after annealing in UHV-STM ($V_{Sample} = +1.4$ V, $I_{Tunnel} = 400$ pA), (h) Close-up STM image confirms the clean MoTe₂ surface ($V_{Sample} = -0.8$ V, $I_{Tunnel} = 400$ pA). RHEED patterns are attached in the inset of corresponding STM images for crystalline quality reference.

To further understand the effect of annealing in UHV to recover a clean MoTe₂ surface, we prepared another sample capped with a Te layer and kept in a dry N₂ box for 24 hours and then, re-introduced in the UHV-STM chamber to remove the protective Te layers. This is very similar to sample #2; the only difference is that the Te layer was desorbed in the STM system instead of the XPS chamber and that XPS spectra were not recorded on this sample. This sample is labelled as sample #4 and shown in Fig. 7.

The surface topography of sample #4 displays clean domains of MoTe₂ on graphene, very similar to sample #2 (Fig. 7(a)). A height profile along the blue line shows the height of monolayer between 5 Å to 7 Å. This height is consistent with the model outlined in previous work [9]. The root mean square (RMS) surface roughness is ~ 0.3 nm. Next, a capping layer of Te is deposited on this sample (Fig. 7(b)). Irregularly formed islands cover the surface, inducing higher surface roughness (~ 0.5 nm). Only RHEED diffraction streaks from such Te capping layers are observed, 2H-MoTe₂ streaks are no more detected as seen in the corresponding inset. After keeping the sample in a dry N₂ box for 24 hours, it is reintroduced in the UHV-STM chamber and slowly annealed up to 200°C (10min). RHEED pattern in the inset of Fig. 7(c) after removing the protective Te layers is quite bright with clear diffraction streaks for MoTe₂, nearly the same as the pristine pattern in Fig. 7(a). The topography image is also very similar to the pristine surface with almost the same height of the monolayer as indicated in the height profile along the red line

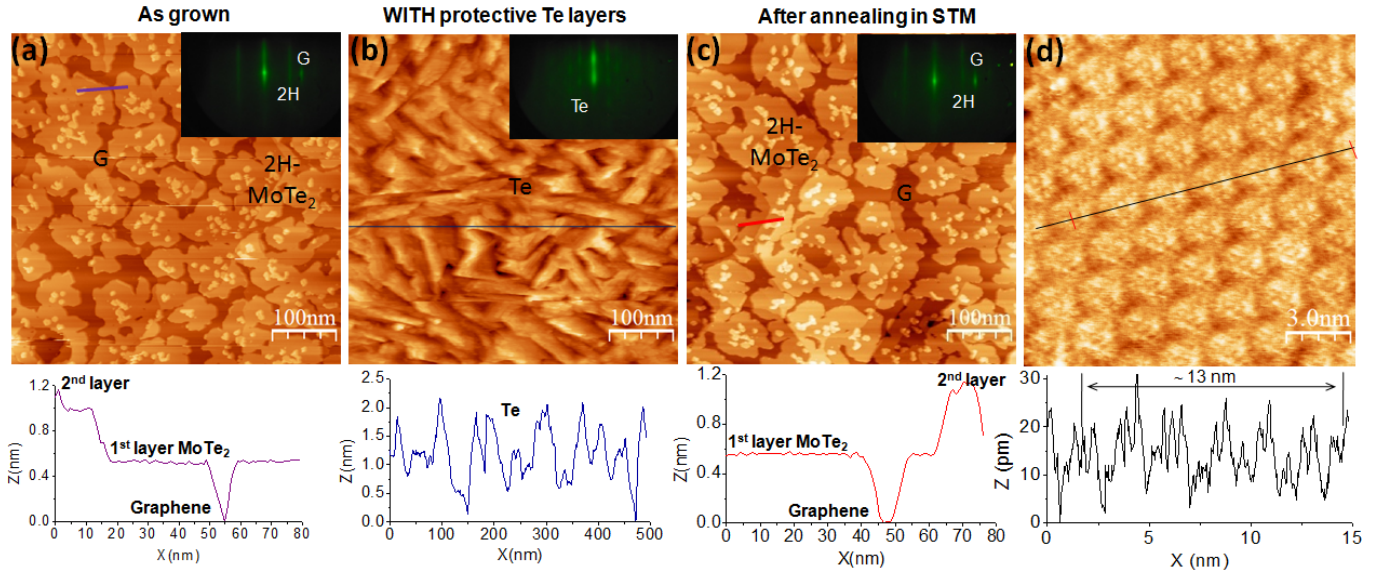


FIG. 7: STM images of sample #4: (a) As-grown surface of $2H$ - MoTe_2 ($V_{\text{Sample}} = -0.5$ V, $I_{\text{Tunnel}} = 700$ pA), (b) STM image after the deposition of Te capping layer ($V_{\text{Sample}} = -0.5$ V, $I_{\text{Tunnel}} = 1000$ pA), (c) recovered sample after reloading and annealing in UHV-STM ($V_{\text{Sample}} = -0.5$ V, $I_{\text{Tunnel}} = 600$ pA), and (d) Atomic resolution was nicely observed after recovering $2H$ - MoTe_2 ($V_{\text{Sample}} = -0.2$ V, $I_{\text{Tunnel}} = 2000$ pA). RHEED patterns are attached in the inset of corresponding STM images. In each image, the height profile along the line is given below, respectively. G stands for graphene and $2H$ stands for $2H$ - MoTe_2 .

and a nice atomic resolution from the $\sqrt{39}R33.2^\circ$ Moiré pattern of monolayer $2H$ - MoTe_2 on graphene was obtained (Fig. 7(d)), confirming perfect recovery of sample #4.

From XPS analysis, one can see that a reasonably pure Mo-Te peak is present in sample #3 (see supporting information in Fig. S4). Although its STM image shows instabilities, domains of monolayer $2H$ - MoTe_2 can still be observed. Unlike sample #1 (full exposure to air), the surface of sample #3 (preserved in N_2 box) still remains quite good quality after transportation through air. Between samples #2 and #4 (capped with protective Te layers), sample #4 shows much better surface quality after decapping in UHV-STM, comparable to its pristine surface. Compared to sample #3 (without capped Te layers), the surface of sample #4 has slightly better quality after annealing to desorb the oxide layers as can be seen on its stable STM image. This can be understood by the direct exposure of the MoTe_2 surface to air during transferring process (even very short time) of sample #3 which also makes it difficult to remove any remaining oxide due to strong covalent Te-O and Mo-O bonds in the films. **From experiments, one can suggest that capping the sample with protective Te layers and storing in a dry N_2 box (sample #4) would perfectly protect the MoTe_2 films from any contact with oxygen, favoring annealing to recover the surface quality of the sample.** However, the disadvantages of sample #4 might be considered if the sample cannot be annealed for *ex-situ* characterization such as scanning electron microscopy (SEM), transmission electron microscopy (TEM) or Raman spectroscopy. In this context, preparation of samples without protective Te layers like sample #3 within preserving in dry N_2 box is preferable and more convenient for further measurement and fabrication.

IV. CONCLUSIONS

In conclusion, we obtained nice stoichiometric films of mono-/double-layer 2H-MoTe₂ by using a multi-step process and appropriate MBE conditions. The effect of exposing samples to air and N₂ atmosphere is carefully examined. It is clear that effects of oxidation impact significantly on the crystalline quality of the films, leading to certain difficulties in *ex-situ* measurements. The full exposure of MoTe₂ films to air causes a complete change of the surface properties, making it no longer suitable for further characterization. In particular, it is impossible to recover clean MoTe₂ films. In this context, our work demonstrated an effective method to improve the efficiency of *ex-situ* sample transfer between vacuum chambers. **While capping with a protective layer is a well known practice, our experimental evidence by RHEED, STM and XPS shows that an inert atmosphere such as a dry nitrogen box, substantially preserves the crystalline quality of transferred films both capped with Te layers or not and makes it easier to recover the clean MoTe₂ surface.**

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