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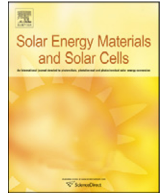

Thin films formed by selenization of $CuIn_xB_{1-x}$ precursors in Se vapor

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ABSTRACT

Previous attempts in producing light absorbing materials with bandgaps near the 1.37 eV efficiency optimum have included the partial substitution of gallium or aluminum for indium in the CIS system. The most efficient of these solar cells to date have had absorber layers with bandgaps < 1.2 eV. It is logical that an even smaller substitutional atom, boron, should lead to a wider bandgap with a smaller degree of atomic substitution. In this study, copper–indium–boron precursor films are sputtered onto molybdenum coated glass substrates and post-selenized. In the selenized films, although X-ray diffraction (XRD) measurements confirm that a CIS phase is present, Auger electron spectroscopy (AES) results indicate that boron is no longer homogeneously dispersed throughout the film as it was in the case of the unselenized precursor.

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1. Introduction

A recent paper by Contreras et al. [1] has set the optimum absorber bandgap for terrestrial solar cells at 1.37 eV. In this paper they announce the highest efficiency for a chalcopyrite solar cell as 19.5%. This high efficiency is achieved with 30% Ga substitution for In within the CIGS system, yielding a bandgap of 1.14 eV. In order to attain the ideal bandgap, a substitution level of 67% Ga for In would be needed. At that level, the efficiency for CIGS solar cells is reduced to approximately 14% [1].

There are evidently several reasons for the decrease in efficiency when the Ga content becomes high enough to reach the ideal bandgap. In the above-mentioned paper the authors show that the dark current and diode ideality factor, J_0 and A, respectively, in Eq. (1) below for current density, J, as a function of developed voltage, V, both increase substantially for $E_g > 1.2$ eV:

$$J = J_0 e^{q((V-RJ)/AkT)} + GV - J_L. \tag{1}$$

The other terms in this equation are the standard q, electron charge; k, Boltzmann's constant; R, series resistance; G, shunt conductance; and J_L, the light generated current density.

The authors explain the rise in A as a function of Ga content for all bandgaps as probably due to an increase in space charge region recombination. This increase in A is most likely due to changes in interface states between the CIGS and CdS or other window material, with more interface states for more Ga. The explanation for the increase in J_0 is probably associated with large changes in the electrical transport properties of the absorber (CIGS) layer. This is logically due to reductions in diffusion length due to alterations in the lattice crystal structure when Ga substitution exceeds 30%. In order to achieve a 1.37 eV bandgap, a substitution of 67% Ga would be calculated from Eq. (2) below [2]:

$$E_g(x) = (1-x)E_g(\mathrm{A}) + xE_g(\mathrm{B}) - bx(1-x). \tag{2}$$

In this equation A refers to In and B refers to Ga, Al, or B. (The bowing coefficient b can be shown to have little effect on the equation.) As a consequence of the high density of Ga needed to achieve the desired bandgap and the fact that the efficiency decreases when the Ga concentration exceeds 30%, attempts have been made to increase the bandgap using aluminum as a substitution for In. Using Eq. (2) above, only 25% Al would be needed to reach a bandgap of 1.37 eV.

To date, an efficiency of 16.9% has been achieved in $CuIn_xAl_{1-x}Se_2$ [3] and this is with a bandgap of about 1.15 eV with Al substituting for 13% of the In. An increase in Al content always degrades the device efficiency when compared to a CIGS cell with equal bandgap. The cause is explained to be due to significantly greater disorder in the absorber layer when the Al content is increased [4]. More recent work on this combination of materials [5] is more closely related to our efforts here. The Cu, In, and Al are deposited sequentially and selenized in an Se vapor. The resultant films do not have complete incorporation of aluminum into the $CuInSe_2$ structure, but the Al accumulates at the back of the film.

An analysis of Eq. (2) using boron and an estimate of the bandgap of $CuBSe_2$ [6] yields a substitution level for B for In of only 18.6% to yield a bandgap of 1.37 eV. Unfortunately, at this time boron has not been fully introduced into the CIS structure. An analysis of the film properties and a discussion of the methods used to produce these films are in the following section.

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2. Deposition techniques

All films fabricated in this study were deposited via magnetron sputtering of individual Cu, In, and *B* targets or by sputtering targets consisting of some mixture of those elements. The films were then post-selenized in a manner similar to that reported in the literature for CIGS [7,8]. Several methods were used to deposit CuInB films onto Mo coated soda-lime glass substrates:

1. Cu and $Cu_{0.45}In_{0.55}$ were DC sputtered and boron was RF sputtered. All targets were sputtered simultaneously (sample no. 070425CIB1).
2. $Cu_{0.45}In_{0.55}$ was DC sputtered and boron was RF sputtered. Both targets were sputtered simultaneously (sample no. 070718CIB1).
3. A boron layer was RF sputtered first and a $Cu_{0.45}In_{0.55}$ layer was DC sputtered onto the boron (sample no. 070427CIB1).
4. A $Cu_{0.45}In_{0.55}$ layer was DC sputtered first and boron was RF sputtered onto the $Cu_{0.45}In_{0.55}$ (sample no. 070810CIB1).
5. Cu_3B_2 and $Cu_{0.45}In_{0.55}$ targets were DC sputtered simultaneously (sample no. 070806CIB1).

Specific deposition parameters are detailed in the table. In these depositions the substrates were all at the temperature of the sputtering system with no additional heating. The layered samples are indicated by Cycles #1 and #2. The background pressure was always less than 1.3×10^{-4} Pa and all deposition took place at approximately 0.27 Pa. In each case, the substrate to target distance was 5 cm. Auger electron spectroscopy (AES) and/or XRD were used to analyze these films. The results are discussed below (Table 1).

3. Results

3.1. Deposition and study of precursors and selenized films

The first CIB precursor film was made by co-sputtering Cu, $Cu_{0.45}In_{0.55}$, and B. The Auger depth profile in Fig. 1 shows the atomic concentration for precursor sample 070425CIB1. The film was then subjected to an ex situ selenization procedure similar to that found in the literature for CIS [7] and CIGS [8]:

(1) The film, residing in a graphite boat with selenium reservoirs in a rough vacuum environment (~1 Pa), was heated to a temperature of 250 °C at a rate of 25 °C/min.
(2) The temperature was held at 250 °C for 20 min.
(3) The temperature was increased to 400 °C at a rate of 30 °C/min.
(4) The temperature was held at 400 °C for 30 min.

The purpose of steps 1 and 2 are to evaporate the Se to form a thin layer on the film surface. Steps 3 and 4 drive the Se into the film and allow the bonding reactions to take place. Several substrates

Table 1
Precursor deposition parameters

Sample	Sputter time (min)		Cu(0.45) In(0.55)	Cu(0.4) B(0.6)	Cu	B	Cu (AES) (%)	In (AES) (%)	B (AES) (%)
	Cycle #1	Cycle #2	DC current (mA)	DC current (mA)	DC current (mA)	RF power (W)			
070810CIB1	32 (CuIn)	225 (B)	208			150	NA	NA	NA
070806CIB1	58	NA	100	163.5			45.00	27.50	27.50
070718CIB1	98	NA	60			150	22.50	22.50	55.00
070425CIB1	186	NA	45		35	150	58.00	14.00	28.00
070228CI1	40	NA	100				45.00	55.00	0
070427CIB1	223 (B)	16 (CuIn)	100			150	NA	NA	NA

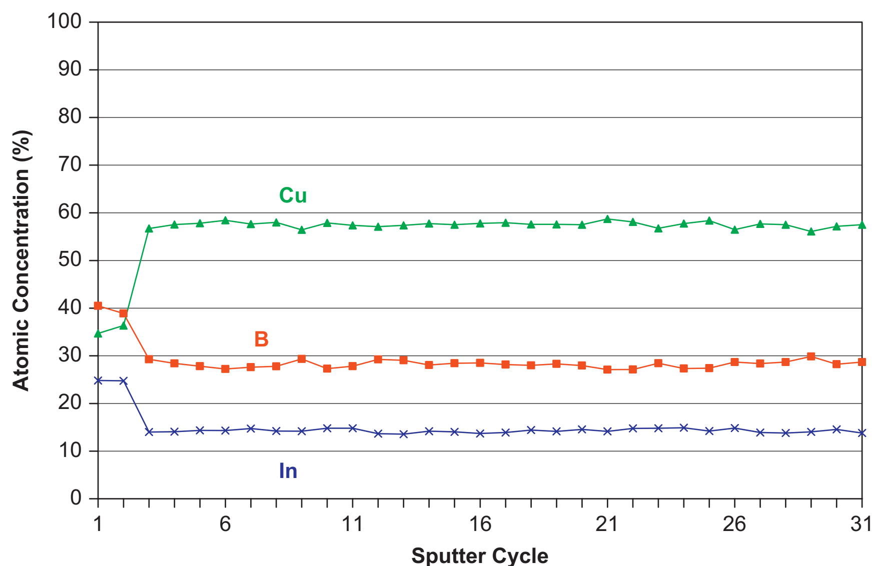

Fig. 1. Auger electron spectroscopy depth profile of a co-sputtered Cu, In, B precursor film 070425CIB1 showing uniform distribution of the atomic concentration of each element.

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