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Aerosol assisted chemical vapor deposition of Sb_2S_3 thin films: Environmentally benign solar energy material

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ABSTRACT

Antimony sulfide (Sb_2S_3, stibnite) is an important environmentally benign material which finds applications in solar cells, thermoelectric devices, switching devices, microwaves and television cameras. Orthorhombic (stibnite) Sb_2S_3 thin films have been deposited by Aerosol-Assisted Chemical Vapor Deposition (AACVD), spin coating, melt and the doctor's blade methods using *tris*(thiobenzoato)antimony (III) complex as a single source precursor. The p-XRD pattern of thin films deposited by all the methods show the deposition of Sb_2S_3 (stibnite). The morphology of the films is typically based on sheets, thick plates or bundles of sticks with varying sizes depending on the technique used and/or the deposition temperature. The EDX analysis showed that the films deposited at all temperatures by all methods are antimony rich. The band gaps of the films deposited by AACVD range from 1.81 to 1.90 eV.

1. Introduction

For the last few decades binary chalcogenides material such as M_2X_3 (M=As, Sb, Bi; X=S, Se, or Te) have attracted much attention due to their unique electrical and optical properties [1–3] and their potential applications in photovoltaic and thermoelectric devices [4–6].

Among these materials the antimony sulfide (Sb_2S_3 stibnite,) has applications in solar cells, [7, 8] thermoelectric devices [9], switching devices [10], microwave [11] and television cameras [12]. It is also useful material for 'write-once-read-many times' type of optical storage devices. The band gap reported for thin films of this material range from 1.73 eV to 2.57 eV [13–15] with strong absorption coefficient ($1.8 \times 10^5\ cm^{-1}$), and is relatively environmentally benign material [16–19]. Its good photoconductivity and wide range of band gap covers the visible and near IR range of the solar energy spectrum [20]. Thin films of Sb_2S_3 have demonstrated unique photosensitivity and thermoelectric properties [21–24]. Various deposition techniques have been used to deposit antimony sulfide including: chemical bath deposition [25–27], spray pyrolysis [28,29], electrodeposition [30], tarnishing reactions [31], dip–dry technique [32] and successive ionic layer adsorption and reaction method [33].

There are only three reports by Molloy et al. [34–36] on deposition of antimony sulfide thin films using single-source precursors. They reported the deposition of Sb_2S_3 thin films by AACVD using unsymmetrical antimony(III) dithiocarbamates, $[Sb(S_2CN(Me)R)_3]$ (R=Bu, Hex, Bz) [34] and by Low Pressure (LP) CVD route using volatile antimony thiolates, $Sb(SR)_3$ (R=But, CH_2CF_3) [35]. The films deposited by AACVD were heavily contaminated with Sb_2O_4, $Na_3Sb_2S_4$ and KSb_5S_8. The oxygen contamination increases with the increase in deposition temperature. Those deposited from the thiolates by LPCVD were predominantly Sb_2S_3 but contaminated with antimony. The morphologies of the films were dependent on the type of substrate (glass or silicon). Films deposited on glass substrate had a band gap of 1.6 eV. Molloy et al. also used dithicarbamates $[Sb(S_2CNR(R))]_3$, dithiophophates $[Sb(S_2P(OR)_2)]_3$, and dithiocabonates $[Sb(S_2COR)_3]$ by solvothermal and hydrothermal routes and $[Sb(S_2COR)_3]$ by AACVD [36]. The oxygen contamination was the problem in each case.

Herein we report the first oxygen free deposition of orthorhombic stibnite (Sb_2S_3) thin films by AACVD, spin coating, melt and doctor blade methods from *tris*(thiobenzoato)antimony(III) complex as single source precursor.

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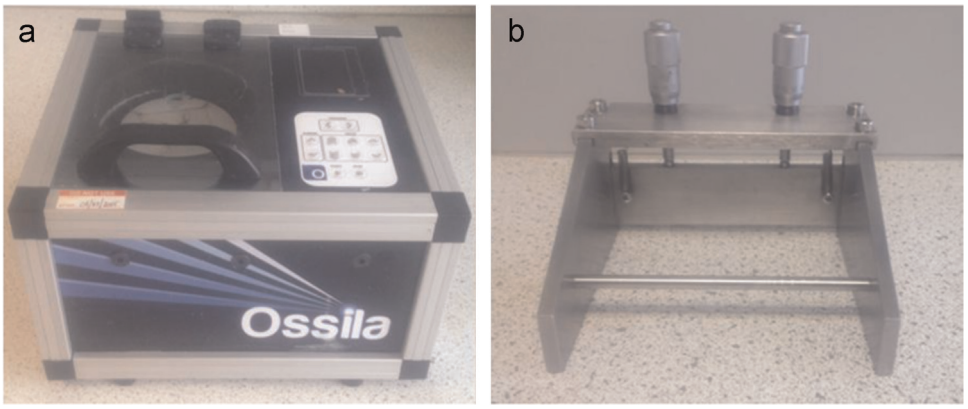
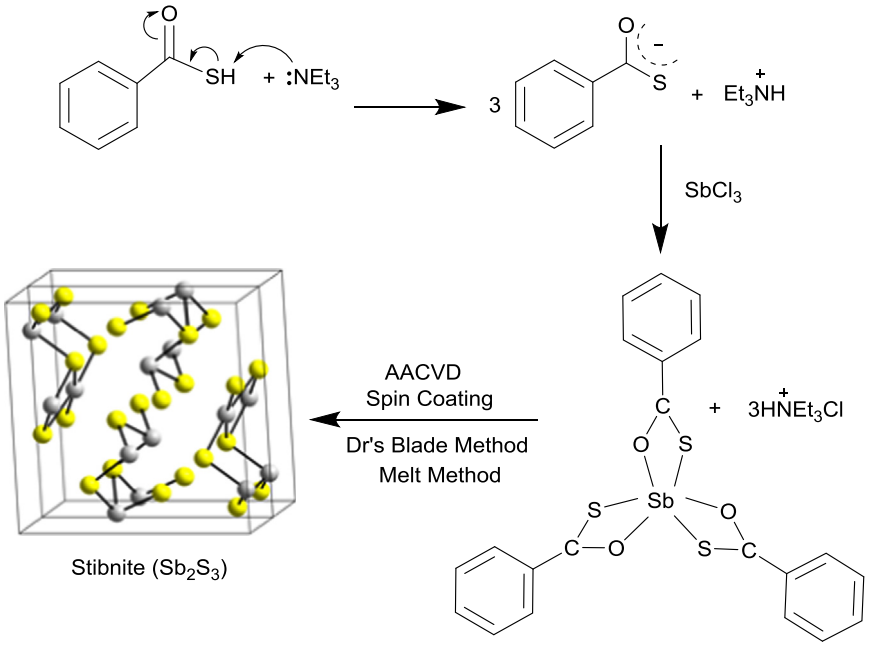


Fig. 1. (a) Ossila spin coater used for spin coating, (b) doctor blade coater.



Scheme 1. Scheme for the synthesis of Sb_2S_3.

Table 1
Summary of deposition results.

Deposition methods	Deposition temperatures (°C)	Sb: S (EDX analysis)	Stoichiometric formula	Morphology
AACVD	300	41: 59	$Sb_{2.05}S_{2.95}$	Sheets
	350	44: 56	$Sb_{2.2}S_{2.8}$	Thinner plates
	400	43: 57	$Sb_{2.15}S_{2.85}$	Thick short rods
Spin coating	300	43: 57	$Sb_{2.15}S_{2.85}$	Large sheets
	350	41: 59	$Sb_{2.05}S_{2.95}$	Large sheets
	400	43: 57	$Sb_{2.15}S_{2.85}$	Large sheets
Melt method	300	44: 56	$Sb_{2.2}S_{2.8}$	Sheet bundles
	350	39: 61	$Sb_{1.95}S_{3.05}$	Sheet bundles
	400	47: 53	$Sb_{2.35}S_{2.65}$	Sheet bundles
Doctor's blade method	300	40: 60	Sb_2S_3	Thick sheets
	350	41: 59	$Sb_{2.05}S_{2.95}$	Thick bundles
	400	38: 62	$Sb_{1.9}S_{3.1}$	Thick bundles

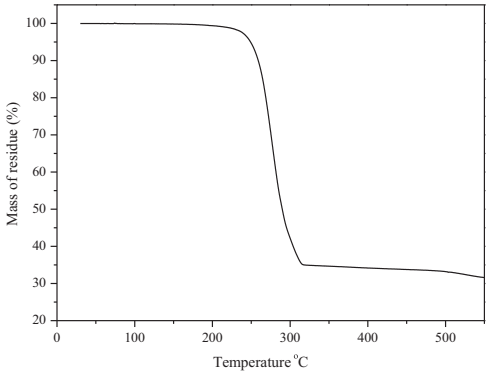


Fig. 2. Thermogravimetric analysis of *tris*(thiobenzoato)antimony(III) complex at heating rate of 10 °C min^{-1} under nitrogen.

2. Experimental

All reagents were purchased from Sigma-Aldrich and used as received. Solvents were distilled prior to use. Elemental analysis and TGA measurements were performed by the University of Manchester micro-analytical laboratory. Infrared spectra were recorded on a Specac single reflectance ATR instrument (4000–400 cm^{-1}, resolution 4 cm^{-1}) and melting points on the Barloworld SMP10 Melting Point Apparatus. p-XRD studies were performed on a Bruker AXSD 8 diffractometer using CuKα radiation and scanned between 20° and 70° in a step size of 0.05 with a varying count rate depending upon the sample. SEM analysis of