Atomic step induced spiral growth in PVD SnS

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1. Introduction:

Screw dislocation driven growth in 2D materials could result in spiral structure and bring about plenty of intriguing properties such as vertical conductivity through the screw dislocation core and nonlinear optical generation, piezoelectricity and ferroelectricity through the inversion symmetry breaking by the spiral growth. However, the control of spiral growth in 2D materials is still immature because of the random occurrence of screw dislocation. In this research, a novel method to obtain spiral SnS on atomic steps is proposed. Not only high percentage of spiral SnS flakes are achieved, but the nucleation position of spiral SnS could be well controlled. Furthermore, spiral SnS could be grown on artificial steps created on various substrates which gigantically extend its flexibility for application. Finally, contrary to common understanding, spiral SnS turns out to exhibit inversion symmetric structure through the second harmonic generation (SHG) spectroscopy and the cross-sectional TEM analysis. This is the first work to point out that the single spiral morphology with monolayer step height does not guarantee non-centrosymmetric structure in 2D materials.

2. Results and discussion:

Spiral SnS was grown by physical vapor deposition (PVD) method with pure SnS powder as source and N_2 as carrier gas on step-rich substrate, HOPG. When SnS nucleates at small steps formed by 1~2L graphene, SnS could partially climb up and grow over the step. A screw dislocation would be created at the boundary between the regions where SnS climbs over the step and where SnS doesn't [1]. As a result, continuous spiral growth could originate from the exposed edge of SnS and the screw dislocation core (i.e. center of spiral) would locate on top of atomic steps, as shown in **Fig. 1a**. **Fig. 1b** shows the height profile of spiral SnS center region with average height of SnS steps are around 0.6 nm. The enlarged layer distance from normal thickness of 0.54 nm might be resulted from the formation of spiral structure. It could also be discovered that the height of SnS steps at the opposite sides of spiral center are not aligned, indicating the continuous spiral growth in the vertical direction due to screw dislocation.

Transferring exfoliated graphene to various substrates like mica or silica (SiO_2/Si) and followed by PVD growth, spiral SnS could also be obtained on artificial graphene steps. As shown in **Fig. 2**, it could be found that spiral SnS grown on graphene/mica and graphene/silica substrates with their centers of screw dislocations also locating on top of step lines which is similar to the situation on HOPG. This result indicates that atomic step induced screw dislocation driven spiral growth could not only be conducted on different substrates but possess well control on nucleation sites. These characteristics can facilitate the future development of researches and applications based on spiral SnS.

Surprisingly, both the SHG measurements and the cross-sectional HAADF-STEM image in **Fig. 3** imply that spiral SnS possesses the inversion symmetricity. While no SHG signal could be observed in spiral SnS flakes, STEM also shows clear AB stacking of SnS layers. One possible reason for single spiral SnS with monolayer step height to exhibit centrosymmetric structure is the occurrence of the orientation switching with opposite flake orientation at the step edge, as schematically shown in **Fig. 3**.

In summary, screw dislocation driven spiral growth of SnS triggered by 1~2L graphene steps was demonstrated not only on HOPG substrate but on various substrates with artificial steps, indicating the novel control of the spiral growth. Moreover, it turned out that spiral SnS exhibited centrosymmetric AB stacking structure, which is contradict with common belief in the structure of spiral 2D materials.

Ref: [1] Y.-R. Chang, *et al.*, JSAP spring meeting, 15a-A404-6 (2020)

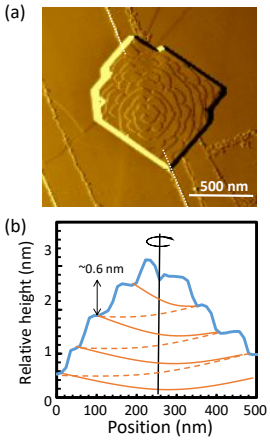

Figure 1. (a) AFM amplitude image of spiral SnS. (b) Height profile of spiral SnS near spiral center area.

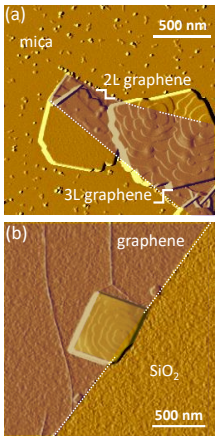

Figure 2. AFM amplitude image of spiral SnS grown on (a) mica and (b) SiO_2 with artificial graphene steps.

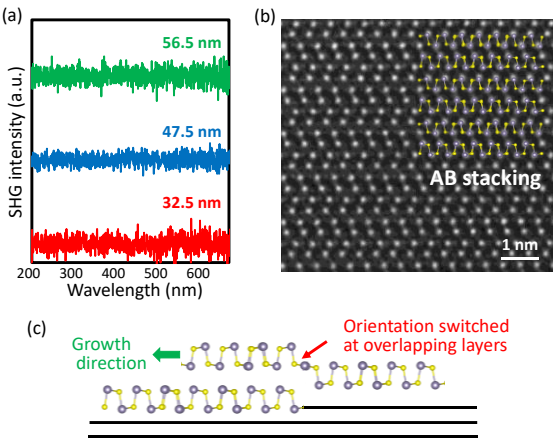

Figure 3. (a) SHG spectrum of spiral SnS. (b) Cross sectional HAADF-STEM image of spiral SnS. (c) Schematic illustration of possible mechanism to form AB stacking in spiral SnS originated from graphene atomic step.