PVD growth of AA stacking SnS through screw dislocation induced by substrate edge steps

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1. Introduction:

Although SnS has been highly demanded as power generator due to its high piezoelectric coefficient comparable to PZT, its piezoelectricity is limited to the odd number layers with non-centrosymmetric structure, that is, not bulk property. So far, we have demonstrated the ferroelectricity of monolayer SnS grown on mica substrate, which guarantees its piezoelectricity as well [1]. To further improve the power generation capacity, the bulk SnS with non-centrosymmetry (AA stacking) is highly required. The key idea is screw-dislocation-assisted spiral growth, which has already been observed to result in AA stacking in MoS_2. However, in general, the growth mode on atomically flat mica substrate is the layer-by-layer growth with 2D nucleation. Here, HOPG substrate containing high density of atomic edge steps, unlike mica, is applied and these steps may work as origins for the spiral growth. In this study, the growth mode of SnS and its crystallinity on mica and HOPG are compared in detail to gain the insight to obtain the piezoelectric bulk SnS.

2. Growth mode & Crystallinity

The physical vapor deposition of SnS was carried out on different substrates using the SnS source powder under the N_2 carrier gas flow. **Figure 1** compares AFM image of the SnS flakes on mica and HOPG substrates. Typical 2D nucleation of SnS with the atomically flat surface is clearly observed on mica. Although it is difficult to discuss the staking sequence due to the low crystallinity suggested from Raman data in **Fig. 2**, recent TEM study indicates the AA stacking.

On the other hand, for HOPG substrates, most of SnS crystals include several spiral growth features, as shown in **Fig. 1**. It should be empathized that the positions of screw dislocation center are aligned just on the step lines, suggesting the preferred formation sites. Moreover, the dislocation centers are located at monolayer and bilayer graphene steps, not at trilayer step. In order to elucidate the formation of screw dislocation, magnified image of the different thin SnS layer (~6 nm) and conjectured formation path of screw dislocation are shown in **Fig. 3**. Based on the observation, the growth sequence is as follows. SnS could firstly nucleate at the step sites of HOPG and afterward, part of flake grows across the atomic step which further induces the overlaps of layers and screw dislocation. Since monolayer and bilayer graphite steps exhibit lower or similar thickness as SnS layers, it is reasonable for SnS growing across these steps and forming screw dislocation only in these sites.

When SnS grow along screw dislocations, no nucleation is required, which could lead to exactly the same orientation of layers (AA stacking). Therefore, as shown in **Fig. 2**, the quite sharp Raman peaks are observed for SnS with the dislocations, which are similar to the Raman peaks of mechanically exfoliated bulk SnS with AB stacking since the difference in Raman peak positions for AA and AB are negligible. Interestingly, thin SnS (< 6 nm) grown on atomically flat terrace of HOPG often shows 2D nucleation. The Raman spectrum exhibits more complicated peak splitting features (**Fig. 2**), suggesting the twisted stacking sequence of SnS. Although the thickness of SnS on mica and HOPG is almost the same, the Raman peak for HOPG is much stronger, indicating the high crystallinity of SnS on HOPG.

As a summary, the screw-dislocation-assisted spiral growth on HOPG indeed ensures the AA stacking sequence of PVD SnS and also provides superior crystallinity, which could further facilitate the development of SnS-based power generator.

Ref.: [1] N. Higashitarumizu, *et al.*, JSAP Fall meeting, 19a-E308-5 (2019).

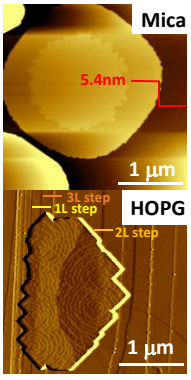

Fig. 1 AFM images of SnS flakes grown on mica and HOPG.

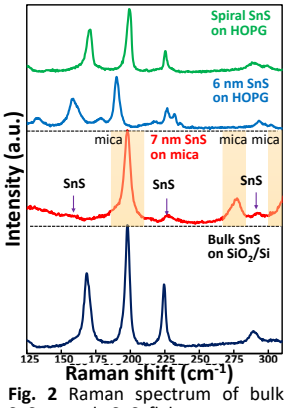

Fig. 2 Raman spectrum of bulk SnS crystal, SnS flakes grown on mica and HOPG by PVD.

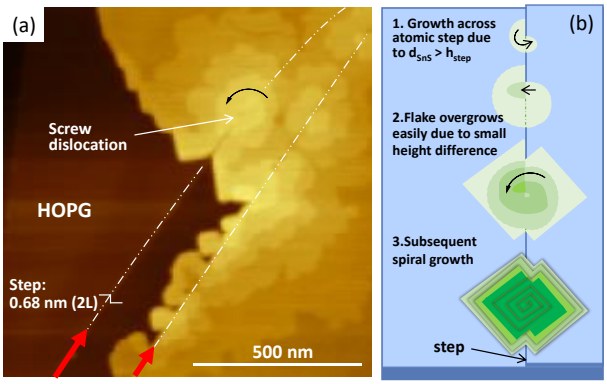

Fig. 3 (a) AFM height images of SnS flakes grow on steps of HOPG substrate. (b) Schematic illustration of conjectured growth mode of spiral SnS.