

# Ammonia free CdS buffer layer for Cu(In,Ga)Se<sub>2</sub> solar cells by chemical bath deposition

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## Abstract

### **Ammonia free CdS buffer layer for Cu(In,Ga)Se<sub>2</sub> solar cells by chemical bath deposition**

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The buffer layer in Cu(In,Ga)Se<sub>2</sub> solar cells can improve cell performance. In this work we make CdS buffer layer by chemical bath deposition (CBD) without ammonia. CBD without ammonia were sought out since ammonia is a volatile compound.

Different recipes for making CdS were tested; only one of the tested recipes actually produced something that is worth further investigating. This recipe used sodium citrate, an innocuous compound instead of ammonia. The best performance was 0.15 % off from the reference.

This is almost as good as the used baseline process. However the worst almost completely killed the solar cells. Cell performance dropped by more than absolute 10 %.

This demonstrates that chemical bath deposition can have profound effects on the solar cell performance. When trying to improve the best cells only detrimental effects showed up. This might show that, a part in the recipe used, NaOH has detrimental effects on solar cells.

Ammonia free chemical bath deposition is possible, however so far it has not produced as good results as the reference. The difference is however very small, which makes it worth further investigating with more and better solar cell material.

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## List of abbreviations

$\alpha$	Attenuation coefficient
$\eta$	The efficiency of the solar cell
$\theta$	Bragg angle for XRD
$\lambda$	Wavelength of radiation
$\rho$	Density
$\tau$	Period for interference pattern
$A_a$	Activated area by X-ray
Ac	Acetate ion, $\text{CH}_3\text{COO}^-$
BA	Grid evaporator used in the lab
BAK	Balzers–Anlage (Kubische) 550
BRIC	Brazil, Russia, India and China
CBD	Chemical bath deposition
CVD	Chemical vapor deposition
CIGS	Copper indium gallium selenium, compounds of composition $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ with $0 \leq x \leq 1$ .
$d$	Thickness of film and inter-planar distance
$E_g$	Band gap of a semiconducting material
FF	Fill factor
GI–	Grazing incident XRD
XRD	
$I$	Intensity of light and used for current
$I_0$	Intensity of light as prefactor
$I_L$	Difference in current of a solar cell under illumination and in the dark
$I_{sc}$	Short circuit voltage
$I_{mp}$	Current of maximum power
$J_{sc}$	Short circuit voltage normalized by area
$k$	Boltzmann’s constant
$K_{sp}$	Solubility product
$M_w$	Molecular weight
MRC	DC–Sputtering used to deposit Mo
$P_{in}$	Input power of a solar cell
$P_{out}$	Output power of a solar cell
$q$	Elementary charge
QE	Quantum efficiency
RF	Radio frequency
SLG	Soda lime glass
T	Temperature
TEM	Transmission electron microscopy
$V_{mp}$	Maximum power voltage
$V_{oc}$	Open circuit voltage
von	RF–sputter used to deposit ZnO
Ar–	
denne	
$x$	Path length
XRD	X–Ray Diffraction
XRF	X–Ray Fluorescence

ÅSC Ångström solar center a part of the solid state electronics division at  
Uppsala University

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## 1 Populärvetenskaplig sammanfattning

Solceller är elektriska apparater som förvandlar solljus till elektricitet. Dessa solceller kan vara gjorda av många olika material. Ett av dessa är en så kallad tunnfilmssolcell som betecknas CIGS för koppar, indium, gallium och selen.

Tunnfilmssolcellerna består av olika lager, likt en dagobertmacka där varje lager fyller sin speciella roll. Ett av lagrena i dessa solceller kallas för buffertlager och består vanligtvis av den kemiska föreningen kadmiumsulfid ( $\text{CdS}$ ). Buffertlagret har en rad olika effekter, men ett bra buffertlager förbättrar solcellernas prestanda.

Vanligtvis läggs buffertlagret på solcellen med en våtkemisk metod som kallas för "chemical bath deposition", kemisk baddeponering. Denna metod går till så att i en behållare med vatten och rätt startmaterial sänks solcellen ner. Kadmiumsulfiden kommer då idealt att fästa på solcellen och bilda ett heltäckande lager.

Det här examensarbetet har utförts för Tunnfilmssolcellsgruppen vid Uppsala Universitet och har undersökt möjligheten till att ändra startmaterialen för deponeringen. Ett av de vanliga materialen, ammoniak för att lägga på kadmiumsulfiden på solcellen är en flyktig förening. Eftersom ammoniak är en flyktig förening innebär det att förhållanden för att lägga på lagret kan ändras med tiden. Alla jämförelser för alternativa deponeringsmetoder har varit mot standardsättet att göra kadmiumsulfid som kallas baseline. I det här arbetet har vi kommit fram till följande saker:

- Många metoder för att göra  $\text{CdS}$ -lager som finns beskrivna i litteraturen är svåra att reproducera och över huvudtaget få att fungera på något vis.
- I det enda fallet där deponeringen har fungerat har stora modifieringar fått göras för att kunna reproducera resultaten från litteraturen, detta då litteraturen varit väldigt sparsam med beskrivningar.
- I litteraturen användes kadmiumklorid som kadmiumkälla för de recept som kom att undersökas mest för det här projektet. Det upptäcktes efter ett tag att kadmiumacetat lika gärna kunde användas som kadmiumklorid. Detta har flera fördelar då kadmiumacetat är billigare, mindre giftigt och inte klibbar fast i glasvaror på lab.
- Det som fungerade bäst i jämförelse med baseline var att göra buffertlager med ett recept bestående av kadmiumacetat, tiourea, natriumcitrat och natriumhydroxid. Här erhöles solceller med en skillnad i verkningsgrad på 0.15 %, receptet innehöll små mängder natriumhydroxid.
- Natriumhydroxid behövs för att göra buffertlager med det bästa alternativa receptet, men om för mycket används bildas inget lager över huvudtaget och bara partiklar av kadmiumsulfid bildas. Natriumhydroxiden verkar dock kunna ha negativa effekter, dessa är inte förstådda. Som sämst förlorar solcellen mer än hälften av sin prestanda.

Det är värt att nämna att den alternativa metoden inte har kunnat testas fullt ut. Anledningen till det är att i labbet har maskinen som gör CIGS-materialet haft stora problem. Likväl finns det förhoppningar om att den här alternativa metoden kan, med modifikationer ersätta det vanliga sättet att göra buffertlagret på.

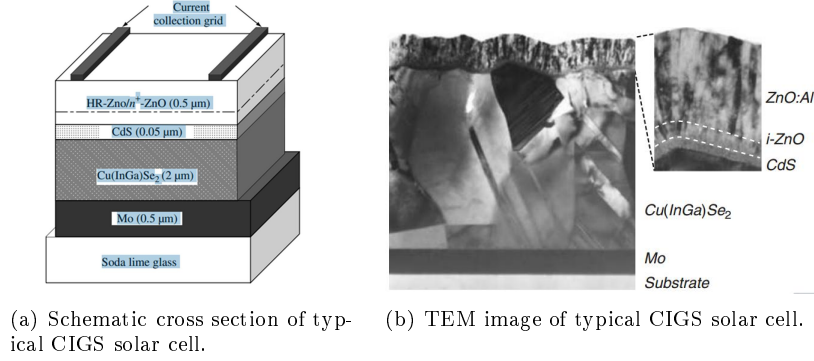
## 2 Introduction

### 2.1 Background

Human population is on the increase, from 1950 to 2010 the population increased 2.8 fold from 2.5 billion to 7 billion [1]. At the same time more and more people are being lifted out of poverty [2] which increases their living standard and with this comes an increase in material wealth. Between 1980 and 2010 the proportion of the population experiencing absolute poverty dropped from over 40 % to around 20 %. As more and more people are adapting to a more westernized lifestyle the demand and need for energy will surely increase. Not all predictions about human population dictate it will keep increasing at a high rate, various scenarios are possible as seen by [1]. Low predictions state that population will rise to 7.4 billion by 2050 and high predictions about population gives the number 10.6 billion in 2050. In any scenario whether if population keeps on increasing, even at a slow rate while more and more people are being lifted out of poverty; the demand for energy will surely increase.

How can this electricity be generated? Solar cells are certainly one way, the sun is a nuclear reactor that generates an enormous amount of energy, it radiates light of approximately  $4 \cdot 10^{26}$  W [3]. However the sun is about  $1.5 \cdot 10^{11}$  m [3] far away from the earth so only a minute amount of that light hits the surface of the earth. Light hitting the earth corresponds to roughly  $1 \text{ kW/m}^2$  and with a mere efficiency of 10 % solar cells could in theory supply a great deal more than man's current energy use.

Several companies have demonstrated commercial solar cells of efficiencies  $> 10 \%$  [4] with a wide range of materials. Commercial solar cells are commonly made out of silicon (amorphous/crystalline/poly-crystalline), CdTe or  $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$  (CIGS) [4] which will be the solar cell material used in this thesis. Record for lab scale production of CIGS is 20.4 % demonstrated by EMPA [5], for production the record is a few percent behind for this material. In this work the focus will be on the buffer layer consisting of CdS for CIGS solar cells shown in figure 1.



**Fig. 1:** Left pictures shows a cross section of a typical CIGS solar cell, from bottom to top substrate of soda lime glass coated with molybdenum as back contact, CIGS as active material, buffer layer of CdS, high resistive ZnO layer, high-conductive ZnO layer and topmost current collectors. To the right a TEM image of the same structure is shown. Figure taken from [4].

## 2.2 CIGS

CIGS, short form for copper indium gallium selenium, compounds of composition  $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$  with  $0 \leq x \leq 1$  is a direct band gap semiconductor used as an absorber layer for solar cells. The band gap varies by the empirical equation 1 from [4] which gives a band gap of 1.010 eV for  $\text{CuInSe}_2$  and 1.636 eV for  $\text{CuGaSe}_2$

$$E_g = 1.010 + 0.626y - 0.167y(1 - y), \quad (1)$$

where  $y = \frac{\text{Ga}}{\text{Ga}+\text{In}}$  is the Ga/III ratio, thus it is possible to tailor the band gap of CIGS solar cells by varying the Ga/III.

Here one could imagine that it is just tailoring the band gap to match the solar spectrum but it is of course more complex than that. Going up in gallium content for instance often leads to a material that is in-homogeneous and performs worse than one with a lower gallium content. However, a too low gallium content also has adverse effects.

Since the material consists of four different elements it can and does contain not only the wanted CIGS material but other compounds that may alter the cell performance.

The first example one encounters with doping is often Si were the intrinsic material can be tailored by adding dopant elements such as arsenic, boron or phosphorus. These dopant atoms substitute silicon in the lattice and give rise to electrons or holes; by the fact that these dopant atoms are often aliovalent and thus their charge gives a charged lattice. In CIGS this is not the case for the doping, here the effect comes from defects. These defects can be interstitial or more commonly vacancies, where depending on which atoms are vacant give rise to a p- or n-type semiconductor. Most commonly is p-type CIGS that comes from a Cu-poor material, then these vacancies act as acceptors. Having a p-type CIGS together with the n-type semiconductor CdS creates a pn-junction.



CIGS has quite short history, it started in 1953 when Hahn synthesized  $\text{CuInSe}_2$  and later proposed it as a photovoltaic material in 1974 [4]. In the beginning of the 1980s Boeing Corp. had already reported lab scale efficiencies  $> 10\%$ . It would take almost two decades for the first commercial CIGS solar cell to reach the market.

Now CIGS and other solar cells are sold commercially in large parts of the world, where the developed world is leading installation <sup>1</sup>. The market for solar cells is still in its infancy, this can be seen by the number of companies gone bankrupt, merged with other companies or simply closed down [6]. However there are still a number of companies alive and the market for CIGS solar cells is growing.

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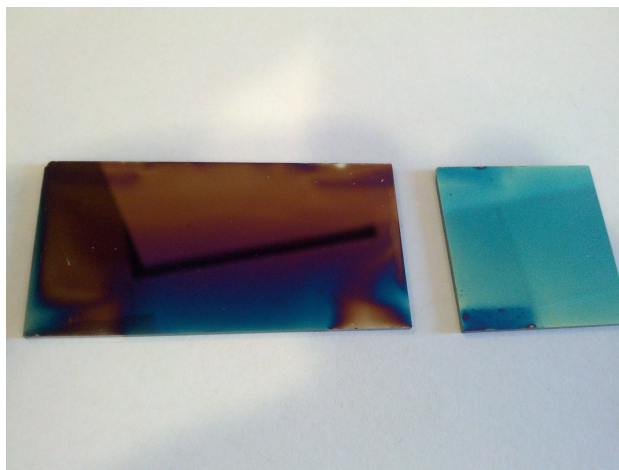
<sup>1</sup> This can be partly false depending on how the BRIC countries are categorized.

### 2.3 Aim of project

This degree project is done at the Ångström Solar Center (ASC) division at Uppsala University. The purpose of this project is to investigate if it is possible to grow CdS by chemical bath deposition by an alternative recipe. Recipes are to be evaluated compared to the baseline recipe, which utilizes ammonia.

Recipes in the literature are to be tested in the lab first for molybdenum or glass substrates for a quick evaluation if a film forms at all. Later CIGS solar cells fabricated by an alternative CBD method are to be compared with the baseline CBD process. The problem with the ASC method CBD method is mainly ammonia, a volatile compound. Volatile compounds in solution will boil off and make concentration in the reaction beaker change over time.

Also depending on how the reaction is stirred the formed films will change as seen in figure 2. All conditions are to be held constant except for the buffer layer, which will be grown by CBD but by different recipes.



**Fig. 2:** Left part of picture shows a flaky CdS, which has a big thickness variation produced by not stirring the reaction vessel for the baseline process. Right part of picture shows CdS which has been deposited by continuously stirring the reaction vessel during the deposition. The color gives a rough estimate of the thickness of the film.

For the project there were fundamental limitations, the CBD equipment is used daily by other people at ASC and Solibro Research AB. These use small variations of the CBD process but the temperature is kept constant at 60 °C, therefore to not disrupt other people's experiments this temperature was kept constant. Not every chemical needed to evaluate different recipes was available in the lab or could be easily obtained and thus not all recipes could be evaluated.

It would however be possible to use different temperatures by using a heating plate which is available in the lab, but still the experiments would need to be performed in the special designated fume hood for CBD. This was not done since it would risk disrupting other experiments.

### 3 Theory

This section will only give a very brief description of the theory of a solar cell, for more details see for instance [4, 7]. Solar cells are semiconductor devices that give off electrons and thus generates a current by absorption of light that generates electron–hole pairs. These electron hole pairs will start moving across a junction because of a concentration difference and can thus be used as device to generate electricity. The gradient formed by ZnO and the buffer layer has such a high band gap that the photons just passes by these and hit the absorber layer.

When photons hit the absorber layer; an electron will move from the valence band to the conduction band leaving behind a hole. This generates a depletion zone where there are more positive charge carriers on one side and more negative charge barriers on the other side. The depletion zone generates an electrical field in which the electrons and holes start to move due to charge separation. If the solar cell is connected through a circuit it can thus generate electricity, in a simplified way much as a battery does while discharging.

#### 3.1 Role of the buffer layer

What does the CdS layer do in CIGS solar cells? It is not necessary to have a CdS layer or some other buffer to create working CIGS solar cells. The buffer layer instead work as a heterojunction for the ZnO and CIGS layers. Several alternative buffer layers with different deposition methods have been tested [8]. So far the CdS layer deposited by CBD has the highest performance [5] with 20.4% efficiency in lab scale. Alternative buffer material try to get rid of the CdS layer and replace the toxic [9] element with a non–toxic or less toxic material.

But what does the layer do? The main point of the buffer layer is that it acts as a pn–junction as previously described, which is the most important for the buffer layer. Besides this the real part of the refractive index of CIGS, CdS and ZnO is approximately 2.9, 2.4 and 1.9 respectively [10]. The complex part of the refractive index however changes over the spectrum and determines the absorption of light.

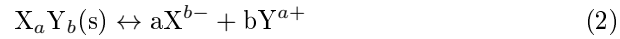
The buffer layer thus reduces optical reflections which means that more light actually reach the absorber material. The additional light that reach the absorber layer is the positive effect and means that more electron–hole pairs can be generated meaning a more effective solar cell can be achieved.

However, the buffer layer not only has the beneficial part of decreasing the reflections, it counteracts some of this by absorbing parts of the light. Absorption of light in a layer is thickness dependent so the layer should be thin to reduce this effect. Too thin layers however, decrease the efficiency of the solar cell compared to thicker layers [10]. It is worth noting that the layer should not be too thick as well as this leads to increased absorption of light.

Additionally to this, the buffer layer decreases recombination of electron–hole pair in the interface. There are many theories about other effects of the buffer layer. Some include that the CBD process etches away oxides from the CIGS layer and also that it might protect the CIGS surface from the negative oxygen ions during ZnO sputtering. It is not fully understood why the buffer layer is needed, but it improves the performance of the cells. The most important probably being that it creates a heterojunction.

### 3.2 Precipitation chemistry

Several compounds are hard to dissolve in a solvent such as water and rather precipitate in solution than being dissolved in the solvent. One common example of this is the salt AgCl in water which can be used to detect silver or chloride ions in solution. Compounds that are basically insoluble in a solvent such as water can be used as a method for fabrication of films. Given ions  $X^{b-}$  and  $Y^{a+}$  which precipitates by the reaction formula



then one defines the solubility product  $K_{sp}$  as

$$K_{sp} = \frac{\{X^{b-}\}^a \{Y^{a+}\}^b}{\{X_a Y_b\}}. \quad (3)$$

For dilute concentrations the activity  $\{\}$  of a species is approximately equal to the concentration  $[\ ]$  and thus  $\{\} \approx [\ ]$  which gives that equation 3 can be written as

$$K_{sp} = [X^{b-}]^a [Y^{a+}]^b \quad (4)$$

since the activity of a solid is defined as 1. This product  $K_{sp}$  can be seen as a measurement on how much of a salt can be dissolved in a solvent such as water. A small number means that the vast majority of the ions will precipitate in solution if there is enough of the corresponding counterion present. Solubility product for insoluble compounds<sup>2</sup> range from  $10^{-3}$  to  $10^{-100}$  with the value of  $10^{-27}$  for CdS  $10^{-27}$  [11].

#### 3.2.1 Chemical bath deposition

Given that some compounds are hard to dissolve in water this can be used as a method for fabrication of films. Salts in a solution that contain both the anionic and the cationic part of a compound dissolved in a solution will precipitate to form the corresponding insoluble compound.

However this does not necessarily generate a film on a substrate since the ions will react in the liquid phase and just precipitate in the solution.

For the compound to form a film instead one needs to control the reaction so that nucleation will take place at the substrate instead of in the solution. At least partially on the substrate instead of just in the solution. This means that the ions must react at the surface to at least some extent, so just adding corresponding ions in solution will not produce a film. The reaction conditions needs to be controlled so that nucleation and later growth is on the substrate and not just in solution.

This can be done and this deposition method is called chemical bath deposition. It can be seen as a liquid phase version of the commonly used chemical vapor deposition (CVD). Instead of gas phase reactants reacting at a surface as in CVD water soluble compounds react at a surface.

<sup>2</sup> This term is "loosely" used, all compounds are solvable to a certain extent, however when the proportion is very small we call the compound insoluble.

To mitigate precipitation in the solution a complexing agent is often added which ensures a slow release of one of the ions in solution. The growth of the CdS layer can be by different mechanisms, for instance ion by ion, cluster formation or a mix of the two [12]. Whichever mechanism the growth takes there is a nucleation time until the film starts to form which depend on the reaction conditions. Afterwards there is growth of film which also depend on the species in reaction and temperature.

The biggest advantage of the CBD method is that is a cheap, low temperature method which easily scales up. In theory it is possible to just use a bigger reaction vessel and keeping the reaction conditions constant as one scales the process. Negative parts of CBD is that it produces a lot of waste and that is has a low material yield. Since it is performed in a solvent such as water it is of course not a vacuum method. One needs to break the vacuum if CBD is to be used.

### 3.3 Solar cell performance

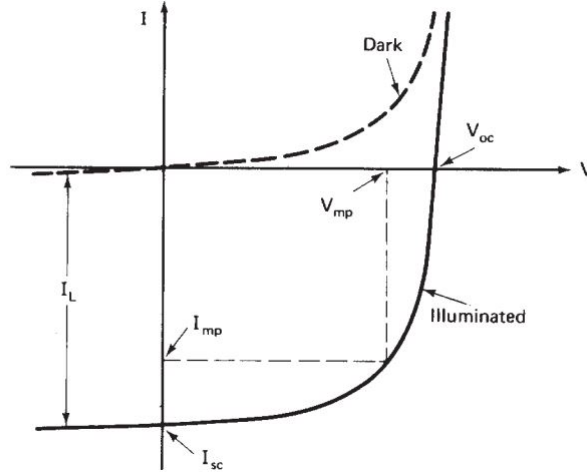
Solar cells performance are generally characterized by four parameters and a curve called the quantum efficiency. Below the parameters are briefly summarized and later described in more detail.

- $\eta$  is the efficiency of a solar in %, it is a measure of how effective the solar cell is in generating electrons from photons.
- FF measures the squareness of the current–voltage curves from the solar cell in units of %.
- $J_{sc}$  is the short circuit current density, i.e it is the current at zero voltage divided by area, typical unit is  $\text{mA}/\text{cm}^2$ .
- $V_{oc}$  is the voltage that gives zero current, often given in mV.

In a simplified picture a solar cell can be seen as a simple diode that obeys the diode equation 5, [7]

$$I = I_0 \left( \exp \left( \frac{qV}{kT} \right) - 1 \right) - I_L, \quad (5)$$

where  $I$  is the current,  $I_0$  is a prefactor,  $q$  is the charge,  $V$  is the voltage,  $k$  Boltzmann's constant,  $T$  temperature and  $I_L$  is the difference between a solar cell working in the dark or under illumination. The different parameters can also be seen in the figure 3.



**Fig. 3:** Solar cell seen as a diode in the dark or under illumination. The figure gives a graphical illustration of the parameters  $I_L$ ,  $I_{mp}$ ,  $I_{sc}$ ,  $V_{mp}$  and  $V_{oc}$ . Figure from [7].

Setting the current  $I = 0$  in equation 5 we get the following expression for  $V_{oc}$

$$V_{oc} = \frac{kT}{q} \ln \left( \frac{I_L}{I_0} + 1 \right). \quad (6)$$

The parameters  $I_L, I_0$  are dependent on the type of semiconductor and the quality of it and also temperature. From the open circuit voltage one defines the fill factor FF as

$$FF = \frac{V_{mp} I_{mp}}{V_{oc} I_{sc}}, \quad (7)$$

which measures how square the diode curve is. The maximum theoretical power one can draw from a solar cell is  $V_{oc} I_{sc}$ , however due to losses, it is less than that. For the working cell it is less than that and is  $V_{mp} I_{mp}$  and thus the fill factor is an important parameter.

The fill factor also determines the efficiency of the solar cell. Efficiency of a solar cell is given by

$$\eta = \frac{P_{out}}{P_{in}}, \quad (8)$$

where  $P_{in}, P_{out}$  is the input power from photons and the output power from the solar cell respectively. The term  $P_{out}$  depends on the maximum power voltage and current and equation 8 can with algebraic manipulation be written as

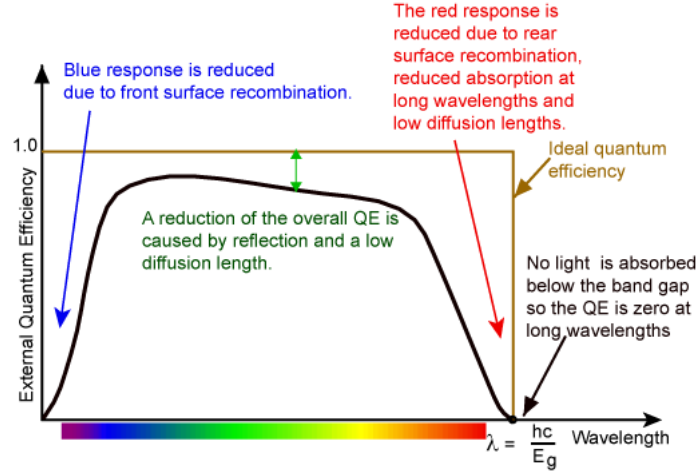
$$\eta = \frac{V_{mp} I_{mp}}{P_{in}} = \frac{V_{oc} I_{sc} FF}{P_{in}}. \quad (9)$$

The efficiency of the solar cell thus depends on the three other parameters.

Here we used the current  $I$  and not the current density  $J$ . The reported value in literature and when comparing is often the current density. This is because this gives the possibility to compare fabricated cells of different sizes.

### 3.3.1 Quantum efficiency

Besides performance measurements that are numbers an often presented graph is the quantum efficiency curve. The most important things can be seen in figure



**Fig. 4:** Quantum efficiency curve showing the response of a solar cell to illumination. The quantum efficiency is the ratio of the number of carriers collected by the solar cell to the number of photons incident on the solar cell. Figure from [13].

4, the main point of a QE is that it shows the number of carriers that the solar cells actually collect from the number of photons incident on the cell.

One distinguishes the internal quantum efficiency and the external quantum efficiency which is the directly measurable one. Often the external quantum efficiency is just called quantum efficiency since the internal is not directly measurable. But can be computed from the external with additional measurements. The internal quantum efficiency is given by the number of charge carriers collected by the solar cell divided by the number of photons of a given energy shone on the solar cell from the outside and are absorbed by the cell while external is the number of charge carriers collect by the solar cell divided by the number of photons shone on the cell from outside.

QE curves can thus give an estimate of the efficiency of a solar cell device for each wavelength measured, which makes it a very powerful technique for comparing cells with for instance different buffer layers.

Ideally the QE curve would just be a horizontal line with  $QE = 1$  up to the band gap of the semiconductor where it would go down to zero. Recombination of charge carriers, reflection of light, the diffusion lengths of holes and electrons and the band gap determines the shape of the QE curve. One can separate the QE curve into different regions where different mechanisms play the most important part. Normally QE curves are only presented from wavelengths of 300–350 nm upto 1200 nm. The lower number is because below 300–350 nm the power from the solar spectrum is very low below these wavelengths. Upper limit is usually the band gap of the absorber material since after that no light is absorbed and thus it is not meaningful to present data from here.

### 3.4 GI-XRD

XRD analysis utilizes an X-ray source to give lattice information about a substance. Since the penetration depth of a normal XRD is in the micrometer range this method does not work well for thin films where the signal of the film will be drowned in the signal of the substrate. To counteract this grazing incident XRD can be used, it is basically a low angle XRD to change the penetration depth of the X-ray. With a small angle it is still possible to obtain Bragg reflections by the Bragg formula

$$2d \sin \theta = n\lambda, \quad (10)$$

where  $d$  is the inter-planar spacing,  $\theta$  is the angle between the scattering plane and the incident ray,  $n$  is an integer and  $\lambda$  is the wavelength of the x-ray used. The same physics described in [14] for normal XRD applies for GI-XRD however here one uses a low angle to change the penetration depth.

### 3.5 XRF for thickness measurement

XRF can be used as a thickness measurement for films not thicker than the penetration depth of radiation. If the film is thicker than the X-ray penetration depth, then one does not get information from all of the film and thus it cannot be used for thickness measurements. However if one illuminates a thin film where the thickness is less than the penetration depth, one gets some sort of counts of how many atoms have been activated by the radiation. This requires that it is the same compound in the film and that the density of the film is uniform and is compared to a reference sample. One can derive the equation 11

$$\text{Counts} = \frac{A_a \cdot d \cdot \rho}{M_w} = d \cdot \left( \frac{A_a \cdot \rho}{M_w} \right), \quad (11)$$

where  $A_a$  is the activated area by the radiation,  $d$  is the thickness,  $\rho$  is the density and  $M_w$  is the molecular weight. Since the activated area can be controlled by the XRF settings and if one uses the same settings then if the density is the same the number of counts is directly proportional to the thickness.

XRF was also used to check the composition and thickness of CIGS material to make sure that no processing was done on cells that would not work. This is done by checking the Cu/III ratio ( $\frac{\text{Cu}}{\text{Ga+In}}$ ) ratio and the Ga/III ratio ( $\frac{\text{Ga}}{\text{Ga+In}}$ ).



## 4 Literature review

CdS can be deposited in a number of different ways. The cadmium source can be varied between the acetate, chloride, iodide or sulfate salt. In all cases but one found in the literature [15] thiourea was used as a sulphur source.

The complexing agent is commonly ammonia, but different complexing agents have been used such as ethylenediamine, ethanolamine, triethanolamine, EDTA, tartaric acid and sodium citrate. Ammonia free recipes were sought out in this literature review and thus recipes including ammonia as a complexing agent are left out.

Temperature varies between RT–90 °C, temperatures below room temperature are in theory possible. Deposition speed would probably be very slow however. Temperatures higher than 90°C will result in boiling of the water and also damaging the substrate, it also makes it harder to handle.

Focus was placed on recipes that did not include ammonia and did not include doping elements, however as seen in [16, 17] lot of deposition include dopant elements to change the properties of the layer. These were not studied further since a pure CdS was sought out without added dopant atoms.

**Tab. 2:** *CBD recipes found in the literature with different deposition conditions. Unless otherwise stated thiourea is used as a sulphur source. Table sorted according cadmium source.*

Cd salt	Complexing agent	T/(° C)	Comment+source
(Ac <sup>-</sup> ) <sub>2</sub>	-	80	[15] Thioacetamide as a sulphur source no complexing agent employed.
(Ac <sup>-</sup> ) <sub>2</sub>	Ethylenediamine	35–50	[18]
(Ac <sup>-</sup> ) <sub>2</sub>	NH <sub>3</sub>	60	ASC baseline process
(Ac <sup>-</sup> ) <sub>2</sub>	NH <sub>3</sub> /NH <sub>4</sub> Ac	50–90	[19]
(Ac <sup>-</sup> ) <sub>2</sub>	NH <sub>3</sub> /NH <sub>4</sub> Cl	80	[20]
(Ac <sup>-</sup> ) <sub>2</sub>	Triethanol	75	[21]
Cl <sup>-</sup>	Ethanolamine	60	[22]
Cl <sup>-</sup> /I <sup>-</sup>	NH <sub>4</sub> Cl/NH <sub>4</sub> I	>40	[23]
Cl <sup>-</sup>	Sodium citrate	60	[24–27]
Cl <sup>-</sup>	Tartaric acid	60	[28]
SO <sub>4</sub> <sup>2-</sup>	EDTA/NH <sub>3</sub> /NH <sub>4</sub> Cl	80	[29]
SO <sub>4</sub> <sup>2-</sup>	Ethylenediamine	50–90	[30]
SO <sub>4</sub> <sup>2-</sup>	NH <sub>3</sub> /NH <sub>4</sub> OH	85	[31]
SO <sub>4</sub> <sup>2-</sup>	NH <sub>3</sub>	60–85	[32]
SO <sub>4</sub> <sup>2-</sup>	NH <sub>3</sub>	70	[33]
SO <sub>4</sub> <sup>2-</sup>	NH <sub>3</sub> /N <sub>2</sub> H <sub>4</sub>	60	[34]
SO <sub>4</sub> <sup>2-</sup>	Potassium nitrilotriacetate	RT–90	> 24h deposition time at 50 ° C [35]

## 5 Experimental

In this section the experimental details of the project will be described. All parts that are named baseline are part of the ÅSC standard procedure for lab scale processing of CIGS solar cell materials which is described in greater detail in [36]. Here only the core details are extracted to describe the baseline process which was used during the entire project, while the experiments that deviate from the baseline are described more thoroughly.

### 5.1 Baseline CIGS

An overview of the baseline processing is given in table 5.1 while the more complete description of the process is given in [36]. This section will describe how the baseline process is used to give  $0.5 \text{ cm}^2$  cells. Lab scale production of modules is similar but some steps need to be modified to some extent.

**Tab. 3:** Baseline process with short comments and lab name. Layers from bottom to top starting with soda lime glass. Letters indicate that the layer is deposited by either A or B not both.

Layer	Method	Normal layer thickness	Name
1. Soda lime glass	Cleaned at ÅSC	1–2 mm	Soda lime glass
2. Molybdenum	DC-Sputtering	350 nm	MRC
3A. CIGS	Co-Evaporation	2000 nm	BAK
3B. CIGS	Co-Evaporation	2000 nm	MPilote
4. CdS	CBD	50–100 nm	CBD
5. i-ZnO/ZnO:Al	RF-Sputtering	440 nm	von Ardenne
6A. Al/Ni/Al grid	Evaporation	3000 nm	BA
6B. Al/Ni/Al grid	Evaporation	3000 nm	Flutter
7. Scribing	Mechanical scribing	NA	Scriber

#### 5.1.1 Soda lime glass

The soda lime glass is a low iron drawn glass of type extra white glass. Since the glass is drawn and not ordinary float glass, it means that both sides of the glass are identical. The glass is used as is after a wash procedure which uses  $60^\circ \text{C}$  deionized water and Cole-Parmer Micro-90 detergent. Four consecutive baths are used with ultrasonic baths inbetween to remove any impurities on the glass. After the cleaning substrates are spin dried in nitrogen atmosphere and placed in a nitrogen cabinet if not sputtered with molybdenum directly.

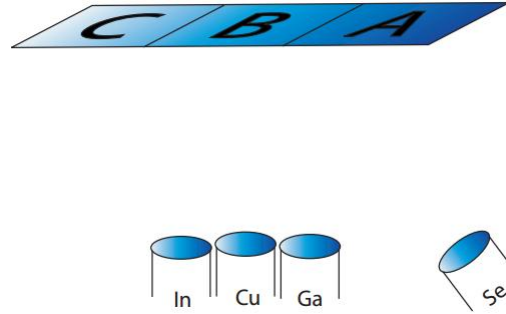
#### 5.1.2 Sputtering of molybdenum

Back contact of molybdenum is sputtered with the MRC 603 DC sputtering system using a 99.99 % Mo target. The sputtering power used is 1500 W and the sputtering pressure is 0.8 Pa. Substrates move at a rate of 7 cm/min. The process is a two stage process so it actually deposits two different layers of molybdenum. First being a layer designed to be adherent to the glass substrate

i.e a prime layer. Second a layer that is designed to have good electrical properties, the resulting molybdenum stack has a sheet resistance of approximately  $0.6 \Omega/\square$ . The two stage process gives a molybdenum film which has good adhesive properties to the glass while still having good electrical properties.

### 5.1.3 Evaporation of CIGS

Evaporation of the CIGS layer can be done in either the MPilote or the BAK (Balzers-Anlage (Kubische) 550). Both these systems are co-evaporation systems which use different evaporators to evaporate the source material of Cu, In, Ga and Se. The BAK is a system where the substrates are fixed in place and do not move around. In contrast to the MPilote where the substrates move on a carousel with a rotation speed of approximately one revolution per hour. The BAK is a co-evaporator which uses two different evaporators. These are positioned according to figure 5.



**Fig. 5:** Position of substrates A, B and C in the BAK with the four different evaporators in place. Figure from [37].

It has been shown that the BAK produces CIGS which has changing composition over the substrate [38, 39]. This means that the pieces A, B and C are not identical in composition. Furthermore composition varies from left to right and from top to bottom among the pieces A, B and C.

The MPilote has been shown to have much less variation in composition and thickness. MPilote is a co-evaporator as the BAK but here the substrates move around a circular path, the evaporators are fixed in place while the substrates move in front of the evaporators. First the substrates move through a heating and deposition zone where the substrate temperature reach around  $520^\circ\text{C}$ . Actual deposition takes roughly 20 minutes and thereafter the substrates move through the carousel to cool down in temperature. By setting the temperature of the evaporators, one can control Cu/III, Ga/III and thickness of the deposited CIGS layer.

### 5.1.4 Chemical bath deposition of CdS

The baseline method for chemical bath deposition of CdS is performed by using  $\text{Cd}(\text{Ac})_2$  (CAS 5743-04-4) as a cadmium source, thiourea  $((\text{NH})_2\text{CS})$  (CAS 62-56-6) as a sulfur source and 28 % ammonia  $(\text{NH}_3)$  (1336-21-6) as a complexing agent.

Here the process for deposition of the CdS layer will be described for a "small" bath which is suitable for substrates up to  $5 \times 5 \text{ cm}^2$ . 0.13 g of the cadmium source is dissolved in a 25 mL flask with deionized water. The 1.33 g of sulfur is dissolved in a 50 mL flask with deionized water. These chemicals are mixed at least one hour before deposition but no more than 12 h before. This is to make sure that the chemicals are fully dissolved for the deposition. Just before deposition 15 mL of ammonia is diluted to complete a volume of 100 mL. This gives a total volume of 175 mL for the reaction beaker.

Substrates are then mounted on the substrate holder. In the CBD container the chemicals are added in alphabetical order, i.e ammonia, cadmium and last thiourea. Substrates are then immersed in the bath where the temperature is set to  $60^\circ\text{C}$ . Every 30 s the bath is stirred until the deposition time of 8 minutes 15 second is complete. The deposited substrates are now rinsed with water in a two stage process and later dried with a nitrogen gun.

Since cadmium is a chemical element which is toxic to aquatic life and humans the waste is disposed in a certain cadmium container and sent for handling.

In theory it is possible to just scale up the deposition process by using a bigger beaker and more precursors. The biggest beaker used at ÅSC is a 1560 mL beaker for  $12.5 \times 12.5 \text{ cm}^2$  modules. The normal size "small" is a beaker which has a total reaction volume of 175 mL.

### 5.1.5 Sputtering of ZnO

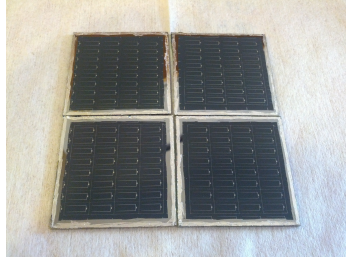
The deposition of the front contact of ZnO is a two step process deposited in the von Ardenne RF sputter. The deposited layers are an intrinsic ZnO layer and a Al-doped ZnO layer, Al:ZnO. Before deposition the targets are conditioned with an oxygen flow of 5 sccm also present during ignition.

First step of the process is to deposit the intrinsic ZnO layer which is done with a 200 W RF-generator together with an argon flow of 14 sccm. A throttle valve is used to regulate the pressure to approximately 0.133 Pa. After the deposition of intrinsic ZnO the doped ZnO layer is deposited with a 300 W RF-generator and otherwise with the same settings. The metallic sources are of 99.9 % purity and the doped target has 2 wt%  $\text{Al}_2\text{O}_3$  in the ZnO.

Before the actual substrates are deposited, a dummy run is performed by depositing ZnO according to the same recipe but on two glass substrates. The sheet resistance of these two glass pieces is then checked with a four point probe to make sure that the sheet resistance is right. Together with each deposition one glass piece is placed to be deposited as well to make sure that deposition conditions do not change too much from run to run.

### 5.1.6 Grid evaporation of Al/Ni/Al

Grid deposition can be done in the flutter or in the BA (Balzers BA510). Normally the BA is used for grid deposition. The BA is a Balzer BA510 electron-beam heated evaporator using multiple crucibles mounted on a turntable. Evaporation rate is controlled by changing the electrical parameters of the electron gun. Thickness of the grown film is controlled by a quartz-crystal microbalance. Flutter is also an electron-beam evaporator but with more manual settings. Both these can be used together with a mask to produce a grid as seen in figure 6. Layers are in total about 3000 nm thick where the Ni layer is the thickest.



**Fig. 6:** Four  $5 \times 5 \text{ cm}^2$  substrates each containing  $8 \times 4$   $0.5 \text{ cm}^2$  cells. Grid has been deposited on the substrates by the flutter and afterwards the edges has been scraped off with a scalpel and an indium paste has been soldered on for cell characterization.

### 5.1.7 Scribing of cells

Mechanical scribing of cells is done by using a stylus to scribe out  $0.5 \text{ cm}^2$  cells. This is done by defining how many cells are to be cut out from the deposited grid. Depending on substrate size and how many cells are on them the cells are scribed out with a needle. Normally for a  $5 \times 5 \text{ cm}^2$  substrate  $8 \times 4$   $0.5 \text{ cm}^2$  cells are scribed out. However if the mask is placed incorrectly for the grid deposition fewer cells might be produced. Typically  $5 \times 5 \text{ cm}^2$  substrates give 32  $0.5 \text{ cm}^2$  cells which gives good enough statistics about the process.

## 5.2 Different substrates for CBD

Three types of substrates has been used for this project: the cleaned soda lime glass, molybdenum and CIGS. Only the CIGS gives fully working solar cells, but molybdenum and glass can be used to extract information on the deposition process. Depositing CdS on glass makes it easy to make optical measurements such as transmission measurements. These optical measurements can for instance give quantitative information on the thickness of the film, for instance one can use glass coated with CdS to find out the maximum deposition time possible.

Molybdenum on the other hand has the advantage that one can in principal see the thickness from the color due to Michel-Lévy interference [40]. The thickness is periodic for some period  $\tau$  which means that for a thickness  $d$  which has a color the same color will show up at  $d + \tau n$  ( $n$  being an integer) but less intense. This is because as the thickness grows the intensity exponentially decays as  $I = I_0 e^{-\alpha \cdot x}$  where  $I$  is the intensity of light,  $I_0$  is a prefactor,  $\alpha$  is the attenuation coefficient and  $x$  is the path length relating to the thickness and refractive index. Molybdenum has been used as a quick check to see how deposition thickness varies with time. Glass has been used for optical transmission measurement and GI-XRD while CIGS has been used to make fully working solar cells.

## 5.3 Sodium citrate deposited CdS

In general the cadmium salt  $\text{Cd}(\text{Ac})_2$  was used as a cadmium source. In the beginning  $\text{CdCl}_2$  was used as a cadmium source since that was what was used

in the articles [24–27]. These served as inspiration for using sodium citrate dihydrate (CAS 6132–04–3) as a complexing agent. Switching from the chloride salt to the acetate salt was based on the fact that the acetate salt also produced working films and has several advantages compared to the chloride salt.

The chloride salt is more toxic and more expensive. In contact with water it forms a thick white paste that tends to stick onto the walls of flask and the weighing boats used in the lab. Cadmium acetate is still a toxic substance, however it does have advantages compared to the chloride salt. These being less toxic, less expensive and not sticky in contact with water.

In all cases, the chemicals were mixed according to the following scheme:

1. Weigh in A g of  $\text{Cd}(\text{Ac})_2$  together with B g of sodium citrate dihydrate in a 100 mL flask.
2. Weigh in C g of thiourea in a 50 mL flask.
3. Weigh in D g of sodium hydroxide in a 25 mL flask or dilute a bigger solution to the appropriate mass concentration.

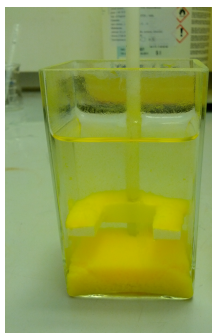
The mass of the chemicals were changed for different runs. The chemicals were added in the order of the cadmium acetate together with sodium citrate dihydrate, thiourea and last sodium hydroxide. Each time the reaction vessel was stirred every 30 s, despite the original articles describing that they did not stirr their reaction vessels [24–27]. However the application for these articles were thicker layers for thin film transistors and CdTe solar cells, not CIGS solar cells which requires a thinner layer than the other applications.

## 6 Results and discussion

Here the main results are presented which led to a working CdS buffer layer of some sort. The different recipes are presented in appendix A. These include the ones that did not produce a fully covering film, no film at all and the ones that were made into cells together with performance of these recipes. For all results short form of "on molybdenum" refers to the baseline process where CdS has been deposited on glass coated with molybdenum. While that "on glass" is on the glass that is used for the baseline process. Since the only recipe that was tested that gave a CdS film was one that utilized sodium citrate dihydrate as a complexing agent all the results are from sodium citrate deposited CdS.

### 6.1 Effect of complexing agent

Initially attempts were made to recreate results from [24–27] on molybdenum by just copying the experimental details. When as near experimental details as possible had been used all that happened was that millimeter sized CdS particles fell to the bottom of the beaker as in figure 7. No film formed at all.



**Fig. 7:** *Initial experiments with low amount of complexing agents only produced millimeter sized CdS particles and not a film, these particles are at the bottom of the reaction vessel.*

Rereading the articles many times it was clear that the information in the articles was not enough to just copy the experimental setup used. The experimental details were really vague and thus more trial and error had to be used.

After initial trials on molybdenum, it was clear that at least twice the amount of complexing agent (roughly 1 g) was needed to form a film. These findings then led to a first trial on CIGS to see how the complexing agent together with the thiourea concentration gave different films.

**Tab. 4:** *Experimental setup for determining the effect of complexing agent and thiourea on cell performance and thickness. Deposition time was 8 minutes 15 s, 110 mg NaOH was used and 0.16 g of CdCl<sub>2</sub>.*

Thiourea/g	Sodium cit/g	CIGS substrate	Color of CdS on Mo
1.33	2.52	9696a	dark blue
1.33	1.26	9697d	light light blue
0.67	2.52	9696d	brown-purple
0.67	1.26	9697c	dark blue

These four samples came from two different CIGS "9696" and "9697" made in the MPilote with the same settings after each other. This means that all these substrates are comparable since XRF analysis showed that they had the same composition and thickness. Cells were processed and the results are given below together with the baseline 9697b.

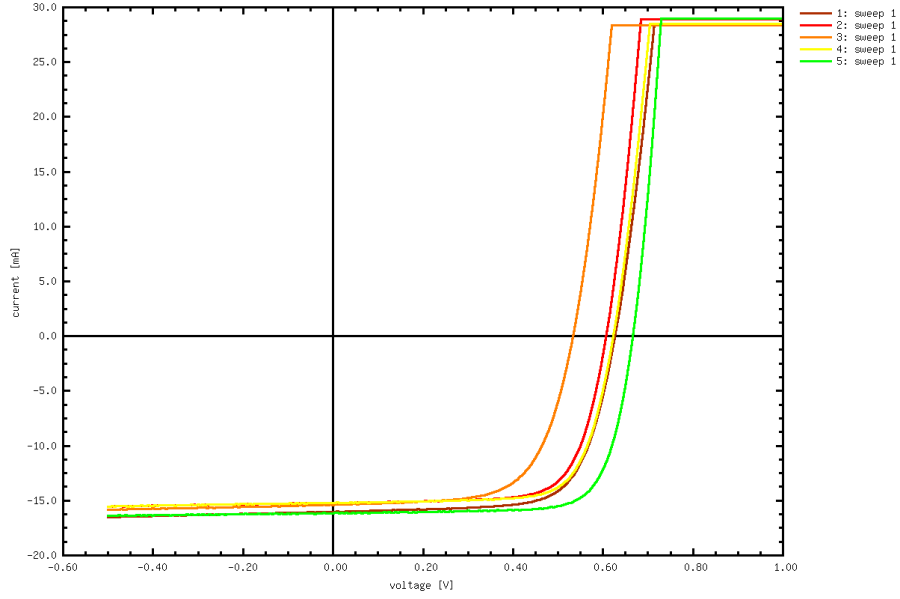
These cells were also analyzed by J-V curves, the average mean and maximum from the cells are presented in table 5. However not all cells were measured on, which was a weakness in the evaluation of the cells. For the different recipes at least 20 cells out of 32 were measured on, thus it is possible that the best cells produced was not measured on. Remeasurements could not be made because the cells were baked in an oven to see if this would improve the cells, which they did not.

**Tab. 5:** *Effect of open circuit voltage, short circuit density, fill factor and efficiency on the complexing agent and thiourea. The J-QE is only for wavelength < 1000 nm because only one detector was used, presented because of large spread in J<sub>sc</sub> for different samples.*

Substrate	V <sub>OC</sub> (mV)	J <sub>sc</sub> (mA/cm <sup>2</sup> )	FF (%)	$\eta$ (%)	J-QE (mA/cm <sup>2</sup> )
9696a					
Mean	0.607	30.76	69.46	12.98	—
Max	0.628	32.13	72.82	14.13	30.01
9697d					
Mean	0.614	30.33	71.18	13.25	—
Max	0.626	31.88	72.79	13.80	29.53
9696d					
Mean	0.515	30.83	62.55	9.95	—
Max	0.534	32.25	65.53	10.72	30.11
9697c					
Mean	0.593	30.57	69.60	12.63	—
Max	0.616	31.95	73.59	13.48	29.93
9697b					
Mean	0.665	32.46	74.34	16.05	—
Max	0.670	32.87	75.58	16.52	—

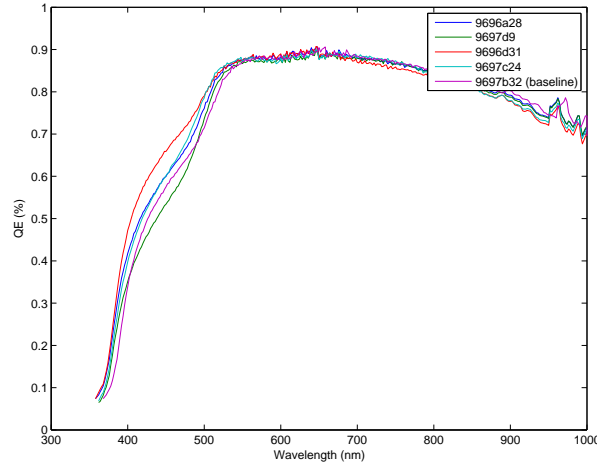
For the best cells I-V-curves are presented in table 8. These show that all cells lose in open circuit voltage and fill factor compared to the baseline.





**Fig. 8:** IV curves for the best cells measured. Orange curve is 9696d31, red curve is 9697c24, yellow curve is 9697d9, dark red curve is 9696a28 and the green curve is the baseline 9697b32. Curves shows that all samples lose open circuit voltage compared to the baseline and also a loss in fill factor.

QE measurements were made on the best cells measured in figure 9.



**Fig. 9:** QE measurements for different complexing agents and compared to the baseline process. Figures show CdS of different thickness as indicated in the blue region. All the QE curves show the same band gap. Region of wavelengths  $> 1000$  nm were excluded due to the fact that only one of the detectors of the QE setup were used. Here 9696a28 is blue, 9697d9 is green, 9696d is red, 9697c24 is light blue and 9697b32 is the purple one.

From the blue region of the QE curve one can draw the conclusion that the thinnest cell was 9696d which has the low amount of thiourea and high amount of complexing agent. The thickest however is the 9697d which has high amount of thiourea and low amount of complexing agent. Inbetween these are the cells that has high amount of thiourea and high amount of complexing agent and the one that has low amount of thiourea and low amount complexing agent. Close to the thickness of the cells with high or low in both thiourea is the baseline recipe. QE "thickness" is however not a good measurement of thickness of films since there are other factors that determine how many photons one collect in the blue region. Together in the deposition Mo-pieces were placed and the colors of these match that of the QE, and thus the thickness of Mo together with QE gives a rough estimate of the order thickness.

Thus it is evident that the complexing agent and the thiourea content affect the thickness of the formed film for a given deposition time. More complexing agents means a thinner film while more thiourea means a thicker film. This makes sense, if the sodium citrate acts as a complexing agent for the cadmium ions then more complexing agent will make the ions bound to the metal complex rather than being in the solution ready to react. If the sodium citrate did not act as a complexing agent for this system then one would expect no film to form at all or the thickness to be independent of the amount of citrate used. It might be that the sodium citrate changes the deposition conditions by some other mechanism than that of its complexing capability.

The best efficiencies for the alternative recipes were from 9696a indicating that under these experimental conditions it is best using high amounts of both thiourea and citrate. One sees that the biggest difference from the baseline is a loss in open circuit voltage and fill factor while the short circuit current is

actually higher than that of the baseline. It is worth noting that the spread in data from the J–V–setup is quite large and thus since the difference in  $\eta$  is only 0.33 % between the two best sodium citrate recipes it is hard to draw conclusions. The baseline is still better than these, also it is worth noting is that short circuit current varies a lot for the alternative recipe. Also it is evident that the measured J–V parameter has a large spread in it while the ones from the QE varies a lot less.

This could indicate that the uncertainty in the J–V–measurement is quite large. Reasons for this could be many: drift of setup during use, slightly misplaced cells, small difference in the placement of the measuring probes etc.

This indicates that the effect of complexing agent can tell more about the thickness of the formed layer than the actual performance because of the large spread in the J–V–measurement. Still this served as a design principle for further cells, a high amount of thiourea and complexing agent are to be used to make sure that layers actually forms and does not just fall off. Also it produced the best cells for the alternative recipe for this experiment, however given the large spread in the J–V–measurement this is questionable.

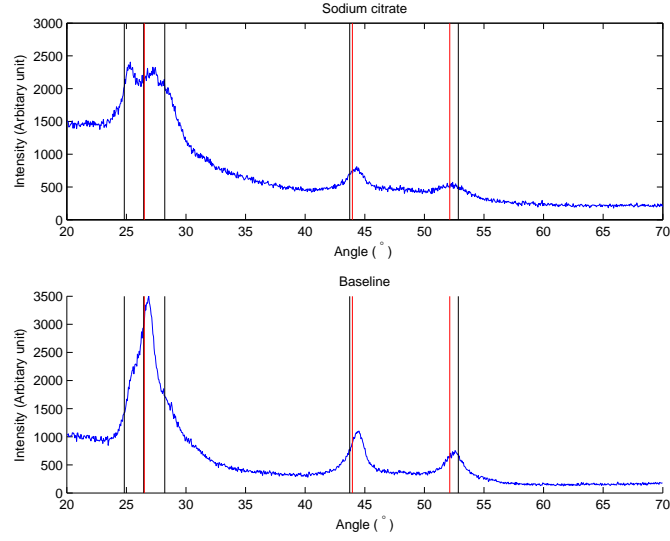
## 6.2 GI–XRD

Sodium citrate deposited CdS on glass came out looking clear yellow, transparent and less "milky"<sup>3</sup> than the baseline CdS. All visual signs indicated that CdS had actually formed, but to see if the same crystallographic phase had formed GI–XRD was performed on a baseline CdS sample deposited on glass and a CdS grown by sodium citrate deposited on glass.

The sodium citrate deposited CdS used a deposition time of six minutes and used 0.23 g Cd(Ac)<sub>2</sub>, 1.33 g thiourea, 2.52 g sodium citrate and 0.11 g NaOH. One side of the glass substrate was etched with dilute HCl solution to remove CdS on that side, this was done on the baseline and the sodium citrate deposited CdS. A short deposition time was used to for the alternative recipe to get a thin CdS to see if some other compounds would form on the glass substrate.

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<sup>3</sup> The visual signs of the two samples on glass looked like that the baseline CdS film seemed to be more diffuse like a "slurry" which spread light in more directions.



**Fig. 10:** GI-XRD with  $\text{CuK}\alpha_{1,1}$  radiation on baseline CdS and sodium citrate deposited CdS between  $20^\circ$  and  $70^\circ$ . Step size was  $2\Theta = 0.0001$ . Black vertical lines are main peaks from the hexagonal phase (h) from [41] (PDF 00-006-0314) while the red peaks are from the cubic phase (c) [42] (PDF 00-010-0454). Note that two peak pairs lie very close to each other  $26.4497^\circ$  (h)/ $26.5058^\circ$  (c) and  $43.7368^\circ$  (h)/ $43.9603^\circ$  (c).

**Tab. 6:** Expected peaks for the hexagonal and cubic phases of CdS between  $20$  and  $70^\circ$ . Intensity of each is scaled according to the main peak with intensity value of 100 %. Peaks with intensity less than 10 % of main peak not represented.

	Angle	Intensity		Angle	Intensity
Cubic [42]			Hexagonal [41]		
	26.5058	100		24.8289	75
	30.8069	40		26.4497	60
	43.9603	80		28.2171	100
	52.1321	60		36.6492	25
	54.5807	10		43.7368	55
	64.0286	20		47.8873	40
				50.9458	18
				51.8776	45
				52.8456	18
				66.8695	16

Figure 10 indicate that for both samples the hexagonal and cubic crystallographic phase had formed, however certain peaks are very near each other and thus one cannot distinguish easily between the two. The baseline had much less prominent peaks at  $24.8289^\circ$  and  $28.2171^\circ$ . Sodium citrate deposited CdS from other groups [24, 26, 27] show a hexagonal phase that grows preferentially in the (0 0 2) direction,  $26.4497^\circ$ .

However here we see a mixed phase, it is possible for CdS to start growing at a hexagonal phase and that later growth is the cubic phase [43]. Nothing can be said about the growth direction with GI-XRD since texture is not seen. In figure 10 one sees that between 25 and 30 degrees the baseline XRD has a predominant peak while the citrate one is composed of three different peaks. Reasons for this could be that the sodium citrate deposited CdS is thinner than the baseline one and thus a thicker sample might show that the citrate gives preferential growth in one direction, as seen in [24,26,27] where they grow micrometer thick samples. It could also be that the growth modes of the two different recipes differ and thus it is a fundamental difference of the different recipes

One difference between the two films is that the sodium citrate deposited one seems thinner. Evidence for this is the color of the molybdenum coated pieces which was placed in the bath at the same time, XRF Cd count <sup>4</sup> of that piece table 7 and optical transmission measurements in figure 11.

**Tab. 7:** *Color of molybdenum pieces together with Cd XRF counts for the same samples. Only the samples baseline and citrate 6 min were analyzed by XRD while the two other glass pieces were analyzed optically.*

Sample	Mo-color	XRF/(Cd counts Cps/mA)
Baseline 6 min	Dark blue	89.907
Baseline	Light blue	128.092
Citrate 6 min	Light Brown	58.630
Citrate 8 min	Brown-Purple	80.701

The color of CdS deposited on Mo of light brown for the sodium citrate deposited CdS sample compared to the dark blue or light blue of the two baseline sample's indicate that the baseline recipe had grown a thicker CdS layer. This is also supported by the XRF Cd counts where the baseline has a higher count, for the two six minute samples the XRF count is 50 % larger for the baseline deposited than the sodium citrate deposited. Figure 11 also show that the the optical thickness of the baseline is thicker than the sodium citrate deposited ones, but the six minute baseline being thinnest. Together with the GI-XRD this shows that the sodium citrate sample was thinner than the baseline samples, the XRD signal count is not enough in itself to determine the thickness of the samples. This is because the XRD only captures signals from crystalline phases, if amorphous phases forms they cannot be seen in the XRD. However together with molybdenum color, XRF Cd count and the optical transmission curve 11 it is evident that the baseline recipe grows a thicker layer.

The bath conditions could give other compounds deposited than CdS, the most likely ones being CdO and Cd(OH)<sub>2</sub>. For both samples a comparison was made with these candidates, none of the other compounds did even give a close match. But the hexagonal phase [41] and the cubic phase [42] did. This indicates that both the recipes grow a mixed phased CdS, but possibly with different preferential growth and different amount of cubic material.

However just because the other phases cannot be seen does not mean that are not there in some place of the growth of the CdS layer. Hypothesis exist that

<sup>4</sup> By first placing a thin ZnO layer

growth of CdS by CBD starts off by formation of  $\text{Cd}(\text{OH})_x$  clusters in solution or near the surface, however we cannot rule out that this does not happen here as well. There is however no support from these measurements that some other compound formed than CdS of hexagonal and cubic phase.

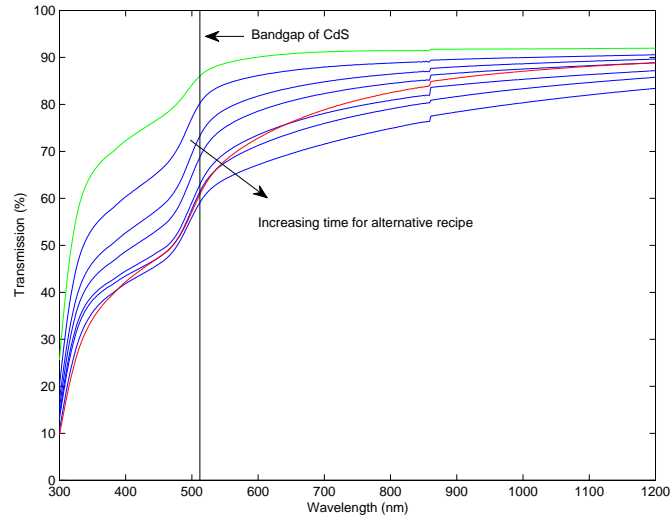
### 6.3 Optical transmission measurements

Optical transmission measurements were made from 300 to 1200 nm with a Perkins Elmer Lambda-950 spectrophotometer on glass substrates. These were made to see the growth of CdS, also to compare it with the optical thickness of the baseline CdS. Experimental condition was to remove one glass substrate at a time at different times from the bath. The samples were dried off with a nitrogen gun and the backside was etched with dilute HCl to simplify the analysis of the data. This avoid multiple reflections and the light only has to pass through one CdS layer not two.

Two different time series were used and later served as a design guideline for making CIGS cells. These used 55 mg or 110 mg NaOH which was determined by taking an appropriate volume from a stock solution of 2200 mg/L. This was because only sodium hydroxide pellets were available and thus a stock solution had to be made. However when going up in NaOH amount of around 300 mg the films simply peeled off. Thus a quite low amount of NaOH had to be used to even produce a film and a time series was made to evaluate the growth of these compared to the baseline. For the different time series the recipe used was 0.23 g of  $\text{Cd}(\text{Ac})_2$ , 2.52 g of sodium citrate dihydrate and 1.33 g of thiourea.

#### 6.3.1 110 mg of NaOH

The first working recipe used about 110 mg of NaOH. This weight was initially used since most sodium hydroxide pellets weighed in at around that. Also it produced a fully covering film, the growth of these were studied on glass and the optical transmission curve is seen in figure 11. Deposition times were 6, 7, 8, 9, 10 and 11 minutes for the alternative recipe. For the baseline deposition times were 6 minutes and 8 minutes 15 s.



**Fig. 11:** Transmission curve of CdS grown with 110 mg of sodium hydroxide. The deposition times were 6, 7, 8, 9, 10 and 11 minutes. Red curve is the baseline process while green curve is baseline grown at 6 minutes. For the alternative recipes the blue curves are used and the one with highest transmission is the 6 minute sample while the one with the lowest is the 11 minute. The kink in the graph at approximately 875 nm is due to change of lamp in the spectrophotometer and not a physical phenomena.

Figure 11 indicates that after around 10 minutes the sodium citrate deposited CdS produced a curve which is the most similar under transmission to the baseline process. Just by visually inspecting the films it looked like the longer the deposition time for the sodium citrate recipe the more intense yellow color did the films have. Also these samples looked less milky than the baseline samples which seemed to spread out the light more diffusely. However this is all by visual inspection, which means that it is not a "hard" number or anything like that, just visual appearance.

The optical transmission curves show that optically it looks like growth saturates as time increases, if only absorption would be the mechanism of loss of transmission then one would expect that the change in transmission would be linear in thickness by the Lambert–Beer law. However if the action of loss in transmission is more complex than that, i.e if the action is that of reflection losses as well then this does not hold.

To investigate if this is the case then complex optical measurements would need to be made, which are not available for the spectrophotometer in the lab. Here it would seem straightforward to just measure the number of Cd count on the samples by XRF. To do this the samples need to be coated with ZnO to avoid contaminating the XRF system. This coating could damage the film by removing atoms from the surface and thus these samples were not coated with ZnO. If one had used Mo pieces at the same time or two glass pieces for each time then this could be done. However this many samples do not fit in the CBD holder and several time series would have further complicating the analysis.

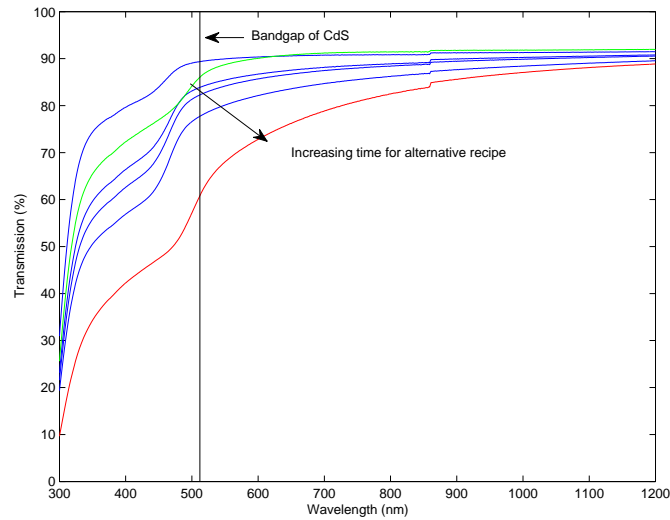
The different times were checked with a simple stop watch and thus the un-

certainty in time is quite large, however they show that for this type of recipe layers of different thickness can be grown. It also shows that the longer deposition time, the less transparent the layer gets, which is of no surprise. Only if the growth had stopped at a certain moment would the layer of different deposition times behave optically the same.

These findings served as a guideline for making solar cells. However the growth of CdS on CIGS is not the same as on SLG because the substrates are inherently different, one being amorphous and the other being polycrystalline.

### 6.3.2 55 mg of NaOH

Using half as much sodium hydroxide as previously described was sought out to try to get milder deposition conditions and also thinner films. To investigate this longer deposition times were used because growth of CdS was slower on Mo with lower NaOH amount.



**Fig. 12:** Transmission curve of CdS grown with 55 mg of sodium hydroxide. The deposition times were 8, 11, 13 and 16 minutes. Red curve is the baseline *i* while green is the baseline process with 6 minutes deposition time. The curve at 8 minutes is the one termed "thinnest" and the thickest is the one deposited for 16 minutes. The kink in the graph at approximately 875 nm is due to change of lamp in the spectrophotometer and not a physical phenomena.

All the samples produced here are more transparent than the baseline process. The six minute baseline sample looks like a sample deposited by the alternative recipe somewhere between 8 and 11 minutes. Here as for the samples grown with 110 mg of NaOH it seems as growth slows down as time increases as seen in figure 11. None of these samples were checked with XRF for the same reason as the other time series. It is worth noting that here, which is not seen in figure 11 that there seems to be a shift of the band gap. To determine this one would need to make band gap measurements, simply extracting these from transmission curves is not accurate enough. However it looks like there might



be a shift in the band gap for thinner films. Here the deposition times were 8, 11, 13 and 16 minutes for the alternative recipe while the baseline had times of 6 minutes and 8 min 15 s, as in figure 11

This time series also worked as a design guideline for making solar cells.

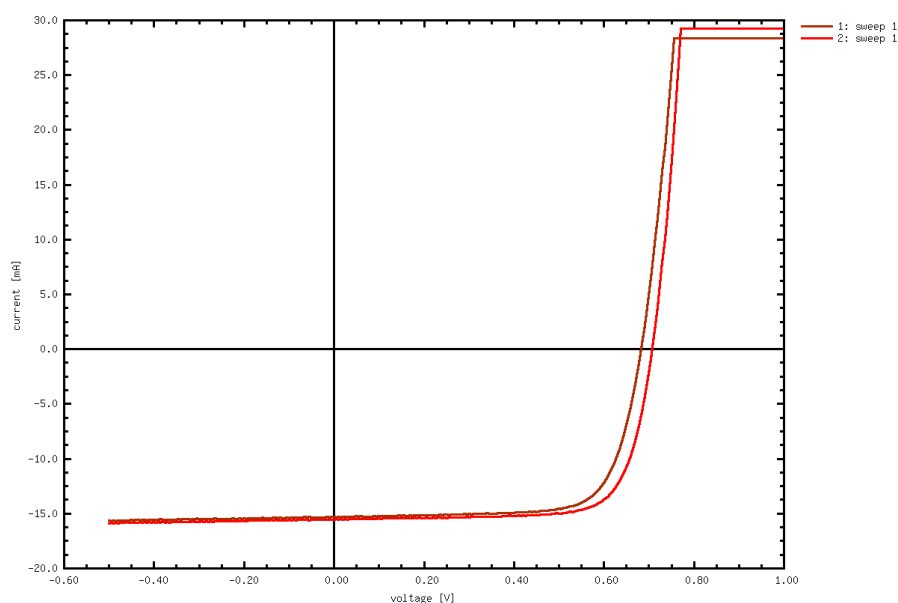
#### 6.4 Solar cells produced with 110 mg NaOH

To investigate how solar cells produced with 110 mg of NaOH would perform against baseline, a recipe with 0.23 g  $\text{Cd}(\text{Ac})_2$ , 1.33 g thiourea, 110 mg of sodium hydroxide and a deposition time of 12 minute was used. This was to produce a CdS layer that is approximately as thick as the baseline recipe from optical transmission curves in figure 11. Baseline sample was 9698b and the alternative sodium citrate was 9698d.

**Tab. 8:** *Solar cell performance data for cells produced at a deposition time of 12 minutes with 110 mg sodium hydroxide compared to the baseline.*

Sample	$V_{oc}$ (mV)	$J_{sc}$ (mA/cm <sup>2</sup> )	FF (%)	$\eta$ (%)
9698d (12 minute sodium citrate)				
Mean	0.680	30.66	73.88	15.48
Max	0.686	31.06	75.20	15.89
9698b (baseline)				
Mean	0.706	31.05	75.00	16.45
Max	0.712	31.65	75.95	16.83

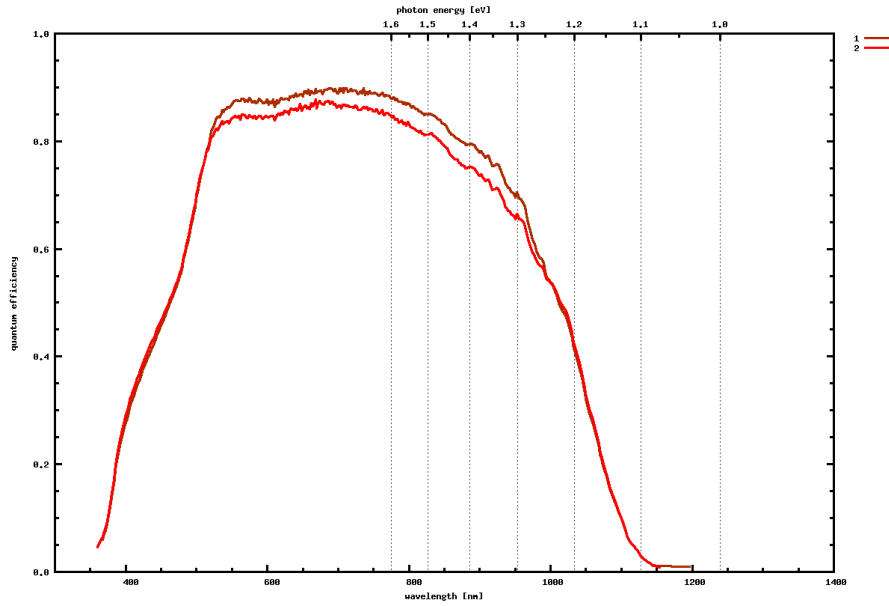
For the best produced cells for the both recipes, 9698d1 and 9698b32 IV curve 13 and QE curve 14 are presented below.



**Fig. 13:** IV curve showing that the alternative sodium citrate has a lower open circuit voltage and fill factor. Baseline curve is the red while the dark red is the sodium citrate deposited one. Samples were 9698b32 and 9698d1.

The IV curve 13 together with the table 8 show that the alternative recipe loses open mainly circuit voltage but also fill factor.

QE measurements were made for the best cells and is presented in 14 together with the baseline.



**Fig. 14:** QE curve showing that the alternative sodium citrate has a lower QE for intermediate wavelengths. Baseline curve is the top one in dark red while the light red is the sodium citrate deposited one. Samples were 9698b32 and 9698d1.

The IV curve 13 show a loss of open circuit voltage and fill factor while the QE curve 14 shows that for intermediate wavelengths the alternative recipe has an overall lower QE. According to the transmission curve 11 it is likely that the thickness of the alternative CdS recipe is similar to the baseline. This is supported by the QE curve for blue wavelengths. However since QE is not a conclusive way to measure thickness one cannot necessarily say this. Ideally the buffer should not determine the behavior for intermediate wavelengths, the losses here are more of that of reflections and a low diffusion length. Since the QE behaves the same in the blue region, the deposited layer somehow causes increased reflections or changes the diffusion length of the minority carriers in the CIGS layer.

## 6.5 Solar cells produced with 55 mg NaOH

As seen in figure 14 the cells produced with 110 mg of NaOH suffered losses in the QE for intermediate wavelengths. To try to get thinner cells and also milder deposition conditions half the amount of NaOH was used. This was to see if the losses in intermediate wavelengths could be lowered and also an increase in the QE for blue wavelengths could be obtained.

Here two sets of samples were produced to be compared to the baseline. Using a deposition time of 12 minute, 1.33 g thiourea, 0.23 g  $\text{Cd}(\text{Ac})_2$  and 2.52 g of sodium citrate for the alternative recipe while the baseline was kept as is. The two samples were 9737C and 9723d1 which are to be compared to the baseline runs of 9737A and 9723d2. Here is it worth noting that these two CIGS, 9397 and 9723 are different from eachother in composition and thickness. This

means that it is possible to compare 9737C with 9737A but not with 9723d1 or 9723d2 and vice verse. These were the best results obtained in the project.

**Tab. 9:** *Best cells produced with 12 minute deposition time with 55 mg of NaOH.*

Sample	$V_{oc}$ (mV)	$J_{sc}$ (mA/cm <sup>2</sup> )	FF (%)	$\eta$ (%)
9737A (baseline)				
Mean	0.609	33.20	69.78	14.10
Max	0.616	34.86	71.88	14.91
9737C				
Mean	0.572	33.81	65.40	12.65
Max	0.587	35.84	69.77	13.59
9723d1 (baseline)				
Mean	0.650	30.03	71.76	13.99
Max	0.665	30.24	73.08	14.37
9723d2				
Mean	0.640	30.35	67.41	13.11
Max	0.657	31.52	71.04	14.22

Here it is interesting to see in table 9 that using the same recipe for two different CIGS the change in efficiency compared to baseline show result that are promising. For instance when comparing the best cells of 9723d1 (baseline) to 9723d2 the difference in efficiency,  $\Delta\eta$  is 0.15 % which is almost no difference at all. When comparing the average the difference is almost absolute 1 % which is still quite high. However for the best cells for this CIGS the difference is probably within the uncertainty of the measurements. A change in open circuit voltage of 8 mV can be explained by temperature differences for instance.

It is worth noting here that despite using the same recipe being used the performance difference compared to the baseline differs to some extent. This could indicate that the two different CIGS substrates do not work the same for the alternative recipe and thus certain CIGS might be more suitable for the alternative recipe. It could also be that despite using the same recipe it does not produce the same result, however this is less likely.

To see if these could be improve two other experiments were performed, a pre-heated deposition and a deposition which used a pre-etching with ammonia. In those sections of this project QE curve can be seen 16 together with IV curves as in figure 15. These show not only the effect of preheating and pre-etching but also how the none modified versions perform.

### 6.5.1 Preheated solutions

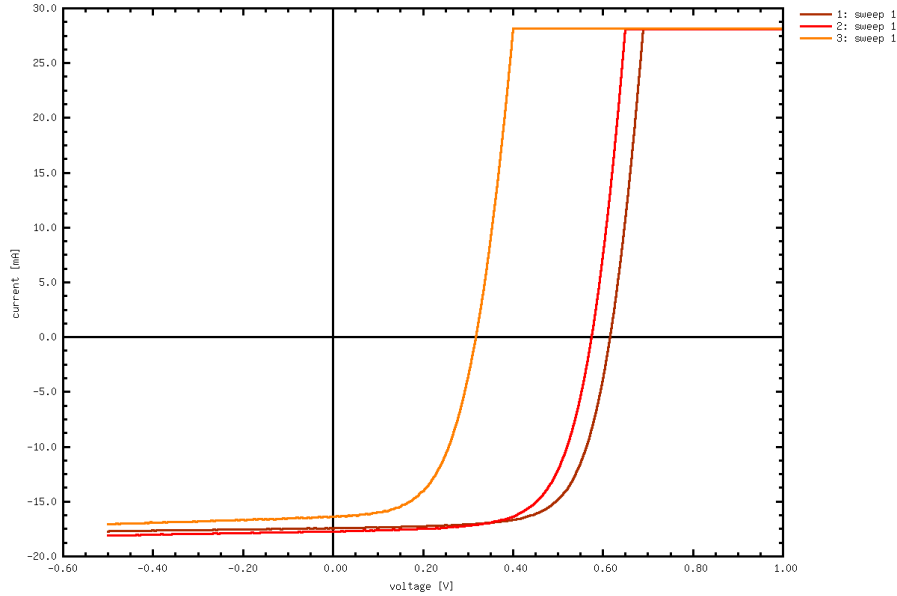
Certain research groups preheat the CBD solutions before adding a final ingredient to start the reaction. Various claims has been made about the effects of this pre-treatment, some state that it etches the CIGS surface additionally or that Cd-ions diffuse into the CIGS, which would alter the performance of the cells. To test if this would improve the sodium citrate recipe, bath depositions were made on molybdenum to see how one should pre-heat and yet still achieve the same thickness. Using a recipe of 1.33 g thiourea, 0.23 g Cd(Ac)<sub>2</sub>, 2.52 g of sodium citrate and 55 mg NaOH on molybdenum it was seen that the same

thickness as one deposited for 12 min could be achieved by preheating the solutions for 8 minutes and then depositing for 8 minutes by adding NaOH to start the reaction. Without NaOH added to the reaction there is no visual sign that the reaction actually starts.

**Tab. 10:** *Effect of pre-heat compared to a none pre-heated sample and the baseline.*

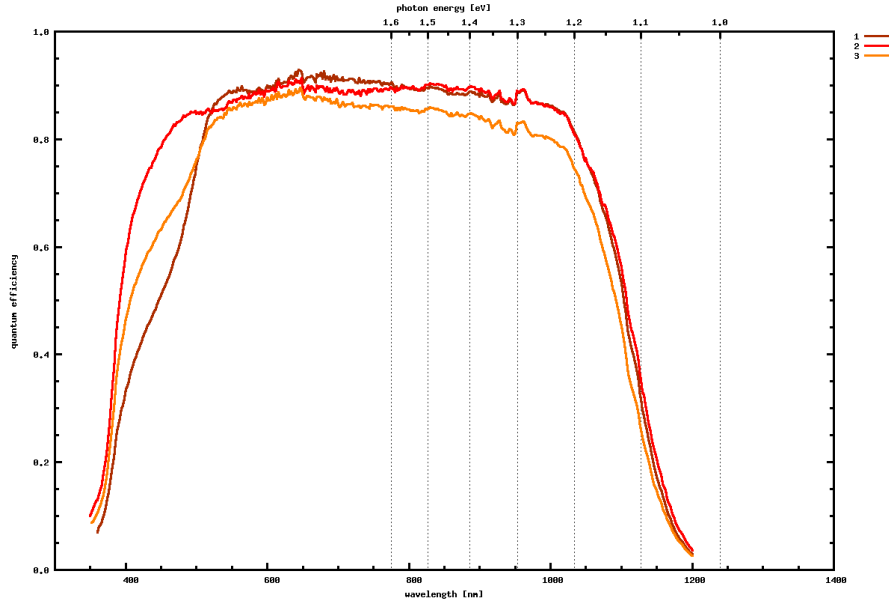
Sample	$V_{oc}$ (mV)	$J_{sc}$ (mA/cm <sup>2</sup> )	FF (%)	$\eta$ (%)
9737C (not pre-heated)				
Mean	0.572	33.81	65.40	12.65
Max	0.587	35.84	69.77	13.59
9737B (pre-heated)				
Mean	0.222	32.55	40.30	3.39
Max	0.317	34.62	55.29	5.73

IV and QE measurements were made on the best cells and are presented in in figure 15 and figure 16



**Fig. 15:** *I–V measurement on the three substrates. Here the orange is the preheated and the red one is the none-preheated. The cells deposited by preheating the solution were almost completely killed. Inlay of dark red to show how baseline performs.*

As can be seen by the table 10 and figure 15 this preheat treatment almost killed the cells. Efficiency dropped by almost absolute 10 % compared to the baseline. This is due to a huge drop in open circuit voltage and fill factor. Open circuit voltage decreases by almost 300 mV compared to the none preheated and fill factor by absolute 15 %. The QE curve in figure 16 interestingly showed that the cells produced by preheating had lower QE for all intermediate wavelengths.



**Fig. 16:** QE of the CdS deposited by preheating the solutions and deposited as is for 12 minutes. Orange curve is the preheated, red is the none-preheated. The preheated shows an overall decrease in QE for intermediate wavelengths while the none-preheated looks like it is an extremely thin layer, possibly with a different band gap. Inlay of dark red baseline for comparison.

Preheating the substrates must somehow have a huge detrimental effects on the cells. Sodium citrate deposited without preheating suffers from the same effect of a loss in fill factor and open circuit voltage, but not nearly as big as the drop by preheating. Causes for this huge drop in performance are not fully understood, but it must be by degradation of the CIGS, the CIGS surface or the interface somehow. This preheated solution contains sodium, which has been proven to have a number of effects on CIGS: including film structure, conductivity, changes how defects are distributed among others. It might be, but this has not been investigated further that the preheated solutions which contain sodium compounds somehow changes these often beneficial effects of CIGS to the negative. However this would mean that the CIGS is very sensitive to sodium containing solutions and that sodium from the solution should start to diffuse into the CIGS or make the sodium diffuse out from the CIGS.

It is more likely that warm sodium hydroxide solution damages CIGS or the surface of the CIGS or the interface. This could explain the efficiency drop by the none-preheated which is in the bath for 12 minutes. Here the cells are exposed to 60 °C NaOH for several minutes during the deposition.

Since the preheated solutions did not have positive effects on the cells no further experiments were done on CIGS to see if it could be improved with preheating. Preheating was seen as a dead end for this type of chemistry. However it might help explain the drop in open circuit voltage and fill factor for all experiments, if the sodium hydroxide damages the surface of the CIGS then this would explain the losses for the previous experiments.

### 6.5.2 Pre-etching with ammonia

Previous experiments showed that the baseline outperformed the sodium citrate recipe when using low amount of sodium hydroxide. The idea was now to see if pre-etching with ammonia with the same experimental conditions as the baseline could improve this. The samples were pre-etched in ammonia for four minutes in the bath, and then the recipe used 1.33 g thiourea, 2.52 g sodium citrate, 0.23 g  $\text{Cd}(\text{Ac})_2$  and 55 mg of sodium hydroxide to deposit CdS. Deposition time was 12 minutes. This was made to see if the sodium citrate deposited CdS could be improved by pre-etching, however it might have been interesting to pre-etch the baseline run as well. However, the idea was to see if pre-etching with ammonia could improve the sodium citrate deposited cells, not the baseline.

**Tab. 11:** Effect of pre-etching compared to a none pre-etched sample and the baseline.

Sample	$V_{oc}$ (mV)	$J_{sc}$ (mA/cm <sup>2</sup> )	FF (%)	$\eta$ (%)
9723d2 (no pre-etch)				
Mean	0.640	30.35	67.41	13.11
Max	0.657	31.52	71.04	14.22
9723c1 (pre-etched)				
Mean	0.559	29.82	65.70	10.99
Max	0.615	30.69	69.09	13.05

The findings in table 11 indicate that the pre-etching did not improve cell performance but only made them worse. Efficiency dropped by more than absolute 1 % compared to the unetched cells. The idea was that the pre-etching with ammonia would remove impurities from the CIGS surface and thus improving performance. Since the treatment with ammonia had only detrimental affects this can be either by the fact that ammonia or water in itself damages the CIGS in some way. If ammonia would damage the surface then recipes that used more ammonia would benefit from using less. However a lot of groups produce high quality CdS with ammonia and do not see that more ammonia necessarily make their cells worse. Thus it is more likely that exposure to water or temperature somehow damages the cells, the etched sample have been in a water bath for a total of 16 minutes which is almost twice of the baseline. Results are not fully understood, but indicate that in this experiment the CIGS only deteriorated from the none-etched.

### 6.5.3 BAK run

Only one run was made with BAK-CIGS, this is mainly due to the fact that BAK-CIGS is harder to compare when searching for small differences. The reason for this being is that the substrates that come out of the BAK have different compositions and that they degrade faster when exposed to air. When depositing CdS by CBD on BAK it means that the order in which deposition has been done alter the result, doing recipe "A" before "B" might show that "B" is worse than "A" but from degradation of the CIGS and not from the fact that one recipe is better than the other. The order for this run was 130508 – 3AL

(baseline), 130508 – 3BL (sodium citrate with pre-etching in ammonia) and finally 130508 – 3BR (baseline). The reason for this was to have a reference in the beginning, a sample which used sodium citrate and finally one more reference to see if the CIGS had degraded. The idea was to have a sample which wasn't pre-etched in ammonia as well, however this sample was destroyed and thus no data could be collected.

Sodium citrate deposited CdS with pre-etching in ammonia was done by using 1.33 g thiourea, 2.52 g sodium citrate, 0.23 g  $\text{Cd}(\text{Ac})_2$  and a deposition time of 12 minutes.

**Tab. 12:** *Solar cell performance parameters from BAK-CIGS with two baseline runs (13050803-AL/BR) compared to one which has been pre-etched in ammonia (130508-3BL) and later deposited for 12 min with sodium citrate*

Run	$V_{oc}$ (mV)	$J_{sc}$ (mA/cm <sup>2</sup> )	FF (%)	$\eta$ (%)
130508-3AL				
Mean	0.640	32.44	71.88	14.92
Max	0.649	32.83	75.89	15.92
130508-3BL				
Mean	0.564	33.16	66.81	12.50
Max	0.570	33.33	67.59	12.75
130508-3BR				
Mean	0.624	30.41	72.62	13.79
Max	0.633	30.61	74.28	14.23

One sees from table 12 that both the baseline runs outperform the sodium citrate by more than 1% absolute  $\eta$ . This means that the deterioration of the cells from run to run in this case cannot explain the difference in performance. Even though the samples are not uniform and not processed at the same time the baseline runs outperforms the sodium citrate deposited layer by having a larger  $V_{oc}$  and fill factor. Pre-etching with ammonia for this short time seems to not to improve the results of the sodium citrate recipe, as seen previously in the MPilote results 11.

## 6.6 Long term stability of solutions

According to the baseline process the solutions of thiourea and cadmium salt are to be mixed at least 1 h before deposition and no more than 12 h before deposition. This means that for each deposition one has to weigh up the appropriate amount of chemicals and mix them with water according to the recipe used. Weighing up chemicals is time consuming and when it comes to small masses as 0.13 g of cadmium acetate as the baseline process calls for this can create variations from run to run.

Previously it had been tested to use premixed chemicals so one could eliminate this step when depositing CdS, however these experiments produced results that changed with time [39]. The problem was that of the cadmium seemed to form a white precipitate in solution with time, which was thought to be  $\text{Cd}(\text{OH})_2$ . Also since ammonia is volatile the concentration of a premixed ammonia solution is changing over time.

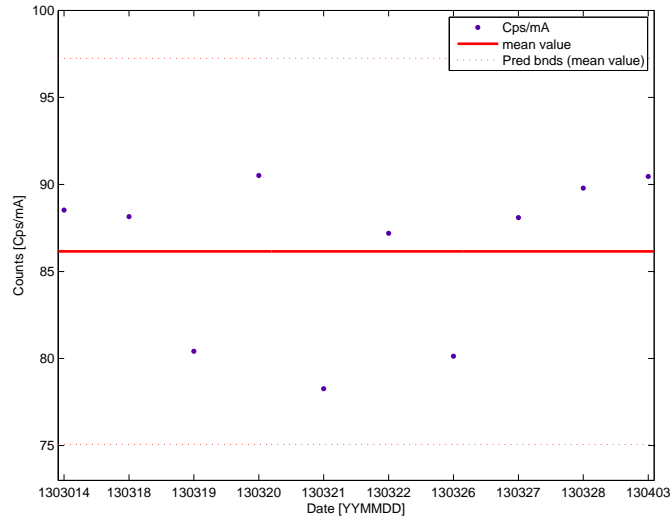


The idea was then to see if all chemicals could be premixed with sodium citrate as a complexing agent to minimize the number of times one weighs up chemicals. This was done by mixing 13.33 g of thiourea in a 0.5 L flask with water, 1.60 g of cadmium chloride together with 25.52 g sodium citrate in a 0.5 L flask with water and finally 1.10 g of NaOH in a 0.5 L flask with water. For each run 50 mL of each solution were mixed together with 25 mL of water for a final volume of 175 mL.

Each deposition was 8 minute 15 s with stirring every 30 s with bath temperature of 60 °C on molybdenum. Samples were all purple or slightly brown with uniform color over the whole substrate, and kept in a nitrogen cabinet until all depositions had been made. When the last deposition had been made on the molybdenum the remaining samples were removed from the cabinet and a thin layer of ZnO<sup>5</sup> was deposited on the samples. This was to avoid contaminating the XRF system with Cd [44] and this thin layer would not interfere with the measurements [44]. Each sample was then placed in the XRF and the number of Cd counts were collected, minimal background noise was present.

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<sup>5</sup> 90s of deposition time was used to give a thin ZnO layer



**Fig. 17:** XRF measurement of CdS deposited on Mo. Deposition time of 8 minute 15 s at 60 °C. All the Cd counts lie within the calculated 95 % deviation from the arithmetic mean.

XRF counts are proportional to the number of Cd atoms present in the film and thus if the density is constant also present a measure of the thickness of the film.

This means that with these experimental conditions it is possible to use premixed chemicals, at least when depositing them on Mo. It would thus be likely to use a recipe which uses premixed chemicals if one uses sodium citrate as a complexing agent. This is a clear improvement from the baseline recipe which requires that the chemicals are weighed up no more than 12 h in advance.

Since the color and the XRF count of the samples are all the same or very similar it indicates that all these samples are basically the same. However this says nothing about if the same would apply if premixed chemicals for this recipe were to use on CIGS. It is likely that the same would apply if depositions were made on CIGS, however this was not tested since producing fully working cells takes 1–2 days plus analysis depending on lab issues.

## 7 Conclusions

Aim of this project was to find ammonia free CBD recipes and evaluate them. This has been done for the cases when the chemicals were available in the lab or could be easily purchased. As indicated in Appendix A a lot of recipes were tested, but could not just reproduce the results from the corresponding paper. In some cases the experimental setup just could not be copied or was too vaguely described.

This meant that the only recipe that worked used sodium citrate as complexing agent and this came in late in the project. The original papers used cadmium chloride as a cadmium source, which was first used here. However given that this salt is more toxic, more expensive and harder to handle than the salt used for the baseline process,  $\text{Cd}(\text{Ac})_2$  the chloride salt was changed for the acetate salt. The experimental details in the papers described sodium citrate as complexing agent were also very vague and thus a lot of trial and error had to be used to get a recipe that even produce a CdS film and not just particles. Moreover when finally a recipe that could produce CdS that were deemed good enough on Mo the CIGS evaporator MPilote had big problems and not everything could be tested.

In general, it is hard to draw conclusions about the performance of the layer, more can be said about the processing windows for sodium citrate deposited CdS. The recipe works similarly for cadmium chloride, cadmium acetate and cadmium sulfate on Mo for equimolar masses indicating that the rate is at least for short deposition times not depending on the anion of the cadmium salt. Sodium citrate acts as a complexing agent and the more complexing agent available the slower the reaction, at least up to 2.52 g which was the highest amount tested. The process is sensitive to NaOH concentration in the reaction, for a small beaker somewhere around 50 mg is needed to start the reaction. Going up to around 300 mg no films forms at all and only millimeter sized CdS are produced.

Some of the result indicate that the CBD process can have profound negative affects of the cell performance. For instance when pre-heating the solutions the cells were almost killed. Given the huge difference in performance for the produced solar cells it is evident that the CBD process itself is something that is to be taken seriously.

This project also demonstrate a problem with peer reviewed articles, sometimes the experimental details are very vague and cannot be reproduced. It is not so strange that research groups do not want to give away all the details about their work and that since scientific papers are short not every detail can be captured. However in theory it should be possible to at least recreate the results from the articles and not starting "from scratch".

### 7.1 Further outlook

The cells produced for this project were not as good as the baseline process, for the few cells that could actually be made a loss of open circuit voltage and fill factor is seen. This might be from the layers being very thin, which was something that was striven for to capture more light in the blue region while just keeping the baseline as is. However this might have detrimental effects on the cells, it is not possible to rule out that if a thinner baseline was used

the same effect would show up. Thus one cannot distinguish here between the thickness of the layer and the actual deposition process. This would be worth doing, to see if it is the thickness of the CdS layer or the recipe itself that make the cell lose in open circuit voltage and fill factor.

Other things that would be worth doing is changing the temperature, we've deposited CdS in room temperature and at 60 °C because no other temperatures could be tested easily. Both these temperatures can give fully covering CdS layers, however when using the elevated temperature it is likely that warm NaOH damaged the interface or the CIGS. Thus it would be worth altering the temperature of the deposition here to see if cells improve by a lower temperature CBD. Other things that are worth testing are changing from NaOH to other bases like KOH.

KOH was tested instead of NaOH in this project and it also produced a fully covering film on SLG. However given that the potassium hydroxide came in submillimeter particles that flew away by the ventilation in the fume hood this was not further tested. If premixed KOH solution is used then one does not have this problem and thus it is worth further exploring.

Besides this it might be worth testing out pH-buffers to ensure that the pH is stable during the whole deposition. We've seen that depositing CdS by sodium citrate is sensitive to the amount of NaOH present and thus it might be worth using a pH buffer to minimize variations in pH during deposition.

No changes in the sulfur source was made, however it is possible that a different sulfur source would work better for this chemistry. The only organosulfur compounds seen in the literature for depositing CdS by CBD was thiourea and thioacetamide. However given that there are a myriad of sulfur compounds available this might be worth testing.

Besides this, more and better CIGS are needed to fully evaluate the sodium citrate recipe. In this project getting CIGS pieces itself was a problem, and the CIGS obtained was of low efficiency, sometimes as low as 14 % for the baseline process. This low efficiency is nowhere near the best obtained efficiencies by the group, and to make a fair evaluation of the sodium citrate recipes better CIGS and more would be needed.

## Acknowledgment

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## A Recipe collection

This part will describe CBD recipes that were tested. A lot of different recipes were tested at first, but a lot of them were not evaluated further since they did not produce full covering films as in table 13 or simply no film at all. Together with this films that actually led to working cells are presented.

**Tab. 13:** Recipes that did not produce fully working films. Blank entries indicate that these parameters were not included or not tested. Here TU is short for thiourea, TRC means trisodium citrate dihydrate, deposition time means that depositions were made for times between 0 and that time. All deposition temperatures were 60 °C. Reference indicates where the recipe came from.

Cd/g	TU/g	Comp agent/g	Dep time/min	pH	Ref
0.10 Cd(Ac) <sub>2</sub>	0.25	0.15 tartaric acid	16		[28]
0.10 Cd(Ac) <sub>2</sub>	0.25	0.15 tartaric acid + 10 mL NH <sub>3</sub>	16		[28]
0.66 Cd(Ac) <sub>2</sub>	0.83	0.25 tartaric acid	16		[28]
0.32 CdCl <sub>2</sub>	0.89	0.25 tartaric acid + NH <sub>3</sub>	16	9.5	[28]
0.32 CdCl <sub>2</sub>	0.89	0.25 tartaric acid + NaOH	16	10	[28]
0.13 Cd(Ac) <sub>2</sub>	1.33	Ethanolamine	60	11	[22]
0.13 Cd(Ac) <sub>2</sub>	1.33	Ethanolamine	60	11.5	[22]
0.13 Cd(Ac) <sub>2</sub>	1.33	Ethanolamine	60	12	[22]
0.10 CdSO <sub>4</sub>	1.33	Ethanolamine	40	11	[22]
0.10 CdSO <sub>4</sub>	1.33	Ethanolamine	40	11.5	[22]
0.10 CdSO <sub>4</sub>	1.33	Ethanolamine	40	12	[22]
0.18 CdI <sub>2</sub>	1.33	Ethanolamine	40	11	[22]
0.18 CdI <sub>2</sub>	1.33	Ethanolamine	40	11.5	[22]
0.18 CdI <sub>2</sub>	1.33	Ethanolamine	40	12	[22]
0.13 Cd(Ac) <sub>2</sub>	1.33		50		[15]
0.16 CdCl <sub>2</sub>	1.33	0.15 EDTA	40		[29]
0.16 CdCl <sub>2</sub>	1.33	0.65 EDTA	40		[29]
0.20 CdSO <sub>4</sub>	1.33	0.10 EDTA	40		[29]
0.20 CdSO <sub>4</sub>	1.33	0.75 EDTA	40		[29]
0.18 g CdSO <sub>4</sub>	1.33	0.52 TRC + 0.10 g NaOH	8		[24–27]
0.36 g CdSO <sub>4</sub>	1.33	0.52 TRC + 0.10 g NaOH	8		[24–27]
0.16 g CdCl <sub>2</sub>	1.33	0.52 TRC + 0.10 g NaOH	8		[24–27]
0.18 g CdSO <sub>4</sub>	1.33	0.52 TRC + 0.20 g NaOH	8		[24–27]
0.18 g CdSO <sub>4</sub>	2.60	0.52 TRC + 0.20 g NaOH	8		[24–27]
0.32 g CdCl <sub>2</sub>	1.33	0.52 TRC + 0.20 g NaOH	8		[24–27]
0.32 g CdCl <sub>2</sub>	2.60	0.52 TRC + 0.20 g NaOH	8		[24–27]
0.13 g Cd(Ac) <sub>2</sub>	1.33	0.52 TRC + 0.10 g NaOH	8		[24–27]
0.13 g Cd(Ac) <sub>2</sub>	1.33	0.52 TRC + 0.20 g NaOH	8		[24–27]
0.13 g Cd(Ac) <sub>2</sub>	1.33	2.52 TRC + 0.30 g NaOH	8		[24–27]
0.13 g Cd(Ac) <sub>2</sub>	1.33	0.52 TRC + 0.50 g NaOH	8		[24–27]

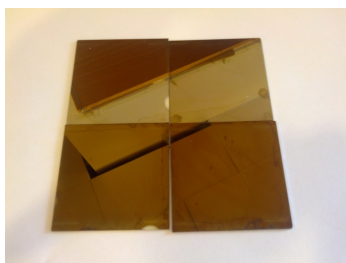
**Tab. 14:** Recipes that led to films being deposited. Blank entrees indicate that these parameters were not included or not tested. Here TU is short for thiourea, TRC means trisodium citrate dihydrate and  $\Delta\eta$  is the change in max efficiency compared to baseline. All deposition temperatures were 60 °C. Reference indicates where the recipe came from.

Cd/g	TU/g	Comp agent/g	Dep time/min	NaOH	$\Delta\eta$	Ref
0.13 g Cd(Ac) <sub>2</sub>	1.33	2.52 TRC	8 min 15 s	110 mg		[24–27]
0.18 g CdI <sub>2</sub>	1.33	2.52 TRC	8 min 15 s	110 mg		[24–27]
0.20 g CdSO <sub>4</sub>	1.33	2.52 TRC	8 min 15 s	110 mg		[24–27]
0.16 g CdCl <sub>2</sub>	1.33	2.52 TRC	8 min 15 s	110 mg	2.39	[24–27]
0.16 g CdCl <sub>2</sub>	1.33	1.26 TRC	8 min 15 s	110 mg	2.72	[24–27]
0.16 g CdCl <sub>2</sub>	0.67	2.52 TRC	8 min 15 s	110 mg	5.80	[24–27]
0.16 g CdCl <sub>2</sub>	0.67	1.26 TRC	8 min 15 s	110 mg	3.04	[24–27]
0.23 g Cd(Ac) <sub>2</sub>	1.33	2.52 TRC	12 min	110 mg	0.94	[24–27]
0.23 g Cd(Ac) <sub>2</sub>	1.33	2.52 TRC	12 min	55 mg	1.32	[24–27]
0.23 g Cd(Ac) <sub>2</sub>	1.33	2.52 TRC	12 min	55 mg	0.15	[24–27]
0.23 g Cd(Ac) <sub>2</sub>	1.33	2.52 TRC	4 min NH <sub>3</sub> etch + 12 min	55 mg	1.32	[24–27]
0.23 g Cd(Ac) <sub>2</sub>	1.33	2.52 TRC	12 min (BAK-run)	55 mg	3.17	[24–27]
0.23 g Cd(Ac) <sub>2</sub>	1.33	2.52 TRC	8 min preheat + 8 min	55 mg	9.18	[24–27]

## B Room temperature deposition with sodium citrate

When depositing CdS by sodium citrate it was noted that deposition started to take place before bath had even reached 60 °C. Therefor attempts were made to grow CdS at room temperature. None of the experiments made a thick enough film, however it was possible to grow a very thin film at room temperature.

For all experiments the mass of thiourea was held constant at 1.33 g,  $\text{Cd}(\text{Ac})_2$  was kept constant at 0.23 g but the amount of sodium hydroxide and sodium citrate varied. Sodium citrate varied between 0.5 g to 2.50 g, sodium citrate varied from 220 mg to 500 mg. The higher amount was first tried because it was believed more aggressive experimental conditions was needed to form a film. The only film that actually formed was using 220 mg NaOH and 1.26 g sodium citrate. This resulted in the films formed in figure 18



**Fig. 18:** *Experiment that formed a film at room temperature. Experimental details were 0.22 g NaOH, 1.26 g sodium citrate, 0.23 g  $\text{Cd}(\text{Ac})_2$  and 1.33 g thiourea. Films were grown between 8 and 16 minutes.*

After 16 minutes it seemed that the reaction slowed off and no additional film would form. To confirm this a glass substrate was put in the reaction vessel, after ten minutes no film had formed on the glass. This confirms that the reaction was "dead". These experiments show that it is indeed possible to grow CdS at room temperature, however it seems hard to form a thick enough film. Nucleation is at least possible at room temperature.



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