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Effects of triethanolamine on the morphology and phase of chemically deposited tin sulfide

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ABSTRACT

Effects of triethanolamine (TEA) on tin sulfide films grown by chemical bath deposition were explored. Nanostructures were observed in the samples employing TEA in precursor solutions, and different morphologies, i.e. spherically assembled nanoflakes, continuous nanoflake films and solid nanospheres could be resulted at low, medium and high TEA concentrations respectively. The phases of the nanoflakes and solid nanospheres were characterized as orthorhombic SnS and orthorhombic Sn_2S_3 by SAED and HRTEM. In order to explore the growth mechanisms, models regarding different TEA concentrations, especially the molecular modeling of the role played by TEA in complex formation, were proposed. Good agreements between the experimental observation and theoretical predications are obtained, which not only indicates scientific insights to the formation mechanisms but also provides practical guides to morphological modifications of tin sulfide films.

1. Introduction

Tin sulfide is an intriguing semiconductor material that has gained much attention owing to its narrow direct band gap of 1.3 eV [1] that enables its novel applications including photocatalyst [2,3] and absorber layers of solar cells [4–6]. A variety of methods have been utilized to prepare tin sulfide thin films, such as hydrothermal synthesis [5], electrochemical deposition [7], sputtering [8] and physical vapor deposition [9]. Chemical bath deposition (CBD) is also among the most widely adopted methods, largely because of its simple requirements for experimental setup as well as its possibility to be carried out at ordinary atmospheric pressure and relatively low temperature [10].

The morphology and phase of the tin sulfide thin films deposited by CBD are affected by multiple factors including pH [11], precursor concentration and temperature [12]. Complexing agent is another crucial variable in determining the growth rate, structure, morphology and thus several properties of tin sulfide thin films [13,14]. Intensive studies on the interactions of metal ions and organic complexing agents have been conducted. For example, Dumitriu et al. [15] have modeled the complexes and supramolecules formed by Cu^{2+}, Ni^{2+} and triethanolamine (TEA), and de Leon et al. [16] have proposed molecular models describing the interactions between TEA and Pb^{2+} as well as PbS. However, the complexing and formation of supramolecules between Sn^{2+} and TEA, an extensively applied complexing agent, receive less exploration. Furthermore, the extant models of complexing molecules and supramolecules are rarely applied to offer explanations for the impacts of complexing agents on the morphology and phase of tin sulfide prepared by CBD.

In this study, we focus on the role of the concentration of TEA on tin sulfide nanostructures. While the morphologies and phases of the as-prepared nanostructures are examined, explanations for the varying morphology and phase associated with different amount of TEA are also provided using models of Sn–TEA complexes and supramolecules.

2. Experimental details

The soda lime glass slides used as substrates were sonicated in Micro-90, acetone and ethanol for 15 min sequentially. To prepare the precursor, 0.95 g $SnCl_2$ was dissolved in 5 mL acetone. 20 mL, 0.4 M thioacetamide (TAA) solution in water used as the sulfur source was firstly added in a beaker. Then, a certain volume of 98% TEA, 4 mL 28% ammonia and DI water were added subsequently to reach a total volume of 60 mL. $SnCl_2$ solution was then added to the beaker. The system was stirred until a homogeneous solution was formed, after which the pH was measured to be 9. A glass substrate was vertically immersed into the solution, held by a clip with a thin ceramic stick threaded through it, the two ends of which were placed on the rim of the beaker. The system was then

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kept in a 75 °C water bath for 1 h. After deposition, the sample was sonicated in DI water for 10 min and dried with nitrogen blow. The amounts of TEA added and the morphologies of the obtained films are listed in Table 1.

Scanning electron microscopy (SEM) images of the as-prepared films were acquired using a field emission scanning electron microscope (FE-SEM) (ZEISS SUPRA™ 40) with the accelerating voltage of 3 kV. The transmission electron microscopy (TEM) images, selected area electron diffraction (SAED) patterns and high resolution TEM (HRTEM) images were obtained using a transmission electron microscope (JEOL 100CX 2010F) with accelerating voltage of 200 kV.

3. Results and discussions

Characterization of as prepared samples: The SEM images of samples prepared with different TEA concentrations (S1–S4) are shown in Fig. 1. In S1 with 2 mL TEA added, dispersed spherical assemblies of nanoflakes are observed, the diameter of which is in the range of 0.5–1 μm. In S2 with 4 mL TEA, free-standing nanoflakes are deposited. In S3 with 8 mL TEA, the nanoflakes possess better uniformity and more continuous coverage. For S4 with 10 mL TEA, solid spheres with a diameter of 0.5–1 μm are formed, some of which have nanoflakes inset. The coverage of the film is reduced. The morphological features are further confirmed by the TEM images (Fig. 2a, d, g and j). A detailed analysis on the formation mechanisms at different TEA concentration will be discussed in *Growth mechanism* to explain the different morphologies observed.

The structures of the as-synthesized samples are investigated by HRTEM and SAED. As in Fig. 2b, the SAED pattern taken for a nanoflake in S1 can be indexed with the lattice planes of orthorhombic SnS (PDF-39-0354) with a zone axis of [213]. This is also confirmed by the HRTEM image (Fig. 2c), in which the lattice fringe spacing is 3.40 Å, corresponding to the {120} plane of the orthorhombic SnS. The SAED patterns for the freestanding nanoflakes in S2 and S3 can be matched to orthorhombic SnS as well (Fig. 2e and h). Such results are confirmed by the HRTEM images (Fig. 2f and i), where the lattice fringe spacings are measured to be 3.22 Å and 3.39 Å, in good correspondence with the {021} and {120} planes of orthorhombic SnS, respectively. However, the phase of the nanosphere in S4 is judged to be orthorhombic Sn_2S_3 (PDF-14-0619) according to the indexing of its SAED pattern (Fig. 2k) where the zone axis is $[21\bar{4}]$.

Growth mechanism: The mechanism of chemical deposition of binary chalcogenide thin films exhibits a strong dependence on the concentration of complexing agents relative to that of metal ions [17–19]. With the presence of TEA, Sn^{2+} ions take Sn–TEA complexes rather than free ions as the primary form, and the formation of the nanostructures is dominated by a complex-decomposition mechanism. For S1–S3, the following reactions are deduced [19–21]:

$$CH_3CSNH_2 + 2OH^- \rightarrow HS^- + CH_3COO^- + NH_3 \tag{1}$$

$$Sn^{2+} + n(TEA) \leftrightarrow Sn(TEA)_n^{2+} \tag{2}$$

$$Sn(TEA)_n^{2+} + 2OH^- \rightarrow Sn(OH)_2 + nTEA \tag{3}$$

$$Sn(OH)_2 + HS^- \rightarrow SnS + H_2O + OH^- \tag{4}$$

The stability constant K for the Sn–TEA complexing process (Eq. (2)) is dictated by the van't Hoff equation [22]

$$\frac{d\ln K}{dT} = \frac{\Delta H_m^0}{RT^2} \tag{5}$$

where R is the gas constant, T is the temperature and ΔH_m^0 is the standard enthalpy change. With ΔH_m^0 for complexing process generally negative [23–25], the stability constant declines when the system is heated to the reaction temperature (75 °C in our case), which provides the driving force for more complexes to decompose and release Sn^{2+}. Besides, the consumption of free

Table 1
Summary of TEA amounts and morphologies of tin sulfide thin films.

Sample	TEA (mL)	Obtained morphology
S1	2	Spherically assembled nanoflakes
S2	4	Predominantly unassembled nanoflakes and a few clusters tending to form spherical assemblies
S3	8	Unassembled nanoflakes
S4	10	Solid spheres with unassembled nanoflakes on the top

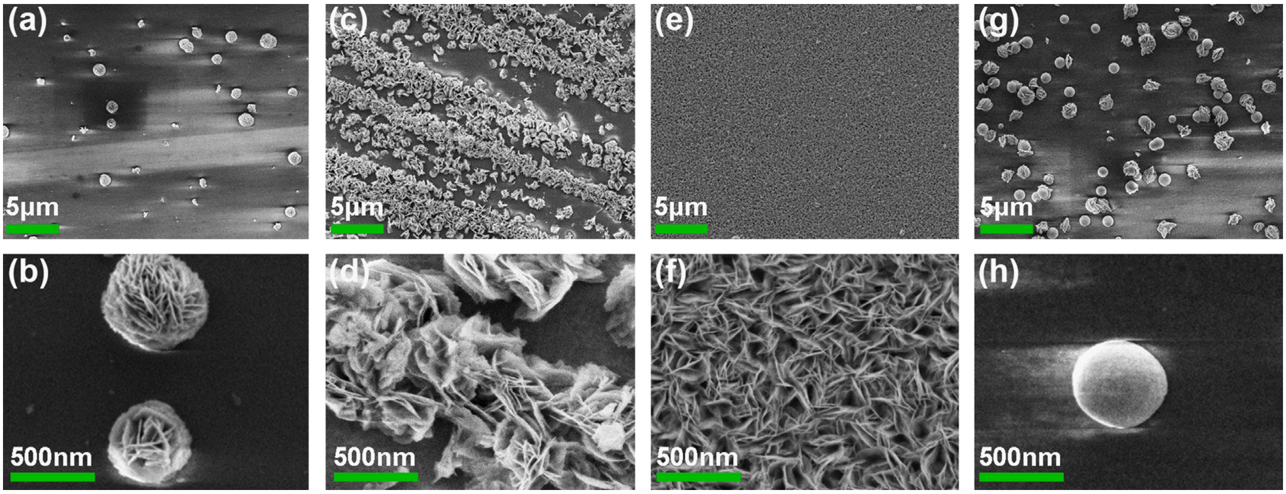

Fig. 1. SEM images of (a, c, e, g) sample S1–S4 and (b, d, f, h) their magnified morphological features.

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