Supporting Information

Structural Phase Transition of Multilayer VSe₂

Dian Li,¹ Xiong Wang,¹ Chi-ming Kan,¹ Daliang He,² Zejun Li,³ Qing Hao,⁴ Hongbo Zhao,⁵ Changzheng Wu,³ Chuanhong Jin² and Xiaodong Cui¹

- 1. Physics Department, University of Hong Kong, Hong Kong SAR, P. R. China
- State Key Laboratory of Silicon Materials, School of Materials Science and Engineering, Zhejiang University, Hangzhou, Zhejiang 310024, P. R. China
- Hefei National Laboratory for Physical Sciences at the Microscale, CAS Center for Excellence in Nanoscience, and CAS Key Laboratory of Mechanical Behavior and Design of Materials, University of Science & Technology of China, Hefei, Anhui 230026, P. R. China
- Department of Aerospace and Mechanical Engineering, University of Arizona, Tucson, Arizona 85721, United States
- Department of Electrical and Computer Engineering, University of Arizona, Tucson, Arizona, 85721, United States

Corresponding Author

*Email: chhjin@zju.edu.cn

*Email: xdcui@hku.hk

1. DFT Calculations

All our computational work used density functional theory (DFT). All DFT calculations were performed with the Vienna Ab initio simulation package (VASP)^[1], and the projected-augmented wave (PAW) method was used.^[2]

The electron exchange and correlation effects were treated with the generalized gradient approximation (GGA) functional of Perdew, Burke, and Ernzerhof (PBE).^[3] We used a plane-wave basis set with a kinetic energy cut-off of 310 eV. The Brillouin zone was sampled by using a $9\times9\times2$ Monkhorst-Pack k-point grid.^[4] Periodic calculation was applied to the unit cell to simulate the bulk situation. In phonon calculations, $3\times3\times2$ and $3\times3\times4$ supercells are employed for bulk *2H*-VSe₂ and *1T*-VSe₂, respectively.

Lattice constant and total energy

The unit cell of VSe₂ has two equal lattice constants, a = b, and for the ML case, a vacuum layer of at least 30 Å along the *c* direction while the bulk structures have two identical lattice constants a = b and the third independent *c*. All structures were firstly determined by the structure optimization with both the lattice vectors and atom coordinates relaxed with the tolerance of less than 0.01 eV/Å on each atom.

It's worth noting that the atom number of each 2*H*-phase unit cell is double for that of the *1T*-phase, so for convenience of comparison between different polymorphs, total energies of the 2*H*-VSe₂ unit cell were halved to get total energies of bulk 2*H*-VSe₂ per VSe₂ formula. Unless otherwise specified, the term total energy below refers to total energy per VSe₂ formula.

Figure S1 shows the evolution of the calculated total energy as a function of lattice constant for two different polymorphs of VSe₂ in both bulk and ML form. The optimized lattice constant is a = 3.22 Å for ML *T*-VSe₂ and a = 3.23 Å for ML *H*-VSe₂. The calculated lattice constants of bulk 2*H*-VSe₂ are a = 3.24 Å, c = 12.6 Å, while those of bulk *1T*-VSe₂ are a = 3.24 Å, c = 6.0 Å.



Figure S1 Evolution of the calculated total energy as a function of the lattice constant for (a) bulk and (b) ML form VSe₂.

The calculated total energies of certain forms are listed on the below table, which indicates that bulk VSe_2 prefers *IT*-VSe₂ to *2H*-VSe₂ due to a lower energy by 65 meV while *2H*-phase is energetically favorable in ultrathin VSe₂ due to lower energy by 18 meV.

	1T	2H	$E_H - E_T$
bulk	-2498.668 eV	-2498.603 eV	65 meV
monolayer	-2498.314 eV	-2498.332 eV	-18 meV

Table S1Calculated total energies of certain forms of VSe2

Phonon dispersion

Phonon dispersion spectrum analysis is a reliable tool to confirm the structure stability. When a structure is stable, all of its phonon frequencies on the k-points in the Brillouin zone should be positive.^[5-6] In order to check the structural stability of VSe₂, accurate phonon calculations on monolayer H-VSe₂ and T-VSe₂ were performed, and the full phonon dispersion spectra of the two

structures along the high-symmetry directions in the Brillouin zone were calculated. As shown in Figure S2, no imaginary vibration frequency appears for either monolayer H-VSe₂ or T-VSe₂, implying that these two monolayer structures have high phonon stability. According to the phonon calculations, both H-VSe₂ and T-VSe₂ should be stable. ^[6-7]



Figure S2 Phonon dispersion along with high-symmetry directions in the BZ of (a) bulk *1T*-VSe₂ and (b) bulk *2H*-VSe₂, the Raman active branches are marked in red.

Thermal dynamic properties

Free energy, vibration entropy, and thermal capacity are calculated with quasi-harmonic approximation. The vibration entropy and thermal capacity of ML VSe₂ are shown in Figure S3, which depicts a clear picture that lattice vibration effect plays much more significant role in H-VSe₂ than T-VSe₂ because the former has both much larger vibration entropy and thermal capacity than the latter. For example, at 300 K, entropy is about 64 J·mol⁻¹·K⁻¹ for T-VSe₂ but is 76 J·mol⁻¹·K⁻¹ for H-VSe₂. The thermal capacities of two polymorphs attain the same value at a temperature higher than 600 K because they tend to the classical value 9R (about 75 J·mol⁻¹·K⁻¹, 3R per atom, R is the ideal gas constant) at the high-temperature limit, according to the Dulong-Petit law. Such a coincidence exactly demonstrates the reliability of our calculations.



Figure S3 Vibration entropy *S* and thermal capacity C_V for ML VSe₂.

Energy barrier using the c-NEB technique

As shown in the inset of Figure 2b, the phase transition is mainly related to the movement one of the two selenium layers. In the process of the phase transition, the upper Se atom transfers from the original (1/3, 2/3, Z) site to the (2/3, 1/3, Z) site, and both the V atom and the lower Se atom do not leave their original site. The transition state of the phase transition corresponds to the Se atom moving to the (1/2, 1/2, Z) site. At the transition state of the phase transition, the length of the Se–V bond is decreased to 2.189 Å from the initial value of 2.302 Å for monolayer *T*-VSe₂ and finally increases to 2.265 Å for monolayer *H*-VSe₂. The overall phase transition needs to overcome an energy barrier of 147 meV. The barrier is much lower than that of VS₂,^[7-8] probably due to large atomic radius of selenium atoms.

Furthermore, we use the same technique to calculate the energy barrier at few-layers level, as shown in Table S2, and the result show no significant difference from monolayer to 10-layers case.

Layer number	1	2	3	5	10
Energy barrier (meV)	147	151	147	152	146

Table S2Energy barriers with different layer number

Electrical band structure

Our DFT calculation presented in Figure S4a shows that 1T-VSe₂ exhibits robust metallic behavior due to the bands crossing the Fermi energy. Meanwhile, as shown in Figure S4b, bulk 2H-VSe₂ has a small bandgap around 0.3149 eV without considering spin. If spin is considered, a bandgap is widened to around 0.7635 eV separately between the valence band maximum (VBM) around Γ point and the conduction band minimum (CBM) around M point in Brillouin zone.



Figure S4 Electronic band structures of (a) bulk *1T*-VSe₂, and (b) bulk *2H*-VSe₂. The spinup and spin-down bands are distinguished as black and red lines, respectively.

2. Device Fabrication

VSe₂ single crystals are grown via chemical vapor transport method with iodine used as the transport agent. In a typical procedure, a mixture of vanadium and selenium powder with mole ratio of 1:2, as well as iodine powder were encapsulated in quartz tube with vacuum. Then the tube was placed into a muffle furnace. Subsequently, the furnace was heated to 850 °C and kept for 2 days and then slowly cooled down to 500 °C within 2 days, finally, cooled down to room temperature. VSe₂ crystals with several millimeters can be obtained.

1T-phase VSe₂ nanoflakes in the experiments were obtained by mechanically exfoliating from VSe₂ single crystals with organic polymer membrane, then transferred onto 300-nm thick SiO₂ capped silicon substrates for the Raman measurement, which is similar to the technique of producing graphene. It is hard to obtain flakes thinner than 10 nm, and the thickness of exfoliated flakes range from 10 to 150 nm, which are determined by AFM.

For the electrical measurement, the nanoflakes were transferred to the pre-patterned electrode depositing 45 nm/5 nm Au/Cr on the same silicon substrates mentioned above. All devices were annealed at 375 K for an hour to make sure the good contact between the sample and the subtracts/electrode was made.

The thickness of the nanoflakes used for Raman ranges from 15nm to 90nm, and those for electrical measurement are kept around 30nm. The whole procedure mentioned above is progressed in the glove box to prevent the sample from oxidation.

The *2H*-phase VSe₂ nanoflakes were obtained by baking the *1T*-phase VSe₂ nanoflakes mentioned above at a tube furnace ventilating argon at 650 K for two hours.



Figure S5 Left: The AFM image of the sample for Raman scattering, inset: the optical image of the same sample. Right: the standard four-probe configuration of the resistivity measurement.

3. Raman Characterization of *1T*- and *2H*-Phase

To distinguish the *1T*- and *2H*-phase of nanoflakes VSe₂, Raman spectra of these two flakes were measured. Raman spectroscopy was performed at normal incidence with diode-pumped solid-state laser centered at 532 nm. The laser beam was focused to a diameter of about 2 μ m on the samples with a ×100 objective. The laser power on the sample was adjusted at 100 μ W, preventing samples from damage through laser irradiation. The reflected radiation was collected by the same objective and analyzed with a Shamrock 193i spectrograph from ANDOR company with 1800 l/mm grating equipped with the Andor Newton EMCCD to record the signal.

In the measured spectral range, the *1T* flake shows only one dominate peak at 202.86 cm⁻¹. By contrast, the 2*H* flake exhibits two characteristic Raman peaks, at 190.9 cm⁻¹ and 221.1cm⁻¹.

Determine the temperature of the phase transition

Thermodynamic calculation predicts that in the bulk form VSe₂, the phase transition from 1T to 2H will occur at 650 K. In order to determine the suitable baking temperature, we varied the baking temperature from 550 K to 700 K at the interval of every 50 K. In the situation of 550 K and 600 K, some part of the sample shows out the peak of 1T while somewhere else shows out the peak of 2H in the Raman spectrum. This means that the transition has already begun at 500 K, but not wholly, the sample is on an intermediate state. In the case of 700 K, the baked sample all show the characteristic peak of 2H-VSe₂. But from the optical microscope or the scanning electron microscope (SEM) image (as shown in Figure S6a, b), we can clearly see that the nanoflakes become fragmentary as there was serious evaporation of Se atoms. The Energy-dispersive X-ray spectroscopy (EDXS) measurement in Figure S6c shows out the reduction of selenium element in

the composition. This also confirmed the evaporation of Se atoms. Therefore, the suitable baking temperature was confirmed at around 650 K.



Figure S6 Nanoflakes become fragmentary as the evaporation of the Se atom under the baking temperature of 700K. (a) Optical microscope and (b) SEM image clearly show out the fragments. (c) The EDXS spectra of samples after different baking temperature.

Excluding oxidation effects during the Raman

Exposing *IT*-phase VSe₂ at FLs level (about 10 nm) to air is easy to show out the *IT* characteristic peak accompanied with another significant peak at 243 cm⁻¹ when doing the Raman measurement, as shown in Figure S7. This significant 243 cm⁻¹ peak is identified as the Raman signal of the oxidation of vanadium. We surmise that the oxidation is induced by the heating effect of the laser. Raman spectrum is measured from a thin *IT*-phase VSe₂ that covered by a flake of *h*-BN to isolating air under ambient condition, as the *h*-BN film is impervious to oxygen diffusion even at high temperature.^[9] The absence of the oxidation peak from the Raman spectrum verifies our assumption.



Figure S7 Comparison of thin *1T*-phase VSe₂ covered by a flake of *h*-BN (red) or not (black) under ambient condition. Inset is an optical image of the sample covered by the *h*-BN.

This also indicated that exposure to oxygen and high temperatures at the same time would accelerate the oxidation of *1T*-phase VSe₂ flake. As the laser would induce local high temperature, unless otherwise specified, all Raman measurements are carried in the high vacuum chamber to exclude the influence from oxygen.

For the same thickness level 2H-VSe₂, the Raman spectra show no difference between the sample placed in a high vacuum chamber and exposed to air. This striking contrast indicates that when the VSe₂ thinned down to FLs level, the 2H-phase is thermodynamically stable than 1T-phase, which is consistent with our thermodynamic calculation.

For further confirmation of that the 243 cm⁻¹ peak comes from the oxidation, the sample was heated to 373 K in the air for 1 hour to make it fully oxidized before Raman measurement. As shown in Figure S8a, the Raman spectrum shows a significant oxidation peak at 243 cm⁻¹ rather than any characteristic peak of either *1T*- or *2H*-phase. The EDXS measurement is carried on the corresponding sample. As shown in Figure S8b, we can clearly see that, for the oxidation sample,

the selenium atoms are almost replaced by the oxygen atoms while oxygen barely exists in the 1T-VSe₂ or 2H-VSe₂ sample.



Figure S8 (a) Characteristic Raman peaks of *2H*-VSe₂ (blue), *1T*-VSe₂ (red) and oxidized *1T*-VSe₂ (orange) and (b) the corresponding EDX spectra.

Thickness dependence Raman spectra of 2H-phase VSe₂

The Raman spectra of 2H-phase VSe₂ with thickness ranges from 15 to 90 nm were measured. No energy shift was shown in Figure S9. The lack of sensitivity to the change of thickness may be ascribed to the shortage of samples thinner than 10 nm.



Figure S9 Thickness dependence Raman spectra of 2H-VSe₂.

4. Electrical Measurement

For the resistivity measurement, a constant current source provided by the KEITHLEY 236 source measure unit is used to pass constant small current I, which can protect the sample from burnout by overloaded current, to the two external electrodes. The same KEITHLEY 236 source measure unit is also used as a precise voltmeter to measure the voltage V between the two inner electrodes, and the thin film resistivity of the sample is calculated according to

$$\rho = \frac{\pi L}{2\ln 2} \frac{V}{I}$$

where L is the length of the electrode.

For the current-voltage curve measurement, the source voltage measurement current method is used. A KEITHLEY 236 source measure unit is used to add a variable voltage on the sample, and the same KEITHLEY 236 source measure unit is also used as an ammeter to measure the current flow through the sample.

The low temperature and high vacuum environment (less than 10⁻⁶ mbar) were provided by JANIS research PTCM-4S-3 refrigerator system (about 15 K) or ST-500 Microscopy Cryostat (about 77 K) and controlled by LakeShore 332 temperature controller.

Fitting of the temperature-dependent conductivity of 2H-VSe₂ sample

The conductivity data was first fitted by the thermal activation model given by $\sigma = \sigma_0 \exp\left(-\frac{E_a}{k_BT}\right)$, where σ_0 is the temperature-dependent parameter extracted from the fitting curves, *T* is the temperature, E_a is the thermal activation energy, and k_B is the Boltzmann constant. As shown in Figure S10a, we found that in the high-temperature regime (above 100 K), the model fits the data very well ($r^2 > 0.996$). However, the data in the temperature regime lower than 100K fit poorly ($r^2 < 0.75$).



Figure S10 (a) The thermal activation model fitting of the conductivity data in the high (above 100 K) and (b) the Mott VRH model fitting for the low temperature (below 100 K) regime.

So for the data in the low-temperature regime (below 100 K), we try to use the Mott VRH model given by $\sigma = \sigma_0(T) \exp\left[-(T_0/T)^{\frac{1}{d+1}}\right]$ to fit them, where σ is the measured conductivity, T is the temperature, d is the dimensionality of the system, and σ_0 is a temperature-dependent conductivity prefactor given by AT^{-m} , where m varies from 0.8 to 1, A is a constant, and T_0 is the characteristic temperature given by the slope of the linear fits for σ versus $T^{-1/3}$. d = 2 is selected for multilayer VSe₂, as the case has been verified previously for ultrathin MoS₂.^[10] Figure S10b shows the above Mott VRH equation with m = 0.8 fits the temperature-dependent conductivity data very well ($r^2 > 0.997$).

The current-voltage curves measurement

The current-voltage curves are shown in Figure S11. At both room and liquid nitrogen temperatures, Ohmic-like behaviors (linear $I_d - V_{ds}$) are observed in 1T-VSe₂ (Figure S11a, c), which indicates the metallic property of 1T-VSe₂. By contrast, clear nonlinear $I_d - V_{ds}$

characteristics are indicative of Schottky behavior of 2H-VSe₂ (Figure S11b, d), which is consistent with the semiconducting of 2H polymorph.



Figure S11 I-V characteristic of (a) *1T*-phase VSe₂ and (b) *2H*-phase VSe₂ at room temperature (300 K); (c) and (d) at the liquid nitrogen temperature (77 K).

5. In-Situ Heating and SAED Characterization

The TEM sample used for *in-situ* heating and SAED characterizations was prepared by the standard focused ion beam (FIB) based lift-off process using a FEI Quanta 3D FEG system, with the working voltage and ion probe current gradually decreasing from 30 kV& 5 nA (for initial cutting) to 5 kV&10 pA (for final polishing), respectively. *In-situ* heating experiments were conducted with a conventional furnace-type heating holder (Gatan 628) inside the TEM (FEI Tecnai G² F20) operated at 200 kV, and the accuracy of the measured temperature is ± 5 K. Kinematic theory-based diffraction simulation was done using the software (Crystalmaker & Single-crystal diffraction) during which the DFT calculated structures including the unit cells of *IT*-VSe₂ and *2H*-VSe₂ were used.

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