Nanoscale



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Cite this: *Nanoscale*, 2017, **9**, 8126 Received 23rd March 2017, Accepted 26th May 2017 DOI: 10.1039/c7nr02070h

rsc.li/nanoscale

MoS₂ heterostructure with tunable phase stability: strain induced interlayer covalent bond formation[†]

Bin Ouyang, ம *^a Shiyun Xiong, *^b Zhi Yang, ^{c,d} Yuhang Jing^{e,f} and Yongjie Wang^g

The structural phase transition in MoS₂ promises applications in novel nanoelectronic devices. Elastic strain engineering can not only serve as a potential route for phase transition engineering, but also reveal potential ferroelastic behavior of MoS₂ nanostructures. However, the elastic strain required for phase transition in monolayer MoS₂ is far beyond its elastic limit, thus inhibiting the experimental realization. In this study, employing density functional theory calculations, we uncover that by forming heterostructure with buckled 2D materials, such as silicene, germanene and stanene, the critical phase transition strain required in monolayer MoS₂ can be drastically reduced. Particularly when MoS₂ forms sandwiched structures with silicene or stanene, the uniaxial and biaxial critical strain can be reduced to ~ 0.06 and ~ 0.03 , respectively, which is well below the experimental elastic limit. This theoretical study not only proposes an experimental achievable strategy for flexible phase transition design in MoS₂ nanostructure, but also identifies those MoS₂ heterostructures as 2D candidates for potential shape memory devices and pseudoelasticity applications.

1. Introduction

In addition to the promising optoelectronic,¹⁻⁴ piezoelectronic^{5,6} and valleytronic^{7,8} properties offered by MoS_2 , the probing of polytypic structures has recently inspired several new applications.⁹⁻¹³ With various experimental designs,^{9,10,14} structural phase transition to the 1T phase can occur in the original 2H phase accompanied with a shift of the S sub lattice. However, due to the instability of free standing 1T lattice, Peierls distortion would always take place and further lead to the $1T \rightarrow 1T'$ (1T") phase transition.^{12,15} The polymorphism of MoS₂ enriches its electronic properties and leads to new possible applications. For instance, 1T-MoS₂ is metallic and has been used for hydrogen evolution¹⁶⁻¹⁸ and lithium/ sodium batteries,^{16,19,20} while 1T'-MoS₂ and 1T"-MoS₂ possess narrow band gaps (<0.1 eV) with flexible tunability under external field, which is promising for a low dimensional topological insulator design.15,21,22

To date, the means of achieving flexible phase transitions in bulk and nanostructured MoS₂ are largely limited to charge based methods.^{9,10,12,13,23} Those methods, however, rely on the intercalation of ions between MoS2 layers, thus introducing various defects into the material in the meantime.9,10 The ferroelastic behavior as being studied by Duerloo et al.,²⁴ Li et al.²⁵ and Ouyang et al.,¹² inspires the potential of utilizing strain engineering as an alternative option. This method is relatively cleaner and more flexible compared to the charge injection method. However, according to first principle calculations,^{12,24} the critical planar elastic strain required for triggering $2H \rightarrow T$ transition in MoS₂ monolayer turns out to be 0.15 for biaxial deformation and >0.2 for uniaxial deformation,^{12,24} which are significantly larger than its elastic limit reported experimentally.²⁶ As a result, with the strain loaded on MoS₂, the membrane will break before the phase transition can happen. This greatly inhibits the realization of flexible phase transitions by strain engineering.

Recently, 2D heterostructures have attracted tremendous attention due to their versatile structures and promising electronic and optoelectronic properties.^{5,11,13,27-29} Due to the

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^aNational Center for Supercomputing Applications, University of Illinois at Urbana–Champaign, Urbana, Illinois 61801, USA. E-mail: bouyang@illinois.edu ^bFunctional Nano and Soft Materials Laboratory (FUNSOM) and Collaborative Innovation Center of Suzhou Nano Science and Technology, Soochow University, Suzhou, JiangSu 215123, China. E-mail: xiongshiyun216@163.com

^cCollege of Physics and Optoelectronics, Taiyuan University of Technology, Taiyuan, ShanXi 030024, China

^dKey Lab of Advanced Transducers and Intelligent Control System, Ministry of Education and Shanxi Province, Taiyuan University of Technology, Taiyuan, ShanXi 030024, China

^eDepartment of Astronautical Science and Mechanics, Harbin Institute of Technology, Harbin, Heilongjiang 150001, China

^fBeckman Institute for Advanced Science and Technology, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801, USA

^gDepartment of Electrical Engineering and Computer Engineering, University of Michigan, Ann Arbor, Michigan 48109, USA

 $[\]dagger$ Electronic supplementary information (ESI) available. See DOI: 10.1039/ c7nr02070h

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interlayer interactions, the relative phase stability can be modified when a heterostructure is formed. As a result, it can serve as a potential way to engineer the phase transition in 2D materials. In this study, we are interested in combining MoS₂ with 2D materials consisting of buckled hexagonal lattice since it will ensure more orbital overlapping with MoS₂ at the interface. The aim of the study is to reduce the critical strain of phase transition in MoS₂ within its elastic limit, thus, offering a possible strategy to realize the phase transition by strain in MoS₂ systems experimentally. Silicene,³⁰ germanene³¹ and stanene³² are three important representatives of buckled monolayer (BML) materials, among which silicene/MoS₂³³ and germanene/MoS2 34 heterostructures have already been fabricated successfully in experiments. Therefore, we focus our study on MoS₂ heterostructures with these three candidates. As demonstrated by the phase stability diagram based on DFT calculations, the structural phase transition in MoS₂ can be flexibly tuned by strain that is well below its elastic limit. With the charge transfer analysis, we found that the reduction of the critical strain originates from strain-induced covalent interaction between MoS₂ and buckled monolayers. Unlike graphene derivatives with only planar orbitals,^{11,27} covalent bridges can be directly formed between MoS₂ and 2D BML due to orbital overlapping. Accompanied by the formation of covalent bonds, the phase stability of T phases is enhanced and therefore the 2H \rightarrow T structural transition occur with much smaller planar strain than that in the free standing MoS₂. On basis of the theoretical predictions, a new route for tuning the phase stability of MoS₂ nanostructures is suggested by combining interfaces and lattice strain. Moreover, due to the different properties between the 2H-MoS₂ and the T-MoS₂ integrated with BMLs, this study will also shed light on designing 2D heterostructures with switchable properties.

2. Methodology

2.1. Modeling of atomic structures

Due to the lattice mismatch between MoS₂ and BMLs, supercells consist of different unit cells of MoS₂, and BMLs are selected to minimize the lattice distortion in simulations. Supercells of 6×6 , 10×10 , 6×6 for MoS₂ are selected for constructing heterostructures with silicene, germanene and stanene. Correspondingly, the supercell sizes of BMLs are set as 5×5 , 8×8 and 4×4 for silicene, germanene and stanene (as illustrated in Fig. 1(a)-(c)). Since we are focusing on the structural transition of MoS₂ lattice, the 2H-MoS₂ lattice is set as a reference. With this structural model, the corresponding lattice mismatches are smaller than 1.3%, 1.0% and 2.0%. In this study, we have considered MoS₂/BML bilayer and BML/MoS₂/BML sandwiched heterostructures, which account for interfacial interactions from one side and both sides of MoS₂. Both types of heterostructures can be easily synthesized experimentally with deposition based methods.33-36

It is worth noting that due to the variation in orientation, there are different possibilities to stack the heterostructures.



Fig. 1 Atomic illustration of supercells adopted for (a) Si/MoS_2 ; (b) Ge/ MoS_2 and (c) Sn/MoS_2 . Three types of sublattice sites are shown in (d).

All those possibilities can be identified from Fig. 1(d). As shown in Fig. 1(d), there are three symmetric sites labelled as A, B and C in the hexagonal basal plane of MoS_2 . In order to ensure the most orbital overlapping with monolayer MoS_2 , the bonds among BML atoms (Si, Ge, Sn) are set perpendicular to either the AB, AC or BC direction. As a result, there are 6 stacking configurations for bilayer MoS_2/BML heterostructures and 21 stacking configurations for BML/MoS₂/BML sandwiched heterostructures. All the potential stacking configurations are listed in detail in Fig. S1 (ESI⁺).

2.2. Structure optimization

First-principles DFT calculations employing the Perdew-Burke-Ernzerhof (PBE) functional³⁷ and projector augmentedwave (PAW)³⁸ method were performed using the Vienna ab initio simulation package (VASP) for structure optimization and energy calculations. The dispersive van der Waals interactions between MoS2 and BMLs were included using the DFT-D2 method of Grimme.³⁹⁻⁴¹ In each calculation, up to $5 \times 5 \times 1$ k-point grid and an energy cutoff of 400 eV were adopted. Both the k-grid and cutoff energy have been tested to be converged in energy. A vacuum space of 20 Å is used for each slab model to eliminate image interactions. When performing the structure optimizations, the system is regarded as converged when the maximum force per atom is less than 0.01 eV Å⁻¹. The interlayer distance d_0 , which is defined as the shortest vertical distance between S atoms and BML atoms, is initialized as 3.0 Å for all the heterostructures. The initial distance is tested to have no effect on the final relaxed structure.

3. Results and discussion

The configurations of three types of bilayer MoS_2/BML heterostructures after first principle DFT relaxations are demonstrated in Fig. 2. The interface interactions are illustrated by the deformation charge density shown in Fig. 2(a)–(c). In each panel, the side view of the 2H-MoS₂/BML and the T-MoS₂/BML bilayers with the lowest energy states are shown in the figures



Fig. 2 Ground state structures and deformation charge densities for bilayer (a) MoS_2/Si , (b) MoS_2/Ge , and (c) MoS_2/Sn ; in each figure from (a)–(c), the top two plots are side views of heterostructures with the deformation charge density illustrated with the same isosurface threshold value. The two subplots underneath are bottom and top views of the two monolayers in the T-MoS_/BML heterostructure. (d) Box chart plot for the total energy E_0 and equilibrium interlayer distance d_0 of different configurations; top: Si/MoS₂, middle: Ge/MoS₂ and bottom: Sn/MoS₂.

on top. Since there is significant lattice distortion in T-MoS₂/ BML heterostructures, the top and bottom views of each monolayer at each T-MoS₂/BML heterostructure are also included below the side views for more information.

As shown by the charge deformation for all three groups of MoS_2/BML heterostructures, the 2H-MoS₂ tends to interact with BMLs *via* van der Waals bonds since no charge transfer can be observed. On the contrary, the T-MoS₂ (1T, 1T', 1T'') tends to form covalent bonds with BMLs as evidenced by the significant charge transfer at the interface. The formation of covalent bonds between T-MoS₂ and BML can also be evidenced by the significant lattice distortion perpendicular to the basal plane. Moreover, as shown in Fig. 2(a)–(c), compared to the buckling direction, the atomic position in the planar direction is almost unchanged and the projected lattice is kept hexagonal.

Those phenomena observed in Fig. 2(a)–(c) can be further confirmed by the quantitative calculations of the total energy E_0 and interlayer distance d_0 shown in Fig. 2(d). For each system, the total energy as well as the layer distance between MoS₂ and BML of all stacking possibilities are presented. The exact value for all the stacking sequences can be found in Fig. S1.[†] For 2H-MoS₂/BML heterostructures, E_0 and d_0 do not change too much within different orientations between MoS₂ and BML layers. While these two quantities strongly depend on the relative layer orientations in T-MoS₂/BML (T = 1T, 1T' and 1T") heterostructures, the strong orientation dependency of energy and interfacial distance again indicates that there is a strong covalent interaction between T-MoS₂ and BML layers, which is in agreement with the calculated charge deformation. In addition, on comparing the interfacial distance d_0 between BML and different phases of MoS₂, it can be found that for all the three groups, 2H-MoS₂/BML always possesses the largest interlayer distance (~3 Å). This also delivers the information that 2H-MoS₂/BML possesses the weakest interlayer interaction.

In order to quantitatively determine the influence of interfacial bonds on the phase stability of MoS_2 , we have calculated the relative energy difference ΔE per unit cell of MoS_2 between the 2H and T phases, which is defined as follows:

$$\Delta E = (E_{\rm T}^{\varphi} - E_{\rm 2H}^{\varphi})/N_{\rm unit} \tag{1}$$

in which E_T^{ϕ} and E_{2H}^{ϕ} refer to the total energy of the T phase (1T, 1T' or 1T") and 2H phase, respectively. N_{unit} represents the number of MoS₂ units in the supercell. ϕ can either be the bilayer heterostructure, the sandwiched heterostructure or the free standing MoS₂. As shown in Table 1, compared to the free

Table 1 Calculated relative energy difference ΔE per unit cell for free standing MoS₂ and bilayer heterostructures. ΔE_{min} and ΔE_{avg} indicate the minimum and average ΔE among all stacking sequences

Structure energy (eV)	$\begin{array}{c} \mathrm{MoS}_2 \\ \Delta E \end{array}$	MoS_2/Si		MoS_2/Ge		MoS_2/Sn	
		ΔE_{\min}	$\Delta E_{\rm avg}$	ΔE_{\min}	$\Delta E_{\rm avg}$	ΔE_{\min}	$\Delta E_{\rm avg}$
1T	0.839	0.337	0.385	0.513	0.568	0.552	0.561
1T'	0.551	0.330	0.383	0.483	0.509	0.370	0.371
1T″	0.634	0.385	0.396	0.468	0.498	0.356	0.371

standing structures, ΔE is greatly decreased by forming a bilayer heterostructure with all the three considered BMLs, which changes in the order MoS₂/Ge < MoS₂/Sn < MoS₂/Si. The reduction of ΔE indicates that the transition from 2H to T structures will be much easier when a bilayer heterostructure is formed. Consequently, this strategy can be cooperated with the strain engineering to tune among different phases. Since the energy difference is largely reduced, the required strain could be much smaller than that in the free standing state of MoS₂, thus opening a potential way to experimentally realize the phase transformation through deformation.

Since the energy difference between the 2H and T phase is largely reduced in bilayer heterostructures, it might be possible that this energy difference can be further reduced if a sandwiched BML/MoS₂/BML is formed. To test this idea, we also studied the configurations and the total energy of BML/ MoS₂/BML sandwiched heterostructures. As demonstrated in Fig. 3, similar to the bilayer systems, BML interacts with T-MoS₂ from both sides *via* covalent interactions, while it interacts with 2H-MoS₂ *via* weak van der Waals forces. Moreover, E_0 and d_0 of BML/T-MoS₂/BML structures highly depend on the stacking orientations with the fluctuation larger than the bilayer systems. To quantify the influence of interfaces on phase stability, the relative energy difference ΔE is also evaluated for each configuration and is demonstrated in Table 2.

As expected, the relative energy difference ΔE is much smaller than that in the corresponding free-standing MoS₂ monolayers and the reduction is even more significant than that in the corresponding bilayer structures, indicating that the transition from 2H to T phases should be even easier in sandwiched structures compared to the bilayer systems.

It is also worth to mention that both MoS_2/Ge bilayer and $Ge/MoS_2/Ge$ sandwiched structures show the least reduction of ΔE compared to the other two systems, *i.e.*, ΔE is larger than that in the Si and Sn systems (Tables 1 and 2). As a result, the phase transition from 2H to T phases in MoS_2 -Ge heterostructures should be more difficult than that in MoS_2 -Si and

Table 2Calculated relative energy difference ΔE per unit cell for thefree standing MoS2 and sandwiched heterostructures

Structure energy (eV)	$MoS_2 \\ \Delta E$	Si/MoS ₂ /Si		Ge/MoS ₂ /Ge		Sn/MoS ₂ /Sn	
		ΔE_{\min}	$\Delta E_{\rm avg}$	ΔE_{\min}	$\Delta E_{\rm avg}$	ΔE_{\min}	$\Delta E_{\rm avg}$
1T	0.839	0.187	0.341	0.409	0.496	0.406	0.449
1T'	0.551	0.153	0.248	0.399	0.440	0.167	0.198
1T"	0.634	0.131	0.218	0.362	0.418	0.138	0.178



Fig. 3 Ground state and deformation charge density for sandwiched structures of (a) $Si/MoS_2/Si$, (b) $Ge/MoS_2/Ge$, (c) $Sn/MoS_2/Sn$; (d) calculated total energy and interlayer distances for all the potential BML/2H/BML stacking heterostructures. In each figure from (a)–(c), the top two plots are side views of the heterostructures with the deformation charge density illustrated with the same isosurface value, while the three plots underneath are the bottom views of the three monolayers individually.



Fig. 4 Phase stability diagram for (a) MoS₂/Si; (b) MoS₂/Ge; (c) MoS₂/Sn; (d) Si/MoS₂/Si; (e) Ge/MoS₂/Ge and (f) Sn/MoS₂/Sn heterostructures. The solid lines indicate the phase boundaries predicted while the dashed line indicates the 2H/1T' phase boundary of freestanding monolayer MoS₂.²⁴

MoS₂-Sn heterostructures. This phenomenon indicates that the charge transfer is less significant in MoS₂-Ge heterostructures, which should originate from different lattice mismatch between MoS₂ and BMLs in the supercell we considered. In general, the charge transfer should be more significant when the BML atom (Si, Ge or Sn) is situated directly on top/bottom of the S atom in MoS2 since the "head-to-head" bonding will have the largest orbital overlapping. Among the three types of BMLs, germanene atoms have much less possibility to form "head-to-head" bonding compared with the other two heterostructures, which can be identified by the number of MoS₂ and BML unit cell ratios in the supercell. From the modelling section, we can identify the number of MoS₂ and BML unit cell ratios as 36/25, 25/16 and 9/4 for Si, Ge and Sn, respectively. In one minimum supercell, there is only one "head-to-head" bonding, which means the number of "head-to-head" pairs is 1 per 36, 25 and 9 MoS₂ units for Si, Ge and Sn, respectively. Although in a single pair bond, the charge transfer follows the trend S–Si > S–Ge > S–Sn, the dense "head-to-head" pairs in the MoS2-Sn system finally result in a larger charge transfer compared to the MoS₂-Ge system.

With the reduction of energy difference between the 2H and T phases by building heterostructures, the phase transition easily occurs with the assistance of other environmental variables. More specifically, it should require much smaller elastic strain than the free standing MoS_2 to induce the corresponding phase transitions. In order to provide a direct evidence for this idea, we calculated the energy surfaces of each phase as a function of planar strain (Fig. S2†), based on which the phase stability diagrams with planar strain as state variables are established. At a specific strain, the phase with the lowest energy is regarded as the most stable one and the cross lines of the lowest two surfaces represent the phase boundaries between the two phases. When the phase boundary lines are plotted as a function of planar strain, the phase stability diagram can be constructed.

As indicated in Fig. 4, the critical strain required for inducing $2H \rightarrow T$ (1T, 1T' and 1T") phase transition is greatly reduced with the formation of interfaces between MoS₂ and BMLs. Moreover, being consistent with the above charge transfer analysis, heterostructures formed by Germanene and MoS₂ need the largest critical strain to take the transition from 2H to T phases due to the weakest interlayer interactions. On the contrary, the critical strain of the heterostructures with silicene is the smallest due to the strong interlayer interactions. Moreover, with the enhanced total orbital overlapping by forming the sandwiched structures, the phase stability will be more sensitive to the elastic strain compared to the bilayer structure. To facilitate the detailed comparisons, we have listed the critical lattice deformation required for $2H \rightarrow T$ transition in Table 3. From this dataset, it can be clearly referred that even though the uniaxial strains required are still slightly larger than the experimental elastic limit ~ 0.11 ,²⁶ they are almost halved with the forming of the bilayer heterostructures compared with the free-standing case (>0.2). Furthermore, the

Table 3 Critical lattice deformation required for inducing $2H \rightarrow T$ (1T, 1T', 1T'') phase transition in MoS₂ lattices

Strain	MoS_2	MoS ₂ / Si	MoS ₂ / Ge	MoS ₂ / Sn	Si/MoS ₂ / Si	Ge/MoS ₂ / Ge	Sn/ MoS ₂ /Sn
$\Delta a/a_0$	>0.2	0.13	0.15	0.12	0.05	0.12	0.05
$\Delta b/b_0$	>0.2	0.15	0.19	0.13	0.06	0.11	0.06
Biaxial	0.15	0.06	0.08	0.08	0.03	0.06	0.03

Table 4 The activation energy barrier $E_{\rm b}$ (normalized by the number of MoS₂ units) of selected MoS₂/BML heterostructures for phase transitions between 2H and T phases. For each BML, the first row is the activation energy barrier without strain while the second row indicates the activation energy barrier under the critical biaxial strain

BML	Bilayer stru	cture	Sandwich structure		
	$2H \rightarrow T$	$T \rightarrow 2H$	$2H \rightarrow T$	$T \rightarrow 2H$	
Silicene	1.19 eV	0.86 eV	1.46 eV	1.34 eV	
	0.51 eV	0.51 eV	1.09 eV	1.09 eV	
Germanene	1.24 eV	0.77 eV	1.45 eV	1.09 eV	
	0.47 eV	0.47 eV	0.83 eV	0.83 eV	
Stanene	1.27 eV	0.90 eV	1.36 eV	1.22 eV	
	0.57 eV	0.57 eV	1.05 eV	1.05 eV	

designing of sandwiched structures can further reduce the critical strain required for 2H to T phase transition due to the reduced energy difference. Most importantly, in the sandwiched Si/MoS₂/Si and Sn/MoS₂/Sn, the critical strains are smaller than 0.06, which is far below the elastic limit of monolayer MoS₂²⁶ (0.11) and Si/Sn⁴² (0.175/0.17). Consequently, the Si/MoS₂/Si and Sn/MoS₂/Sn sandwiched structures provide a possible platform for realizing the phase transition by strain engineering experimentally. Since the critical strain in the two sandwiched structures is within the elastic limit of both the monolayer MoS₂ and BMLs, we argue that the structures should be stable under such small strains. In fact, when we experimentally measure the elastic properties of monolayer 2H-MoS₂, the loading and unloading curves overlap each other, indicating that the 2H phase under the elastic strain is stable.²⁶

In addition to the energy information, we also considered the kinetics of the 2H/T phase transition in MoS₂ lattice. Climbing image nudged elastic band (ci-NEB) calculations are performed to estimate the activation energy barriers required for phase transitions between 2H and T phases. For each bilayer or sandwiched heterostructure, the stacking sequence with the lowest energy is selected for ci-NEB calculation. Two types of strain states are selected for ci-NEB calculations, *i.e.*, the strain free condition and the heterostructures under their critical biaxial strain as shown in Fig. 4 and Table 3. The calculated barriers are demonstrated in Table 4 below.

It is interesting to note from Table 4 that the strain can always lower the activation energy barrier for phase transition. That is to say, together with the heterostructuring, not only will the T phases be energetically more favorable, but also the overall $2H \rightarrow T$ phase transition kinetics would be enhanced. Based on this result, we propose a strategy that can further facilitate the 2H to T phase transition kinetics for Si/MoS₂/Si and Sn/MoS₂/Sn sandwiched structures: in the two systems, the critical strains are well below their elastic limit; as a result, one can apply a larger strain beyond the critical strain to reduce the phase transition barriers. After the phase transition, we can release the strain to the magnitude we want or even to zero. In this case, the T phases would be unlikely to transform back to the 2H phase even at the strain free state due to the increased energy barriers.

It is also worth noting that the electronic properties would be changed when a heterostructure is formed, which is evidenced by our calculated density of states in Fig. S3[†] and band structures calculated by Li *et al.*⁴³ To preserve the electronic properties of T-MoS₂, a possible solution is to separate/isolate the MoS₂ layer from the BML layers either by the exfoliation method⁴⁴ or by etching the BML layers⁴⁵ after the MoS₂ transform into the T phase. In addition, the heterostructures with 2H and T phases can be treated as a new material with new properties that are different from their monolayer counterparts. As a result, each phase of the heterostructures may serve as new candidates for electronic devices with exceptional properties.^{43,46} Moreover, the strain induced phase transition may also serve as an ideal candidate for devices with switchable properties similar to the newly proposed phononic logic gates,^{47,48} such as ultrathin actuators or heat pumps in nanomechanical systems.

4. Summary

To conclude, flexible phase transition can be achieved in 2D MoS₂ by forming heterostructures with silicene, germanene and stanene. Due to the covalent bond formation between MoS₂ and BML, the charge transfer will diminish the energy gaps between different phases of MoS₂. The reduced energy gap greatly decreases the critical strain that is required for phase transition from the 2H to T phases. More importantly, both the uniaxial and biaxial critical strains in Si/MoS₂/Si and Sn/MoS₂/Sn sandwiched structures are well below their elastic limit, and thus are able to be realized experimentally. Particularly, the biaxial strain in both systems can be as low as 0.03, which is almost 5 times lower than that in the free standing MoS₂. The energy barrier calculations reveal that strain can also reduce the phase transition energy barrier, and thus it is also beneficial for the phase transition kinetics.

Moreover, since the phase stability is triggered with small elastic deformation, the ferroelastic behaviors of MoS₂/BML heterostructures can serve as one candidate for testing the 2D ferroelasticity in real-world experiments. Phase transition can be introduced with deformation, while being recovered with heating or other methods, thus making these heterostructures as potential 2D shape memory alloys (SMA), with operating principle similar to that of the 3D-SMA based on martensite-austenite phase transitions. Consequentially, MoS₂/BML heterostructures could also be used as ultrathin actuators or heat pumps in nanomechanical systems.

Acknowledgements

The authors would like to thank the support from the National Natural Science Foundation of China (U1510132). Various computing resources including the National Center for Supercomputing Applications in University of Illinois at Urbana–Champaign, Supercomputer Consortium Laval UQAM McGill and Eastern Quebec and Professor Xiong's group cluster in Soochow University are also greatly appreciated.

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