Synthesis and Growth Mechanism of SiS₂ Rods

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1. INTRODUCTION

Silicon disulfide (SiS₂) is an important synthetic compound used in fundamental and applied research. It is one of the important raw materials for sulfide-based solid electrolytes.¹⁻¹²

There are five polymorphs of SiS₂. One is the ambient-pressure (NP) phase (≤3.83 MPa, 973–1570 K), with an orthorhombic structure (Ibam, Space Group no. 72), which can remain stable up to 6.9 GPa at RT.¹⁰ The other four are high-pressure (HP) phases, while HP1-, HP2-, and HP3-phases are quenchable under ambient conditions. Monoclinic HP1-/HP2-phases (P12₁/c1, no. 14) form under 2.8/3.5 GPa at 1473 K, respectively. They have different unit-cells (Z = 4 vs Z = 12) and the c value of the former [5.8261(8) Å] is smaller than that of the latter [14.747(2) Å].¹¹ The tetragonal HP3-phase (P42₁/̅m, no. 122) forms under 4.0–7.5 GPa at 1373–1703 K.¹¹,¹⁴,¹⁵ The trigonal HP4-phase (P3m1, no. 164) cannot be obtained by quenching from a high temperature. It can only form through in situ high-pressing (27.5–29.6 GPa) at RT,¹⁰ either from a stable NP-phase or one of the above three metastable HP-phases.

The SiS₂ has an extreme-high selling price due to its complex synthesis methods restrained by its sensitivity toward hydrolysis and oxidation to generate the toxic H₂S with a penetrating odor.¹⁰⁻¹⁹

Synthesis methods for NP-SiS₂ have been summarized⁵ and classified into two groups: compound⁵,¹³,¹⁶⁻²⁰ and elemental¹⁰,¹¹,²⁰⁻²⁴ methods. As for the latter, both silicon (Si) and sulfur (S) sources are elementary substances. It has advantages of easy availability of raw materials, simple process, no environmental pollution, safety, and less corrosion of equipment. At present, the “elemental method” for NP-SiS₂ has become the main priority for academic research and scale production. The related reaction takes place at a certain temperature in a sealed quartz or quartz-lined steel container, similarly in a low-/medium-pressure hydrothermal kettle.

There are two routes in the “elemental method”.

The first is with a dual-temperature zone having a temperature gradient between the cold- and hot-ends of the container. The synthesis reaction happens at the hot-end. The S-vapor circulates between the two ends. The ambient reaction pressure (NP) depends on the saturated S-vapor pressure (Pₛₛ, sat.@S) at the cold-end rather than the pressure at the hot-end. This route ensures effectively the safe use of quartz tubes. However, it is at the expense of the reaction pressure reduction due to the lower cold-end temperature (vs hot-end temperature). The reaction time has to be extended. The requirement with a longer tube would decrease the effective reaction volume and therefore increase the equipment complexity and difficulty to use.

The second is with a uniform-temperature zone while the NP varies. When NP ≤ Pₛₛ, ctrl., the reaction can take place safely (Pₛₛ, ctrl.—the control pressure set for safe use of quartz tubes; being equal to 3.83 MPa in this work).

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where Blocks I–IV correspond to the four P-T relevant quadrants (labeled in Figure 2, see Section 2). The \( P_0 \) is the ideal gas pressure of S calculated by the ideal gas equation (\( = n_S R T V_q^{-1} \), MPa), where \( T > T_{b.p.}@S \) (717.75 K).\(^23\) The \( n_S \) is the mole number of S, \( R \) is the ideal gas constant (8.3144 J mol\(^{-1}\) K\(^{-1}\)), and \( V_q \) is the active volume (dm\(^3\)). Next, the \( P_{\text{expl}} \) is the pressure limit of tube explosion. When \( NP > P_{\text{ctrl}} \) and meanwhile \( > P_{\text{expl}} \) quartz tubes would explode (Block IV). In practical application, the \( P_{\text{expl}} \) value of a commercially available quartz tube is about several megapascals (MPa), far below the tensile strength of a silica rod (\( \sim 120 \) MPa at 923–1073 K).\(^24\),\(^25\)

Figure 1. Preparation of the flow chart of SiS\(_2\) (a) Solid–liquid boiling process; (b) solid–gas steaming process.

2. MATERIALS AND CHARACTERIZATION

The preparation flow chart of SiS\(_2\) is shown in Figure 1 and the ambient pressure (NP) via temperature (T) diagram for synthesizing SiS\(_2\) in Figure 2.

S Powder. The commercially available S powder (99 wt %, Beijing Xinguang Chem. Reag. Fact., China) was washed first by aqua regia with a HCl/HNO\(_3\) ratio of 3:1 (vol %) (36.0–38.0 wt % HCl, Shanghai Chem. Reag. Fact., China; 65.0–68.0 wt % HNO\(_3\), Shanghai Chem. Reag. Fact., China). Then, it was washed many times with ultrapure water (\( > 18 \) M\(^2\) cm), until no Cl\(^-\) could be detected in the washing solution and pH = 7. The improvement of the rate constant (\( k \)) and conversion rate (\( \eta \)) in an exothermic reaction, which is also applied in this work.

However, there remains still some challenges in the application of the “elemental method”, e.g., low purity of SiS\(_2\), set for the safe use of quartz tubes complicated process to eliminate residual S,\(^6\) long production period (soaking for 150 h,\(^13\), \( > 3 \) d,\(^10\),\(^11\) or 7 d;\(^22\) calcining for 70–80 h or 12 d),\(^10\),\(^11\)) too many production procedures,\(^6\) high-temperature/pressure safety problems,\(^5\),\(^6\) and detailed growth kinetics of rods (\( \text{c.f.} \) CdS, ZnO, et al.).\(^26\),\(^27\)

We prepared SiS\(_2\) 2 years before through an “elemental-synthesis gasifying separation” (ESGS) process.\(^5\) This work is to reinvestigate/optimize the control techniques for solid–liquid/solid–gas reactions, chemical/phase-purity and microstructure of SiS\(_2\). The chemical (\( \text{c.f.} \) evaporation) approach using benzene is first used to eliminate residual S to prepare pure SiS\(_2\). The growth mechanism of SiS\(_2\) rods is proposed.
washed substance was vacuum-dried and sieved through 200 mesh (<74 μm).

**Si Powder.** A certain number of polysilicon blocks (7N, Xinte Energy Co. Ltd., China) were broken and put into a stainless-steel vessel, together with Fe-balls (ϕ 5.9 mm) and ethanol (99.7 wt %, Shanghai Chem. Reag. Fact., China) at the ratio of 1 (Si): 8 (Fe-balls): 1 (ethanol) (wt %). Ball-milling proceeded for 12 h at 150 rpm for revolution and 300 rpm for rotation in a planetary mill (QM-DY9, Nanjing Instr. Fact., China). The Si slurry was washed in sequence by 10 wt % HCl and 6 wt % HF (≥ 40.0 wt %, Shanghai Chem. Reag. Fact., China). Then, it was washed with ultrapure water and ethanol and vacuum-dried and sieved as the above. The Te-flon utensils and containers were used when HF was involved in experiments.

As a comparison, some Si powder was prepared by using WC-Co balls (ϕ 6.1 mm) for 2 h. Then, the Fe-ball-milled Si powder was denoted as “Si” and the WC-Co-ball-milled Si powder was denoted as “Si#”.

**SiS₂ Powder.** The obtained S and Si powders were mixed at the mole ratio (δ) of 3.3 : 1, that is, δ = 3.3, and then sealed in quartz tubes and vacuumed to 10 Pa with Ar. Each tube (Vq = 0.0121 dm³) contains 2 g of powder, equivalent to that mSi = 34.6 g/dm³. At least three tubes were used for one sample. Quartz tubes were laid diagonally in the furnace at a certain angle of 15°–25°. Half of them contained reactants at a down (D) site (for the solid–liquid boiling process; Figure 1a) and the other half at an up (U) site (for the solid–gas steaming process; Figure 1b). Samples were heated at low (L) or high (H) temperature (1023/1073 K) for 3 h then cooled down to RT. Both heating and cooling rates were 5 °C/min. Products were taken out by cutting quartz tubes and then treated (T) with benzene (Sinopharm, China; ≥ 99.5 wt %) in an Ar-filled glovebox (H2O < 0.1 ppm, O2 < 0.1 ppm). Last, they were vacuum-dried and sieved through 200 mesh (<74 μm). For the following reasons, benzene was used in this work — it is the simplest aromatic hydrocarbon with a stable ring connected by delocalized big π-bonds. The hydrogen atoms on the ring are easy to be replaced but difficult to react with the oxygen in air (at RT). Addition reactions are difficult to proceed while it is used. It does not dissolve or react with the target product SiS₂. However, it can dissolve residual S and other impurities.30 Samples were labeled hereafter with suffixes such as H, L, U, D, and T to represent those prepared at different conditions, for example, SiS₂_HUT refers to the SiS₂ prepared at a high (H) temperature of 1073 K, while the quartz tube was at an up (U) site, and treated (T) by benzene.

Chemical compositions were analyzed by an inductively coupled plasma-optical emission spectrometer (ICP Prodigy 7, Leeman Labs Inc., USA). The crystal structure and phase purity were determined by X-ray powder diffraction (XRD) using CuKα radiation (λα1 = 1.5406 Å, 40 kV, 40 mA) in a flat plate θ/2θ geometry with a step size of 0.01313°/step and a time per step of 128.52 s/step (Empyrean, PANalytical B.V., Netherlands). Samples were protected from water and oxygen through a special sample stage (Deen Optics Co., China) with shielding Ar in Kapton tapes.

The structure refinement with spherical harmonics function was performed by the Rietveld method implemented in GSAS/
EXIGUI software\(^{31}\) using the model of \(\text{Si}_\text{s}[\text{S}^\text{s}]\), based on an orthorhombic structure (\(\text{Ibam}, \text{ICSD 291210}\)).\(^{11}\) The preferred orientation of polycrystalline grains was characterized by the texture index (\(J\)), texture strength (\(J^{1/2}\)), and pole figures.

The microstructure and compositions were tested by a field-emission scanning electron microscope (S-4800, Hitachi Ltd., Japan), and a field-emission scanning/transmission electron microscope equipped with an X-ray spectrometer for energy-dispersive spectroscopy (EDS) (Talos F200S G2, Thermo-Fisher Sci. Inc., USA).

3. RESULTS AND DISCUSSION

3.1. Chemical Purity. 31 elements were analyzed by ICP for the acid-pickled raw materials (S and Si) and the synthesized Si\(_2\)S\(_2\) powders (Figure 3). It showed that the W impurity induced by WC-Co ball-milling was much more difficult to be removed by the acid-pickling process than the Fe induced by Fe ball-milling.\(^{5,28,29}\) All samples except the Si\(^{\#}\) (WC-Co-ball-milled Si powder) had a low content of element impurity (<690 ppm; w/o Na) and a low total impurity content (\(\sim 99.95\) wt % purity; w/o Na). The acid-pickled Si, the synthesized Si\(_2\)S\(_2\)_LUT, Si\(_2\)_HU, and Si\(_2\)_HUT had a relatively high content of Na, as a result of a high content of total impurity content. It might come from utensils, containers, or test errors. More studies are underway.

3.2. Phase Purity and Crystal Structure. The acid-pickled S was indexed to the orthorhombic \(\alpha\)-S\(_8\)(s) with annular molecules (\(FdddZ\), no. 70; ICSD 63083) (Figure 4a). At low temperatures (<432 K), the prevailing S-molecular species were those of cyclocta-S, cyclo-S\(_8\), and small molecules (from S\(_2\) to S\(_8\)) with minimal and negligible quantities identified in the solid, liquid, and gaseous phases.\(^{34-36}\) When heated, it will transform to various forms of polymeric S\(_n\)-chains, catena or mixed cyclolinear, for example, monoclinic \(\beta\)-S\(_8\)(s) at 369 K, monoclinic \(\lambda\)-S\(_8\)(l) with long-chain molecules near its melting point (\(T_{\text{m.p.}}@S = 388.36\) K), and amorphous \(\mu\)-S\(_8\)(l) at 432–433 K. Last, it would turn into a gas at its boiling point (\(T_{\text{b.p.}}@S = 717.75\) K).\(^{35,36}\) The acid-pickled Si was indexed to the cubic phase (\(Fd\overline{3}m\text{S},\) no. 227; ICSD 51688). The S and Si started to react below 628–663 K.\(^{22,23,32-37}\)

\[
\begin{align*}
\text{S(l)} & \xrightarrow{1023 K/2.57 \text{MPa}} S(\text{g}) & (2) \\
\text{Si(s)} + 2\text{S(l)} & \xrightarrow{1023 K/2.57 \text{MPa}} \text{SiS}_2(\text{s}){}^{28,29} & (3) \\
\text{Si(s)} + 2\text{S(g)} & \xrightarrow{1023 K/2.57 \text{MPa}} \text{SiS}_2(\text{s}) & (4)
\end{align*}
\]

Two of the eqs 2–4 are independent.

XRD patterns of the synthesized Si\(_2\)S\(_2\) samples could be indexed to pure (100 wt %) orthorhombic Si\(_2\)S\(_2\) phases except for Si\(_2\)_HU. The Si\(_2\)_HU contained a small amount of residual \(\alpha\)-S\(_8\), which was easily removed by benzene. All patterns were almost the same, including background, peak positions, shapes, and relative intensities. However, these relative intensities were obviously different with those deduced from the ICSD 291210 (\(\text{Ibam},\) no. 72).\(^{11}\) Thus, the preferred orientation correction\(^{31,38,39}\) was introduced into the Rietveld refinement of the Si\(_2\)_HUT sample (Figure 4b). The refinement did not show any anomalies. The fit converged with acceptable goodness-of-fit (\(\chi^2 = 2.62\)) and agreement indices (\(R_p = 5.49\%\), \(R_{wp} = 8.72\%\), \(R_{exp} = 3.34\%\), and \(R_F^2 = 9.14\%\)). The obtained structural and thermal parameters are reasonable (Table 1).\(^{11,40}\)

It showed orthorhombic Si\(_2\)S\(_2\) phases could be synthesized through the boiling/steaming process in a uniform-temperature zone (1023–1073 K, 3 h) and under the corresponding saturated S-vapor pressure (\(P_{\text{sat.}}@S = 2.57–3.83\) MPa).\(^{34}\)

The chemical bonds in the orthorhombic Si\(_2\)S\(_2\) are anisotropic. Distorted edge-sharing [Si\(_2\)S\(_4\)] tetrahedra link as chains along the c-axis (the inset of Figure 4b). There is very rigid covalent bonding between the tetrahedra in the direction [0 0 1], while there is weak ionic and van der Waals bonding with an "open"
structure in the other two directions (a and b).\textsuperscript{11,40} From the structure refinement with spherical harmonics function, the allowed eighth-order harmonic coefficients ($C_l^{(8)}$) were calculated. They are related to the reflection-intensity correction factors that describe the texture effects. Then, the texture index ($J$) and texture strength ($J^{1/2}$) which depends on $C_l^{(8)}$ were concluded, that is, $J = 1.6149$ (c.f. $J = 1$ for random, otherwise $J > 1$; $J = \infty$ for a single crystal) and $J^{1/2} = 1.2708$.

Pole figures present that the statistical orientation distribution of the plane normals from a particular set of planes gives a mapping of the probability of possible grain orientations.\textsuperscript{31,38,39} Figure 4c showed pole figures constructed for the first three allowed reflections in orthorhombic SiS$_2$ with the comparatively low symmetry, that is, (1 1 0), (2 0 0), and (2 1 1), in which the relative populations of planes in various orientations were proportional to the numbers (represent relative intensities of the diffraction signal) against the contour lines.

It confirmed that the synthesized orthorhombic SiS$_2$ powders presented polycrystalline alignment with oriented [0 0 1] texture microstructures.

### 3.3. Microstructure (SEM and TEM/EDS).

Scanning electron microscopy/transmission electron microscopy (SEM/TEM) images and EDS mappings of the acid-pickled Si and the synthesized SiS$_2$ powders are shown in Figure 5i–viii. The length ($L$), diameter ($D$), and length-to-diameter ratio ($L/D$) of Si and SiS$_2$ rods/particles from SEM image analysis are shown in Figure 6.

The S was kept in the liquid and gaseous states in this work thus the initial size (as opposed to chemical purity) needs not be too concerned.

The acid-pickled Si has a small particle size and a uniform particle size distribution of 3.3 ± 0.9 μm (Figures 5i and 6). It means that the Fe-based medium for ball-milling Si powder is highly effective for decreasing particle size and maintaining a high chemical purity (by post-acid-pickling).\textsuperscript{5,28,29}

SiS$_2$ particles prepared with the quartz tubes at a down (D) site (solid–liquid boiling process, Figure 1a), whether at low (L) or high (H) temperature (1023/1073 K), have irregular shapes and feature a little rod-like, such as SiS$_2$ LD (Figure 5ii) and SiS$_2$ HD (Figure 5v). Their mean particle diameters are 3.8 ± 1.2 μm and 4.9 ± 1.3 μm, respectively (Figure 6). The forced-convective S-liquid stirred constantly the solid Si/SiS$_2$ and destroyed the rods (see Section 3.4).

SiS$_2$ particles prepared with the quartz tubes at an up (U) site (solid–gas steaming process, Figure 1b), whether at low (L) or high (H) temperature (1023/1073 K), have rod-like shapes and feature very little irregular, such as SiS$_2$ LU (Figure 5iii), SiS$_2$ LUT (Figure 5iv), SiS$_2$ HU (Figure 5vi), and SiS$_2$ HUT (Figure 5vii and viii). The solid–gas steaming process provided a more stable growth environment for the SiS$_2$ rods (see Section 3.4). Their mean particle sizes (length/diameter) are 13.4 ± 4.5/3.8 ± 0.9 μm for SiS$_2$ LU, 12.9 ± 3.0/3.2 ± 0.6 μm for SiS$_2$ LUT, 16.0 ± 5.4/3.9 ± 0.9 μm for SiS$_2$ HU, and 16.8 ± 5.0/4.5 ± 1.3 μm for SiS$_2$ HUT, respectively. The corresponding length-to-diameter ($L/D$) ratios are 3.5, 4.0, 4.1, and 3.7, respectively. The length increases 19−30% with preparation-temperature increasing, while the diameter increases by varying degrees. Thus, the resulting L/D values change a little (Figure 6).

The TEM imagine and EDS mappings of SiS$_2$ HUT (Figure 5viii) showed a homogeneous elemental distribution of S and Si in SiS$_2$ rods. No impurities were detected.
Comparing the images of SiS$_2$ LUT (Figure 5iv) with SiS$_2$ HUT (Figure 5v) and SiS$_2$ HU (Figure 5vi) with SiS$_2$ HUT (Figure 5vii), they showed that the residual S under the saturated S-vapor pressure ($P_{\text{sat.}, 1073 \text{K}} = 3.83 \text{MPa}$) was much lower than the one in the absence of S vapor ($P_{\text{sat.}, 1023 \text{K}} = 2.57 \text{MPa}$) and the side reactions to SiS(g) (eq 6) was suppressed. For samples prepared at the down (D) site of quartz tubes, the main process was boiling with a solid–liquid reaction between solid Si and S-liquid, while saturated S-vapor stayed at the up (U) site. For samples prepared at the up (U) site of quartz tubes, the main process was steaming with a gas–solid reaction between solid Si and saturated S-vapor, while S-liquid stayed at the down (D) site (Figure 1).

From the thermodynamics viewpoint, there may exist the following reactions to prepare SiS$_2$ by an “elemental method”, for example, at 1023 K (2.57 MPa)—1073 K (3.83 MPa) in this work.

Si(s) + S(g) = SiS$_2$(s), $\Delta G^0$ (kJ/mol) = $-$325.24 + 0.1632T (<0, when $T < 993 \text{K}$)$^{33}$ (5)

SiS$_2$(s) + S(g) = 2SiS(g), $\Delta G^0$ (kJ/mol) = 102.55 − 0.1632T(<0, when $T > 628 \text{K}$)$^{33}$ (6)

SiS$_2$(s) + S(s) = 2SiS(g), $\Delta G^0$ (kJ/mol) = 395.2 − 0.2646T(<0, when $T > 1494 \text{K}$)$^{37}$ (7)

SiS$_2$(s) = $\frac{1}{2}$S$_2$(g) + SiS(g), $\Delta G^0$ (kJ/mol) = 387.7 − 0.2354T(<0, when $T > 1647 \text{K}$)$^{37}$ (8)

The main reaction to synthesize SiS$_2$(s) (eq 5) proceeds below 1993 K and the side reaction to SiS(g) (eq 6) starts to proceed when $T > 628 \text{K}$. The former dominates because there is a larger Gibbs free-energy (absolute value) than the latter. Besides, the forward reactions in eqs 7 and 8 would be very difficult to happen below 1993 K (also in this work), while the partial pressures of SiS(g) are $10^{-3}$ atm in eq 7$^{33,37}$ and $10^{-5}$ atm in eq 8, respectively.$^{33}$ This means, if the SiS(g) was generated via eq 6, it would tend to produce SiS$_2$(s) and Si(s) as in the backward reaction of eq 7 or react with S$_2$(g) to form SiS$_2$(s) as in the backward reaction of eq 8. Therefore, the contribution of SiS(g) in the “elemental method” (as in this work) to synthesize SiS$_2$(s) can be neglected, which is different from that in a “compound method”.$^{3,13,16−20}$

For the Si–S reactions, there is an interface between reacting phases. In order for the reaction to proceed, three paths take place in series—transport of reactants (Si/S) to the interface, reaction at the phase boundary (PB), and transport of product (SiS$_2$) away from the interface.$^{46}$ In addition, the exothermic reactions (eqs 3 and 4) at PB liberate heat (given an adiabatic assumption, e.g., in a uniform-temperature zone in this work), change the boundary temperature and limit the reaction rate ($r$). Any of these steps may determine the overall reaction rate ($r$) which depends on the slowest one.
Solid−liquid reaction (boiling process; Figure 1a): The process was at 1023 K under 2.57 MPa or at 1073 K under 3.83 MPa. Mass-transport rates of reactants (Si and S) and product (SiS$_2$) increased greatly through the forced-convection mass-transport step in the S-liquid. The PB reaction proceeded mainly between the solid Si and S-liquid, while the saturated S-vapor stayed nearby (eq 3). Therefore, the dominant factor which determines $r$ was the reaction rate of solid-liquid-PB ($r_{s-l}$). The PB was fixed by the movement of atoms/molecules across the interface in a way equivalent to the grain growth. In this process, the forced-convective boiling S stirred constantly the solid Si/SiS$_2$ and destroyed the rods, such as SiS$_2$-LD (Figure 5ii) and SiS$_2$-HD (Figure 5v).

Solid−gas reaction (steaming process; Figure 1b): Here, mass-transport rates were governed through the forced-convection mass-transport step in the saturated S-vapor. The PB reaction proceeded mainly between the solid Si and saturated S-vapor, while the S-liquid stayed below (eq 4). The dominant factor which determined $r$ was the reaction rate of solid−gas-PB ($r_{s-g}$). When a single Si-particle (surrounded by S-vapor) acted as a heterogeneous reaction surface, the oriented growth of SiS$_2$ occurred, such as SiS$_2$-LU (Figure 5iii), SiS$_2$-LUT (Figure 5iv), SiS$_2$-HU (Figure 5vi), and SiS$_2$-HUT (Figure 5vii and viii).

Then, consider the reactions from the kinetics viewpoint. The calculations of Rau et al. concluded that the mean S-atom number per molecule is 3 in the liquid state [i.e., S$_3$(l)] and 4.7 in the gaseous one [i.e., S$_{4.7}$(g)] in the range of 1023−1073 K. Referring to eqs 3 and 4, the kinetic equations could be expressed as eq 9. The relationship among reaction pressure, concentrations of reactant (S)/product (SiS$_2$), and reaction time showed in Table 2 and Figure 7. Here, the $t$ refers to time. The $a$, $b$, and $c$ are initial ($t=0$) concentrations of Si(s) (= [Si]$_0$ = 1.23 mol/dm$^3$), S$_3$(l) (= [S$_3$]$_0$), and S$_{4.7}$(g) (= [S$_{4.7}$]$_0$), respectively ($a \leq 1.5b + 2.35c$). Here, the initial concentration of single S, that is, $[S]_0 = 4.059$ mol/dm$^3 = 3b + 4.7c$, while $\delta = 3.3$.

The $x$, ($a - x$), ($b - ux$) and $c - ((2-3x)/4.7)x$ are instantaneous ($t = t$) concentrations of SiS$_2$ (eq 9). The $x$ values (= [S$_{4.7}$]$_0$) were calculated by the ideal gas equation under $P_{sat, S_{4.7}}$. When the reactions went on at 1023 K, the S-vapor pressure in the tube remained constant ($= P_{sat, S_{4.7}}$). However, when the reactions completed 82.9% (= 1.02/1.23 × 100%) at 1073 K, the S-vapor pressure became smaller (between 3.03−3.83 MPa) than $P_{sat, S_{4.7}}$ because all the liquid S had been gasified earlier. The amount of S-liquid was the difference between those of the total S and S-vapor.

The $b_{l, \infty}$ and $b_{g, \infty}$ correspond to the amount of residual S$_3$(l) and S$_{4.7}$(g) when the reactions just finished at the synthesis temperature, respectively. The total residual S, that is, $S_{rest} = b_{l, \infty} + b_{g, \infty} = 3b + 4.7c - a$.

The differential-type kinetic equations are as the following:

![Figure 5. SEM (i−vii), TEM images, and EDS mappings (viii) of Si and the synthesized SiS$_2$ powders. They are as follows: the Fe-ball-milled and acid-pickled Si [i(a) and i(b)]; the SiS$_2$ prepared at a low (L) temperature of 1023 K, while the quartz tube was at a down (D) site [ii(a) and ii(b)], at an up (U) site [iii(a) and iii(b)], or at an up (U) site and then treated (T) by benzene [iv(a) and iv(b)]; the SiS$_2$ prepared at a high (H) temperature of 1073 K, while the quartz tube was at a down (D) site [v(a) and v(b)], at an up (U) site [vi(a) and vi(b)], or at an up (U) site and then treated (T) by benzene [vii(a) and vii(b); viii(a1), viii(b1), and viii(c1)].](https://doi.org/10.1021/acsomega.2c01725)
Table 2. Kinetic Equations and the Relationship between Initial/Final Concentrations ([C]/[C]₀) of Reactant (S) /Product (SiS₂) and Reaction Time (t)

| t = 0 | Conc. (mol/dm³) | a | b | c | 0 |
|-------|-----------------|---|---|---|---|
| C₁₀₂₃ K⁻¹ | 1.23 | 0.880 | 0.302 | 0 |
| C₁₀₂₃ K⁺² | 1.23 | 0.880 | 0.302 | 0 |
| C₁₀₇₃ K⁻¹ | 1.23 | 0.680 | 0.429 | 0 |
| C₁₀₇₃ K⁺² | 1.23 | 0.680 | 0.429 | 0 |

| t = t | Conc. (mol/dm³) | a - x | b - ux | (c - \(\frac{2 - 3u}{4.7}\)x) | x |
|-------|-----------------|-------|--------|----------------------------|---|
| C₁₀₂₃ K⁻¹ | 1.23 - x | 0.880 - 2/3x | 0.302 | x |
| C₁₀₂₃ K⁺² | 1.23 - x | 0.880 - 2/3x | 0.302 | x |
| C₁₀₇₃ K⁻¹ | 1.23 - x | 0.680 - 2/3x | 0.429 | x |
| C₁₀₇₃ K⁺² | 1.23 - x | 0.680 - 2/3x | 0.429 | x |

| t = ∞ | Conc. (mol/dm³) | 0 | h₈₁₀ | c₈₁₀ | a |
|-------|-----------------|---|------|------|---|
| C₁₀₂₃ K⁻¹ | 0 | 0.060 | 0.302 | 1.23 |
| C₁₀₂₃ K⁺² | 0 | 0.060 | 0.302 | 1.23 |
| C₁₀₇₃ K⁻¹ | 0 | 0.000 | 0.340 | 1.23 |
| C₁₀₇₃ K⁺² | 0 | 0.000 | 0.340 | 1.23 |

\[
r = \frac{dx}{dt} = \frac{d[SiS₂]}{dt} = -\frac{d[Si]}{dt} = -\frac{d[S₄.₇]}{udt} = \frac{4.7d[S₄.₇]}{(2 - 3u)dt} \\
= k(a - x)^α(b - ux)^β\left(c - \left(\frac{2 - 3u}{4.7}\right)x\right)^γ, \quad a ≤ \frac{1}{2} \\
\cdot(3b + 4.7c)\quad 0 < x < a
\]

where \(k\) refers to the rate constant of reaction. \(k = k_{SiS} = k_{Si} = (1/\ u)k_{S₄.₇} = (4.7/(2 - 3u))k_{S₄.₇}\). The \(α, β,\) and \(γ\) are the sub-orders of reaction (all > 0). Parallel solid–liquid (eq 3) and solid–gas (eq 4) reactions proceeded simultaneously as the following:

\[
r = r^{s⁻¹} + r^{s⁻g}
\]

where \(k^{s⁻¹}\) and \(k^{s⁻g}\) are the rate constants of the solid–liquid phase-boundary (PB) and solid–gas phase-boundary (PB), respectively. The following superscript symbols have the same meanings. The \(a\) and \(a₇\) correspond to the amount of Si reacted with \(S₃(l)\) and \(S₄.₇(g)\), respectively.

For the boiling process to synthesize SiS₂ at 1023/1073 K and a down (D) site in quartz tubes, eq 12 (same as the following eqs 14 and 15) was the primary reaction.

\[
r^{s⁻¹}_{1023K} = k^{s⁻¹}_{1023K}(1.23 - x)^α\left(0.880 - \frac{2}{3}x\right)^β, \quad 0 < x < 1.23
\]

This was a complete solid–liquid reaction. Where \(a \to 0, a_1 = a = 1.23\) mol/dm³ and \(u = 2/3\). The \([S₄.₇]\) kept constant (= c = 0.302 mol/dm³) until the end of the reaction. \(b = (3.3 \times 1.23 - 4.7 \times 0.302)/3 = 0.880\) mol/dm³.

\[
r^{s⁻¹}_{1073K} = k^{s⁻¹}_{1073K}(1.23 - x)^α\left(0.680 - \frac{2}{3}x\right)^β, \quad 0 < x < 1.02
\]

This was an incomplete solid–liquid reaction. Where \(a_7 \to 0, a_1 = a = 1.23\) mol/dm³ and \(u = 2/3\). The \([S₄.₇]\) kept constant (= c = 0.429 mol/dm³) until 82.9% (= 1.02/1.23 × 100%) SiS₂ was obtained. \(b = (3.3 \times 1.23 - 4.7 \times 0.429)/3 = 0.680\) mol/dm³. The \([S₄.₇]\) consumption was 0.680 mol/dm³ and that of \([S₄.₇]\) was 0.089 mol/dm³ (= 0.429 – 0.340 mol/dm³). In other words, the last 17.1% SiS₂ was synthesized through a solid–gas reaction.

Figure 6. Length (L), diameter (D), and length-to-diameter ratio (L/D) of Si and SiS₂ rods/particles from SEM image analysis.
For the steaming process to synthesize SiS₂ at 1023/1073 K and a up (U) site in quartz tubes, eq 13 (same as the following eqs 16 and 17) was the primary reaction.

\[ r_{1023}^{r-e} = k_{1023}^{r-e}(1.23 - x)^\alpha, \quad 0 < x < 1.23 \]  

(16)

This was a complete solid–gas reaction. Where \( a_1 \rightarrow 0, a_2 = a = 1.23 \text{ mol/dm}^3 \) and \( u = 2/3 \). The \( S_{4.7}^{\text{g}} \) kept constant \( (\approx c = 0.302 \text{ mol/dm}^3) \) until the end of the reaction. The amount of \( S_{4.7}^{\text{g}} \) which reacted with \( \text{Si(s)} \) equals that of the gasified \( S_3^{\text{l}} \), while the latter decreased from 0.880 to 0.060 mol/dm³.

\[ r_{1023}^{r-e} = k_{1023}^{r-e}(1.23 - x)^\alpha, \quad 0 < x < 1.02 \]  

(17)

This was a complete solid–gas reaction. Where \( a_1 \rightarrow 0, a_2 = a = 1.23 \text{ mol/dm}^3 \) and \( u = 2/3 \). The \( S_{4.7}^{\text{g}} \) kept constant \( (\approx c = 0.429 \text{ mol/dm}^3) \) until 82.9% \( (\approx 1.02/1.23 \times 100\%) \) SiS₂ was obtained. The temperature increasing would result in the decreasing of the solid

\[ r_{1073}^{r-e} = k_{1073}^{r-e}(1.23 - x)^\alpha, \quad 0 < x < 1.02 \]  

(18)

Because (0.880–2/3x)/(0.680–2/3x) > 1, \( \beta > 0 \) and the \( k_{1023}^{r-e}/k_{1073}^{r-e} \) is slightly less than 1 (according to the Arrhenius rule from the kinetics viewpoint), so \( r_{1023}^{r-e}/r_{1073}^{r-e} < 1 \). The temperature increasing would result in the decreasing of the solid–liquid–PB reaction rate \( (r^{\text{e}}) \) in the boiling process. In other words, the high temperature is beneficial to the steaming process.

4. CONCLUSIONS

In this work, the SiS₂ rods were prepared by using the excess sulfur formula either through a solid–liquid boiling process or a solid–gas steaming process.

The relatively high pressure (2.57 MPa@1023 K and 3.83 MPa@1073 K) is more favorable for the formation of SiS₂ rods in the closed sealed-tube system (with a uniform-temperature zone) than that in an open system. The chemical (cf. evaporation) approach using benzene is first used to eliminate residual S to prepare pure SiS₂.

The SiS₂ rods have controllable microstructure and high chemical/phase purity. The optimized synthesis condition can affect the macroscopic morphology but cannot enough change the microstructural anisotropy.

The gaseous SiS is hardly present in this “elemental” method between 1023 and 1073 K which is different with that in a “compound method”. The SiS₂ rods were synthesized through solid–liquid/solid–gas reactions among the Si(s), S₃(l), and S⁴.₇(g). The low temperature is beneficial to the solid–liquid reaction and the high temperature to the solid–gas reaction.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.2c01725.

Crystallographic data for SiS₂ and further details of the crystal structure investigation may be obtained from Cambridge Crystallographic Data Centre (UK) and inorganic Crystal Structure Database of FIZ Karlsruhe (Germany) on quoting the appropriate ICSD number (SiS₂_1073 K 3.8 MPa, ICSD 2151800, 2022.2.14), DOI: 10.5517/ccdc.csd.cc2b73xm (CIF)
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Notes

The authors declare no competing financial interest.

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