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Demonstration of Electromechanical Device Based on 2D Piezoelectric Materials for Nanogenerator Applications

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Abstract

A flexible device based on two-dimensional (2D) piezoelectric material, tin sulfide (SnS) has been developed. For the first time, we demonstrated thickness tunable crystal growth of SnS from bulk to monolayer, whose gauge factor is two order of magnitude larger than that of conventional metal strain gauge. This large piezoresistive response is owing to the high crystalline quality of SnS. All these experiments were performed on the 2D platform of mica from material synthesis to fabrication of flexible device. This all-2D electromechanical device goes beyond the flexibility limit of bulk materials, enabling highly sensitive strain sensor and generator applications.

1. Introduction

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~145 pm/V, comparable to piezoceramics, 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 controlled to balance adsorption/desorption of SnS. Synthetic mica, $KMg_3AlSi_3O_{10}F_2$, 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.

2. Material Synthesis and Device Fabrication

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_{SnS} = 470°C and T_{sub} = 410°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**.

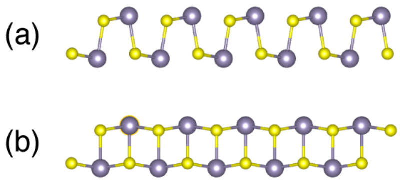

Fig. 1 Crystal structure of monolayer SnS along (a) armchair and (b) zigzag directions. Gray and yellow balls represent Sn and S atoms, respectively.

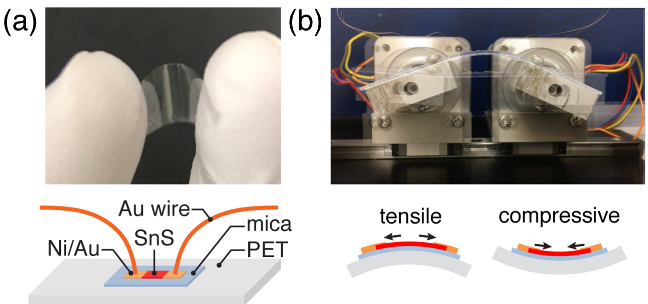

Fig. 2 Photographs and schematic views of (a) flexible device of SnS on mica and (b) home-made programable bending machine.

3. Results and Discussions

Figure 3 shows typical piezoresistive response of ~10 layers SnS under the repeated compressive/tensile strains ε = ±0.58% 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

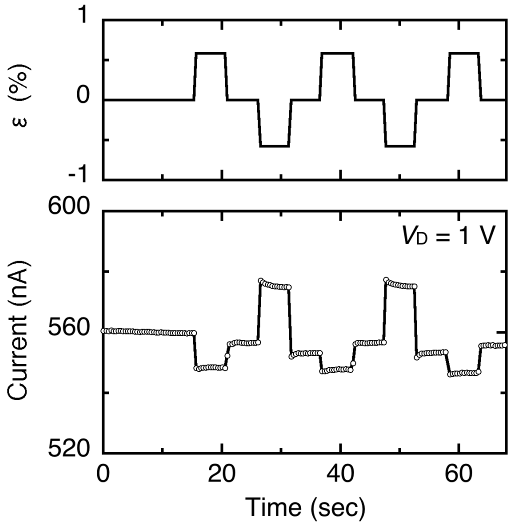

Fig. 3 Piezoresistive response of ~10 layers SnS under ±0.58% strains.

factor (GF) as follows:

$$\mathrm{GF} = \frac{\Delta R / R_0}{\varepsilon}. \quad (1)$$

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

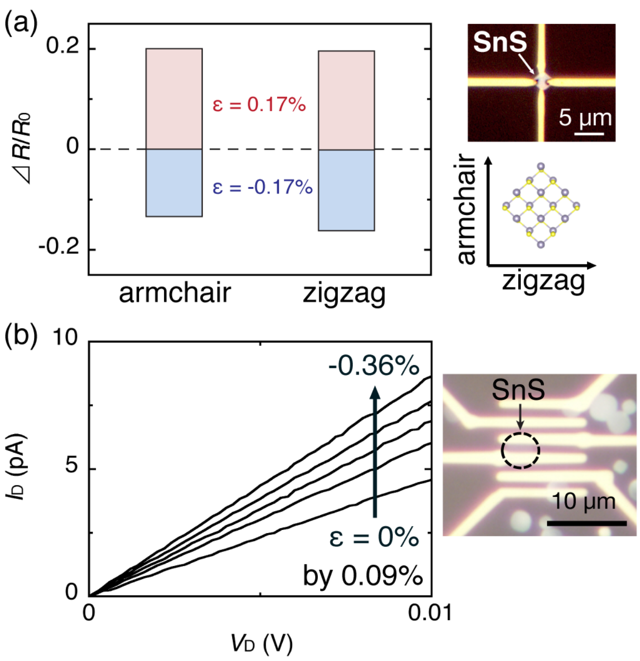

Fig. 4 (a) Piezoresistive response of ~19 layers SnS under ±0.17% strains along armchair and zigzag directions (b) I_D–V_D curves of bilayer SnS under compressive strain.

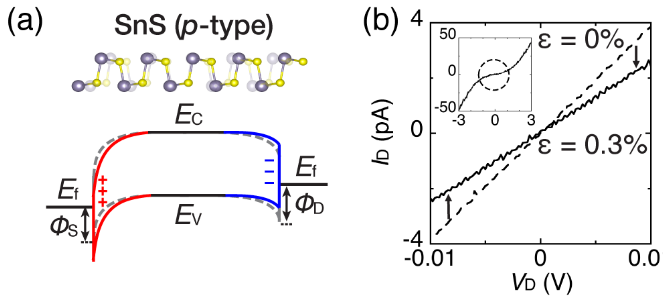

Fig. 5 (a) Band diagram model of asymmetric SBH modulation for metal/piezoelectric semiconductor with fixed drain bias. (b) Symmetric change of I_D–V_D curve for monolayer SnS with Ni contact.

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.

4. Conclusions

We have demonstrated electromechanical device of few-to-monolayer SnS on mica. From crystal growth to fabrication of flexible device, mica is the promising platform owing to its layered structure. The piezoresistive response was observed for bilayer SnS with the large GF of ~130. For the piezoelectric response in monolayer SnS, the symmetrical change of transport characteristics under strain was observed, suggesting that channel transport is dominant rather than Schottky contact. Further investigation of metal selection to make Schottky contact will necessary to realize the piezoelectric generator of SnS.

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