

THESIS FOR THE DEGREE OF LICENTIATE OF ENGINEERING

Recycling of selenium from CIGS solar cell materials

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CHALMERS UNIVERSITY OF TECHNOLOGY

Gothenburg, Sweden 2012

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Cover: Suggested recycling process for selenium from CIGS solar cell materials

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ABSTRACT

Today the importance of solar cells as a power source is growing due to the environmental advantages compared to fossil fuels. One of the most promising new solar cell materials, resulting in high efficiency solar cells, is copper indium gallium selenide (CIGS). CIGS is used in thin film solar cells, which require less semiconductor material than conventional silicon solar cells and as a result are much more cost effective. Lately the issue of recycling material from spent solar cells and taking care of production waste has received increasing attention, especially since solar cell technologies utilize expensive, rare, or toxic elements. The production of solar cells requires high purity materials, putting high demands on the recycling processes if the recycled material is to be used directly in new solar cells. One way to obtain high purity materials is to separate the element of interest in the gas phase while other elements remain in the liquid or solid state. To facilitate the separation more volatile compounds of the element can be formed through chemical reactions. As the first step in the development of a recycling process for CIGS materials this study aimed to use such a method for separation of selenium from CIGS.

The feasibility to recycle selenium from CIGS through separation of selenium as either hydrogen selenide or selenium oxide was examined. Several different methods for separation of selenium as hydrogen selenide (H_2Se) were tested, but none of them was successful. However, separation of selenium via oxidation of CIGS at elevated temperatures proved to be feasible. The oxidation resulted in the formation of selenium dioxide (SeO_2), which after cooling of the gas could be collected as crystals. After oxidation at 1000°C only a few percent by weight of the selenium remained in the CIGS material. To recover the selenium the selenium dioxide was reduced. Two different reduction methods were tested. First the selenium dioxide was reduced by an organic compound, in a so called Riley reaction. Next sulphur dioxide gas was used as a reducing agent. Both methods resulted in high yield and high purity of the recycled selenium. Thus, the aim of the study was achieved and the method will be further developed in the future. The next step in the development of a recycling process for CIGS materials will be the separation of the remaining elements.

KEYWORDS: Recycling, Solar cells, Photovoltaic, Thin film, CIGS

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Paper I All experimental work, data treatment, evaluation and major part of writing of the manuscript.

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1. Introduction

Solar cells are considered by many to be part of the future energy mix [1]. The amount of energy coming from the sun makes it the largest available energy source, but the question is how to best utilize that energy [2]. One way to exploit solar energy is to use solar cells, which transform solar energy into electricity. The ability of some materials to convert light into electricity is called the photovoltaic (PV) effect and was discovered by Henry Becquerel in 1839 [3]. Since then extensive work has resulted in a number of different types of solar cells which are used in a variety of applications; from terrestrial applications supplying power to the national grid to applications in space [4]. Today the importance of solar cells as a power source is growing due to the environmental advantages compared to fossil fuels [5]. New PV materials, devices and production methods are constantly being developed in order to increase cell efficiency and minimize the energy and material consumption, thereby making PV power more competitive both economically and environmentally compared with other power sources. The progress in this area has been reviewed by several authors [5-11]. At present the most common solar cell material is silicone, but other types of PV materials, such as cadmium telluride (CdTe) and copper indium gallium selenide (CIGS), are making advances on the global market [12]. CdTe and CIGS are used in thin film solar cells, which require much less semiconductor material than conventional silicon solar cells and as a result are much more cost effective [13]. Lately the issue of recycling spent solar cells and production waste has been receiving attention, especially since most PV technologies utilize expensive, rare, or toxic elements [14]. This is definitely the case with CIGS thin film solar cells where the utilization of the rare and valuable metals indium and gallium makes recycling of CIGS materials necessary in order to keep production costs down [15]. In 2010 the European Commission identified both indium and gallium, along with only twelve other materials, as critical raw materials with regards to supply shortage and economic impact in the European Union [16]. The production of solar cells requires the input materials for semiconductor production to be of extremely high purity. This means that recycled materials must have a purity of 99.999% (5N) to be used directly in solar cell production [17]. To today's date, none of the recycling processes developed for CIGS (or CdTe) are generating materials with such purity.

1.1 Objective

The objective of this PhD project is to develop a recycling process for CIGS materials. The process should result in the separated elements having a purity of at least 5N with respect to the elements chromium, manganese, iron, nickel and zinc. These are the critical elements that decrease the efficiency of solar cells. The process should be economically feasible and scalable to an industrial scale. The goal is also to implement the developed process in a pilot scale at the CIGS solar cell manufacturer Midsummer AB [18]. At present the main intention is to recycle waste material from the production process, but in the future the process should also be applicable to recycling of discarded solar cells from manufacturing and spent solar cells from energy production. The work presented in this thesis is focused on the separation of selenium from the other elements in the CIGS material. Even though selenium is the least expensive of the elements in CIGS it constitutes half of the material and therefore contributes significantly to the cost of the material. Future work will be concentrated on the separation of the other elements in the material.

2. Background

2.1 Solar cells

The active material in a solar cell is a semiconductor. When sunlight hits the semiconductor material the absorbed energy promotes an electron to the conduction band making the material conductive [19]. The construction of the device then ensures that the free electron can only be transported in one direction, thereby generating an electric current in an outer circuit connected to the device. The standard type of solar cell is the pn-junction solar cell [4], see Figure 2.1.

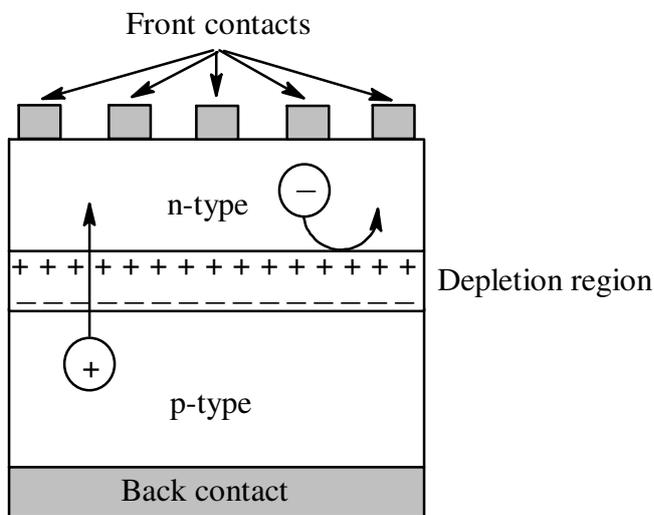


Figure 2.1. Schematic cross-section of standard pn-junction solar cell [19].

A semiconductor material that is deficient in electrons is called p-type (p for positive). One example of such a material is silicon doped with an element with fewer valence electrons, e.g. boron. Doping is the deliberate introduction of an impurity into a material. If, on the other hand, the material is in excess of valence electrons it is called n-type (n for negative). Doping of silicon with e.g. phosphorus, gives this kind of material. When regions of n-type and p-type doping meet in a semiconductor crystal electrons from the n-type will migrate into the p-type in order to balance the difference in electron concentration [19]. The migration of electrons into the p-type will give rise to a depletion region and a negative charge that counteracts further migration will be established. The electric field in the depletion region ensures that electrons can only be transported in one direction, from p-type to n-type [20]. If the same semiconductor is used as both p-type and n-type, as in the example with silicon

above, the junction is called a homojunction. When different materials are used, e.g. CIGS/CdS, the junction is called a heterojunction [20].

In addition to the semiconductor, a solar cell consists of several different layers. The thickness of the absorber layer in thin film solar cells is typically $<2 \mu\text{m}$ [21] which means that it is more than a 100 times thinner than silicon wafers [6]. Thus, while mono- and multicrystalline wafers are self-supporting (see Figure 2.1) thin film solar cells, e.g. amorphous silicon, CdTe and CIGS, need a supporting base called a substrate, see Figure 2.2 [22].

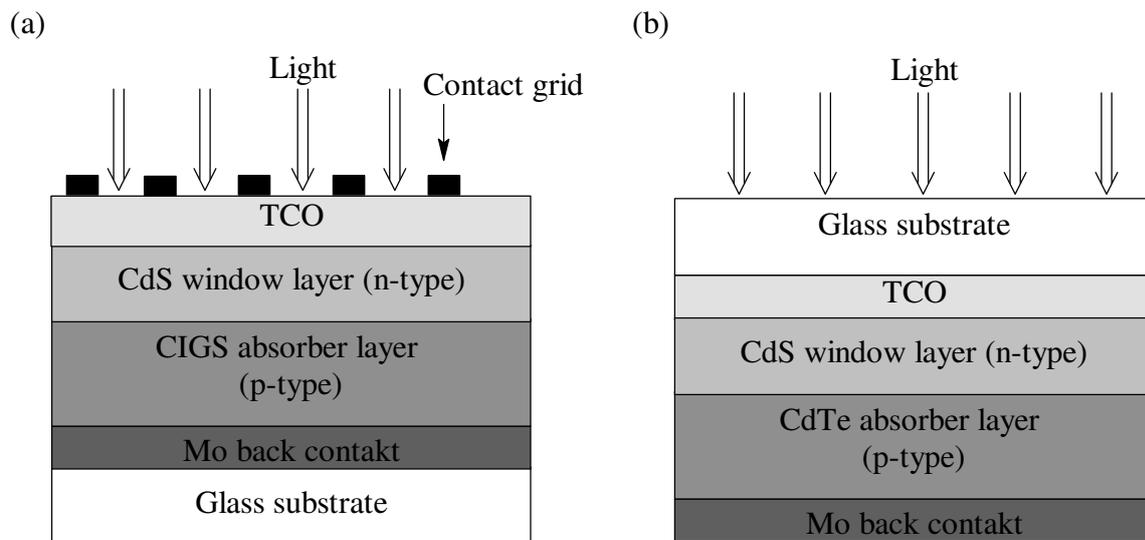


Figure 2.2. Schematic cross-section of (a) CIGS solar cell and (b) CdTe solar cell [22].

For the solar cell to produce electricity it must be connected to an outer circuit. This is facilitated by contacts at the front and back of the semiconductor material. The back contact is usually a thin layer of molybdenum. The front contact can be provided by screen printing of a metal grid (Figure 2.1), alternatively a transparent conductive oxide (TCO) can be used, e.g. zinc oxide (Figure 2.2b) or a combination of the two (Figure 2.2a) [14]. For energy production several solar cells are connected to form a solar cell module. Normally the module is laminated with EVA (ethylene-vinyl acetate) polymer on to a glass plate and encased in an aluminium frame for protection [23].

The top efficiency for different types of solar cells and solar cell modules are reviewed annually [24]. Currently the record holder for a small single junction laboratory device (area of 1 cm^2) is a gallium arsenide cell with an efficiency of 28.3%. This can be compared with 25.0% for crystalline silicon, 19.6% for CIGS and 16.7% for CdTe. The corresponding numbers for solar cell modules are 22.9% for crystalline silicon, 15.7% for

CIGS and 12.8% for CdTe. The lower efficiency of the modules is due to the difficulty in scaling up the production methods. Modules made on an industrial scale seldom reach efficiencies over 10% for thin film technologies and 16% for silicon wafer technology due to the balance between efficiency and cost [13].

2.2 CIGS solar cells

In CIGS solar cells the semiconductor layer is made from $\text{Cu}(\text{In,Ga})\text{Se}_2$. This is a material consisting of CuInSe_2 with some percentages of the indium replaced by gallium. By modifying the amount of gallium the bandwidth (see section 2.1) of the solar cell can be adjusted and a higher efficiency device can be achieved [21, 25].

The possibility to modify the composition of the CIGS absorber and produce high efficiency devices at laboratory scale has made the technology one of the most promising thin film technologies [6, 24]. The challenge with this technology is that the CIGS material contains four different elements which make the system complex and production therefore demands a high level of process control [25]. The scale up to large-scale production with preserved solar cell efficiency has been difficult to achieve due to the complexity of the processes [6] and high investment costs [13]. There are several different manufacturing processes for CIGS solar cells, but the two most common approaches are (1) co-evaporation and (2) selenization [6]. In the co-evaporation process evaporation sources are heated under vacuum and the evaporated atoms are deposited on the substrate. The selenization process starts with the deposition of a film containing only copper, indium and gallium, with e.g. sputtering, followed by selenization with for example hydrogen selenide [26]. The co-evaporation process has been used to produce high efficiency laboratory scale solar cells, but the selenization process has been more successful in industrial scale production [14].

The advantage of thin film technologies is that each solar cell only contains minor amounts of the valuable semiconductor, but there is a problem. Independent of the production method, large amounts (up to 34%) of the starting material are lost in different waste streams [27]. The recycling of this waste material is of great importance for the future advance of the technology.

2.3 Recycling of solar cells

The interest in recycling of solar cell modules has increased during recent years, but normally only the aluminium frame and the glass encasing the solar cells are taken care of. Only two recycling processes for solar cells have been commercialized [28]. The first process,

developed by Deutsche Solar, is used to treat crystalline silicon solar modules and the second process, developed by First Solar, is used to treat cadmium telluride solar cells.

The process developed by Deutsche Solar was described by Bombach *et al.* [29]. The laminate on the modules was removed in a thermal process followed by manual separation of the glass. The contacts, anti-reflective coating and pn-junction were removed by etching. No details of the chemicals used in the etching step were given. After treatment the silicon wafers were reused in new solar cells. Broken wafers were melted and made into new wafers.

The process used by First Solar to recycle solar cell modules has been described by Mezei *et al* [30, 31]. The modules were dismantled and the semiconductor material was leached from the glass. The leaching was performed using a mixture of sulphuric acid and hydrogen peroxide and resulted in a 99% leaching of cadmium and tellurium [30]. After leaching, the metals were precipitated with sodium hydroxide forming stable compounds making further recycling of tellurium impossible. Due to the difficulties in recycling tellurium after precipitation, further development of this process was studied [31]. A combination of solvent extraction and electrowinning was examined as an alternative to the precipitation step. This process gave promising results at a pilot scale and may be implemented at full scale in the future.

Other recycling methods for solar cells have been described in the literature, but have not yet been commercialized. Mono- and multicrystalline silicon are the dominating solar cell materials on the market with a market share of 81% [12]. During the last 15 years insufficient feedstock supply and the high price of silicon suitable for solar cell production [32] has made recycling an important issue. The focus on recycling of mono- and multicrystalline silicon solar cells has been mostly on the reuse of wafers with [33-36] or without [37, 38] removal of the pn-junction and other layers. There has also been a lot of work done on the recycling of the waste material (kerf loss) from wafer production [39-48].

A lot of attention has been given to the recycling of CdTe solar cells, partly due to the toxicity of cadmium and partly because of the high cost and limited supply of tellurium [27, 49]. Two different approaches to the recycling of CdTe can be distinguished. The first approach includes removal of the semiconductor from the substrate and a purification step, but no separation of the elements [17, 50, 51]. In this case the challenge of closing the loop for the semiconductor material is transferred to the producers of solar cell semiconductor materials. The second approach includes a variation with a separation step separating the elements into separate process streams [52-54]. Furthermore, a completely different process,

where an electrochemical cell was used to redeposit CdTe from an old solar cell onto a new substrate, has been developed by Menezes [55].

Recycling of CIGS solar cells and waste material is motivated by the high price of indium and gallium and several different processes have been developed. In the same way as with recycling of CdTe, some processes only consider the removal of the semiconductor material from the substrate followed by purification and reuse in normal solar cell semiconductor production [17, 56]. In both these cases no details of the purification or reuse processes were provided. As for CdTe, Menezes has developed an electrochemical method for transferring CIGS from old solar cells on to new substrates [57]. A cyclic variation of the electrochemical potential was used to dissolve the old CIGS film and deposit the material on a new cell. However, no details were given concerning the result of the recycling. A more detailed study of the mechanisms, e.g. potentials and electrolyte composition, of the process has also been done [58]. So far only two recycling processes have been developed where the elements are separated [23, 59]. Drinkard *et al.* used a combination of hydrometallurgical methods, including leaching and electrolysis, to separate indium and gallium from copper and selenium. In the next step a pyrometallurgical method was used to separate selenium from copper. The SENSE (Sustainability EvaluationN of Solar Energy systems) project also used leaching as the means of separating the CIGS material from the substrate. In the next step separation of indium was done by solvent extraction. Selenium was then reduced with sulphur dioxide and separated from the solution via filtration. Gallium was precipitated and separated as gallium hydroxide.

3. Theory

3.1 Dissolution of CIGS in acids

CIGS can be leached in an oxidizing acid e.g. nitric acid [23, 50, 59], but no records of non-oxidizing acids e.g. hydrochloric and sulphuric acid have been found. If subsequent reduction of the dissolved elements is of interest, it is not possible to use oxidizing acids for the dissolution. However, a combination of a non-oxidizing acid and hydrogen peroxide can be used [59, 60]. After the dissolution the hydrogen peroxide can be removed from the solution by decomposition at elevated temperatures.

3.2 Separation of selenium from CIGS

The use of recycled CIGS materials in new solar cells requires separation and purification of the elements [6, 17]. Selenium is the element in CIGS that is most unlike the other elements [26]. Thus, the separation of selenium is the best starting point for recycling. There are several possible hydrometallurgical methods that could be used for the separation e.g. ion exchange [61] or precipitation from aqueous solution [59], but it would be of advantage if the separation could be done in such a way that selenium could be obtained directly at high purity. Separation of selenium, or a compound thereof, in a gas phase is therefore of interest.

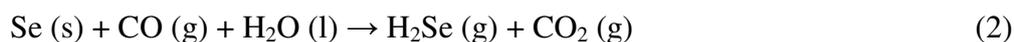
3.2.1 Reduction of selenium to hydrogen selenide

Under certain conditions selenium can be reduced to hydrogen selenide which is a gas at room temperature. The reduction of the selenium to hydrogen selenide could therefore possibly be used as a method for separation of selenium from the other elements in CIGS. In addition, hydrogen selenide is used in the selenization step of the CIGS solar cell production [26]. Thus, the recycled selenium in the form of hydrogen selenide could be used directly in new solar cells.

The preparation of hydrogen selenide can be done in several different ways. The most common production methods involve the reaction of water with aluminum selenide (Al_2Se_3) or the hydrolysis of iron selenide (FeSe) by a dilute mineral acid [62], but there are also methods to produce hydrogen selenide directly from selenium, either in solid state or dissolved in liquid. According to Patnaik hydrogen selenide can be produced via reduction of selenium with hydrogen gas at 440 °C [26].



This reaction between selenium and hydrogen in the gas phase has also been described by Greenwood, but here the reaction is said to be surface catalyzed in the temperature range between 350 and 650° C with an optimum temperature of 520 °C [62]. No information concerning the catalyst was found. Sonoda et al. prepared hydrogen selenide from metallic selenium with water and carbon monoxide gas in the presence of a mild base. The hydrogen selenide gas formed was liberated from the solution by acidification with sulphuric acid [63].



There are some examples of sodium borohydride being used as reducing agent for production of hydrogen selenide for the analysis of selenium with atomic absorption spectroscopy [60, 64]. Several metals interfere with this reaction, among them copper [64]. To avoid interference the copper can be removed from the solution as copper hydroxide precipitate [60]. Also, some electrochemical methods have been suggested [65, 66]. Hydrogen peroxide, even though it is known for its oxidizing properties, can under certain conditions also work as a reducing agent [26, 62].

Hydrogen selenide is a flammable and highly toxic gas [62], the production and handling therefore demands high levels of safety.

3.3.2 Pyrometallurgical processing – Distillation of selenium dioxide

Distillation is a well-tried method for separation of different elements and compounds. During distillation the difference in volatility of the different compounds is utilized. An advantage with this kind of separation is that the separated element can be obtained with very high purity if optimal process parameters are used. An example of an established distillation process is the Mond process, which is used for purification of nickel [67]. Nickel metal is reacted with carbon monoxide forming the volatile nickel tetracarbonyl ($\text{Ni}(\text{CO})_4$) that can be separated from other non-volatile carbonyl compounds. After the separation the nickel tetracarbonyl is decomposed at temperatures above 180 °C and the nickel is recovered [68].

One distillation method that could be used for separation of selenium from CIGS is oxidation of the selenium to selenium dioxide via heating in an atmosphere containing oxygen. The oxidation of selenium is a known method for purification of selenium [69]. The impurities in the selenium form non-volatile oxides and are thereby separated from the selenium. At temperatures above 317 °C selenium dioxide is a gas that upon cooling sublimates and can be collected as crystals. Oxidation reaction:



Sublimation:



After reduction the process results in high purity selenium. Reduction of selenium dioxide to selenium can be achieved by the use of the selenium dioxide as a mild oxidizing agent for organic compounds, as first described by Riley et al. [70].

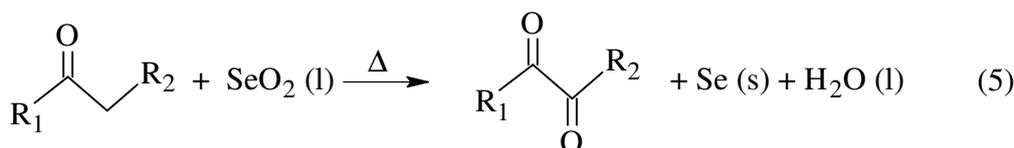
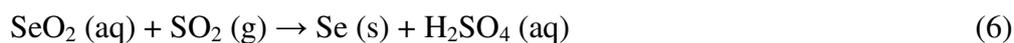


Figure 3.1. Riley reaction oxidation of keton to diketon.

Since then, these types of reaction have been extensively studied and used in numerous applications [69, 71, 72]. Selenium dioxide can also be reduced using a wide variety of inorganic reducing agents [69]. One of the reducing agents described in the literature is sulphur dioxide gas [59, 62, 73, 74].



The advantage of this reduction method is the decreased risk of contamination of the produced selenium.

3.4 Selenium

Selenium is a rare element in the earth's crust that is recovered as a by-product of copper extraction [75]. Selenium is found in several allotropic forms [62]. The amorphous form exists in two different colours, red and black. The red selenium is transformed to black selenium when heated or with aging. The black selenium is the form most commonly used in industry. In the crystalline form selenium is found as dark red, transparent crystals and the metallic form is glossy grey [26]. Upon heating the amorphous and crystalline allotropes are transformed into metallic selenium [62].

4. Materials and methods

4.1 Materials

CIGS materials from solar cell production were supplied by Midsummer AB [18]. For all experiments the CIGS material was crushed in an agate mortar and mixed carefully for homogeneity. The crushed material was sieved and the preferred particle size was chosen. For the dissolution experiments a particle size of 180-250 μm was used. For the fluidized bed batch reactor experiments a particle size of 125-180 μm was used. For the oxidation experiments the crushed material was only characterized and a mix of different particle sizes was used, see Table 4.1.

Table 4.1. Particle size distribution of starting material for the oxidation experiments.

| Particle size (mm) | Share of material with the given particle size (wt%) |
|--------------------|--|
| > 2.0 | 8 \pm 0.6 |
| 0.25-2.0 | 67 \pm 1.2 |
| 0.075-0.25 | 15.5 \pm 0.6 |
| < 0.075 | 9.5 \pm 0.5 |

For the ICP-OES analysis the CIGS material was dissolved in concentrated nitric acid (pro analysis, 65%, Acros Organics), or in the case of the residues from the oxidation experiment hot aqua regia. The aqua regia was prepared by mixing nitric acid (pro analysis, 65%, Acros Organics) and hydrochloric acid (puriss, 37%, Sigma-Aldrich) with a molar ratio of 1:3 respectively. Suprapure nitric acid (65%, Merck) and MilliQ water (>18 M Ω , Millipore Milli-Q Plus 185) was used to prepare a 0.1 M suprapure nitric acid used to dilute the samples before characterization. The chemical composition of the starting material was determined with ICP-OES, see Table 4.2.

Table 4.2. Chemical composition of the CIGS material used for the experiments. The uncertainty corresponds to one standard deviation.

| Cu(wt%) | In(wt%) | Ga(wt%) | Se(wt%) |
|----------------|----------------|---------------|----------------|
| 17.4 \pm 0.2 | 28.3 \pm 0.5 | 5.3 \pm 0.1 | 49.0 \pm 0.8 |

For the purity measurements with ICP-MS the samples were dissolved in suprapure nitric acid (65%, Merck) and diluted to an acid concentration of 1 M with MilliQ water (>18 M Ω). The samples analyzed with GC-MS were dissolved and diluted in acetone (pro analysis, Fischer Scientific) to a concentration of 16 mg/l.

4.2 Methods

4.2.1 ICP-OES

Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES) is used to analyze the concentration of different elements in solution. After passing through a nebulizer the analytes in the liquid sample are atomized in the plasma. The high excitation energy of the atoms in the plasma will cause them to emit electromagnetic radiation, which is detected in the optical emission detector. More information on ICP-OES is given by Dean (2005) [76]. A Thermo iCAP 6500 was used to analyze the composition of the different solar cell materials, before and after the experiments.

4.2.2 ICP-MS

Inductively Coupled Plasma – Mass Spectrometry (ICP-MS) is used to analyze the concentration of different elements in solutions. For further information on this technique see Dean (2005) [76]. After atomization in the plasma the mass spectrometer measures the mass-to-charge ratio of the ions. The ions are separated by an electric field and detected with an electron multiplier detector. A Perkin Elmer ELAN 6000 was used to determine the purity of the selenium from the distillation experiments.

4.2.3 Gas-MS

Gas – Mass Spectrometry (Gas-MS) is used for analysis of the chemical composition of gases. Atoms or molecules in the gas are ionized, separated in an electric field and detected with an electron multiplier detector. For more information see Harris (2007) [77]. For the gas-MS analysis of the gas from the selenium reduction in the fluidized bed batch reactor an Omnistar 301 O from Pfeiffer Vacuum was used.

4.2.4 GC-MS

Gas chromatography – Mass Spectrometry (GC-MS) is a combination of gas chromatography and mass spectroscopy. Gas chromatography is used to separate mixtures of chemicals in the gas phase into individual components prior to characterization in the mass spectrometer. Liquid samples are evaporated prior to analysis. This technique is described in more detail by Harris (2007) [77]. The purity of the organic product from the Riley oxidation was analyzed with a GI800A GCD System from Hewlet Packard using an sp2330 column.

4.2.6 XRD

In x-ray powder diffraction (XRD) finely ground crystalline powder is exposed to monochromatic x-rays. The crystal planes in the crystallites will diffract the incoming x-rays according to Bragg's law and the phase composition of the crystalline material in the sample can be determined. More details of this technique are given in Smart and Moore (2005) [19]. XRD was used to identify crystalline compounds in the CIGS materials, before and after the oxidation experiments. A Bruker D2 Phaser diffractometer with a Cu K α -source ($\lambda=1.5418$ Å) and a Lynxeye[®] silicon strip detector were used. The results were evaluated using the Joint Committee of Powder Diffraction Standards database [78].

5. Experimental

5.1 Dissolution of CIGS

5.1.1 Oxidizing acid

Samples of 1.0 g of CIGS material with particle size 180-250 μm were placed in beakers. Nitric acid (pro analysis, 65%, Acros Organics) was diluted with MilliQ water ($>18\text{ M}\Omega$) to 3, 5, 7 and 10 M. Different volumes of the acids were added to the samples according to Table 5.1.

Table 5.1. Experimental plan for the dissolution experiment.

| Acid concentration (M) | Volume 1 (ml) | Volume 2 (ml) | Volume 3 (ml) | Volume 4 (ml) |
|------------------------|---------------|---------------|---------------|---------------|
| 3 | 30 | 60 | 90 | 120 |
| 5 | 20 | 40 | 60 | 80 |
| 7 | 10 | 20 | 30 | 40 |
| 10 | 5 | 10 | 15 | 20 |

The time needed for the dissolution was recorded. Samples of the liquid were taken at intervals and the metal concentration in the liquid was analyzed with ICP-OES to ensure that complete dissolution had been reached. The experiment was allowed to continue for 24 h after which samples containing CIGS that had not been dissolved were decanted and the particles were dried and weighed. As a reference samples 1.0 g of the starting material was dissolved in 4 ml concentrated HNO_3 (pro analysis, 65%, Acros Organics) and the time needed for the dissolution was recorded. To examine the effect of reaction temperature on the dissolution process an additional experiment was done where a sample containing 1.0 g of CIGS and 30 ml of 3 M nitric acid was heated to $100\pm 2\text{ }^\circ\text{C}$. The time needed for the dissolution was recorded.

5.1.2 Non-oxidizing acid

A sample of 1.0 g of CIGS material with particle size 180-250 μm was placed in a beaker. 10 ml concentrated HCl (reagent, 37%, Acros Organics) was added to the sample. The time needed for the dissolution was recorded. The experiment was allowed to continue for 24 h after which samples containing CIGS that had not been dissolved were decanted and the particles were dried and weighed. The same experiment was also done with concentrated H_2SO_4 (reagent grade, 95%, Acros Organics).

The dissolution of metals in non-oxidizing acids can be facilitated by addition of hydrogen peroxide. To examine this method H₂O₂ (pro analysis, 30%, Scharlau) was added to samples consisting of 1.0 g of CIGS material, with particle size 180-250 μm, and 10 ml concentrated HCl (reagent, 37%, Acros Organics). The samples were stirred with a magnetic bar at 300 rpm. One of the samples was heated to 100±2 °C prior to addition of H₂O₂, while the other sample was kept at room temperature. The H₂O₂ was added in portions off 0.5 ml until all material was dissolved. The gas evolving after each addition was allowed to leave the vessel before a new addition was made. The volume of H₂O₂ needed for the dissolution was recorded. The same experiment was repeated with concentrated H₂SO₄ (reagent grade, 95%, Acros Organics).

5.2 Reduction of CIGS - hydrogen selenide

5.2.1 Reduction of CIGS with hydrogen gas

A sample of 15 g of the starting material with a particle size of 125-180μm was placed in a fluidized bed batch reactor in a vertical tube furnace. The reactor was made from an 820 mm long quartz tube fitted with a porous quartz plate of 30 mm in diameter placed 370 mm from the bottom of the tube. The temperature in the reactor was controlled with thermocouples inserted into the reactor through thin glass tubes. A gas mixture of 5vol% H₂ and 95vol% N₂ gas was passed through the reactor from the bottom at a flow rate of 600 ml/min. The temperature in the reactor was set to 520 °C. The gas from the reactor was analyzed with gas-MS. The gas not passing into the gas-MS was bubbled through two Drechsel bottles each filled with 100 ml 0.5 M CuSO₄ in order to trap any residual H₂Se. The hydrogen selenide reacts with Cu²⁺ in the solution forming black copper selenide that can easily be detected, collected and analyzed. The copper solution was prepared from CuSO₄ (puriss, Fluka) and MilliQ water (>18 MΩ). After 20 min the experiment was terminated.

The gas was changed to 100vol% H₂ gas at a flow rate of 274 ml/min. Due to technical problems the gas-MS was removed and instead three Drechsel bottles each filled with 100 ml 0.5 M CuSO₄ was used to trap H₂Se formed during the experiment, see figure 5.1.

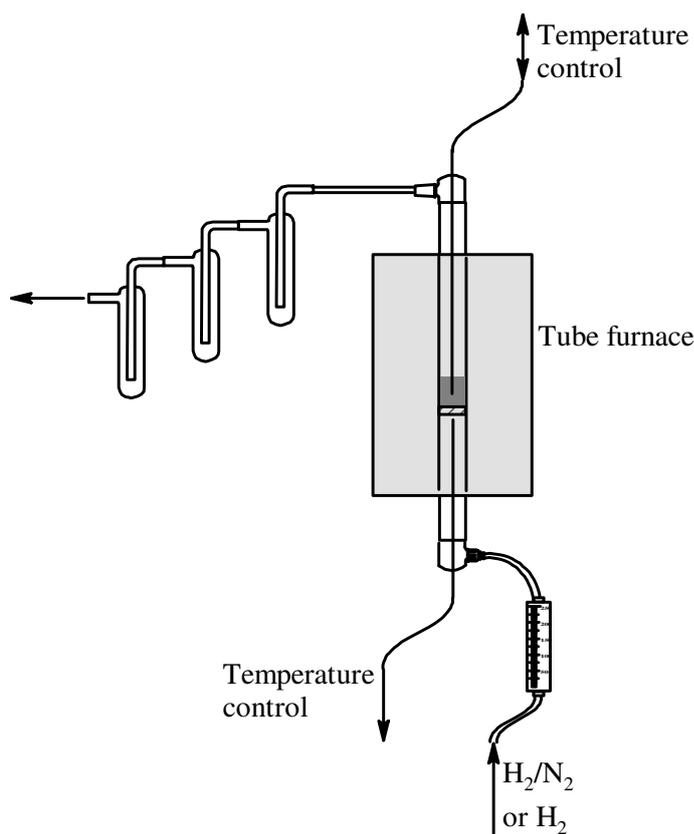


Figure 5.1. Experimental setup for the fluidized bed batch reactor reduction experiments.

The furnace was heated from 300 ± 5 to 650 ± 5 °C in steps of 50 ± 5 °C. Each temperature was maintained for 10 minutes. During the experiment the Drechsel bottles were observed for any formation of black copper selenide. After the experiment the residue was analyzed with ICP-OES and the composition was compared with the composition of the starting material. Any precipitation formed was analyzed with ICP-OES to determine the substance.

5.2.2 Reduction of CIGS with sodium borohydride (NaBH_4)

A sample of 1.0 g of CIGS was dissolved in hydrogen chloride and hydrogen peroxide (as described above). After the complete reaction the solution was heated for 10 min to allow all H_2O_2 to decompose. The solution was placed in a reaction flask and 0.5 g of sodium borohydride (>98.5%, Sigma Aldrich) was added in portions of 0.02 g. The reaction flask was connected via plastic tubing to two Drechsel bottles each filled with 100 ml 0.5 M CuSO_4 . The copper solution was prepared from CuSO_4 (puriss, Fluka) and MilliQ water (>18 M Ω). During the reaction the Drechsel bottles were observed for formation of copper selenide. Any precipitation formed was analyzed with ICP-OES to determine the substance.

A sample of 1.0 g of CIGS was dissolved in hydrogen chloride and hydrogen peroxide (as described above). To the solution 10 ml of 10 M NaOH was added to remove the copper. The NaOH solution was prepared from NaOH (98%, Acros Organics) and MilliQ water (>18 MΩ). The precipitate formed was decanted. Sodium hydroxide solution was added until no more precipitate was formed. The remaining liquid was placed in a reaction flask and 0.5 g of sodium borohydride (>98.5%, Sigma Aldrich) was added in portions of 0.02 g. The reaction flask was connected via plastic tubing to two Drechsel bottles each filled with 100 ml 0.5 M CuSO₄. The copper solution was prepared from CuSO₄ (puriss, Fluka) and MilliQ water (>18 MΩ). During the reaction the Drechsel bottles were observed for formation of copper selenide. Any precipitation formed was analyzed with ICP-OES to determine the substance.

5.2.3 Reduction of CIGS with ammonia and hydrogen peroxide

Hydrogen peroxide (pro analysis, 30%, Scharlau) and ammonia (pro analysis, 25%, Fischer) were used to prepare 50 ml of a solution containing 25vol% hydrogen peroxide and 3vol% ammonia. A sample of 1.0 g of CIGS with particle size 180-250 μm was placed in a reaction flask. The solution was added to the flask in portions of 10 ml. After each addition the reaction was allowed to settle before another addition was made. During the reaction the Drechsel bottles were observed for formation of copper selenide. Any precipitate formed was analyzed with ICP-OES to determine the substance.

5.3 Distillation of selenium dioxide

5.3.1 Oxidation experiment

A sample of 13.5 g of crushed CIGS, with the particle size distribution given in Table 4.1, was placed in a furnace boat. The furnace boat was placed in a tube furnace and heated together with oxygen gas (99%, AGA) with a flow rate of 200 ml/min, see Figure 5.2.

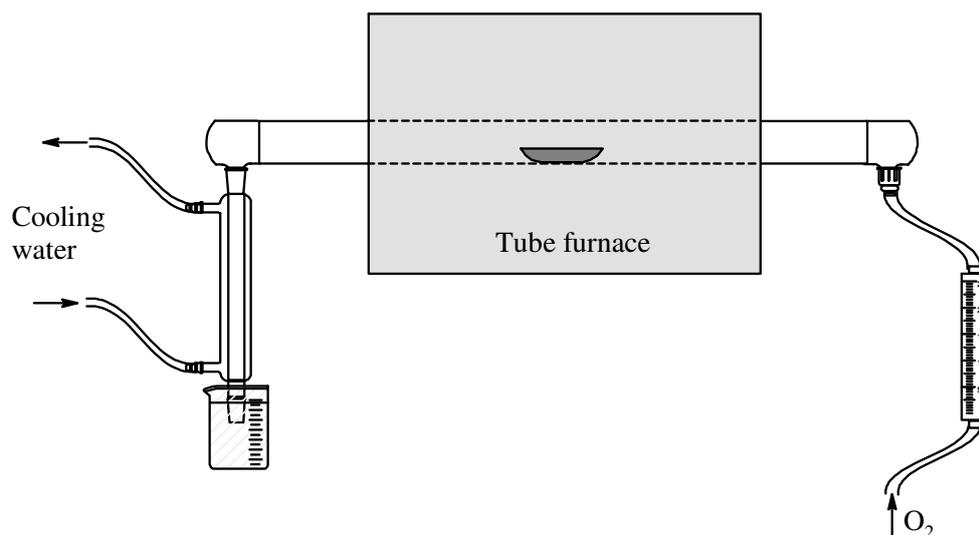


Figure 5.2. Experimental setup for oxidation experiments in the tube furnace.

The temperature in the furnace was regulated with a thermocouple on the outside of the quartz tube. The oxygen gas was passed (from right to left) through the quartz tube placed in the tube furnace. The formed selenium dioxide was sublimed outside the furnace (on the left). After the tube furnace, the gas was cooled in a cooler and then bubbled through a beaker containing MilliQ water ($>18\text{ M}\Omega$) to trap any remaining selenium dioxide. A series of experiments was performed where the tube furnace was heated to 500, 600, 700, 800, 900 and $1000\pm 10\text{ }^\circ\text{C}$ for 24 h. The composition of the residue was analyzed with ICP-OES and the selenium content was compared with the selenium content of the starting material. The residues and the starting material were also analyzed with XRD. The selenium dioxide from the reaction was analyzed with ICP-MS to determine the purity with respect to the critical impurities (Cr, Mn, Fe, Ni, Zn) along with the level of separation from copper, indium and gallium. To determine the accuracy of the ICP-OES and ICP-MS measurements triplicates were analyzed.

5.3.2. Reduction of selenium dioxide – Riley reaction (Oxidation of deoxybenzoin to benzil)

For the reduction experiment selenium dioxide from the oxidation of CIGS at 1000°C was used. 7 ml glacial acetic acid (pro analysis, 100%, Merck) was used to dissolve 2.00 g (0.018 mol) of selenium dioxide and 3.54 g (0.018 mol) deoxybenzoin (98%, Acros organics). The solution was refluxed for 3 h at $126\pm 2\text{ }^\circ\text{C}$. After cooling the liquid was decanted from the solid selenium formed during the reaction. Diethylether (99+%, Acros organics) was used to wash the selenium and to extract the organic product from the acetic acid. After the extraction MilliQ water ($>18\text{ M}\Omega$) and a saturated solution of sodium bicarbonate was used to wash the

organic product. A final wash with brine and drying with sodium sulphate was done before the product was concentrated under reduced pressure. The selenium from the reaction was analyzed with ICP-MS to determine the purity with respect to the critical impurities (Cr, Mn, Fe, Ni, Zn) along with the level of separation from copper, indium and gallium. The organic product was analyzed with GC-MS to determine the purity. To determine the accuracy of the ICP-OES and ICP-MS measurements triplicates were analyzed.

5.3.3 Reduction of selenium dioxide – Sulphur dioxide

A sample 1.00 g (0.009 mol) of selenium dioxide from the oxidation of CIGS at 1000° C was used dissolved in 50 ml MilliQ water (>18 MΩ) in a Drechsel bottle. After heating of the solution to 80±2°C sulphur dioxide gas (99.8%, AGA) at a flow rate of 40 ml/min was bubbled through the solution. The reaction was allowed to continue for 15 min after which the selenium was separated from the liquid. MilliQ water (>18 MΩ) water was used to wash the selenium before it was dried and weighed. The selenium from the reaction was analyzed with ICP-MS to determine the purity with respect to the critical impurities (Cr, Mn, Fe, Ni, Zn) along with the level of separation from copper, indium and gallium. To determine the accuracy of the ICP-OES and ICP-MS measurements triplicates were analyzed.

6. Results and discussion

6.1 Dissolution of CIGS

6.1.1 Oxidizing acid

CIGS was readily dissolved in 4 ml concentrated nitric acid in less than 10 minutes. The result from the dissolution experiments with lower acid concentrations can be seen in Table 6.1.

Table 6.1. Results from dissolution of CIGS material in nitric acid.

| Acid concentration (M) | Acid volume (ml) | Time for complete dissolution | Remaining material* (wt%) |
|------------------------|------------------|-------------------------------|---------------------------|
| 3 | 30 | - | 88.4 |
| 3 | 60 | - | 79.7 |
| 3 | 90 | - | 71.3 |
| 3 | 120 | - | 84.8 |
| 5 | 20 | - | 24.1 |
| 5 | 40 | - | 18.1 |
| 5 | 60 | - | 13.4 |
| 5 | 80 | - | 34.0 |
| 7 | 10 | - | 9.9 |
| 7 | 20 | - | 5.9 |
| 7 | 30 | <24 h | 0 |
| 7 | 40 | 6 h | 0 |
| 10 | 5 | < 24 h | 0 |
| 10 | 10 | 15 min | 0 |
| 10 | 15 | 10 min | 0 |
| 10 | 20 | 5 min | 0 |

*The weight of the starting material (1.0 g) remaining after 24 h dissolution

From the table it can be seen that at least 10 ml of 10 M acid was needed for quick dissolution. Larger volumes, 30ml or more, of 7 M acid also dissolved the CIGS material, but several hours were needed before the dissolution was complete. None of the samples treated with acid of lower concentration were completely dissolved. One thing worth noticing is that larger acid volume did not always lead to better dissolution. The samples treated with the largest amounts of 3 M and 5 M acid was not dissolved to the same extent as the samples

treated with less acid. This might be due to inadequate mixing of those samples because of the large liquid volume.

Heating improved the dissolution process and 40 ml of 3 M acid dissolved the sample in 3 h.

6.1.2 Non-oxidizing acids

Neither concentrated hydrochloric nor concentrated sulphuric acid dissolved the CIGS material completely. After 24 h in hydrochloric acid 96wt% of the material had not been dissolved. The dissolution in sulphuric acid was even lower and 97wt% of the material still remained after the test. At room temperature the CIGS material was dissolved in hydrochloric acid after addition of 4 ml hydrogen peroxide. The dissolution was completed in 25 minutes. This means that CIGS can be dissolved in a non-oxidizing acid if an oxidizing agent is added. This makes reduction of the dissolved specimen, which is impossible if an oxidizing acid is used, possible. An elevated temperature (100 °C) did not reduce the amount of hydrogen peroxide or time needed for dissolution. The dissolution of CIGS in sulphuric acid was completed after addition of 11 ml hydrogen peroxide during 50 minutes. The reaction upon addition of hydrogen peroxide to the sulphuric acid solution was much more violent compared to the reaction when hydrochloric acid was used. At 100 °C the amount of hydrogen peroxide needed for the dissolution was reduced to 8 ml and the time was reduced to 40 minutes. It was concluded that hydrochloric acid was more suitable for the dissolution than sulphuric acid. Hydrochloric acid in combination with hydrogen peroxide was therefore used for dissolution for the sodium borohydride reduction experiments.

6.2 Reduction of CIGS - hydrogen selenide

6.2.1 Reduction of CIGS with hydrogen gas

During the first part of the experiment no hydrogen selenide could be detected by the gas-MS. There was also no black copper selenide forming in the Drechsel bottles after the gas-MS. It was concluded that no hydrogen selenide was formed under the set conditions. Therefore the concentration of hydrogen gas was increased and a larger temperature interval was investigated. During this part of the experiment the gas-MS was removed due to technical problems and all the gas was led through the copper sulphate solution instead. No copper selenide was formed in the Drechsel bottles, at any of the tested temperatures. The ICP-OES analysis of the CIGS material after the experiment showed no change in selenium content compared to the starting material. The result from this experiment shows that

hydrogen selenide could not be formed when heating CIGS in hydrogen gas. It was concluded that in order for the reaction to work a catalyst is needed. Since no catalyst was available the method was abandoned.

6.2.2 Reduction of CIGS with sodium borohydride

No hydrogen selenide was formed from addition of sodium borohydride to the CIGS solution. Instead red selenium was precipitated from the solution. This might be due to the interference of copper ions with the reduction of selenium to hydrogen selenide. Therefore a new experiment was performed where copper was precipitated as copper hydroxide prior to the reduction, but this experiment did not result in hydrogen selenide formation upon addition of sodium borohydride either. The reduction method was therefore concluded not to work on CIGS materials.

6.2.3 Reduction of CIGS with ammonia and hydrogen peroxide

Upon the first addition of the ammonia and hydrogen peroxide solution to the dry CIGS material 0.03 g of precipitate was formed in the first Drechsel bottle. ICP-OES analysis on the precipitate confirmed that it was copper selenide and it could be concluded that a minor amount of hydrogen selenide had been produced. Further addition of the ammonia and hydrogen peroxide solution to the CIGS material did not yield any more hydrogen selenide.

6.3 Distillation of selenium dioxide

6.3.1 Oxidation experiment

The characterization of the starting material showed that it contained approximately 50wt% selenium, Table 4.2. The analysis of the residues after the oxidation experiments revealed that the selenium content decreased with higher oxidation temperature, see Figure 6.1. After oxidation at 1000 °C the residue only contained 4wt% of the original amount of selenium.

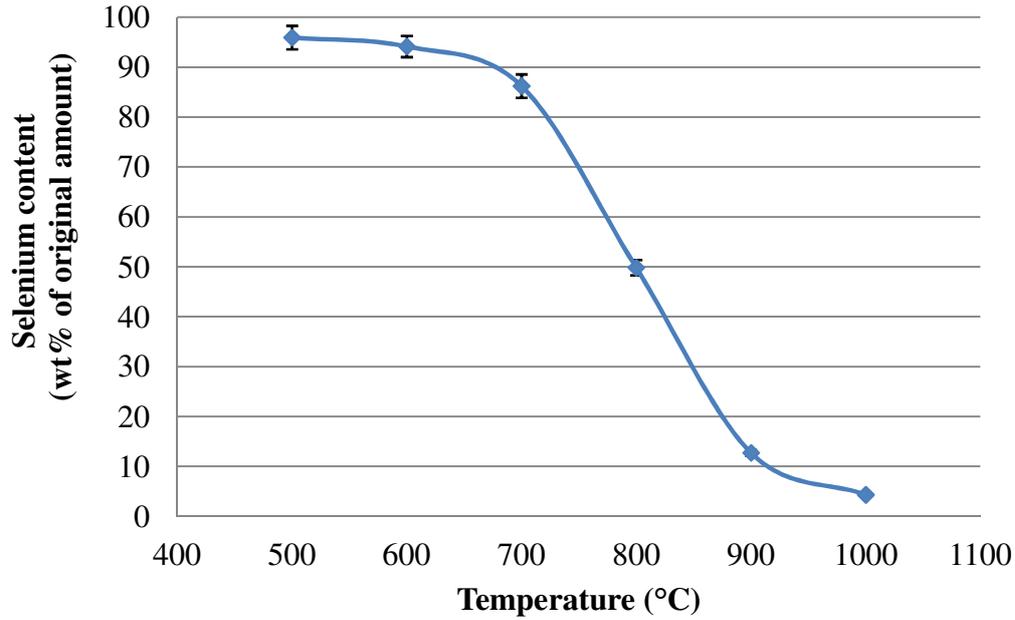


Figure 6.1. The selenium content in the residues from the oxidation of CIGS as a function of temperature. The selenium content is given in percent of the selenium content in the starting material.

Approximately 85wt% of the selenium removed from the CIGS material during each oxidation experiment was recovered as selenium dioxide. To improve the yield another design of the process equipment has to be developed. Analysis of different layers in the residues after oxidation showed an increasing amount of selenium towards the bottom of the reaction vessel. This indicates that mixing of the material could improve the selenium separation.

Table 6.2. The composition of the top and bottom layers of the residue after oxidation at 1000 °C. The uncertainty corresponds to one standard deviation.

| | Cu (wt%) | In (wt%) | Ga (wt%) | Se (wt%) |
|---------------------|-----------------|-----------------|-----------------|-----------------|
| Top layer | 51.5±0.4 | 45.9±0.5 | 2.3±0.2 | 0.28±0.04 |
| Bottom layer | 27.0±0.2 | 56.1±0.7 | 11.4±0.1 | 5.5±0.1 |

The XRD analysis of the starting material and the residues, after oxidation at 800 and 1000 °C, showed that the material had been oxidized and that several different compounds had been formed, see Figure 6.2.

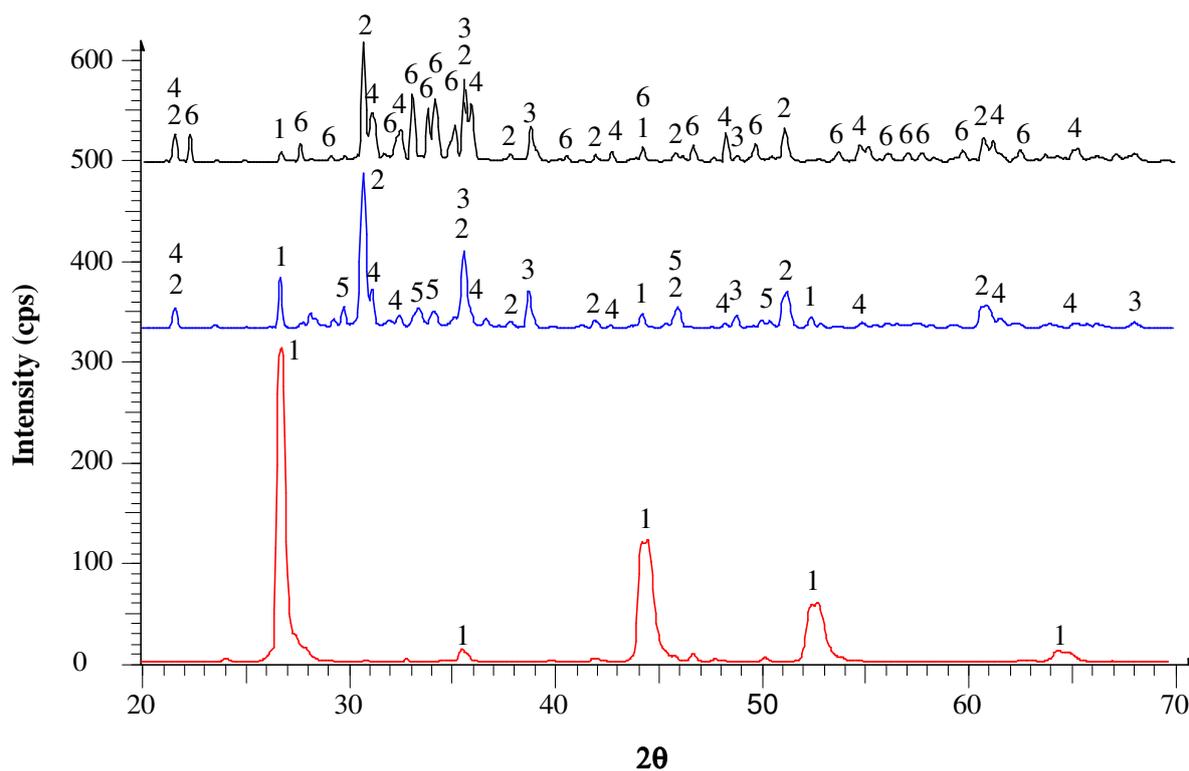


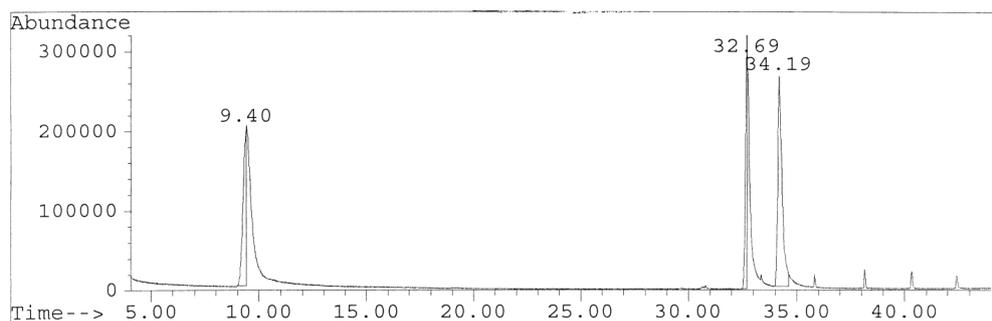
Figure 6.2. XRD patterns for starting material (bottom), residue after oxidation at 800 °C (middle) and residue after oxidation at 1000 °C (uppermost). 1) Cu(In,Ga)Se₂, 2) In₂O₃, 3) CuO, 4) CuGaInO₄, 5) SeCu₂, 6) Cu₂In₂O₅.

The spectrum of the starting material shows the characteristic peaks of Cu(In,Ga)Se₂ (1). After the oxidation at 800 °C these peaks were reduced and the peaks indicating indium oxide (2), copper oxide (3) and copper indium gallium oxide (4) can be seen. In addition copper selenide (5) has been formed. The spectrum of the residue after oxidation at 1000 °C indicates that there has been some recrystallization and indium copper oxide (6) has been formed.

The solubility of the residue in nitric acid after oxidation was considerably lowered with higher oxidation temperatures. To ensure complete dissolution of the residues aqua regia had to be used. This means that further processing of the residues cannot be done by any method requiring dissolution.

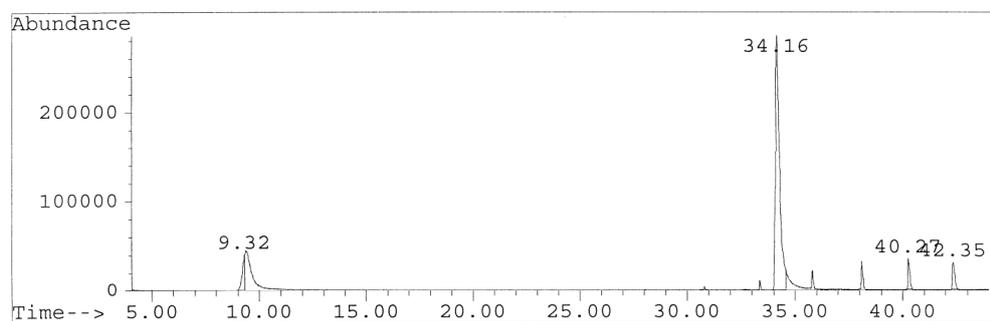
6.3.2. Reduction of selenium dioxide – Riley reaction (Oxidation of deoxybenzoin to benzil)

The reaction gave 1.19 g of selenium corresponding to a yield of 90.7wt% and 3.1 g of the organic product equivalent to a yield of 96.6wt%. The GC-MS analysis showed that the formed benzil was pure from organic impurities, Figure 6.3 and 6.4.



| Retention Time | Area | Area % | Ratio % | Type | Width |
|------------------------|---------|--------|---------|------|-------|
| Total Ion Chromatogram | | | | | |
| 9.401 | 2095254 | 27.676 | 56.747 | rBV | 0.399 |
| 32.690 | 1783149 | 23.553 | 48.294 | rBV | 0.217 |
| 34.185 | 3692276 | 48.771 | 100.000 | rBV | 0.648 |

Figure 6.3. GC-MS analysis of mixture containing deoxybenzoin and benzil. The retention time was 32.69 min for deoxybenzoin and 34.19 min for benzil. The peak after 9.40 min was determined to be diacetone alcohol (2-Pentanone, 4-hydroxy-4-methyl), a contamination commonly found in acetone. Acetone was used for dilution of the samples. The small peaks after 35 min are silicon compounds from the column.



| Retention Time | Area | Area % | Ratio % | Type | Width |
|------------------------|---------|--------|---------|------|-------|
| Total Ion Chromatogram | | | | | |
| 9.318 | 306820 | 6.696 | 7.998 | rBV | 0.333 |
| 34.162 | 3836112 | 83.718 | 100.000 | rBV | 0.604 |
| 40.266 | 211736 | 4.621 | 5.520 | rBV | 0.243 |
| 42.348 | 227533 | 4.966 | 5.931 | rBV | 0.250 |

Figure 6.4. GC-MS analysis of organic product from the Riley reaction. The peak after 34.16 min shows that the sample only contained benzil.

6.3.3 Reduction of selenium dioxide – Sulphur dioxide

During the reaction selenium dioxide was reduced to red selenium which upon heating to 80 °C was transformed to black selenium. The reaction was completed in 10 minutes and yielded 0.67 g of selenium corresponding to 93.8wt% of the selenium in the selenium dioxide. The

selenium content of the liquid after the reduction was determined to be less than 1.4wt%. To improve the yield the collection of the selenium has to be improved.

6.3.4 Purity of the recycled selenium

The critical impurities in solar cells are chromium, manganese, iron, nickel and zinc. The purity of the recycled selenium was analyzed with respect to these elements along with copper, indium and gallium. The selenium from both reduction experiments and the selenium dioxide from the oxidation test at 1000 °C were analyzed. The results from the ICP-MS measurements were used to calculate the concentrations of the impurities in the selenium, see Table 6.3.

Table 6.3. The concentration of impurities in the recycled selenium. The uncertainty corresponds to one standard deviation.

| | Cr (ppm) | Mn (ppm) | Fe (ppm) | Ni (ppm) | Zn (ppm) | Cu (ppm) | Ga (ppm) | In (ppm) |
|--|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|
| Selenium dioxide | 0.17 ±0.01 | <0.1 | <50 | 0.26 ±0.01 | 0.30 ±0.01 | 5.49 ±0.22 | 0.35 ±0.01 | 3.57 ±0.22 |
| Selenium - Riley reaction | 0.79 ±0.03 | <0.1 | <50 | 0.51 ±0.02 | 0.43 ±0.02 | 13.5 ±2.86 | 3.45 ±0.26 | 6.55 ±0.94 |
| Selenium - Sulphur dioxide reaction | 0.23 ±0.01 | <0.1 | <50 | 0.34 ±0.02 | 0.18 ±0.02 | 5.58 ±0.46 | 0.29 ±0.01 | 2.04 ±0.10 |

The concentration of all the critical impurities except iron was shown to be below 1ppm for each element. Iron on the other hand could only be determined to be below 50ppm. The higher detection limit for iron was due to the interference of iron with argon oxide in the ICP-MS. The concentration of copper, indium and gallium were higher than the concentration of the critical elements, but since they are used in the solar cell they do not pose a problem. However, they were analyzed to give a measurement of the success of the separation method. From the results shown in Table 6.3 the purity of the recycled selenium was determined, see Table 6.4.

Table 6.4. The purity of the selenium dioxide from the oxidation and for the recycled selenium and with respect to *Cr, Mn, Ni and Zn, ** Cr, Mn, Ni, Zn, Cu, Ga and In and ***all the analyzed elements including iron. The uncertainty corresponds to one standard deviation.

| | Purity* (wt%) | Purity** (wt%) | Purity*** (wt%) |
|--|--------------------------------|---------------------------------|----------------------------------|
| Selenium dioxide | 99.99993 ±2.07E-06 | 99,99899 ±5.01E-05 | > 99.99 |
| Selenium - Riley reaction | 99.99983 ±4.50E-06 | 99,99747 ±3.02E-04 | >99.99 |
| Selenium - Sulphur dioxide reaction | 99.99992 ±2.81E-06 | 99,99913 ±4.75E-05 | >99.99 |

Due to the difficulty measuring iron the purity of the recycled selenium could only be determined to be higher than 99.99wt%, but with respect to the other analyzed elements it could be concluded that the purity was 5N or higher. It could also be concluded that the sulphur dioxide reduction method gave a slightly higher purity.

7. Conclusions and process suggestions

7.1 Conclusions

It is possible to dissolve CIGS material in concentrated nitric acid, but not in concentrated hydrochloric or sulphuric acid. Dissolution in nitric acid at room temperature could be performed in 7 M acid, but at 100 °C only 3 M acid was needed. These results were not used further since it was concluded that hydrometallurgical methods were not going to be used for recycling of CIGS.

To dissolve CIGS in non-oxidizing acid, addition of an oxidizing agent (hydrogen peroxide) is needed. Hydrochloric acid was determined to be the best choice for the dissolution. This method was later used during one of the reduction experiments.

The possibility of reducing the selenium to hydrogen selenide was evaluated and several different methods were tested. None of the methods yielded hydrogen selenide in substantial amounts and the efforts were therefore abandoned.

The separation of selenium by distillation of selenium dioxide was proven to be successful. Nearly all of the selenium was separated from the CIGS material after oxidation at 1000 °C. Due to the high detection limit of iron with ICP-MS the purity of the recycled selenium could only be determined to be higher than 4N with respect to all the critical elements (Cr, Mn, Fe, Ni and Zn). However, with respect to the other critical elements the purity was higher than 5N for all the analyzed selenium materials, enough for the material to be used in the production of new semiconductor material for solar cell production. To more accurately determine the iron concentration, neutron activation analysis will be done. Some copper, indium and gallium could be detected in the selenium providing a purity level just below 5N and the separation was considered to be successful. To reach even higher purities the selenium could be passed through the oxidation process again.

The difficulty in dissolving the residue after the oxidation will have to be taken into account when the next step in the recycling process is developed.

7.2 Process suggestions

Based on the results obtained during this study a suggestion for a process for separation of selenium from CIGS materials can be made. The most promising methods are the distillation of selenium as selenium dioxide followed by reduction of the selenium dioxide to selenium by sulphur dioxide, see Figure 7.1.

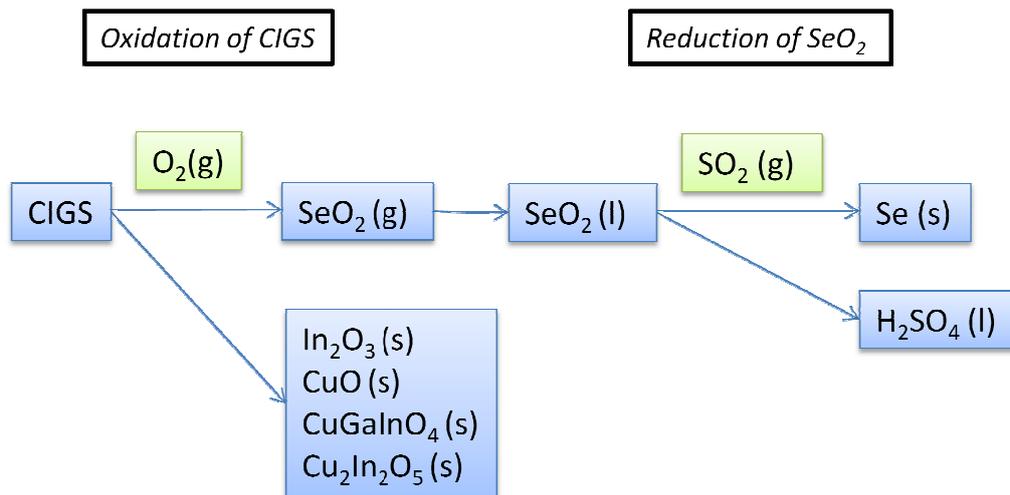


Figure 7.1. Suggested process for separation of selenium from CIGS materials.

8. Future work

The results from the distillation experiments have been promising and the development of this separation method will be continued with the optimization of the oxidation step with regards to energy consumption and cost. Better mixing between the gas and the solid could mean lower oxidation temperature, shorter reaction time and perhaps the possibility of using a cheaper gas. The possibility to use the process in industrial scale will be dependent on the energy consumption and cost in relations to the purity of the recycled material compared to other purification methods.

The next step in the development of a recycling method for CIGS will be to separate the remaining elements in the residue from the oxidation step.

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List of Abbreviations and Terms

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| PV | Photovoltaic |
| CIGS | Copper Indium Gallium Selenide (Cu(In,Ga)Se ₂) |
| CdTe | Cadmium Telluride |
| CdS | Cadmium Sulphide |
| 4N | 99.99% |
| 5N | 99.999% |
| TCO | Transparent Conductive Oxide |
| ICP-OES | Inductively Coupled Plasma – Optical Emission Spectroscopy |
| ICP-MS | Inductively Coupled Plasma – Mass Spectroscopy |
| Gas-MS | Gas – Mass Spectroscopy |
| GC-MS | Gas Chromatography – Mass Spectroscopy |
| XRD | X-Ray Diffraction |