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論文題目	In-situ transmission electron microscopy observation of fracture process in multilayer MoS_2 films
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論文の内容の要旨

Mechanical strain plays a pivotal role in modulating both the structural and electronic properties of two-dimensional (2D) materials. While small, controlled strains are widely utilized to tune functionalities such as bandgap and carrier mobility, such minor deformations are insufficient for probing the intrinsic mechanical response and failure mechanisms of atomically thin materials. In particular, the understanding of fracture behavior under uniaxial tensile stress at the atomic scale remains incomplete, largely due to limitations in experimental techniques that can simultaneously provide mechanical control and atomic-resolution imaging. In this study, we address these challenges by developing an integrated in situ transmission electron microscopy (TEM) tensile testing platform and applying it to the fracture investigation of few-layer molybdenum disulfide (MoS_2) nanosheets.

Our work begins with a comprehensive assessment of existing experimental approaches and the identification of key limitations in current tensile testing methods for 2D materials. To enable high-stability mechanical testing under TEM, we first constructed a dedicated *in situ* experimental system comprising a JEOL 2100Plus TEM equipped with a custom-built tensile holder. This holder features a piezoelectric actuator and a titanium support plate to enable voltage-controlled tensile displacement with sub-nanometer accuracy.

Recognizing the instability of conventional tensile chips, such as those relying on independent silicon fragments, we designed a new tensile chip architecture based on a monolithic silicon frame integrated with a SiN_x observation window. A key feature of our design is the introduction of long, narrow slits on the SiN_x membrane, which localize strain and improve stress uniformity within the imaging region. Finite element simulations and in situ performance validation confirmed the linear displacement behavior and mechanical robustness of the platform. Additional improvements, such as the implementation of T-shaped termini and the minimization of out-of-plane movement, further enhanced the reliability of atomic-resolution deformation tracking.

High-quality few-layer MoS_2 samples were prepared via modified mechanical exfoliation using PDMS, followed by a dry-transfer process facilitated by a PPC/PDMS stamp. We adopt contrast-thickness calibration protocol using optical microscopy (OM), atomic force microscopy (AFM), and Raman spectroscopy, allowing for real-time layer number identification during sample manipulation. Moreover, we introduced a practical method for determining the crystallographic zigzag (ZZ) edge orientation of MoS_2 flakes by correlating natural edge morphology with optical and TEM observations. This orientation calibration was critical for exploring the anisotropic fracture behavior of MoS_2 under uniaxial strain.

Using the custom tensile platform, we performed a series of in situ stretching experiments on few-layer MoS_2 nanosheets with controlled orientations and thickness. Our observations revealed a striking deviation from the brittle fracture behavior typically associated with 2D materials. Specifically, samples stretched along directions near the armchair (AC) axis exhibited clear signatures of ductile fracture, including stepped edge morphologies, irregular crack fronts, and sustained compressive strain near crack tips. These features were observed consistently across multiple samples and were supported by GPA-based strain mapping, which revealed localized strain bands and interlayer sliding regions indicative of energy dissipation during deformation.

One of the most remarkable findings of this study is the consistent formation of ~10 nm-wide stepped fracture zones, which emerged during the near AC direction uniaxial tensile failure of few-layer MoS_2. These characteristic fracture regions suggest that crack propagation occurs along distinct paths. The fracture morphology further supports a scenario where cracks propagate preferentially along the ZZ direction, consistent with theoretical predictions of lower fracture energy along this direction. Similar ductile features were also observed in MoS_2 samples stretched along the ZZ orientation at low strain rates, reinforcing the generality of the observed behavior.

In addition to crack initiation and propagation, we identified the role of pre-existing structural features, such as holes and pre-cracks generated during the pre-straining process, as fracture precursors. These defects influenced the stress field and promoted crack nucleation, especially in regions characterized by ripple-like stress distributions formed propagated along two AC directions away from tensile axis. These intersecting ripples exhibit a periodicity of approximately 10 nm, which accounts for the formation of alternating stripes with ~10 nm spacing and varying contrast observed after the pre-strain treatment.

In summary, this study presents a comprehensive framework for investigating fracture mechanics in 2D materials at the atomic scale. By developing a stable, precise, and orientation-calibrated *in situ* TEM tensile testing platform, we successfully visualized the dynamic evolution of fracture processes in few-layer MoS_2. Our findings challenge the conventional view of 2D materials as inherently brittle and instead reveal a ductile failure mechanism characterized by stepwise fracture zones, interlayer sliding, and stress field redistribution. These insights not only deepen our understanding of mechanical failure in 2D systems but also provide practical guidance for designing mechanically robust nanoelectronic and optoelectronic devices based on van der Waals materials.

KEYWORDS: few layers 2H-MoS_2 nanosheet, tensile loading, ductile fracture, real-time *in situ* TEM, atomic resolution

List of publication(s):

1. Xiong, Wei, Xie, Lilin, and Oshima, Yoshifumi. Development of an in-situ TEM method for elucidating tensile fracture processes of 2D materials at atomic scale. ***Jpn. J. Appl. Phys.*** **(2025)** doi:10.35848/1347-4065/ade945.

Presentations:

- International Conference

1. Wei Xiong, Limi Chen, Lilin Xie, Kohei Aso and Yoshifumi Oshima, “Precise measurement of ripple structure of MoS_2 nanoribbon when stretching”, 20th International Microscopy Congress (IMC20), 10-15 September 2023, Korea. (Poster)

- Domestic Conference

1. Wei Xiong, Lilin Xie and Yoshifumi Oshima, “Ripple structure of MoS_2 nanosheets evaluated by in situ stretching transmission electron microscopy”, 9th International Symposium on Organic and Inorganic Electronic Materials and Related Nanotechnologies, 5-8 June 2023, Ishikawa. (Oral)
2. Wei Xiong, Limi Chen, Lilin Xie, Kohei Aso and Yoshifumi Oshima, “Precise measurement of ripple structure of MoS_2 nanoribbon when stretching”, JAIST International symposium of Nano-Materials for Novel Devices, 11-12 January 2024, Ishikawa. (Poster)
3. Wei Xiong, Lilin Xie and Yoshifumi Oshima, “Interlayer fracture of multilayer MoS_2 evaluated by in situ transmission electron microscopy”, 10th International Symposium on Organic and Inorganic Electronic Materials and Related Nanotechnologies, 11-14 June 2025, Fukui. (Poster)

論文審査の結果の要旨

2 次元材料は、同一平面内における強固な結合と、層間における比較的弱い結合という特性を有する。このため、脆性破壊と延性破壊の区別は、単なる体積変形ではなく亀裂の伝播挙動に基づいて議論される。すなわち、多層構造の各層内で独立に塑性変形（亀裂発生や空隙膨張など）が進行する場合は延性破壊と見なし、亀裂が層間を貫通する場合は脆性破壊と見なされる。延性破壊プロセスでは、TEM 観察においてステップ状のコントラストが確認されることが予想される一方、脆性破壊プロセスでは破断が瞬時に進行する様子が観察されると考えられる。

これまで、引張試験による 2 次元材料の破断過程に関しては計算シミュレーションの報告が多く、実験報告はほとんどない。その理由として、従来の in situ TEM 引張ホルダーでは、試料を固定する両支持台間の剛性不足により原子分解能観察が困難であること、両支持台間のギャップが大きく（>3 µm）、10%のひずみ導入に 300 nm 以上の変位が必要となること、さらに引張速度（通常>5 nm/s）の精密制御が難しく、破断過程の動的進化を捉えることが困難であったことが挙げられる。

本研究では、細いノッチを 1 か所設けたシリコンチップを用い、その両端に 2 次元材料を架橋してギャップを広げることで引張変形を実現した。初期ギャップを約 200 nm まで縮小することで、10%ひずみ導入に必要な変位を約 20 nm に抑え、両支持板は高剛性を有するため機械的安定性が確保され、原子分解能 TEM 観察が可能となった。ただし、伸張時に応力がノッチ先端に集中し、亀裂発生によりシリコンチップが破断する問題があった。そこで、ノッチ先端に「T」字型の幾何形状を導入し、これを機械的レバーとして機能させる設計を考案した。その結果、ギャップ伸張時にも基板破断が回避され、引張速度も 0.1 nm/s 未満に制御可能となり、従来課題の多くを解決することに成功している。その結果、MoS_2 多層膜が延性破壊している様子を TEM 観察することに成功している。

審査過程では、MoS_2 多層膜の引張変形の TEM 観察結果の解釈について議論が行なわれた。多層膜のある層でボイドが形成し、そのボイドが引っ張り方向に対し垂直方向に広がり、やがて帯状になり、破断していく様子は確認できたが、ボイドの形成については、電子線による損傷の可能性や、すでに存在していた空孔が凝集したものなどかについて不明であった。また、多層膜の固定状態も明白ではなく、この点で懸念が残った。

本研究は、新奇の引張機構を組み込んだ in situ TEM ホルダーを開発し、2 次元材料の破断過程を明らかにしたものであり、2 次元材料の機械的性質を理解する上で学術的貢献は大きい。よって博士（マテリアルサイエンス）の学位論文として十分に価値あるものと認めた。