Cd x Zn 1-x S/PbS Thin Film Solar Cell

Article · August 2014

CITATIONS
0

READS
16

3 authors, including:

Cliff Orori Mosiori
Technical University of Mombasa

39 PUBLICATIONS 14 CITATIONS

Some of the authors of this publication are also working on these related projects:

Thin film characterization View project

Undergraduate Student Projects _ Technical University of Mombasa View project

All content following this page was uploaded by Cliff Orori Mosiori on 10 February 2016.

The user has requested enhancement of the downloaded file. All in-text references underlined in blue are added to the original document and are linked to publications on ResearchGate, letting you access and read them immediately.
Cd$_x$Zn$_{1-x}$S/PbS Thin Film Solar Cell

Mosiori Cliff Orori$^1$, Njoroge Walter Kamande$^2$, Okumu John$^3$

Department of Physics, Kenyatta University, P. Box 43844 -00100, Nairobi, Kenya
Email: cliffmosiori@gmail.com

Accepted 25 July 2014

In this work, $n$-type Cd$_x$Zn$_{1-x}$S and $p$-type PbS layers were optimized through chemical solution technique for solar cells. Cd$_x$Zn$_{1-x}$S was grown at 820°C while PbS was grown at room temperature utilizing aqueous conditions. Optical constants suitable for solar cells fabrication were investigated. Cd$_x$Zn$_{1-x}$S films had a band gap varying from 2.47 eV ($x = 0.6$) to 2.72 eV ($x = 1.0$), transmittance above 79% in VIS - NIR region with resistivity range of $9.5 \times 10^1$ to $1.22 \times 10^2$ Ω-cm. PbS had a band gap of 0.89 eV, transmittance below 55% with a resistivity range of $6.78 \times 10^3$ to $1.26 \times 10^4$ Ω-cm appropriate for solar cell absorber layers. Their solar cell had a short circuit current, $I_{sc} = 0.031$ A, open voltage, $V_{oc} = 0.37$ V, efficiency, $\eta = 0.9\%$ with a fill factor, $ff = 0.66$.

Keywords: Film, Solar, Cell

INTRODUCTION

Thin films can be used to fabricate photovoltaic devices that can convert solar energy into electrical energy for various uses. This can be achieved if their structure, inter-band transitions and other optical properties are maximized to harvest enough solar radiation to provide energy. Activities that take place when electrons transit between energy bands in thin films are of fundamental importance in harvesting solar radiation (Chapin and Pearson, 1954). Solar energy is abundant but it has not been harvested well although harvesting it by use of solar cells does not require sophisticated and expensive facilities. Thin film nanotechnology has fabricated cheap photovoltaic cells that produce power for homes, small commercial uses or electric current (Schroder, 1998). Solar energy if a form of energy that is reliable, easy to maintain, install and it can extend to cover IR and UV radiation regions to make solar cells more efficient (Armin, 2009; Siu and Kwok, 1978). Solar cells absorb photons from the sun and convert them directly into electricity. They consist of a $p$-type layer which has a majority hole carriers and an $n$-type layer that has a majority electron carriers. When a photon with energy greater than the band-gap of the semiconductor passes through such a cell, it may be absorbed by the material and this takes the form of a band-to-band electronic transition producing an electron-hole pair.

Several thin films have been fabricated and used to manufacture solar cells using various methods of preparation for solar cells that include chemical deposition; liquid deposition and chemical vapour among others have also been used. Many researchers have devoted their efforts to solution technique because it is a
non-expensive method for thin film preparation. It has
developed many noble materials. Doping using elemental
dopants like boron (Khallaf et al., 2009), indium (Shadia
et al., 2008), arsenide and chlorine (Amanullah et al.,
2005) has produced suitable films for use as window
layers. Ternary derivatives of CdS have generated a lot
of research interest because of their varied applications
in the field of optoelectronic devices. Cd_{1-x}Zn_xS which is
gaining prominence as a good candidate for wide band
gap materials for solar cells. Its band gap can be tailored
to vary from 2.43 eV to 3.32 eV depending on its
constituents and preparation techniques. The addition of
Zn onto CdS enhance open-circuit voltage (V_{oc}) and
short-circuits current (I_{sc}) in hetero-junction devices and
result into a decrease in window absorption losses. Lead
chalcogenides films grown by CBD possess a well-
deﬁned band structure in which their energy gap varies
continuously between 0.41 eV to 2.7 eV depending on
the method of preparation. Since their band gap ranges
within the optimum theoretical band gap for maximum
absorber material of about 1.5 eV, they can be used to
fabricate solar cells (Popa et al., 2006).

**Experimental details**

**Preparation of substrates**

Glass slides were used as substrates, degreased in
hydrochloric acid for 24 hours, washed with detergent,
rinsed in distilled water and dried in air for 2 hours.
They were inserted vertically from synthetic foam
which covered the beakers containing the bath solution.

**Growth of Cadmium Zinc Sulphide layer**

The bath composed of 0.038 M cadmium nitrate, 0.076 M
ammonium nitrate, and 0.076 M thiourea in de-ionized
water. 25 ml of the each solution was taken into
a separate beaker and de-ionized water added to top up
to 100 mL, then heated to about 82° C. Using a burette,
NH_4OH (29.4%) was added drop-wise to maintain a pH of
about 9. Glass substrates were inserted for 25 minutes.

Varying concentrations of zinc nitrate [Zn(NO_3)_2] solutions
were added to vary zinc ions and the value of x, (i.e. x =
Zn^{2+}/[Cd^{2+} + Zn^{2+}]) was varied from 1.0 - 0.6 according
to the equation Cd_{1-x}Zn_xS. A reaction mechanism for the
formation of Cd$_2$S was suggested to be as shown in
equation 2.1 where cadmium salts in the presence of
ammonium hydroxide solution form the complex
compounds.

\[ \text{NH}_3 + \text{H}_2\text{O} \rightarrow \text{NH}_4\text{OH} ^{} \text{H}^+ \]  \hspace{1cm} (2.1)  
\[ \text{Cd(NO}_3\text{)}_2 + 4(\text{NH}_3) \rightarrow \text{Cd}(\text{NH}_3)_4[\text{NO}_3]_2 \]  
\[ \text{Zn(NO}_3\text{)}_2 + 4(\text{NH}_3) \rightarrow (\text{Zn}(\text{NH}_3)_4)[\text{NO}_3]_2 \]  
\[ \text{Cd}(\text{NH}_3)_4^{2+} \rightarrow \text{Cd}^{2+} + 4\text{NH}_3 \]  \hspace{1cm} (2.2)  
\[ \text{Zn}(\text{NH}_3)_4^{2} \rightarrow \text{Zn}^{2+} + 4\text{NH}_3 \]  \hspace{1cm} (2.3)  
\[ \text{Cd}(\text{OH})_2 \rightarrow \text{Cd}^{2+} + 2(\text{OH})^- \]  \hspace{1cm} (2.4)  
\[ \text{Zn}(\text{OH})_2 \rightarrow \text{Zn}^{2+} + 2(\text{OH})^- \]  \hspace{1cm} (2.5)  
\[ \text{SH} + \text{OH} \rightarrow S^{2} + H_2O \]  \hspace{1cm} (2.6)  
\[ x \text{Cd}^{2+} + (1-x) \text{Zn}^{2+} + S^{2} \rightarrow \text{Cd}_x\text{Zn}_{1-x}S \]  \hspace{1cm} (2.7)

Thiourea is a sulphide-ion source in an alkaline medium
where the sulphide ions are released slowly as shown in
equation 2.5 and 2.6. Cadmium ions react with sulphide
and zinc ions to form Cd$_x$Zn$_{1-x}$S as shown in equations
(2.3), (2.4), and (2.6):

The reactions in equations 2.1 to 2.7 are interrelated.
Ammonia concentration affects the concentration of
cadmium ions Cd$^{2+}$, precipitation of cadmium hydroxide
[Cd(OH)$_2$], concentration of the tetra-ammine-cadmium
complex ions [Cd(NH$_3$)$_2$]$^{2+}$, and the concentration of
hydroxide ions [OH$^-$] in the bath. Electrical properties
were studied using a four point probe connected to
Kethley 2400 source meter interfaced with a computer
using Labview program while optical transmittance was
measured using UV-VIS-NIR spectrophotometer 3700.

**Growth of PbS thin film layer**

Growth was done in a reactive chemical bath in a 100 ml
beaker by sequential additions of solution of 5 ml of 0.5 M
lead nitrate as a source of Pb$^{2+}$, 5 ml of 2 M sodium
hydroxide as source of alkaline medium, 6 ml of 1 M
thiourea as source of S$^{2-}$ and 2 ml of 1 M tri-ethanolamine
as a complexing agent. Solutions were prepared from
analytical grade chemicals. Lead ions of varying
concentration from 0.3 M to 0.7 M at intervals of 0.1 M
were prepared. 5ml of lead nitrate poured into a 100ml
beaker followed by 5ml of 2M sodium hydroxide and the mixture was thoroughly stirred using an electric stirrer to obtain a milky solution. This was followed by adding 6ml of 1M thiourea followed immediately by 2ml of 1M tri-ethanolamine while stirring continued for about two minutes to ensure uniformity of the mixture. A substrate was inserted vertically leaning on the side of the beaker and maintained at room temperature for 120 minutes. Lead nitrate concentration was varied at intervals of 0.1 for the subsequent films from 0.3 - 0.7M of Pb\textsuperscript{2+} ion

<table>
<thead>
<tr>
<th>Film</th>
<th>Conc. of Zn</th>
<th>[n]</th>
<th>E\textsubscript{g} [eV]</th>
<th>$\rho$ [Ω-m]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd\textsubscript{0.6}Zn\textsubscript{0.4}S</td>
<td>0.4</td>
<td>2.39</td>
<td>2.72</td>
<td>136.19</td>
</tr>
<tr>
<td>Cd\textsubscript{0.7}Zn\textsubscript{0.3}S</td>
<td>0.3</td>
<td>2.41</td>
<td>2.69</td>
<td>122.91</td>
</tr>
<tr>
<td>Cd\textsubscript{0.8}Zn\textsubscript{0.2}S</td>
<td>0.2</td>
<td>2.46</td>
<td>2.60</td>
<td>116.98</td>
</tr>
<tr>
<td>Cd\textsubscript{0.9}Zn\textsubscript{0.1}S</td>
<td>0.1</td>
<td>2.51</td>
<td>2.52</td>
<td>109.37</td>
</tr>
<tr>
<td>CdS</td>
<td>0.0</td>
<td>2.53</td>
<td>2.47</td>
<td>113.56</td>
</tr>
</tbody>
</table>
concentrations. Reflection and transmission spectra were measured at room temperature in the spectral range of 260 – 2000 nm (4.54 – 1.08 eV) using NIR-VIS IR spectrophotometer DUC 3700 instrument at ambient temperature. The electrical resistivity measurements were done using the Keithley 2400 source meter interfaced with a computer.

### RESULTS

#### Electrical Properties

The resultant PbS thin films were homogeneous, well adhered to the substrate and specularly reflecting. As shown in figure 1, resistivity of PbS was \(9.171 \times 10^3 \, \Omega\)-

---

**Table 2:** Variation of current against voltage in Cd\(_x\)Zn\(_{1-x}\)S/ PbS Solar cell as measured by solar simulator.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>0.031</td>
<td>0.0</td>
</tr>
<tr>
<td>0.05</td>
<td>0.031</td>
<td>0.00155</td>
</tr>
<tr>
<td>0.10</td>
<td>0.031</td>
<td>0.0031</td>
</tr>
<tr>
<td>0.15</td>
<td>0.031</td>
<td>0.00465</td>
</tr>
<tr>
<td>0.20</td>
<td>0.030</td>
<td>0.006</td>
</tr>
<tr>
<td>0.25</td>
<td>0.028</td>
<td>0.007</td>
</tr>
<tr>
<td>0.27</td>
<td>0.027</td>
<td>0.00729</td>
</tr>
<tr>
<td>0.29</td>
<td>0.026</td>
<td>0.00754</td>
</tr>
<tr>
<td>0.31</td>
<td>0.023</td>
<td>0.00713</td>
</tr>
<tr>
<td>0.33</td>
<td>0.020</td>
<td>0.0066</td>
</tr>
<tr>
<td>0.35</td>
<td>0.015</td>
<td>0.00525</td>
</tr>
<tr>
<td>0.36</td>
<td>0.010</td>
<td>0.0036</td>
</tr>
<tr>
<td>0.37</td>
<td>0.001</td>
<td>0.00037</td>
</tr>
</tbody>
</table>

**Table 3:** Cell parameters of Cd\(_x\)Zn\(_{1-x}\)S / PbS Solar cell

<table>
<thead>
<tr>
<th>Cell parameters</th>
<th>Value of parameter/unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>(I_{sc})</td>
<td>0.031 A</td>
</tr>
<tr>
<td>(V_{oc})</td>
<td>0.37 V</td>
</tr>
<tr>
<td>(V_{max})</td>
<td>0.29 V</td>
</tr>
<tr>
<td>(I_{max})</td>
<td>0.026 A</td>
</tr>
<tr>
<td>(P_{max})</td>
<td>0.00754 W</td>
</tr>
<tr>
<td>(ff)</td>
<td>0.66</td>
</tr>
<tr>
<td>(\eta)</td>
<td>0.9</td>
</tr>
</tbody>
</table>
cm and decreased to $6.78 \times 10^3 \ \Omega\text{-cm}$ but thereafter increased almost linear to $1.26 \times 10^4 \ \Omega\text{-cm}$ at 0.7M PbS which translates to an electrical conductivity range of $1.09 - 0.79 \times 10^{-5} \ S\text{-cm}^{-1}$. This observation was attributed to the large levels of scattering centres due to amorphous nature of the films as lead concentration increases. Amorphous thin films have higher concentration of scattering centres.

On the hand, electrical resistivity of $\text{Cd}_x\text{Zn}_{1-x}\text{S}$ increased with increase of Zn ions from $1.09 \times 10^2$ to $1.36 \times 10^2 \ \Omega\text{-cm}$ shown in figure 2. Introduced Zn impurities result into more scattering centres which in turn reduced the mean free path hence scattering at the grain boundaries in addition to the bulk scattering centres that were present. Charge carries moving through the thin film grains suffer extra scattering at the grain boundaries.
hence a reduced mean free path. Tuning the electrical properties of the thin films through doping is very important for various applications. Similar sheet resistivity measurement have been observed (Vidhya and Velumani, 2009, Song et al., 2006) by Van der Pauw technique (order of 107 Ω-cm-106 Ω-cm) or conductivity order of 1×10-2 to 7 × 10-3 [Ω-cm]-1 as compared to conductivity obtained that ranged from 7.4 × 10-4 to 9.1 × 10-3 S/cm.

Optical Properties

Cd1-xZnxS films were smooth, uniform, adherent, bright yellow orange in colour where the yellowness decreased with increasing zinc content. Zn reduced reflectance and absorbance while it increased transmittance within the visible and infrared range. Reflective index (n) was calculated using the equation proposed by Ravindra et al. (2006) as:

\[ n = [(1+R^{1/2})/ (1-R^{1/2})] \]  \hspace{1cm} (3.4)

while optical refractive index (n) and energy band gap (Eg) related as:

\[ n = 4.08 - 0.62Eg \]  \hspace{1cm} (3.5)

Refractive index decreased with increase in Zn concentration and this explains why the colour of the films faded as concentration increased. Dielectric constants are used to describe any losses caused by optical conductivity (σ) in thin films where real and imaginary parts of the dielectric constant are given by:

\[ \varepsilon_r = \varepsilon_i + \varepsilon_i \]  \hspace{1cm} (3.6)

and they were estimated using the relations:

\[ \varepsilon_r = n^2 - k^2 \]  \hspace{1cm} (3.7)

\[ \varepsilon_i = 2nk \]  \hspace{1cm} (3.8)

The dielectric constant (ε) reduced as wavelength increased at a constant Zn concentration and it explains why there are high optical conductivity losses at longer wavelengths. The absorption coefficient (α) was calculated using the equation:

\[ \alpha = 2.303A/d \]  \hspace{1cm} (3.9)

where α is the absorbance coefficient value at a particular wavelength(λ) and d is the thickness of the semiconductor film. Extinction coefficient on the other hand was calculated using the relation:

\[ k = \alpha\lambda/4\pi \]  \hspace{1cm} (3.10)

Both coefficients were very small over a wide range of wavelengths and as such very low photon energy absorption losses are experienced. They form high quality window layer materials (Kumar and Sankaranayanan, 2009), Kasim et al. (2008), Salia, (2009), Vidhya and Velumeni, (2009) with transmittances of 90%, 80%, 79% and 65% respectively in the wavelength range of 300 – 1200 nm.

\textbf{Cd1-xZnxS / PbS Solar cell}

A layer of Cd1-xZnxS was chosen as the window layer with the largest band gap of 2.72 eV, highest transmittance of above 79%, lowest refractive index, lowest optical absorption, extinction coefficient. PbS with lowest refractive index, lowest transmittance of below 55%, and high absorption and extinction coefficients as an absorber layer. Silver paste was used as the ohmic contact. Solar cell’s I-V characteristics were measured using a solar simulator (table 2). Figure 3 illustrates current/or and power variation with voltage. Table 2 display experimental I-V characteristics of the solar cell while other cell parameters are presented in table 3.

The solar cell had a short circuit current, Isc = 0.031 A, open voltage, Voc = 0.37V, a fill factor, ff = 0.66 or 66 % and an efficiency, η = 0.9 as shown in Table 3. The cell produced a higher current than what was reported by Harumi et al. (1995) with a Voc of 0.45V and Isc of 0.001mA/cm². Fill factor is a measure of the quality of a cell and therefore a large fill factor of 1 is desirable and it corresponds to I-V sweep that is more square-like where typical fill factors ranges from 0.50 to 0.82 (50 % - 82%). Considering the square-like nature of the I-V curve and a fill factor of 0.66, it was concluded that the cell formed a good p-n junction for solar cells.

\textbf{CONCLUSIONS}

Cd1-xZnxS and PbS thin films were successfully prepared on glass substrates using CBD technique under different preparation conditions. Optimum conditions gave Cd1-xZnxS and PbS solar cell that gave a short circuit current, Isc = 0.031 A, open voltage, Voc = 0.37 V, a fill factor, ff = 0.66 or 66 % and an efficiency, η = 0.9. The solar cell had a fill factor above 0.5 (i.e. ff = 0.66) support a good p-n junction for solar applications.

\textbf{ACKNOWLEDGMENTS}

We acknowledge the Department of Physics, Kenyatta University where this study was carried out and the Department of Material Science University of Nairobi, [Chiromo Campus] for kindly providing the UV-VIS-NIR spectrophotometer 3700 and the Solar Simulator for analysis.

\textbf{REFERENCES}