ABSTRACT: The controlled synthesis of large-area, atomically thin molybdenum ditelluride (MoTe$_2$) crystals is crucial for its various applications based on the attractive properties of this emerging material. In this work, we developed a chemical vapor deposition synthesis to produce large-area, uniform, and highly crystalline few-layer 2H and 1T'-MoTe$_2$ films. It was found that these two different phases of MoTe$_2$ can be grown depending on the choice of Mo precursor. Because of the highly crystalline structure, the as-grown few-layer 2H MoTe$_2$ films display electronic properties that are comparable to those of mechanically exfoliated MoTe$_2$ flakes. Our growth method paves the way for the large-scale application of MoTe$_2$ in high-performance nanoelectronics and optoelectronics.

Two-dimensional transition metal dichalcogenides (TMDs) have been attracting increasing interest because of their unique structures and remarkable properties, which make them promising materials for a wide range of applications related to, e.g., electronics, optoelectronics, valleytronics, spintronics, and catalysis. As a member of the TMD family, MoTe$_2$ possesses interesting features. Bulk MoTe$_2$ has an indirect band gap of $\sim$1.0 eV, and single-layer MoTe$_2$ is a direct-gap semiconductor with an optical band gap of 1.1 eV. Because of the smaller band gap compared with other group 6 TMDs, single- and few-layer MoTe$_2$ holds promise for use in easily controllable ambipolar field-effect transistors (FETs) and extends the operating range of TMD optoelectronic devices from the visible to the near-infrared range. In particular, the band gap, which is quite close to that of Si ($\sim$1.1 eV), the strong absorption throughout solar spectrum, and the strong spin-orbit coupling suggest that MoTe$_2$ is a highly attractive material for use in electronic devices, photovoltaic devices, and spintronic and valley-optoelectronic devices.

A crucial step toward the practical application of MoTe$_2$ in electronics and optoelectronics is the controlled production of high-quality, large-area, atomically thin MoTe$_2$ films. To date, single- and few-layer MoTe$_2$ have only been achieved using “top-down” exfoliation methods. However, exfoliation produces only small MoTe$_2$ flakes with arbitrary shape that are randomly distributed on a surface, thus preventing production for large-scale applications. Liquid exfoliation is a promising method for mass production of atomically thin MoTe$_2$, but the low quality of MoTe$_2$ obtained using this technique cannot satisfy the requirements for electronic and optoelectronic applications. Therefore, a technology for the mass production of high-quality, large-area, atomically thin MoTe$_2$ films is highly desirable.

Compared with other group 6 TMD materials, stoichiometric MoTe$_2$ films are more difficult to achieve. The electronegativity difference between Te and Mo is much smaller (0.3 eV) among these materials. Therefore, the bonding energy of Mo–Te bonds is quite small, which translates to a weaker tendency for the material to form and difficulty in obtaining stoichiometric MoTe$_2$. Moreover, at high temperatures, instead of evaporating as a compound, MoTe$_2$ decomposes and loses Te as a vapor. These properties make it challenging to directly obtain atomically thin MoTe$_2$ films by physical vapor deposition, and there is very often a Te deficiency in as-prepared MoTe$_2$. In regard to the synthesis of MoTe$_2$, another unique feature distinguishing MoTe$_2$ from other TMDs is the small energy difference (<0.1 eV per MoTe$_2$ unit) between the two crystal phases of MoTe$_2$, i.e., the semiconducting 2H and metallic 1T′ phases. As a result, MoTe$_2$ can be reversibly switched from the 2H phase to the 1T′ phase by changing the temperature, which on one hand makes it a promising two-dimensional material for phase-change memory applications but on the other hand poses challenges for the controllable synthesis of a pure MoTe$_2$ crystal phase. In this work, we investigated the synthesis of MoTe$_2$ via chemical vapor deposition (CVD) and found that pure 2H and pure 1T′ MoTe$_2$ films can be selectively synthesized by selecting different Mo precursors. The resulting 2H MoTe$_2$ films can be as thin as a few atomic layers, with high crystalline quality and...
excellent electrical characteristics comparable to those of exfoliated samples.

The strategy for the synthesis of MoTe₂ films is schematically illustrated in Figure 1a. Briefly, a 1 nm Mo film was deposited onto a SiO₂/Si substrate by electron beam evaporation. Then the Mo film was fully oxidized in air to give MoO₃. The resulting MoO₃ film was placed in a ceramic crucible containing Te powder. A mixture of argon and hydrogen (3 sccm Ar, 4 sccm H₂) was used as the carrier gas and formed a reducing atmosphere during the CVD growth. Hydrogen was essential for the MoTe₂ growth, similar to the growth of Se-based TMD materials.²⁸ Molecular sieves were added to the crucible before growth and were found to absorb byproducts during growth and to help release Te vapor in a controllable way. The growth temperature was controlled at 700 °C (Figure 1b). The MoO₃ film was tellurized into a MoTe₂ film after annealing in Te vapor at this temperature. Figure 1c shows a typical optical image of an as-synthesized MoTe₂ film. The film is uniform and continuous across the whole area (∼1 cm), as can be seen from the homogeneous color contrast in the image.

The crystal quality and uniformity of few-layer MoTe₂ films were further characterized by Raman spectroscopy using a 532 nm excitation laser. To investigate the spatial variations of the CVD-grown film on a scale of a few centimeters, Raman spectra were collected at 15 randomly chosen positions on the sample (Figure 1d). The MoTe₂ film shows several Raman peaks between 100 and 400 cm⁻¹: the in-plane E₂g₁ mode at ~119 cm⁻¹, the out-of-plane A₁g mode at ~171 cm⁻¹, the prominent peak of the in-plane E₂g₂ mode at ~234 cm⁻¹, and the out-of-plane B₁g mode at ~289 cm⁻¹. Besides these first-order Raman peaks, several second-order resonant peaks with relatively low intensities at ~140, 183, 204, 327, and 344 cm⁻¹ are also observed. These Raman features coincide with those observed in few-layer 2H MoTe₂ and thus unequivocally identify the as-grown film as 2H MoTe₂.¹⁹,²⁰ The presence of the B₁g peak at ~289 cm⁻¹ indicates that the synthesized film is atomically thin, since the B₁g mode is Raman-inactive in single-layer and bulk 2H MoTe₂.¹⁹ Additionally, the nearly identical positions and intensities of the peaks in these Raman spectra taken at all of these locations strongly suggest that the CVD-grown large-area atomically thin MoTe₂ film (1.6 × 1.8 cm²) is highly homogeneous.

Micro-Raman mapping was performed to evaluate the uniformity of the MoTe₂ film. The intensity map of the E₂g¹ peak (Figure 2b), the A₁g peak (Figure 2c), and the B₁g peak (Figure 2d) of the MoTe₂ film (Figure 2a) all show uniformly distributed color, indicating the high homogeneity of the MoTe₂ film within the spatial resolution of the Raman instrument (∼1 μm). The ratio of the intensities of the B₁g and E₂g¹ peaks is sensitive to the thickness of the MoTe₂ film and decreases as the number of MoTe₂ layers increases.¹⁹ The homogeneity in color presented in the intensity ratio map (Figure 2e) further confirms that the thickness of the MoTe₂ film is uniform over the whole mapping area. Atomic force microscopy (AFM) images of the grown film on the edge (Figure 2f) reveal that the MoTe₂ is a uniform thin film with a height of ~3.1 nm. The MoTe₂ surface has a roughness of 0.3 nm, which is similar to that of the SiO₂ substrate, further indicating that a high-quality material was grown. Since the interlayer spacing in MoTe₂ is about 0.7 nm, our grown film (Figure 2f) should be a four-layer film of MoTe₂.

X-ray photoelectron spectroscopy (XPS) was utilized to examine the elemental composition and bonding types in the CVD-grown film. The XPS survey spectra reveal the presence of Mo and Te elements that originate from the MoTe₂ film (Figure S1). The prominent Mo 3d peaks at 228.3 eV (3d₅/₂) and 231.5 eV (3d₃/₂) are assigned to Mo–Te bonds (Figure 3a).²¹ The Te 3d₅/₂ and 3d₃/₂ peaks, located at 573 and 583.4 eV, respectively, are also attributed to Mo–Te bonds (Figure 3b).²¹ These features are consistent with the XPS spectra obtained from a bulk MoTe₂ crystal. Additionally, the Mo:Te atomic ratio is 1:2.02, indicating that the CVD-grown MoTe₂ film is stoichiometric.

The crystallographic structure and the chemical composition of the MoTe₂ film were further characterized by transmission electron microscopy (TEM), selected-area electron diffraction (SAED), and energy-dispersive X-ray spectrometry (EDX). Figure 3c shows a typical TEM image of our MoTe₂ film. The continuity of the film suggests that our CVD-grown MoTe₂ film is of high quality. Figure 3e displays the SAED pattern which shows the hexagonal symmetry of the CVD-grown MoTe₂. SAED patterns taken at several locations on this sample revealed that the thickness of the MoTe₂...
hexagonal patterns with the same orientations (Figure S2), indicating that the lateral crystal domain size of this MoTe₂ specimen can reach up to 30 μm, comparable to that of exfoliated MoTe₂. High-resolution TEM shows a hexagonal atomic lattice of alternating bright and dark spots with a lattice spacing of 0.35 nm, which is consistent with the structure of 2H MoTe₂ (Figure 3f). The EDX spectrum reveals that the as-grown film contains Mo and Te (Figure S3).

Transport measurements were used to characterize the electrical properties of our few-layer MoTe₂ film. The large-area, uniform, and atomically thin MoTe₂ film greatly facilitated the fabrication of electrical devices. FET devices with various channel lengths from 300 nm to 6.5 μm were fabricated on a Si/SiO₂ substrate using electron-beam lithography (EBL) followed by metal deposition (1 nm Ti/60 nm Au). After EBL, the MoTe₂ devices were tailored into bars with a width of 20 μm using a reactive ion etching process (Figure 4a). The nonlinear I₈₋₉-V₈₋₉ characteristics suggest that Schottky contacts are formed between the Ti/Au metal pads and MoTe₂ (Figure 4b). The MoTe₂ device exhibits p-type conduction with an ON/OFF current ratio of ~10³ and an estimated carrier concentration of >4.8 × 10¹² cm⁻² (Figure 4d). Unlike other group 6 TMDs (MoS₂, MoSe₂, WS₂), which usually behave as n-type semi-

Figure 3. XPS and TEM characterizations of a 2H MoTe₂ film. (a) XPS spectra of Mo 3d core levels for the CVD-grown MoTe₂ film (red) and the bulk MoTe₂ crystal (yellow). (b) High-resolution Te 3d XPS spectra of the same region on the MoTe₂ film (blue) and the bulk MoTe₂ crystal (cyan). (c) Low-resolution TEM image of the CVD-grown MoTe₂ film supported on a TEM grid. (d) High-resolution TEM image of the same MoTe₂ film. (e) Corresponding SAED pattern. (f) FFT-filtered image of the area marked in (d). The inset shows the overlay of an atomic structure model of MoTe₂.

Figure 4. Electrical properties of devices made from a 2H MoTe₂ film. (a) Typical optical image of a MoTe₂ device on 90 nm SiO₂/Si. The darker region is MoTe₂. In the following, the channel length and width of this FET are ~6.5 and 20.0 μm, respectively. (b) Output characteristics (I₈₋₉ vs V₈₋₉) of our MoTe₂ FET device at various values of the gate voltage (V₈₋₉). (c, d) Transfer characteristics (I₈₋₉ vs V₈₋₉) curves for the same devices at various values of V₈₋₉ on (c) linear and (d) logarithmic scales.
difference between the 1T’ and 2H phases of MoTe2 is small and that 1T’ MoTe2 is thermodynamically stable under certain mechanical strain conditions. In view of the drastic change in the volume of each Mo unit in going from Mo (15.6 Å³, 380%) or MoO3 (50.8 Å³) to MoTe2 (74.9 Å³), it is likely that a large strain is induced during the transformation from Mo to a MoTe2 film. As a result, the 1T’ phase, which is metastable without strain, becomes the more stable phase for MoTe2 synthesized from a Mo film. In contrast, the change in volume in going from MoO3 (50.8 Å³) to MoTe2 (74.9 Å³) is about 47%, which is much lower than that for the Mo system. This stress can be relaxed during the high-temperature growth. This might be the reason that 2H MoTe2, which is the more stable phase in the absence of strain, can be obtained by tellurization of MoO3. Since MoO3 tends to lose oxygen during evaporation, we first deposited Mo by electron-beam evaporation and then fully oxidized the Mo film in air.

Another key parameter involved in MoTe2 growth is the amount of the Te source. Te vapor should be maintained during the growth of both the 2H and 1T’ phases to avoid Te deficiency in the as-grown film because MoTe2 is unstable and Te is prone to sublime at high temperature.

In summary, we have presented a simple yet very effective technique to produce large-area, atomically thin MoTe2 films. The resulting MoTe2 can be pure 2H phase or pure 1T’ phase with high crystallinity depending on the choice of Mo precursor. The as-grown few-layer MoTe2 films are stoichiometric and have high uniformity. The electrical transport properties of our 2H MoTe2 films are comparable to those of mechanically exfoliated MoTe2 flakes. Since our high-quality, atomically thin MoTe2 films are highly homogeneous and the size of the films is limited only by the size of the substrate, our growth method paves the way for large-scale applications of MoTe2 in the context of high-performance nanoelectronic and optoelectronic devices and circuits.

### ASSOCIATED CONTENT

**Supporting Information**

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Experimental details and supporting figures (PDF)

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**AUTHOR INFORMATION**

*Corresponding Authors*

jingkong@mit.edu

millie@mgm.mit.edu

**Notes**

The authors declare no competing financial interest.

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