Review

Fundamental Aspects and Comprehensive Review on Physical Properties of Chemically Grown Tin-Based Binary Sulfides

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Abstract: The rapid research progress in tin-based binary sulfides (Sn S ) by the solution process has opened a new path not only for photovoltaics to generate clean energy at ultra-low costs but also for photocatalytic and thermoelectric applications. Fascinated by their prosperous developments, a fundamental understanding of the Sn S thin film growth with respect to the deposition parameters is necessary to enhance the film quality and device performance. Therefore, the present review article initially delivers all-inclusive information such as structural characteristics, optical characteristics, and electrical characteristics of Sn S. Next, an overview of the chemical bath deposition of Sn S thin films and the influence of each deposition parameter on the growth and physical properties of Sn S are interestingly outlined.

Keywords: o-SnS; c-SnS; SnS ; SnS ; CBD; solar cells

1. Introduction

To make a significant contribution to the energy needs of society with low production cost, thin film photovoltaic (TFPV) technology has been developed. Currently, the CdTe/CdS and Cu(InGa)Se (CIGS)/CdS heterojunction TFPV technologies have received worldwide attention because these solar cells achieved record efficiencies of 22.1% [1] and 23.35% [2], respectively. However, their wider impact is hindered due to major concerns raised on the presence of harmful elements (Cd and Se) and scarcity of constituent elements (Te, In and Ga). In view of that, considerable efforts have been made to develop environmentally friendly absorbers and buffers that are free from the aforementioned toxic and inadequate elements. Along this path, the tin-based binary sulfides (Sn S ) such as tin monosulfide (orthorhombic (ORT)-SnS and cubic (CUB)-SnS), tin disulfide (SnS ), and tin sesquisulfide (SnS ) have drawn much attention because these are abundant, inexpensive, and nontoxic [3]. According to the merits of SnS (see Table 1), the o-SnS, c-SnS, and SnS are strongly expected as potential and alternative absorbers to the conventional CdTe and CIGS, and SnS is expected as an appropriate and alternative buffer to the regular CdS. Furthermore, their simple composition and promising physical properties made them suitable for other applications such as photocatalytic, thermoelectric, etc. (see Figure 1). Among Sn S, o-SnS, SnS and SnS occur naturally, whereas c-SnS was synthesized in the laboratory. The historical information and the applications of Sn S available in the literature are presented in Table 2.

The deposition of Sn S in thin film form became prominent owing to their wide applications. The selection of deposition technique along with the growth conditions is critical because the properties of Sn S thin films are susceptible to their growth method. Sn S films should be prepared by low-cost techniques such as solution processes to further reduce the production cost of TFPV devices. The preparation of Sn S thin films via chemical methods, especially by chemical bath deposition(CBD), includes a slightly
The deposition of $\text{Sn}_x\text{S}_y$ thin films using CBD is relatively new, and their process–property relationships must be understood for the desired application. Further, the formation of single-phase o-$\text{SnS}$, c-$\text{SnS}$, $\text{SnS}_2$, and $\text{Sn}_2\text{S}_3$ thin films in CBD is highly dependent on preparative conditions. In addition, identification and separation of the o-$\text{SnS}$, c-$\text{SnS}$, $\text{SnS}_2$, and $\text{Sn}_2\text{S}_3$ phases are also critical criteria. However, there is a lack of comprehensive studies on the optimization of growth parameters until now. Therefore, extensive research studies on the growth, deposition mechanism, and preparative parameters that affect phase separation and the physical properties of $\text{Sn}_x\text{S}_y$ thin films are crucial to a successful device design in the production of clean energy.

In this scenario, the present article provides an overview of the bulk properties of $\text{Sn}_x\text{S}_y$ and a comprehensive review of the deposition, growth mechanism, and effect of growth parameters on the physical properties of $\text{Sn}_x\text{S}_y$ thin films. According to the authors’ knowledge, this is the first review of $\text{Sn}_x\text{S}_y$ thin films by CBD.

**Figure 1.** Applications of $\text{Sn}_x\text{S}_y$ [4–12]. Solar cell (o-$\text{SnS}$, c-$\text{SnS}$, $\text{Sn}_2\text{S}_3$ as light absorber and $\text{SnS}_2$ as buffer); photodetector (o-$\text{SnS}$, c-$\text{SnS}$, $\text{Sn}_2\text{S}_3$ as light absorber and $\text{SnS}_2$ as buffer); Li- and Na-ion batteries (o-$\text{SnS}$, c-$\text{SnS}$, and $\text{SnS}_2$ as anode materials); gas- and bio sensors (o-$\text{SnS}$, c-$\text{SnS}$, and $\text{SnS}_2$ as sensing materials); tunnel field-effect transistors (TFET) (o-$\text{SnS}$, c-$\text{SnS}$, and $\text{SnS}_2$ as top or back gates); electrochemical and super capacitors (o-$\text{SnS}$, c-$\text{SnS}$, and $\text{SnS}_2$ as electrode materials); capacitor; thermoelectrics (o-$\text{SnS}$, c-$\text{SnS}$, and $\text{Sn}_2\text{S}_3$ as grids); and water-splitting (o-$\text{SnS}$, c-$\text{SnS}$, and $\text{SnS}_2$ as photocathodes).
Table 1. The advantages of Sn\(_x\)S\(_y\) compared to the conventional absorbers (CdTe, CIGS, and CZTS) and the buffer (CdS).

| Characteristics             | PV Absorbers | PV Buffers |
|-----------------------------|--------------|------------|
|                             | CdTe         | CIGS       | CZTS       | o-SnS | c-SnS | Sn\(_2\)S\(_3\) | CdS | SnS\(_2\) |
| Earth abundance             | No           | No         | Yes        | Yes   | Yes   | Yes          | Yes | Yes        |
| Eco-friendly                | No           | No         | Yes        | Yes   | Yes   | Yes          | Yes | No         |
| Band gap (eV)               | 1.45–1.5 eV   | 1.1–1.5    | 1.0–1.5    | 1.16–1.79 | 1.64–1.75 | 0.95–2.03 | 2.35–2.50 | 2.04–3.30 |
| Absorption coefficient      | \(>10^6\)    | 10\(^9\)   | \(>10^4\)  | 10\(^5\) | 10\(^5\) | 10\(^4\)    | –   | –          |
| Conductivity type           | p-type       | p-type     | p-type     | p-/n-type | p-type   | p-type       | n-type | n-type |
| Carrier density (cm\(^{-3}\)) | 10\(^{14}\)–10\(^{17}\) | 10\(^{12}\)–10\(^{18}\) | 10\(^{16}\)–10\(^{18}\) | 10\(^{11}\)–10\(^{18}\) | 10\(^{11}\)–10\(^{18}\) | 10\(^{14}\)–10\(^{18}\) | 10\(^{12}\)–10\(^{18}\) | 10\(^{13}\)–10\(^{17}\) |
| Structure                   | Zinc blend   | Chalcopyrite | Kesterite | Orthorhombic | Cubic | Orthorhombic Hexagonal | Hexagonal |
| Maximum theoretical efficiency (%) | –29          | –29        | 31 [62]   | 31 [63] | >25 [64] | –            | –    | –          |

Table 2. The historical information and the applications of Sn\(_x\)S\(_y\).

| Tin Sulfides | Mineral Form [65–67] | Appearance [68] | Other Names | Discovered/Reported [69,70] | Applications [24,71–91] |
|--------------|----------------------|-----------------|-------------|-----------------------------|-------------------------|
| o-SnS        | Herzenbergite         | Black color with dark red–brown internal reflections. Kolbecke | Reported by Ramdohr | PV, photocatalysts [24], photodetectors [71], water splitting [72], supercapacitors [83], field-effect transistors [85], lithium-ion and lithium-ion batteries [86,87], gas sensors [88], biosensors [89], thermoelectric [90], and electro chemical capacitors [91]. |
| SnS\(_2\)    | Berndtite            | Pale yellow with intense brownish to yellow–orange internal reflections. Mosaic gold | Discovered at the Stiepelmann mine in Arandis, Namibia, as described by Ramdohr in 1935. | PV, photocatalysts [73], water splitting [74], supercapacitors [75], field-effect transistors [76], lithium-ion and lithium-ion batteries [77,78], gas sensors [79], thin film diodes [80], and high-speed photodetectors [81]. |
| SnS\(_3\)    | Ottemanite           | Gray with orange–brown internal reflections. - | Reported by Moh from the Cerro de Potosí mine (Bolivia) in 1964. | PV, optoelectronic [82], thermoelectric and IR detectors [84]. |

2. Physical Properties of o-SnS, c-SnS, SnS\(_2\), and SnS\(_3\)

The physical properties such as structural, optical, and electrical properties of Sn\(_x\)S\(_y\) can significantly influence the device’s performance. The crystal structure of a material can influence its optical and electrical properties, which can affect the material-related device performance [92]. Understanding and obtaining knowledge on the electronic band structure and optical characteristics of Sn\(_x\)S\(_y\) is essential before using them for device applications because the main optical parameter, band gap energy (\(E_g\)), is very sensitive to the crystal structure and defects, which directly influences the performance of a PV device. Electrical characteristics such as conduction type, resistivity, carrier concentration, and mobility of Sn\(_x\)S\(_y\) play a key role in achieving high-performance photovoltaic devices. These electrical properties critically depend on the formation of defects in Sn\(_x\)S\(_y\). Therefore...
fore, a good understanding of the physical properties is required for the development of effective devices.

2.1. Crystal Structure and Structural Characteristics

In α-SnS, c-SnS, SnS$_2$, and Sn$_2$S$_3$, Sn exhibits ‘2+’ (divalent Sn(II)) or/and ‘4+’ (tetravalent Sn(IV)) oxidation states (Table 3). The capability of Sn to elect different oxidation states is the origin of structural diversity/different structures (Figure 2a) of resulting compounds [93]. α-SnS (α-SnS, space group, Pnma-D$_{2h}$16) and c-SnS (π-SnS, space group, P2$_1$3) are the two polymorphic forms of SnS, resulting from distortions in the crystal lattice depending on growth conditions. The α-SnS consists of a double layer of Sn and S atoms (two-dimensional SnS sheets) with zigzagged chains in which each Sn atom bonds to two S atoms in the b–c plane of the layer with a bond length of 2.671 Å and one additional S atom at a short bond length of 2.633 Å perpendicular to the plane (along a-axis) in the layer stack. The interlayer bond length of Sn-Sn atoms is 3.48 Å, and the distance between the layer stacks is 2.79 Å. The lone pair of 5s$^2$ in the Sn atom occupies the fourth coordination site and weakens interaction along the b-axis. In the case of c-SnS, each Sn atom bonds with three nearest S atoms at 2.7 Å and forms a trigonal pyramidal environment, with the Sn-S bond at the trigonal base and the 5s$^2$ lone pair pointing toward the apex. The stereo chemical activity of Sn(II) 5s$^2$ lone pair creates a highly distorted internal structure of c-SnS. The local coordination in c-SnS is similar to α-SnS; however, a three-dimensional network is formed by a covalent bond [60]. Additionally, SnS also exhibits some of other polymorphs [94] such as, β-SnS (formed at T > 880 K), γ-SnS [95], δ-SnS [96,97], RS-SnS (rock salt-SnS, Fm$ar{3}$m) [98]. One key point is that c-SnS and RS-SnS belong to the cubic crystal system. Further, c-SnS is a simple cubic lattice type, and RS-SnS is a face-centered cubic lattice (important note: the structure of c-SnS was incorrectly assigned as ZB-SnS previously in the literature. To avoid confusion in the literature, the readers should replace ZB-SnS with c-SnS in previous literature). More details can be found in the literature clarifying these assignments [28,93,99,100]. Furthermore, the weak interactions between distorted lone pair of 5s$^2$ in Sn and neighboring S form the metastable SnS crystals or polymorphs of SnS [101].

Next, the SnS$_2$ adopts a layered hexagonal structure with P$ar{3}$m1 space group, similar to the structure of the CdI$_2$ system. In this structure, the layers are arranged in the b–c plane, which is perpendicular to the a-axis, and each layer is composed of S, Sn, and S atomic parallel monolayers. Each Sn atom forms bonds in an octahedral environment with six S atoms, similar in rutile SnO$_2$ structure [93]. It has a symmetric edge-sharing Sn(IV)S$_6$ octahedral with 2D planes that are separated by weak van der Waals interaction between 3.6 Å distant S atoms [61]. Finally, the Sn$_2$S$_3$ exhibits an orthorhombic crystal structure similar to α-SnS with the same space group of Pnma. It contains tetravalent (4+) and divalent (2+) Sn atoms in equal proportions, and they form Sn(IV)S$_6$ octahedral 1D chains covered by Sn(II) tetrahedral [51]. The lone pair in Sn(II) occupies one coordination site as in the ground state form of α-SnS. These lone pairs are responsible for weak interchain interactions. The optimized theoretical lattice parameters along with experimental values for all these Sn$_x$S$_y$ phases are presented in Table 3. The structural characterization of Sn$_x$S$_y$ thin films is generally performed by X-ray diffraction (XRD). The standard XRD patterns of α-SnS, c-SnS, SnS$_2$, and Sn$_2$S$_3$ (Figure 2b) showed the highest intensity for peaks located at 2θ of: 31.53°, 26.63°/30.84°, 15.03°, and 21.49°, arising from diffraction from (111), (222)/(400), (001), and (130) planes, respectively [25,28,102–104].
Figure 2. (a). Crystal structures of ground state Sn$_x$S$_y$ forms (reprinted with permission [51] © 2017, Royal Society of Chemistry) and (b) standard powder diffraction patterns for Sn$_x$S$_y$.

The o-SnS, c-SnS, SnS$_2$, and Sn$_2$S$_3$ thin films have similarities in XRD patterns (Figure 3a). Thus, clear differentiation of one phase to another is difficult by using diffraction analysis alone. In this respect, it is preferable to identify these phases in pure form using a complementary method such as Raman spectroscopy because the Raman spectrum is sensitive to mainly crystal quality, structural symmetry, and strength of the chemical bond between atoms [105]. The o-SnS has 21 optical vibrational modes with the irreducible representation of $\Gamma = 4A_g + 2B_{1g} + 4B_{2g} + 2B_{3g} + 2A_u + 4B_{1u} + 2B_{2u} + 4B_{3u}$ [106,107]. In these phonons, two are inactive ($2A_u$), seven are infrared-active ($3B_{1u}$, $3B_{3u}$, and $1B_{2u}$), and twelve are Raman-active ($4A_g$, $2B_{1g}$, $4B_{2g}$, and $2B_{3g}$). In the case of c-SnS, there are 189 optic branches, and they can be reduced to 3 in the form of $\Gamma = 16A + 16E + 47T$ [51]. Next, the SnS$_2$ has six vibrational modes with the irreducible representation, $\Gamma = A_{1g} + E_g + 2A_{2u} + 2E_u$ [108]. The six optic modes are divided into two Raman-active modes ($A_{1g}$ and $E_g$), two infrared-active ($A_{2u}$ and $E_u$), and two acoustic modes ($A_{2u}$ and $E_u$). Additionally, the Sn$_2$S$_3$ has 57 optic modes with reduced form of $\Gamma = 10A_g + 5A_u + 5B_{1g} + 9B_{1u} + 10B_{2g} + 4B_{2u} + 5B_{3g} + 9B_{3u}$ [51,109]. The simulated Raman spectra [51] (Figure 3b) clearly showed the significant differences in frequencies and spectral intensities because the o-SnS, c-SnS, SnS$_2$, and Sn$_2$S$_3$ phases have differences in structure and bonding. The Raman spectrum of the o-SnS showed three prominent peaks at 160 cm$^{-1}$ (narrow mode, $B_{2g}$), 189 cm$^{-1}$ (highest intensity mode, $A_g$), and 220 cm$^{-1}$ (narrow mode, $A_g$). The spectrum also showed a weak $A_g$ mode at approximately 92 cm$^{-1}$, which has a narrow line width up to room temperature. In the case of c-SnS, there are three strong $A$ phonon modes at 174 cm$^{-1}$, 187 cm$^{-1}$, and 202 cm$^{-1}$ and two prominent $E$ modes at 166 cm$^{-1}$ and 183 cm$^{-1}$ along with a group of weak modes in between the ranges of 50–125 cm$^{-1}$ and 200–250 cm$^{-1}$. Next, the SnS$_2$ showed a single and strong mode at 305 cm$^{-1}$ ($A_g$), which has a constant line width with the temperature. Furthermore, the Sn$_2$S$_3$ showed a significantly high-intensity $A_g$ mode at 291 cm$^{-1}$ and a moderate-intensity $A_g$ mode at 300 cm$^{-1}$ with a narrow line width. Its spectrum also showed weak modes at 182 cm$^{-1}$, 210 cm$^{-1}$, 226 cm$^{-1}$, 244 cm$^{-1}$, and 252 cm$^{-1}$, which are observed at high temperatures. Notably, the Raman mode of Sn$_2$S$_3$ (307 cm$^{-1}$) overlaps marginally with the active mode of SnS$_2$ (310 cm$^{-1}$). However, the phase can be easily identified based on the band width of modes. Sn$_2$S$_3$ has a band width that is significantly
greater than that of SnS$_2$ (Figure 3b). From the experimental Raman spectra (Figure 3c), o-SnS, c-SnS, SnS$_2$, and SnS$_3$S$_2$ films showed Raman active modes at 93 cm$^{-1}$, 161 cm$^{-1}$, 192 cm$^{-1}$, and 218 cm$^{-1}$ [110]; 59 cm$^{-1}$, 71 cm$^{-1}$, 90 cm$^{-1}$, 112 cm$^{-1}$, 123 cm$^{-1}$, 176 cm$^{-1}$, 192 cm$^{-1}$, 202 cm$^{-1}$, and 202 cm$^{-1}$ [111]; 224 cm$^{-1}$ and 310 cm$^{-1}$ [112]; and 61 cm$^{-1}$, 91 cm$^{-1}$, 179 cm$^{-1}$, 220 cm$^{-1}$, and 307 cm$^{-1}$ [113], respectively, which matched well with theoretically calculated data. The Raman results suggested that o-SnS, c-SnS, SnS$_2$, and Sn$_3$S$_2$ phases have distinct modes. Moreover, S-rich impurity phases can easily be found in SnS due to the sharp Raman mode of SnS$_2$ (310 cm$^{-1}$).

2.2. Electronic Band Structure and Optical Characteristics

According to the electronic band structures of Sn$_x$S$_y$ (Figure 3d), the valence band maxima (VBM) of o-SnS, c-SnS, and SnS$_2$S$_3$ are formed mostly of S 3p and Sn 5s hybrid states with a tiny contribution from Sn 5p states, whereas SnS$_2$ is primarily composed of S 3p orbitals. The conduction band minimum (CBM) of SnS$_2$ and SnS$_2$S$_3$ is formed by the Sn 5s bands, whereas SnS$_2$ is mainly composed of Sn 5p orbitals. The VBM of SnS$_2$ is lower than those of o-SnS, c-SnS, and SnS$_2$S$_3$; however, the CBMs of all o-SnS, c-SnS, SnS$_2$, and Sn$_3$S$_2$ are almost aligned. The partial hybridizations with S 3s and Sn 5p states result in SnS polymorphs due to the change in density of state.

On the other hand, the band-edge positions deviated from the special points in the reciprocal space except for the CBM of SnS$_2$. However, they fall between the Brillouin zone center and the zone boundaries [64,114]. From the ab initio band-structure calculations and Kohn–Sham density-functional theory, o-SnS and c-SnS exhibited the indirect and direct energy gaps of 1.6 eV and 1.8 eV; and 1.72 eV and 1.74 eV, respectively, which is due to an inherent error in calculating band structure [58]. The energy difference between direct and indirect band gaps is small; thus, the change in the nature of the band gap could be due to the effect of temperature through thermal expansion and electron-phonon coupling [64]. According to the band-structure calculations from the Hartree–Fock exchange HSE06 functional technique, o-SnS, SnS$_2$, and SnS$_2$S$_3$ showed indirect energy gaps of 1.11 eV, 2.24 eV, and 1.09 eV, respectively [115]. The optical characterization of Sn$_x$S$_y$ thin films is generally studied by a UV-Vis-NIR spectrometer. Although theoretical calculations showed the indirect band gap energy of Sn$_x$S$_y$, most of the experimental studies (Figure 3e) proved that Sn$_x$S$_y$ thin films have direct band gap energies, with the following ranges (Tables 4 and 5): 1.16–1.79 eV; 1.64–1.75 eV; 2.04–3.30 eV; 0.95–2.03 eV; for o-SnS, c-SnS, SnS$_2$, and Sn$_3$S$_2$, respectively. The band gap energies of these phases depend on various factors such as strain, sulfur impurities, and Sn vacancies [116–122].

2.3. Conduction Type and Electrical Characteristics

In Sn$_x$S$_y$, three types of defects, namely, (i) Sn and S vacancies (V$_{Sn}$ and V$_S$), (ii) Sn and S interstitials (S$_n$ and S$_i$), and (iii) Sn on S antisites (S$_n$S) and S on Sn antisites (S$_i$Sn) are commonly formed, as shown in Figure 4a. According to the defect energy concepts (Figure 4b), the formation energy of vacancies (V$_{Sn(II)}$ or V$_{Sn(IV)}$, V$_S$) depends on the coordination number, i.e., it generally increases with increasing coordination number. Thus, V$_{Sn(II)}$ has lower formation energy compared to V$_{Sn(IV)}$ because the coordination number is three for Sn(II) and six for Sn(IV). As a result, V$_{Sn(II)}$ becomes a major defect that acts as an acceptor and contributes to the p-type conducting nature to SnS. In SnS, the primary defects are V$_{Sn}$ and V$_S$, whereas S$_n$ and S$_i$ have higher energies. SnS exhibits the p-type at the Sn-poor condition, whereas the n-type at the Sn-rich condition. The defect-formation energies in SnS$_2$ differ from those in SnS. The major defects are V$_S$, S$_1$, and S$_{Sn(II)}$, which are inert to carrier generation. The defect-formation energies in SnS$_2$S$_3$ are typically interpreted as a mixture of those in SnS and SnS$_2$. On the other hand, the formation energy of interstitials (S$_n$, S$_i$) associates with the gap of interlayer free spaces, and that gap follows the notation of SnS > SnS$_2$ > SnS$_2$. S$_n$ always prefers to locate at the center of the gaps, whereas S$_i$ likes to make a covalent bond with neighboring S atoms. The tin interstitial, S$_n$ in both SnS$_2$ and SnS$_2$S$_3$, has lower formation energy compared to SnS, and it acts as a deep
Nanomaterials 2021, 11, x FOR PEER REVIEW 7 of 47

and orthorhombic Sn2S3 (reprinted with permission [113]. © 2016, Elsevier). (d) Band structures of SnxSy (reprinted with permission [123]. © 2016, Elsevier), and (e) bandgap estimation of o-SnS (reprinted with permission [124]. © 2016, Sciendo).

Figure 3. (a) XRD profiles of o-SnS and c-SnS (reprinted with permission [26]. © 2016, Elsevier), hexagonal SnS2 (reprinted with permission [123]. © 2016, Elsevier), and orthorhombic Sn2S3 (reprinted with permission [113]. © 2016, Elsevier). (b) Simulated Raman spectra for SnxSy at different temperatures of 10 K, 150 K, and 300 K (reprinted with permission [51]. © 2017, Royal Society of Chemistry). (c) Experimental Raman spectra of o-SnS (reprinted with permission [110]. © 2017, Elsevier), c-SnS (reprinted with permission [26]. © 2016, Elsevier), hexagonal SnS2 (reprinted with permission [123]. © 2016, Elsevier), and orthorhombic Sn2S3 (reprinted with permission [113]. © 2016, Elsevier). (d) Band structures of SnxSy (reprinted with permission [114]. © 2016, American Physical Society), and (e) bandgap estimation of o-SnS (reprinted with permission [123]. © 2016, Elsevier), c-SnS (reprinted with permission [26]. © 2016, Elsevier), hexagonal SnS2 (reprinted with permission [123]. © 2016, Elsevier), and orthorhombic Sn2S3 (reprinted with permission [124]. © 2016, Sciendo).

donor in SnS2 and Sn2S3 and contributes to an n-type conductivity. All the antisites in SnxSy have higher formation energies because they are correlated with chemical bonds. Therefore, these defects do not play a major role in the conduction type of SnxSy phases. The electrical characterization of SnxSy thin films is generally performed by the popular van der Pauw–Hall method.

From the reported electrical parameters of SnxSy films (Table 3), the o-SnS has a hole density in the order of 1011–1018 cm−3, hole mobility in the range of 4–500 cm2 V−1 s−1, and electrical resistivity in the range of 13–105 Ω cm. In contrast, the c-SnS has a hole density in the order of 1011–1018 cm−3, hole mobility in the range of 10−2–78 cm2 V−1 s−1, and electrical resistivity in the range of 70–107 Ω cm. In the case of the SnS2, it has a carrier concentration of the order of 1013–1017 cm−3, electron mobility in the range of 15–52 cm2 V−1 s−1, and electrical resistivity in the range of 1.1–107 Ω cm, whereas the Sn2S3 has a carrier density in the order of 1014–1016 cm−3 and resistivity in the range of 0.4–105 Ω cm, and a very little information related to SnS2 carrier mobility value is available in the literature. The reported variation in electrical parameters is expected due to the differences in the growth process and chemical composition.
Figure 4. (a) Possibility of different defect formation in Sn_{x}S_{y}, and (b) defect formation energies in Sn_{x}S_{y} as a function of Fermi energy under Sn-rich (S-poor) and Sn-poor (S-rich) conditions (reprinted with permission [114]. © 2016, American Physical Society).
Table 3. Optimized theoretical and experimental lattice parameters, reported optical bandgaps, and electrical parameters of Sn\textsubscript{x}S\textsubscript{y} (Th: theoretical, Exp: experimental).

| Sn\textsubscript{x}S\textsubscript{y} Phase | Structure (Space Group) | Oxidation State of Sn | Parameters of unit cell | Structural Properties | Optical Properties | Electrical Properties | Resistivity (Ω·cm) |
|-----------------------------------------|------------------------|----------------------|------------------------|----------------------|----------------------|----------------------|------------------|
| o-SnS                                   | Orthorhombic (Pnma)    | 2+                   | α = β = γ = 90°; a ≠ b ≠ c | a = b = c           | 1.64 [24], 1.66 [25], 1.67 [26], 1.73 [27], 1.74 [28], 1.75 [29]. | 5.87 × 10\textsuperscript{11} [29], 7.93 × 10\textsuperscript{12} [30], 6 × 10\textsuperscript{14} [51]. | 1.47 × 10\textsuperscript{-2} [51], 75 [50], 77.7 [29]. | 70 [51], 1 × 10\textsuperscript{4} [50], 1.37 × 10\textsuperscript{4} [29], 1 × 10\textsuperscript{5} [25], 1 × 10\textsuperscript{7} [28]. |
| c-SnS                                   | Cubic (P2\textsubscript{1}3) | 2+                   | α = β = γ = 90°; a = b = c | 11.506, 11.603, 1.64 [24], 1.66 [25], 1.67 [26]. | 1.64 [24], 1.66 [25], 1.67 [26], 1.73 [27], 1.74 [28], 1.75 [29]. | 5.87 × 10\textsuperscript{11} [29], 7.93 × 10\textsuperscript{12} [30], 6 × 10\textsuperscript{14} [51]. | 1.47 × 10\textsuperscript{-2} [51], 75 [50], 77.7 [29]. | 70 [51], 1 × 10\textsuperscript{4} [50], 1.37 × 10\textsuperscript{4} [29], 1 × 10\textsuperscript{5} [25], 1 × 10\textsuperscript{7} [28]. |
| Sn\textsubscript{2}S\textsubscript{2}   | Hexagonal (P\textsuperscript{3}m1) | 4+                   | α = β = γ = 90°; a ≠ b ≠ c | 8.11, 8.878, 0.95 [30], 1.16 [31], 1.2 [139], 1.65 [32], 1.9 [33], 1.96 [140], 2.0 [141], 2.03 [34]. | 8.11, 8.878, 0.95 [30], 1.16 [31], 1.2 [139], 1.65 [32], 1.9 [33], 1.96 [140], 2.0 [141], 2.03 [34]. | 9.4 × 10\textsuperscript{14} [52], 1 × 10\textsuperscript{15} [45], 4.0 × 10\textsuperscript{16} [53]. | 20.5 [53], 0.359 [124], 0.66 × 10\textsuperscript{4} [45], (0.22–0.36) × 10\textsuperscript{10} [52,141], (0.4–2.5) × 10\textsuperscript{8} [137]. | 11.2 [56], 0.77 × 10\textsuperscript{4} [37], 0.42 × 10\textsuperscript{7} [54], 0.26 × 10\textsuperscript{7} [138]. |
| Sn\textsubscript{2}S\textsubscript{3}   | Orthorhombic (Pnma)    | 2+ and 4+            | α = β = γ = 90°; a ≠ b ≠ c | 8.11, 8.878, 0.95 [30], 1.16 [31], 1.2 [139], 1.65 [32], 1.9 [33], 1.96 [140], 2.0 [141], 2.03 [34]. | 8.11, 8.878, 0.95 [30], 1.16 [31], 1.2 [139], 1.65 [32], 1.9 [33], 1.96 [140], 2.0 [141], 2.03 [34]. | 9.4 × 10\textsuperscript{14} [52], 1 × 10\textsuperscript{15} [45], 4.0 × 10\textsuperscript{16} [53]. | 20.5 [53], 0.359 [124], 0.66 × 10\textsuperscript{4} [45], (0.22–0.36) × 10\textsuperscript{10} [52,141], (0.4–2.5) × 10\textsuperscript{8} [137]. | 11.2 [56], 0.77 × 10\textsuperscript{4} [37], 0.42 × 10\textsuperscript{7} [54], 0.26 × 10\textsuperscript{7} [138]. |
3. Influence of Deposition Parameters on Sn$_x$S$_y$ Thin Film Growth and Properties

In CBD, the selection of tin source precursor, sulfur source precursor, complexing agent, and their concentrations is crucial to prepare the high-quality Sn$_x$S$_y$ thin films using CBD. Moreover, the selection of suitable activation conditions such as solution/bath temperature, solution/bath pH (acidic or basic medium), deposition time, and stirring speed is also important [36,142] because they significantly affect the phase formation, growth, and properties of Sn$_x$S$_y$ films. In addition to the above parameters, the nature of the substrate and its cleaning procedure also affect the phase formation, growth, and properties of Sn$_x$S$_y$ films. Therefore, the understanding of the influence of all those parameters on the growth process of Sn$_x$S$_y$ films and their physical properties is necessary to deposit the quality films for device applications. In Tables 4 and 5, the deposition parameters used for different thin films of tin sulfides made from chemical methods were summarized.

3.1. Overview of CBD Process of Sn$_x$S$_y$ Thin Films

The CBD refers to “a typical synthesis employing mild conditions [143]”. As schematically illustrated in Figure 5a, the experimental setup of CBD consists of the following parts: (i) magnetic stirrer with thermostat (to stir the mixed reactant solution continuously), (ii) oil bath (to maintain the desired temperature), (iii) substrate holder (to keep the substrates stable), (iv) stock chemical solutions to compose the reaction bath (mixture of different reagent solutions and its level always remains below the outer oil level), and (v) cleaned substrates [144]. The deposition of o-SnS, c-SnS, SnS$_2$, and SnS$_3$ by CBD was reported in 1987 [145], 2006 [146], 1990 [36,130], and 2012 [34], respectively. Sn$_x$S$_y$ films were deposited using various Sn precursors such as tin (II) chloride dihydrate (SnCl$_2$·2H$_2$O), tin(IV) chloride pentahydrate (SnCl$_4$·5H$_2$O), and tin ingots; various S precursors such as sodium sulfide (Na$_2$S), ammonium sulfide (NH$_4$)$_2$S, sodium thiosulfate (Na$_2$S$_2$O$_3$), thioacetamide (C$_2$H$_5$NS), and thiourea (CH$_4$N$_2$S); and various complexing agents such as triethanolamine (C$_6$H$_{15}$NO$_3$), ammonia (NH$_3$)/ammonium hydroxide (NH$_3$OH), ammonium fluoride (NH$_4$F), ammonium citrate (C$_6$H$_7$N$_3$O$_7$), trisodium citrate (Na$_3$C$_6$H$_5$O$_7$), citric acid (C$_6$H$_8$O$_7$), tartaric acid (C$_4$H$_6$O$_6$), ethylenediaminetetraacetic acid (C$_{20}$H$_{21}$N$_2$O$_{8}$), and disodium ethylenediaminetetraacetate (C$_{12}$H$_{22}$N$_2$O$_{8}$). Among the above-mentioned chemicals, tin (II) chloride, thioacetamide, and triethanolamine, along with ammonia, were widely used as Sn precursor, S precursor, and complexing agents, respectively (Figure 5b). Other types of Sn precursors such as tin ingots [130,147] and tin (IV) chloride [131] were employed to deposit the SnS$_2$ films. Except for the above reports, tin (II) chloride was used as an Sn source. In the case of S precursors, sodium thiosulfate was used as a second alternative to the regularly used thioacetamide.

The preparation of Sn$_x$S$_y$ thin films by CBD occurs when a substrate is immersed in the solution mixture of Sn ion (Sn$^{2+}$) and S$^{2-}$-source, S ion (S$^{2-}$)-source, and an appropriate complexing agent. In the deposition process, the Sn$^{2+}$ /Sn$^{4+}$ ions are complexed through the coordinated bond formation by the complexing agent, which controls the rate of reaction [148]. At super saturation condition (Ionic product, Q$_{lp}$ > Solubility product K$_{sp}$), Sn$_x$S$_y$ films can be deposited (Figure 5c). However, simply maintaining supersaturation condition in the bath will not provide acceptable quality Sn$_x$S$_y$ films; managing the solubility product of tin hydroxides is required because when an Sn precursor is dissolved in water, it rapidly binds with hydroxide ions, creating Sn(OH)$_2$ and Sn(OH)$_4$. The differences in K$_{sp}$ values between SnS (1 × 10$^{-25}$ mol$^2$ dm$^{-6}$), irrespective of the polymorphs, and SnS$_2$ (1 × 10$^{-46}$ mol$^3$ dm$^{-9}$) are very close to those between their hydroxides (Sn(OH)$_2$ (1 × 10$^{-28}$ mol$^3$ dm$^{-9}$) and Sn(OH)$_4$ (1 × 10$^{-56}$ mol$^3$ dm$^{-15}$)). Therefore, it is vital to monitor supersaturation with respect to an individual phase as well as the growth kinetics. In addition, the K$_{sp}$ of Sn$_x$S$_y$ is affected by the concentration of precursor, solvent type, bath temperature, and bath pH [148,149]. Therefore, the optimum condition for the deposition of Sn$_x$S$_y$ thin film can be achieved by manipulating the above deposition parameters.
At low pH values (<2.5), the reaction is controlled by the rate of hydrolysis of Sn precursor leading to the formation of hydrogen sulfide (H\textsubscript{2}S), whereas at higher pH values (>2.5), the reaction is controlled by the formation and decomposition of the tin–thioacetamide complex. Therefore, the pH of the bath and metal–thioacetamide complexes are also considered as the growth rate- and growth mechanism-determining components in the film formation \[154\].

The Sn ions react with the S ions and initiate the formation of tin sulfides (o-SnS, c-SnS, SnS\textsubscript{2}, and Sn\textsubscript{2}S\textsubscript{3}). The generation rate of Sn and S ions is controlled primarily by the source concentration, pH, and solution temperature. When the precursor concentration is changed, multiphase or other single-phase films can be formed by the following reactions \[155,156\]:

\[
\text{Sn}^{2+} + \text{S}^{2-} \rightarrow \text{SnS} \quad (K_{sp} = 1 \times 10^{-25} \text{ at } 25 \, ^°\text{C})
\]

\[
\text{Sn}^{4+} + 2\text{S}^{2-} \rightarrow \text{SnS}_2 \quad (K_{sp} = 1 \times 10^{-46} \text{ at } 25 \, ^°\text{C})
\]

\[
\text{Sn}^{2+} + \text{Sn}^{4+} + 3\text{S}^{2-} \rightarrow \text{Sn}_2\text{S}_3
\]

\[
\text{Sn(II)}\text{S} + \text{Sn(IV)}\text{S}_2 \rightarrow \text{Sn(II)(IV)}_2\text{S}_3 \text{ (or) SnS + SnS}_2 \rightarrow \text{Sn}_2\text{S}_3
\]

Figure 5. Schematic representation of (a) CBD, (b) main chemical reagents used for the preparation of Sn\textsubscript{x}S\textsubscript{y} thin films from 1987 to the present, and (c) importance of K\textsubscript{sp} and Q\textsubscript{sp} relation on the films by CBD.

According to previous reports, the formation of o-SnS, c-SnS, SnS\textsubscript{2}, and Sn\textsubscript{2}S\textsubscript{3} thin films is achieved through either an ion-by-ion mechanism (Figure 6a) or a simple cluster (hydroxide) mechanism (Figure 6b) based on the reaction process and parameters maintained in the bath \[150\]. The formation reaction of Sn\textsubscript{x}S\textsubscript{y} thin films through the ion-by-ion mechanism and cluster (hydroxide) mechanism is as follows:

**Ion-by-ion mechanism:**

\[
x\text{Sn}^{p+} + y\text{S}^{q-} \rightarrow \text{Sn}_x\text{S}_y
\]

\[
[\because \ p = 2 \text{ or } 4, \ q = 2; \ x = 1 \text{ or } 2, \ y = 1, 2, \text{ or } 3; \锡x\text{S}_y = \锡S, \锡S_2, \text{ or } \锡_2\text{S}_3]
\]

**Cluster (hydroxide) mechanism:**

\[
x\text{Sn}^{p+} + y(\text{OH})^{q-} \rightarrow \text{Sn(OH)}_n
\]

\[
\text{Sn(OH)}_n + y\text{S}^{q-} \rightarrow \text{Sn}_x\text{S}_y + n(\text{OH})
\]

\[
[\because \ p = 2 \text{ or } 4, \ q = 2; \ n = 2 \text{ or } 4; \ x = 1 \text{ or } 2, \ y = 1, 2, \text{ or } 3; \锡x\text{S}_y = \锡S, \锡S_2, \text{ or } \锡_2\text{S}_3]
\]

The physical properties of the CBD-deposited o-SnS, c-SnS, SnS\textsubscript{2}, and Sn\textsubscript{2}S\textsubscript{3} thin films can be affected by the growth mechanism, level of supersaturation, and surface energy of the complexing agents \[17\]. Therefore, it is crucial to understand the actual mechanism undertaken in the solution for tuning the properties of the deposited films. Moreover, in the process of o-SnS, c-SnS, SnS\textsubscript{2}, and Sn\textsubscript{2}S\textsubscript{3} thin film deposition, controlling the reaction to reduce or remove the spontaneous precipitation is essential, which can only be achieved by completing the tin ions using an appropriate complexing agent (L). The
kinetics of o-SnS, c-SnS, SnS\(_2\), and Sn\(_2\)S\(_3\) thin film formation can be comprehended through the following reactions.

The complexing reactions in an aqueous Sn precursor solution are as follows:

\[
\text{SnCl}_2 \cdot 2\text{H}_2\text{O} + \text{L} \rightleftharpoons \text{Sn(L)}^{2+} + 2\text{Cl}^- + 2\text{H}_2\text{O}
\]

\[
\text{SnCl}_4 \cdot 5\text{H}_2\text{O} + \text{L} \rightleftharpoons \text{Sn(L)}^{4+} + 4\text{Cl}^- + 5\text{H}_2\text{O}
\]

The free Sn\(^{2+}\)/Sn\(^{4+}\) ions are slowly released by the tin complex in a controlled way. As the tin complex dissociates, then

\[
\text{Sn(L)}^{2+} \rightleftharpoons \text{Sn}^{2+} + \text{L}
\]

\[
\text{Sn(L)}^{4+} \rightleftharpoons \text{Sn}^{4+} + \text{L}
\]

Here, the concentration of complex tin ions in the solution, Sn\(_{\text{L}}^{2+}\) or Sn\(_{\text{L}}^{4+}\), can be controlled by adjusting the concentration of the complexing agent and bath temperature \([151]\). If these ions can be generated, then the deposition of Sn\(_x\)S\(_y\) thin films can be achieved. On the other hand, controlling the reaction by a slow and uniform generation of sulfur ions in the solution is also a significant factor when thin films are deposited. Thioacetamide (C\(_2\)H\(_5\)NS) is one of the most frequently employed S precursors. The hydrolysis of the S precursor can produce H\(_2\)S and then S\(^{2-}\) ions by the following reactions \([152]\):

\[
\text{CH}_3\text{CSNH}_2 + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{CONH}_2 + \text{H}_2\text{S}
\]

When the reaction attains an equilibrium \([153]\), the following reactions are expected at a temperature of 25 \(^\circ\)C:

\[
\text{H}_2\text{S} + \text{H}_2\text{O} = \text{H}_3\text{O}^+ + \text{HS}^- (K_0 = 10^{-7})
\]

\[
\text{HS}^- = \text{H}^+ + \text{S}^{2-} (K_1 = 10^{-17})
\]

\[
\text{HS}^- + \text{OH}^- = \text{H}_2\text{O} + \text{S}^{2-} (K_2 = 10^{-3})
\]

At low pH values (<2.5), the reaction is controlled by the rate of hydrolysis of S precursor leading to the formation of hydrogen sulfide (H\(_2\)S), whereas at higher pH values (>2.5), the reaction is controlled by the formation and decomposition of the tin–thioacetamide complex. Therefore, the pH of the bath and metal–thioacetamide complexes are also considered as the growth rate- and growth mechanism-determining components in the film formation \([154]\).

The Sn ions react with the S ions and initiate the formation of tin sulfides (o-SnS, c-SnS, SnS\(_2\), and Sn\(_2\)S\(_3\)). The generation rate of Sn and S ions is controlled primarily by the source concentration, pH, and solution temperature. When the precursor concentration is changed, multiphase or other single-phase films can be formed by the following reactions \([155,156]\):

\[
\text{Sn}^{2+} + \text{S}^{2-} \rightarrow \text{SnS} (K_{\text{sp}} = 1 \times 10^{-25} \text{ at } 25 \, ^\circ\text{C})
\]

\[
\text{Sn}^{4+} + 2\text{S}^{2-} \rightarrow \text{SnS}_2 (K_{\text{sp}} = 1 \times 10^{-46} \text{ at } 25 \, ^\circ\text{C})
\]

\[
\text{Sn}^{2+} + \text{Sn}^{4+} + 3\text{S}^{2-} \rightarrow \text{Sn}_2\text{S}_3
\]

\[
\text{Sn(II)}\text{S} + \text{Sn(IV)}\text{S}_2 \rightarrow \text{Sn(II)(IV)}\text{S}_3 \text{ (or) } \text{SnS} + \text{SnS}_2 \rightarrow \text{Sn}_2\text{S}_3
\]
Figure 6. Schematic representation of (a) ion-by-ion mechanism and (b) cluster-by-cluster (hydroxide) mechanism.
| Sn,Sy Phase | Precursors | Complexing Gent | Deposition Parameters | Structure | Band Gap (eV) | Electrical Parameters | Ref |
|-------------|------------|-----------------|----------------------|-----------|--------------|-----------------------|-----|
| o-SnS       | T(II)C = 0.1 M | TEA = 15 mL, NH₃ = 8 mL | Tᵇ = 27 °C, tₙ = 20 h, pH = 10.5 ± 1 | Amorphous | 1.51 (i) | n | – | – | – | 1987 [145] |
| o-SnS       | T(II)C = 0.025 mol SDS/AS = 0.025 mol | – | Tᵇ = –, tₙ = –, pH = 3.1, 10, 12 | ORT(013) | 1.08 | p | 10⁷–10³ | – | – | 1989 [36] |
| o-SnS       | T(II)C = –, TU = – | – | Tᵇ = –, tₙ = –, pH = – | Polycrystalline | 1.3 (i) | – | – | – | – | 1990 [157] |
| o-SnS       | T(II)C = 1 g TA = 1 M | TEA = 12 mL, NH₃ = 10 mL | Tᵇ = 75 °C, 25 °C, tₙ = 5 h, 40 h, pH = – | Polycrystalline | 1.3 | p | – | – | – | 1991 [128] |
| o-SnS       | T(II)C = 1 g TA = 1 mol L⁻¹ | TEA = 0.5 mL, NH₃ = – | Tᵇ = 50 °C, 25 °C, tₙ = 2–4 h, 5–10 h, pH = – | Crystalline | – | – | – | – | – | 1991 [158] |
| o-SnS       | T(II)C = 1 g TA = 4 mL, 8 mL | TEA = 12 mL, NH₃ = 12 mL | Tᵇ = 75 °C, 25 °C, tₙ = 5 h, 40 h, pH = – | – | – | – | – | – | 1991 [159] |
| o-SnS       | T(II)C = 1 g TA = 1 M | TEA = 12 mL, NH₃ = 10 mL | Tᵇ = 60 °C, tₙ = 7 h 30 min, pH = – | ORT(111) | – | – | – | – | – | 1992 [160] |
| o-SnS       | T(II)C = 1 g TA = 1 M | TEA = 12 mL, NH₃ = 10 mL | Tᵇ = 60 °C, tₙ = 7 h 30 min, pH = 9.5 | ORT(111) | – | p | – | – | – | 1993 [161] |
| o-SnS       | T(II)C = 1 g TA = 1 M | TEA = 12 mL, NH₃ = 13 mL | Tᵇ = 50–75 °C, tₙ = 1.5 h, 20 h, pH = – | ORT(111) | – | p | – | – | – | 1994 [162] |
| Sn$_x$S$_y$ Phase | Precursors | Complexing Gent | Deposition Parameters | Structure | Band Gap (eV) | Electrical Parameters | Ref |
|-----------------|------------|----------------|----------------------|------------|---------------|----------------------|------|
|                 |            |                |                      |            |               | Type R (Ωcm) μ (cm$^2$V$^{-1}$S$^{-1}$) N (cm$^{-3}$) |     |
| o-SnS           | T(II)C = 15 g TU = 5 g, 10 g | – | $T_b = -$ $t_d = 5$ min pH = 3 $S_p = 1.33$ mm/s | ORT(040) | 1.4 | – – – – | 1999 [163] |
| o-SnS           | T(II)C = 0.1 M SDS = 0.05 M | – | $T_b = 80$ °C $t_d = -$ pH = 12 | – – p | – – – – | 2001 [164] |
| o-SnS           | T(II)C = 1.125 g ST = 2 M | AF | $T_b = T_r$ $t_d = 18$ h pH = 7 | ORT(111) | 1.38 (d) 0.96–1.14 (i) | – – – – | 2003 [165] |
| o-SnS           | T(II)C = 1 g TA = 8 mL NH$_3$ = 10 mL | TEA = 12 mL | $T_b = 35$ °C $t_d = 15$ h pH = 9.5 | ORT(111) | 1.18 (d) | p $10^7$–$10^4$ | – – | 2003 [166] |
| o-SnS           | T(II)C = 0.56 g SS = 0.025 M | – | $T_b = 80$ °C $t_d = -$ pH = 12 | ORT(111) | – – – – | – – | 2006 [167] |
| o-SnS           | T(II)C = 1.13 g TA = 0.1 | TEA = 30 mL NH$_3$ = 16 mL | $T_b = RT$ 293–298 K $t_d = 5$–6 h pH = – | ORT(111) | 1.17 (d) 1.12 (i) | – $10^8$–$10^6$ | – | 2007 [168] |
| o-SnS           | T(II)C = 1 g TA = 1 M | TEA = 12 mL NH$_3$ = 10 mL | $T_b = 308$ K $t_d = 20$ h pH = – | ORT(111) | – – – – | – – | 2007 [169] |
| o-SnS           | T(II)C = 1 g TA = 1 M | TEA = 10 mL NH$_3$ = 5 mL | $T_b = 45$ °C $t_d = -$ pH = – | ORT(111) | 1.33–1.39 (d) | – – – – | 2008 [43] |
| o-SnS           | T(II)C = 1 g TA = 8 mL NH$_3$ = 10 mL | TEA = 12 mL | $T_b = 55$ °C $t_d = 8$ h pH = – | ORT(111) | – p | $10^3$ 90 $10^{11}$ | 2008 [43] |
| Sn₅S₇ Phase | Precursors | Complexing Gent | Deposition Parameters | Structure | Band Gap (eV) | Electrical Parameters | Ref |
|------------|------------|----------------|----------------------|-----------|---------------|----------------------|-----|
| o-SnS      | T(II)C = 1.12 g ST = 0.5 M |
|            | TTA = 10 mL |
|            | Tₜ = Tₜ |
|            | tₜ = 24 h |
|            | pH = 7     |
|            | ORT(111)   |
|            | 1.1 (d)    |
|            | – 10⁶      |
|            | – –        |
|            | – 2008 [170] |
| o-SnS      | T(II)C = 1 g TA = 8 mL |
|            | TEA = 12 mL NH₃ = 10 mL  |
|            | Tₜ = 313 K tₜ = 8–22 h |
|            | pH = –     |
|            | ORT(111)   |
|            | 1.2–1.7 (d) |
|            | p – – –    |
|            | – 2009 [171] |
| o-SnS      | T(II)C = 0.15 M ST = 2 M |
|            | NH₂OH = 6 mL  |
|            | Tₜ = 30 °C tₜ = 24 h |
|            | pH = 7     |
|            | ORT(040)/(141) |
|            | 1.31 (d)   |
|            | – – – –    |
|            | – 2009 [172] |
| o-SnS      | T(II)C = 2 × 10⁻² M TA = 1 × 10⁻²–8 × 10⁻² M |
|            | – – – –    |
|            | Tₜ = 80 °C tₜ = 60 min |
|            | pH = 1.87  |
|            | Amorphous  |
|            | – – – –    |
|            | – 2009 [142] |
| o-SnS      | T(II)C = 1 g TA = 8 mL |
|            | TEA = 12 mL NH₃ = 10 mL  |
|            | Tₜ = 55 °C tₜ = 8 h |
|            | pH = –     |
|            | ORT(111)   |
|            | 1.12 (i)   |
|            | – – – –    |
|            | – 2009 [173] |
| o-SnS      | T(II)C = 0.15 M ST = 2 M |
|            | AH = 6 mL   |
|            | Tₜ = Tₜ |
|            | tₜ = 24 h |
|            | pH = –     |
|            | ORT(111)   |
|            | – – – –    |
|            | – 2009 [174] |
| o-SnS      | T(II)C = – TA = – |
|            | TEA = – NH₃ = –  |
|            | Tₜ = 75 °C tₜ = 24 h |
|            | pH = –     |
|            | ORT(111)   |
|            | 0.82–1.22 (i) |
|            | – – – –    |
|            | – 2009 [175] |
| o-SnS      | T(II)C |
|            | TA = 0.1 M |
|            | TEA = 30 mL NH₄OH = 16 mL  |
|            | Tₜ = – tₜ = 5 h |
|            | pH = –     |
|            | ORT(111)/(040) |
|            | 1.76 (i)   |
|            | – – – –    |
|            | – 2010 [176] |
| o-SnS      | T(II)C = 1 M TA = 1 M |
|            | TEA = 10 mL TSS = 5 mL NH₃/NH₄Cl = 5 mL |
|            | Tₜ = 60 °C tₜ = 2–10 h |
|            | pH = 9.31  |
|            | ORT(111)/(040) |
|            | 1.30–1.97 (d) |
|            | 0.83–1.36 (i) |
|            | p 9.9–12.3 |
|            | – 2010 [177] |
Table 4. Cont.

| Sn<x> S<y> Phase | Precursors | Complexing Gent | Deposition Parameters | Structure | Band Gap (eV) | Electrical Parameters |
|------------------|------------|-----------------|-----------------------|-----------|--------------|----------------------|
|                  |            |                 |                       |           |              | Type | R (Ω cm) | µ (cm² V⁻¹ S⁻¹) | N (cm⁻³) | Ref        |
|                  |            |                 |                       |           |              |      |          |              |          |            |
| o-SnS            | T(II)C = 1 M TA = 1 M | TEA = 10 mL TSS = 5 mL NH₃/NH₄Cl = 5 mL | T_b = 27 °C t_d = 24 h pH = 10.7 | ORT(110) | 1.37 (d) | 1.05 (i) | p | 10⁵ | 9 × 10⁵ | – | 2010 [178] |
| o-SnS            | –          | TEA = 12.5 M, 13 M | T_b = – t_d = – pH = – | – | 1.93–2.16 (d) | – | – | – | – | – | 2010 [179] |
| o-SnS            | T(II)C = 0.95 g TA = 0.1 M | TEA = 8 mL NH₃ = 6 mL | T_b = 75 °C t_d = 1 h pH = – | ORT(111)/(040) | 1.3 (i) | – | p | – | – | – | 2010 [180] |
| o-SnS            | T(II)C = – TA = – | TEA, NH₃ TTA | T_b = T_r, 90 °C t_d = 24 h, 3 h pH = – | ORT(400) | 1.1–1.9 (d) | – | – | – | – | – | 2011 [181] |
| o-SnS            | T(II)C = 0.2 M ST = 0.2 M | Na₂EDTA = 25 mL of 0.2 M | T_b = 40–80 °C t_d = 30 h pH = 1.5 | – | 1.2–1.5 (d) | – | – | – | – | – | 2011 [182] |
| o-SnS            | T(II)C = 0.15 M ST = 0.15 M | Na₂EDTA = 25 mL of 0.2 M | T_b = 75 °C t_d = 150 min pH = – | – | 1.2–1.6 (d) | – | – | – | – | – | 2011 [183] |
| o-SnS            | T(II)C = 0.1 M ST = 0.25 M | AC = 50 mL of 0.2 M | T_b = 35 °C t_d = 10 h pH = 5, 6 | ORT(111) | 1.75 (d) | 1.12 (i) | – | – | – | – | 2011 [184] |
| o-SnS            | T(II)C = 0.1 M ST = 0.25 M | AC = 50 mL of 0.2 M | T_b = 35 °C t_d = 10 h pH = 5 | ORT(111) | 1.75 (d) | 1.15 (i) | – | 420 | – | – | 2011 [185] |
| o-SnS            | T(II)C TA | TEA = – NH₃ = – | T_b = 20–50 °C t_d = – pH = – | ORT(111) | 1.15 (i) | 1.35(d) | p | 6.3 ± 0.1 | 11 ± 7 | 10¹⁶–10¹⁷ | 2011 [186] |
| Sn$_x$S$_y$ Phase | Precursors | Complexing Gent | Deposition Parameters | Structure | Band Gap (eV) | Electrical Parameters | Ref |
|-----------------|-----------|----------------|----------------------|----------|--------------|-----------------------|-----|
|                 | o-SnS     |                |                      |          |              |                       |     |
|                 |           |                | T(II)C = 0.1 M       |          |              |                       |     |
|                 |           |                | ST = 0.25–0.75 M     |          |              |                       |     |
|                 |           |                | AC = 50 mL of 0.3 M  |          |              |                       |     |
|                 |           |                | $T_b = 60–80 \, ^\circ C$ |          |              |                       |     |
|                 |           |                | $t_d = 5 \, h$       |          |              |                       |     |
|                 |           |                | pH = 5               |          |              |                       |     |
|                 |           |                | ORT(111)/(040)       |          |              |                       |     |
|                 |           |                | 1.01–1.26 (i)        |          |              |                       |     |
|                 |           |                |                      |          |              |                       |     |
|                 |          |                | T(II)C = –           |          |              |                       |     |
|                 |          |                | TA = –               |          |              |                       |     |
|                 |          |                | TEA = –              |          |              |                       |     |
|                 |          |                | NH$_4$Cl = –         |          |              |                       |     |
|                 |          |                | $T_b = 45 \, ^\circ C$ |          |              |                       |     |
|                 |          |                | $t_d = 5 \, h$       |          |              |                       |     |
|                 |          |                | pH = –               |          |              |                       |     |
|                 |          |                | ORT(111)             |          |              |                       |     |
|                 |          |                | 0.7–1.3 (i)          |          |              |                       |     |
|                 |          |                |                      |          |              |                       |     |
|                 | o-SnS     |                | T(II)C = 1 g         |          |              |                       |     |
|                 |           |                | TA = 1 M             |          |              |                       |     |
|                 |           |                | TEA = 12 mL          |          |              |                       |     |
|                 |           |                | NH$_3$ = 10 mL       |          |              |                       |     |
|                 |           |                | $T_b = 60 \, ^\circ C$ |          |              |                       |     |
|                 |           |                | $t_d = 6 \, h$       |          |              |                       |     |
|                 |           |                | pH = 6               |          |              |                       |     |
|                 |           |                | ORT(111)/(101)       |          |              |                       |     |
|                 |           |                | 0.9–1.1              |          |              |                       |     |
|                 |           |                |                      |          |              |                       |     |
|                 | o-SnS     |                | T(II)C = 1 M         |          |              |                       |     |
|                 |           |                | TA = 1 M             |          |              |                       |     |
|                 |           |                | TEA = 10 mL          |          |              |                       |     |
|                 |           |                | NH$_3$ = 2 mL        |          |              |                       |     |
|                 |           |                | $T_b = RT = 27 \, ^\circ C$ |          |              |                       |     |
|                 |           |                | $t_d = 24–72 \, h$   |          |              |                       |     |
|                 |           |                | pH = 9.7             |          |              |                       |     |
|                 |           |                | ORT(111)             |          |              |                       |     |
|                 |           |                | 1.14–1.18 (i)        |          |              |                       |     |
|                 |           |                | 1.32–1.44 (d)        |          |              |                       |     |
|                 |           |                |                      |          |              |                       |     |
|                 |          |                | T(II)C = 0.06 M–0.12 M |          |              |                       |     |
|                 |          |                | TA = 0.1 M           |          |              |                       |     |
|                 |          |                | TEA = 1.85 M         |          |              |                       |     |
|                 |          |                | NH$_3$ = 1.5 M       |          |              |                       |     |
|                 |          |                | $T_b = 30 \, ^\circ C$ |          |              |                       |     |
|                 |          |                | $t_d = 90 \, min$    |          |              |                       |     |
|                 |          |                | pH = –               |          |              |                       |     |
|                 |          |                | ORT(040)/(111)       |          |              |                       |     |
|                 |          |                | 1.5–1.95 (d)         |          |              |                       |     |
|                 | o-SnS     |                | T(II)C = 0.1 M       |          |              |                       |     |
|                 |           |                | TA = 0.1 M           |          |              |                       |     |
|                 |           |                | TEA = 1.85 M         |          |              |                       |     |
|                 |           |                | NH$_3$ = 1.5 M       |          |              |                       |     |
|                 |           |                | $T_b = 30 \, ^\circ C$ |          |              |                       |     |
|                 |           |                | $t_d = 90 \, min$    |          |              |                       |     |
|                 |           |                | pH = –               |          |              |                       |     |
|                 |           |                | ORT(040)/(111)       |          |              |                       |     |
|                 |           |                | 1.5–1.95 (d)         |          |              |                       |     |
|                 | o-SnS     |                | T(II)C = 1 g         |          |              |                       |     |
|                 |           |                | TA = 1 M             |          |              |                       |     |
|                 |           |                | TEA = 12 mL          |          |              |                       |     |
|                 |           |                | NH$_4$OH = 10 mL     |          |              |                       |     |
|                 |           |                | $T_b = 60 \, ^\circ C$ |          |              |                       |     |
|                 |           |                | $t_d = 6 \, h$       |          |              |                       |     |
|                 |           |                | pH = –               |          |              |                       |     |
|                 |           |                | ORT(111)             |          |              |                       |     |
|                 |           |                | 1.9 (d)              |          |              |                       |     |
|                 |           |                | 1.1 (i)              |          |              |                       |     |
|                 | o-SnS     |                | T(II)C = 0.1 M       |          |              |                       |     |
|                 |           |                | TA = 0.6 M           |          |              |                       |     |
|                 |           |                | TTA = 1 M            |          |              |                       |     |
|                 |           |                | $T_b = 50–70 \, ^\circ C$ |          |              |                       |     |
|                 |           |                | $t_d = 50 \, min$    |          |              |                       |     |
|                 |           |                | pH = 1.5             |          |              |                       |     |
|                 |           |                | ORT(111)             |          |              |                       |     |
|                 |           |                | 1.30–1.35 (d)        |          |              |                       |     |

Table 4. Cont.
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| SnₓSᵧ Phase | Precursors | Complexing Gent | Deposition Parameters | Structure | Band Gap (eV) | Electrical Parameters | Ref |
|-------------|------------|-----------------|-----------------------|-----------|--------------|-----------------------|-----|
| o-SnS       | T(II)C = 0.05–0.2 M TA = 0.4–0.7 M | Na₂EDTA = 20 mL of 0.1 M | Tₑ = 50–80 °C tₜₜ = 0.5–3 h pH = 9–12 | ORT(200) | – | – | – | – | 2013 [194] |
| o-SnS       | T(II)C = 0.1 M ST = 0.3 M | Na₂EDTA = 5 mL of 0.1 M TSC = 5 mL of 0.66 M | Tₑ = Tₑ tₜ = 24 h pH = 10 | – | 1.50–1.90 (d) | – | – | – | 2013 [195] |
| o-SnS       | T(II)C = 0.5 M TU = 1 M | NH₃ = 3 M | Tₑ = Tₑ tₜ = 60–180 min pH = – | – | 1.98–2.01(d) 1.82–1.98 (i) | p | – | – | – | 2013 [196] |
| o-SnS       | T(II)C | TA = 0.1 M TEA = 30 mL NH₄OH = 16 mL | Tₑ = – tₜ = 5 h pH = – | ORT(111)/(200) | 1.64–1.7 (f) | – | – | – | 2013 [197] |
| o-SnS       | T(II)C = 0.1 M TA = 0.1 M EDTA = 0.05 M–0.08 M NH₃ = 1.4 M | | Tₑ = – tₜ = 3–4 h pH = – | ORT(111)/(101) | 1.5–1.60 (d) | p | 400 | – | – | 2013 [198] |
| o-SnS       | T(II)C = 1 g TA = 1 M | TEA = 6 mL NH₃ = 10 mL | Tₑ = – tₜ = – pH = – | ORT(240) | 1.78–1.75 (d) | – | 10⁸–10⁸ | – | – | 2014 [199] |
| o-SnS       | T(II)C = 1 g TA = 1 M | TEA = 12 mL NH₃ = 10 mL | Tₑ = 20–40 °C tₜ = 24 h pH = 11 | ORT(111) | ORT 1.1 (i) | p | 10²–10² | – | – | 2014 [146] |
| o-SnS       | T(II)C = 0.5 g TA = 1 M | TEA = 6 mL TSC = 0.006–0.008 M NH₃ = 5 mL | Tₑ = 30 °C tₜ = 24 h pH = – | ORT(111) | 1.17–1.40 (d) | – | 10⁴ | 148–228 | 10¹² | 2014 [44] |
| o-SnS       | T(II)C = – TA = – | TSC = – | Tₑ = 50 °C tₜ = 2.5 h pH = 5 | ORT(111) | 1.25–1.83 (d) 1.1–1.65 (i) | n | 10³ | – | – | 2014 [200] |
| Sn$_x$S$_y$ Phase | Precursors | Complexing Gent | Deposition Parameters | Structure | Band Gap (eV) | Electrical Parameters | Ref |
|-----------------|------------|-----------------|-----------------------|-----------|---------------|-----------------------|-----|
|                 |            |                 |                       |           |               |                       |     |
| o-SnS           |            |                 |                       |           |               |                       |     |
| o-SnS           | T(II)C = 0.03 M ST = 0.03 M TTA = 0.44 M |               | $T_b = T_r$ $t_d = 24$ h $pH = 7$ | ORT(400) | 1.49–1.39 (i) | – – – – – – | 2014 [201] |
| o-SnS           | T(II)C = 1 g TA = 1 M TEA = 12 mL NH$_3$ = 10 mL |               | $T_b = 40$ °C $t_d = 17$ h $pH = –$ | ORT(111) | 1.25–1.1 (i) | – $10^3$ – – | 2015 [202] |
| o-SnS           | T(II)C = 0.1 M TA = 0.1 M TEA = 15 mL NH$_3$ = 8 mL |               | $T_b = 26$ °C $t_d = 22$ h $pH = –$ | ORT(021) | 1.76–3.32 (d) | – – – – – | 2015 [203] |
| o-SnS           | T(II)C = – ST = 0.01–0.09 M TTA = 1 M |               | $T_b = 22$ °C $t_d = 24$ h $pH = 7$ | – – – – | – – – – – – | – – – – | 2015 [204] |
| o-SnS           | T(II)C = 20 mL TA = 20 mL TTA = 1 M |               | $T_b = 40–80$ °C $t_d = 50$ min $pH = 1.5$ | – | 1.33–1.41 (d) | – – – – – | 2015 [17] |
| o-SnS           | T(II)C = 0.1 M TA = 0.15 M TSC = 0.2 M NH$_3$ = – |               | $T_b = 80$ °C $t_d = 4$ h $pH = 7$ | ORT(040) | 1.65 (d) | p – – – | 2016 [205] |
| o-SnS           | T(II)C = 1 g TA = 8 mL TEA = 12 mL NH$_3$ = 10 mL |               | $T_b = 40$ °C $t_d = 10$ h $pH = 11$ | ORT(111) | ORT = 1.1 (i) | p $10^6$ – – | 2016 [25] |
| o-SnS           | T(II)C = 0.1 M TA = 20 mL TTA = 1 M |               | $T_b = 70$ °C $t_d = –$ $pH = –$ | ORT(111) | 1.31–1.26 (d) | p 6–38 124 $10^{15}$–$10^{16}$ | 2016 [144] |
| o-SnS           | T(II)C = 1 g TA = 0.3 g TEA = 5.5 mL NH$_3$ = 5 mL |               | $T_b = 70$ °C $t_d = –$ $pH = –$ | ORT(002) | 1.14–1.75 (d) | – – – – – | 2016 [206] |
Table 4. Cont.

| Sn$_x$S$_y$ Phase | Precursors | Complexing Gent | Deposition Parameters | Structure | Band Gap (eV) | Electrical Parameters | Ref |
|------------------|------------|----------------|----------------------|----------|--------------|-----------------------|-----|
| o-SnS            | T(II)C = –  
TA = –         | TTA = 1 M      | Tb = 70 °C  
$t_d = –$  
pH = –         | ORT(111)   | 1.3 (d)       | p         | 38–14.2  
55–23        | 10$^{15–19}$ | 2016 [123]   |
| o-SnS            | T(II)C = 0.1 M  
TA = 0.15 M   | TSC = 0.15–0.21 M | Tb = 80 °C  
$t_d = 4$ h  
pH = 5.8         | ORT(111)   | 1.64–1.1 (d)  | –         | –              | –              | 2017 [207] |
| o-SnS            | T(II)C = 0.1 M  
TA = 0.15 M   | TSC = 0.2 M    | Tb = 80 °C  
$t_d = 4$ h  
pH = 6.5–7.5 | ORT(111)   | 1.51 (d)      | –         | –              | –              | 2018 [27]  |
| o-SnS            | T(II)C = 1 g  
TA = 1 M     | TEA = 312 mL  
NH$_3$ = 10 mL | Tb = 40 °C  
$t_d = 17$ h  
pH = 1.5      | ORT(111)   | 1.1 (i)       | –         | –              | –              | 2018 [208] |
| o-SnS            | T(II)C = 4 mmol  
TA = 4–8 mmol | TSC = 0.15–0.21 M | Tb = 80 °C  
$t_d = 1–2$ h  
pH = 0.4–1.0 | ORT(111)   | 1.39–1.41 (d) | –         | –              | –              | 2018 [209] |
| o-SnS            | T(II)C = 0.1 M  
TA = 0.15 M   | TEA = –        | $T_b = 343$ K  
t$_d = 120$, 240, 369 min  
pH = 4         | ORT(013)   | –            | –         | –              | –              | 2018 [210] |
| o-SnS            | T(II)C = 20 mL  
TA = 20 mL    | TTA = 0.6–1.6 M | Tb = 70 °C  
$t_d = 50$ min  
pH = –         | ORT(111)   | 1.28–1.45 (d) | p         | 38–62          | 29–108        | 1.92 × 10$^{15–19}$  
4.12 × 10$^{15}$ | 2019 [211] |
| o-SnS            | T(II)C = 0.1 M  
TA = 0.6 M    | TTA = 1 M      | Tb = 40–80 °C  
$t_d = 50$ min  
pH = 1.5     | ORT(111)   | 1.30–1.41 (d) | p         | 38              | 55             | 1.5 × 10$^{15–19}$  
3.4 × 10$^{15}$ | 2019 [212] |
| Sn₅S₇ Phase | Precursors | Complexing Gent | Deposition Parameters | Structure | Band Gap (eV) | Electrical Parameters | Ref |
|------------|------------|----------------|----------------------|-----------|---------------|----------------------|-----|
| o-SnS      | T(II)C = 1 g TA = 1 M | TEA = 18 mL NH₃ = 10 mL | Tb = 40–70 °C tₜ = 3 H pH = 10 | ORT(040) | 1.32–2.08 (d) | – – – – | 2019 [213] |
| o-SnS      | T(II)C = 0.2 M TA = 0.4 M | TTA = 0.5 M | Tb = 50–80 °C tₜ = 90 min pH = 1.5 | ORT(040) | 1.55–1.92 (d) | – – – – | 2019 [214] |
| o-SnS      | T(II)C = 0.1 M TA = 0.15 M | TSC = 0.2 M | Tb = 80 °C tₜ = 4 h pH = 5.0–6.5 | ORT(111) | 1.34–1.51 (d) | – – – – | 2019 [215] |
| o-SnS      | T(II)C = 4 mmol TA = 6 mmol | – | Tb = 80 °C tₜ = 120 min pH = 0.7 | ORT(111) | 1.41–1.49 (d) | – – – – | 2019 [216] |
| o-SnS      | T(II)C = 2 g ST = 0.2 M | TEA = 70 mL CA = 0.4 M NH₃ = 10 mL | Tb = 55 °C tₜ = 4 h pH = 11 | ORT(111) | 1.33 (i) | – – – – | 2019 [217] |
| o-SnS      | T(II)C = 20 mL TA = 10 mL PVA = 2 g | TTA = 0.5 M | Tb = 80 °C tₜ = 45–90 min pH = 10 | ORT(040) | 1.55–1.79 (d) | – – – – | 2019 [218] |
| o-SnS      | T(II)C = 0.1 M TA = 1 M | TEA = 10 mL TSC = 0.66 M | Tb = – tₜ = – pH = 9.2–9.6 | ORT(102) | 1.36–1.99 (d) | – – – – | 2020 [219] |
| o-SnS      | T(II)C = 0.1 mol TA = 0.4 mol | AA = 0.8 mL | Tb = 75 °C tₜ = 70 min pH = 9.2–9.6 | ORT(110) | – – – – | – – – – | 2020 [220] |
| o-SnS      | T(II)C = – TA = 0.1 M | TEA = – NH₃ = 15 mL | Tb = 25 °C tₜ = 4 h pH = – 200–600 °C | – | 1.5–1.7 (d) | – – – – | 2021 [221] |
| Sn₅S₅ Phase | Precursors | Complexing Gent | Deposition Parameters | Structure | Band Gap (eV) | Electrical Parameters | Ref |
|-------------|------------|----------------|-----------------------|-----------|--------------|----------------------|-----|
| o-SnS       | T(II)C = 1 g, TA = 0.6 g, NH₃ = 15 mL | TEA = 12 mL, TEA = 12 mL, NH₃ = 15 mL | Tₜ = 70 °C, tₜ = 2 h, pH = 10.93 | ORT(111) | 1.38 (d) | – – – – | 2021 [222] |
| o-SnS       | T(II)C = 4 m mol, TA = 6 mL mL | – | Tₜ = 80 °C, tₜ = 120 min, pH = 0.7 | ORT(111) | 0.78–1.13 (d) | – – – – | 2021 [223] |
| o-SnS       | – | – | Tₜ = 65 °C, tₜ = 3 h, pH = 5.5–8.5 | ORT(111) | 1.41–1.75 (d) | – – – – | 2021 [224] |
| c-SnS       | T(II)C = 2.26 g, TA = 10 mL | TEA = 30 mL, NH₃ = 16 mL | Tₜ = 25 °C, tₜ = 6 h, pH = – | CUB (111)/(200) | 1.64–1.73 (d) | p | 10⁵ | 10⁴ | 10⁹ | 2008 [43] |
| c-SnS       | T(II)C = 2.26 g, TA = 10 mL | TEA = 30 mL, NH₃ = 16 mL | Tₜ = 25 °C, tₜ = 6 h, pH = – | CUB (111)/(200) | 1.7 (d) | – – – – | 2009 [171] |
| c-SnS       | T(II)C = 2.26 g, TA = 10 mL | TEA = 30 mL, NH₃ = 16 mL | Tₜ = 25 °C, tₜ = 6 h, pH = – | CUB (111)/(200) | 1.7 (d) | – – – – | 2009 [173] |
| c-SnS       | T(II)C = –, TA = 0.1 M | TEA = 8964 g, NH₄OH = 15 M | Tₜ = 25 °C, tₜ = 2–4 h, 30 min, pH = – | CUB (111)/(200) | 1.7 (d) | – – – – | 2011 [225] |
| c-SnS       | T(II)C = –, TA = 0.1 M | TEA = –, NH₄OH = 15 M | Tₜ = 25 °C, tₜ = –, pH = – | – | – – – – | – | 2011 [226] |
| c-SnS       | T(II)C = –, TA = 0.1 M | TEA = 8964 g, NH₄OH = 15 M | Tₜ = 25 °C, tₜ = –, pH = – | CUB (111)/(200) | 1.76 (d) | 1.44–1.51 (d) | – – – – | 2012 [227] |
| Sn,S\_y Phase | Precursors | Complexing Gent | Deposition Parameters | Structure | Band Gap (eV) | Electrical Parameters | Ref |
|----------------|------------|-----------------|-----------------------|-----------|---------------|-----------------------|-----|
|                | c-SnS      |                 |                       |           |               |                       |     |
| c-SnS          | T(II)C = – | TEA = 8964 g    | T_b = 25 °C           | CUB       | 1.76 (d)      |                       | 2012 [228] |
|                | TA = 0.1 M | NH\_3OH = 15 M  | t_d = –               | (111)/(200) |              |                       |     |
|                | c-SnS      | TEA = 12 mL     | T_b = 20–40 °C        | CUB       | 1.67 (d)      | p 10^7–10^2           | 2014 [146] |
|                | TA = 1 M   | NH\_3 = 10 mL   | t_d = 24 h            | (111)/(200) |              |                       |     |
|                | c-SnS      | TEA = 0.1 M     | T_b = 17 °C           | CUB       | 1.74 (d)      | –         10^3         | 2015 [28]  |
|                | TA = 0.1 M | NH\_3OH = 15 M  | t_d = 10 h            | (222)/(400) |              |                       |     |
|                | c-SnS      | TEA = 0.1 M     | T_b = 25 °C           | CUB(111)/(200) | 1.70 (d)      | –         –           | 2015 [229] |
|                | TA = 0.1 M | NH\_3 = 16 mL   | t_d = –               |           |               |                       |     |
|                | c-SnS      | TEA = 30 mL     | T_b = 17 °C           | CUB(222)/(400) | 1.73 (d)      | –         –           | 2016 [230] |
|                | TA = 0.1 M | NH\_3 = 16 mL   | t_d = 15 h            |           |               |                       |     |
|                | c-SnS      | TEA = 30 mL     | T_b = 17 °C, 10 °C    | CUB(222)/(400) | 1.66–1.72 (d) | p 10^6              | 2016 [25]  |
|                | TA = 0.1 M | NH\_3 = 16 mL   | t_d = 4 h, 18 h       |           |               |                       |     |
|                | c-SnS      | TEA = 30 mL     | T_b = 25 °C           | CUB(222)/(400) | –             | –         –           | 2016 [231] |
|                | TA = 0.1 M | NH\_3 = 16 mL   | t_d = 6 h             |           |               |                       |     |
|                | c-SnS      | TEA = 30 mL     | T_b = 17 °C           | CUB(222)/(400) | –             | –         –           | 2016 [232] |
|                | TA = 0.1 M | NH\_3 = 16 mL   | t_d = 10 h            |           |               |                       |     |
|                | c-SnS      | EDTA = 20 mL of 0.5 M | T_b = 25–65 °C     | CUB(222)/(400) | 1.74–1.68 (d) | p 10^5–10^4          | 2016 [50]  |
|                | ST = 1 M   |                  | t_d = 6 h             |           |               | 8.98–28.6            |     |
|                |            |                  | pH = 10.5             |           |               | 10^{12}–10^{13}      |     |
Table 4. Cont.

| Sn$_x$S$_y$ Phase | Precursors | Complexing Gent | Deposition Parameters | Structure | Band Gap (eV) | Electrical Parameters | Ref |
|-------------------|------------|-----------------|----------------------|-----------|--------------|----------------------|-----|
|                   |            |                 |                      |           |              | Type $R$ ($\Omega$cm) | $\mu$ (cm$^2$V$^{-1}$S$^{-1}$) | $N$ (cm$^{-3}$) |
| c-SnS             | T(II)C = 2.26 g ST = 1 M | EDTA = 15–25 mL of 0.5 M NH$_3$ = 5 mL | $T_b$ = 45 $^\circ$C $t_d$ = 6 h pH = 10.5 $S_p$ = – | CUB(222)/(400) | 1.67–1.73 (d) | p | $10^5$–$10^4$ | 0.34–28.6 | $10^{14}$–$10^{12}$ | 2016 [26] |
| c-SnS             | T(II)C = 0.1 M TA = 0.15 M | TSC = 0.2 M | $T_b$ = 80 $^\circ$C $t_d$ = 4 h pH = 7 | CUB(222)/(400) | 1.64 (d) | – | – | – | – | 2017 [24] |
| c-SnS             | T(II)C = 0.1 M TA = 0.1 M | TEA = 30 mL NH$_3$ = 16 mL | $T_b$ = 17 $^\circ$C, 80 $^\circ$C $t_d$ = 3 h, 21 h pH = – | – | – | – | – | – | 2017 [233] |
| c-SnS             | T(II)C = 0.1 M ST = 0.125 M | EDTA = 0.1 M | $T_b$ = 45 $^\circ$C $t_d$ = 6 h pH = – | CUB(222)/(400) | 1.67–1.75 (d) | p | $10^5$–$10^4$ | 5.22–77.7 | $10^{11}$–$10^{13}$ | 2017 [29] |
| c-SnS             | T(II)C = 0.1 M TA = 0.15 M | TSC = 0.2 M | $T_b$ = 80 $^\circ$C $t_d$ = 4 h pH = 6.5–7.5 | CUB(222)/(400) | 1.64–1.73 (d) | – | – | – | – | 2018 [27] |
| c-SnS             | T(II)C = 0.1 M TA = 0.15 M | TSC = 0.2 M | $T_b$ = 80 $^\circ$C $t_d$ = 4 h pH = 7 | CUB(222)/(400) | 1.5 (d) | – | – | – | – | 2018 [234] |
| c-SnS             | T(II)C = 0.5 M TA = 0.5 M | TEA = 30 mL NH$_3$ = 16 mL | $T_b$ = 35 $^\circ$C $t_d$ = 4 h pH = 9.78 | CUB(222)/(400) | 1.74 (d) | – | – | – | – | 2018 [235] |
| c-SnS             | T(II)C = 2.26 g TA = 0.1 M | TEA = 30 mL NH$_3$ = 16 mL | $T_b$ = 17–8 $^\circ$C $t_d$ = 3–21 h pH = – | CUB(222)/(400) | 1.76 (d) | – | – | – | – | 2018 [236] |
| c-SnS             | T(II)C = 2.26 g TA = 10 mL | TEA = 30 mL NH$_3$ = 16 mL | $T_b$ = 17–8 $^\circ$C $t_d$ = 3–21 h pH = – | CUB(222)/(400) |       |       |       |       |       | 2019 [217] |
Table 4. Cont.

| Sn₅S₇ Phase | Precursors | Complexing Gent | Deposition Parameters | Structure | Band Gap (eV) | Electrical Parameters | Ref |
|-------------|------------|----------------|-----------------------|-----------|--------------|----------------------|-----|
|             |            |                |                       |           |              | Type     | R (Ωcm) | µ (cm²V⁻¹S⁻¹) | N (cm⁻³) |          |
| c-SnS        | T(II)C = 0.04 M TA = 0.08 M | TEA = 1.1 M NH₃ = 9.5 mL | Tᵦ = 30 °C tᵣ = 4 h pH = - | CUB(222)/(400) | 1.74 (d) | -        | -        | -          | - | 2020 [237] |
| c-SnS        | T(II)C = 0.1 M TA = 0.15 M | TSC = 0.2 M | Tᵦ = - tᵣ = - pH = - | CUB(222)/(400) | -        | -        | -        | -          | - | 2020 [238] |
| c-SnS        | T(II)C = 1 g TA = 0.3 g | TEA = 5.5 mL NH₃ = 5 mL | Tᵦ = 24 °C tᵣ = 4.25 h pH = 9.25 | CUB(222)/(400) | 1.70-1.74 (d) | - | 10³–10⁴ | -          | - | 2020 [239] |
| c-SnS        | T(II)C = 0.2 M TA = 0.1 M | TEA = 5.5 mL NH₃ = 5 mL | Tᵦ = 17-8 °C tᵣ = 3-21 h pH = 11 | CUB(222)/(400) | 1.76 (d) | p | 10⁸ | -          | - | 2020 [240] |
| c-SnS        | T(II)C = 2.25 g ST = 0.1 M | EDTA = 0.5 M NH₃ = 5-7.5 mL | Tᵦ = 50 °C tᵣ = 6 h pH = 10.3 | CUB(222)/(400) | 1.75-1.8 (d) | p | 10³–10⁴ | 15–75 | 10¹²–10¹³ | 2020 [241] |
| c-SnS        | T(II)C = 1 g TA = 0.6 g | TEA = 12 mL NH₃ = 15 mL | Tᵦ = 70 °C tᵣ = 2 h pH = 8.24 | CUB(200) | 1.72 (d) | -        | -        | -          | - | 2021 [222] |
| c-SnS        | T(II)C = 1.21 g TA = 0.5 M | TTA = 1 M | Tᵦ = 80 °C tᵣ = 2-6 h pH = 5-8 | CUB(222)/(400) | 1.72-1.90 (d) | - | 10²–10⁸ | -          | - | 2021 [242] |
| c-SnS        | T(II)C = 0.5 g TA = 1 M | NTA = 0.6 M | Tᵦ = 40 °C tᵣ = 90–182 min pH = 10 | CUB(222)/(400) | 1.77-1.81 (d) | - | 10⁶ | -          | - | 2021 [243] |
| c-SnS        | T(II)C = 0.01 mol TA = 0.1 M | TEA = 0.6 M | Tᵦ = 17–8 °C tᵣ = 3–21 h pH = 10 | CUB(222)/(400) | 1.70-1.80 (d) | - | -        | -          | - | 2021 [244] |
Table 5. Deposition conditions and the physical properties of SnS$_2$ and Sn$_2$S$_3$ films grown by CBD.

| Sn$_x$S$_y$ Phase | Precursors | Complexing Agent | Deposition Parameters | Structure | Band Gap (eV) | Electrical Parameters | Ref |
|------------------|------------|------------------|----------------------|-----------|--------------|----------------------|-----|
|                  |            |                  |                      |           |              | Type | R ($\Omega$cm) | $\mu$ (cm$^2$V$^{-1}$s$^{-1}$) | N (cm$^{-3}$) |     |
| SnS$_2$          |            |                  |                      |           |              | $\text{SnS}_2$-n | $10^7$–$10^8$ | –          | –          | 1989 [36] |
| SnS$_2$          | T(II)C = 0.025 mol
SDS/AS = 0.025 mol | –                 | $T_b = T_r$
$t_d = 2$ h
pH = – | Amorphous | 2.04 | SnS$_2$-n | $10^7$–$10^8$ | –          | –          | 1990 [130] |
| SnS$_2$          | Tin-ingots (99.9%)
ST = 10 mL | –                 | $T_b = 27$ °C
$t_d = 10$–120 min
pH = 10 | Amorphous | 2.35 (d) | n | $10^7$–$10^8$ | –          | –          | 1992 [147] |
| SnS$_2$          | T(II)C = 1.13 g
TA = 0.1 M
NH$_3$ = 15 mL | EDTA = 25 mL
CA = 0.375, 0.5, 0.625 mol/L | $T_b = T_r$
$t_d = 5$ min
pH = 3 | – | 2.05 (i) | HEX(001) | –          | –          | –          | 1997 [38] |
| SnS$_2$          | T(II)C = 15 g
TU = 5 g, 10 g | –                 | $T_b = T_r$
$t_d = 5$ min
pH = 3 | – | 2.40 (d) | –          | –          | –          | –          | 2011 [131] |
| SnS$_2$          | TC(IV) = 0.02 mol
TA = 0.5 mol L$^{-1}$
CA = 0.375, 0.5, 0.625 mol/L | –                 | $T_b = 35$ °C
$t_d = 2$ h
pH = 1.3 | – | 3.3–3.7 (d) | HEX(001) | –          | –          | –          | 2012 [41] |
| SnS$_2$          | T(II)C = 1 g
TA = 0.5 M
NH$_3$ = 12 mL–20 mL | TEA = 24 mL
TEA = 3.75 M
NH$_3$ = 12 mL | $T_b = 60$ °C
$t_d = 2$ h
pH = – | – | 2.8–3.0 (d) | HEX(001) | –          | –          | –          | 2013 [245] |
| SnS$_2$          | T(II)C = 0.8 M
TA = 0.5 M
NH$_3$ = 12 mL | TEA = 3.75 M
NH$_3$ = 12 mL | $T_b = 60$ °C
$t_d = 6$ h
pH = – | – | 2.58 (d) | HEX(001) | –          | –          | –          | 2017 [246] |
| Sn$_x$S$_y$ Phase | Precursors | Complexing Agent | Deposition Parameters | Structure | Band Gap (eV) | Electrical Parameters | Ref |
|------------------|------------|------------------|-----------------------|-----------|-------------|-----------------------|-----|
|                  |            |                  |                       |           |             |                       |     |
| SnS$_2$          |            |                  |                       |           |             |                       |     |
| SnS$_2$          | T(II)C     | TTA = 1 M        | $T_b = -$             | HEX(001)  | 2.95–2.80 (d) | n 11.2 48 10$^{17}$ | 2017 [56] |
|                  | TA         |                  | $t_d = 30$–120 min   | pH = –    |             |                       |     |
|                  |            |                  |                       |           |             |                       |     |
| SnS$_2$          | T(II)C = 0.84 g | TEA = 24 mL | $T_b = 60 ^\circ$ C | – – – – – | – – – – – | – – – – – | 2018 [247] |
|                  | TA = 0.5 M | NH$_3$ = 16 mL  | $t_d = 2$ h           | pH = –    |             |                       |     |
|                  |            |                  |                       |           |             |                       |     |
| SnS$_2$          | T(II)C = 0.1 M | TTA = 0.1 M | $T_b = 60 ^\circ$ C | HEX(001)  | 2.25–2.53 (d) | – – – – – | 2019 [248] |
|                  | TA = 0.1 M |                  | $t_d = 6$ h           | pH = –    |             |                       |     |
| SnS$_3$          |            |                  |                       |           |             |                       |     |
| SnS$_3$          | T(II)C = 1 M | TEA = 10 mL     | $T_b = 30 ^\circ$ C | ORT(131)  | 2.03–2.12 (d) | – – – – – | 2012 [34] |
|                  | TA = 1 M   |                  | $t_d = 20$–24 h      | pH = 10.7 |             |                       |     |
|                  |            |                  |                       |           |             |                       |     |
| SnS$_3$          | T(II)C = 1.4 g | TEA = 30 mL | $T_b = RT$            | ORT(211)  | 1.2 (d)     | – – – – – | 2012 [139] |
|                  | TA = 1 M   | NH$_3$ = 50 mL  | $t_d = 24$ h         | pH = –    |             |                       |     |
|                  |            |                  |                       |           |             |                       |     |
| SnS$_3$          | T(II)C = 0.05 M | SDS = 0.05 M | – – – – – – | ORT(021)  | 1.3 (d)     | – – – – – | 2018 [249] |
|                  |            |                  |                       |           |             |                       |     |
| SnS$_3$          | T(II)C = 0.1 M | TEA = 30 mL | $T_b = 17 ^\circ$ C | ORT(211)  | 1.75 (d)     | p $10^4$ 6 × 10$^{-6}$ | 2020 [250] |
|                  | TA = 0.1 M | NH$_3$ = 16 mL  | $t_d = 15$ h         | pH = –    |             |                       |     |
|                  |            |                  | 450 ^\circ$ C | (S-powder: 15 mg), 5–75 min |             |                       |     |
3.2. Sn and S Precursors and Their Concentration Effect

The selection of Sn precursor and its concentration plays a vital role in the growth, phase formation, crystallinity, preferred orientation, morphology, band gap, and other properties of Sn$_x$S$_y$ thin films [251]. This is because the releasing rate of Sn ions strongly depends on the selection of Sn precursors. As mentioned in Section 3.1, the SnCl$_2$·2H$_2$O (T(II)C) has been considerably utilized as an Sn precursor for the deposition of Sn$_x$S$_y$ films. According to the literature (Tables 4 and 5), until recently, there have been no reports related to the study of different types of Sn precursors on the formation of Sn$_x$S$_y$ films and the Sn precursor concentration effects on the formation of SnS$_2$ and Sn$_3$S$_3$ films and their properties. However, there have been very few quantitative analyses of Sn precursor concentration effect on the formation of o-SnS films and their properties. The primary report related to the effect of Sn precursor concentration ([T(II)C] = 0.06–0.12 M) on the growth of o-SnS films was made in 2012 [191]. A lower T(II)C concentration stimulates the formation of multi phases with a dominant SnS$_2$ phase, whereas a higher T(II)C concentration reduces the crystallinity. The T(II)C concentration of 0.1 M is beneficial for the deposition of pure, good crystalline o-SnS with (111) preferred orientation (Figure 7a). A small variation in T(II)C concentration (at 0.15 M) changes the preferred orientation of o-SnS from (111) to (200) [194]. Moreover, the change in T(II)C concentration can increase the grain size and decrease the band gap (1.95–1.5 eV) (Figure 7b,c) [191]. Therefore, the manipulation of preferred orientation, crystallinity, and band gap can be achieved by the change in Sn precursor concentration.

Figure 7. (a–c) XRD patterns, SEM images, and ($\alpha$hv)$^2$ versus (hv) graph of o-SnS films grown at various SnCl$_2$ concentrations (reprinted with permission [191]. © 2012, Elsevier), and variation in o-SnS film (d) thickness with different TA concentrations (reprinted with permission [145]. © 1987, Elsevier). (e,f) Morphology and crystallinity changes of o-SnS films with ST concentrations (reprinted with permission [187]. © 2012, Elsevier). (g) Variation in SnS film thickness with different TEA concentrations (reprinted with permission [145]. © 1987, Elsevier). (h,i) XRD patterns of the o-SnS films and c-SnS films deposited at different TTA (reprinted with permission [211]. © 2019, Elsevier) and EDTA concentrations, respectively (reprinted with permission [26]. © 2016, Elsevier). (j) XRD patterns of SnS$_2$ films deposited at various volumes of ammonia solution (reprinted with permission [41]. © 2012, Elsevier). (k) ($\alpha$hv)$^2$ versus (hv) for c-SnS films prepared using various EDTA amounts reprinted with permission [26]. © 2016, Elsevier). (l) SEM images of o-SnS films deposited with various TTA concentrations (reprinted with permission [211]. © 2019, Elsevier). (m,n) Scheme of the formation (reprinted with permission [185]. © 2011, Elsevier) and XRD patterns of o-SnS and c-SnS films (reprinted with permission [27]. © 2018, Elsevier). (o) Morphologies of o-SnS and c-SnS films (reprinted with permission [184]. © 2011, Elsevier), and (p) variation in the band gap o-SnS films at different pH values (reprinted with permission [27]. © 2018, Elsevier).
In addition to the suitable Sn precursor selection, the choice of S precursor and its concentration are highly desirable to obtain good quality Sn$_x$S$_y$ films. In CBD, the releasing rate (or reaction rate) of S ions greatly affect the growth kinetics and phase formation, and it can be controlled by the S precursor concentration. According to the previous reports (Tables 4 and 5), TA and ST have been chiefly used as S ion sources (Figure 5b). In those, TA is preferable compared to ST because it works in both acidic and alkaline bath conditions. The influence of TA concentration on o-SnS film growth (thickness) was initially reported in 1987 [145]. An extremely low or high TA concentration produces the o-SnS films of smaller terminal thickness, whereas a moderate TA concentration promotes the growth of maximum thickness (Figure 7d). The reason for the lower film thickness obtained at a lower S precursor concentration is the insufficient number of S ions in the reaction bath that can combine with all the available Sn ions. At a higher S precursor concentration, the releasing rate of S ions is high enough to stimulate the precipitation process, which also results in a lower film thickness [145].

Furthermore, the S precursor concentration can influence the morphology and phase formation of o-SnS films (Figure 7e). A higher TA concentration stimulates the formation of multi phases such as Sn$_2$S$_3$ and Sn$_3$S$_4$ (Sn$_2$S$_3$ + SnS $\rightarrow$ Sn$_3$S$_4$) [209] and a lower TA concentration assists the growth of single-phase o-SnS films, but with lower crystallinity [142,198]. A TA concentration of 0.1 M is preferable for the deposition of a single-phase, polycrystalline o-SnS with (101) preferred orientation [198], and a ST concentration of 0.75 M is advisable for (111)/(040) preferred orientation (Figure 7f). The effect of changes in the S source concentration on the band gap of o-SnS films is controversial until the present. A reduction in band gap from 1.70 eV to 1.25 eV with increasing TA concentrations was reported in [200], although no significant change in band gap was found with TA concentration in [198]. On the other hand, no studies in the literature have focused on the influence of S precursor concentration on the properties of c-SnS, SnS$_2$, and Sn$_2$S$_3$ films.

### 3.3. Complexing Agents and Their Concentration Effect

As stated in Section 3.1, in order to develop influential Sn$_x$S$_y$ films, the control of the availability of Sn ions in the reaction bath is essential. It can be successfully attained by the addition of an appropriate concentration of a complexing agent [128,148]. Moreover, adhesion, morphology, crystallinity, and the deposition rate of Sn$_x$S$_y$ films can be significantly affected by the concentration of the complexing agent [128]. Therefore, knowledge of the behavior of complexing agents in the bath can help to obtain good quality Sn$_x$S$_y$ films. The behavior of complexing agents is described in terms of their stability constants (K$_S$), which is the equilibrium constant for the formation of a complex in a solution [252]. It is defined for the equilibrium between an Sn ion (Sn$^{2+/4+}$) and a ligand (L) as [148]

$$K_S = \frac{a_{Sn^{2+/4+} - L}}{a_{Sn^{2+/4+}} a_L}$$  \hspace{1cm} (1)

where a is the activity of subscripted species and can be approximated by its concentration. A large value of K$_S$ implies a strong binding affinity for the metal (Sn) ion, while a small value of K$_S$ implies a weak binding affinity [148]. Generally, complexing agents can prevent the formation of powder/bulk precipitation of tin hydroxides in the reaction bath, and they can easily maintain the supersaturating condition. If a complexing agent has a weak binding affinity, it does not arrest the bulk precipitation of tin hydroxides. On the other hand, if it has an extremely strong binding affinity, it restricts the deposition of the desired film [253]. Therefore, in order to prevent powder/bulk precipitation of tin hydroxides, the complexing binding affinity must be intermediate.

Various complexing agents have been explored to control Sn ions depending on the bath conditions during the deposition of Sn$_x$S$_y$ films (Tables 4 and 5). However, there are only a few reports on the study of complexing agent concentration. Initially, the influence of TEA complexing agent concentration on the thickness of o-SnS films was made in 1987 [145]. An optimized TEA complexing agent concentration controls the formation of
o-SnS films, yielding a thick o-SnS film (Figure 7g). In addition to the growth (thickness), the change in TEA complexing agent concentration can also influence the phase formation and crystallinity of o-SnS, c-SnS, and SnS$_2$ films. The lower tartaric acid (TTA) complexing agent concentration creates weak tin complexation, leading to partial homogeneous precipitation, resulting in low-crystalline o-SnS films. As the complexing agent concentration increases, the improved tin complexation controls the reaction, yielding the formation of better crystalline films o-SnS. Over the limit, the availability of free Sn ions is reduced due to strong complexation, resulting in the formation of sulfur-rich tin phases such as Sn$_2$S$_3$ and SnS$_2$ (Figure 7h) [211]. Single-phase, polycrystalline o-SnS films with (111) preferred orientation are produced at 1.85 M of TEA [191] and 1.4 M of TTA [211], while a c-SnS (222)/(400) is formed at 0.125 M of EDTA [26] concentrations (Figure 7i). The crystallinity of o-SnS films can be improved by replacing the lower stability (Sn$^{2+}$-TEA) complexing agent with the higher stability (Sn$^{2+}$-EDTA) one [198,254], due to the fact that EDTA (hexa- ligand) may generate a ligand more quickly than TEA (triligand) [255]. An increase in citric acid and ammonia concentration also improves the crystallinity in the case of SnS$_2$ films (Figure 7j) [41,131]. The concentration of the complexing agent similarly influences the morphological and optical properties of the o-SnS, c-SnS, and SnS$_2$ films. The direct optical energy gap for o-SnS films reduces with increasing complexing agent concentration (TSC, 0.06–0.08 M; TEA, 12.5–13 M; TTA, 0.6–1.4 M) from 2.16 eV to 1.17 eV [50,182,214], but rises from 1.67 eV to 1.73 eV [26] for c-SnS films with EDTA (0.075–0.125 M) (Figure 7l). The change in complexing agent concentration (TSC, TTA) improves the compactness and morphology of o-SnS films (Figure 7m). This may improve their electrical properties, such as electrical mobility ($\sim$228 cm$^2$V$^{-1}$s$^{-1}$) and carrier concentration ($\sim$4.1 $\times$ 10$^{15}$ cm$^{-3}$). No previous study has examined the effect of complexing agents on the formation and physical properties of Sn$_2$S$_3$ films.

3.4. Solution pH Effect

In CBD, solution pH/bath pH (a measure of the acidity or basicity of a solution) is an important parameter because it directly affects the growth mechanism as well as reaction rate. Therefore, it can influence the formation of phases and physical properties of films [27]. In addition, the bath pH must be at a specific optimum value to maintain supersaturation condition ($Q_{sp} > K_{sp}$, Figure 5c) for the formation of Sn$_x$S$_y$ films. The preparation of Sn$_x$S$_y$ films was reported both in acidic (pH < 7) and alkaline (pH > 7) baths (see Tables 4 and 5). When the bath pH is varied between 1 and 14, the concentration of OH$^-$ ions increases, which results in a reduction in the concentration of free Sn$^{2+}$ or Sn$^{4+}$ ions in the solution. A higher bath pH, on the other hand, encourages the hydrolysis of a sulfur source precursor.

A few researchers have investigated the bath pH effect on o-SnS and c-SnS films growth and their physical properties (Table 4). The bath pH effect on the adhesion and growth rate of o-SnS films was first reported in 1989 [36]. According to this report, the good adhesion of o-SnS films on glass can be obtained with a bath pH >3. The growth rate is low at pH~7 and high at pH~10 for o-SnS films due to the formation of Sn(OH)$_2$ or 4 precipitate from the hydrolysis of an Sn precursor because a part of Sn(OH)$_2$ or 4 precipitate turns into Na$_2$SnO$_2$, which dissolves back in the solution. The change in growth rate by bath pH leads to the variation in grain size of o-SnS films [183]. The bath pH can also influence the growth mechanism, which leads to phase transformation [184,185]. An o-SnS forms at a lower pH of 6.5 via the cluster-by-cluster mechanism, whereas c-SnS forms at a higher pH of 7.0 through the ion-by-ion mechanism (Figure 7n,o) [27]. The phase transition caused by the change in bath pH leads to a change in the morphologies of the film surfaces (Figure 7o) and the energy band gaps (o-SnS: 1.51 eV and c-SnS: 1.64 eV) (Figure 7p) [27,184,185]. The increase in solution pH results in the decrease of free Sn$^{2+}$ ion concentration as well as the concentration of OH$^-$ ions, which are favorable for the hydrolysis of the S ion source [256], leading to the increase in the concentration of
S\(^{2-}\) ions. Thus, the interaction of Sn\(^{2+}\) and S\(^{2-}\) ions can form the c-SnS via an ion-by-ion mechanism because the potential barrier of heterogeneous nucleation is lower than that of homogeneous nucleation [25,185]. However, these mechanisms are speculated, and direct in situ measurement evidence such as in situ quartz crystal microbalance and electrochemical impedance is lacking. Therefore, such studies are required for understanding the growth mechanism of SnS\(_x\) films [257]. On the other hand, no studies in the literature have examined the effect of bath pH on the properties of SnS\(_2\) and SnS\(_3\) films.

### 3.5. Solution Temperature (T\(_b\)) Effect

In CBD, solution temperature/bath temperature (T\(_b\)) also played a crucial role in the preparation of thin films with high quality and desired features. It critically enhances the rate of dissociation of the precursors and thus strongly affects the thickness, growth rate, type of nucleation, crystalline phase, crystallite size, morphology, and optoelectrical properties of thin films. The change in film growth rate as a function of T\(_b\) can be determined through the Arrhenius equation [258],

\[
k(T) = A e^{-\frac{E_a}{RT}}
\]

where k(T) is the temperature-dependent growth rate for the given deposition conditions, A is a pre-exponential constant related to the initial reagent concentration, E\(_a\) is the activation energy (kJ/mol), and R is the gas constant (R = 8.3145 J mol\(^{-1}\) K\(^{-1}\)).

The deposition of Sn\(_x\)S\(_y\) films has been reported in the T\(_b\) range of room temperature (T\(_r\))—90 °C (Tables 4 and 5). The effect of T\(_b\) on the formation of o-SnS, c-SnS films, and their properties (Table 4) was studied extensively. The T\(_b\) changes the growth rate due to the variation in the deposition mechanism, i.e., the ion-by-ion mechanism, which is less thermally activated with low activation energy (at lower bath temperatures). In contrast, cluster-by-cluster is believed to occur at relatively higher temperatures [259]. Thus, the thickness of a film has a close relationship with the T\(_b\). First, it increases significantly with the T\(_b\) due to the increase in bath supersaturation [145,213] and reaches saturation point very quickly because the hydrolysis of the S precursor is greatly improved by the increase in T\(_b\) [182] (Figure 8a). Then, it decreases down to a terminal point because of the ion–ion condensation process and high homogeneous precipitation rate [145,146]. In addition, the T\(_b\) significantly affects the microstructures of o-SnS and c-SnS films.

Generally, the films prepared at lower T\(_b\) have smaller grains, and those grains increase in size with T\(_b\) due to the covering of voids by secondary nucleation (Figure 8b) [50,212]. The change in grain shape may indicate a change in the growth mechanism [146]. The T\(_b\) can also influence the composition of c-SnS films. The c-SnS films show a non-stoichiometric composition at higher and lower Tb values due to the relatively faster and slower release of Sn\(^{2+}\) ions from the tin complex due to the variation of thermal energy in the solution [50]. Single-phase, polycrystalline o-SnS films with (111) preferred orientation and c-SnS films with (222)/(400) preferred orientation are produced separately at T\(_b\) of 70 °C [212] and 65 °C [50] using a different source of materials (Table 4), respectively.

On the other hand, the T\(_b\) shows an impact on phase transformations when other bath parameters remained constant. The films predominantly exhibit the o-SnS phase above the T\(_b\) range of 30–40 °C, whereas the c-SnS phase is below this range (20–30 °C) for particular deposition conditions [146]. The T\(_b\) can directly affect the crystallinity of both o-SnS and c-SnS films. The crystallinity of both films is improved with T\(_b\) due to the supply of sufficient thermal energy for further crystallization (Figure 8c) [50,212]. Thus, an average crystallite size is improved with T\(_b\)—however, up to a certain extent [212]. As the T\(_b\) improves the kinetic energy of the reactants and accelerates the interaction between all ions in the reaction bath, the nuclei formation (crystallite grow) is enhanced on the surface of the substrate [260]. However, at higher T\(_b\), the crystallite size is decreased due to the dissolution of grown film.
The $T_b$ also influences the optical characteristics of the o-SnS and c-SnS films. In o-SnS films, the $T_b$ improves the sharpness of the absorption edge with a high optical absorption coefficient ($>10^4$ cm$^{-1}$) [17] (Figure 8d), which is suitable for PV devices. The optical energy gap of o-SnS and c-SnS films decreases from 1.41 eV to 1.30 eV and from 1.74 eV to 1.68 eV, respectively, with the increase in $T_b$ (30–70 °C) [17,50]. As mentioned above, $T_b$ can improve the grain size and simultaneously reduce height (smoothness of the surface) and the number of grain boundaries [261]; this minimizes imperfections in the film and enhances the quality of the film, which can lead to change in density of localized states within the energy gap [262]. Therefore, band gap tuning is easily possible in CBD deposited o-SnS and c-SnS films regarding $T_b$, which is essential for designing highly efficient solar cells [263]. The optical parameters, namely, refractive index (n), extinction coefficient (k), and real/imaginary dielectric constants of o-SnS films, are in ranges of 2.72–3.24, 0.24–0.13, and 7.34–10.48/0.85–1.32 [17], respectively (Figure 8e). Here, the variation in the optical parameters may be arrived from the change in strain and packing density with $T_b$ [264].

As previously mentioned, $T_b$ improves the crystallinity along with grain size and thickness. Thus, the scattering of charge carriers by grain boundaries decreases with respect to $T_b$, which makes a significant change in the electrical characteristics of films [265]. These possible reasons may improve the carrier density and a consequent reduction in resistivity in both o-SnS and c-SnS films. The reduction of the dispersing effects of carriers can lead to an increase in the mobility of carriers in those films (~55 cm$^2$ V$^{-1}$ s$^{-1}$ for
where \( \alpha \) is the fractional decomposition (or reaction), \( k \) is a rate constant, and \( n \) is the Avrami exponent.

There are a considerable number of reports on the study of the \( t_d \) effect on \( \alpha \)-SnS films, but there are only a few reports for \( \varepsilon \)-SnS [210,225], SnS\(_2\) [56], and SnS\(_2\)S\(_3\) [34] films (Tables 4 and 5). Typically, a \( t_d \) from a few minutes to several hours has been reported to prepare these Sn\(_x\)S\(_y\) films (Tables 4 and 5). The growth of Sn\(_x\)S\(_y\) films with \( t_d \) simply described in terms of thickness. In the initial state, the change in film thickness is insignificant because of the requirement of long incubation time for nucleation [198], and the thickness increases linearly due to the availability of sufficient amounts of Sn\(^{2+}\) or Sn\(^{4+}\) and S\(^{2-}\) ions. Next, the film thickness increases faster, then decreases at a longer deposition time, and attains a maximum value as a terminal/final thickness. Here, the attained terminal thickness is not only \( t_d \)-dependent but also \( T_b \)-related [145]. Thus, a terminal thickness should be considered when the reaction undergoes at a constant temperature. A terminal thickness in the range of 120–900 nm can be obtained for different \( t_d \) varying from 1 h to 24 h at a constant range of \( T_b \) (75 °C) for \( \alpha \)-SnS and \( \varepsilon \)-SnS films [128,145,175,198,225], and a thickness of 152 nm can be attained at a \( t_d \) of 90 min for SnS\(_2\) films (Figure 8g) [56]. The variation in the thickness (growth) of these films with respect to \( t_d \) can be explained by considering two competing processes taking place in the deposition bath. One process includes heterogeneous precipitation, which leads to film growth (thickness improves). The other involves the dissolution of the preformed film, which results in the decrease of film thickness.

The \( t_d \) has a significant impact on the surface morphology, crystallinity, crystallite size, and phase purity of Sn\(_x\)S\(_y\) films. As the \( t_d \) increases, the size and quantity of grains (or aggregations) can be improved to form a more homogeneous film [177] (Figure 8h). This indicates an occurrence of nucleation growth with \( t_d \) [56,190]. If \( t_d \) exceeds the optimum value, a non-uniform film with porous nature might be formed due to the dissolution of pre-adhered grains in the film [190]. This phenomenon can be experimentally observed for \( \alpha \)-SnS, SnS\(_2\), and SnS\(_2\)S\(_3\) films when the \( t_d \) varies between 2 and 10 h [177], 30–120 min [56], and 20–24 h [34], respectively. The \( t_d \) can considerably improve the crystallinity of the Sn\(_x\)S\(_y\) films and simultaneously enhance the crystallite size. However, beyond the limit of \( t_d \), the crystallinity becomes poor, and the crystallite size decreases (Figure 8i) [56,146,177,190,225]. The reduction of crystallite size is due to the lowering of the van der Waals force in between crystallites because the substrate remained in the solution longer than necessary [177]. In addition to the crystallinity of films, the \( t_d \) also influences the phase purity of a film. At low \( t_d \), the released Sn\(^{2+}\) or Sn\(^{4+}\) ions are relatively low in the reaction bath compared to the available S\(^{2-}\) ions. These available S\(^{2-}\) ions are not balanced by the all released Sn\(^{2+}\) or Sn\(^{4+}\) ions, leading to the development of other secondary phases, whereas at longer \( t_d \) they are counterbalanced, promoting the growth of the pure phase [56].
As mentioned previously, the $t_d$ directly influences the thickness of Sn$_x$S$_y$ films. Thus, it tremendously shows an impact on their optical transmittance/absorbance. Always, shorter $t_d$ periods generate the thinnest film of high transmittance, which might be affected by abundant porosities [175,177]. Simultaneously, the more extended $t_d$ periods produce thick films of high absorption [34,175,190], essential for solar cell application. The longer $t_d$ period also improves the size of crystallites that can affect the optical absorption and the band gap energy of films [190].

The quantum size effect and changing barrier height (or variation in grain size) are also responsible for the variation in the band gap of films with $t_d$ at other identical growth conditions [22,177]. The increase in $t_d$ period reduces the band gap of o-SnS, SnS$_2$, and Sn$_2$S$_3$ films from 1.83 eV to 1.30 eV [177], 2.95 eV to 2.80 eV [56], and 2.12 to 2.03 eV [34], respectively. In contrast, the longer $t_d$ period generates greater compression impacts with the thickness in o-SnS films, which may enhance the band gap (0.82–1.22 eV) [175]. In addition to the optical gap, $t_d$ shows a significant effect on the optical constants such as refractive index ($n$, SnS$_2$:2.57–2.63, Sn$_2$S$_3$: 4.89–7.18) and extinction coefficient ($k$, SnS$_2$: 0.69–0.61, Sn$_2$S$_3$: 0.0015–0.0019) (Figure 8j,k) [34,56]. However, no previous studies had included the variations in optical constants of o-SnS and SnS$_2$ films with $t_d$. On the other hand, the $t_d$ reduces the electrical resistivity and improves the carrier density and mobility of carriers in the case of both o-SnS and SnS$_2$ films [56,177] due to the improved crystallinity and suppression of secondary phases with $t_d$. In contrast, in the case of c-SnS and Sn$_2$S$_3$ films, there are no reports available in the literature.

### 3.7. Other Parameters

#### 3.7.1. Substrate Nature and Its Cleaning Process Effect

Generally, thin films require proper mechanical support that provides sufficient adhesion. These supports are commonly called substrates. Substrates have a significant effect on the film properties in practice [268]. Therefore, the choice of a suitable substrate with a specific form for a thin film with a particular application is critical since the substrate must be structurally and chemically compatible with the thin film material in terms of thermal and mechanical stability [266,270]. Moreover, the substrate nature strongly affects the preferred orientation of a thin film, which plays a major role in device performance [271]. Therefore, currently, the exploration of feasible substrates has become an active research area. The CBD has the benefit of allowing thin film deposition on unevenly shaped surfaces. However, the substrate nature greatly affects the deposition process and film quality. Usually, substrates with rough surfaces have better anchoring of the initial deposit in the tiny valleys. Substrates such as glass, tin oxide (TO), indium tin oxide (ITO), and silica/quartz are relatively reactive, owing to the presence of hydroxyl surface groups. Furthermore, when the lattice of the deposited material matches well with that of the substrate, the free energy change is smaller; this facilitates fast nucleation with good morphology and structure. Although the substrate nature has more impact on the process of CBD and the deposited thin film characteristics, there are only a few studies on this area in the case of o-SnS and SnS$_2$ films and no reports for c-SnS and Sn$_2$S$_3$ films (Tables 4 and 5). The reports related to the effects of molybdenum (Mo), ITO, and TO and borosilicate glass substrates [204] on the properties of o-SnS films and the glass, TO, and titanium (Ti) substrates [130] on SnS$_2$ films are available in the literature. At 0.01 M of Sn and S sources concentrations, both Mo and TO substrates generate o-SnS films with a better surface coverage, whereas the borosilicate glass and ITO substrates produce a discontinuous film with separate agglomerated o-SnS particles. When the concentration of sources is 0.03 M, all substrates except the borosilicate glass form a complete and uniform coverage of o-SnS films. At a high concentration of 0.09 M, all substrates produce a complete coverage of o-SnS films but with a lower adhesive nature [204]. In the case of SnS$_2$, the amorphous and n-type nature films formed on the glass and Ti substrates, respectively.

In addition to the substrate nature, the cleaning process of the substrate also significantly affects the quality of thin films. Improper cleaning of substrates results in the
formation of pinholes in the film, which creates major issues on the fabrication of large-area devices and produces short circuits in solar cells [272]. Unfortunately, there is a lack of research on this area for CBD deposited o-SnS, c-SnS, SnS₂, and Sn₂S₃ thin films.

3.7.2. Stirring Speed and Humidity Effect

In the CBD, chemical solutions with a homogeneous distribution of precursors are necessary before starting the process. Continuous mixing of the reaction solution is mandatory for realizing a uniform thin film deposition [273]. This could be achieved by stirring the solutions at appropriate speeds. At the beginning of the deposition, the stirring speed does not have a significant impact on the growth rate of thin films. However, for longer deposition times, it directly affects the growth rate. In addition, stirring with uneven speed may produce a variation in thin film uniformity and improper diffusion of complex ions toward the substrate [274], and stirring provokes precipitation and reduces the final thickness of the film. Therefore, care must be taken in stirring the solution to obtain the desired quality of thin films.

On the other hand, environmental humidity also influences the formation and physical properties of CBD processed films [273] since the CBD can be performed in an open environment where the gas–liquid interface is influenced by moisture. Even after the deposition of films, they considerably degrade because of their colloidal nature [275]. Therefore, the maintenance of environmental humidity is vital for the deposition of defect-free films. Although the control of stirring speed and environmental humidity is essential for producing quality SnₓSᵧ films, there is no systematic study on these effects in the literature.

3.8. Summary

SnₓSᵧ are binary metal chalcogenides that have attracted considerable attention due to their abundant, low cost, and nontoxic constituent elements. In comparison to other vacuum and chemical approaches, they may be simply synthesized utilizing a simple non-vacuum CBD methodology. Sn precursors, S precursors, and complexing agents are ideally T(II)C, TA, and TEA, respectively. The following lines are made based on the examination of published data (Tables 4 and 5) and the explanation in Sections 3.1–3.7. Changes in Sn precursor concentration, complexing agent concentration, and Tᵇ can be used to manipulate high-intensity plans and crystallinity. Maintaining complexing agent concentration, bath pH, and tᵈ may regulate phase transition and growth rate. Controlling S precursor and complexing agent concentrations results in good morphological, optical, and electrical characteristics. As a result, optimizing each deposition parameter is critical for producing high-quality SnₓSᵧ thin films for a variety of applications. However, no previous research has looked at the effect of S precursor concentration on c-SnS, SnS₂, and Sn₂S₃ films; complexing agent concentration on Sn₂S₃ films; bath pH on the properties of SnS₂ and Sn₂S₃ films; Tᵇ on both SnS₂ and Sn₂S₃ films; and tᵈ on c-SnS and Sn₂S₃ films. Furthermore, for all o-SnS, c-SnS, SnS₂, and Sn₂S₃ thin films, there is a dearth of research on the substrate nature-cleaning procedure, stirring speed, and humidity influence.

According to the description in this part, it is confirmed that further research is required to improve the quality of SnₓSᵧ films and more studies are necessary related to the optimization of all deposition parameters. Hence, research focusing on this area is essential.

4. Conclusions

SnₓSᵧ thin films deposited with CBD are a relatively recent development, and their process–property correlations must be understood for the desired application. Further, the fabrication of single-phase o-SnS, c-SnS, SnS₂, and Sn₂S₃ thin films in CBD is very condition-dependent. Additionally, it is crucial to identify and separate the o-SnS, c-SnS, SnS₂, and Sn₂S₃ phases. However, until recently, there has been a dearth of detailed studies on the optimization of growth parameters. The present review outlined the background and basic properties of SnₓSᵧ (o-SnS, c-SnS, SnS₂, and Sn₂S₃) along with the principle,
nucleation, growth, and growth mechanism of Sn$_x$S$_y$ thin films by CBD. Furthermore, the influence of growth parameters such as precursor concentration (tin source, sulfur source, and complexing agent), bath pH, bath temperature ($T_b$), deposition time ($t_d$) on the phase formation, and physical properties of Sn$_x$S$_y$ thin films were comprehensively described. As a result, the reader should be able to prepare single-phase tin sulfide materials with ease after studying the present article. Hence, the present review should motivate readers to conduct extensive investigations on Sn$_x$S$_y$ films to develop cost-effective, eco-friendly, and earth-abundant tin sulfide materials to meet all future energy requirements. The connection between the physical properties of Sn$_x$S$_y$ thin films and their photovoltaic application will be discussed in our subsequent article.

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**Abbreviations**

| Abbreviation | Chemical Name                                      |
|--------------|---------------------------------------------------|
| A            | Ammonia                                           |
| AA           | Acetic acid                                       |
| AC           | Ammonium citrate                                  |
| ACE          | Acetone                                           |
| AF           | Ammonium fluoride                                 |
| AH           | Ammonium hydroxide                                |
| ALD          | Atomic layer deposition                           |
| AS           | Ammonium sulfide                                  |
| BT           | Baking temperature                                |
| CA           | Citric acid                                       |
| CALPHAD      | CALculation of PHAse diagram                       |
| CBD          | Chemical bath deposition                          |
| CBM          | Conduction band minimum                           |
| CBO          | Conduction band offset                            |
| CSS          | Close space sublimation                           |
| CUB          | Cubic                                             |
| DDT          | Dodecanethiol                                     |
| DIW          | Deionized water                                   |
| DW           | Distilled water                                   |
| EDS          | Energy-dispersive X-ray spectroscopy              |
| EDTA         | Ethylenediaminetetraacetic acid                   |
| EL           | Electrolyte                                       |
| FF           | Fill factor                                       |
| G            | Glass                                             |
| GA           | Glacial acetic acid                               |
| GIXRD        | Grazing incidence X-ray diffraction               |
| HCL          | Hydrochloric acid                                 |
| HEX          | Hexagonal                                         |
| HH           | Hydrazine hydrate                                 |
| HWVD         | Hot wall vapor deposition                         |
| ITO          | Indium tin oxide                                  |
| JCPDS        | Joint committee on powder diffraction standards   |
| Abbreviation | Compound |
|--------------|----------|
| Li           | Lithium  |
| MeOH         | Methanol |
| Mo           | Molybdenum |
| Na           | Sodium   |
| Na₂EDTA      | Disodium ethylenediaminetetraacetate |
| NTA          | Nitriloacetic acid |
| ODE          | Octadecene |
| OLA          | Oleylamine |
| ORT          | Orthorhombic |
| PG           | Propylene glycol |
| PL           | Photoluminescence |
| QE           | Quantum efficiency |
| RS           | Rock salt |
| SAED         | Selected area electron diffraction |
| SCR          | Space charge region |
| SDS          | Sodium sulfide |
| Si           | Silicon |
| SILAR        | Successive ionic layer adsorption and reaction |
| SIMS         | Secondary ion mass spectrometry |
| SS           | Stainless steel |
| SnS          | Tin monosulfide |
| SnS₂         | Tin disulfide |
| Sn₂S₃        | Tin sesquisulfide |
| ST           | Sodium thiosulfate |
| TA           | Thioacetamide |
| T(II)C       | Tin (II) chloride dehydrate |
| TC(IV)       | Tin(IV) chloride pentahydrate |
| TEA          | Triethanolamine |
| TEM          | Transmission electron microscopy |
| Ti           | Titanium |
| TO           | Tin oxide |
| TOP          | Triocetylphthyline oxide |
| Tr           | Room temperature |
| TSC          | Trisodium citrate |
| TTA          | Tartaric acid |
| TU           | Thiourea |
| UAED         | Ultrasound-assisted electrodeposition |
| VBM          | Valence band maximum |
| XRD          | X-ray diffraction |
| ZB           | Zinc blended |

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