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Authors	Ye, Shili;Xu, Kunqi;Lei, Le;Hussain, Sabir;Pang, Fei;Liu, Xinmeng;Zheng, Zhiyue;Ji, Wei;Shi, Xinghua;Xu, Rui;Xie, Liming;Cheng, Zhihai
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PAPER

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Shili Ye[1,2,3], **Kunqi Xu**[1], **Le Lei**[2], **Sabir Hussain**[1,3], **Fei Pang**[2], **Xinmeng Liu**[2], **Zhiyue Zheng**[1], **Wei Ji**[2], **Xinghua Shi**[1], **Rui Xu**[1,2,4], **Liming Xie**[1] and **Zhihai Cheng**[2,4]

[1] CAS Key Laboratory of Standardization and Measurement for Nanotechnology, CAS Key Laboratory for Nanosystem and Hierarchy Fabrication, CAS Center for Excellence in Nanoscience, National Center for Nanoscience and Technology, Beijing 100190, People's Republic of China

[2] Department of Physics and Beijing Key Laboratory of Optoelectronic Functional Materials & Micro-nano Devices, Renmin University of China, Beijing 100872, People's Republic of China

[3] University of Chinese Academy of Sciences, Beijing 100049, People's Republic of China

[4] Authors to whom any correspondence should be addressed.

E-mail: xur@nanoctr.cn **and** zhihaicheng@ruc.edu.cn

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Abstract

The fracture behaviors of single-layer molybdenum disulfide (MoS_2) grown on SiO_2/Si wafer by chemical vapor deposition (CVD) were systematically investigated here via a technique that combining AFM-based nanoscratch tests with friction force microscopy (FFM). To get a complete cognition of fracture behavior and deepen the understanding of different fracture stages in the process, nanoacratch with progressive and constant force was done step by step. The radius of AFM tip we used is ~10 nm which is relatively blunt to produce a tensile fracture rather than pierce the film at the initial stage. As a result, there were novel crack modes with specific normal load in the surface of CVD-grown MoS_2: semi-circular and periodical zigzag cracks, and both crack modes exhibit anisotropy during the generation and propagation. The scratch study of single-layer MoS_2 film has exhibited the gradual process of fracture behavior on nanoscale layered films and confirmed the mesoscopic anisotropy of the mechanical failure of 2D materials.

Introduction

Two-dimensional (2D) materials have attracted wide research interest since the discovery of graphene prepared by the mechanical exfoliation technique [1] because of their outstanding characteristics including electrical and superior mechanical properties [2–4]. As the rapidly growing demand for high-performance and miniaturized devices in flexible electronics field [5, 6], it is of great importance to further explore the fracture mechanics properties of 2D materials deposited on substrate. Up to date, experimental researches about fracture mechanics have been carried out on 2D materials, such as nanoindentation test on exfoliated grapheme [7], MoS_2 [8] and nanoscratch test on graphene [9], MoS_2 and h-BN [10].

Micro/nano-scratch technique is a universal method based on the atomic force microscopy (AFM) platform, which can clearly exhibit the behaviors and characteristics of nanoscale crack in flexible 2D material bounded onto a rigid substrate. For the film-substrate system, during nanoscratch progress, AFM tip is drawn over the film surface with normal load, an uneven and dynamic stress distribution are generated and especially the stress is concentrated at the localized region around the AFM tip. The radii of tips make such potential differences in the fracture progresses, extremely sharp nanoscale tip can directly cut off the film beneath the tip, which is consistent with these micro/nano-scratch researches [9–11]. And relatively blunt tip may fail to pierce the film, accompanied with the generation of delamination between the film and substrate, which will give rise to new fracture mechanics behavior. But little work has been done on 2D materials about the fracture in this side.

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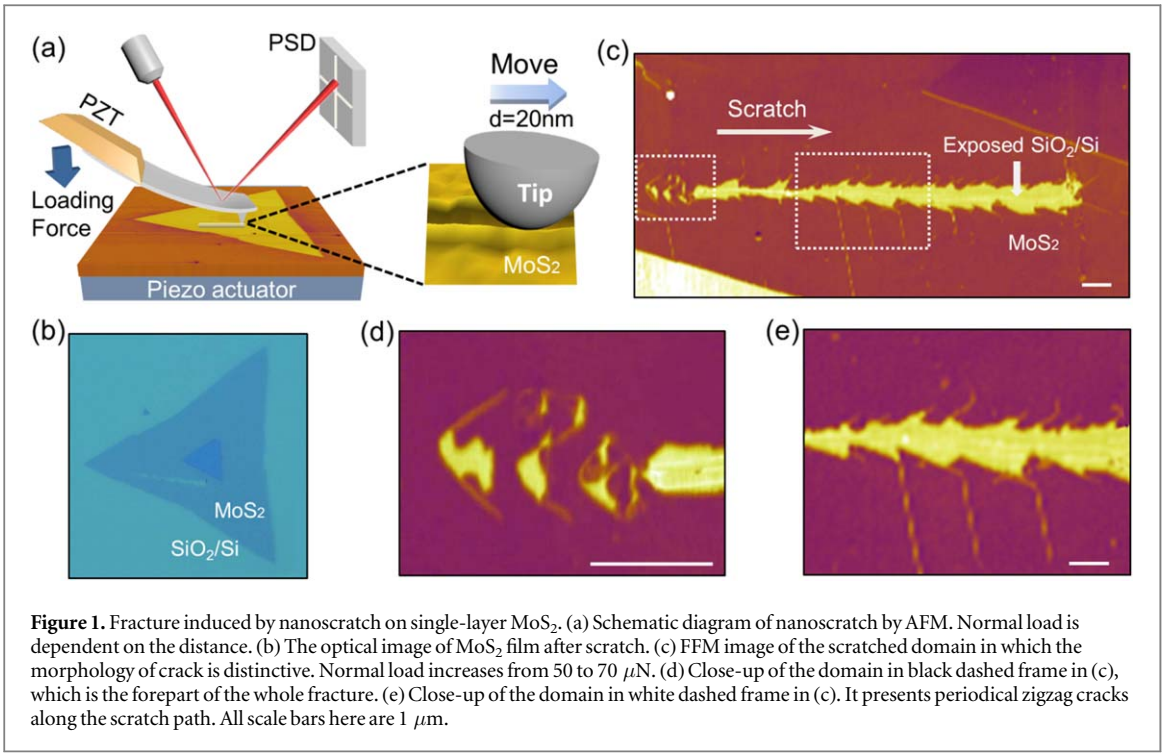


Figure 1. Fracture induced by nanoscratch on single-layer MoS_2. (a) Schematic diagram of nanoscratch by AFM. Normal load is dependent on the distance. (b) The optical image of MoS_2 film after scratch. (c) FFM image of the scratched domain in which the morphology of crack is distinctive. Normal load increases from 50 to 70 μN. (d) Close-up of the domain in black dashed frame in (c), which is the forepart of the whole fracture. (e) Close-up of the domain in white dashed frame in (c). It presents periodical zigzag cracks along the scratch path. All scale bars here are 1 μm.

Here, AFM tip with radius of 10 nm was applied for performing nanoscratch on single-layer MoS_2 film grown on SiO_2/Si substrate by chemical vapor deposition (CVD), and we observed a kind of novel normal load-dependent crack behavior. Under a series of progressive normal loads, the fracture trajectory shape generated a transformation from semi-circular to periodic serration. What's more, anisotropy of crack was clearly revealed, which namely means that the cracks generate and propagate along the energy-favored zigzag directions. These new unique crack characteristics may be originated from tensile fracture of the film driven by the 'stress cloud' instead of shear breaking. This present work is significant to get a deeper understanding of the fracture mechanics property of MoS_2 membrane and is helpful for the design of reliable and protective nanoclectrical devices.

Experiment method

The MoS_2 monolayer was deposited on SiO_2/Si substrate by CVD method. Specifically, MoO_3 powders (99.5% purity) and sulfur powders (99.5% purity) are applied as precursors. The synthesis implemented at a reaction temperature of 850 °C for 30 min, after which the heater in the furnace was turned off and the N_2 flow rate was increased to 200 sccm for cooling down. Then the grown samples were taken out if the furnace had naturally cooled down to room temperature.

Here, the experiment was done with Asylum Research MFP-3D infinity AFM in ambient environment (20 to 30% relative humidity, 20 °C to 25 °C). Antimony doped Si AFM probes [Bruker RTESPA-525, specified tip radius R = 8 to 12 nm, and typical normal force constant k = 150 to 200 N m^{-1}, calibrated using the reference cantilever method] were used at different normal load with scan areas several micrometers across.

Results and discussion

In nanoscratch experiment, in-plane break of the film is driven by the control of normal load of AFM tip. To investigate the dependence of normal load on nanoscratch, we applied a progressive series of forces to perform a scratch along a linear routine on the single-layer MoS_2, shown in figure 1(a). The normal load increased from 50 to 70 μN with a distance of 20 μm. Considering the crack behavior is potentially dependent on the tip radius [10–12], the apex radius of ~10 nm was chosen, which is not too sharp to pierce the film easily and not too blunt to peel off such huge piece of film. The experiment result is presented in figures 1(b) and (c), which corresponds to the optical image and morphology of the sample after scratch test, respectively.

As the morphology shown, there is not obvious phenomenon on the sample with normal load less than 50 μN and crack modes in the front and the middle of fracture exhibit distinctive differences. Figure 1(d) shows the close-up image of the front of the fracture in which a so-called 'semi-circular crack' was generated only under

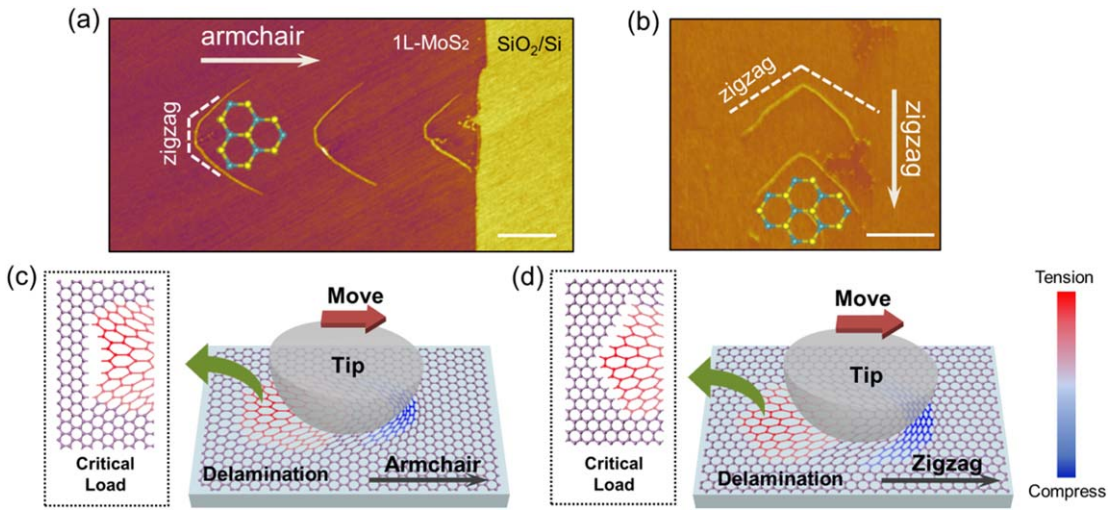


Figure 2. The formation of semi-circular cracks. (a) The FFM image of a string of cracks along armchair direction. The scratch is from left to right, as shown by the arrow. The head shape of the crack is flat. (b) A string of cracks along zigzag direction, from up to down. The head shape of the crack is angular. (c) Schematic diagram of the formation of semi-circular cracks. With the sliding of tip on sample, the tensile stress behind the tip increases up to the critical value. All scale bars here are 0.5 μm.

the certain critical load (~50 μN). Figure 1(e) is the middle of the fracture where we can find periodical serrated cracks. The serrated smooth edges of the crack imply the anisotropic brittle fracture of single-layer MoS_2. Details of the normal loads and the other experiment results have been presented in figure S1 is available online at stacks.iop.org/MRX/6/025048/mmedia which exhibit good repeatability.

The particularity of the fracture in present nanoscratch experiment lies in the fact that the two novel crack forms can be triggered according to the different magnitudes of the normal load, which is rather different from the previous researches about fracture mechanics. To further observe the characteristics of these two crack behaviors, we use constant normal load to carry out the nanoscratch process more finely. Here, under the critical load (~50 μN), with an extremely slow scan velocity; we generated the arrays of semi-circular cracks on single-layer MoS_2, as shown in figures 2(a) and (b). Figures 2(a) and (b) correspond to nanoscratch tests along the two high-symmetric crystallographic orientations (armchair and zigzag), determined by primary growth boundaries, respectively [13, 14]. Interestingly, although the size and distance between adjacent semi-circular cracks of the two crystallographic orientations are very similar, the head shapes of semi-circular cracks exhibit obvious differences. That is, the head shape of cracks along armchair is flat, but the head shape of cracks along zigzag is angular with a 120° angle at the top. As a result, all the directions of the head cracks are consistent with zigzag orientation in this mode, which agrees well with the previous theoretical calculation results on the crack propagation of MoS_2 [15–18]. Apart from the starting position of the fracture, the curved shape of crack in the propagation did not show such brittleness here. As been researched by *Wang et al* on this situation, it can be attributed to the loading force is not large enough and the sliding motion of weakly bonded sulphur atoms mitigates crack tip stress relaxation [17].

Such unique crack form is originated from the special local stress distribution around the AFM tip. As figure 2(c) shows, when the tip rubs the flexible film surface, the friction between the tip and the sample creates compressive stress in front of the tip and tensile stress behind it. The tip quasi-statically pulls the film behind the tip accompanied with the continuous delamination of the film simultaneously [19]. Tensile stress behind the tip and distributing like cloud shape expands to a larger area than the scale of the diameter of the AFM tip [20]. The maximum tensile stress occurs behind the contact back border at the edge of the formed groove; and the generated cracks are curved, which can be explained by the two directional loading mechanisms acting in the stress field [19, 21, 22]. Relatively blunt tip facilitates the expansion of 'stress cloud' rather than directly cutting off the film at the edge of tip. As the tip moves in stick-slip mode on the surface of membrane, then the tip will bounce to the next point with a distance, sliding again with the accumulation of stress and viscous force, remaining an array of semi-circular crack trajectories. And owing to crystallographic orientations dependence of fracture strength: the energy release along the zigzag direction is 2.09 $\pm$ 0.13 eV/Å, lower than the armchair direction of 2.48 $\pm$ 0.16 eV/Å [23], the head of the semi-circular crack exhibits obviously prior breaking of zigzag orientation.

Similarly, we used a larger constant normal load (80 μN) here to scratch the single-layer MoS_2 film along armchair direction and generated the serrated-shape crack, shown in figure 3(a). And figure 3(b) is the close-up image of one part of the serrated cracks, which reveals the more fine structures of the crack. After the tip

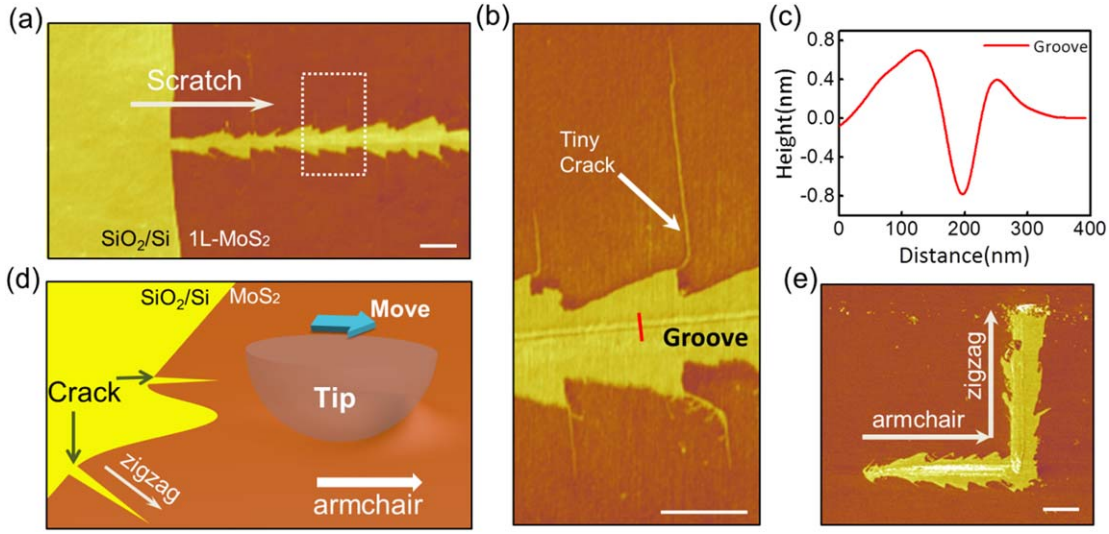


Figure 3. Periodical zigzag cracks in the fracture progress. (a) FFM image of a scratch-induced fracture with direction from left to right. The details are as follows. (1) The width of all these units is around 1.5 μm and the period of longitudinal length is around ~1 μm. (2) Most edges of the fracture present an angle of 30° to the groove generated by scratch. (3) Tiny cracks generate at the end of each unit and propagate along zigzag direction. (b) Close-up of one unit of the periodical cracks in (a). (c) The width of groove, gotten from the topography image, showing the width of the groove is around 50 nm. (d) Schematic diagram of the formation of zigzag cracks. (e) A scratch with path both along armchair and zigzag direction. All scale bars here are 1 μm.

scratches the film bound onto the rigid substrate, a groove with ~50 nm width in the middle of the fracture is generated from the direct plough of the tip, but the area that actual serrated-shape crack covers is much larger than the groove. The width of each unit of the periodical cracks is from 1 μm to ~1.5 μm with the period in longitudinally direction is 1 μm. And most cracks here are along the zigzag orientation with a neatly broken edge. Compared with the the line profile of tip contact region in figure 3(c), which is nanoscale, it indicates the delamination of the film during the scratch process.

All of these lead us to consider the periodical serrated-shape crack to stem from accumulation and release of the elastic strain energy. Kinking of the film is a pivotal aspect of crack propagation unique for two-dimensional materials, which is thought to be governed by the complex strain field at the moving crack tip [17]. As shown in figure 3(d), when the tip rubs the film, the viscous force between the tip and film make a buckling configuration before the tip which helps the continuous accumulation of the tensile elastic strain energy at the rear of tip. The film releases strain energy finally through fracture and gets the temporary elastic recovery. However, fracture is energy-favored that fracture strength along armchair is larger and such a difference causes the predominant crack in zigzag direction [16]. When the elastic strain energy decreases to a certain degree, it will accumulate again, which results in the periodicity of the serrated-shape crack.

It is worth noting that crystallographic orientation-dependent brittle fractures driven by strain energy in the MoS_2 flake sample assist the formation of serrated-shape crack regardless of the scratch directions. During the progress of nanoscratch, the continuous delamination makes the tensile stress propagate from the contact region to a certain distance. At the boundary of the stress zone, the stress is very slight but is able to drive the tiny cracks along zigzag direction to generate and propagate with strain release, Raman spectroscopy has been used to confirm this result as in figure S3. The directions are consistent with the edges of the serrated-shape crack (figure 3(b)). Further investigation confirms that the direction of the edges of serrated-shape crack is determined by energy-favoured crystallographic orientations (zigzag direction) but not related with the scratch directions (figure 3(e)).

To understand the fracture mechanism more deeply in present scratch experiment and further verify the crystallographic orientation-dependent brittleness fractures in the MoS_2 flake sample, we exerted force to the sample through scanning the film continually under a small normal load (8 μN). Figure 4(a) is a single-layer MoS_2 in its initial state, after five scanning cycles the tiny cracks propagated clearly from the edge, shown in figure 4(b), and all of them stretched along zigzag direction which was the same as tiny cracks generated from the nanoscratch. This phenomenon indicates there were micro-cracks inside of the sample during the CVD growth. When the sample interacts with the tip, the micro-cracks begin to propagate from the dents at the edge of sample. As a result, even the stress at the edge of the stress zone is small enough in figure 3(a); it still can induce the generation and propagation of zigzag cracks. Such phenomenon can also provide a novel method to obtain

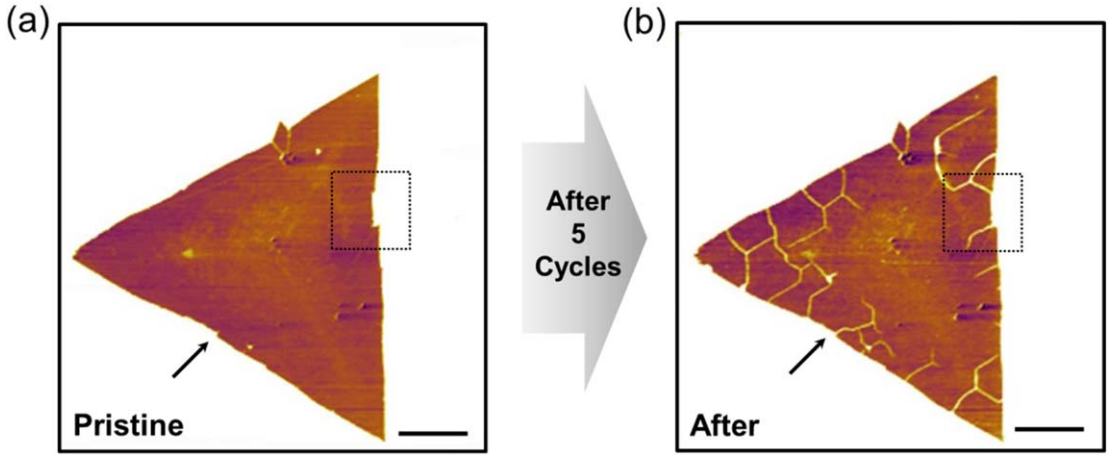


Figure 4. The propagation of tiny cracks induced by the release of thermal strain. (a) A MoS_2 film without any visible tiny cracks on it. (b) FFM image of sample after scanning for five cycles. (c) Sketch Map of the propagation of tiny cracks.

clean, tiny and smooth zigzag edges. *Miho Fujihara et al* has demonstrated in graphene the high-quality edges offer an ideal system for the study of the unique electric and magnetic properties of the edge state [24].

Summary

The study of fracture in sheet-like membrane is not only critical in gaining an understanding of the fundamental two-dimensional interatomic interactions, but it has ramifications for a host of mechanical applications. Through the nanoscratch study on CVD-grown monolayer MoS_2 film, novel fracture behaviors were observed by using the tip with such blunt apex to generate tensile break in the film. Semi-circular and periodical zigzag cracks in the fracture were generated according to the different loading force, and both of them present anisotropy in the generation and propagation progress that is helpful for the design of reliable and protective nanoelectronic devices. By considering MoS_2 as a model material for a broader class of two-dimensional atomic crystals, these results provide fundamental insights into the further understanding of their cracking mechanisms.

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ORCID iDs

Fei Pang https://orcid.org/0000-0002-8578-366X
Rui Xu https://orcid.org/0000-0001-9982-5421
Liming Xie https://orcid.org/0000-0001-8190-8325
Zhihai Cheng https://orcid.org/0000-0003-4938-4490

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