Room Temperature Commensurate Charge Density Wave on Epitaxially Grown Bilayer 2H-Tantalum Sulfide on Hexagonal Boron Nitride

Wei Fu, Jingsi Qiao, Xiaoxu Zhao, Yu Chen, Deyi Fu, Wei Yu, Kai Leng, Peng Song, Zhi Chen, Ting Yu, Stephen J. Pennycook, Su Ying Quek, and Kian Ping Loh

ABSTRACT: The breaking of multiple symmetries by periodic lattice distortion at a commensurate charge density wave (CDW) state is expected to give rise to intriguing interesting properties. However, accessing the commensurate CDW state on bulk TaS2 crystals typically requires cryogenic temperatures (77 K), which precludes practical applications. Here, we found that heteroepitaxial growth of a 2H-tantalum disulfide bilayer on a hexagonal-boron nitride (h-BN) substrate produces a robust commensurate CDW order at room temperature, characterized by a Moiré superlattice of $3 \times 3$ TaS2 on a $4 \times 4$ h-BN unit cell. The CDW order is confirmed by scanning transmission electron microscopy and Raman measurements. Theoretical calculations reveal that the stabilizing energy for the CDW phase of the monolayer and bilayer 2H-TaS2-on-h-BN substrates arises primarily from interfacial electrostatic interactions and, to a lesser extent, interfacial strain. Our work shows that engineering interfacial electrostatic interactions in an ultrathin van der Waals heterostructure constitutes an effective way to enhance CDW order in two-dimensional materials.

KEYWORDS: charge density wave, two-dimensional transition metal dichalcogenides, molecular beam epitaxy, interfacial electrostatic interaction, Moiré superlattice

A charge density wave (CDW) state is a macroscopic quantum state showing strong coupling between periodic lattice distortion and electron density modulation.1-4 The CDW state engenders spontaneously broken symmetries, leading to novel phenomena.5-9 For example, the CDW in 1T-TiS2 breaks inversion symmetry with an axial vector resulting in a chiral state.8 Phase transitions between different CDW states can be electrically switched, and the abrupt change of resistance and hysteresis during such phase transitions can be used for building logic gates and circuits without the need for field effect transistors.10,11 However, practical applications of CDW-based devices are hampered by the fact that CDW ordering is usually accessed only at cryogenic temperatures.12,13 The CDW transition temperature, $T_{\text{CDW}}$, for the normal and the CDW phase occurs at 33 K for NbSe2 and at 78 K for 2H-TaS2 bulk crystals,15,16 greatly limiting their practical applications. Hence, there is a search for materials that exhibit room-temperature commensurate CDWs. Theoretical studies have focused on the impact of strain and charge doping on the soft phonon mode that stabilizes the CDW transition of monolayer or bulk metallic transition metal dichalcogenides (TMDs).17,18 For example, it has been shown that tensile strain can stabilize the CDW phase in 1T-TiSe2 and 1T-TaS2, and charge doping can suppress the CDW phase in 1T-TiSe2, H-TaS2, and 2H-NbSe2.20 Strategies such as reducing the thickness have also been applied in an attempt to enhance $T_{\text{CDW}}$.2,21

Herein, we discover that when atomically thin hexagonal TaS2 is epitaxially grown on hexagonal-boron nitride (h-BN), a room temperature $3 \times 3$ commensurate CDW state is stabilized, as revealed by STEM and Raman measurements. The $T_{\text{CDW}}$ is increased from 78 K for bulk 2H-TaS2 to higher than room temperature for bilayer TaS2 grown epitaxially on h-BN. The room temperature CDW phase cannot be observed in epitaxially grown TaS2/graphene or physically transferred...
TaS$_2$/h-BN (rotationally misoriented).$^{22}$ Density functional theory (DFT) calculations show that the stabilization of the CDW phase arises mainly from interfacial electrostatic interaction between TaS$_2$ and h-BN in the Moiré superlattice of $3 \times 3$ TaS$_2$ on $4 \times 4$ h-BN, with negligible charge transfer between TaS$_2$ and h-BN. In contrast, there is a large charge transfer from graphene to TaS$_2$, which suppresses the CDW phase.$^{22}$ Our work indicates that the CDW phase transition temperatures of atomically thin metallic TMDs can be significantly enhanced by growing the CDW host epitaxially on h-BN, on which the Moiré electrostatic modulation plays an important role in stabilizing the CDW order.

**RESULTS AND DISCUSSION**

**Molecular Beam Epitaxy Growth of Wafer-Scale, Bilayer TaS$_2$ on h-BN.** Using molecular beam epitaxy (MBE), bilayer TaS$_2$ crystals were epitaxially grown on an h-BN or graphite crystal. Ultrapure tantalum and sulfur molecular beams were evaporated by an e-beam evaporator and a valved sulfur cracker cell, respectively. Due to the hexagonal symmetry of the crystal, as-grown TaS$_2$ domains show two types of orientations (0° and rotated by 60°) on the h-BN or graphite substrate (as depicted in Figure 1a). With longer growth time, the domains merge to form a continuous film (Figure 1b). Compared with the theoretical monolayer thickness ($\sim$0.66 nm) of TaS$_2$, the film thickness of $\sim$1.18 nm as measured by the height profiles of atomic force microscopy (AFM) images in Figure S1 indicate that the TaS$_2$ forms bilayers on h-BN. On a large h-BN/sapphire wafer, a wafer-scale atomic TaS$_2$/h-BN hybrid film was successfully grown (Figure 1b), and the film characterizations are shown in Figure S2. The growth follows the Frank–van der Merwe growth mode as revealed by AFM images of the nuclei and partially coalesced film in Figure 1b. Aberration corrected scanning transmission electron microscopy—high angle annular dark field (STEM-HAADF) images of a step edge in Figure 1c show epitaxial growth along the Ta–Ta/S–S zigzag direction.$^{23-25}$

The STEM-HAADF image of the heterolayers in Figure 1d shows a honeycomb lattice that is characteristic of the H-phase polymorph, in which the sulfur atoms are arranged in a trigonal prismatic arrangement around the Ta atoms. Raman measurements (Figure 3) and XPS spectra (Figure S3) also evidence that the as-grown film is H-phase TaS$_2$. TaS$_2$ grown on h-BN reveals a signature honeycomb structure as imaged by STEM-HAADF, which is indicative of an AA*-stacked bilayer (Figure 1e). The corresponding fast Fourier transform (FFT) diffraction pattern inserted in Figure 1d demonstrates that the bilayer 2H-TaS$_2$ diffraction spots are aligned with respect to the crystallographic orientation of the underlying h-BN crystal, revealing that the TaS$_2$ layer grows epitaxially on the h-BN. Additionally, a well-defined Moiré pattern is observed on the TaS$_2$/h-BN heterolayers with a periodicity of $\sim$10 Å (Figure 1d,e). The Moiré superlattice is constructed by a $3 \times 3$ superlattice is consistent with the excellent lattice match between $3 \times 3$ TaS$_2$ and $4 \times 4$ h-BN, with TaS$_2$ experiencing a tensile strain of only $\sim$0.9% (Table S1).

**Scanning Transmission Electron Microscopic Study of Room-Temperature Commensurate CDW Ordering.** Medium angle ADF (MAADF) imaging collects a high fraction of coherently elastic scattered electrons in which the image contrast is sensitive to small atomic displacements.$^{26,27}$ Hence, MAADF imaging was used to probe the existence of periodic intensity changes due to the room-temperature CDW ordering in the bilayer 2H-TaS$_2$ on h-BN. In this case, the TaS$_2$ bilayer was directly grown by MBE on an h-BN (or few-layer graphene) flake that was pretransferred onto a TEM grid to avoid sample degradation caused by solution-based transfer...
methods (Figure 2a). The trigonal prismatic structure of the 2H phase is clearly observed in the STEM-MAADF image in Figure 2b. The superlattice spots in the FFT diffraction pattern (orange squares in Figure 2c) indicate the existence of a $3 \times 3$ TaS$_2$ superlattice. The $q_{\text{CDW}} = a^*/3$, revealing the presence of $3 \times 3$ periodicity due to the CDW. (d) Side (left) and top (right) view of the atomic structure of AA’ bilayer $3 \times 3$ trihollow CDW H-TaS$_2$. Blue, green, and pink triangles are used to group Ta atoms. The Ta-Ta distances decrease by 3.7% and 1.7% in the blue and green triangles, respectively, while the Ta-Ta distances in the pink triangle increase by 2.9%. (e) Simulated FFT image and the schematic intensity line profile (not drawn to scale) along the blue arrow in the upper panel of bilayer trihollow CDW H-TaS$_2$.

To identify if the h-BN substrate plays a special role in enhancing CDW order in epitaxially grown 2H-TaS$_2$/h-BN, we also examined if the chemical exfoliated bilayer H-TaS$_2$ and epitaxially grown bilayer H-TaS$_2$ on graphene shows similar $3 \times 3$ periodicity. On an exfoliated, freestanding bilayer TaS$_2$ flake (schematic shown in Figure 3a), the signature honeycomb structure of 2H-TaS$_2$ is seen in the MAADF-STEM image in Figure 3b. From the corresponding FFT diffraction pattern in Figure 3c, only the $1 \times 1$ diffraction spots of 2H-TaS$_2$ are seen. This indicates that the room temperature CDW state observed on bilayer 2H-TaS$_2$/h-BN is not intrinsic to bilayer 2H-TaS$_2$ crystals. Moreover, on the MBE grown bilayer H-TaS$_2$/monolayer graphene sample (depicted in Figure 3d), two types of domain orientations ($0^\circ$ and rotated by $60^\circ$) are observed in Figure 3e, similar to the sample grown on h-BN. High-quality atomic honeycomb structure is also observed in the MAADF-STEM image in Figure 3f. However, the inset FFT pattern only displays normal $1 \times 1$ 2H-TaS$_2$ diffraction spots, and no CDW superlattice is detected. We can conclude that epitaxial growth alone is insufficient to guarantee the $3 \times 3$ CDW phase, despite the fact that graphene and h-BN share very similar lattice constants (Table S1).

Closely examining the $3 \times 3$ CDW atomic structure in our MBE grown bilayer H-TaS$_2$/h-BN sample reveals that besides the diffraction spots corresponding to the $3 \times 3$ real space lattice (Figure 2c), the Fourier transform of the STEM-
MAADF image shows additional diffraction spots, labeled as A and B (red circles) in Figure 2c. We performed DFT calculations using the generalized gradient approximation (GGA) together with nonlocal van der Waals (vdW)
correlation for the exchange-correlation functional (optB86b-vdW30,31). Our DFT calculations show that out of the four 3×3 CDW atomic structures (Figure 4) commonly considered in the literature, only the trihollow CDW structure produces these A and B spots in the simulated diffraction pattern of the monolayer (Figure 4e) and AA′ stacked bilayer (Figure 2d,e). These results provide clear evidence that the 3×3 CDW phase in H-TaS2 adopts the trihollow CDW structures (Figure 4e,d), which is also consistent with the CDW structure reported for H-NbSe2.29 Indeed, our DFT GGA calculations for monolayer H-TaS2 show that the trihollow structures (Figure 4e) are 7 meV, 13 meV, 15 meV, and 38 meV more stable than those of the trifilled-CDW (Figure 4d),29 star-CDW (Figure 4c),32 hex-CDW (Figure 4b),33 and 3×3 normal phase H-TaS2 (Figure 4a), respectively. The energy differences among different phases were also calculated by the GGA+U (DFT+U) method (Figure 4), where a Hubbard U term is added to the DFT Hamiltonian to take into account strong on-site Coulomb interactions of localized Ta d electrons.34 U = 2.5 eV was estimated using a linear-response method.35 Details of all these CDW structures are provided in Table S2. The trihollow-CDW structure of interest here is characterized by triangular groups of Ta and S atoms, as shown in Figure 4e. Atoms in the same group move away from one another, move toward one another, or do not move relative to one another (see Figure 4e caption and Table S2).

We compute the phonon spectra of bilayer normal phase H-TaS2 (Figure S5a) and find that a soft phonon mode with large imaginary frequency is obtained at q = [0.33, 0, 0], consistent with the formation of a 3×3 CDW phase in bilayer H-TaS2. The most stable CDW phase (Figure 2d) in the AA′-bilayer H-TaS2 system was identified by considering different relative stacking orientations of two monolayers in the trihollow structure (Figure S4).

**Raman Study of Phonon Vibration Modes in Room-Temperature CDW Ordering.** The CDW phase is accompanied by the emergence of optically active Raman modes, thus Raman spectroscopy is widely used to characterize the vibrational properties of the CDW materials.3 We first consider the vibrational properties of 2L AA′ H-TaS2 in its normal phase (P3̅m1 space group (No. 164)). The vibrational modes of even layer (n atoms) AA′ TaS2 (normal phase) decompose into four types of irreducible representations at the Γ point: \( \Gamma_{\text{even-l}} = \frac{n}{2}(A_{1g} \oplus A_{2u} \oplus E_{g} \oplus E_{u}) \). Therein, the \( A_{1g} \) (Figure 5c,f,g) and \( E_{g} \) (Figure 5b,d,e) modes are Raman active. \( A_{2u} \) (Figure S5b,f,g) and \( E_{u} \) (Figure S5c,d,e) modes are infrared active. Figure 5a shows the experimental Raman spectra of TaS2 at room temperature and 80 K. It is clear that the Raman spectrum of the exfoliated flake is different from that of TaS2 epitaxially grown on h-BN. For the exfoliated flake, all the Raman frequencies predicted for the normal phase TaS2 are experimentally observed (see Figure 5bfö for frequencies) except for the shear mode located at low wavenumbers (\( E_{g} (16.1 \text{ cm}^{-1}) \)); the latter is beyond the detection limitation of the equipment. A broad peak around 185 cm\(^{-1}\) in Figure 5a corresponds to a two-phonon mode, which is commonly observed in the normal phase of group-VB H-
Table 1. CDW Formation Energies of TaS₂ and TaS₂/h-BN Heterostructures

<table>
<thead>
<tr>
<th></th>
<th>monolayer (GGA)</th>
<th>bilayer (GGA)</th>
<th>monolayer (GGA+U)</th>
<th>bilayer (GGA+U)</th>
</tr>
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<tbody>
<tr>
<td>TaS₂</td>
<td>−38</td>
<td>−66</td>
<td>−81</td>
<td>−145</td>
</tr>
<tr>
<td>TaS₂ (0.9% tensile strain corresponding to the Moire superlattice match with h-BN)</td>
<td>−42</td>
<td>−75</td>
<td>−85</td>
<td>−151</td>
</tr>
<tr>
<td>TaS₂/h-BN structure I [I']</td>
<td>−57 [-5]</td>
<td>−86 [-41]</td>
<td>−102 [-52]</td>
<td>−168 [-119]</td>
</tr>
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Figure 6. Effect of the h-BN substrate on the CDW phase. (a) Top view of the atomic structure of monolayer 3 × 3 CDW TaS₂, shown without the h-BN substrate. (b) h-BN substrate with S atoms overlaid in the TaS₂/h-BN commensurate superlattice. (c, d) Atomic structures of TaS₂/h-BN-I and TaS₂/h-BN-II, two of the commensurate heterostructures considered in this work. The signs, +, −, and 0, refer to the increase or decrease in Ta–Ta distances or S–S distances within each colored triangle, relative to the freestanding monolayer TaS₂ phase. The red, dark blue, and gray dashed triangles are used to denote the groups S1 (+), S2 (−), and S3 (0), respectively. The red arrowheads in (b) show the direction of the forces exerted by the negatively charged N atoms and positively charged B atoms on the adjacent (negatively charged) S atoms. (b) to (c) shows a schematic to illustrate how the h-BN substrate favors the CDW state in TaS₂.

TMDs. No peaks are detected from 40 to 150 cm⁻¹ in the exfoliated sample. Bilayer AA’-stacked CDW TaS₂ belongs to the P3m1 space group. The inversion centers of the bilayer CDW structures are labeled by black dots in Figure 5. Seven Raman peaks are clearly observed in Figure 5a for bilayer TaS₂ epitaxially grown on h-BN, which is different from the Raman spectra of exfoliated TaS₂. Using first-principles calculations, we find that these Raman peaks can be assigned to Raman active modes in TaS₂. The corresponding theoretical/experimental frequencies are given as follows: A₁g (31.9/31.8 cm⁻¹; Figure S6a), mode a (69.0/64.8 cm⁻¹; Figure S5i), mode b (104.7/104.3 cm⁻¹; Figure S5j), mode c (119.1/125.3 cm⁻¹; Figure S5k), mode d (155.0/149.0 cm⁻¹; Figure S5l), E₁ (301.2/301.7 cm⁻¹ Figure S6e), and A₁g (392.0/392.4 cm⁻¹; Figure S6f), respectively. In contrast to the Raman spectrum for exfoliated TaS₂, there is significant Raman intensity in the low frequency range of 40 to 150 cm⁻¹ arising from CDW-related modes a–d. The Ta atoms in each supercell of the CDW phase can be distinguished into three groups (Figure 2d,e). We denote these three groups by green, blue, and pink triangles in Figure 5h–l. Modes a, b, and c (Figure S6i–k) involve predominantly the vibration of one of these groups of Ta atoms in each layer. The vibration of the Ta atoms in different groups leads to significant differences in frequency among these modes, consistent with the different Ta–Ta bond lengths in the different groups in the CDW structure. Mode d involves displacements of all the Ta atoms. Modes a–d are related to the E₁ (Figure S5h) and E₁/E₃ modes (Figure S5j) of the normal 2H phase bilayer TaS₂ at the K point (0.33, 0.33, 0), which folds to the Gamma point in the 3 × 3 CDW bilayer H-TaS₂ structure, enabling the phonon to be optically detected in the Raman spectra. The Raman peaks in the frequency range 40 to 150 cm⁻¹ are strong signatures of the CDW phase. In addition, two-phonon modes detected in normal H-TaS₂ exfoliated from flakes disappear in bilayer H-TaS₂ epitaxially grown on h-BN, which is also an evidence to indicate the appearance of a CDW phase. Thus, the Raman spectra in Figure 5a show that the CDW phase exists at between room temperature and 80 K for bilayer TaS₂ epitaxially grown on h-BN but not in exfoliated TaS₂.

Effect of the h-BN Substrate on the Stabilization of the CDW Phase in H-TaS₂. The very large increase in T_{CDW} for bilayer H-TaS₂ epitaxially grown on h-BN substrates (compared to both bulk and exfoliated bilayer H-TaS₂) indicates that the CDW phase of H-TaS₂ is remarkably stable on h-BN. We define the CDW formation energy per 3 × 3 TaS₂ unit cell to be ΔE = E_{CDW} − E_{Normal}. ΔE values calculated by GGA and GGA+U methods show consistent results (Table 1). Here, we discuss the GGA results. In unstrained TaS₂ with no substrate, the ΔE values are −38 meV and −66 meV for monolayer and bilayer TaS₂, respectively (Table 1). Earlier theoretical studies have focused on the impact of strain on ΔE. The h-BN substrate induces 0.9% tensile strain on TaS₂. Calculations show that this amount of strain increases the magnitude of ΔE by 4 and 9 meV for freestanding monolayer and bilayer TaS₂, respectively (Table 1). Significantly, when an h-BN substrate is included explicitly in the DFT calculations, taking TaS₂/h-BN structures I (I) as examples (I: Figure 6c; II: Figure 6d), ΔE becomes −57 (−61) meV for monolayer TaS₂ and −86 (−91) meV for bilayer TaS₂ (Table 1), which corresponds to a stabilization of the CDW phase by 19–23 meV and 20–25 meV, respectively. This clearly indicates that compared to interfacial stabilization by h-
BN, strain alone accounts for only less than \(\sim 19\%\) (monolayer) and \(\sim 45\%\) (bilayer) of the change in \(\Delta E\). The maximum change in \(\Delta E\) for strains up to 5\% does not exceed 10 meV per layer (Figure S7), which indicates that the stabilization energy due to an interfacial effect by h-BN is larger than what can be achieved by strain alone for monolayer and bilayer TaS\(_2\). We have considered a total of 18 different stacking orders for monolayer TaS\(_2\) on h-BN (see Figure S8 for details), and we found that \(\Delta E\) varies from \(\sim -48\) meV to \(-61\) meV in all the geometry-optimized structures. These \(\Delta E\) values indicate that the stabilization of the CDW phase is quite robust with respect to the specific stacking orientation. In all these heterostructures, the charge transfer between TaS\(_2\) and h-BN is negligible. Structures I and II (Figure 6c,d, Table 1) are among the most stable of the heterostructures with different stacking orders.

In order to understand the nature of the interfacial interaction between TaS\(_2\) and h-BN, and specifically to determine what causes the stabilization of the CDW phase, we create artificial structures I’ and II’, where the B and N atoms are swapped without allowing the positions of the atoms to relax. \(\Delta E\) becomes \(-3\) meV and \(-9\) meV in structures I’ and II’, respectively (Table 1), much smaller than \(\Delta E\) in isolated unstrained monolayer TaS\(_2\). This indicates that, in these artificial structures, the CDW phase becomes strongly suppressed by the h-BN substrate. Importantly, this reveals that the positions of the B and N atoms relative to the S atoms play an important role in the interfacial stabilization mechanism in TaS\(_2\). As shown in Figure 4, the trihollow-CDW structure is characterized by triangular groups of Ta and S atoms. Figure 6a,b illustrates these groups in greater detail. There are three groups of S atoms (Figure 6a). In group S1 (red dashed triangle), the S–S distances increase relative to the normal phase (S1: + indicating an increase in S–S distances); in group S2 (dark blue dashed triangle), the S–S distances decrease (S2: – indicating a decrease in S–S distances); and in group S3 (gray dashed triangle), the S–S distances remain the same (details in Table S2). These groups, S1, S2, and S3, are closely related to the corresponding three groups of the Ta atoms, denoted by blue, green, and pink triangles, respectively (Figure 6a). By examining the details of the relaxed structures of the 18 heterostructures, we find that for a given stacking orientation of normal phase TaS\(_2\) on h-BN, the most stable CDW structure corresponds to one where atoms in group S1 (+) are nearer N than B, and atoms in group S2 (−) are nearer B than N. The same outcome is also obtained if a normal phase TaS\(_2\) is allowed to relax to the CDW phase naturally, as shown in Structures I and II in Figure 6c,d. This preference is consistent with the negative Bader charge for N and positive Bader charge for B. Specifically, the negatively charged N atoms stabilize group S1 (+) by pushing the negatively charged S atoms away from N and also away from one another (see schematic in Figure 6b). On the other hand, the positively charged B atoms stabilize group S2 (−) by pulling the negatively charged S atoms closer to B and closer to one another. This way, quite remarkably, the relative positions of B and N atoms, as well as S atoms in the commensurate TaS\(_2\)/h-BN superlattice, favor the CDW phase in TaS\(_2\) (Figure 6c), which, coincidentally, hosts groups of sulfur atoms, S1 (+) and S2 (−), in exactly the arrangement that is also favored by the positions of B and N atoms in the h-BN substrate.

**CONCLUSIONS**

In summary, we have discovered a room temperature commensurate CDW state on epitaxially grown 2H-TaS\(_2\) on h-BN. DFT calculations show that the stabilization of the 3 \(\times\) 3 CDW phase can be largely attributed to the interfacial electrostatic interaction between TaS\(_2\) and h-BN in the Moiré superlattice of few-layer 3 \(\times\) 3 TaS\(_2\) on 4 \(\times\) 4 h-BN and the absence of charge transfer across the interface. On an epitaxially grown TaS\(_2\)/graphene substrate, however, charge transfer interaction suppresses the CDW phase on TaS\(_2\). In addition to charge transfer interactions and interfacial strain that have been used previously for tuning the CDW and superconducting transition temperature, our work suggests that a third control mechanism lies in Moiré-modulated interfacial electrostatic interactions. Additional theoretical and experimental work is needed to fully explore the potential applications engendered by a room temperature commensurate CDW state.

**METHODS**

The epitaxial growth was carried out in a customized MBE system with a base pressure of \(< 3 \times 10^{-10}\) Torr. Ultrapure Ta (99.995%, Goodfellow) and sulfur (99.5%, Alfa Aesar) were evaporated from a mini-electron-beam evaporator and a valve sulfur cracker cell, respectively. The temperature of the sulfur crucible cell was set to 383 K. A two-step growth process was applied: in the first stage, the substrate was kept at around 973 K for 3 h to form scattered domains; in the second stage, the substrate temperature was increased to 1073 K and maintained for another 2 h to allow lateral growth and merging of the isolated domains to form a whole film. After growth, both the Ta and sulfur sources were turned off, and the sample was annealed at 1073 K for 30 min before cooling to room temperature at a rate of 10 K/min.

The multilayer h-BN was epitaxially grown on a wafer sized c-plane sapphire by a low-pressure CVD method. Ammonia borane (97% purity, Sigma-Aldrich) was used as the B and N sources. After the furnace was increased to 1673 K under a mixed H\(_2\)/Ar gas, ammonia borane was heated to 403 K and the growth of h-BN maintained for 30 min at a controlled pressure of 0.1 Torr. After that, the furnace was cooled down under a mixed H\(_2\)/Ar gas. The basic characterizations of the grown wafer scale h-BN/sapphire film are reported in our previous paper.

Atomic force microscopy was performed using Bruker Dimension FastScan atomic force microscopy in noncontact mode at room temperature. The Raman spectroscopy measurements were performed by a WITec Alpha300 Series confocal Raman system with 2400 g/mm grating with a 532 nm excitation laser. A combination with a Bragg notch filter allows the measurements of the low-frequency Raman modes down to approximately \(\sim 10\) cm\(^{-1}\). The beam spot size of the excitation laser is focused around 1 \(\mu\)m by a 50X long working distance (LWD) objective. To avoid laser-induced sample damage, the power of the laser was strictly controlled below 2 mW. An integration time of 180 s was used to obtain the spectra. The temperature dependent Raman measurements were achieved by interfacing the Linkam optical DSC600 and LNPS5 cooling system. The TaS\(_2\) samples were introduced into a vacuum chamber with a cryostat. Furthermore, in order to avoid sample degradation caused by the solution-based transfer method, the TaS\(_2\) atomic layers were directly grown by MBE on an h-BN (or graphene) flake that was pretransferred onto a Mo-TEM grid. STEM-ADF imaging was carried out on an aberration-corrected JEOL ARM-200F equipped with a cold field emission gun, operating at 80 kV, and an ASCOR probe corrector. The convergence semiangle of the probe was \(\sim 30\) mrad.

STEM-MAADF images were collected using a half angle range from \(\sim 30\) to 110 mrad, while STEM-HAADF images were collected from \(\sim 85\) to 280 mrad. XPS characterizations were performed using a SPECS XR-50 X-ray Mg Ka (1253.7 eV) source with a pass energy of 19 eV. XPS measurements were performed using a PERKIN ELMER PHI 5600 VersaProbe XPS System equipped with a monochromatic Al-K\(_\alpha\) X-ray source and a pass energy of 19 eV. The base pressure of the analysis chamber was \(\sim 2 \times 10^{-8}\) Torr. The measurements were acquired at room temperature using a four-channel analyzer with a pass energy step of 2 eV and an analysis area of \(200 \times 200 \mu\)m\(^2\).
30 eV and a spot size of 5 mm. A PHOIBOS 150 hemispherical energy analyzer (SPECS, GmbH) was used as the energy analyzer. The binding energies of the XPS spectra were calibrated using Au 4f/2 peaks. XPS peak fitting was carried out using a mixed Gaussian—Lorentzian function after a Shirley background subtraction.

Density functional theory calculations were performed using the projector augmented wave method and a plane-wave basis set as implemented in the Vienna ab initio simulation package (VASP). Density functional perturbation theory was employed to vibrational frequencies at the Gamma point (VASP) and phonon dispersion (Quantum Espresso). The kinetic energy cutoff for the plane-wave basis set was set to 700 eV for calculating geometric and vibrational properties. A k-mesh of $27 \times 27 \times 15$ was adopted to sample the first Brillouin zone of the unit cell of bulk 2H-TaS$_2$. The mesh density of the k points was kept fixed when calculating the properties for few-layer normal and CDW phase H-TaS$_2$. In the geometry optimization and vibrational frequency calculations, van der Waals interactions were considered at the vdW-DF level with the optB86b functional, which has been shown to be accurate in describing the structural properties of layered materials. For the self-consistent cycle was 1 $\times$ 10$^{-8}$ eV. All atoms in the supercell were allowed to relax until the residual force per atom was less than 5 $\times$ 10$^{-3}$ eV/Å$^{-1}$. Total energies were also computed using the GGA+U method to consider a strong on-site Coulomb interaction of d localized electrons of Ta. Electronic band structures were calculated using the Perdew–Burke–Ernzerhof (PBE) functional with spin–orbit coupling (SOC). The phonon dispersion shown in Figure S8a was calculated using the PBE-D3 functional.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsnano.0c00303.

AFM images under different growth stages, basic characterizations of the wafer-scale film, XPS spectra, calculated lattice constants and the Ta–Ta distance in the normal and CDW phases, simulated FFT images, vibrational properties, and effects of the strain on the CDW formation energy (PDF)

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REFERENCES


