Full paper

Directional dependent piezoelectric effect in CVD grown monolayer MoS\textsubscript{2} for flexible piezoelectric nanogenerators

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\begin{abstract}
Due to the interesting semiconducting and optical properties of transition metal dichalcogenides, they have received particular attention for novel electronics and optoelectronics. In addition it is expected that piezoelectric properties of two-dimensional (2D) layered materials are very useful to realize next generation mechanically powered transparent flexible charge-generating devices. Here we report directional dependent piezoelectric effects in chemical vapor deposition grown monolayer MoS\textsubscript{2} for flexible piezoelectric nanogenerators (NGs). It was found that the output power obtained from the NG with the armchair direction of MoS\textsubscript{2} is about two times higher than that from the NG with the zigzag direction of MoS\textsubscript{2} under the same strain of 0.48\% and the strain velocity of 70 mm/s. This study provides a new way to effectively harvest mechanical energy using novel flexible piezoelectric NGs based on 2D semiconducting piezoelectric MoS\textsubscript{2} for powering low power-consuming electronics and realizing self-powered sensors.
\end{abstract}

\section{1. Introduction}

Considerable scientific efforts are being expanded towards realizing electronic components for transparent flexible self-powered electronic switches, skins, sensors, etc. Experimental studies on the physical properties of two-dimensional (2D) materials have grown exponentially since 2D materials offer unique advantages for use in such next-generation devices [1–5]. Various semiconducting 2D materials have been studied, including transition metal dichalcogenides (TMDs) such as molybdenum disulfide (MoS\textsubscript{2}), molybdenum diselenide (MoSe\textsubscript{2}), tungsten diselenide (WSe\textsubscript{2}), which are likely to bring breakthroughs in future electronics and optoelectronic devices [6–11]. The physical properties of 2D MoS\textsubscript{2} nanosheets have been actively explored particularly as a result of their possible integration in both nano/microelectromechanical devices and energy harvesting devices [4,7]. Monolayer MoS\textsubscript{2} has a direct band gap and high mobility [6,11] and has been used to successfully fabricate field-effect transistors [8,11–14] so it has emerged as an interesting complement to graphene in various semiconducting applications.

In previous theoretical studies, most of 2D monolayer materials may exhibit piezoelectric properties, unlike its bulk parent crystal [15–17]. Remarkably, the calculation of the piezoelectric coefficient for monolayer MoS\textsubscript{2} according to density-functional theory revealed that the monolayer structure exhibits a stronger piezoelectric coupling than the bulk wurtzite structured materials [15]. Nevertheless, experimental evidence of the piezoelectricity of 2D monolayer MoS\textsubscript{2} has not yet been sufficiently provided although very recently few studies on the experimental observation of intrinsic piezoelectric properties of MoS\textsubscript{2} reported that the piezoelectricity from MoS\textsubscript{2} only exists when there are an odd number of layers in the 2D crystal [5,8]. Here we report directional dependent piezoelectric effects in chemical vapor deposition (CVD) grown monolayer MoS\textsubscript{2} using lateral piezoresponse force microscopy (PFM) [18,19] measurements. In addition, it was found that the piezoelectric power output from piezoelectric nanogenerators (NGs) fabricated with monolayer MoS\textsubscript{2} is strongly dependent on the MoS\textsubscript{2} atomic orientation along either armchair or zigzag direction, which further confirms that the magnitude of the piezoelectric polarization in monolayer MoS\textsubscript{2} significantly depends on the atomic orientation axis of MoS\textsubscript{2}. 

\begin{figure}
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\includegraphics[width=\textwidth]{figure1.png}
\caption{ schematic diagram of the experimental setup for the PFM measurements. (a) Top view of the fabricated MoS\textsubscript{2} nanosheet. (b) Cross-sectional view of the fabricated MoS\textsubscript{2} nanosheet. (c) Schematic diagram of the PFM measurement setup.}
\end{figure}
2. Methods

2.1. Synthesis of monolayer MoS$_2$ by CVD

Triangular-shaped monolayer MoS$_2$ flakes has been synthesized in the conventional atmospheric pressure CVD method [20,21]. In detail, 5 mg of MoO$_3$ (Sigma-Aldrich, 203815) and 200 mg of solid S (Sigma-Aldrich, 344621) were loaded into the tube reactor which are at 210 °C (zone 1) and 780 °C (zone 2). As a synthesized template, SiO$_2$ (300 nm)/Si wafer was faced-down above MoO$_3$ crucible and total growth time is 15 min including ramping up period for both zone 1 and 2. After cooling step, the triangular monolayer MoS$_2$ flakes were directly synthesized on SiO$_2$/Si substrate.

2.2. PFM measurement

The atomic force microscopy (AFM)-based investigations were carried out using an AFM (Park Systems, XE-100). The piezoelectric property of the monolayer MoS$_2$ flake samples was confirmed by PFM equipped with non-conductive silicon tips (with about 3 N/m of spring constant) (Multi 75-G, Budget Sensors), operating in contact mode for imaging of topography and relative polarization by PFM. A lock-in amplifier (Stanford Research, SR830) was used to detect the piezoresponse signal.

2.3. Electrical characterization measurement

The output voltage signals of MoS$_2$ piezoelectric NGs were measured using a programmable electrometer (Keithley, 6514B) with 200 TΩ input impedance. A picoammeter (Keithley, 5-1/2 digit Model 6485) was used for low-noise output current measurements, with an input impedance of 1 kΩ. A bending tester was used to induce strain between the electrodes depending on bending radius.

3. Results and discussion

2D layered MoS$_2$ is expected to exhibit piezoelectric effects due to the non-centro-symmetric arrangement of the Mo and S atoms (Fig. 1a). Piezoelectricity in 2D MoS$_2$ structures arises from the development of asymmetrical electrical dipoles that are induced when the material is subjected to an external stress [22]. An optical microscope image in Fig. 1b shows that the present work is based on CVD-grown triangular-shaped single-crystalline monolayer MoS$_2$ flakes [23–25]. Geometric features of the MoS$_2$ cause the magnitude of the piezoelectric property to significantly depend on the crystallographic orientation of MoS$_2$. In particular, if we measure the piezoelectric property in parallel to the armchair direction of MoS$_2$, the value of the piezoelectricity can be different from that which is perpendicular to the zigzag direction of MoS$_2$. However, the directional dependent piezoelectric properties of the 2D layered material makes cannot be experimentally studied in a straightforward manner due to its atomic-scale thickness.

The 2D monolayer MoS$_2$ was transferred onto a SiO$_2$ (300 nm thickness)/Si substrate, and contact pads were deposited onto the individual monolayer MoS$_2$ by using standard electron beam lithographic techniques. Although the tip of the AFM can usually act as the top electrode during PFM measurements, lateral measurement of the piezoresponse is difficult to measure reliably with a consideration of the field distribution if an AFM tip is used as the top electrode [26]. Furthermore, since the target material is thin on an atomic scale, the field concentration under the AFM tip can cause unexpected issues, such as water-mediated electrochemical reactions or electrochemical reactions of the SiO$_2$ layer under the MoS$_2$ layer [27]. Thus we deposited two lateral electrodes onto the MoS$_2$ in order to apply an electric field laterally through the monolayer MoS$_2$.

We used a non-conductive AFM tip as a mechanical sensor to detect the lateral piezoresponse (Fig. 1c). As mentioned above, two lateral electrodes were used for applying electric field in order to

![Fig. 1. Atomic structure and image of a single-crystalline monolayer MoS$_2$ flake. (a) Atomic structure of the monolayer MoS$_2$. (b) Optical microscope image of a triangular monolayer MoS$_2$ flake on a SiO$_2$/Si substrate with schematically overlapping lattice orientation of Mo and S atoms. The monolayer MoS$_2$ flake was directly synthesized on a SiO$_2$/Si substrate through a CVD process. (c) Piezoelectricity of the monolayer MoS$_2$ using lateral PFM. Schematic image of the measurement configuration for the lateral PFM on the monolayer MoS$_2$. (d,e) Topography and friction force microscopy images of the monolayer MoS$_2$ on the SiO$_2$/Si substrate, respectively.](image-url)
measure the lateral piezoresponse of the monolayer MoS2. Thus, the AFM tip should not be conductive because the AFM tip was utilized to only measure the deformed strain value of MoS2 by applying extrinsic bias. The external electric field was applied to one end of the monolayer MoS2 to conduct the PFM measurement, the data of the piezoresponse was recorded by scanning the sample with the AFM tip. Since the AFM tip is non-conductive, the electric field distribution along the monolayer MoS2 is not disturbed by the AFM tip.

The contact pads width of approximately 5 µm ensures the high-quality pads when applying the electric field while providing an ample sample area for the PFM studies. Considering van der Waals interaction with a weak physical contact between MoS2 and SiO2 and the formation of wrinkles in the monolayer MoS2 flake transferred on the other substrate [6,8], it is reasonable that there is a room for a single monolayer MoS2 flake to be effectively stretched or compressed by applying electrical field through the two lateral electrodes. Fig. 1d presents a topographical image of the MoS2 flakes after the lateral electrodes were deposited. Although the MoS2 monolayer is difficult to observe in the topographical image, it can be clearly observed in the friction image (Fig. 1e). We also prepared another sample so that the electric field could be applied in the zigzag direction of MoS2.

The monolayer MoS2 is hard to be distinguished from SiO2/Si substrate in the AFM topography image. Thus, friction force microscopy was used to distinguish the monolayer MoS2 because of distinct friction difference between the MoS2 and the SiO2. In order to further observe the piezoelectric property of the monolayer MoS2, we carried out the lateral and vertical PFM measurements of the sample. As shown in Fig. 2b, the lateral PFM phase showed a clearly different contrast of MoS2 and SiO2 areas. In contrast, the vertical PFM phase did not show any distinguishable contrast as presented in Fig. 2c because of absence in the vertical piezoresponse for both materials. Mo atom and S atom shift much larger for the a,b mode than for the c mode in monolayer MoS2 by extrinsic bias, indicating that the lateral PFM is an effective way to investigate the piezoelectric property of the MoS2 monolayer.

MoS2 has a hexagonal crystal structure, and either Mo or S atoms can be accommodated along each side of the triangular monolayer MoS2 flake [14]. Therefore, as previously noted, the piezoelectric coefficient is expected to be dissimilar when it is measured along the “armchair” (Mo and S parallel) and “zigzag” (Mo and S in the same line) directions of the triangular monolayer MoS2 flake (Fig. 3a and b). Fig. 3c and d respectively shows the variations in the piezoresponse as a function of the electric field applied across the MoS2 samples with these two different device geometries. Fig. 3c shows the piezoresponse as a function of the magnitude of the voltage that is applied in the armchair direction for the monolayer MoS2 and the α-quartz, revealing a distinct piezoresponse from the monolayer MoS2 when compared to that of the α-quartz, which increases as the applied voltage increases, indicating piezoelectric properties from the MoS2 monolayer. The piezoelectric coefficient can therefore be obtained from the slope of the solid lines that represents the fitted linear equation because the piezoelectricity has a linear relation to the electric and mechanical status. Based on the previous reports [28,29], it can be suggested that this force–distance curve can provide a method to estimate the lateral piezoelectric coefficient, d11. The slope obtained for MoS2 by fitting the data is 17.93 × 10−6 arbitrary unit/V, and that for α-quartz is 10.41 × 10−6. Since the d11 of the quartz is known to be approximately 2.3 pm/V [28], it can be used to calibrate the obtained piezoresponse considering piezoelectric tensor. Accordingly, the d11 of MoS2 in the armchair direction is calibrated into 3.78 pm/V by using the ratio between the materials. In contrast, the piezoresponse in the zigzag direction exhibited a lower response, with a piezoelectric coefficient of 1.38 pm/V (Fig. 3d).

The d11 measured for the 2D monolayer MoS2 flake is comparatively larger than that for quartz in the case of the armchair direction while it is smaller in the zigzag direction. In fact, these anisotropic piezoelectric properties can be understood by considering the atomic arrangement of the triangular 2D MoS2 flakes. The d11 calibrated along the armchair direction for the monolayer MoS2 is 1.5 times greater than that of quartz [30]. The experimental findings obtained in this work are consistent with the results of simulations [15] that were previously reported.

Therefore, the PFM results confirm that 1) MoS2 is piezoelectric, and the 2) piezoelectricity of MoS2 depends on the atomic orientation axis. The same experimental process was used to confirm that a distinct piezoresponse was not observed in the bare SiO2 substrate with no piezoelectric property (Fig. 52), which further confirms that the experimental results reported in this work are reliable. The direct piezoresponse observations from the PFM experiments were further validated using Raman measurements as well (Fig. 53). The piezoelectric effect of the monolayer MoS2 depending on the orientation is explained by three-fold rotational symmetry of piezoresponse. The existence of the piezoelectricity in TMDs studied by the optical second-harmonic generation (SHG) has been reported [31]. In particular, the SHG intensity in the monolayer MoS2 shows the polarization depending on angle θ.

To further confirm the piezoelectric properties of the monolayer MoS2 depending on the atomic orientation axis, we fabricated a monolayer MoS2-based flexible piezoelectric NG (Fig. 4a). Triangular shape monolayer MoS2 flakes were transferred on a polyethylene terephthalate as a flexible polymer substrate [32]. The monolayer MoS2 flakes were connected with lateral electrodes very carefully in order to clearly compare the power output from the piezoelectric NGs depending on the MoS2 atomic orientation along either armchair or zigzag direction. Fig. 4c and d shows optical images showing energy harvesting active regions with the armchair and zigzag atomic orientations of the piezoelectric NGs.
respectively. The piezoelectric power output performances were investigated by applying mechanical strain (Fig. 4e–h). The voltage and current output shown in Fig. 4e–h were obtained with bending strain of 0.48% at a frequency of 0.5 Hz. The measured output voltage approached up to 20 mV (Fig. 4e) and the output current was over 30 pA (Fig. 4g) from the NG with the armchair direction of MoS2. On the other hand, the output voltage and current are less than 10 mV and 20 pA, respectively, from the NG with the zigzag direction of MoS2. This result suggests that manipulation of the MoS2 atomic orientation along an armchair
direction in a large scale is very critical to dramatically enhance piezoelectric power output performance from single-crystalline MoS2 monolayer-based piezoelectric NGs.

Moreover, we also investigated the power output change from the MoS2 NG as a function of the applied strain (Fig. 5) and the load resistance (Fig. S6). It was found that the output performance is increased with increasing the applied strain, revealing typical piezoelectric power output behavior and good mechanical durability of the flexible piezoelectric MoS2 NGs in this work. As shown in Fig. S6, output voltage from the monolayer MoS2 NG as a function of the external load resistance under the 0.48% strain along the armchair direction is almost constant for a load resistance up to ~1 MΩ. However, the output voltage is dramatically increased over 10 MΩ in the load resistance because an increase of the load resistance leads to a decrease of the output current due to the ohmic loss.

We further explored the output voltages and output currents with continuous application of cycled compressive force to the MoS2 NG. Notably, there were no significant differences in the output voltages measured from the MoS2 NG over 7500 cycles with bending strain of 0.42% at a frequency of 0.5, confirming the good mechanical durability of our MoS2 NG in this work (Fig. 6). Again, ‘switching polarity’ tests were also conducted to confirm that the measured output signals were generated from the monolayer MoS2 NG rather than from the measuring system (Fig. S7). The output signals were reversed when we reversed the polarity of the voltage and current meters.

4. Conclusions

In conclusion, the unique directional dependent piezoelectric effect of the CVD-grown triangular-shaped single-crystalline monolayer MoS2 flake was qualitatively studied by using lateral PFM. We successfully perform an experiment where the piezoelectric coefficient, $d_{11}$, was measured, showing the anisotropic piezoresponse in the single-crystalline monolayer MoS2. It was found that the $d_{11}$ of MoS2 in the armchair direction is 3.78 pm/V, while the $d_{11}$ of MoS2 in the

![Fig. 5. Output voltage obtained from the monolayer MoS2 NGs at a fixed velocity of 70 mm/s as a function of applied strain. (a) and (b) Change of voltage output with the strain applied along the armchair direction and the zigzag direction, respectively.](image1)

![Fig. 6. Mechanical durability test of the output voltage (a) and output current (b) obtained from the MoS2 NG with continuous application of cycled compressive force to the NG.](image2)
ziggard direction is 1.38 pm/V, clearly revealing its distinct anisotropic piezoelectric properties. In addition, flexible piezoelectric NGs were successfully fabricated using the CVD-grown single-crystalline monolayer MoS2 flakes. In accordance with the PFM result, the piezoelectric power output from the monolayer MoS2 NGs was strongly dependent on the MoS2 atomic orientation. It was found that the output power obtained from the NG with the armchair direction of MoS2 is about two times higher than that from the NG with the zigzag direction of MoS2 under the same strain of 0.48% and the strain velocity of 70 nm/s. This study provides a new way to effectively harvest mechanical energy using novel flexible piezoelectric NGs based on 2D semiconducting piezoelectric MoS2 for powering low-power-consuming devices and realizing self-powered electronics.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.nanoen.2016.02.046.

References

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