Deterministic synthesis of SnS and SnS_2 by chemical vapor deposition

°(M1) Kazuki Koyama [1], Takamichi Miyazaki [1], Takeshi Odagawa [1],
Chaoliang Zhang [2], Shutaro Karube [1], and Makoto Kohda [1,3,4,5]
Grad. Sch. of Eng., Tohoku Univ. [1], FRIS, Tohoku Univ. [2], CSIS, Tohoku Univ. [3],
FRiD, Tohoku Univ. [4], QUARC, QST [5]
E-mail: kazuki.koyama.s1@dc.tohoku.ac.jp

SnS is a promising layered ferroelectric material for spintronics because a persistent spin helix state with a short spin wavelength and electrical control of spin polarization has been theoretically predicted [1,2]. Therefore, the methods to grow the SnS crystals with large scale and high purity become essential. Chemical vapor deposition (CVD) using only Sn and S is one of the candidates [3]. However, the stable compound SnS_2 can also be grown, and few works have discussed the decisive conditions for SnS and SnS_2 during CVD. We here focus on the effect of the concentration ratio between S and Sn, which is controlled by the distance (d) between the precursors S and Sn.

During CVD, we keep the Ar gas flow in a tube furnace to be 100 sccm under atmospheric pressure. The S powder is placed at upstream and the Sn powder with a SiO_2/Si substrate is placed at downstream. They are respectively heated at 200 and 850 degrees for 30 minutes. As we modify d from 25 to 20 cm, the shape of the grown crystals changes from rhombic to hexagonal, implying the change from SnS to SnS_2. We then investigate the structural phase differences by Raman spectroscopy. In the case of d = 25 cm, peaks at ~95, 165, 192, 219 cm^{-1} are found (Fig. 1), corresponding to the A_g and B_{3g} modes of SnS. When d is adjusted to 23.5 cm, the widths of the previous four peaks broaden, and an additional peak at ~314 cm^{-1} is observed (Fig. 1), corresponding to the A_{1g} mode of SnS_2. This result suggests that the crystal is a mixture of SnS and SnS_2. Moreover, when d is shortened to 20 cm, only the peak at ~314 cm^{-1} is left (Fig. 1), showing that the crystal is pure SnS_2. We also characterize the chemical composition and crystallinity of the crystals by energy-dispersive X-ray spectroscopy and electron backscatter diffraction using scanning electron microscopy. The obtained results are consistent with each other. We concluded that the concentration ratio between S and Sn has a decisive influence on the type of grown crystals. This novel insight is expected to contribute to the production of high-quality SnS crystals.

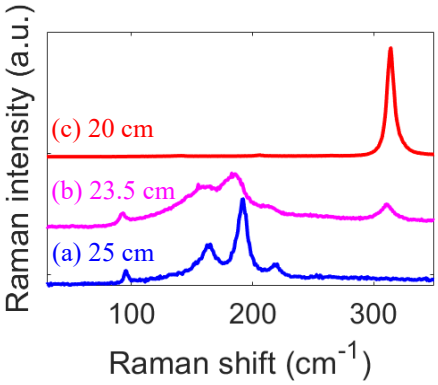

Fig. 1. Raman spectra for (a) d = 25 cm. (b) d = 23.5 cm. (c) d = 20 cm.

References: [1] N. Higashitarumizu *et al.*, Nat. Commun. **11**, 2428 (2020). [2] M. A. U. Absor *et al.*, Phys. Rev. B **100**, 115104 (2019). [3] D. Yu *et al.*, J. Mater. Sci.: Mater. Electron. **30**, 10879 (2019).