



## Indium sulfide buffer layers deposited by dry and wet methods

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#### Abstract

Indium sulfide ( $In_2S_3$ ) thin films have been deposited on amorphous glass, glass coated by tin oxide (TCO) and crystalline silicon substrates by two different methods: modulated flux deposition (MFD) and chemical bath deposition (CBD). Composition, morphology and optical characterization have been carried out with Scanning Electron Microscopy (SEM), IR-visible-UV Spectrophotometry, X-ray diffraction (XRD) and Fourier transform infrared (FTIR) spectrometer. Different properties of the films have been obtained depending on the preparation techniques. With MFD,  $In_2S_3$  films present more compact and homogeneous surface than with CBD. Films deposited by CBD present also indium oxide in their composition and higher absorption edge values when deposited on glass.

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#### 1. Introduction

Thin film solar cells based on Cu(In,Ga)Se<sub>2</sub> and CuInS<sub>2</sub> semiconductors have reached conversion efficiencies of 19.5% and 14%, respectively[1–3]. Such values are achieved by using a CdS buffer layer, deposited by chemical bath deposition (CBD). Due to the toxicity of CdS other alternatives are sought to replace it, like ZnO, ZnSe, SnS<sub>2</sub>, ZrO<sub>3</sub>, SnO<sub>2</sub>, In<sub>2</sub>S<sub>3</sub> etc. [4-6]. In<sub>2</sub>S<sub>3</sub> is an interesting candidate with band gap between 2.0 and 2.45 eV, depending on thin film composition. The In<sub>2</sub>S<sub>3</sub> buffer properties are strongly determined by the preparation procedure. Different methods are used in film preparation, like dry methods: spray pyrolysis [7], reactive evaporation [8], atomic layer deposition (ALD) [9], metal-organic chemical vapor deposition (MOCVD) [10] etc., and wet methods as chemical bath deposition (CBD) [11], electrodeposition [12], ion layer gas reaction (ILGAR) [13]. Both kinds of methods have given In<sub>2</sub>S<sub>3</sub>-buffers which reached high efficiencies of 16.4% for ALD [14] and of 15.7% for CBD techniques [15] on Cu(In,Ga)Se<sub>2</sub> absorber. These high efficiency values are approaching those obtained with standard CdS buffers and justify further development to investigate the properties of In<sub>2</sub>S<sub>3</sub> films grown by both dry and wet procedures.

In this work, indium sulfide thin films were prepared by modulated flux deposition (MFD), in vacuum from elemental evaporation sources. In comparison with conventional reactive evaporation, the MFD chamber design incorporates a substrate rotating holder that allows its sequential exposure to the elemental evaporant fluxes and to the heating lamps array. In this way, the growing mechanism of the film involves chemical reactions between a few monolayers of both elements during each rotation cycle, allowing a precise control of the film thickness as required for buffer layer preparation.

Besides, CDB method has been developed from an indium salt and thioacetamide as sulfur source, as a simple and low-cost method based in the precipitation of ions that produces uniform, adherent, low temperature and reproducible large-area thin films.

#### 2. Experimental

The indium sulfide films have been grown on soda lime glass, glass coated by tin oxide (TCO) and unpolished crystalline silicon substrate, CBD films have been synthesized

Table 1  $In_2S_3$  films prepared on amorphous glass (SLG), glass coated by tin oxide (TCO) and crystalline silicon substrates by two different methods: modulated flux deposition (MFD) and chemical bath deposition (CBD)

Method/substrate	SLG	Si	TCO
CBD (0-25 min)	CBD1	CBD2	CBD3
CBD (25-50 min)	CBD4	CBD5	CBD6
MFD	MFD1	MFD2	MFD3

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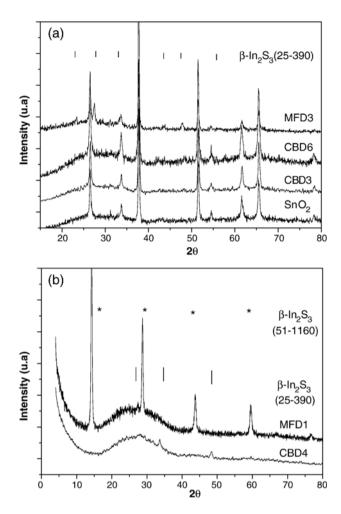


Fig. 1. XRD of films CBD3, CBD6, and MFD3 deposited on TCO substrate (a) and films CBD4 and MFD1 deposited on glass substrate (b).

from an acidic solution of thioacetamide [TA]=0.5 M (CH<sub>3</sub>. CSNH<sub>3</sub>, Fluka), and [InCl<sub>3</sub>]=0.025 M (Fluka). Other additives necessary to improve the film quality are hydrochloric acid

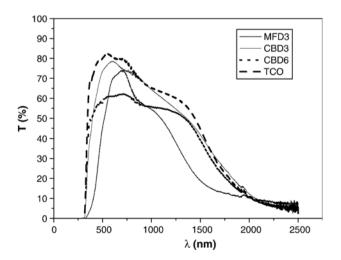


Fig. 2. Optical transmittance spectra for indium sulfide samples obtained by CBD and MFD methods on TCO substrates.

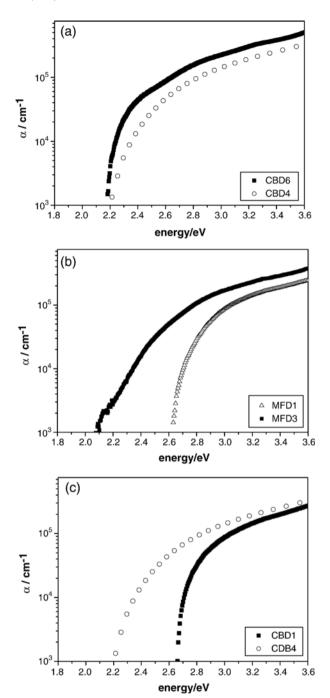


Fig. 3. Absorption coefficient spectra of films obtained by CBD method (a), MFD method (b) on glass and TCO, and films obtained by CBD on glass in different times of reaction (c).

[0.01 M] and acetic acid [0.3 M]. The synthesis has been realized in a thermostatised bath (70 °C) equipped with a Quartz crystal microbalance (Maxtek. Inc.) which allows the in-situ registration of the film thickness evolution [16]. Different CBD layers have been selected for the present work, obtained with 25 min the deposition time on the substrate: the initial from 0 to 25 min or from 25 to 50 min of solution reaction time (Table 1).

By MFD, the deposition parameters were optimized in order to minimize the substrate temperature as well as the amount of evaporated sulfur. The base pressure of the system was

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