ISSN 1674-1056
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Citation: Chin. Phys. B . 2019, 28(11): 118101 . **doi:** 10.1088/1674-1056/ab457c
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Chemical vapor deposition growth of crystal monolayer SnS_2 with NaCl-assistant*

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(Received 24 June 2019; revised manuscript received 12 September 2019; published online 18 October 2019)

As an important member of the two-dimensional layers of metal dichalcogenides family, the two-dimensional (2D) group IV metal chalcogenides (GIVMCs) have been attracting intensive attention. However, the growth of monolayer tin disulfide (SnS_2) remains a great challenge contrasted to transition metal dichalcogenides, which have been studied quite maturely. Till date, there have been scant reports on the growth of large-scale and large-size monolayer SnS_2. Here, we successfully synthesized monolayer SnS_2 crystal on SiO_2/Si substrates via NaCl-assisted CVD and the edge can be as long as 80 μm. Optical microscope, Raman spectroscopy, x-ray diffraction, atomic force microscopy (AFM), and energy-dispersion x-ray (EDX) were performed respectively to investigate the morphology, crystallographic structure, and optical property of the 2D SnS_2 nanosheets. In addition, we discussed the growing mechanism of the NaCl-assisted CVD method.

Keywords: group IV metal chalcogenides, tin disulfide, two-dimensional materials, chemical vapor deposition

PACS: 81.07.–b, 81.15.Gh **DOI:** 10.1088/1674-1056/ab457c

1. Introduction

Recently, two-dimensional (2D) layered metal dichalcogenides (LMDs) such as molybdenum disulfide (MoS_2) have attracted significant attention due to their electronic structure, super-large specific surface, quantum effect compared to the bulk materials.[1,2] They have great application prospects in the fields of optics, electronics, catalysis, etc. Until now, more 2D LMDS such as MoS_2[3] and WS_2[4] have been extensively studied in terms of preparation technology and potential applications in field effect transistors (FETs), photodetectors, solar cells, and flexible devices.[5–13] However, the investigation of 2D SnS_2 which is an important number of IV–VI A group is still in its nascent stage.[14,15]

SnS_2 is consisted of planar three-fold layers (TLs), where strong covalent bonding exists in plane but weak van der Waals interaction dominates out of plane. SnS_2 has a large bandgap of ~ 2.5 eV and an octahedral lattice made of two atomic layers of sulfur and one atomic layer of tin (shown in Fig. 1), which have the advantages to suppress the drain to source tunneling for short channels.[16] In addition, it is better to fulfill the industrial requirements for next-generation electronic/optoelectronic devices than other members of 2D LMDs because of the earth-abundant, low-cost, nontoxic, and environmental friendly characteristics. However, it is still a challenge to synthesize high-quality, large-scale monolayer SnS_2.[17–21]

Up to now, most of the reported SnS_2 nanosheets are synthesized via exfoliation from bulk crystals,[22] chemical vapor deposition (CVD),[17,23,24] hydrothermal methods,[14] and spin coating techniques.[25] The most common methods are exfoliation and CVD. However, the size of layered SnS_2 obtained by exfoliation is usually limited because the thickness and size are difficult to control in this way. More importantly, the resultant drawbacks, such as less controllability of the uniform morphology, sever clustering, poor crystallinity, or poor harvest, may impact the device performance (low responsivity or slow response speed).[15]

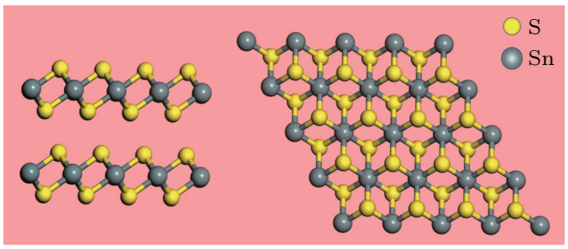


Fig. 1. Crystal structure of monolayer 2H-SnS_2.

Chemical vapor deposition has been proposed as an effective way to synthesize various large-scale atomic layered 2D materials because of the advantage of the precise control on morphology, defects, and structure of the final products, particularly on large-area growth of 2D materials such as MoS_2 and graphene.[26] Herein, we report a facile and repeatable method to synthesize large-size and high-quality monolayer SnS_2 crystal. Recently, NaCl-assisted CVD has been proved to lower the reaction requirements effectively for synthesizing some 2D layer materials.[27] In the reports so far, no one has used this method to synthesize 2D group IV metal chalcogenides (GIVMCs). Motivated by this, by mixing NaCl with

*Project supported by the National Basic Research Program of China (Grant No. 2016YFA0202302), the National Natural Science Foundation of China (Grant Nos. 61527817, 61875236, 61905010, and 61975007), and the Overseas Expertise Introduction Center for Discipline Innovation, 111 Center, China.

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tin oxalate (SnC_2O_4)[28] powder as the precursor, we successfully synthesized large-size and high quality monolayer SnS_2 on SiO_2/Si substrates. The monolayer SnS_2 can be as long as 80 μm. The Raman peak position shift and intensity change are observed as a function of the thickness and illustrate that the synthesized SnS_2 crystals have a 2H phase.[15] Atomic force microscopy (AFM) was used to prove that the synthesized SnS_2 nanosheets are of single atom layer.[20] The x-ray diffraction (XRD) and energy-dispersion x-ray (EDX) images can be well indexed to a pure SnS_2 crystal phase without any detectable impurities such as SnS, Sn, Sn_2S_3, Na and Cl elements.[29] In summary, we have used NaCl-assisted CVD method to synthesize the large-size and high quality monolayer SnS_2. Until now, there are only a few reports on the growth of atomically thin SnS_2 layers. These jobs will provide inspiration for future researchers.

2. Results and discussion

Large-size SnS_2 monolayer was synthesized via an optimized CVD method (diagrammatic sketch shown in Fig. 2). A mixture of tin oxalate (SnC_2O_4) powder and NaCl powder with a mass ratio of 8 : 1 was used as the Sn precursor in an alumina boat. A clean Si wafer with 300 nm SiO_2 was used as the substrate located on the top of the boat. SnC_2O_4 has recently been found to be suitable for the growth of 2D SnS_2, which has many advantages over traditional Sn precursors such as SiO_2, SiI_2, and $SiCl_2$. These precursors have some shortcomings, for example, most SnS_2 nanosheets are slanted on the substrate and several layers in thickness cannot be achieved.[30,31] It is not conducive to the preparation of optoelectronic devices. The S powder was placed in another alumina boat and located 15 cm upstream from the Sn precursor in a lower temperature zone. The furnace was heated from room temperature to 600 °C over 25 min and maintained at this temperature for 5–10 min during growth. Finally, the furnace was naturally cooled to room temperature.

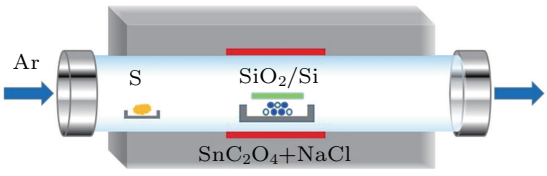


Fig. 2. Schematic diagram of the synthesis of SnS_2 by CVD with NaCl-assistant.

Oxides and iodides like SnO_2 and SnI_2 are difficult to evaporate because of their extremely high melting points about 850 °C and 700 °C.[27,31,32] During the heating process, SnC_2O_4 will decompose into tin oxide. Mixing tin oxide and NaCl will produce a molten solution. The vapor pressure of the molten salt is much higher than that of many metal oxides. A general reaction can be written as

$$\mathrm{NaCl} + \mathrm{SnO}_z \rightarrow \mathrm{SnO}_x\mathrm{Cl}_y + \cdots, \quad (1)$$

$$\mathrm{SnCl}_x\mathrm{O}_y + \mathrm{S} \rightarrow \mathrm{SnS}_2 + \mathrm{SO}_2 + \mathrm{S}_a\mathrm{Cl}_b. \quad (2)$$

NaCl can lower the melting points of Sn precursors, thereby reducing the reaction temperature significantly. Adding NaCl can result in an even higher nucleation rate due to the high volatility nature of metal oxychlorides.

Figures 3(a)–3(c) present the typical optical images of the as-grown monolayer SnS_2 on the SiO_2/Si substrate. According to the previous literature, like other 2D materials, the thickness and the number of layers of the resultant SnS_2 can be easily discriminated via their optical contrast in the optical image.[33] Figure 3(a) is a low-magnification microscope image showing many tin disulfide crystals in a large area. Figures 3(b) and 3(c) show the optical images of the monolayer SnS_2, which have irregular triangles, hexagons, or an irregular shape composed of several monolayer SnS_2. Because if a certain area on the substrate is easy to nucleate, multiple cores will start to grow and SnS_2 will be connected into pieces. The size of the SnS_2 monolayer is generally from about ten to eighty microns, and the largest crystal is about 80 μm in edge. The thickness of the individual SnS_2 nanosheets was measured by AFM. As shown in Fig. 3(d), the thickness of the measured sample is 1.0 nm, corresponding to a monolayer SnS_2 nanosheet. This measured height is larger than the theoretical interlayer distance in SnS_2 bulk materials (≈ 0.8 nm), which can be attributed to the instrumental offset phenomenon (≈ 0.5) that is constantly observed in the AFM image of monolayers two-dimensional materials. A high-magnification SEM image of a synthetic atomic-layer SnS_2 with edge length about 20 μm on SiO_2/Si is shown in Fig. 4(a), the image reveals that the SnS_2 nanosheets are composed of two triangular SnS_2 nanosheets and have a flat surface and sharp edge. EDX spectrum was employed to explore the chemical compositions of the SnS_2 nanosheet demonstrated in Fig. 4(b), the corresponding EDX spectrum of the atomic-layer SnS_2 presents clear signals of Sn and S with an atomic ratio of ∼ 2 : 1, matching well the stoichiometric value of SnS_2. Raman spectroscopy is a valid and simple technique to determine the number of layers and crystal quality of 2D metal chalcogenides.[15,34] For instance, the E_g and A_{1g} band positions of MoS_2 change monotonously with the layer number. Layered SnS_2 crystals could be assorted to two different polytypes: 4H and 2H.[15] For 4H–SnS_2 crystals, the Raman peak at 313.5 cm^{-1} has the maximum intensity which is ascribed to a mixture of A_{1g} and E_g optical modes and the E-mode causes a doublet at 200 cm^{-1} and 214 cm^{-1}. As for the 2H-SnS_2 crystals, the most intense peak at 315 cm^{-1} is assigned to the A_{1g} mode, and the E_g mode causes a single band at 205 cm^{-1}. Figure 4(c) presents the Raman spectra of SnS_2 nanoflakes with different layers. The E_g mode has a single peak at 204.6 cm^{-1} illustrates that the synthesized SnS_2 crystals have a 2H phase. When the thickness decreases down

to a few layers, the E_g peak becomes undetectable, this phenomenon has been well explained by previous research results, which can be attributed to the increase in the number of scattering centers for in-plane scattering.[35,36] Obviously, both the position and intensity of the A_{1g} peak are related to the thickness of the SnS_2 nanoflakes. As the thickness increases from monolayer to thick flakes, except for the increasing intensity, the wavenumber of the A_{1g} peak increases from 303.8 cm^{-1} to 314.5 cm^{-1}. Joseph M. Gonzalez once proved this phenomenon in his research.[37] The A_{1g} peak is blue shifted because when the thickness increases, the increased interlayer van der Waals force in the SnS_2 nanoflakes suppresses the atomic vibration, yielding higher force constants.[38,39] These

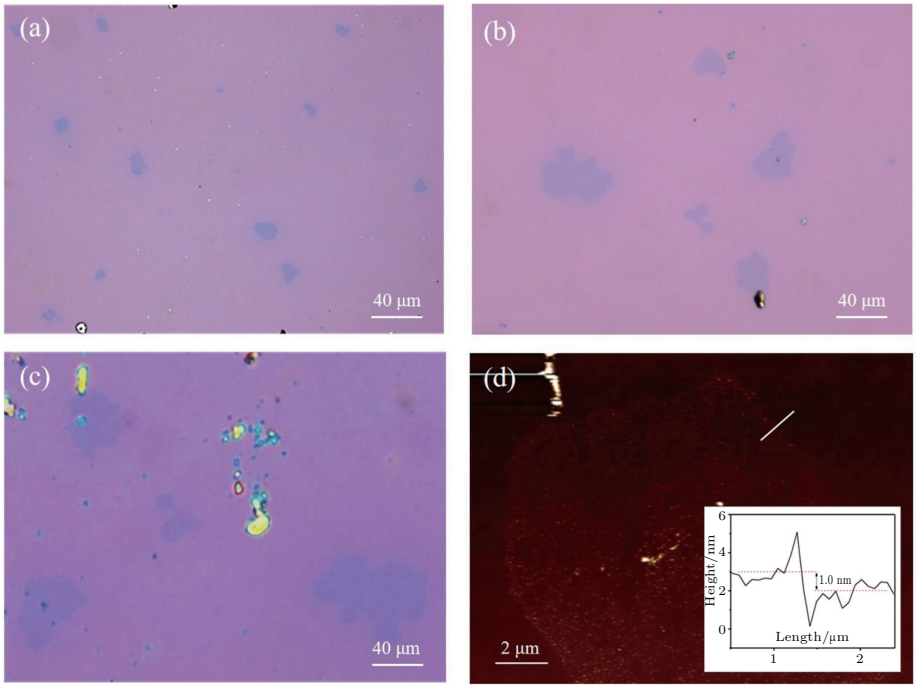


Fig. 3. (a), (b) Large-scale images to show the high yield of SnS_2 monolayer. (c) Typical optical image of SnS_2 monolayer and the monolayer can be as long as 80 μm. (d) AFM image of an atomic-layer SnS_2 crystal. The height profile (inset) shows a thickness of 1.0 nm.

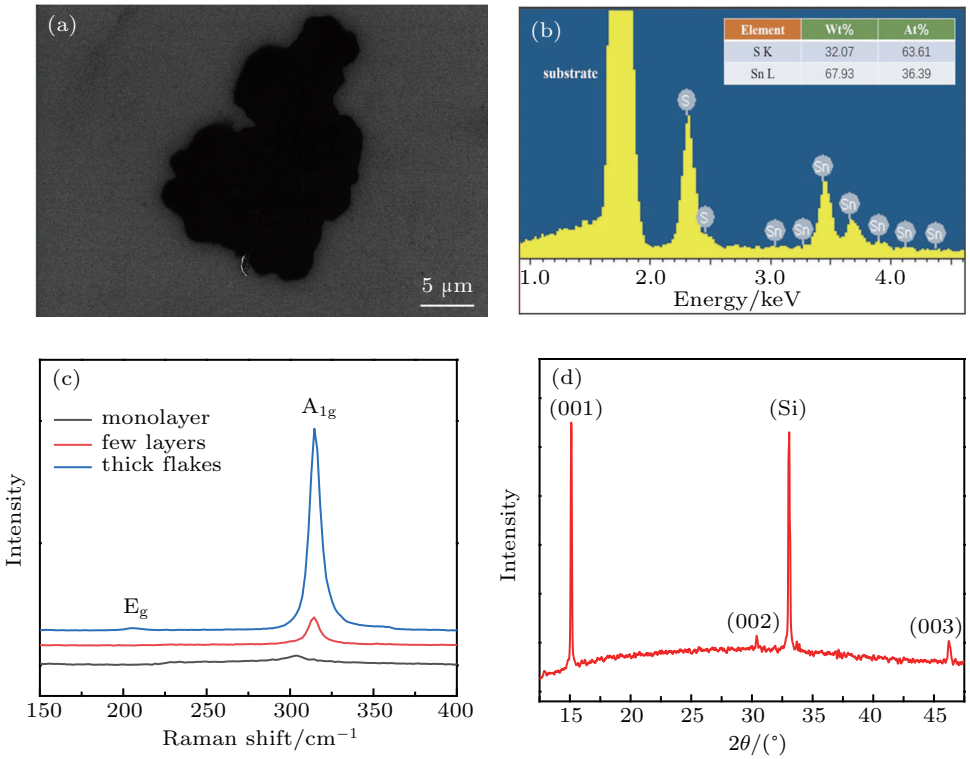


Fig. 4. (a) A high-magnification SEM image of a synthetic atomic-layer SnS_2 composed of two triangular SnS_2 nanosheets. (b) EDX spectrum of the atomic-layer SnS_2 crystal, inset: the atomic ratio of Sn and S. (c) Raman spectra of SnS_2 crystals with various thickness. (d) XRD patterns of the SnS_2 nanosheets.

phenomena provide an effective method to identify the thickness of the SnS_2 nanoflakes. Furthermore, XRD characterization was applied to investigate the structure of the sample grown on SiO_2/Si and the result is exhibited in Fig. 4(d), except for the diffraction peaks from the substrate, the major XRD diffraction peaks at $2\theta = 15.11°$, 30.38°, and 46.23° can be indexed to the (001), (002), and (003) planes of 2H SnS_2 (JCPDS No. 23–0677), respectively. The sharp XRD patterns confirm the highly crystalline nature of the synthetic SnS_2 nanoflakes without any detectable impurities such as SnS, Sn, and Sn_2S_3.[29]

3. Experimental details

Two-dimensional SnS_2 were synthesized on SiO_2/Si substrates by chemical vapor deposition method inside a high-temperature horizontal tube furnace with a 4.5-cm inner diameter and a 98-cm-long heating zone. A mixture of SnC_2O_4 powder (purity 99.9%, Alfa Aesar) and NaCl powder (purity 99.9%, Alfa Aesar) with a mass ratio of 8 : 1 in an alumina boat with a top face down SiO_2/Si substrate was placed at the center of the quartz tube (the heating zone). The sulfur (500 m g) was placed in an alumina boat 15 cm upstream from the Sn precursor, where the temperature was lower, which was around 200 °C during the growth. Before heating, high purity Ar was flow through the system at a rate of 600 standard cubic centimeter per minute (sccm) for 40 min to eliminate oxygen in the furnace. Then the temperature of the center zone was heated to 600 °C in 25 min and maintained at this temperature for 5–10 min. Argon (100 sccm) was used as the carrier gas and to maintain an inert atmosphere. In the cooling step, the furnace was cooled to 200 °C with a cooling rate of 3 °C/min and then rapidly cooled to room temperature.

4. Conclusion and perspectives

In summary, we synthesized large-size and high-quality monolayer SnS_2 with the edge length of up to 80 μm via an CVD method by NaCl-assistant. As we know, no method for stable preparation of monolayer SnS_2 has been reported. Optical microscope, AFM, SEM, XRD, and EDX were used to characterize the size, semblance, thickness, and composition of the sample. NaCl can lower the melting points of Sn precursors and increase the vapor pressure of the Sn precursor. These changes lead to a higher nucleation rate. This method might pave the way for the electronics and optoelectronics applications and inspire other researchers.

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