論 文 の 内 容 の 要 旨

論文題目
Non-centrosymmetric Two-dimensional Layered Materials
for Piezoelectric and Ferroelectric Device Applications
(圧電・強誘電デバイス応用に向けた中心対称性の破れた二次元層状物質の研究)

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Non-centrosymmetric two-dimensional (2D) layered materials are explored toward the piezoelectric and ferroelectric applications. Monolayer tin sulfide (SnS), an emerging 2D material with a purely in-plane spontaneous polarization, is investigated from material synthesis to device applications. The objective of this work is to demonstrate piezoelectric and ferroelectric devices based on 2D SnS, and investigate their mechanisms.

Since the discovery of graphene and other 2D materials, van der Waals (vdW) materials have attracted a great deal of interests on their unique properties at the atomic-thick scale, from the perspectives of science and engineering. Especially, the research fields of their electrical and optical applications have been rapidly growing after the first demonstration of graphene field-effect transistors (FETs) in 2004. Although graphene has no piezoelectricity due to its centrosymmetric atomic structure, some 2D materials lack the centrosymmetry, which gives a birth of piezoelectricity (**Fig. 1**). In 2014, the first experimental demonstration was reported for piezoelectric nanogenerators based on a monolayer molybdenum disulfide (MoS_2). This achievement has given a new insight to the researches on 2D materials into the piezoelectric applications, enabling self-generated functional devices for the Internet of Things (IoT). However, the mechanism of 2D piezoelectric materials is unidentified, and the output power density is still at the order of several hundred nW/cm^2, much smaller than the required power for the IoT devices.

Monolayer SnS has been theoretically expected to have a large piezoelectric constant d = 145 pm/V, which is two order larger than that of MoS_2 ($d \sim 4$ pm/V) and comparable to that of PZT ($d \sim 300$ pm/V), owing to the puckered structure with quite a small Young's modulus (**Fig. 2**). Given that PZT and other piezo-ceramics are breakable due to their brittle fracture, 2D SnS is superior to these conventional piezoelectric for the sake of wearable device applications. Furthermore, SnS has been theoretically expected to exhibit a ferroelectricity unlike MoS_2, suggesting a potential for applications such as nonvolatile memory and nonlinear optoelectronics. Despite the novel characteristics of monolayer SnS, experimental demonstrations are still challenging due to the difficulty of monolayer fabrication.

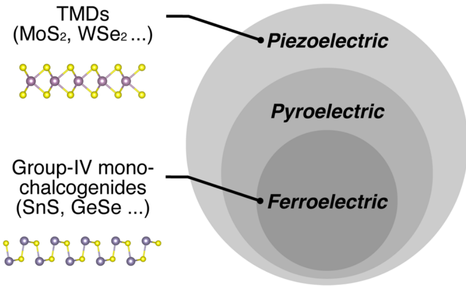

Fig. 1 Non-centrosymmetric 2D materials.

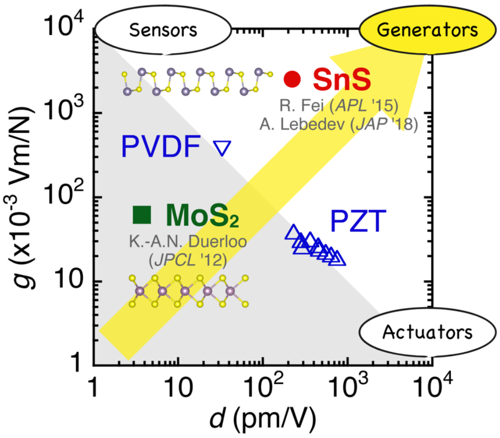

Fig. 2 Comparison of piezoelectric coefficients between 2D materials and conventional 3D materials.

Unlike other vdW materials of graphene and MoS_2, it is difficult to isolate the monolayer SnS *via* mechanical exfoliation due to the ionic interlayer interactions along with vdW forces (**Fig. 3a**). This strong interlayer force is found to be caused by the lone pair electrons in Sn atoms, which also contribute to the puckered structure of Sn along the armchair direction. These lone pair electrons constitute the top of the valence band of SnS, resulting in a favorable bonding with oxygen. Thus, the SnS surface is easy to be oxidized during the thinning process, though this oxidation is self-stopping owing to a robust feature of SnO_x layer, and a steep interface is identified at SnO_x/SnS. When a bulk SnS is treated by an oxygen annealing intentionally, a self-passivated hetero-structure SnO_x/monolayer-SnS is achieved, as shown in **Fig. 3b**.

Together with the top-down process, bottom-up crystal growth is proposed, where he SnS adsorption/desorption is precisely controlled. For the first time, micrometer-size SnS crystal down to the monolayer has been grown *via* physical vapor deposition (PVD) on mica substrate, whose surface is atomically flat. Monolayer SnS grown *via* PVD reveals high crystalline quality better than that obtained *via* top-down methods (**Fig. 3c**): peculiar Raman peaks are observed only for the PVD grown monolayer. Further strikingly, PVD-SnS exhibits a strong interaction with mica substrate: x-ray diffraction measurement confirmed that the lattice orientation of SnS tends to aligned for that of mica. These results suggest that mica is a promising platform for 2D SnS.

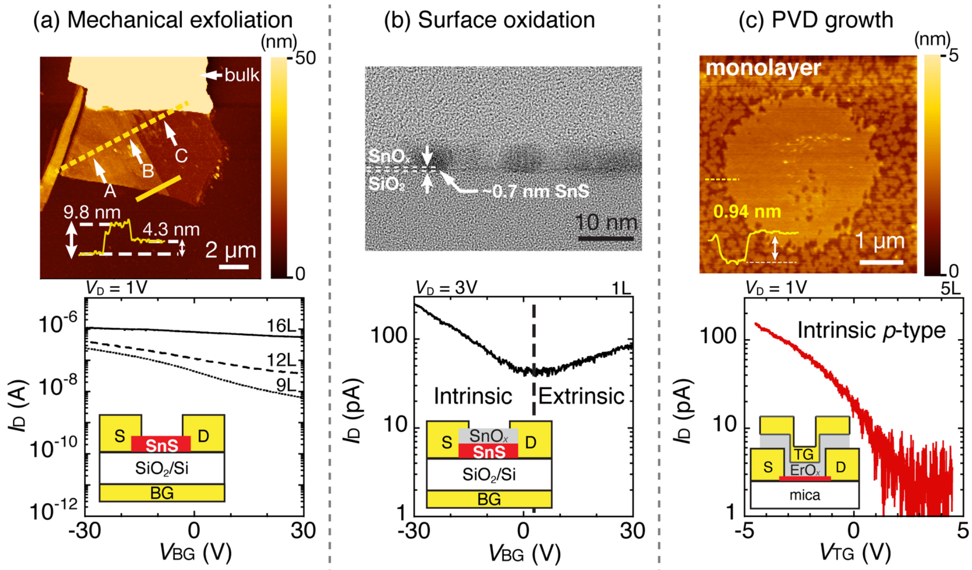

Fig. 3 Characterizations of 2D SnS *via* (a) mechanical exfoliation, (b) surface oxidation, and (c) PVD growth.

An electromechanical response of 2D SnS is described. Flexible devices are demonstrated on mica, which is used as a platform throughout the whole process from crystal growth to the device fabrication. This approach leads to the highly sensitive electromechanical response of SnS, with a gauge factor of approximately 130 much higher than that of metal strain gauges and graphene sheets.

Note that 2D piezoelectric materials (SnS and MoS_2) are semiconductor materials, different from the typical piezoelectric insulators. For the piezoelectric generator, Schottky contact is necessary at the metal/semiconductor interface to prevent the carrier injection from electrode to semiconductor. When the piezoelectric charges are generated, they are expected to be accumulated at the Schottky barrier contact. Although the piezoresistive effect have no polarity at source/drain, the piezoelectric effect modulates the Schottky barrier height (SBH) asymmetrically at the source/drain (S/D). To clarify this asymmetric modulation of the SBH, static I_D–V_D curve is measured under an external strain for MoS_2 as a model material. In this work, metal electrodes are fabricated with a transfer process, because a strong Fermi level pinning is crucial at the metal/MoS_2

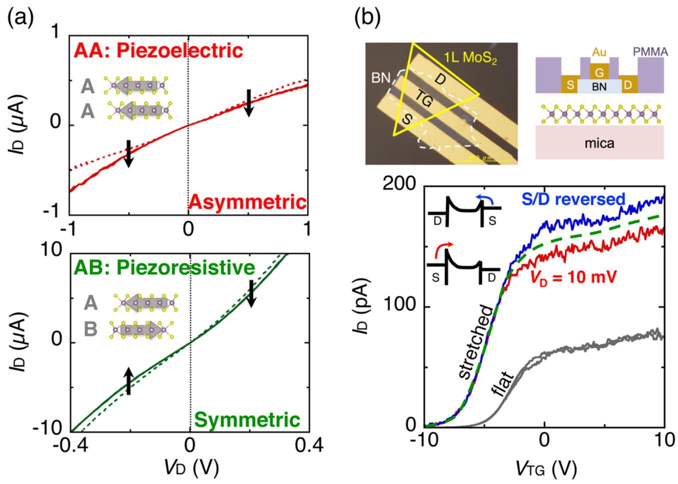

Fig. 4 Demonstration of SBH modulation with piezoelectricity. (a) AA/AB-stacked bilayer MoS_2. (b) I_D–V_{TG} behavior of monolayer MoS_2 under the external strain with reversing S/D.

interface when the metals are evaporated. When bilayer MoS_2 with different stacking sequences are investigated, transport characteristics of AA-parallel and AB-antiparallel stacked MoS_2 are found to be dominated by piezoresistive and piezoelectric effects, respectively (**Fig. 4a**). These results suggest that piezoelectricity can be preserved in the stack-controlled multilayer MoS_2, so that the output power density per unit area can be improved overcoming the monolayer limit. For further understanding, top-gated MoS_2 FETs are fabricated *via* the defect-free transfer method (**Fig. 4b**). Under the positive gate bias accumulating the channel region, a polarity of conductivity is observed reflecting the asymmetric SBH modulation at S/D.

Finally, an in-plane ferroelectric device is demonstrated for a micrometer-size monolayer SnS grown *via* PVD. Polarized Raman spectroscopy for monolayer SnS indicates high crystalline quality and strong anisotropy, and second harmonic generation (SHG) spectroscopy reveals that monolayer SnS is non-centrosymmetric unlike bulk SnS. Ferroelectric switching is successfully demonstrated for the monolayer device at room temperature. Remarkably, for thin SnS below a critical thickness (~15 layers, L), the SHG signal and ferroelectric switching are observed in both odd- and even-number layers (**Fig. 5a–c**), thus overcoming the odd–even effect, which suggests that ultrathin SnS is grown in an unusual stacking sequence lacking centrosymmetry. A cross-sectional TEM observation of multilayer SnS directly proves the transition of staking sequence from AA to AB staking. (**Fig. 5d**) Given that SnS is the semiconductor with multiferroicity, innately exhibiting pyroelectricity and piezoelectricity, this first demonstration of the ferroelectricity in SnS will open up possibilities of providing novel multifunctionalities in vdW heterostructure devices.

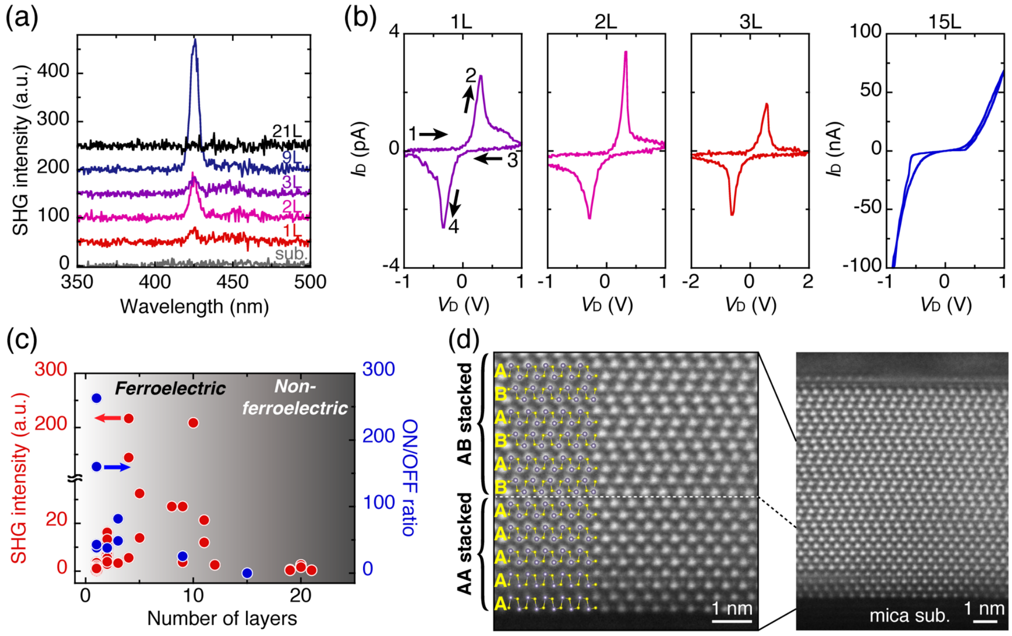

Fig. 5 Transition of stacking sequence from AA to AB staking. (a) SHG spectra and (b) I_D–V_D curves for SnS crystals with different number of layers. (c) Thickness dependences of the SHG intensity and I_{ON}/I_{OFF} ratio. (d) Cross-sectional HAADF-STEM image of 16L SnS along the armchair direction.