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Two dimensional WS₂ lateral heterojunctions by strain modulation

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“Strain engineering” has been widely used to tailor the physical properties of layered materials, like graphene, black phosphorus, and transition-metal dichalcogenides. Here, we exploit thermal strain engineering to construct two dimensional (2D) WS₂ in-plane heterojunctions. Kelvin probe force microscopy is used to investigate the surface potentials and work functions of few-layer WS₂ flakes, which are grown on SiO₂/Si substrates by chemical vapor deposition, followed by a fast cooling process. In the interior regions of strained WS₂ flakes, work functions are found to be much larger than that of the unstrained regions. The difference in work functions, together with the variation of band gaps, endows the formation of heterojunctions in the boundaries between inner and outer domains of WS₂ flakes. This result reveals that the existence of strain offers a unique opportunity to modulate the electronic properties of 2D materials and construct 2D lateral heterojunctions.

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Monolayer or few-layer transition-metal dichalcogenides (TMDs), a new class of two dimensional (2D) layered materials, have attracted extensive attentions due to their unique electronic and optical properties.^{1–7} The band structure renormalization and the difference in work functions as the variation of the number of layers bring us a unique opportunity to construct new artificial hybrid materials.^{5,8–10} For example, heterostructures via vertically or horizontally stacking different 2D TMDs expand the properties of individual 2D crystal tremendously, which are building blocks for next generation electronic and optoelectronic devices, including transistors, photovoltaic devices, and so on. To realize a wide range of applications, both controllable synthesis and atomically sharp interface construction with a facile method are required. To date, the fabrication of 2D lateral heterojunctions has been achieved usually by sequentially integrating two different crystals, with similar lattice structure, to bond in a single atomic layer via chemical vapor deposition (CVD).^{11–17} Besides, spatially selective chemical doping is also another feasible growth method.^{18,19} However, these methods are complex, which usually need two or more steps. Moreover, there are many defects or dangling bonds in the heterointerface due to lattice mismatch or contamination, which inevitably frustrate their high performance in optoelectronic and photovoltaic devices. Thus, it is important to find a convenient approach to fabricate 2D lateral heterojunctions to optimize their performance.

Here, we report a simple and feasible method to construct 2D WS₂ in-plane heterojunctions by thermal strain engineering. The WS₂ flakes were grown on SiO₂ (300 nm)/Si substrate, via traditional low pressure chemical vapor deposition

(LPCVD) method. Briefly, high purity WO₃ powders (99.5%) and sulphur powders (99.5%) applied as precursors were placed in a 25 mm quartz tube in temperature zones of 1030 °C and 180 °C, respectively. The substrates pre-treated through sonication in isopropanol were placed in downstream region of the quartz tube at a temperature of 840 °C. The WS₂ flakes were prepared for 15 min with Ar flow at a maximum pressure ~10 kPa. After growth, the furnace was moved outside the sample immediately, which ensured the sample as grown rapidly cool down to room temperature. During the fast cooling process, mismatch of thermal expansion coefficient (TEC) between WS₂ flakes and substrates results in local stress accumulation in WS₂ flakes.

Fig. 1(a) shows a scanning electron microscope (SEM) topography of few layer WS₂ flakes. The dimensions of WS₂ flakes can be tuned by modulating the growth parameters. Under the experimental condition used in this work, the majority of the flakes are 30–50 μm in size. Fig. 1(b) shows Raman spectra of 1–4 layers with laser excitation at 532 nm. The A_{1g} mode and E_{2g}^l mode in Raman spectra represent out-of plane vibrations of S atoms and in-plane vibrations of W and S atoms, respectively. Here, the E_{2g}^l modes display obvious blueshifts while the A_{1g} modes exhibit opposite shifts when increasing the number of layers, which is similar to previous experimental reports.^{20,21}

Kelvin probe force microscopy (KPFM) has been widely used to measure surface potential and work function in a localized nanoscale surface.²² Here, we employed KPFM to explore the local work function of WS₂ flakes. Fig. 2(a) shows a typical atomic force microscope (AFM) image of one WS₂ flake grown on SiO₂ (300 nm)/Si substrate. Irregular ripples with 2–3 nm surface corrugation can be extracted from the height profile along the green arrowed dashed line

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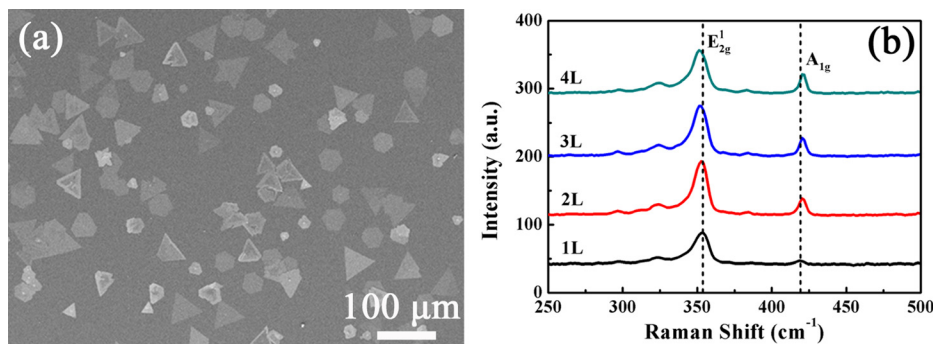


FIG. 1. (a) An SEM image of WS₂ flakes grown on SiO₂ (300 nm)/Si substrate. The Scale bar is 100 μm. (b) Raman spectra of 1–4 layers WS₂ flakes obtained with 532 nm excitation.

in the up panel of Fig. 2(c), which indicates that the interactions and absorption energies between WS₂ flake and the underlying substrate cannot be ignored.^{23,24} Fig. 2(b) represents the surface potential map of the same triangular WS₂ flake measured by KPFM. In KPFM, the contact potential difference V_{CPD} between the tip and sample is given by $V_{CPD} = \Phi_{tip} - \Phi_{smp}$, where Φ_{tip} and Φ_{smp} are work functions of AFM tip and the sample explored, respectively.²² The work function of the sample can be derived with a pre-calibrated tip. Unlike the morphology in Fig. 2(a), the surface potential map over the triangular flake shows two distinct spatial contrasts (Fig. 2(b)). This can be further demonstrated by the cross section shown in the lower panel of Fig. 2(c), which indicates the work function of the inner domain is much larger than that of the outer. The observed feature is much familiar with 2D in-plane heterojunctions constructed with two different kinds of materials with similar lattice structure.^{25–29} However, there is only one kind of material in our system. The fact that the spatial contrasts of surface potential just exist in the same WS₂ layer indicates the influence of layer difference on the surface potential and work function should be eliminated.^{9,10}

To further verify the effect of spatial contrast work function, flakes with stacked layers were explored, as can be seen from Figs. 2(d)–2(f). Fig. 2(d) presents the morphology of stacked WS₂ flakes. The corresponding height profile shown in the upper panel of Fig. 2(f) indicates the WS₂ flakes are constituted by stacking three different flake layers vertically. The top two flakes are hexagons with unequal and equal edge lengths, respectively. Owing to the variation of the number of layers, spatial resolved work function is seen in Fig. 2(e)

and the lower panel of Fig. 2(f) as expected, which is consistent with previous reports and theoretical results.^{9,10,30} However, more prominent feature: irregular sharp interface of work function map, with deeper color in the inner domain than that of the outer domain, is observed again in the same WS₂ layer.

Fig. 3 shows AFM images and the corresponding KPFM surface potential maps of a hexagonal WS₂ flake. Though the shape itself is different from the flake shown in Fig. 2(a), similar feature with junction-like surface potential interface parallel to WS₂ flake's boundary is observed in the surface potential map (Fig. 3(b)). Furthermore, regular nanoscale ripples are seen in the interior region of this hexagonal WS₂ flake (Fig. 3(c)), and the corresponding KPFM surface potential map also presents ripple-like fine structures (Fig. 3(d)). Such results further demonstrate that the difference in surface potentials and work functions between the inner and outer domain is an intrinsic feature in our system.

What is then the origin of the variation of work functions in one WS₂ flake? Just like graphene, atomically thin 2D WS₂ flake is vulnerable to strain owing to interacting with the underlying substrate. It has been reported that the TEC of WS₂ is smaller than that of the SiO₂/Si substrate.³¹ Therefore, mismatch of TEC between WS₂ and substrate will exert an in-plane compression stress on WS₂ during cooling process, as schematically shown in Fig. 4(a). The release of compression stress inevitably leads to the formation of strain in WS₂ flakes.³² Due to the fact that there is nonnegligible interaction between WS₂ flakes and substrates, the manifestation of strain can only be a contraction of the lattice constant (see “A” process of Fig. 4(a)) or accompanied by the formation of

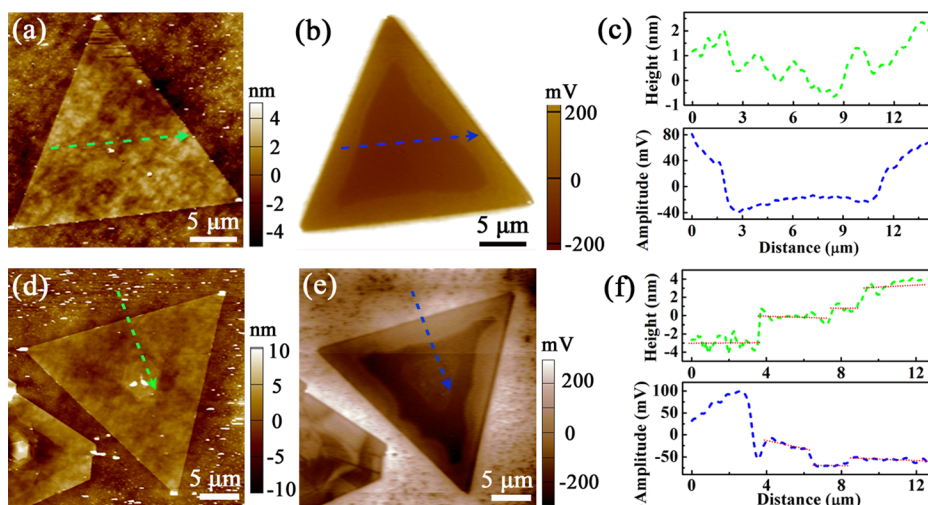


FIG. 2. (a) An AFM image of a typical triangular WS₂ flake on SiO₂ (300 nm)/Si substrate. Scale bar: 5 μm. (b) KPFM surface potential map of the triangular WS₂ flake in panel a. (c) Upper panel: Plot of the height profile along the green arrowed dashed line depicted in (a). Lower panel: Plot of the surface potential measured along the blue arrowed dashed line depicted in (b). (d) A typical image of WS₂ flake with different layer stacked. Scale bar: 5 μm. (e) Corresponding KPFM image of WS₂ flake in panel (d). (f) Upper panel: Plot of the height profile along the green arrowed dashed line in (d). Lower panel: Plot of the surface potential measured along the blue arrowed dashed line in (e).

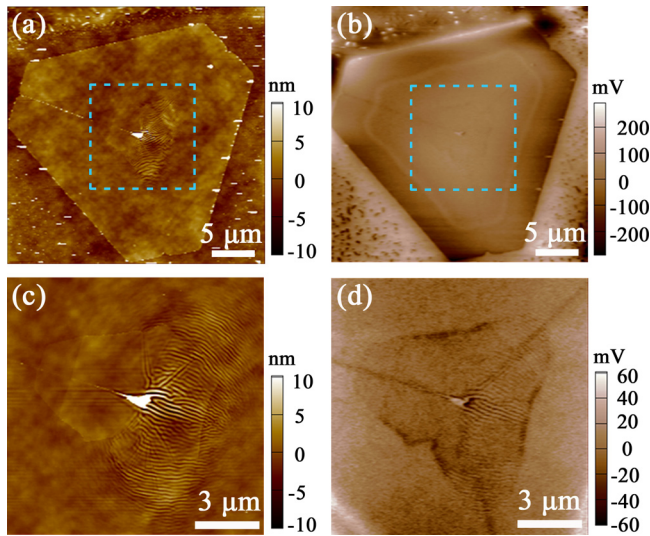


FIG. 3. (a) A typical image of hexagonal WS_2 flake grown on SiO_2 (300 nm)/Si substrate. Scale bar: 5 μm . (b) Corresponding KPFM image of WS_2 flake in (a). (c) A zoom-in topography in the blue frame of (a) showing ripples owing to compression stress relaxation. Scale bar: 3 μm . (d) Corresponding KPFM image of WS_2 flake in (c).

out-of-plane WS_2 ripples (the “B” process of Fig. 4(a)). Meanwhile, the intermediate regions of WS_2 flakes are prone to suffer a larger strain due to the compression stress relaxation from all directions around, which may differ from other works with a slower cooling process.³⁰ Recent studies have shown that strain plays a vital role in tailoring the physical properties of 2D layered materials, including graphene, black phosphorus, and TMDs.^{33–40} The work functions and band gaps can be modulated by strain engineering. Here, with relaxed compression stress of WS_2 flakes, a much larger lattice strain is induced in the interior domain. As a consequence, the Fermi velocity $v_F = [\partial E_{\vec{k}}/\hbar\partial\vec{k}]_{\partial E_{\vec{k}}=E_F}$ depending on the wave vector $\vec{k}$ decreases with the increased strain, leading to an increase in work function.³³ Thus, we observed a difference in surface potential and work function between the inner and outer domain of WS_2 flakes.

To further understand our experimental result, we calculated the effects of strain on the band gap and work function of WS_2 by density functional theory (DET), as implemented in the CASTEP code. Electron-electron exchange correlation interaction is considered by generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) function.⁴¹ In the calculation, 2H- MX_2 trigonal prismatic WS_2 structures were considered. The convergence conditions for energy and force during geometry optimization are set to 10^{-4} eV and 0.01 eV/Å, respectively. After geometry optimization, the stabilized lattice constant ~ 3.19 Å for intrinsic few layers WS_2 films is in excellent agreement with other theoretical values.^{42–44} Here, the strain is defined as the variation of relative lattice parameter $\sim (a - a_0)/a_0 \times 100\%$, with a_0 and a are lattice constants of intrinsic and strained WS_2 flake, respectively.

Usually, compression stress exerted on the WS_2 flakes will result in a decrease of lattice constant, and vice versa. Based on the change of distances between atoms, the hybridization of 3p orbitals of S atoms and 4d orbitals of W atoms will be drastically modulated.⁴⁵ As a result, the energy states for the bottom of conduction band and the top of valence band shift. Such a shift of energy levels will lead a change in the nature of the band gap, which is demonstrated by Fig. 4(b). Here, the positive (from 1% to 3%) and the negative (from -1% to -4%) strain correspond to tensile stress and compressive stress applied to the WS_2 flakes, respectively. According to Fig. 4(b), compressive and tensile stress bring about almost opposite effects on the band gap: the band gap is increased greatly when compressive stress is applied, but decreased under much larger tensile stress. Meanwhile, the work functions in Fig. 4(c) also show a similar tendency. In our system, SiO_2/Si substrate exerts compressive stress on WS_2 flake during fast cooling. Consequently, it is expected to observe increased work functions in the strained regions of WS_2 flake via KPFM measurements, which agrees quite well with our KPFM results. Thus, owing to the difference in work functions or Fermi levels of strained WS_2 and intrinsic

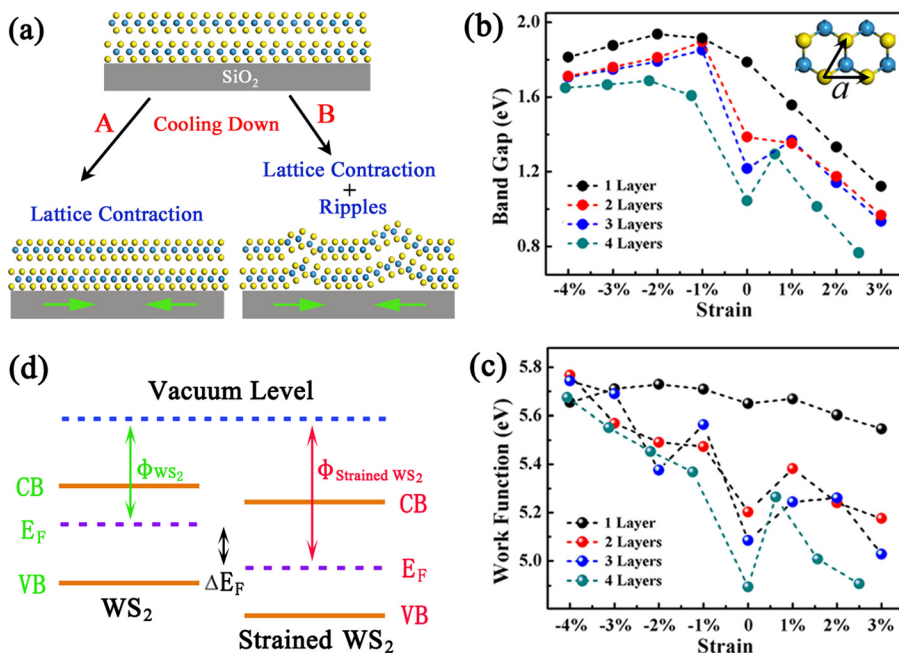


FIG. 4. (a) Schematic diagrams showing the mismatch of TEC on the formation of strain in WS_2 flakes. During cooling process, the SiO_2 substrate contracts and exerts compression stress on the WS_2 flakes. (b) Strain dependence of band gap energies of few layer WS_2 flakes with thickness ranging from 1 to 4 layers. The positive strain corresponds to tensile stress applied to the WS_2 flakes. Otherwise, the negative strain represents compression stress. (c) Evolution of the work functions Φ with the variation of strain. (d) Schematic energy band diagram of WS_2 and strained WS_2 showing their work function values.

WS₂, shown in Fig. 4(d), electrons will diffuse from intrinsic WS₂ to strained WS₂, while holes diffuse in the opposite direction. As a result, the lateral built-in potential is generated in the space charge regions, which is equal to the work functions difference between intrinsic WS₂ and strained WS₂. Furthermore, the band gap modulation by strain is another essential condition for constituting 2D in-plane heterojunction, which is equal to the sum of conduction-band offset and valence-band offset.

In summary, we demonstrated that the electronic properties of few-layer WS₂ films can be tremendously modulated by thermal strain engineering. Work functions of WS₂ flakes are increased owing to compression stress relaxation through forming a larger strain in the interior regions of WS₂ flakes during fast cooling. As a result, the difference in work functions between inner and outer domain of WS₂ flakes leads to the formation of 2D in-plane heterojunctions. This result reveals that the existence of strain offers a unique opportunity to construct and explore 2D in-plane heterojunctions.

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