Introduction

Lattice structures linked to crystal symmetry are fundamental for establishing the physical properties of a solid state system. Polymorphisms allow the coexistence of multiple structural phases, constituting an intriguing property of transition metal dichalcogenides (TMDs). Most TMDs have 2D layered polymorphic structures in which the transition metal ions are connected via six chalcogens, such as trigonal prismatic (2H), octahedral (1T), scarcely distorted octahedral (1T’), and orthorhombic (T_d) structures. Control over such polymorphs has attracted great attention not only because of their underlying physics, but also for their potential applications based on their rich electronic properties as metals, semiconductors, Weyl semimetals, and topological insulators, as well as their superconductivity. One challenge is to engineer an atomically sharp interface between two polymorphs while retaining their distinct electronic properties and without changing chemical stoichiometry. It has already been shown that polymorphs can coexist within the same sample through either controlled growth methods or post treatments.

The 1T’ structure is of great research interest because of its topological phenomena as a Weyl semimetal and as a quantum spin Hall insulator. While the 1T’ structure is mostly observed in MoTe_2 and WTe_2, which are both group-6 TMDs, it is also noted that chemical exfoliation and electron donors like lithium and potassium can drive the structural transition from the 2H phase to the 1T’ phase in other group-6 TMDs. Despite recent intensive investigations on the 1T’ phase, its structural nature is not well understood at a microscopic level.

Bulk vanadium diselenide (VSe_2), which is a group-5 TMD, shows three-dimensional charge density wave (CDW) with 4 × 4 × 3 nesting vector. A recent report of strong ferromagnetism in monolayer VSe_2 has garnered significant attention, although its existence and origin are still under debate. It is also reported that monolayer VSe_2 shows new CDW phase with 2 × √3 and √7 × √3 periodicities, completely different from the 4 × 3 nesting of the bulk VSe_2.
from the $4 \times 4 \times 3$ periodicity of bulk VSe$_2$.\textsuperscript{19,21} This result raises a very intriguing question about the structure of bilayer VSe$_2$, which is still too thin to create the vertical nesting of $\times 3$ periodicity in the bulk.

In this report, we investigate bilayer VSe$_2$ films grown on epitaxial bilayer graphene using a home-built low-temperature scanning tunneling microscope (STM). Bilayer VSe$_2$ reveals the $1T'$ phase, in contrast to the $1T$ phase found in both bulk and monolayer VSe$_2$.\textsuperscript{18–20,23,25} This is surprising because the $1T'$ structure is observed mostly in group-6 TMDs, and never in group-5 TMDs. This result suggests that the structural phase of VSe$_2$ can be greatly altered through the interface and layer arrangements, providing new possibilities regarding VSe$_2$ polymorphism. The bias polarity dependence of topography reveals the microscopic nature of the $1T'$ structure for Se-like and V-like surfaces. More interestingly, the static $1T'$ state can be transformed to the dynamic state of lattice vibrations by increasing tunneling current in STM topography. Latent energy exists during the transition between static and dynamic states, giving rise to hysteresis in the transition. The observed lattice dynamics involve vibrational motion of the top Se atoms and the middle V atoms. The negative bias polarity shows a smaller threshold tunneling current, which is needed to induce lattice dynamics, than the positive bias polarity. This result suggests that the middle V layer, whose d-orbital states are probed at negative bias polarity, plays an important role in driving the lattice dynamics.

**Results and discussion**

Bilayer VSe$_2$ film is grown on epitaxial bilayer graphene on a SiC substrate using home-built molecular-beam epitaxy (MBE). Microscopic investigations of bilayer VSe$_2$ are carried out using a home-built STM operated at 79 K.\textsuperscript{26} Fig. 1a shows a topographic image of top VSe$_2$ film and bottom graphene (Fig. S1 in ESI†). The profile along the horizontal line in Fig. 1a indicates that the flat surface corresponds to bilayer VSe$_2$ shown in Fig. 1a.

The high-resolution image in Fig. 1c reveals that the bilayer VSe$_2$ surface has alternative bright ($\alpha$) and dark ($\beta$) lattice lines, indicating the signature of the $1T'$ phase. A fast Fourier transformation (FFT) applied to Fig. 1c exhibits a $1 \times \sqrt{3}$ periodicity of the $1T'$ phase, labelled by a blue box in Fig. 1d. The $1T'$ phase is mostly reported in group-6 TMDs such as MoTe$_2$ and WTe$_2$, whereas both bulk and monolayer VSe$_2$ are...
stable in the 1T phase. It is, therefore, surprising that bilayer VSe$_2$ possesses a 1T’ structure, showing unique flexibility regarding the polymorphic phases of VSe$_2$ upon dissimilar interface and layer alignments. Additional modulations of CDW are not observed in bilayer VSe$_2$ except for the $\alpha$ and $\beta$ stripes of the 1T’ structure. The $4 \times 4 \times 3$ periodicity of bulk CDW is suppressed in this bilayer geometry in favor of the distorted 1T’ phase, where the underlying interface with graphene may also play important roles such as strain and charge transfer.

Although the 1T’ structures of TMDs have recently received much attention due to their interesting topological properties,$^{27}$ 1T’ structures are not well understood at the microscopic level. Fig. 2a shows the structural model of the 1T’ lattice, where red, blue, and green balls represent the top Se, middle V, and bottom Se atoms, respectively. Although both Se (red box) and V (blue box) layers have a $1 \times \sqrt{3}$ unit cell, the distances between neighboring Se-Se and V-V atoms are different due to the distorted lattices of the 1T’ phase. The unit cell of the V layer is an asymmetric rectangle in which the V atom inside the unit cell (blue box) is shifted to the left edge, while the Se layer has a centered rectangular unit cell (red box). Such differences in the symmetry of unit cell are then used to distinguish between the transition metal (V) and chalcogen (Se) layers of the 1T’ structures in STM topography. It has been demonstrated that symmetric (asymmetric) rectangle unit cell at positive (negative) bias can be assigned to Te-like (Mo-like) layer for 1T’ tangle unit cell at positive (negative) bias can be assigned to V atom inside the unit cell (blue box) is shifted to the left edge, while the Se layer has a centered rectangular unit cell (red box). Therefore, it is important to clarify the bias polarity dependence of the bilayer VSe$_2$ for better understanding on the microscopic nature of 1T’ structure.

The lattice unit cells of Se and V layers are shifted alongside each other in both the $a$- and $b$-axes, as shown with red and blue rectangles in the model of Fig. 2a. Fig. 2b reveals the predicted shift of lattice unit cells when reversing the scanning bias polarities from +3 mV to −3 mV. The black dashed line precisely aligns with the edge of the unit cell (red rectangle) in the empty state +3 mV area, but cuts across the middle of the unit cell (blue rectangle) in the filled state −3 mV area. Fig. 2a shows the shift of the unit cell along the $b$-axis as depicted with a black dashed line. The shift of the unit cell along the $a$-axis is around 1.1 Å based on the line profiles (Fig. 2c) taken from the red and blue dashed lines in Fig. 2b. All these observations match well with the structural model of Fig. 2a, confirming that empty and filled state images represent Se-like and V-like surfaces, respectively.

Intriguing lattice dynamics are observed in the 1T’ bilayer VSe$_2$. Fig. 3 shows a series of topographic images, scanning the same area with gradually increasing (a–d) and decreasing (e–h) tunneling current. When raising the current up to 60 pA (Fig. 3a–c), the 1T’ structure is maintained, although subtle broadening is involved. At 70 pA (Fig. 3d), a transition occurs in topography showing indistinctive and noisy features. When lowering the current, the topography still shows blurred features down to 30 pA (Fig. 3g) and eventually recovers the clear 1T’ structure at 10 pA (Fig. 3h). The series of topographies is attributed to the transition between the static state and the dynamic state of lattice vibrations triggered by the tunneling current. Since the motion of fast lattice dynamics is averaged over the slow scanning time, the lattices in topographic images become blurry at the dynamic state. In addition, this static–dynamic transition shows hysteretic behavior during the cycle of changing tunneling currents. Fig. 3b shows clear 1T’ structure at 50 pA in the ascending cycle while Fig. 3f taken at the same current in the descending cycle is still under lattice dynamics (this is the same for the 60 pA images in Fig. 3c and e). This hysteretic behavior suggests the existence of latent

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**Fig. 2** Bias polarity dependence topography of 1T’ bilayer VSe$_2$: (a) Top (a–b plane) and side (a–c plane) views of the atomic model of 1T’ VSe$_2$, where red, green, and blue balls represent the top Se, bottom Se, and V atoms, respectively. The red and blue rectangles represent a $1 \times \sqrt{3}$ unit cell of Se and V layers, respectively. (b) The bias voltage is switched from +3 mV (empty state) to −3 mV (filled state), and back to +3 mV while scanning with a 30 pA current (size: 5 × 5 nm$^2$). (c) Line profiles measured along the blue and red dashed lines in (b) (color coded).
energy during transition, as schematically described in Fig. 4a. The system requires latent energy to induce the dynamic state, and this latent energy needs to be released to return to the static 1T′ phase. We note that the onset current to induce the lattice dynamic can vary with tips and sample locations in a range of 40–70 pA, while the hysteretic behaviors remain similar.

To investigate the trajectory of the lattice dynamics, line profiles along the dashed lines in Fig. 3a and d are given in Fig. 4b and d (color coded), respectively. The line profiles of Fig. 4d taken from the dynamic state suggest that both bright (α) and dark (β) lattices shake along lateral and vertical directions. It should be noted that the top Se layer showing alternative α and β lines are closely coupled to the paired underlying V atoms labelled by a blue arrow in Fig. 2a. In this structural view, the V atoms play a pivotal role in driving the lattice dynamics of Se atoms, as illustrated in Fig. 4c.

To further understand the static–dynamic transition, we investigated the bias polarity dependence of the lattice dynamics. Interestingly, the dynamic state can be more easily...
formed through both a tunneling current (Fig. 3) and negative bias voltage (Fig. S3 in ESI†). For positive bias polarity, however, the transition is less affected by an applied sample bias voltage (Fig. S3 in ESI†). In group 5-TMDs, the transition metal orbitals often dominate the electronic states near the Fermi level, while the chalcogen orbitals are mostly occupied and involved in the intralayer bonding.\(^2\)\(^,\)\(^29\)\(^,\)\(^30\) This explains why V-like surface is observed at the negative bias shown in Fig. 2b because the states near the Fermi level (V d-orbitals) usually contribute to the tunneling substantially at the negative bias. This suggests that vibrational dynamics can be more favorably induced by probing the V d-states at a negative bias, supporting the pivotal role of V atoms in the observed dynamic state.

Finally, we note that the bilayer VSe\(_2\)/graphene system exhibits very intriguing 1T′ phase, not found in either its bulk or monolayer systems with 1T phase. The monolayer VSe\(_2\) on graphene presents low temperature superstructures of \(\sqrt{3} \times 2\) and \(\sqrt{3} \times \sqrt{7}\), different from the \(4 \times 4 \times 3\) CDW of bulk VSe\(_2\) (Fig. S4 in ESI†). Accounting the interesting structural transition through layer thicknesses, both interlayer interactions within the bilayer VSe\(_2\) and hetero-interface couplings at the VSe\(_2\)-graphene boundary likely play critical roles. Therefore, it is of great interests to investigate the role of interfaces on the polymorphic phase of bilayer VSe\(_2\)/graphene system and its vibrational dynamics by controlling interface interactions such as charge transfer,\(^31\)\(^,\)\(^32\) and lattice mismatch.\(^33\)

### Conclusions

The novel polymorphic 1T′ phase and its lattice dynamics are investigated for bilayer VSe\(_2\) on bilayer graphene via low-temperature STM. Considering the stable 1T phase in bulk and monolayer VSe\(_2\), emergence of the 1T′ structure in bilayer VSe\(_2\) shows importance of the interface and layer configurations for tailoring the polymorphism of two-dimensional TMD systems. Detailed topographical analysis elucidates the microscopic nature of the 1T′ structure, confirming that Se-like and V-like surfaces are resolved at empty and filled state images, respectively. Moreover, we find that the static 1T′ phase transfers to the lattice vibrational state when triggered by a tunneling current. The hysteretic behavior of static–dynamic transitions is attributed to a latent energy involved in the transition. We propose that V d-orbitals play a pivotal role in driving the observed dynamics of Se atoms. Our work helps to understand the microscopic nature of 1T′ structures of bilayer VSe\(_2\) and the polymorphic phases of two-dimensional TMDs.

### Experimental methods

**Molecular-beam epitaxy growth of bilayer VSe\(_2\) films**

VSe\(_2\) films were prepared using a home-built molecular beam epitaxy (MBE) system with base pressures of \(2 \times 10^{-10}\) Torr. We used 6H-SiC (001) single crystal substrates, supplied by the Crystal Bank at Pusan National University. We annealed 6H-SiC substrates at 1300 °C for 2 min three times in ultra-high vacuum (UHV) conditions, and then bilayer graphene formed on the Si-faced surface of SiC. We co-evaporated V (99.97%) and Se (99.999%) using an e-beam evaporator and an effusion cell, respectively. During film growth, we maintained substrate temperature at 250 °C for 10 min for monolayer thickness and then annealed the sample at 320 °C for 30 min. We carried out in situ reflection high-energy electron diffraction (RHEED) measurements with high voltages of 18 kV. After the growth process, we covered the samples with 100 nm-thick amorphous selenium layer at room temperature to protect pristine surface from air exposure during transfer to scanning tunneling microscopy (STM) chamber. Then, the films were annealed at \(~350\) °C for 5 min in a UHV STM chamber to remove selenium capping layer, and after a few cycles of Ar\(^+\) sputtering, recovered the film surfaces.

**Scanning tunneling microscopy measurement**

STM measurements were carried out using a home-built low-temperature STM system (base pressure of \(~7 \times 10^{-11}\) Torr). Tungsten tips were prepared by electrochemical etching and cleaned with electron beam heating. The bias voltages stated in the topographic images were applied to the sample. All STM measurements were conducted at 79 K. All bias voltages were applied to the sample in STM measurements.

### Conflicts of interest

There are no conflicts to declare.

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### References

Electronic Supplementary Information (ESI)

Novel polymorphic phase of two-dimensional VSe$_2$: The 1T$'$ structure and its lattice dynamics

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1. Bilayer VSe$_2$ grown on epitaxial bilayer graphene

Figures S1a and S1b show STM images of bilayer graphene substrate and bilayer VSe$_2$, respectively. Corresponding 2D FFT images are given in Figs. S1c (graphene) and S1d (VSe$_2$) where Bravais peaks of graphene and VSe$_2$ lattices are well aligned (white dashed lines).

![STM images](image)

**Figure S1.** Bilayer VSe$_2$ grown on bilayer graphene. High-resolution STM image of (a) graphene and (b) bilayer VSe$_2$. (c-d) show the corresponding FFTs of (a-b), respectively. The white and yellow circles indicate Bravais lattice peaks of graphene and VSe$_2$, respectively. The blue rectangle represents 1$\times$$\sqrt{3}$ unit cell of 1T’ phase. Scanning conditions: (a) $V_b = -250$ mV, $I_t = 30$ pA, (b) $V_b = 30$ mV, $I_t = 30$ pA
2. Symmetry of $1\times\sqrt{3}$ unit cell in 1T’ bilayer VSe$_2$

$1\times\sqrt{3}$ unit cell of 1T’ phase VSe$_2$ is clearly observed as shown Fig. S2. However, it is found that its symmetry (centered or asymmetric rectangular) can be changed in STM topography, possibly due to the change of tip states. In Fig. S2, most of area shows asymmetric rectangular unit cell (blue rectangle), but some local area presents rather centered rectangular unit cell (red rectangle).

\textbf{Figure S2.} Filled state STM image of 1T’ bilayer VSe$_2$. 
3. Bias polarity dependence of the lattice dynamics

Figure S3a-f and S3g-k show the bias dependences of lattice dynamics for positive and negative polarities, respectively. Interestingly, the dynamic state can be formed at the lower bias voltages (below -0.2 V) for negative bias, and the atomic lattices become very indistinctive due to lattice vibrations as shown in Fig. S3i-k. For positive bias polarity, however, the transition is less affected by applied sample bias voltage; i.e. The $\alpha$ and $\beta$ rows, the signature of 1T’ phase, are still visible up to 0.6 V (Fig. S3f) albeit the lattices look somewhat blurry.

**Figure S3.** The bias dependences of lattice dynamics for positive (a-f) and negative (g-k) polarities (scan size: $8 \times 8$ nm$^2$).
4. Structures of monolayer and trilayer VSe$_2$

A. Monolayer VSe$_2$

Figure S4a shows bilayer graphene substrate, and monolayer-bilayer VSe$_2$ areas. As shown in Fig. S4c, it is quite interesting that monolayer VSe$_2$ shows new charge density wave (CDW) with $\sqrt{3} \times 2$ and $\sqrt{3} \times \sqrt{7}$ periodicity, which is very different from $1T'$ structure of bilayer VSe$_2$ and $4 \times 4 \times 3$ CDW of bulk VSe$_2$. In our recent report, we suggested that the $\sqrt{3} \times 2$ and $\sqrt{3} \times \sqrt{7}$ CDW is driven by strong lattice distortions with metal-insulator transition.$^1$ The existence of $\sqrt{3} \times 2$ and $\sqrt{3} \times \sqrt{7}$ CDW in monolayer VSe$_2$ is also confirmed by other group.$^2$

Figure S4. (a) STM topography shows monolayer and bilayer VSe$_2$ areas on top of bilayer graphene substrate. (b) Line profile taken along the blue arrow in (a) presents the thickness of each VSe$_2$ layer. (c) Monolayer VSe$_2$ image shows $\sqrt{3} \times 2$ and $\sqrt{3} \times \sqrt{7}$ superstructures marked by dotted black lines. (d) FFT image of (c) presents additional peaks corresponding to the superstructures. The pink circles indicate Bravais lattice peaks of VSe$_2$. 

$^1$ This reference is not provided in the document.

$^2$ This reference is not provided in the document.
B. Trilayer VSe$_2$

Figure S5a shows a topography containing bilayer and trilayer of VSe$_2$. In Fig. S5c, trilayer VSe$_2$ also shows alternative bright ($\alpha$) and dark ($\beta$) lattice lines which are the signature of the 1T' phase. Its FFT in Fig. S5d clearly exhibits $1 \times \sqrt{3}$ periodicity of the 1T' phase, consistent with that of bilayer VSe$_2$, and we also observed very similar lattice dynamics in trilayer VSe$_2$ as well.

Figure S5. (a) STM topography shows bilayer and trilayer VSe$_2$ regions. (b) Line profile taken along the blue arrow in (a) shows single layer height of $\sim$ 6.8 Å between bilayer and trilayer regions. (c) STM topography and (d) its FFT images of trilayer VSe$_2$ present 1T' structure. The blue rectangle represents $1 \times \sqrt{3}$ unit cell of the 1T' phase.
References
