All-2D Flexible Device with Piezoelectric Layered Materials for Highly Sensitive Sensor and Generator Applications

Two-dimensional tin sulfide (SnS) has been recently attracted interests in the application to piezoelectric energy harvesters. In odd-number layers, SnS lacks the center of symmetry resulting in the piezoelectricity. A remarkable piezoelectric constant $d\approx145$ pm/V, comparable to piezo-ceramics, has been predicted for monolayer along the armchair direction [1], whose crystal structure is viewed as rows of two orthogonally coupled hinges as shown in Fig. 1. However, isolation of monolayer SnS is difficult due to a strong interlayer ionic bonding by the lone pair electrons in Sn atoms [2]. Recently, we have succeeded in the growth of few-to-monolayer SnS on mica substrate via physical vapor deposition (PVD), where the growth temperature was precisely con-trolled to balance adsorption/desorption of SnS. Synthetic mica, KMg$_3$AlSi$_3$O$_{10}$F$_2$, is an attractive platform with atomically flat surface, thermal tolerance up to 1100°C, and flexibility, which enable a straightforward process from crystal growth to fabrication of flexible devices, as shown in Fig. 2(a). In this work, for the first time, electromechanical response of SnS is investigated with using ultra-thin SnS layers grown on mica. SnS is a semiconductor material unlike the traditional piezoelectric ceramics; therefore, understanding of piezoresistive effect in SnS is essential as well as piezoelectric effect, toward the nanogenerator application. We have systematically investigated the dependences of piezoresistive response on the crystal orientation and number of layers.

SnS crystals were grown on mica substrate (~600 µm thick) by PVD with SnS powder source. The temperatures of source and substrate were controlled independently at $T_{\text{SnS}}=470^\circ\text{C}$ and $T_{\text{sub}}=410^\circ\text{C}$. The growth pressure was reduced to ~10 Pa lower than that in previously reported growth methods [3], to enhance the SnS desorption from SnS crystals. After the growth, electrode pattern was fabricated with using the standard EB process and Ni was deposited as a contact metal. Then, the device was exfoliated together with mica with a thickness of ~10 µm to enable the bending experiment. The electromechanical response was measured on PET substrate using a home-made programable bending machine as shown in Fig. 2.

Figure 3 shows typical piezoresistive response of ~10 layers SnS under the repeated compressive/tensile strains $\varepsilon=\pm0.58\%$ with a fixed $V_D=1$ V. The increase and decrease of resistivity were observed under tensile and compressive strains, respectively. In order to investigate the dependence on crystal orientation, two pairs of source/drain electrodes were fabricated along the armchair and zigzag direction of ~19 layers SnS, as shown in Fig. 4(a). A relatively more sensitive response was observed along zigzag direction as well as the opposite change of resistivity under compressive/tensile strains. These dependences are consistent with the calculated relationship between bandgap and lattice strain [4]. Figure 4(b) shows $I_D$–$V_D$ curves of bilayer SnS with changing the strain. The electromechanical responsivity was quantitatively evaluated by the gauge factor (GF) as follows: $\text{GF}=(\Delta R/R_0)/\varepsilon$. (1) Although the crystal orientation was uncertain for the few-layer SnS due to the rounded crystal shape unlike the thicker one, the gauge factor was obtained to be ~130, which is much larger than the metal strain gauge (GF~5) and comparable to silicon strain gauge (GF~200) [5]. This large GF is owing to the high crystalline quality of SnS.

For monolayer SnS, the piezoelectric effect is expected along with the piezoresistive effect. According to the previous demonstration on piezoelectricity in MoS$_2$, an asymmetric modulation of Schottky barrier height (SBH) at the source/drain is expected due to the ionic polarization charge induced at the contact region when the lattice strain is induced, which should result in an asymmetric change of $I_D$–$V_D$ curve in the negative and positive $V_D$ [5], as shown in Fig. 5(a). Since SnS is highly doped $p$-type semiconductor, the design for Schottky barrier of metal/monolayer SnS is necessary, that is, the highest SBH should be obtained by a proper selection.
of contact metal. In this context, Ni is known to be the best due to the Fermi level pinning [6]. Contrary to expectations, however, a symmetric change was observed for monolayer SnS with Ni contact, even at the SBH limited region between $V_D = \pm 10$ mV, as shown in Fig. 5(b). This result suggests that the fundamental understanding of SBH is necessary for metal/SnS experimentally. Metals with small work function such as Ag and Al are possibly preferable to form the Schottky contacts and demonstrate the piezoelectric generator of SnS. The all-2D electromechanical device of SnS on mica goes beyond the flexibility limit of bulk materials, enabling highly sensitive strain sensor and generator applications.

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References

Figures

Figure 1: Crystal structure of monolayer SnS along (a) armchair and (b) zigzag directions. Gray and yellow balls represent Sn and S atoms, respectively.

Figure 2: Photographs and schematic views of (a) flexible device of SnS on mica and (b) home-made programmable bending machine.

Figure 3: Piezoresistive response of ~10 layers SnS under ±0.58% strains.

Figure 4: (a) Piezoresistive response of ~19 layers SnS under ±0.17% strains along armchair and zigzag directions (b) $I_D-V_D$ curves of bilayer SnS under compressive strain.

Figure 5: (a) Band diagram model of asymmetric SBH modulation for metal/piezoelectric semiconductor with fixed drain bias. (b) Symmetric change of $I_D-V_D$ curve for monolayer SnS with Ni contact.