

Cite this: *Nanoscale*, 2017, 9, 13910Received 10th July 2017,
Accepted 27th August 2017

DOI: 10.1039/c7nr04998f

rsc.li/nanoscale

Passivating 1T'-MoTe₂ multilayers at elevated temperatures by encapsulation†

Dennis Wang,^a Kori Smyser,^{b,c} Daniel Rhodes,^d Luis Balicas,^e
Abhay Pasupathy^d and Irving P. Herman^f*

Several-layer 1T'-MoTe₂ decomposes very little during heating up to ~550 °C under flowing argon when encapsulated by multilayer hBN, as monitored by Raman scattering and optical microscopy, but largely decomposes at much lower temperatures in incompletely covered and uncovered regions. In covered regions there are small amounts of tellurium product above ~250 °C.

Transition metal dichalcogenide (TMD) van der Waals (vdW) materials are potentially important because of their optical and electronic properties. Their prospective applications come from these properties and also from their promising electrocatalytic activity in hydrogen evolution and hydrodesulfurization reactions.^{1–3} In particular, the 2H (or α) phase of MoTe₂ becomes a direct bandgap semiconductor in the one-to-few monolayer limit and the less-studied 1T' (or β) phase is thought to be a possible quantum spin Hall insulator in the monolayer form.⁴ Recent work suggests limited stability of the several-layer TMD materials at elevated temperatures.^{5–8} These observations and the likely need to operate under such conditions during processing and applications are a potential concern, more so for the tellurides than for the sulfides and selenides. Bulk and few-layer 2H-MoTe₂ have been studied at high temperature,⁹ but the 1T' phase has been studied only in the bulk form.¹⁰ Here, we explore the stability of several-layer 1T'-MoTe₂ to understand and improve the high-temperature operation under a variety of conditions, including hexagonal-phase boron nitride (hBN) encapsulation. vdW encapsulation

is known to be a good means of passivating other vdW layers¹¹ and other nanolayers.¹² We monitor the stability of 1T'-MoTe₂ at elevated temperature (T) with *in situ* optical microscopy and Raman scattering; along with this, we see how 1T'-MoTe₂ Raman peak frequencies vary with T .

MoTe₂ was grown as in ref. 13. It was mechanically exfoliated onto 285 nm SiO₂ on Si chips and located by optical contrast during x - y scanning, and encapsulated by hBN *via* standard transfer procedures in a nitrogen-filled glovebox with 7 ppm or less of O₂. The hBN was exfoliated outside the glovebox and then picked up by slowly “stamping” a poly(propylene carbonate) (PPC)-covered piece of polydimethylsiloxane (PDMS) onto the desired piece of hBN and peeling off at 42 °C. Then, inside the glovebox the hBN was positioned atop the MoTe₂, contacting it at 30 °C and letting it stick permanently when the PPC melted upon heating to 85 °C. The chips were soaked in acetone overnight outside the glovebox and cleaned with isopropyl alcohol (IPA) to remove any remaining PPC residue.

Subsequent testing and analysis were performed outside the glovebox, with temperature cycling in a THMS600 Linkam cell. Atomic force microscopy (AFM) determined the thickness and uniformity of the MoTe₂ and hBN. Each 1T'-MoTe₂ flake had a range of thicknesses; the thinnest region was studied and this thickness is mentioned here. On one chip a 9 nm (~6 unit cells) MoTe₂ flake, called Sample 1, was covered by 13 nm (~40 layers) hBN. On a second chip there were two flakes at different sites: a 4–5 nm (~3 unit cells) flake covered by 10 nm (~35 layers) hBN, called Sample 2, and a 4 nm (~3 unit cells) flake covered by 5 nm (~16 layers) hBN, called Sample 3. These flakes, including the locations of the thinnest region and of nearby flakes, and the lateral extent of the hBN coverage, are shown in Fig. S1 and described in Table S1 in the ESI.† The contrast was increased by 40% to make all the provided optical micrographs clearer. Sample 2 was totally covered. The examined, covered thin part of Samples 1 and 3 adjoined thicker parts of the flakes that were uncovered. Within the Linkam cell, *in situ* optical images were taken with a long-working-distance 50 $\times$ objective and Stokes Raman

^aDepartment of Applied Physics and Applied Mathematics, Columbia University, New York, NY 10027, USA

^bColumbia Optics & Quantum Electronics IGERT REU Program, Columbia University, New York, NY 10027, USA

^cMontana State University, Bozeman, MT 59717, USA

^dDepartment of Physics, Columbia University, New York, NY 10027, USA

^eDepartment of Physics and National High Magnetic Field Laboratory, Florida State University, Tallahassee, FL, 32310, USA

^fDepartment of Applied Physics and Applied Mathematics, Columbia University, New York, NY 10027, USA. E-mail: iph1@columbia.edu

†Electronic supplementary information (ESI) available. See DOI: 10.1039/c7nr04998f

spectra were acquired at the same point on MoTe₂ in the covered regions as seen in Fig. S1 in the ESI† during the temperature cycles (514.5 nm argon-ion laser, 0.2–0.3 mW, ~1 μm spot size, 120 s).

In Run 1, the Sample 1 flake was heated in ambient air from 50 to 500 °C, in 50 °C increments, with a 2 min wait at each temperature before Raman analysis (Table S2 in the ESI†). Optical microscopy showed degradation and then the disappearance of the 1T'-MoTe₂ starting at ~300 °C in regions not covered by hBN and at ~400 °C in covered regions, and so measurements were not made during cooling. This flake exhibited severe discoloration and shrank from the outskirts of the flake inwards with increasing temperature, first in the uncovered regions and then in the covered regions. Six to eight MoTe₂ Raman peaks were usually identified at room temperature in each MoTe₂ sample, from ~96 to 253 cm⁻¹,^{14,15} in addition to the Si peak near 520 cm⁻¹. These peaks essentially disappeared at 450 °C in this run, as seen in Fig. S2 in the ESI†.

In order to try to understand this deterioration and delay its onset with increasing temperature (relative to that in Run 1), Samples 2 and 3 were studied on the same chip and so at the same temperature, under an Ar flow (1 atm, 5 sccm), finer temperature control and higher temperatures, and different hBN coverage: Sample 2 was totally covered by hBN (Fig. 1a) and Sample 3 was only partially covered (Fig. S1c in the ESI†). After storing the chip in a vacuum desiccator for five days, in Run 2 the chip was heated from room temperature to 50 °C, and then 100–300 °C in 50 °C increments and cooled by the reverse procedure. Then to explore higher temperatures, in Run 3 the same chip, again after storing the chip in a vacuum desiccator for five days, was heated from room temperature, first to 100, 200 and 300 °C, and then to 325, 100, 350, 100, 375, 100, ..., 600, 100 °C (Table S2 in the ESI†). Raman and optical microscopy measurements were conducted at each temperature after waiting for 5–10 min; at each temperature above 300 °C, the optical micrographs are sharper in the sub-

sequent 100 °C cycle and so they are presented here. The waiting period at each temperature was longer than that in Run 1 to better compensate for sample motion caused by cell thermal expansion. Such expansion led to optical defocusing and lateral motion and the need to move the cell to enable taking Raman spectra at the same single spot in Samples 2 and 3 at each temperature, using landmarks within the thinnest region in the covered flake (Fig. S1 in the ESI†). In Run 3, during optical microscopy the laser was attenuated more than in Run 2, by using additional neutral density filters, to decrease the observed laser spot size and improve spot relocation. Regions in Sample 2 were analyzed with AFM after the Run 3 sequence.

The optical micrograph in Fig. 1a shows Sample 2 and the laser spot used for Raman probing (red arrow) before the heating cycles. Sample 2 remained largely unchanged during Run 2 to 300 °C and also up to ~550 °C in Run 3 (Fig. 1d). At higher temperatures, the Sample 2 flake became a bit smaller and slightly discolored starting at 550 °C, though much of it survived visually unchanged up to 600 °C (Fig. 1f), including the region probed by Raman scattering. Also, there was no observable evidence of photodegradation in this region after ~80 min of integrated irradiation during Runs 2 and 3.

Small, uncovered flakes below Sample 2 decomposed between 200 and 300 °C during Run 2 (Fig. S3 in the ESI†). The uncovered regions of the partially covered flake above and to the right of Sample 2 began to decompose at 300 °C (Run 3) and were no longer present at and above 350 °C (Fig. 1b and c). Then, the covered regions of that flake began to decompose near 400 °C, and continued to decompose as the temperature increased and were virtually no longer present at 600 °C (Fig. 1c–f).

Discolorization and deterioration were clear above 350 °C (Run 3) for the covered regions of Sample 3 and it became very pronounced at 425 °C (Fig. S4 in the ESI†). (The MoTe₂ Raman peaks became so weak that this sample was not probed by Raman scattering at higher temperatures.)

Representative Raman spectra of covered 1T'-MoTe₂ (Sample 2) are shown in Fig. 2 during Run 2 and in Fig. S5 in the ESI† during Run 3. At room temperature, the main peaks aside from the Si peak were due to MoTe₂, at 112 (assigned to A_g),¹⁵ 128 (A_g),^{15,16} 164 [(A_g)¹⁶ or (B_g)¹⁵], 191 (B_g),¹⁵ and 253 cm⁻¹ (A_g).^{15,16} The peaks near 96 and 106 cm⁻¹ were detectable but were too close to the cut-off of the laser blocking filter for quantitative analysis.¹¹ Similar spectra at room temperature were seen for Samples 1 and 3 (Fig. S2 and S6 in the ESI†), but the relative peak areas in the three prepared samples differed; the ratios of the 164 cm⁻¹ and 128 cm⁻¹ peak areas were ~6, 3, and 1 in Samples 1, 2, and 3, respectively.

The MoTe₂ Raman peaks varied with temperature, as discussed below; during Run 3, these Raman peaks were small at 575 and 600 °C. Other peaks were seen during the temperature ramps. The peak near 143 cm⁻¹ in Fig. 2 after heating Sample 2 is assigned below to solid Te. It was weak at the beginning of Run 3 and no longer present above ~300 °C (Fig. S5 in the ESI†). This peak was present and much stronger in the Raman spectra of Sample 3 during Run 2 (Fig. S6 in the ESI†) and a second and

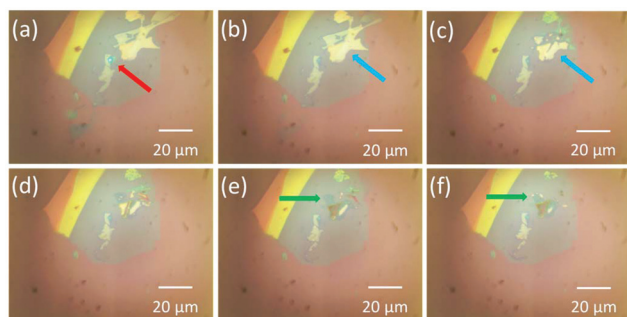


Fig. 1 Optical micrographs of Sample 2 and nearby MoTe₂ flakes, during Run 3: (a) at T_{room} at the beginning of the run, and then after being heated to (b) 325 °C, (c) 475 °C, (d) 550 °C, (e) 575 °C, and (f) 600 °C and then cooled to 100 °C. The red arrow in (a) points to the thin region in Sample 2, where it was probed by Raman scattering. The blue arrows in (b) and (c) identify large regions in the flake above and to the right of Sample 2, when this covered part of MoTe₂ starts to disappear. The green arrows in (e) and (f) show further decomposition and the lateral movement of parts of that flake.

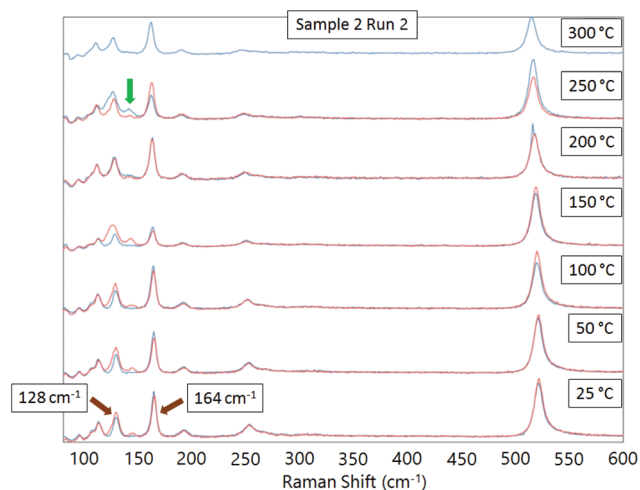


Fig. 2 Raman spectra of encapsulated 1T'-MoTe₂ at various temperatures (Sample 2, Run 2) under an Ar flow. The blue and red spectra were acquired during the temperature ramp up and down, respectively. The brown arrows point to the two largest MoTe₂ peaks and the green arrow shows the emergence of a tellurium peak ~ 143 cm⁻¹ at higher temperatures.

even larger peak appeared at ~ 123 cm⁻¹, which is also assigned to Te below; the relative strength of these two peaks appears to be the same in each spectrum. At and above 200 °C this ~ 123 cm⁻¹ peak overshadowed the 128 cm⁻¹ MoTe₂ peak. Both Te peaks appeared at 100–150 °C during Run 2 for Sample 3 and were present up to 300 °C, and in the ramp down to 25 °C (Fig. S6 in the ESI†). The Raman spectrum at 25 °C in Run 3 was the same as the last Run 2 spectrum, with these two same strong Te peaks, which then did not change much with increasing temperature in Run 3 up to ~ 350 –400 °C (Fig. S7 in the ESI†); these and the other MoTe₂ peaks decreased at the final probed temperature, 425 °C, when the sample deteriorated. This ~ 123 cm⁻¹ Te peak was not seen in Sample 2, but is likely the origin of the low-energy shoulder of the 128 cm⁻¹ MoTe₂ peak at and above 100 °C in Fig. 2. The two Te Raman peaks were not seen for Sample 1 in Run 1, which had been heated in air.

At 298 K, there are A₁ and E_{TO} peaks in bulk trigonal Te at 120.4 and 140.7 cm⁻¹ and at ~ 121 and 146 cm⁻¹ for amorphous Te.¹⁷ These crystalline peaks appear to shift down to ~ 115.4 and 134.3 cm⁻¹ for nanoplates and nanorods of Te.¹⁸ After heating and cooling to room temperature, the ~ 123 and 143 cm⁻¹ Sample 3 peaks were near those for bulk crystalline and amorphous Te, but both were much higher than those for “nano” Te. The ratio of the heights of these two Sample 3 peaks was ~ 3 to 1. This is the same ratio as that for bulk trigonal Te, both with linear polarized incident and unpolarized detected light (as was used here), and differs from the more nearly equal strengths for amorphous Te, ~ 4 to 3 peak height ratio,¹⁷ and so the new Sample 3 peaks were likely due to largely crystalline tellurium.

Except when the damage was apparent from the optical micrographs, the Raman spectra at ambient temperature after heating were essentially the same as those before heating in each run, aside from the appearance of the Te peaks. For example, the

prominent 164 cm⁻¹ 1T'-MoTe₂ peak returned to within roughly 0.5 cm⁻¹ of its original value after heating and cooling. The Raman spectra of MoTe₂ and Te were effectively the same at the end of Run 2 and at the beginning of Run 3. During Run 3, the MoTe₂ peak frequencies in Sample 2 returned to the same values at 100 °C after each increase in T up to 600 °C in Run 3, after calibration using the Si reference peak. The changes in the MoTe₂ Raman peak areas in Sample 2, in the ~ 3 unit cell, optically-thin probed region, suggest that its thickness changed by much less than a monolayer, again until deterioration was noted.

The Te Raman peaks that appeared in Sample 3 were much larger than the initial largest MoTe₂ peaks in this optically thin sample. This does not mean that there was more Te than MoTe₂, but that the Raman cross-sections for the Te peaks are much larger than those for the MoTe₂ peaks and that a solid Te coverage that averages much less than a monolayer of Te in the probed region could be easily noted. The Te peaks seen for Sample 2 likely correspond to submonolayer Te coverage and to MoTe₂ decomposition much less than a monolayer; this decomposition may well have been much less than that for Sample 3 (which had much larger Te peaks) (see below).

There was no evidence of crystalline (or polycrystalline) oxide peaks, MoO₃ (360, 510, 575, and 748 cm⁻¹),¹⁹ MoO₃ (158, 285, 666, 820, and 995 cm⁻¹ for the powder),²⁰ and TeO₂ (426 and 611 cm⁻¹),²¹ from the Raman peaks during Run 1 (with heating in air) or during Runs 2 and 3 (heating in Ar, and potentially due to residual air). There was no evidence of the formation of 2H-MoTe₂ from the Raman peaks in any run, which is consistent with the transformation from the 2H phase to the 1T' phase in bulk MoTe₂ seen above 400 °C in ref. 5.

Every MoTe₂ peak Raman shift decreased with higher temperature for each sample and run, both in the heating and cooling cycles. Increased broadening with increased T was also seen, but was harder to characterize well because of overlapping peaks and small signal sizes. Fig. 3 shows the representative Raman shifts of Raman peaks of covered 1T'-MoTe₂ during heating and cooling cycles, here for Sample 2 in Run 2 and the heating cycle in Run 3 for the two largest peaks; for Run 3, raw data and data calibrated using the known Si Raman peak frequency at 100 °C are shown. Other Sample 2 peaks are not characterized because they were weak or over-

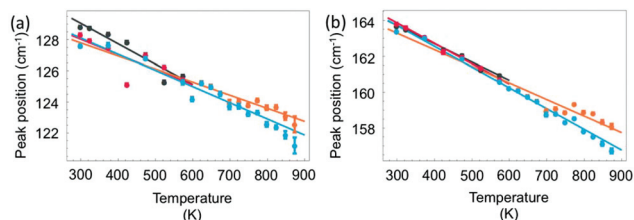


Fig. 3 Raman shifts versus temperature of the two largest Raman peaks, (a) ~ 128 cm⁻¹ and (b) ~ 164 cm⁻¹, of the covered 1T'-MoTe₂ Sample 2 during the up (red) and down (black) ramps of Run 2 and the up ramp of Run 3 (orange), including linear fits vs. temperature for each. The data for Run 3 are also shown recalibrated to the Si Raman peak (blue).

lapped with Te peaks and Sample 3 peaks are not analyzed because of the large Te peaks. The frequencies of the two largest peaks were fit as a function of temperature T , and each fits well with a linear fit in this temperature range (Table S3 in the ESI†), as expected from thermal expansion and a three-phonon coupling model at higher temperatures;²² they had comparable slopes. Averaging the intercepts and slopes for the three cycles, using the calibrated Run 3 results, the fit is $131.72 (\pm 0.13) \text{ cm}^{-1} - [0.011088 (\pm 0.000282) \text{ cm}^{-1} \text{ K}^{-1}]T(\text{K})$ for the 128 cm^{-1} peak and $167.08 (\pm 0.06) \text{ cm}^{-1} - [0.011039 (\pm 0.000525) \text{ cm}^{-1} \text{ K}^{-1}]T(\text{K})$ for the 164 cm^{-1} peak. Aside from variations due to errors in the peak fitting procedure, the small differences in the room-temperature peak frequencies of 1T-MoTe₂ could be due to different thicknesses, different adhesion and strain, different effects due to thermal expansion in the cool down ramps, and different contact with hBN. The thermal expansion contribution depends on the mode, the number of layers in the flake, the relative thermal expansion coefficients of the layer and the substrate, and how well the flake adheres to the substrate during T changes.

Fig. 4 shows the *ex situ* AFM traces of the parts of the Sample 2 flake before Run 2 (in a) and then after Run 3 (in b and c). Fig. 4a and b include the region probed by Raman scattering (within the triangular, thinnest multilayer region outlined in Fig. S1b in the ESI†). Fig. 4c was taken to the right of this region and the entire MoTe₂ flake, near the edge of the hBN layer. Fig. 4b and c show the presence of nanoparticles, which are presumably Te nanoparticles, and so Fig. 4c shows that there were particles away from the Sample 2 flake but still within the encapsulated region and no particles outside the encapsulated region. This suggests that at some temperature as high as 600 °C there was migration of nanoparticles, other adsorbates, and/or product vapor under the hBN, and that products that migrated towards the edge could leave the covered region, possibly through folds or wrinkles, and that the particles were then no longer bound to the substrate and the products could be carried away by the flowing argon. (The Te vapor pressure is 100 Pa (0.75 Torr) at 775 K and 1000 Pa (7.5 Torr) at 888 K,²³ so transport in any MoTe₂/hBN gaps might be possible, along with transport on the surfaces.) It is not clear how important this is at lower temperatures.

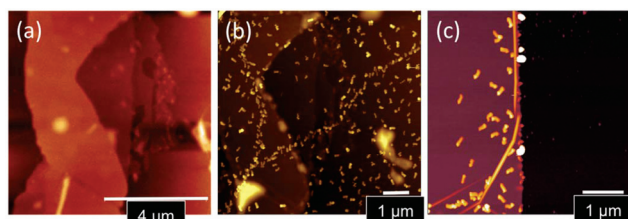


Fig. 4 *Ex situ* AFM traces of the probed region of Sample 2 at room temperature (a) before and (b) after all the heating and cooling cycles of Runs 2 and 3, showing the presence of nanoparticles, presumably composed of Te, under the hBN. The region probed during Raman scattering is in the triangular area, outlined in red, in Fig. S1(b);† here Sample 2 is the thinnest. (c) The rightmost edge of the hBN on Sample 2, after these runs; no nanoparticles are observed outside the boundaries of the hBN.

Optical microscopy definitively shows that the Sample 2 flake decomposed less than the Sample 3 flake at elevated temperatures, and this is likely because it was covered by hBN better, with the MoTe₂ flake extending beyond the hBN in Sample 3. The hBN layer being thicker in Sample 2 did not make it more stable because both hBN layers were multilayer. This greater stability of Sample 2 was also seen in the thin region by the stability of the MoTe₂ Raman peaks at the same T where optical microscopy indicated stability. Both samples were more stable than Sample 1, which was not totally covered by hBN and heated in air rather than in Ar.

Both decomposition and transport may depend on the overall coverage of the flake by hBN and also on the conformal coverage of the hBN layer and how it may vary with the local topography of the MoTe₂ flake, which has a range of thicknesses. Good local conformal coverage may mean slower decomposition at a site and slower transport to and from it. The decomposition may be slower because products cannot leave the hBN-covered surface and/or the decomposition was slowed down due to products that remain on the surface and/or any altered composition of the remaining surface layer. The *ex situ* AFM suggests that there was transport under the hBN, at least near 600 °C. Any transport at lower temperature might affect the results quantitatively, but should not significantly affect the main findings.

The entire Sample 2 flake would decompose at the same rate if MoTe₂ decomposition was not sensitive to the local number of monolayers and if contact with hBN was the same. So, Te would be formed at the same rate, but Te transport might depend on the local topography and affect the amount of observed Te at the site probed by Raman scattering. However, this would not affect the observed thickness of the remaining MoTe₂, which was essentially unchanged in Sample 2 until the high- T limit was reached. (The MoTe₂ Raman peak areas should vary linearly with thickness here, aside from resonance changes with thickness, because the MoTe₂ (and any Te overlayer) are optically thin, as is clear from the large signal from the Si substrate. Increased T would increase Stokes scattering rates due to phonon populations, aside from possible changes in Raman susceptibility.)

The much smaller solid Te Raman signal in Sample 2 than that in Sample 3 might be due to slower local decomposition, and/or also due to faster transport of Te away from this site and/or faster decomposition away from this site combined with slower Te transport to this site; this could be caused by better encapsulation and/or better conformal coverage locally or on other regions of the flake. The Sample 2 Te signal in Run 2 decreased when 300 °C was reached, which may indicate that transport away from this site was important then. The small Te signals at even higher temperatures in Run 3 may indicate larger transport rates from the site than the decomposition rates at it. Combined with no noticeable changes in the MoTe₂ peaks until ~550 °C, this may instead mean that the extent of the Te formation at lower temperatures was limited by features such as defects or slower decomposition due to products remaining on or leaving from the surface.

Some of the reasons why encapsulation conferred improved thermal stability here may be similar to those deduced in a previous study of van der Waals layers covering and passivating nanoparticle monolayers from oxidant gases.¹² That study showed that imperfect passivation by van der Waals overlayers was not due to the effect of molecular diffusion through van der Waals layers, which was too slow to be measured under the stated experimental conditions, but due to diffusion pathways beneath the overlayer. It suggested that the effectiveness of passivation was not sensitive to the van der Waals overlayer thickness, but on how well it covered the samples, and particularly its lateral extent.

At the intermediate temperatures studied, stability may be enhanced by the increased local partial pressure of Te vapor, due to hBN trapping and the relatively high equilibrium Te vapor pressure, through the reverse of MoTe₂ sublimation, MoTe₂(s) = MoTe_{2-x}(s) + xTe(g). (Sublimation may be important in MoTe₂ decomposition.) However, MoTe₂ decomposes at the highest investigated temperatures, so this stability mechanism is not dominant then.

Conclusions

Complete encapsulation by hBN greatly increases the temperature at which significant decomposition of 1T'-MoTe₂ begins, to ~550 °C, compared to partial or no hBN coverage. Still some decomposition products are seen at lower temperatures. This could affect device processing and performance, but some Te loss from the surface may bode well for electrolytic and hydrodesulfurization applications. Improved passivation and passivation even above 550 °C might be expected with improved encapsulation, as may occur for MoTe₂ flakes and samples of uniform thickness. Raman scattering and optical microscopy have been shown to be valuable *in situ* tools to evaluate stability.

Conflicts of interest

There are no conflicts of interest to declare.

Acknowledgements

Support was provided by the MRSEC program of the National Science Foundation (DMR-1420634) and the IGERT program of the National Science Foundation (DGE-1069240), and (LB) the U.S. Army Research Office MURI Grant W911NF-11-1-0362. The NHMFL is supported by the National Science Foundation (DMR-1157490) and the State of Florida.

Notes and references

- 1 Y. Liu, N. O. Weiss, X. Duan, H.-C. Cheng, Y. Huang and X. Duan, *Nat. Rev. Mater.*, 2016, **1**, 1–17.
- 2 Q. Lu, Y. Yu, Q. Ma, B. Chen and H. Zhang, *Adv. Mater.*, 2016, **28**, 1917–1933.
- 3 M. Chhowalla, H. S. Shin, G. Eda, L.-J. Li, K. P. Loh and H. Zhang, *Nat. Chem.*, 2013, **5**, 263–275.
- 4 X. Qian, J. Liu and L. Fu, *Science*, 2014, **346**, 1344–1347.
- 5 S. Cho, S. Kim, J. H. Kim, J. Zhao, J. Seok, D. H. Keum, J. Baik, D.-H. Choe, K. J. Chang, K. Suenaga, S. W. Kim, Y. H. Lee and H. Yang, *Science*, 2015, **349**, 625–628.
- 6 J. Lin, S. Pantelides and W. Zhou, *ACS Nano*, 2015, **9**, 5189–5197.
- 7 M. Yamamoto, S. Dutta, S. Aikawa, S. Nakaharai, K. Wakabayashi, M. Fuhrer, K. Ueno and K. Tsukagoshi, *Nano Lett.*, 2015, **15**, 2067–2073.
- 8 K. Ueno and K. Fukushima, *Appl. Phys. Express*, 2015, **8**, 095201.
- 9 H. Zhang, W. Zhou, X. Li, J. Xu, Y. Shi, B. Wang and F. Miao, *Appl. Phys. Lett.*, 2016, **108**, 091902.
- 10 K. Zhang, C. Bao, Q. Gu, X. Ren, H. Zhang, K. Deng, Y. Wu, Y. Li, J. Feng and S. Zhou, *Nat. Commun.*, 2016, **7**, 13552.
- 11 L. Wang, Z. Chen, C. Dean, T. Taniguchi, K. Watanabe, L. Brus and J. Hone, *ACS Nano*, 2012, **6**, 9314–9319.
- 12 D. Zhang, D. Wang, R. Creswell, C. Lu, J. Liou and I. P. Herman, *Chem. Mater.*, 2015, **27**, 5032–5039.
- 13 D. Rhodes, D. A. Chenet, B. E. Janicek, C. Nyby, Y. Lin, W. Jin, D. Edelberg, E. Mannebach, N. Finney, A. Antony, T. Schiros, T. Klarr, A. Mazzoni, M. Chin, Y.-C. Chiu, W. Zheng, Q. R. Zhang, F. Ernst, J. I. Dadap, X. Tong, J. Ma, R. Lou, S. Wang, T. Qian, H. Ding, R. M. Osgood Jr., D. W. Paley, A. M. Lindenberg, P. Y. Huang, A. N. Pasupathy, M. Dubey, J. Hone and L. Balicas, *Nano Lett.*, 2017, **17**, 1616–1622.
- 14 S.-Y. Chen, C. H. Naylor, T. Goldstein, A. T. Johnson and J. Yan, *ACS Nano*, 2016, **11**, 814–820.
- 15 D. H. Keum, S. Cho, J. H. Kim, D.-H. Choe, H.-J. Sung, M. Kan, H. Kang, J.-Y. Hwang, S. W. Kim, H. Yang, K. J. Chang and Y. H. Lee, *Nat. Phys.*, 2015, **11**, 482–486.
- 16 Y. Sun, Y. Wang, D. Sun, B. R. Carvalho, C. G. Read, C.-h. Lee, Z. Lin, K. Fujisawa, J. A. Robinson, V. H. Crespi, M. Terrones and R. E. Schaak, *Angew. Chem., Int. Ed.*, 2016, **55**, 2830–2834.
- 17 A. S. Pine and G. Dresselhaus, *Phys. Rev. B: Solid State*, 1971, **4**, 356–371.
- 18 G. Li, X. Cui, C. Tan and N. Lin, *RSC Adv.*, 2014, **4**, 954–958.
- 19 G. H. Smudde and P. C. Stair, *Surf. Sci.*, 1994, **317**, 65–72.
- 20 B. C. Windom, W. G. Sawyer and D. W. Hahn, *Tribol. Lett.*, 2011, **42**, 301–310.
- 21 J. C. Champarnaud-Mesjard, S. Blanchandin, P. Thomas, A. Mirgorodsky, T. Merle-Mejean and B. Frit, *J. Phys. Chem. Solids*, 2000, **61**, 1499–1507.
- 22 H. H. Burke and I. P. Herman, *Phys. Rev. B: Condens. Matter*, 1993, **48**, 15016.
- 23 *CRC Handbook of Chemistry and Physics*, 97th edn, 2016, http://hbcponline.com/faces/documents/06_22/06_22_0075.xhtml?search=true (accessed February 2017).