



Direct solution deposition of device quality $\text{Sb}_2\text{S}_{3-x}\text{Se}_x$ films for high efficiency solar cells



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ABSTRACT

$\text{Sb}_2\text{S}_{3-x}\text{Se}_x$ ($0 \leq x \leq 3$) is promising for practically applicable solar cell since it possesses excellent stability, suitable band gap, high extinction coefficient and abundant elemental storage. This study demonstrates a novel methodology towards simultaneous dissolution of Se and Sb_2O_3 for direct deposition of $\text{Sb}_2\text{S}_{3-x}\text{Se}_x$ films. Mechanistic study shows that the formation of selenium-nitrogen free radical in sulfur-containing complex is responsible for the dissolution of selenium. The energy levels of the as-synthesized $\text{Sb}_2\text{S}_{3-x}\text{Se}_x$ were examined by synchrotron radiation photoemission spectroscopy, revealing that more Se in the $\text{Sb}_2\text{S}_{3-x}\text{Se}_x$ leads to the valence band shifting considerably upward while the conduction band remaining nearly unchanged. Moreover, for the first time we present that the solution processed $\text{Sb}_2\text{S}_{3-x}\text{Se}_x$ can generate photovoltaic performance with an efficiency of 5.8%. This research provides a straightforward strategy for the fabrication of $\text{Sb}_2\text{S}_{3-x}\text{Se}_x$ solar cells and offers an effective method for the synthesis of metal selenosulfide films.

1. Introduction

Solution deposition of functional thin film is particularly attractive in that it offers opportunity for employing cost-effective and convenient film fabrication strategies such as spin-coating, ink-jet printing and roll-to-roll printing [1,2]. This approach has been proved very successful in the fabrication of $\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$ (CZTSSe) [3], organic-inorganic hybrid perovskite [4,5] as well as semiconducting polymer films for solar cell applications [6–8]. The past research has indicated that the discovery of appropriate processing strategy is critical for obtaining high quality film and in turn high power conversion efficiency (PCE) in a complete device. For instance, high efficiency CZTSSe solar cells are dominantly achieved in hydrazine-based solution processed active layers [3,9]. In general, the delicate selection of solvent system and precursor materials, coupling with suitable processing condition, has profound impact on the optoelectronic properties of the absorber layer and the final device performance [2,10].

$\text{Sb}_2\text{S}_{3-x}\text{Se}_x$ ($0 \leq x \leq 3$) is a class of unconventional photovoltaic materials with bandgap ranging from 1.1 to 1.7 eV when x changing from 3 to 0 [11–19]. These materials possess suitable energy gap, high extinction coefficient, abundant element storage and excellent stability, promising for light absorption materials in practical solar cells.

According to the Shockley–Queisser limit for theoretical maximum efficiency of a solar cell, semiconductor with bandgap between 1.10 and 1.55 eV possesses the greatest potential for highly efficient single-junction solar cells [20,21]. Therefore, developing effective method for tailoring the atomic ratio of S/Se in $\text{Sb}_2\text{S}_{3-x}\text{Se}_x$ is crucial for obtaining superior photovoltaic activity. To this end, a vapor deposition method was developed where the reaction between S vapor and pre-synthesized Sb_2S_3 film could generate $\text{Sb}_2\text{S}_{3-x}\text{Se}_x$ film with broad S/Se ratios [22]. By utilizing a two-step solution approach, Seok and coworkers firstly sensitized mesoporous TiO_2 nanoparticles by deposition of a layer of Sb_2S_3 . Afterwards, an over layer of Sb_2S_3 was deposited onto the Sb_2S_3 surface by chemical bath deposition (CBD). The inter-diffusion between S and Se drives the formation of composition graded $\text{Sb}_2\text{S}_{3-x}\text{Se}_x$ [11]. Recently, our group synthesized selenium-graded $\text{Sb}_2\text{S}_{3-x}\text{Se}_x$, in which the Sb_2S_3 was firstly synthesized by a CBD, followed by reaction with selenium to form selenium-graded $\text{Sb}_2\text{S}_{3-x}\text{Se}_x$ for solar cell applications [23].

In film fabrication, vapor deposition usually requires high cost vacuum apparatus while two-step solution approach adds complexity in device fabrication. In this case, one-step solution synthesis of absorption film would significantly simplify the device fabrication, increase the reproducibility and reduce the cost. One of the critical challenges in

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the direct synthesis of $\text{Sb}_2\text{S}_{3-x}\text{Se}_x$ lies in the simultaneous dissolution of antimony, selenium and sulfur or their corresponding compounds in a solution [24]. A few efforts have made towards the direct synthesis of $\text{Sb}_2\text{S}_{3-x}\text{Se}_x$. For instance, the Brutchey group developed a thiol-amine solvent mixture for dissolving the metal oxide, selenium and sulfur, through spin-coating and post annealing, the film is converted into $\text{Sb}_2\text{S}_{3-x}\text{Se}_x$ [25]. In addition, hydrazine is a powerful solvent in the synthesis of CZTS films, it is also applicable for the synthesis of $\text{Sb}_2(\text{S}_{1-x}\text{Se}_x)_3$ [17]. However, these studies do not report any device performance, which raises a concern regarding the photovoltaic quality of the as-synthesized $\text{Sb}_2\text{S}_{3-x}\text{Se}_x$ films.

Herein, we demonstrate a novel method towards simultaneous dissolution of selenium and Sb_2O_3 powders for the direct synthesis of $\text{Sb}_2\text{S}_{3-x}\text{Se}_x$ films. Furthermore, the film is able to deliver photovoltaic energy conversion of 5.8% in planar heterojunction solar cell using TiO_2 and 2,2',7,7'-tetrakis(*N,N*-di-*p*-methoxyphenylamine)-9,9'-spirobifluorene (Spiro-OMeTAD) as electron and hole selection materials, respectively.

2. Results and discussion

For the preparation of molecular precursor, carbon disulfide (CS_2), *n*-butylamine (nBA) and *N,N*-dimethylformamide (DMF) are mixed together to form a homogeneous solution. Previously, the reaction between CS_2 and alkylamine in ethanol can generate alkyldithiocarbamic acid (compound I in Reaction i) (Fig. 1a) [26–28]. This complex is able to dissolve a series of metal oxide and hydroxide [26–28]. However, the alcoholated alkyldithiocarbamic acid is unable to dissolve selenium (Fig. S1), which renders the synthesis of metal sulfide-selenide impossible by using this reaction system. In this study, a new dissolution mechanism is disclosed by utilizing DMF as a weak basic solvent, which enables simultaneous dissolution of Se and Sb_2O_3 with CS_2 and nBA in the solution. This dissolution produces optically transparent solutions

with a series of Se/Sb concentrations which are stable for several days (Fig. 1b).

Presumably, the dissolution of selenium can be in the form of either dispersed tiny nanoparticles or molecular compound. To verify this assumption, we firstly conducted Raman scattering characterization of the mixture containing CS_2 , nBA, DMF and selenium. As a result, there is no typical Raman scattering Se chains ($230\text{--}260\text{ cm}^{-1}$) and Se_8 ($250\text{--}275\text{ cm}^{-1}$) observed (Fig. S2) [24,29], indicating that the formation of selenium nanoparticles is less possible. To study whether there is new selenium containing molecule formed, electron spin resonance (ESR) measurement was conducted. As a control characterization, the mixture of CS_2 , nBA and DMF did not show any radical signal (Fig. 1c, c1). Once selenium power is introduced into solution, three peaks with similar height are observed and the middle value of *g* equals to 2.0410 (Fig. 1c, c2). The shape of ESR spectrum is identical to that of (2,2,6,6-tetramethylpiperidin-1-yl)oxidanyl (TEMPO) where there is O-N radical (Fig. 1c), except that the *g* value is shifted to 2.0048. This observation indicates that a complex containing Se-N free radical is formed in the selenium dissolved solution. The *g* variation is ascribed to the smaller electronegativity of Se when compared with O atom, leading to the electron density of N atom in O-N being greater than that in Se-N. The free radical characteristic was also confirmed by UV light irradiation of the solution sample. It turns out that the ESR signal is completely disappeared after irradiation for 150 s (Fig. S3). Furthermore, Fourier Transform infrared spectroscopy (FTIR) characterization (Fig. S4) of this solution exhibits nearly identical spectrum to that of I in reaction i. Therefore, Se-N radical is most likely existed as complex II as shown in Reaction ii (Fig. 1a). When Sb_2O_3 is added to selenium solution, the positions of these peaks in ESR (Fig. 1c, c3) and FTIR (Fig. S4) remain unchanged, suggesting that the molecular skeleton is retained. In this case, the dissolution of Sb_2O_3 is expected to form compound III (Fig. 1a, Reaction iii). The co-existence of sulfur and selenium in compound III offers possibility for the transformation to

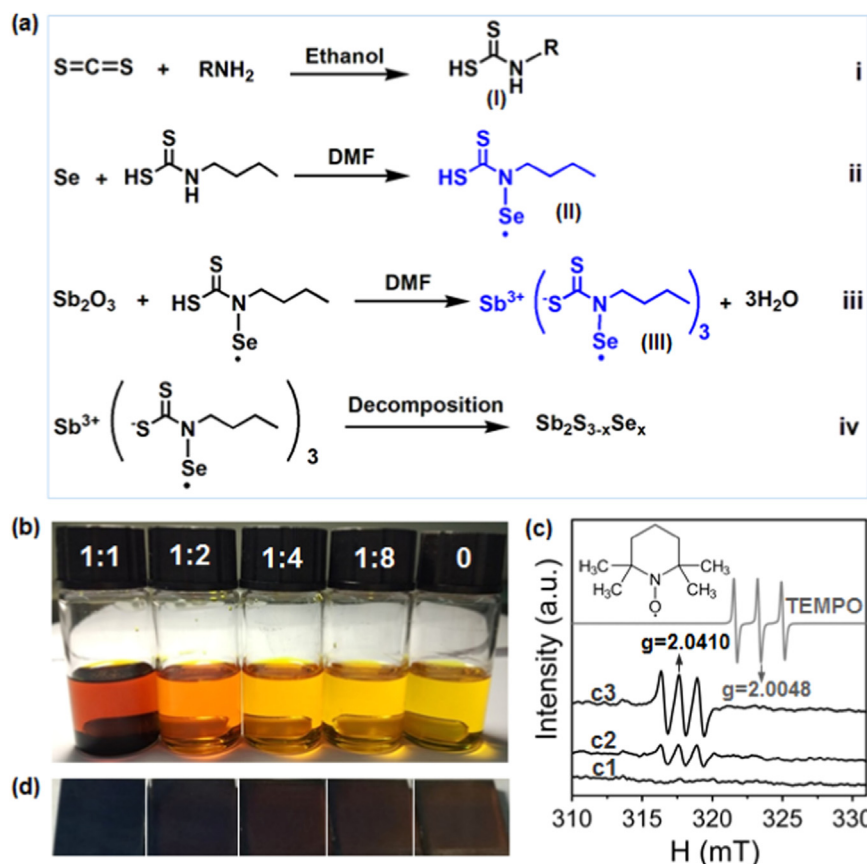


Fig. 1. (a) Proposed reaction pathways toward the synthesis of $\text{Sb}_2\text{S}_{3-x}\text{Se}_x$, (b) digital images of the solutions prepared with Se/Sb atomic ratios of 1:1 (saturated solution), 1:2, 1:4, 1:8 and 0, respectively; (c) electron spin resonance characterization of the as-synthesized solutions composed of (c1) $\text{CS}_2 + \text{nBA} + \text{DMF}$, (c2) $\text{Se} + \text{CS}_2 + \text{nBA} + \text{DMF}$, (c3) $\text{Se} + \text{Sb}_2\text{O}_3 + \text{CS}_2 + \text{nBA} + \text{DMF}$, tempo solution; (d) digital image of the as-synthesized film with Se/Sb atomic ratios of 1:1, 1:2, 1:4, 1:8 and 0 in the precursor solutions.

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