Spring 2014

CZTSSe Thin Film Solar Cells: Surface Treatments

Chinmay S. Joglekar

Purdue University

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By Chinmay S Joglekar

Entitled
CZTSSe Thin Film Solar Cells : Surface Treatments

For the degree of Master of Science in Chemical Engineering

Is approved by the final examining committee:

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Prof. Rakesh Agrawal

Approved by Major Professor(s):

Approved by: Prof. Michael Harris 02/24/2014

Head of the Department Graduate Program Date
CZTSSE THIN FILM SOLAR CELLS: SURFACE TREATMENTS

A Thesis
Submitted to the Faculty
of
Purdue University
by
Chinmay Sunil Joglekar

In Partial Fulfillment of the
Requirements for the Degree
of
Master of Science in Chemical Engineering

May 2014
Purdue University
West Lafayette, Indiana
ACKNOWLEDGEMENTS

I would like to thank my parents for their constant support. I would also like to thank my friends for making this journey joyous and wonderful.

I am very thankful to Prof. Agrawal who has been a great mentor and taught me to ask ‘right questions to get the right answers’. Meetings with him would always give an entirely new perspective on the subject of discussion. He has been a constant source of motivation for me.

I would also like to thank the Solar group for the help and co-operation. I immensely enjoyed the discussions over lunch about research.
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<td>Copper Indium Gallium Sulfide (CuInS₂)</td>
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<td>CIGSe</td>
<td>Copper Indium Gallium Selenide (CuInSe₂)</td>
</tr>
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<td>CZTS</td>
<td>Copper Zinc Tin Sulfide (Cu₂ZnSnS₄)</td>
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<tr>
<td>CZTSe</td>
<td>Copper Zinc Tin Selenide (Cu₂ZnSnSe₄)</td>
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<td>Copper Zinc Tin Sulfo-Selenide (Cu₂ZnSn(S,Se)₄)</td>
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<tr>
<td>FF</td>
<td>Fill Factor</td>
</tr>
<tr>
<td>Jsc</td>
<td>Short Circuit Current</td>
</tr>
<tr>
<td>Mo</td>
<td>Molybdenum</td>
</tr>
<tr>
<td>Se</td>
<td>Selenium</td>
</tr>
<tr>
<td>Voc</td>
<td>Open circuit Voltage</td>
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ABSTRACT

Joglekar, Chinmay S. M.S.Ch.E., Purdue University, May 2014. CZTSSe Thin Film Solar Cells: Surface Treatments. Major Professor: Rakesh Agrawal.

Chalcopyrite semiconducting materials, specifically CZTS, are a promising alternative to traditional silicon solar cell technology. Because of the high absorption coefficient; films of the order of 1 μm thickness are sufficient for the fabrication of solar cells. Liquid based synthesis methods are advantageous because they are easily scalable using the roll to roll manufacturing techniques.

Various treatments are explored in this study to enhance the performance of the selenized CZTS film based solar cells. Thiourea can be used as a sulfur source and can be used to tune band gap of CZTSSe. Bromine etching can be used to manipulate the thickness of sintered CZTSSe film. The etching treatment creates recombination centers which lead to poor device performance. Various after treatments were used to improve the performance of the devices. It was observed that the performance of the solar cell devices could not be improved by any of the after treatment steps.

Other surface treatment processes are explored including KCN etching and gaseous H₂S treatments. Hybrid solar cells which included use of CIGS nanoparticles at the interface between CZTSSe and CdS are also explored.
1. INTRODUCTION

World Primary Energy consumption in 2011 was 12274 million tons of oil equivalent [1]. This is equivalent to 16.3 TW of power consumption. Out of the current total energy consumption, nearly 87% comes from fossil resources (coal, oil and natural gas). 6.4% comes from hydroelectricity and only 1.58% comes from renewable resources. The 2011 reserves-to-production-ratios in 2011 for oil, natural gas and coal are 54.2 years, 63.6 years and 112 years respectively [1]. What these numbers tell us is that there is imminent need to use alternative energy sources which are renewable, scalable and cheap at the same time. Such renewable sources include hydroelectricity, geothermal, wind, solar energy. But use solar energy is by far the most promising alternative which can be used at multi-terawatt scale [2].

Earth receives about 125000 TW of solar radiation [3]. A very tiny fraction of this energy is sufficient to fulfill the energy needs of the planet. Thus even if we harvest very tiny fraction of the incident solar energy and convert and store it in usable form then we can fulfill the energy needs of this planet. Although, photovoltaics were developed for space applications, but they are increasingly being used for terrestrial applications. In fact the annual photovoltaic installations more than doubled in year 2010 to ~17 GW [4].

Traditionally, solar cells are made from crystalline silicon, which is an indirect band gap material ($E_g = 1.1eV$) [5]. It has a low absorption coefficient 100 cm$^{-1}$, which requires hundreds of micron thick Si for good absorption of light. In fact the Si wafer accounts for more than 50% of the module cost[6]. Thus even with years of research in this area, projected cost of crystalline Si modules remains at ~ $0.73 per peak Watt ($W_p$), which is much higher than the DOE target of $0.50/W_p$ [7].
An effective approach is to develop new materials with direct band gap and high absorption coefficient. Due to the high absorption coefficient, the absorber layer thickness can be reduced to few microns.

Various thin film technologies include amorphous Si, chalcogenide based such as CdTe, CIGS(Se) and CZTS(Se). Projected CdTe costs are in the neighborhood of $0.63/W_{p} [7]. Availability of Te at large scale is also a concern for CdTe devices [8][9]. Amorphous Si solar cells suffer from inherent drawback of Staebilar-Wronski effect thereby limiting device performance at around 6-7% power conversion efficiency (p.c.e.)[9].

CIGS is a thoroughly investigated chalcopyrite material for solar cell applications[10]. Currently, CIGSe solar cells have highest power conversion efficiency among chalcogenide thin film solar cells [11]. Record efficiencies for CIGSe lab scale devices are greater than 20% [12]. Processes used for CIGSe device fabrication include co-evaporation, selenization (two stage process), electrodeposition and liquid processing [13]. But availability of In is concern for large scale use of CIGSe solar cells [14].

CZTS is also a chalcogenide semiconductor which is related to CIGS in properties[14] but its constituent elements are more earth abundant and cheaper (see following figure
Wadia et al. [8] have also shown that its constituent elements are abundantly available in Earth’s crust and it could be used at multi-terawatt scale. Because of this CZTS (Se) is area of focus for photovoltaic research. Recently, Mitzi and co-workers reported record efficiency of 12.6% for a CZTSSe device [15].

Figure 2 (Upper part) Relative abundance of elements in Earth’s Crust and (Lower Part) prices of raw elemental materials [16]

CZTS is an I₂–II–IV–VI₄ type quaternary semiconductor. It can be obtained from ternary CIS (Copper Indium Diselenide) by substituting Selenium with Sulfur and Indium with zinc.
and tin [17]. In its structure each Sulfur (Selenium) anion is bonded to four cations and each
cation is bonded to four sulfur (Selenium) anions[18].

As with CIGS, various groups have used different techniques for synthesis of the
absorber material CZTS. Vacuum based techniques include sputtering deposition of
elements/precursors and subsequent annealing, vacuum evaporation method, vacuum based
pulsed laser deposition method. Non vacuum techniques include spray pyrolysis deposition,
spin coating of precursors and annealing, electrochemical deposition, using nanocrystal
synthesis [19].

Advantages of liquid deposition techniques over vacuum based techniques are listed below
[20]

- Significantly lower capital cost of manufacturing equipment
- Higher throughput: liquid based techniques are amenable to adapt to manufacturing
techniques such as roll to roll manufacturing, making high throughput possible.
- Compositional uniformity of films over large area

Our lab uses hot injection based nanocrystal synthesis method for making
CZTS absorber material. The technique is as extension of the hot injection technique
developed for CuInSe₂ and CIGS nanocrystals with photovoltaic activity[21,22]. Guo et. al.
have also developed a novel technique for sintering the nanocrystals by promoting the grain
growth of nanocrystals [21]. This technique involves heat treating the nanocrystals in Se
atmosphere, which results to replacement of S atoms in the nanocrystals by Se atoms with
simultaneous micron size grain growth.

Similar approach was used for synthesis of CZTS nanocrystals and
subsequent heat treatment. Detailed methods of synthesis and subsequent processing can be
found in the published literature [18,23].

**Band Gap Tuning**

CZTS and CZTSSe are closely related systems with difference of S or Se in the anion
lattice. Band gap of CZTS and CZTSSe are calculated to be 1.5 eV and 1.0 eV respectively [14].
Following figure also shows the calculated band gaps of CZTSSe samples under various S
contents.
Figure 3 Calculated band gap for Cu$_2$ZnSn(S$_{1-x}$Se$_x$) at different composition (x)[24]

Band gap of CZTSSe material synthesized in our lab is 1.05 eV [23], which corresponds to x close to 1 in the figure above. This means 85% of the sulfur atoms are replaced by Se atoms during the selenization process. From Shockley-Queisser limits for AM1.5 spectrum [25], it can be seen that relevant range for high efficiency solar cells is (1-1.5eV) Also increase in the S content increases the band gap which should result into increase in Voc.

Motivation for surface treatment studies

Current CZTSSe devices have higher Voc deficit (Eg/q-Voc) values as compared to CIGS solar cells [26]. Literature reports suggest that the reason behind lies in the interface between the absorber layer and buffer layer[27,28]. Thus modification of this interface to increase the Voc is Starting point for various experiments in the study. Front grading of the junction would help reduce the recombination losses in the space charge region[29].

Voc also depends on the band offset at the interface. The band offset can be changed by changing the Valance Band Maximum (VBM) and Conduction Band Minimum (CBM) of the absorber at the interface. For CZTSSe, the VBM is an anti-bonding state between Cu d orbitals and anion p orbitals. And CBM is determined by anti-bonding state between Sn s orbitals and anion s orbitals. Thus changing the S/Se ratio in the CZTSSe film would change band offset at the interface. Following diagram shows the band alignment between CdS and CZTS and CZTSSe.
Figure 4 Band alignment at CdS and CZTSe and CdS CZTS interface [24]
2. EXPERIMENTAL

CZTS thin film devices were fabricated as reported in the literature by our group [23].

A summary is included here for reference.

CZTS nanocrystals are synthesized by hot injection of elemental S (in oleylamine) into oleylamine solution containing Cu, Zn and Sn precursors at 185 – 285°C using a Schlenck line apparatus. After the reaction, the nanoparticles are collected via repeated washing with hexane/isopropanol mixture and centrifugation. The final precipitate is dried under argon flow and redispersed in hexanethiol to produce an ink with a concentration of ~ 200 mg/mL.

Molybdenum (Mo) is sputtered on soda lime glass (SLG) and two coatings of CZTS nanocrystals are applied using glass rod for a total film thickness of ~ 800 nm. As a standard procedure 1”by 2” Mo coated SLG is used as a substrate. After each coating the film is dried on a hot plate at 300°C in air for 1 min. This would be called coated CZTS film.

This film is subjected to a selenization in a graphite box with Se pellets and introduced in a hot furnace for 40 minutes at 500°C. In this process S is replaced with Se and a sintered CZTSSe film is produced. As a standard procedure, the CZTS film is cut into two 1”by 1” pieces before the selenization process. These two 1” by 1” films are considered equivalent and used to identify effects of any non-standard experimental procedures. The sintered CZTSSe absorber film is then completed into a solar cells using a standard procedure which includes chemical bath deposition of CdS (~ 50 nm), RF sputtering of i-ZnO (~ 50nm) and tin doped indium oxide (ITO) (~150nm), and evaporation of patterned Ni/Al grid as the top contact. Mechanical scribing is used to create individual cells with a total area of 0.47 cm².

IV characteristics are measured under AM 1.5 illumination. All the device performance parameters reported are based on total cell area, including the shaded area. (Of the total device area nearly ~ 12% is shaded after the grid deposition).
3. THIOUREA TREATMENTS

Thiourea is used as sulfur source in spray pyrolysis techniques to form CZTS[30]. Building on this idea, it can be proposed that thiourea can be used as sulfur source during/after selenization. By optimizing the amount of thiourea and Se used during the selenization the band gap of the final film can be tuned.

To test this hypothesis, 2” by 1” coated CZTS films were soaked in 1.5 M solution of thiourea in ultrapure water for different time intervals (10 and 20 minutes). These films were then washed with ultrapure water to remove excess thiourea from the surface of the sample. These samples were then selenized for 20 minutes in tube furnace at 500°C. These were completed into devices and characterized. Another test sample was prepared without any treatment with thiourea for comparison. Following tables show the effect of the thiourea treatment on the performance of the devices.

Table 1 Devices parameters without thiourea treatment

<table>
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<tr>
<th></th>
<th>Voc [V]</th>
<th>Jsc [mA/cm²]</th>
<th>FF [%]</th>
<th>Efficiency [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average</td>
<td>0.386</td>
<td>32.2</td>
<td>58.85</td>
<td>7.3</td>
</tr>
<tr>
<td>High</td>
<td>0.39</td>
<td>34.25</td>
<td>61.6</td>
<td>7.8</td>
</tr>
</tbody>
</table>

Table 2 Device parameters for sample treated with thiourea solution for 20 minutes

<table>
<thead>
<tr>
<th></th>
<th>Voc [V]</th>
<th>Jsc [mA/cm²]</th>
<th>FF [%]</th>
<th>Efficiency [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average</td>
<td>0.398</td>
<td>29.6</td>
<td>63.1</td>
<td>7.4</td>
</tr>
<tr>
<td>High</td>
<td>0.4</td>
<td>30.9</td>
<td>64.7</td>
<td>7.7</td>
</tr>
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</table>
It is seen that the average Voc in the thiourea treated devices increases. The increase in Voc of the devices is statistically significant as verified by the Welch’s t test at 99.95 % confidence interval.

Thus the increase in Voc can be due to increase in the sulfur content of the sample due to thiourea treatment. Thus, thiourea can be used as a sulfur source during selenization.

One disadvantage of this method is that there is very small increase in the Voc and also there is no control on the amount of S inclusion in the sample. Also, it is reported in the literature that thiourea forms high molecular weight compounds at higher temperature[31], [32]. Hence, it necessary to develop a method which uses thiourea as a sulfur source but eliminate the incorporation of higher molecular weight compounds.

To see the effect of thiourea during selenization, experiment was done in which thiourea was placed in the graphite box used for selenization. 0.4 g Se pellets and 0.4 g of thiourea pellets were used during selenization. The samples after selenization showed surface inhomogeneity. Also a shiny material was formed at the bottom of the graphite box. This material could be removed by annealing in the tube furnace. From the Raman spectrum of this material, it was found to be Selenium. A yellow residue was also formed inside the graphite box.

Timschenko et al. have shown that thiourea decomposes to form H₂S and other compounds from 180-200 °C. It can be summarized as follows

1. Melting of thiourea, isomerization of thiourea into ammonium thiocyanate, in the temperature range of 140-180 °C

\[ \text{SC(NH}_2\text{)}_2 \rightleftharpoons \text{NH}_4\text{SCN} \]

Thiourea Ammonium thiocyanate

2. Formation of guanidium thiocyanate by reactions (2) and (3) in the liquid phase above 180 °C, with release of large amount of gaseous products.

\[ \text{SC(NH}_2\text{)}_2 \rightleftharpoons \text{NH}_2\text{CN} + \text{H}_2\text{S} \]

Cyanamide
3. Pyrolytic decomposition of Guanidium thiocyanate with formation of solid cyclic compounds in the range 220-300 °C.

Hence, a scheme inside the tube furnace should be used in which only H$_2$S is produced the graphite box. This can be realized by manipulating the temperatures in the 3-zone furnace.

If the device has a layer of higher band gap material at the CZTSSe-CdS interface, then it would enhance the collection of holes due to the electric field present in the material. Starting with this idea, it was decided to use thiourea as a sulfur source for surface modification.

As described earlier, thiourea decomposes to give H$_2$S at 180 to 200 °C. Hence tube furnace heating zones were set to 175-175-200 (°C). Selenized samples were prepared as described earlier. Now a 1” by 1” sample was taken in a graphite box. 0.4 g thiourea pellets were placed inside the graphite box. The graphite box is inserted in the tube furnace heating zone which was at 200 °C. It was kept there for 6 minutes. Then it was pushed into the section at 175°C. It was kept there for 4 minutes. After this the heating in the tube furnace was turned off and the sample was allowed to cool. The reason behind the two stage temperature setting was that if the samples are cooled directly cooled from 200 °C, then thiourea is found to condense on the sample. Having two-step cooling allows the decomposed products to escape the graphite box.
Figure 5 shows the Raman spectra of the samples treated with Thiourea (Blue) and selenized samples. (Red) The spectra were measured using with 632 nm red laser, on HORIBA LabRAM HR Raman Spectrometer. It can be seen that there is strong peak around 230 cm\(^{-1}\) in the samples treated with thiourea. Also it was observed that the sample obtained after thiourea treatment is not very uniform. Further work is needed to obtain uniform samples after Thiourea treatment.

Interestingly, Se has a peak at 230 cm\(^{-1}\). It is reported in literature that thiourea forms complex with Se [33]. Thus the strong peak at 230 cm\(^{-1}\) could be attributed to Se present as the thiourea complex in the sample. Thus thiourea cannot be used along with selenium for surface modification of CZTSSe films. One idea to explore would be to use gaseous H\(_2\)S directly, which is presented in chapter 5.
4. BROMINE ETCHING TREATMENTS FOR CZTSSE ABSORBER LAYERS.

4.1 Background

Figure 6 Raman Spectra of CZTSSe absorber with two different excitation wavelengths.

Above figure shows the Raman Spectra of Cu$_2$ZnSn(S,Se)$_4$ (CZTSSe) absorber layer, obtained using two different laser excitation wavelengths. The absorption coefficient in semiconducting materials is highly dependent on the wavelength used. It increases with decreasing wavelengths.[34] Thus it is expected that the 325 nm laser is more sensitive towards the surface of the CZTSSe absorber.
The spectrum from 633 nm laser shows presence of intense peaks at 196 cm\(^{-1}\) and 174 cm\(^{-1}\), which correspond to the main peaks of CZTSe. It also shows presence of broad peak from 230 cm\(^{-1}\) to 270 cm\(^{-1}\). This peak could consist of peaks from CZTSe and CTSe (Cu\(_2\)SnSe\(_3\)) and ZnSe. In the spectrum from 325 nm laser, the peak intensity of the peak at 196 cm\(^{-1}\) has significantly decreased but at the same time the intensity of the peak at 175~cm\(^{-1}\) remains comparable to the spectrum from 633 nm laser. Also, the broad peak from 230 cm\(^{-1}\) to 270 cm\(^{-1}\) is present in the spectrum from 325 nm laser. Now from spectra reported in the literature, the peak at 196 cm\(^{-1}\) is the most intense peak for CZTSe\(^{[35]}\), whereas for CTSe the peak at 178 cm\(^{-1}\) is the most intense peak\(^{[36]}\). Thus it can be inferred that the surface composition of the CZTSSe absorbers is different from the bulk composition and the surfaces may predominantly consist of secondary phases such as CTSe in addition to CZTSe.

Presence of secondary phases could be a possible reason for the low Voc of our solar cells. Etching treatments are proposed to remove only top 5-10 nm layer of the CZTSSe.

### 4.2 Bromine etching in the literature

Bromine etching has been used for various material systems such as GaP\(^{[37]}\), CdZnTe\(^{[38]}\) and Cu(In,Ga)(S,Se)\(_2\) (CIGS)\(^{[21]}\) and recently for CZTS \(^{[39]}\). Canava et al have reported the use of aqueous bromine etch for CIGS\(^{[40]}\). They have found that Bromine etching leads to formation of specular surfaces with lower surface roughness. They propose a two-step mechanism for oxidation of CIGS. First step being the preferential dissolution of metals which leaves behind a layer of Se(0) on the surface.

\[
\text{Cu(In,Ga)Se}_2 + 2.5 \text{ Br}_2 \rightarrow 2\text{Cu(II)} + \{\text{In(III) + Ga(III)}\} + 2\text{Se}^0 + 5\text{Br}^- 
\]

The second step is the oxidation of Se\(^0\):

\[
\text{Se}(0) + 2\text{Br}^- \rightarrow \text{Se(IV)} + 4\text{Br}^- 
\]

They also report formation of Se\(^0\) layer on the absorber surface after the etching treatments. Siebentritt et al have reported increase in open circuit voltage (Voc) and fill factor (FF) of devices after Bromine in Methanol etch\(^{[39]}\). Our group has used Bromine in Methanol solutions for etching CIGS films in the past\(^{[21]}\).
4.3 Experimental:

Sintered CZTSSe films were prepared as per the standard experimental procedure as described chapter 2. Etching treatments are performed on this device as described below. After the etching treatments are complete, the film is finished into solar cell by standard methods described in chapter 2.

Freshly prepared Bromine in Methanol solutions were used for the etching treatments. All the chemicals used were ACS grade (Bromine, Methanol, KCN, Butylamine and Hexanethiol)

A range of concentrations of Bromine in Methanol solutions was used for finding the etching rate and the effect on surface roughness of CZTSSe absorbers. The variation of etching rate with concentration was found out to be close to linear, as shown in fig. 7. It was also observed that at lower concentrations of bromine, the surface roughness values did not change significantly. The results are summarized in fig. 8. At 0.5 M concentration the surface roughness decreased drastically. This could be attributed to the fact that due to the higher etching rate the absorber is etched down to the unsintered layer, which is different in composition from the bulk CZTSSe layer. The surface roughness and layer thickness for etching rate calculations was measured using KLA Tenor surface profilometer.

Canava et al [40] have proposed an etching mechanism for bromine etching of CIGS. Similar reactions can be written for CZTSSe.

Step I

\[ \text{Cu}_2\text{ZnSnSe}_4 + 4\text{Br}_2 \rightarrow 2\text{Cu(I)} + \text{Zn(II)} + \text{Sn(IV)} + 4\text{Se}^0 + 8\text{Br}^- \]

OR

\[ \text{Cu}_2\text{ZnSnSe}_4 + 5\text{Br}_2 \rightarrow 2\text{Cu(II)} + \text{Zn(II)} + \text{Sn(IV)} + 4\text{Se}^0 + 10\text{Br}^- \]

Step II

\[ \text{Se}^0 + 2\text{Br}_2 \rightarrow \text{Se(IV)} + 4\text{Br}^- \]
It can be seen that copper can either get oxidized to +2 state or remain in +1 state.

Ideally, for etching purposes we want all of the bromides formed to be soluble in methanol / water so that no residue remains on the surface of the absorber. But following solubility data was obtained experimentally:
### Table 3 Summary of solubility of bromides

<table>
<thead>
<tr>
<th>Compound</th>
<th>Solubility in Methanol</th>
<th>Solubility in Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper (I) Bromide</td>
<td>Sparingly Soluble</td>
<td>Sparingly Soluble</td>
</tr>
<tr>
<td>Copper (II) Bromide</td>
<td>Soluble</td>
<td>Soluble</td>
</tr>
<tr>
<td>Zinc (II) Bromide</td>
<td>Soluble</td>
<td>Soluble</td>
</tr>
<tr>
<td>Tin (IV) Bromide</td>
<td>Soluble</td>
<td>Soluble</td>
</tr>
</tbody>
</table>

Thus in addition to layer of $\text{Se}^0$, residue of $\text{Cu(I)}\text{Br}$ is expected to be present on the surface.

### After-Treatments Used

It is necessary to preferentially etch the excess selenium ($\text{Se}^0$) which may be forming on the surface and $\text{Cu(I)}\text{Br}$ layer which is most likely present after the etching treatment.

Various etching treatments can be found in the literature for etching of selenium such as KCN etch, use of Amine-Thiol Mixture for dissolving selenium. The challenge is to selectively etch the selenium layer but keep the CZTSSe absorber layer intact.

**Treatment No. 1**

CZTSSe device was dipped into solution of 0.005M Br$_2$/Methanol for 10 sec. followed by rinse in methanol. The device was then blown dry under nitrogen.

**Treatment No 2**

It consists of Treatment No 1 followed by dipping the device in solution of Butylamine and 1-Hexanethiol (1:1 in volume) for 5 min and then rinsing the device with methanol.

**Treatment No. 3**

It consists of Treatment No 1 followed by dipping the device in 0.5 M aqueous KCN solution for 30 sec. Then the device is rinsed in ultrapure water and blown dry under nitrogen. KCN is known to dissolve selenium according to reaction

$$\text{Se} + \text{KCN} \rightarrow \text{KSeCN}$$
KCN etch is also known to dissolve copper chalcogenides (Cu_{2-x}S and Cu_{2-x}Se). Thus in addition to removing Se^0 from the surface, it will also etch some of the residual Cu(I) in form of Cu(I)Br present on the surface.

**Treatment No. 4**

This treatment was intended to remove the residual CuBr forming on the surface of etched absorbers. After treatment 1, the device is dipped into 3M aqueous KBr solution for 10 min. Complex formation of copper Copper(I) Bromide takes place with bromine ion according to following reactions [41]

\[
\text{CuBr} + \text{Br}^{-1} \rightarrow \text{CuBr}_2^{-1}
\]

\[
\text{CuBr}_2^{-1} + \text{Br}^{-1} \rightarrow \text{CuBr}_3^{-1}
\]

**4.4 Results and Discussion**

Following graphs show IV characteristics of solar cell devices after various etching treatments. The results are summarized in Table 4.

<table>
<thead>
<tr>
<th>Treatment No</th>
<th>Voc [V]</th>
<th>Jsc [mA/cm²]</th>
<th>FF [%]</th>
<th>Efficiency [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>No Treatment/Test</td>
<td>0.403</td>
<td>30.4</td>
<td>61.4</td>
<td>7.5</td>
</tr>
<tr>
<td>1</td>
<td>0.27</td>
<td>0.268</td>
<td>21.7</td>
<td>0.1</td>
</tr>
<tr>
<td>2</td>
<td>0.349</td>
<td>25.2</td>
<td>27.8</td>
<td>2.5</td>
</tr>
<tr>
<td>3</td>
<td>0.365</td>
<td>28.6</td>
<td>49.5</td>
<td>5.2</td>
</tr>
<tr>
<td>4</td>
<td>0.359</td>
<td>7.2</td>
<td>15.2</td>
<td>0.4</td>
</tr>
</tbody>
</table>
Figure 9 IV characteristics of cell after treatment 1

Figure 10 IV Characteristics of cell after treatment 2
Figure 11 IV characteristics of cell after treatment 3

Figure 12 IV Characteristics of cell after treatment 4
It can be seen that just the bromine etching is detrimental for the device performance, even at very low concentration of the Br$_2$/Methanol solution, because the etched surface provides recombination centers for the generated carriers. Use of Amine-Thiol mixture treatment after bromine etching increased the performance up to 2.5%. This may be because Amine-Thiol mixture only dissolves the selenium layer formed on the surface while leaving the insoluble Cu(I)Br still remains on the surface. KCN treatment increased the performance up to 5.2%. Since KCN etches both selenium and Cu$_{2-x}$Se, the increase in performance after the bromine etching treatment due to KCN treatment is higher as compared to that after Amine-Thiol mixture treatment. Finally, KBr treatment is expected to preferentially dissolve the Cu(I)Br residue formed on the surface by forming CuBr$_{x-(x-1)}$ complexes, but as can be seen from the device performance the KBr treatment does not have any significant effect on the device performance as compared to that after just the bromine treatment. Thus, with the treatments tried so far the performance of the absorber layers after the bromine etching could not be improved even up to the baseline level of about 7.5%. This could very well mean that the surface of the etched absorbers even after the post-selenization treatments has more recombination centers as compared to the absorber layer before any etching treatments. In conclusion, our etching observations are in sharp contrast to the beneficial effects reported in the literature [39],[42].
5. OTHER SURFACE TREATMENTS

5.1 Gaseous H$_2$S treatments

The idea is to only modify about 10 nm of the top surface of the CZTSSe absorber layer. Various experimental conditions were used to modify the surface and see if there is any trend found in the performance.

Series of temperatures were used for the surface treatments of the CZTSSe devices. Two 1” by 1” CZTS films were identically processed in tube furnace to make two CZTSSe samples. One of the samples was stored under vacuum and one was loaded on sample holder for the H$_2$S furnace.

The furnace was evacuated and purged with Ar. This procedure was repeated 3 times. After the 3rd purge 80 s.c.c.m. (standard cubic centimeters per minute) Ar was flown through the furnace. The set points of the furnace were set such that the temperature inside the furnace is 300 C. Once the furnace was at steady state the sample was pushed in and the flow was switched to 0.1% v/v Argon/H$_2$S. The sample was pulled out of the heating zone after 30 sec and flow was switched back to Ar. The furnace was opened to rapidly cool the sample. Once the temperature inside the furnace was below 50 °C the sample was removed and immediately dipped in DI water. CdS deposition was completed on the sample.

Following tables summarize the results of the series of experiments conducted.

<table>
<thead>
<tr>
<th>Device</th>
<th>Voc [V]</th>
<th>Jsc [mA/cm$^2$]</th>
<th>FF [%]</th>
<th>Efficiency [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Test</td>
<td>0.363</td>
<td>29.8</td>
<td>57.3</td>
<td>6.2</td>
</tr>
<tr>
<td>1</td>
<td>0.347</td>
<td>29.3</td>
<td>55.5</td>
<td>5.9</td>
</tr>
</tbody>
</table>

1: film exposed to H$_2$S for 30 sec at 300°C
Table 6 Comparison between device parameters

<table>
<thead>
<tr>
<th>Device</th>
<th>Voc [V]</th>
<th>Jsc [mA/cm²]</th>
<th>FF [%]</th>
<th>Efficiency [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Test</td>
<td>0.366</td>
<td>29.9</td>
<td>59.6</td>
<td>6.5</td>
</tr>
<tr>
<td>2</td>
<td>0.380</td>
<td>29.3</td>
<td>61.5</td>
<td>6.8</td>
</tr>
</tbody>
</table>

2: film exposed to H₂S for 30 sec at 400°C

Table 7 Comparison between device parameters

<table>
<thead>
<tr>
<th>Device</th>
<th>Voc [V]</th>
<th>Jsc [mA/cm²]</th>
<th>FF [%]</th>
<th>Efficiency [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Test</td>
<td>0.361</td>
<td>27.6</td>
<td>60.2</td>
<td>6.0</td>
</tr>
<tr>
<td>3</td>
<td>0.365</td>
<td>29.0</td>
<td>59.5</td>
<td>6.3</td>
</tr>
</tbody>
</table>

3: film exposed to H₂S for 30 sec at 500°C

It can be seen that the H₂S treatments marginal impact on the device performance at best.

5.2 KCN Etching Treatments

KCN etching treatments have been used in the literature for both CZTS and CIGS. Timmo et al [42] have reported that treatment in 10% KCN solution increases both Voc and Jsc.

There is a chance that there are grains of Se forming on the surface of CZTS absorber layer after the annealing treatment in Se atmosphere. This could adversely affect the device performance. KCN etching could have following effects on the CZTSSe absorber

1. It can dissolve elemental Se according to the reaction

   \[ \text{Se} + \text{KCN} \rightarrow \text{KSeCN} \]

2. It can dissolve \( \text{Cu}_2\text{Se} \)

1” x 1” CZTSSe devices were made by selenization. One device was used as a test with no KCN etching while other devices were used for etching treatments.
Treatments:

1. 0.05 M KCN in ultrapure water for 30 seconds, then the sample was rinsed in ultrapure water and blown dry in nitrogen
2. 0.005 M KCN in ultrapure water for 30 seconds, then the sample was rinsed in ultrapure water and blown dry in nitrogen
3. 0.05 M KCN in ultrapure water for 30 seconds, then the sample was rinsed in ultrapure water and blown dry in nitrogen, then re-annealed in selenium atmosphere for 10 minutes.

Following table shows a summary of device parameters after the treatments. It can be seen that with treatment 1 the fill factor and Jsc decreases marginally resulting in a lower efficiency. With treatment 2 the Voc as well as Jsc increases on average. This increase is within experimental variation and cannot be attributed as a result of the treatment. The treatment 3 is same as treatment 2 followed by annealing treatment in selenium atmosphere. The annealing treatment was tried so that the etched surface would have an opportunity to reselenize.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Voc [V]</th>
<th>Jsc [mA/cm²]</th>
<th>FF [%]</th>
<th>Efficiency [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>No</td>
<td>0.398</td>
<td>29.6</td>
<td>64.1</td>
<td>7.6</td>
</tr>
<tr>
<td>Treatment/Test</td>
<td>1</td>
<td>0.386</td>
<td>28.0</td>
<td>59.5</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.403</td>
<td>30.1</td>
<td>64.0</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.363</td>
<td>27.5</td>
<td>46.7</td>
</tr>
</tbody>
</table>

It can be seen that KCN etching treatments either had detrimental effect (treatment 1 and 3) on the device performance or the effect was negligible or within experimental error (for treatment 2)

5.3 Hybrid films

Both CIGS and CZTS belong to the chalcopyrite family. CZTS has earth abundant elements Zinc and Tin instead of Indium in CIGS. But currently CIGS provides highest efficiency devices in the chalcopyrite based thin film solar cells. Even in our lab the efficiency of CIGS is higher
than CZTS. One of the proposed reasons why CIGS has higher efficiency than CZTS is because of the interface between CIGS and CdS. To take advantage of this fact thin layer of CIGS can be deposited on top of CZTS followed by CdS buffer layer deposition.

In the first approach ~ 800 nm of CZTS nanoparticles layer was coated on Mo coated SLG. Then ~ 50 nm thick layer of CIGS nanoparticles was coated on top. The hybrid film was annealed under selenium atmosphere. The selenized film was then processed further to make it into a solar cell. Since the surface layer is very thin it is not possible to use characterization techniques such as XRD to probe the changes on the surface. Easiest way is to test the device performance and compare it with a test cell. SEM cross sections were taken for the completed device which is shown below.

![Figure 13 SEM cross section view of completed hybrid device with ~50 nm CIGS nanoparticle layer on top of ~ 800 nm CZTS nanoparticle layer.](image)

Table 9 shows a comparison between a test sample and hybrid film sample. The test sample did not have the CIGS coating on top.
Table 9 Comparison between test device and device with CIGS nanoparticle coated film coated on top of CZTS nanoparticle film

<table>
<thead>
<tr>
<th>Device</th>
<th>Voc [V]</th>
<th>Jsc [mA/cm²]</th>
<th>FF [%]</th>
<th>Efficiency [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Test</td>
<td>0.39</td>
<td>29.0</td>
<td>63.0</td>
<td>7.1</td>
</tr>
<tr>
<td>1-1</td>
<td>0.283</td>
<td>32.5</td>
<td>46.9</td>
<td>4.3</td>
</tr>
<tr>
<td>1-2</td>
<td>0.300</td>
<td>34.4</td>
<td>49.5</td>
<td>4.5</td>
</tr>
</tbody>
</table>

1-1 and 1-2 are two 1” by 1” devices with the hybrid coating.

As can be seen the device performance after the addition of CIGS nanoparticle layer on top of CZTS nanoparticles is detrimental for device performance. Various hypotheses could be made about why this happens. Since the annealing step lasts 40 minutes, the CIGS on the surface can diffuse throughout the CZTS matrix. If this is really the case then shorter annealing times should be used. But then the CZTS film underneath may not sinter all the way through. Solution for this would be to take selenized CZTSSe film and coat a layer of CIGS nanoparticles on top of it and then do a short selenization treatment. Pursuing this idea, ~ 50 nm layer of CIGS nanoparticles was coated on top of sintered CZTSSe film. This hybrid film was reselenized for 10 minutes instead of the standard 40 minutes time.

Table 10 shows comparison of the device performance of the test device and device with the CIGS coating on it.

Table 10 Comparison between test device and device with CIGS nanoparticles coated and reselenized on top of a selenized CZTSSe film.

<table>
<thead>
<tr>
<th>Device</th>
<th>Voc [V]</th>
<th>Jsc [mA/cm²]</th>
<th>FF [%]</th>
<th>Efficiency [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Test</td>
<td>0.380</td>
<td>30.3</td>
<td>64.5</td>
<td>7.1</td>
</tr>
<tr>
<td>2-1</td>
<td>0.135</td>
<td>4.9</td>
<td>30.9</td>
<td>0.2</td>
</tr>
<tr>
<td>2-2</td>
<td>0.147</td>
<td>4.1</td>
<td>33.9</td>
<td>0.2</td>
</tr>
</tbody>
</table>

2-1 and 2-2 are two 1” by 1” devices which have the hybrid coating.

It can be seen that even this approach is detrimental to the device performance and did not serve the intended purpose.

The surface between the p type and n type layer is plays very critical role in the junction formation which in turn is responsible for carrier collection. The idea of using an additional
layer at the CZTSSe interface to gain from better material quality of CIGSSe may have downsides to it. One is since the formation of the junction is not uniform; it can create lot of recombination centers for the generated electron hole pairs.

One way to confirm this hypothesis is to apply coating of CZTS nanoparticles on top of the selenized CZTSSe film and see if that can give device efficiency if any. Hence ~ 50 nm layer of CZTS nanoparticles was coated on top of sintered CZTSSe film and it was completed into a device. A test device without any layer was also used.

Following table shows comparison of device performance between the two devices.

Table 11 Comparison between test device and device reselenized after ~ 50 nm coating of CZTS nanoparticles on top of selenized CZTSSe films

<table>
<thead>
<tr>
<th>Device</th>
<th>Voc [V]</th>
<th>Jsc [mA/cm²]</th>
<th>FF [%]</th>
<th>Efficiency [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Test</td>
<td>0.380</td>
<td>31.3</td>
<td>50.9</td>
<td>6.1</td>
</tr>
<tr>
<td>3-1</td>
<td>0.148</td>
<td>0.2</td>
<td>30.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>

3-1 is the device with the CZTS nanoparticle film on top of sintered CZTSSe film.

Figure 14 SEM cross section of device with reselenized after ~50nm coating of CZTS nanoparticle layer on top of selenized CZTSSe film
This shows that instead of directly using CBD of CdS if an intermediate layer is deposited to modify the interface between the p and n type layer, it is detrimental to the device performance. The reason for which could be the formation of recombination centers due to the introduction of additional layers.
6. CONCLUSION

Chalcopyrite semiconducting materials, specifically CZTS, are a promising alternative to traditional silicon solar cell technology. Because of the high absorption coefficient thin films of these materials are sufficient for the fabrication of solar cells. Liquid based synthesis methods are advantageous because they are easily scalable using the roll to roll manufacturing techniques.

Various treatments were explored in this study to enhance the performance of CZTSSe based solar cells. Thiourea can be used as a sulfur source and can be used to tune band gap of CZTSSe. Bromine etching can be used to manipulate the thickness of sintered CZTSSe film. The etching treatment creates recombination centers which lead to poor device performance. Various after treatments were used in an attempt to improve the performance of the devices. It was observed that the performance of the solar cell devices could not be improved using the after treatments.

Other surface modifications were explored including KCN etching, gaseous H$_2$S treatments. Hybrid solar cells which included use of CIGS nanoparticles at the interface between CZTSSe and CdS were also explored. They resulted in decreased device performances.

In conclusion, various surface treatments were explored to enhance the device performance of CZTSSe solar cells. It was found out that it is beneficial to deposit the n type buffer layer onto the sintered CZTSSe film directly instead of using any surface modification step in between. To ensure homogeneous surface of the p type absorber layer, changes should be made during the annealing step.
LIST OF REFERENCES
LIST OF REFERENCES


