

# Comparison of CdS films deposited from chemical baths containing different doping impurities

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## Abstract

The results obtained for CdS films chemically deposited from solutions containing different impurities known as donor type dopants for CdS (chlorine, iodine, boron and indium) are reported. CdS films were deposited onto glass and CuInSe<sub>2</sub> absorber substrates at 85 °C. The deposition baths were ammonia solutions containing 0.001 M Cd<sup>2+</sup>, 0.02 M ammonium compound and 0.002 M thiourea and CdS was deposited at pH 10.3. After deposition, the layers were heated at 200 °C for 30 min in vacuum. The results confirm that the electrical resistivity of CdS films doped with boron and chlorine was dependent on doping level. At the same time, characteristics of CuInSe<sub>2</sub> solar cells with differently doped CdS did not show any remarkable dependence on doping level and nature. The buried homojunction model is proposed to explain obtained results.

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*Keywords:* Cadmium sulphide; Doping; Chemical bath deposition; CuInSe<sub>2</sub>; Solar cells

## 1. Introduction

Chemical bath deposition (CBD) is widely used as a method for the best buffer layer deposition in Cu(InGa)Se<sub>2</sub> solar cells [1], while the interface chemistry of solar cell is continuously under the interest of researchers [2,3]. Diffusion of Cd and Zn from chemical bath into the Cu(InGa)Se<sub>2</sub> absorber surface layer has been found to improve solar cell characteristics [4,5]. At the same time, the question, does any other doping impurity from chemical bath influences the Cu(InGa)Se<sub>2</sub> solar cell performance, is still open. It is shown in Ref. [6] that chlorine acts as a donor in CuInSe<sub>2</sub>. In Ref. [7], the authors found that boron doping of CdS from chemical bath improved the characteristics of CdTe/CdS solar cells. For CdS chemical deposition, a large variety of recipes have been used, where several cadmium salts such as cadmium acetate, cadmium chloride, cadmium iodide, etc. have been used as cadmium sources. There is a lot of papers dealing with solution chemistry of CdS deposition and with characterization of phase compo-

sition, morphological, optical and other physical properties of chemically deposited CdS and only few of them consider the influence of donor type impurities to the electrical properties of deposited CdS [7,8] or the influence of them to the solar cell performance. At the same time, chlorine and iodine are known as donor type dopants for CdS. In this paper, we report the results of characterization of CdS films on glass substrates obtained by CBD from solutions containing different impurities: chlorine, iodine, boron and indium. Chlorine and boron concentrations in CBD solutions were changed in a large scale, while the influence of other impurities to CdS properties and to the CuInSe<sub>2</sub>/CdS solar cell performance was studied at the level of 10<sup>-5</sup> M (in bath) and at the maximum possible impurity concentrations. The latter was performed by using CdCl<sub>2</sub> and CdI<sub>2</sub> as Cd sources instead of Cd(CH<sub>3</sub>COO)<sub>2</sub> and corresponding ammonium salts in CBD solution.

## 2. Experimental

CdS films were deposited onto glass substrates at 85 °C. The aqueous chemical bath contained 0.001 M Cd<sup>2+</sup> and

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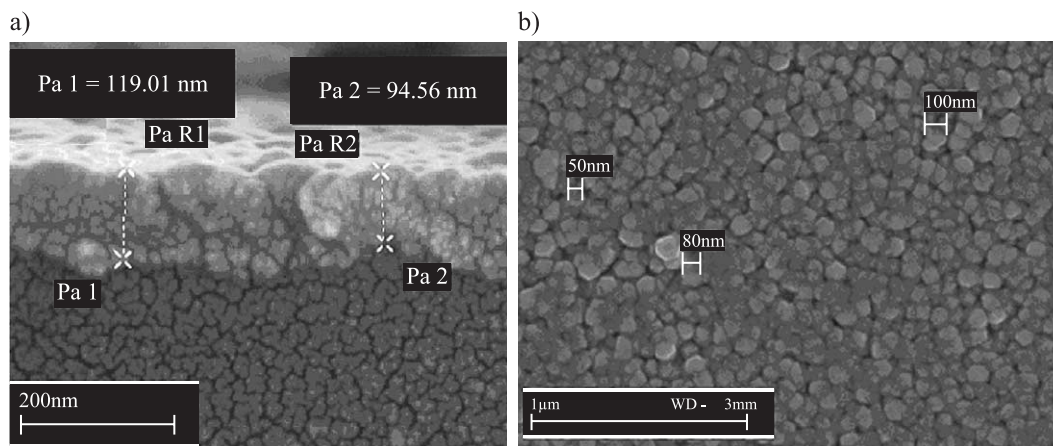


Fig. 1. SEM photos of CdS films on glass substrates: cross-section (a) and surface (b) of CdS layer deposited from bath CdAc<sub>2</sub>:B.

0.02 M ammonium compound and 0.002 M thiourea in ammonia solution. The above-mentioned concentrations were kept constant through all the experimental series. The different concentrations of chlorine and boron were obtained by addition of ammonium chloride or boric acid (H<sub>3</sub>BO<sub>3</sub>) as boron dopant into the acetate based solution keeping the total concentration of ammonium salt constant. The maximum concentration of chlorine (and iodine) has been determined by the full substitution of ammonium acetate by ammonium chloride (iodide) in the chemical bath solution and by usage of CdCl<sub>2</sub> (CdI<sub>2</sub>) as Cd<sup>2+</sup> source. Indium sulphate was used as indium doping source. The as-deposited films were heated at 200 °C for 30 min in vacuum for improvement the crystallinity of CdS grains. All deposited and annealed films were characterised by scanning electron microscopy (SEM). The film thickness and the average grain size were also determined by SEM. The electrical resistivity of all annealed CdS films on glass was measured at room temperature using the two probe technique. For this purpose two dots of liquid In–Ga

eutectic mixture were painted onto the films keeping the distance between them constant. The ohmic behaviour of contacts was followed by the shape of *I–V* curves. CuInSe<sub>2</sub> monograin powders were used as absorber material for the study of the influence of different doping level and nature of CdS to the performance of CuInSe<sub>2</sub>/CdS/ZnO heterojunction solar cell [9]. CdS was deposited from the chemical baths containing dopants in different level and of different chemical nature in parallel onto monograin powders and glass substrates. Deposition time was 20 min. Technology of monograin powder preparation is described elsewhere [10]. Solar cells were characterised by the *I–V* measurements, which were carried out in the darkness and under illumination of 100 mW cm<sup>-2</sup>.

### 3. Results

SEM photos of deposited CdS films are presented in Fig. 1. The resistivity of boron and chlorine doped CdS

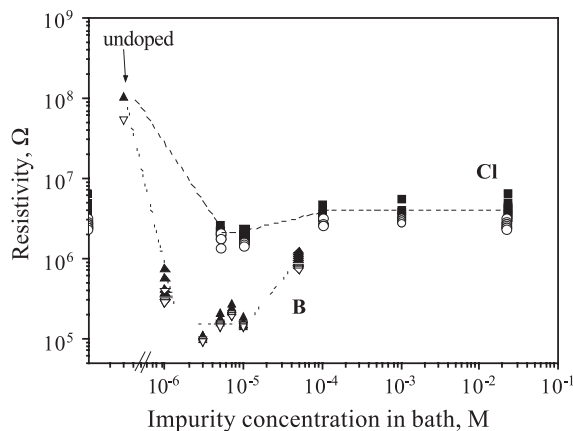


Fig. 2. Resistivity of boron and chlorine doped CdS films deposited at 85 °C for 20 min and annealed in vacuum at 200 °C for 30 min. Solid symbols—dark resistivities, open symbols—resistivities under illumination 100 mW cm<sup>-2</sup>.

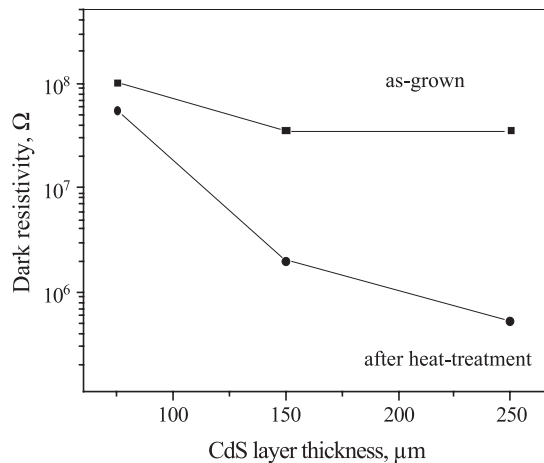


Fig. 3. Resistivity versus thickness of as-grown and annealed CdS films deposited from acetate baths.

Table 1

Data for CdS deposition by CBD from solutions containing maximum and medium concentrations of impurities and CdS film characteristics

Bath	CdAc <sub>2</sub>	CdCl <sub>2</sub>	CdI <sub>2</sub>	CdAc <sub>2</sub> :B	CdAc <sub>2</sub> :Cl	CdAc <sub>2</sub> :In
Source of Cd <sup>2+</sup>	CdAc <sub>2</sub>	CdCl <sub>2</sub>	CdI <sub>2</sub>	CdAc <sub>2</sub>	CdAc <sub>2</sub>	CdAc <sub>2</sub>
Dopant and its concentration (M)	–	Cl 0.022	I 0.022	B $3 \times 10^{-6}$	Cl $1 \times 10^{-5}$	In $1 \times 10^{-5}$
Ammonium salt	NH <sub>4</sub> Ac	NH <sub>4</sub> Cl	NH <sub>4</sub> I	NH <sub>4</sub> Ac	NH <sub>4</sub> Ac	NH <sub>4</sub> Ac
T (K)	358	358	358	358	358	358
(T, °C)	(85)	(85)	(85)	(85)	(85)	(85)
pH	10.3	10.3	10.3	10.3	10.3	10.3
Deposition time on glass (min)	30	30	30	30	30	30
CdS film colour	greenish yellow	greenish yellow	brownish yellow	greenish yellow	greenish yellow	brownish yellow
Average grain size (nm) <sup>a</sup>	80	80	40	80	80	50
Deposition time on CuInSe <sub>2</sub> (min)	20	20	20	20	20	20

<sup>a</sup> Determined by the analyse of SEM pictures of CdS samples deposited onto glass substrate.

films on glass deposited from acetate based baths for 20 min in dependence of dopant concentration in chemical bath solutions is shown on Fig. 2. As it can be seen, resistivity of boron doped CdS is nearly three and chlorine doped CdS two orders of magnitude lower than that of undoped films in the region of dopant concentration  $3 \times 10^{-6}$ – $1 \times 10^{-5}$  in the bath. At higher dopant concentrations the resistivity of films slightly increases. Dependence of electrical resistivity of deposited layers from the chemical nature of bath solution could be as an evidence of different level of incorporation of impurities into CdS layer (Fig. 2).

SEM studies revealed that surfaces of deposited CdS layers were free of colloidal particles. The annealing of films at 200 °C for 30 min decreased resistivities (see Fig. 3). As CdS film resistivity was dependent on layer thickness (see Fig. 3), we tried to keep the deposition conditions constant. As the most conductive CdS layers were deposited in the region of dopant concentrations  $3 \times 10^{-6}$ – $1 \times 10^{-5}$  in the bath, then these concentrations were used for different impurities in the next series of CdS deposition. The obtained results and the results for CBD at the level of maximum possible impurity concentrations in bath are summarised in Table 1. CdS was deposited concurrently onto glass slices and onto CuInSe<sub>2</sub> absorber

material of slightly indium-rich composition (Cu/In/Se 24.9:26.6:48.5 at.%) from the same bath. The results of measurements of thickness of CdS on glass from different baths of this series are depicted on Fig. 4. It is seen that the films deposited from the bath where CdCl<sub>2</sub> is used as Cd source have much lower resistivity than these ones produced from acetate bath with similar thickness. It is obvious that chlorine and iodine impurities of the equal (maximum) concentrations in bath result in different film thicknesses and resistivities (Fig. 4). The CdS film from CdI<sub>2</sub> containing bath is thinner and with higher resistivity. The obtained results are in accordance of results of solubility of chlorine and iodine in CdS [11,12].

Results of electrical measurements of CuInSe<sub>2</sub>/CdS/ZnO solar cells with different CdS buffer layers (Fig. 5) show that the doping of CdS does not affect remarkably the properties of our solar cells. This fact can be considered as an indication of a working buried homojunction. It is known that the role of the CdS buffer layer is not always to be a part of the heterojunction with CuInSe<sub>2</sub>. In many cases, CdS serves both: as (i) a Cd source for doping absorber surface and (ii) as a buffer between ZnO window layer and CuInSe<sub>2</sub> absorber layer. In these cases, the donor doping of CdS and the position of Fermi level in CdS do not have considerable influence on properties of a working junction.

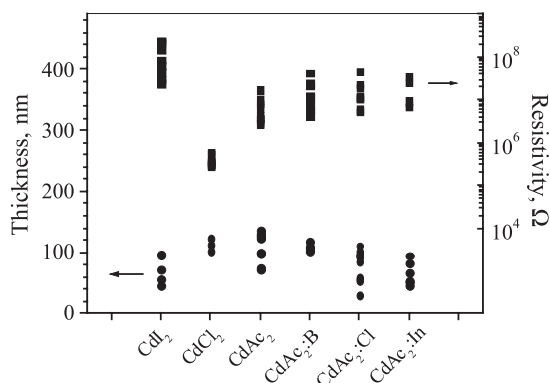


Fig. 4. Resistivity and thickness of CdS films deposited from different baths. Deposition conditions are depicted in Table 1.

#### 4. Conclusions

It was found, that CdS layers, prepared by CBD from the bath containing different donor type dopants for CdS have different electrical resistivities. The results confirm that the electrical resistivity of CdS films doped with boron and chlorine was dependent on doping level. Dependence of electrical resistivity of deposited layers on chemical nature of impurities and on their concentration in bath solution could be as an evidence of different level of incorporation of impurities into CdS layer. The lack of any major effect of CdS-doping on CuInSe<sub>2</sub>/CdS/ZnO solar cell parameter can be considered as an indication of a working buried

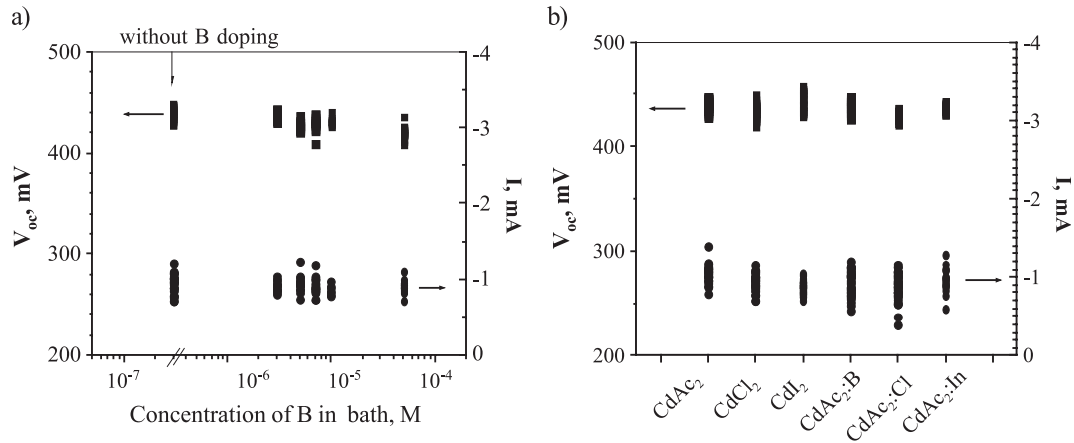


Fig. 5. Characteristics of solar cells: (a) with boron doped CdS and (b) with CdS from different baths depicted in Table 1.

homojunction, where the n-type region is formed on the surface of p-type  $\text{CuInSe}_2$ .

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