Kirigami-inspired highly stretchable nanoscale devices using multi-dimensional deformation of monolayer MoS$_2$

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ABSTRACT: Two-dimensional (2D) layered materials, such as MoS$_2$, are greatly attractive for flexible devices due to their unique layered structures, novel physical and electronic properties, and high mechanical strength. However, their limited mechanical strains (<2%) can hardly meet the demands of loading conditions for most flexible and stretchable device applications. In this paper, inspired from Kirigami, ancient Japanese art of paper cutting, we design and fabricate nanoscale Kirigami architectures of 2D layered MoS$_2$ on a soft substrate of PDMS using a top-down fabrication process. Results show that the Kirigami structures significantly improve the reversible stretchability of flexible 2D MoS$_2$ electronic devices, which is increased from 0.75% to ~15%. This increase in flexibility is originated from a combination of multi-dimensional deformation capabilities from the nanoscale Kirigami architectures consisting of in-plane stretching and out-of-plane deformation. We further discover a new fundamental relationship of electrical conductance and large strain in MoS$_2$ Kirigami structures through both experimental work and finite element simulation. Results show that the electrical conductance of the stretchable MoS$_2$ Kirigami is closely related to its different stages of structural evolutions under strain: e.g., elastic stretching; then a combination of elastic stretching and out-of-plane buckling; and finally stretching and structural damage. This method provides a new opportunity to fabricate highly flexible and stretchable sensors and actuators using different types of 2D materials.

INTRODUCTION

Flexible and portable devices have become the mainstream trend in modern electronics and optoelectronics, showing wide-spread applications in in-situ health monitoring, intelligence interfaces, portable facilities for military camping, and information communication. Realization of fully flexible electronics generally needs the devices to possess the abilities to be folded, bent, and stretched, but still maintain their original properties. Conventional electrical systems based on hard and brittle silicon and its associated technologies cannot satisfy this requirement, which pushes scientists to explore other types of highly elastic materials. In the past decade, various materials including inorganic ceramic materials, metallic materials, conductive polymer and various nanomaterials have been exploited for fabricating different flexible devices (e.g. strain sensors and bendable display screens) to meet the requirements of both good mechanical properties and excellent electrical performances. Very recently, two-dimensional (2D) layered materials (e.g. graphene and MoS$_2$) have been attractive as candidates for building flexible devices, due to their atomically layered structure, layer number dependent electrical properties, super-mechanical strength (e.g. monolayer MoS$_2$ with a 180 ± 60 Nm$^{-1}$) and relatively large stretchability. However, many current flexible devices can only withstand a limited mechanical strain, such as <1% for inorganic ceramic materials, <1% for metallic materials and <5% for conductive polymer and 0.8–5% for 2D layered film of graphene and MoS$_2$. Under severe deformation conditions, this limited strain of the flexible electronics hinders their wide applications. For portable device applications, larger deformation > 5% is often needed in some specific applications such as artificial intelligence interfaces. Recently, attempts have been made to integrate high elasticity and multi-functionality using special functionally structural designs such as Origami or Kirigami architectures. Origami and Kirigami are both traditional Japanese craft
techniques, which enable the fabrication of 3D structures through folding, cutting or bending from 2D sheets of paper. Kirigami mainly refers to paper cutting and Origami refers more on folding of paper. Inspired by the concept of Kirigami, 3D functional structures can be produced in a similar way to achieve a stretchability far beyond the corresponding constituents by out-of-plane deformations of materials. Specifically, some Kirigami structures have been successfully made from graphene, graphene composites and semiconducting GaAs film, respectively. Several application examples based on these Kirigami structures have been demonstrated to apply into stretchable lithium ion batteries, sunlight tracking system in solar cell, soft robotics and optics. Compared to their planar counterparts, Kirigami structures have advantages such as enhancement of the device performance combined with a high stretchability, which is important for flexible and portable device applications. With their intrinsic super-mechanical and physical properties, 2D layered semiconductor materials such as MoS2 are expected to be ideal building blocks for new types of functional Kirigami architectures which will show good performance in portable electronics and optoelectronics. However, up to now, only some theoretical analysis of mechanical properties have been done on the Kirigami structures for 2D monolayer MoS2.

In this article, we perform, for the first time, the experimental investigations in Kirigami structures of 2D layered semiconductor of MoS2. Several MoS2 Kirigami structures were prepared using a plasma etching approach, where the soft polydimethylsiloxane (PDMS) mold was applied as both shielding mask and flexible substrate. Raman and photoluminance (PL) spectra of the MoS2 Kirigami structures exhibited a robust shift upon a tensile loading. The MoS2 Kirigami structures showed a large reversible strain up to 15%, far beyond MoS2’s intrinsic reversible stretchability of 0.75%. Furthermore, we revealed the relationship between the strain and electrical properties of MoS2 Kirigami structures through experiments and finite element simulation. We further discovered a new fundamental relationship of electrical conductance and large strain in MoS2 Kirigami structures. The MoS2 Kirigami structure displayed three major deformation stages upon tensile loading: i.e., elastic stretching, combination of elastic stretching and out of plane buckling, and breaking stage; therefore exhibited distinct electrical conduction behavior at each stage.

**EXPERIMENTAL SECTION**

**Growth of large-area monolayer MoS2 films.** Monolayer MoS2 films were grown on SiO2/Si substrate. The substrate was treated in the piranha solution at 83 °C for 30 min and washed with isopropyl alcohol, acetone, ethanol and deionized water for 10 min, respectively. Then it was treated with O2 plasma for 5 min. The growth process was carried out in a two-zone horizontal CVD system using MoO3 (99.9%), Aladdin and S (99.95%, Aladdin) powders as precursors. MoO3 powder and the substrate were placed on a quartz substrate at the high temperature zone (~670 °C). The distance between MoO3 powder and the substrate was 3 cm. Meanwhile, the S powder was kept in an alumina boat and located at the center of low temperature zone (~250 °C), which was at the upper stream position. During the reaction, Ar gas with a flow rate of 15 sccm was used as the gas carrier. The growth process was kept for more than 30 min under the atmospheric pressure, and then the CVD furnace was naturally cooled down to room temperature.

**Fabrication of 2D MoS2 Kirigami structure on PDMS.** Firstly, different types of hard templates with various microscale structures were fabricated using Si substrate with a thickness of 1 mm through photolithography and wet etching technologies. Then, the template was fumigated using perfluorooctyltrichlorosilane (CF3(CF2)5(CH2)2SiCl3) to avoid the adherence of PDMS to the template. By carefully peeling off the PDMS from the Si template in an ethyl alcohol solution, freestanding PDMS with the designed Kirigami structures was obtained. The freshly prepared PDMS was kept in a vacuum oven for 1 hour to eliminate air bubbles. After that, the PDMS was poured into the templates and heated up to 80 °C for 4~5 hrs. Then the PDMS with the Kirigami structures was peeled off from the Si template in ethyl alcohol solution and dried for 30 min. Next, a large-area MoS2 film, which was synthesized via the CVD process, was transferred onto the Kirigami-structured PDMS substrate by a polymethyl methacrylate (PMMA) assisted transfer process. Then the PDMS/MoS2 was etched using plasma from the reverse side. The smackyglam sections of MoS2 were etched away. Then the PMMA was removed using acetone, thus the same Kirigami structure of the MoS2 films with the underlying PDMS substrate was obtained. After that the strain sensors of PDMS/MoS2 Kirigami structures were fabricated by patterning Ti/Au contact onto the surface of PDMS connected using copper (Cu) wire.

**Finite Element Method.** Commercial finite element analysis software COMSOL Multiphysics was utilized to conduct the theoretical simulation. For the simplification, a 2D PDMS Kirigami substrate model was built with physical constants selected as follows: 0.97 kg/m³, 50 kPa and 0.49 for density, Young’s module and Poisson ratio, respectively. The deformation, stress and strain distributions of Kirigami substrate were simulated under different external strains of 5%, 10%, 15% and 20%.

**DFT calculation.** Theoretical calculations were performed using first principles and density functional theory (DFT) in CASTEP package. The core electrons were replaced by plane wave ultra-soft pseudopotential. The generalized gradient approximation (GGA) and Perdew-Burk-Ernzerhof (PBE) methods were applied to describe the exchange and correlation effects of valance electrons. By performing a convergence test, the k-point was set as 4×4×4 and the cut-off energy was 320 eV. The model was optimized by using a GGA+PBE method and BFGS algorithm until the convergence tolerances was satisfied. The convergence tolerances were set to be 1×10^-6 eV, 0.1 GPa, 0.05 eV/Å, 10^-3 Å for energy, maximum stress, maximum force and maximum displacement, respectively.

**Characterizations.** The obtained samples were characterized using an optical microscopy (Leica DM4500P), a scanning electron microscope (SEM, Hitachi S-4200), Raman and PL spectra (LabRAM XploRA, incident power of 1 mW, excitation wavelength 532 nm). Au electrodes were fabricated using film deposition machines (ZHD−300) and a shadow mask. Electrical measurements of the device were performed using a semiconductor analyzer (Keithley 4200 SCS) combined with a home-made three-dimensional displacement platform at room temperature of ~ 20 °C.
RESULTS AND DISCUSSION

The synthesis process for the highly stretchable MoS$_2$ devices based on the Kirigami structural approach is shown in Figure 1. Large-area MoS$_2$ films were synthesized using a chemical vapor deposition (CVD) which has been reported in our previous papers. The SEM and optical images of large-area MoS$_2$ films are shown in Figure S1 and corresponding thickness of MoS$_2$ is about 0.8 nm (as shown in Figure S2), which indicated the MoS$_2$ is monolayer. The MoS$_2$ films were transferred onto the different PDMS Kirigami structures which were prepared using an injection molding method (see the details in experimental section). Subsequently, various MoS$_2$ Kirigami structures were obtained by plasma etching the exposed MoS$_2$, thus MoS$_2$/PDMS Kirigami structures were obtained with one example shown in Figure 1b. In this way, we obtained the MoS$_2$ with the same Kirigami structure as the underlying PDMS substrate as shown in Figure S3e. Stretchable devices were fabricated by depositing Ti/Au contacts onto the MoS$_2$ Kirigami structure (see Figure 1c). Figure 1d shows the structural changes of the Kirigami structure under a uniaxial strain, providing the MoS$_2$ with variable deformed shapes.

![Figure 1. Schematic illustration of the fabrication process of the MoS$_2$/PDMS Kirigami structure.](image)

The aforementioned technique enables the production of various MoS$_2$ Kirigami structures onto the PDMS substrate. The deformation behaviors between the MoS$_2$/PDMS and paper are similar, which makes it easy to demonstrate the Kirigami structures firstly using the paper models as shown in Figures 2a-2d. The yellow parts represent the electrodes and the white ones are the MoS$_2$ Kirigami structures on the PDMS substrate. As is well known, the Kirigami structure can be considered as a thin and inextensible sheet shaped into a particular 3D geometry. Here, we fabricated four different Kirigami structures: e.g., two linear patterns of Kirigami springs, Kirigami pyramids, and out-of-plane Kirigami springs with alternating C-shapes (see Figure 2).

![Figure 2. Different types of MoS$_2$/PDMS Kirigami structures. (a-d) Different types of structural models of Kirigami structures. (a$_1$-d$_1$) Optical photographs of Kirigami structures. (a$_2$-d$_2$) SEM images of MoS$_2$/PDMS Kirigami structures.](image)

To study the mechanical properties and electrical device application of 2D MoS$_2$ Kirigami structure, the linearly patterned Kirigami spring, one of the most common Kirigami structures, was utilized as the research model. As shown in the SEM image of Figure 3a, the in-plane Kirigami spring structure undergoes a deformation by applying a strain. The elemental mapping spectrum obtained from Energy Dispersive X-ray (EDX) provides the evidence that the MoS$_2$ film was deposited onto the PDMS substrate (S and Mo distributions are shown in Figures 3b and 3c, respectively). Raman and PL spectra of MoS$_2$ Kirigami structures were investigated as a function of applied stain and the testing was carried out at the location of red point A in Figure 3a. Raman characterization was performed on both the MoS$_2$/PDMS and a bare PDMS with a 532 nm laser beam. The black colored curve in Figure S4 of Raman spectra is from MoS$_2$ on the PDMS, and red colored one is from the bare PDMS. The two peaks of E$_{2g}$ and A$_{1g}$ Raman modes of MoS$_2$ are clearly observed from Figure S4. From literature, the frequency difference between the E$_{2g}$ and A$_{1g}$ Raman modes of the 2D MoS$_2$ is strongly dependent on its thickness, which can be utilized for determining the layer number of MoS$_2$. The A$_{1g}$ mode (out of plane mode) at 405.4 cm$^{-1}$ and the E$_{2g}$ mode (in plane mode) at 384.6 cm$^{-1}$ are observed with a frequency difference of ~21 cm$^{-1}$ (see Figure 3d), indicating that it is a monolayer of MoS$_2$. 

When a uniaxial tensile stress was applied to the MoS₂ crystal structure, the crystal would be elongated and the lattice spacing was increased along the uniaxial direction. This structural change can be characterized using Raman and PL spectra. Figure 3d shows Raman spectra of E₂g and A₁g modes of monolayer MoS₂ on the PDMS as a function of the uniaxial strain. The dash lines in Figure 3d label the peak centers. The frequencies of A₁g mode keep unchanged upon the strain applied, whereas those of E₂g mode exhibit an apparent blue-shift with the increase of strain. From the inset of Figure 3d, the A₁g mode is generated from the out-of-plane vibration of S atoms in the opposite directions, and the E₂g mode is resulted from the opposite vibration of two S atoms with respect to the Mo atom in the horizontal plane. The dominant covalent bonds between Mo and S atoms are sensitive to the in-plane uniaxial strain.12 This can be utilized to verify the structural changes of monolayer MoS₂ in the Kirigami structure. The structural change of MoS₂ can also influence its PL spectra, and the corresponding results are shown in Figure 3e under different tensile strains. The PL of MoS₂ on PDMS shows a peak at around 1.86 eV, which is attributed to the lowest-energy excitation transition. This strong PL peak indicates a monolayer MoS₂ with a direct bandgap12. When a uniaxial strain is applied, MoS₂ Kirigami structure has a red-shift of its PL peak. Furthermore, this red-shift increases with the increase of the deformation degree: e.g., from 1.86 eV (0%) to 1.854 eV (5%), 1.849 eV (10%), 1.845 eV (15%) and 1.83 eV (20%).

Electrical properties and structural differences under different strains. The influences of the strain and structural differences on the electrical properties of 2D MoS₂ Kirigami structure were further investigated. The 2D MoS₂ Kirigami structure shows a reversible stretchability up to 15% (see Figure 4a), a 20-fold increase compared to that of the conventional CVD MoS₂ (0.75% reversible stretchability as shown in Figure S6a). The electrical conductivity of the MoS₂ Kirigami structure shows three different stages upon applying the tensile stress: e.g., an initial elastic stretching; then a combination of elastic stretching with out of plane buckling; and finally a breaking stage (see Figure 4a).

In the first stage, the deformation of MoS₂ Kirigami is within a strain value of 5%. The corresponding electrical curve of conductance (I) versus strain (ε) shows a strongly linear dependence with a slope of 0.38 (see Figure 4b). In this stage, deformation of the MoS₂ Kirigami structure mainly occurs via an elastic stretching without apparent flipping or rotation of the MoS₂/ PDMS as illustrated in Figure 4e. At this stage, the structure of monolayer MoS₂ on the PDMS surface shows a little deformation at the border or joint of the Kirigami structure (see Figures 4e and 4h). Therefore, the changes of the currents are very small with the increase of the strain during this stage as shown in Figures 4b and 4e as well as the SEM image in Figure 4h.

In the second stage, with a strain in a range from 5% to 15%, the corresponding curve of conductance (I) versus strain (ε) has a slope of 2.21. The conductance significantly increases upon deformation and reaches the maximum value at a deformation strain of ~ 15% (which is marked as II in Figure 4c). The Kirigami structure at the stage II exhibits out-of-plane deflections to undergo additional tensile deformation with a strain range from 5% to 15% (Figure 4f). Furthermore, the out-of-plane deformation causes a tilting angle with the horizontal plane as shown in Figure S7b. The deformation of MoS₂ at the stage II is much larger than that at the stage I,
consisting of the combination of stretching and out-of-plane buckling.

Further increase of deformation above 15% reaches the stage III (see Figure 4a and 4d), during which the current decreases gradually as the strain is increased (see Figure 4d). With a large strain (> ~15%), MoS2 films begin to break at the edges or joint places as shown in Figures 4g and 4j. The occurrence of breaking is usually defined as the yield point. This structural damage is irreversible. It’s worth noted that the MoS2/PDMS device with the Kirigami structure reaches the maximum reversible deformation of ~ 15%, much higher than that of the original planar MoS2 devices with a reversible strain of only ~ 0.75 %.

To further understand the mechanical and electrical behaviors of the MoS2 Kirigami upon tensile loading, theoretical simulation was performed on the linear Kirigami pattern using the finite element method (FEM). The generated forces from the linear Kirigami pattern were analyzed using a beam theory based on the method from literature. As forces from the linear Kirigami pattern were analyzed using a pattern using the finite element method (FEM). The generated theoretical simulation was performed on the linear Kirigami structure as shown in Figure 5b.

In order to understand the distribution of stress on sample surface, FEM analysis of the linearly patterned Kirigami structure was performed, and the results are shown in Figure 5. When the strain was applied along x-axis, the structure was bent out-of-plane, resulting in locally buckling patterns. We choose a small area of Kirigami structure for analysis as shown in the red-colored square in Figure 5a. This part of the structure will be deformed according to the beam bending theory, and the equations after bending deformation (Figure S8a) can be described using the following equation:

$$ y = \frac{E}{2EI} \left( f^3 - 2f^2 + x^3 \right) $$

Any point of the bent curve can be described using the following equations:

$$ \tan y = \frac{E}{2EI} \left( f^3 - 6f^2 + 4f \right) $$

$$ \Delta x \propto \Delta \cos y $$

$$ \varepsilon_{\text{MoS2}} = \frac{\Delta \gamma}{\Delta x} = \frac{1}{\cos y} - 1 $$

Where \( \gamma \) is the force applied on the beam, \( E \) and \( I \) are the Young’s modulus and rotational inertia, \( \varepsilon \) is the slope of the flexural beam equation in a position \( x \). \( \varepsilon_{\text{MoS2}} \) is defined as the strain of MoS2. The length of the hypotenuse was used to estimate the change of arc length \( \Delta f \). The function images of \( \tan y \) show a decreasing function with \( x \), which means that with the increase of \( x \), \( \gamma \) decreases. At the meantime, \( \varepsilon_{\text{MoS2}} \) increases with the increase of \( x \), which means that the maximum and minimum deformation values occur at the flexural beam center and edge, respectively.
responses. The responses of the currents were increased with the increase of deformation strain if the deformation strain value was less than 15%. The gauge factor, a performance parameter representing the sensitivity of a strain sensor, can be derived from the relation of $\Delta I/I$. The calculated gauge factor for our sensor is about 3.5 for the applied strain of 15%. This value of the gauge factor is comparable to that of graphene fiber strain sensors. The response time of the Kirigami structure-based sensor is a critical parameter. It can be seen from the time-dependent response of devices and corresponding local magnification curves in Figure S10, the response time is ~1s. To evaluate the mechanical stability of strain sensor, we apply multiple cycles under different strain as shown in Figure S11. A stable response across the cycles is observed, indicating mechanical robustness and good stability of our strain sensors. Therefore, these results showed clearly that the devices are attractive candidates for large-deformation wearable and human–machine interface applications.

CONCLUSION

We successfully demonstrate a flexible device made of the 2D MoS$_2$ film which can achieve a significant enhancement in the electrical properties and deformation behavior by adopting the Kirigami architectures. Measurement results of electrical properties indicated that the Kirigami structures significantly improved the reversible stretchability of flexible MoS$_2$ electronic devices, which was increased from 0.75% to ~15%. This new design methodology bridges the gap between nanoscale and macroscale strain engineering, and enables many novel engineering applications in which a large-scale out-of-plane deflection can be controlled precisely to create multiscale and reconfigurable structures, thus will find significant applications in a variety of flexible-electronic technologies.
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**Notes**

The authors declare no competing financial interest.

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