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CDS LAYER OPITIMIZATION FOR $CUINS_2$ SOLAR CELLS BASED ON COATED GLASS BEADS

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ABSTRACT: ECN developed a batch technology for the deposition of CdS layers on $CuInS_2$-coated glass beads. The $CuInS_2$ beads were further processed to solar cells in order to evaluate the IV-characteristics. In order to get acquainted with the deposition process also bare glass beads have been added to the deposition reactor. The CdS coatings are characterized by optical or chemical analysis; thereby focusing on the morphology, layer composition and layer thickness. The optical data were fitted using a thin film approach and calculating the effective CdS layer thickness on glass beads. A linear relationship was found between the thickness values determined by the optical and chemical method. The thickness determined by the optical method is comparable to a flat CdS reference layer thickness and therefore more reliable. A Cd/S ratio of 1.1 and a bandgap of 2.40±0.03 eV were determined. The photoelectrical performance of the SUNRISE cells has been measured. A direct correlation was found between the CdS layer thickness, determined on glass beads, and the measured Voc-values. A uniform and closed CdS layer with a thickness of 39 nm gave the highest (max. 573mV) Voc-values.
Keywords: Buffer Layer, CdS, II-VI Semiconductors, $CuInS_2$, Chalcopyrite, Optical Properties

1 INTRODUCTION

The Scheuten Research Company investigates the fabrication of chalcogenide solar modules based on 0.2 mm CIS coated glass beads, which is called the SUNRISE concept [1]. In comparison to the conventional thin film solar industry instead of processing flat glass the glass beads are coated with the absorber and buffer layers in specially developed batch reactors. The coated glass beads are embedded into a perforated metal film and are further processed to cells and modules of arbitrary size. The expected economical advantages of the SUNRISE technology are:

- Only 330 g of glass beads are needed to cover one square meter cell area, enabling the use of small volume reactors, while maintaining a high throughput
- For the sulfurisation of the Cu/In precursor even 25 times less thermal mass needs to be heated as compared to a 3 mm thick glass panel
- The flexibility of the materials makes the SUNRISE approach compatible for roll-to roll production. In this case, throughput and dimension are not limited by the requirements for absorber and buffer layer deposition.

ECN developed a chemical bath process for the deposition of buffer layers on glass beads. This work focuses on the characterization of deposited CdS layers. To analyze the CdS layer properties bare glass beads were mixed to $CuInS_2$ coated glass beads. The latter are processed to solar cells in order to evaluate the photoelectrical parameters. Different characterization facilities were explored in order to receive information about morphology, layer composition and thickness of the CdS layer on glass beads. To determine the CdS layer thickness two approaches have been chosen:

- Optical measurement and modeling
- Chemical dissolution of the layer and determination of the Cd ion amount

2 EXPERIMENTAL

CdS layers are applied in a chemical bath deposition reactor using the earlier described cold start procedure [2]. A solution of 1.3 mM cadmium acetate, 1M ammonia and 110 mM thiourea is prepared at room temperature. After addition of the beads to the cold solution, the bath is heated to the deposition temperature with a heating rate of 2.5 degrees/min (see Fig.1). The deposition temperature is kept at 55°C. A reactor batch consists of 25g of glass beads. For the following study three CdS deposition conditions are chosen to investigate CdS layer formation. The samples are prepared at different reaction times in the cold start reactor, as marked in Fig.1. In the following the samples are cited as **0'45°C** (directly when 45°C has been reached), **0'55°C** (directly when 55°C has been reached) and **4'55°C** (after 4 min at 55°C)**.**

The morphology of the samples is studied by using a JEOL JSM-6330F Field Emission Scanning Electron Microscope (SEM) (cold-cathode field emission) with a resolution of 2 nm at 15kV. EDX analysis was performed on a JEOL JSM-6480 with a NORAN type 662A-1SES EDX source.

To elucidate the CdS layer thickness on the glass beads two general approaches are chosen:

Optical method: The coated glass beads were manually embedded between two Scotch tapes, aiming for a compact packaging of a single array of glass beads between the tapes. The UV-VIS transmittance and reflectance spectra were taken with a Spectro 320 R5 apparatus with integrating sphere (Instrument Systems GmbH). The spectra were fitted using a thin film fitting programme, assuming a flat substrate/layer/air configuration. The n- and k-values were determined and the bandgap was calculated.

Chemical method: The cadmium ion amount covering 250 mg of glass beads was determined by three methods:

Titration I: dissolved in 5% HCl en titrated with EDTA from a basic solution (indicator: Eriochrome T)

Titration II (following Dutch NEN 3104 norm): dissolved in concentrated HCl en titrated with EDTA from an acid solution (indicator: xylenolorange)

ICP-analysis: dissolved in concentrated HCl and Cd^{2+}determination by Induced Coupled Plasma (ICP)

Analysis with Atomic Emission Spectroscopy using a Varian Vista equipment.
The CdS layer thickness was calculated assuming the formation of a compact layer with a density of 4.82 g/cm^3 on sherical glass beads with a uniform diameter of 0.2 mm.

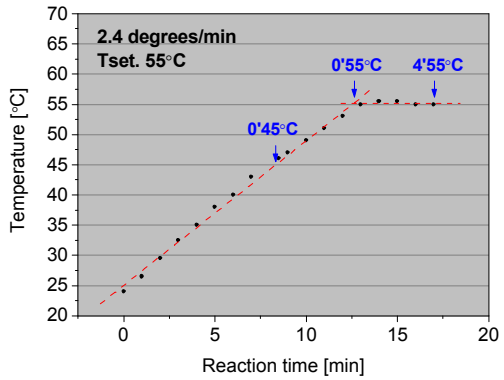

Figure 1: Cold start CdS deposition process and highlighted: three conditions chosen for this work

3 RESULTS AND DISCUSSION

3.1 Morphology of CdS layers on glass beads

In the given cold start process the CdS formation is driven by the decomposition of the sulfur source thiourea. The released HS^- ions react with the cadmium cations in order to form CdS. The SEM photographs in Figure 2.b-d show, that already at 45°C significant CdS precipitation takes place on the glass beads.

a. CdS on glass plate	b. 0'45°C
c. 0'55°C	d. 4'55°C

Figure 2: SEM photographs (x25.000) of CdS layers on glass beads (deposition conditions are given in the picture) and of a CdS layer, deposited at 55°C on a flat substrate (lower right)
At 55°C particles with an approximate diameter of 50 nm are formed, which are gradually covering the whole glass surface (The few visible white particles originate from undesired homogeneous CdS formation). After 4 min at 55°C (batch 4'55°C) the CdS layer is uniform and nearly closed. EDX analysis revealed for all CdS layers on the glass beads a Cd/S ratio of 1.1 (± 0.1), pointing to a nearly stoichiometric CdS composition with a small contribution of cadmium hydroxide.

3.2 Optical method

3.2.1 Thin film model

To determine the CdS layer thickness on glass beads the transmittance and reflectance spectra are fitted by a thin film optics program, assuming a flat air/CdS layer/substrate configuration and a compact CdS layer. As can be seen in the SEM photographs in figure 2 the CdS layers are not always closed. In these cases the calculated thickness value has to be considered as an effective layer thickness, averaging the CdS amount measured over the irradiated area.
On a spherical glass bead, the surface of which is covered by the CdS layer, a perpendicular light beam passes the layer at least two times: if it encounters the glass bead and if it leaves it. Therefore in the optical approach used, the 'flat' layer thickness calculated by the thin film fit is divided by a factor two. This remains an approximation not taking into account either scattering effects or the packaging density of the glass beads in the tape.

3.2.2 Flat CdS reference layer

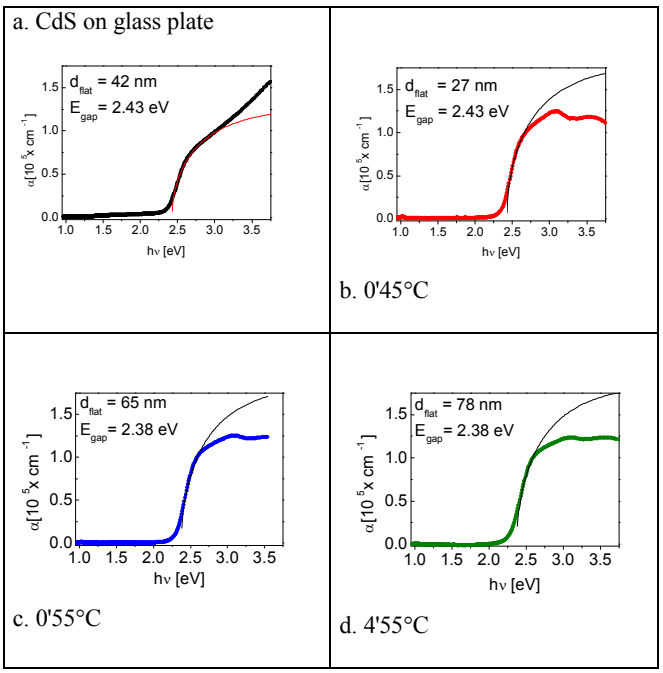

Figure 3: Bandgap determination for CdS layer on a microscopic glass plate (a) and CdS layers on glass beads: sample 0'45°C (b), 0'55°C (c) and 4'55°C (d)
(d (flat) is the layer thickness determined using the thin layer configuration on flat substrates, for glass beads see section 3.2.1)

As reference for the CdS layers on glass beads a microscopic glass plate has been added to the CdS deposition process. Deposition at 55°C shows a uniform and closed layer in the SEM photograph (see Fig.2.a).

The CdS morphology and coverage are similar to the glass bead sample 4'55°C (Fig. 2.d). For the optical fit the thin film program was used. The fit, shown in Figure 3a, delivers a layer thickness of 42 nm and a bandgap of 2.43 eV.

3.2.2.1 Calculation of CdS layer thickness on glass beads

In Fig. 4 the transmittance and reflectance spectra of the three selected CdS batches are given. To investigate, how manual preparation of the tape/glass bead/tape samples influences the optical spectra per batch three separate tape samples were prepared and measured. As is shown in Fig. 4 in general all spectra show the typical CdS absorption edge at approximately 515 nm and the CdS transmittance decreases with increasing deposition time.

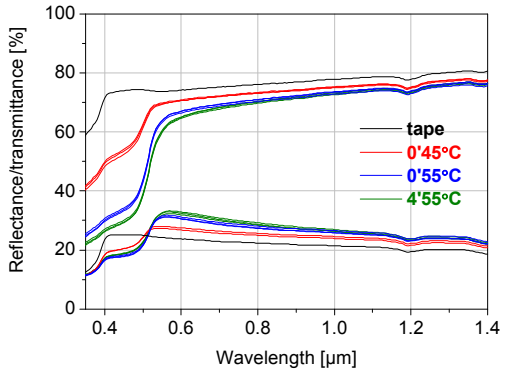

Figure 4: UV-VIS spectra of CdS layers on glass beads

Aside from the differences due to the CdS coating conditions it is hard to recognize individual curves within one batch. In other words, the different tape/glass bead/tape samples show a similar performance. Consequently, it is possible to prepare tape samples of reproducible quality.

Figure 5 gives an overview of the n- and k-values determined by fitting the optical spectra with the thin film model. For all three samples the k-value remains at a value of 0.4 at 350 nm; the refractive index, which gives also an indication about the density of a film, shifts to higher values if the CdS coverage increases. Table 1 gives an overview of the layer thickness determined for the different CdS batches. Since the morphology of sample 4'55°C and the CdS layer on a flat substrate are comparable for sample 4'55°C also a layer thickness close to the 42 nm determined for the flat layer would be expected. The determined value of 39 nm is indeed close to the 42 nm found for the flat configuration. Regarding the values for sample 0'45°C and 0'55°C, it has to be reminded that they are not completely covered with CdS (see Fig. 2) so that this 'effective thickness' value can more reasonably be associated with a CdS coverage degree. The bandgap of 2.43 eV, calculated for sample 0'45°C is identical to the one determined for a flat substrate (see Fig. 3b).

However, for all three samples the α plot deviates from the square root behavior for a direct bandgap, which makes the fit less reliable. The too low bandgap values found for the other samples 0'55°C and 4'55°C (Fig 3.c-d) are therefore not surprising. One reason for the deviating α curve is the insufficient correction for the tape absorption above 3 eV. But apparently here the model does also suffer from the approximations made by neglecting, e.g., light scattering effects.

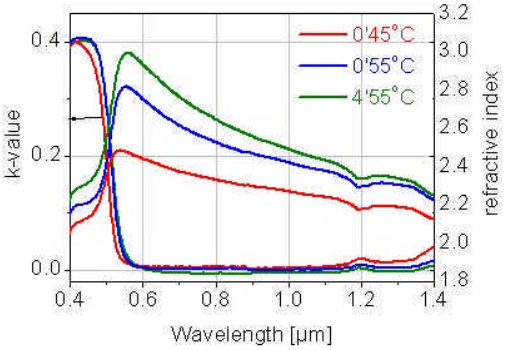

Figure 5. k-value and refractive index calculated from optical spectra

Table 1. Layer thickness for CdS on glass beads determined by the optical method

Sample	**0'45°C**	**0'55°C**	**4'55°C**
Layer thickness	13.5 nm	32.5 nm	39 nm

3.3 Chemical methods

Three different methods were chosen to determine the CdS amount on the glass beads (see table 2). The CdS layer thickness was derived following the method as described in the Experimental section.

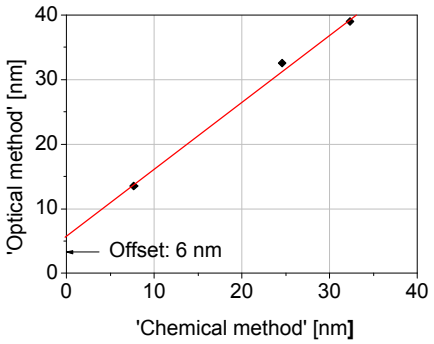

Figure 6: Relationship between the CdS layer thickness on glass beads determined by the optical and chemical method

As summarized in Table 2 the effective CdS thickness starts at 8 nm for sample 0'45°C and increases to 25 nm for sample 0'55°C and 32 nm for sample 4'55°C. As can be seen in Table 2 the thickness deviation, determined within one sample is not more then 2 nm.

As a conclusion, all three approaches, titration I and II and the ICP analysis can be considered as appropriate methods. However, if compared to the optical method the CdS thickness values are linearly correlated (see Fig. 6) but are consequently 6 nm lower.

Presuming, that the layer thickness for sample 4'55°C should be close to 42 nm as established thickness for a closed layer, deviations are attributed to an incorrect model used for the chemical method. Presumably it is not

correct to consider the CdS layer as a dense and compact layer with the given density of 4.82 g/cm^3.

Table 2. Layer thickness for CdS on glass beads determined by the chemical method

Sample	Titration I	Titration II	ICP analysis	Average CdS thickness [nm]
0'45°C	9	7	7	7.7±0.9
0'55°C	22	27	25	24.6±2.1
4'55°C	29	34	34	32.3±2.3

3.4 IV performance of SUNRISE cells

To demonstrate the influence of the CdS quality on the SUNRISE cell performance, two samples were compared: One sample has been processed at optimal conditions, giving a closed CdS layer on glass beads with a layer thickness of 39 nm. The effective thickness determined for the other layer is 34 nm and the SEM-photograph shows, that the layer is not fully closed. The CdS layer thickness on the simultaneously coated $CuInS_2$ beads is not yet known.

The CdS coated $CuInS_2$ beads were embedded in the metal film and contacted. Each contact area of 0.08mm^2 covers approximately 20 glass beads. Figure 7 shows the Voc's and fill factor measured on the individual contact areas. It is obvious that optimal processing significantly reduces both the Voc-values and the Voc-distribution. The better conditions gave Voc's values ranging between 553 mV and 573 mV and a maximum fill factor of 0.5. The short circuit current has not yet been quantified since it strongly depends on the density and number of contacted glass beads.

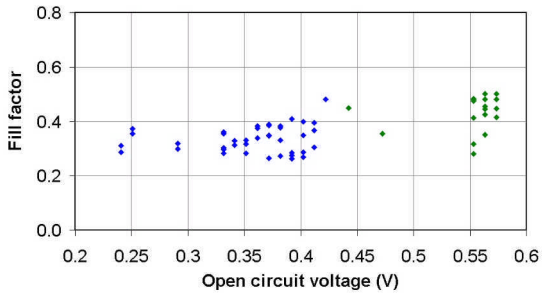

Figure 7: Fill factor and open circuit voltage determined for $CuInS_2$ bead cells (each measurement has performed on an area of 0.08 mm^2, covering approximately 20 beads); Effective CdS layer thickness 34 nm (blue dots) and 39 nm (green dots)

4 CONCLUSIONS

It has been demonstrated that the 'cold start' CdS deposition is applicable to the glass or $CuInS_2$- glass beads. Despite many approximations made for the optical method, the resulting layer thickness corresponds to the expected value. So, regarding the thickness for a closed CdS layer on flat glass (42 nm) and on glass beads (39 nm) the values deviate only 3 nm. The CdS thickness obtained by using the optical method is linearly correlated to the one found with the chemical method. However, the chemical method gives lower values implying that the CdS density chosen for the calculation is not yet correct. Since the thickness deviation between both is consequently 6 nm, a correction factor can be introduced for the chemical method. It has been demonstrated that the CdS layer quality influences the IV-performance of a SUNRISE cell. A uniform and closed layer on glass beads delivers the highest (max. 573mV) and most reproducible Voc-values. Until now the CdS quality on $CuInS_2$ is judged by adding bare glass beads to the CdS deposition batch.

ACKNOWLEDGEMENTS:

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