Chapter 2

CuInS$_2$/In$_2$S$_3$ solar cell in superstrate configuration using microporous TiO$_2$ thin films as electron conducting layer

2.1 Introduction

In superstrate configuration, the entire solar cell structure is deposited over a transparent conducting oxide (TCO) coated glass substrate and illumination is given from substrate side. Here glass substrate functions not only as a supporting structure but also as a window for illumination. ‘Glass/TCO/buffer layer/absorber layer/metal’ configuration is followed for these types of solar cells. Generally a micro or nanoporous electron conducting layer is deposited over TCO layer prior to the buffer layer deposition. Due to infiltration of both absorber and buffer layer over these structures, effective path length of light in the absorber material increases as multiple scattering occurs in the internal interfaces. Hence the absorber layer thickness can be reduced to a few nanometers and still it is capable of maintaining excellent light trapping capacity. Extension of interface increases for these configurations, which can promote effective charge carrier separation [1, 2]. For CuInS$_2$ absorber layer, TiO$_2$ or ZnO are the generally used micro/nanoporous electron conducting layer [3, 2]. Due to large interfacial junction area between the micro or nanoporous electron conducting layer and the absorber layer; probability of recombination of light generated carriers is very high. The role of buffer layer such as In$_2$S$_3$ or CdS is to suppress this recombination. Here the light generated electrons are transferred to the conduction band of large band gap buffer layer before recombination in the
absorber. From buffer layer electrons are injected to the conduction band of TiO₂ or ZnO [4].

2.2 CuInS₂ in superstrate configuration:

A brief review

CuInS₂ was already utilized as an excellent absorber layer in superstrate configuration [1-4]. Direct band gap of 1.5 eV and high absorption coefficient \((10^5 \text{ cm}^{-1})\) are the exceptional qualities that attribute paramount importance for this absorber material. Using a suitable micro or nanoporous electron conducting layer, CuInS₂ becomes ideal candidate for ‘Extremely Thin Absorber (ETA)’ layer solar cells in superstrate configuration [1-4].

Lensmann et al. reported the fabrication of TiO₂/Al₂O₃/In₂S₃/CuInS₂ solar cell having efficiency of 2.9 % [5]. Here nanostructured TiO₂ films were deposited by combining spray and ‘doctor-blade’ techniques. Al₂O₃ layer (as recombination barrier), In₂S₃ buffer layer and CuInS₂ absorber layer were deposited using atomic layer deposition (ALD). Results shows that Al₂O₃ recombination barrier and In₂S₃ buffer layer play crucial role in the better performance of TiO₂/CuInS₂ interface.

Nanu et al. also reported the fabrication of TiO₂/Al₂O₃/In₂S₃/CuInS₂ 3D solar cell having better performance with 4 % efficiency [3]. In this case, TiO₂ was prepared with the help of spray pyrolysis; but all other layers were prepared through atomic layer chemical vapor deposition (ALCVD). They observed that during deposition process, the stoichiometry of TiO₂ and CuInS₂ are modified and the stoichiometry is retained by thermal annealing in sulfur and oxygen.

CSP was employed by Goossens et al. to incorporate CuInS₂ nanocrystals into the matrix of In₂S₃/TiO₂. The device showed efficiency of about 5 % [6]. Ryan O’Hayre et al. reported fabrication of TiO₂/In₂S₃/CuInS₂
solar cells with efficiency of 2.8 % [7]. Here TiO$_2$ layer was deposited by employing spray and ‘doctor-blade’ technique. Both absorber and buffer layers were deposited using CSP. They suggested that by optimizing electron transport and reducing recombination in TiO$_2$, device performance can be improved.

Goossens et al. reported fabrication of 7 % efficient solar cells by following TiO$_2$/In$_2$S$_3$/CuInS$_2$ cell structure [8]. All the component layers were deposited employing spray pyrolysis. Transient absorption spectroscopy was used to study the deep electronic states in CuInS$_2$ and concluded that these states act as electron traps rather than as recombination centers. Temporal storage of charge in these traps reduces the $V_{oc}$ of the device.

Krunks et al. reported fabrication of ITO/ZnO/InS/In$_2$S$_3$/CuInS$_2$ solar cells using CSP and the device shows an efficiency of 2.5 % [2]. Solar cells were also fabricated with ZnO layer without nanostructure and the cell parameters are low. Improvement in current density for structured solar cell is mainly due to the increase in p-n junction area.

Ryo et al. employed CSP for fabricating superstrate type CuInS$_2$ solar cells by following the structure FTO/TiO$_2$/In$_2$S$_3$/CuInS$_2$ [9]. Role of spray rate in the quality of CuInS$_2$ absorber layer was also studied and they observed that films deposited at high spray rate contain large quantity of carbon and oxygen. Presence of these two deteriorates the PV responses of the device. The best device fabricated under this study showed an efficiency of 1.7 %.
2.3 Device structure selected for the present study

![Device structure](image)

(a) Schematic diagram of the fabricated device (b) Top view of the device.

Figure 2.1(a) Schematic diagram of the fabricated device (b) Top view of the device.

A schematic diagram of the fabricated device for the present study is shown in Figure 2.1(a). TCO coated glass plate was used as the substrate. Two types of TCOs were used. Tin doped indium oxide (ITO) (sheet resistance ~ 12 Ω/□; Geomatec, Japan; prepared through sputtering) was used for the initial studies. As this material is costly, fluorine doped tin oxide (FTO) was (prepared through CSP technique in our lab) used as TCO in the cell structure. Over the TCO layer microporous electron conducting layer was spray deposited using commercially available TiO₂ powder (Degussa p25). Spraying helped the In₂S₃ buffer layer and CuInS₂ absorber layer to infiltrate into the micropores of TiO₂. Regarding the absorber layer, CuInS₂ is a best choice because of its direct band gap of 1.5 eV and high absorption coefficient of 10⁵ cm⁻¹ [10, 11]. In₂S₃ buffer layer has a critical role in the performance of the device. Large number of electronic interface states exists at TiO₂/CuInS₂ junction, which lies in the band gap of CuInS₂ and promotes the back flow of electrons [8]. A buffer layer between CuInS₂ and TiO₂ can be used to avoid this process. CdS
and In$_2$S$_3$ are good choices for buffer layers with CuInS$_2$ [12, 3]. Due to the toxicity of CdS, In$_2$S$_3$ was preferred for the present study. Moreover, the conduction bands of In$_2$S$_3$ and CuInS$_2$ have approximately same energy and hence electrons can cross the interface of CuInS$_2$ and In$_2$S$_3$ without energy loss [3]. Finally, for top contact, silver was vacuum evaporated over the cell structure. Here silver was deposited as an array of 9 electrodes each having area of 0.03 cm$^2$ and thickness of 50 nm (Figure 2.1(b)), taking care to isolate each electrode using edge of doctor-blade. Dark and illuminated J-V characteristics of the heterojunctions were recorded employing Source Measure Unit (SMU; NI PXI-1033). For illumination purpose ‘Class AAA’ solar simulator (PET, model SS50AAA) was used.

2.4 Deposition of CuInS$_2$ absorber layer by optimising the spray rate

For spray deposition of CuInS$_2$, Cu/In ratio (in the precursor solution) and substrate temperature are the critical parameters that can affect structural, electrical, morphological and optical properties of the deposited films [13, 14]. For the present study, CuInS$_2$ thin films were deposited using precursor solution containing CuCl$_2$, InCl$_3$ and thiourea [CS(NH$_2$)$_2$]. Sebastian et al. observed that as Cu/In ratio increases the crystallinity of the sample improves [15]. They varied Cu/In ratio as 0.5, 1, 1.5 keeping S/Cu ratio as 5. Cu rich samples (Cu/In = 1.5) showed better crystallinity with enhanced electrical transport properties of the absorber layer. Band gap of ~ 1.35 eV for these sample is ideal for PV conversion. For precursor solution with Cu/In ratio 1.5, there is a chance of precipitation of the solution when it is kept for some time (above 45 minutes). Hence as a safer limit, Cu/In ratio was fixed as 1.4 and S/In as 5 for the deposition of CuInS$_2$ absorber layer in the present study. The variations in structural, electrical and optical properties of CuInS$_2$ thin films
Chapter 2

with substrate temperature was also studied by Sebastian et al. [15]. Substrate temperature was varied as 300 °C, 350 °C and 400 °C. It was observed that as substrate temperature increases crystallinity improves; but at higher temperature, thickness of the samples decreases drastically due to re-evaporation of the precursor solution. As deposition rate was very low, at higher temperature, it takes long time to deposit a particular thickness of the absorber. Hence for the present study, intermediate substrate temperature of 350 °C was selected for CuInS$_2$ deposition. At 350 °C, samples possess good crystallinity and band gap of ~ 1.4 eV, favorable for a good quality absorber layer.

For CuInS$_2$ deposition, Cu/In ratio was fixed at 1.4 and substrate temperature was maintained at 350 °C. It was observed that spray rate can also play a crucial role in the deposition of CuInS$_2$. In spray pyrolysis, spray rate is generally measured as the milli liters of precursor solution sprayed on the substrate in a minute (ml/min). In order to analyse effect of spray rate on CuInS$_2$ films, it was varied as 2 ml/min, 4 ml/min, 6 ml/min and 8 ml/min; correspondingly the samples were named as S-2, S-4, S-6 and S-8 respectively. Ultrasonically cleaned soda lime glass plates were used as the substrates. Spray volume of precursors for all samples was fixed as 80 ml. Thickness of the samples were measured using stylus depth profiler (Dektak 6M). Here diamond tipped stylus is mechanically coupled to the core of a linear variable differential transformer (LVDT). As stylus rides over the sample surface, core position of LVDT changes and electrical signals are produced which is converted to digital format. Thicknesses of S-2, S-4, S-6 and S-8 samples were 254±16 nm, 320±17 nm, 365±20 nm and 432±23 nm respectively.
2.4.1 Structural analysis

X-ray diffraction (XRD) technique was used for the structural analysis of CuInS$_2$ samples deposited at different spray rates. XRD analysis was done using Rigaku (D. Max. C) X-ray diffractometer, employing CuK$_\alpha$ line and Ni filter, operated at 30 kV and 20 mA. When the incident X-ray beam on the samples satisfies the Bragg’s condition ($n\lambda = 2d\sin\theta$, where $n$ is the order of the spectrum, $\lambda$ is the wave length of X-ray, $\theta$ is the Bragg angle and $d$ is the inter planar spacing), it gets diffracted to the detector and an XRD pattern is recorded. Figure 2.2 depicts the XRD patterns of CuInS$_2$ samples deposited with different spray rates. In order to get information about different crystallographic phases and preferred orientations, the data is compared with Joint Council Powder Diffraction (JCPDS) data for standards.

![XRD patterns](image)

Figure. 2.2 XRD patterns of CuInS$_2$ samples prepared at different spray rates.

All samples show preferential orientation along (112) plane which is the characteristic peak of tetragonal CuInS$_2$ (JCPDS data card 270159) [11]. Intensity of XRD peaks increases as the spray rate increases. This is mainly because of the increase in thickness of the deposited samples as spray rate...
increases. At lower spray rate, quantity of the solution hitting the substrate in a minute is very small and hence the deviation in substrate temperature from the preset value is negligible. As a result, re-evaporation is predominant leading to low thickness. But at higher spray rate, the deviation in substrate temperature is significant and possibility of re-evaporation is low. Deposition rate is high at higher spray rate and the samples are thicker when compared to those prepared at lower spray rate for the same volume of the precursor solution.

2.4.2 Optical studies

Optical absorption spectra of the CuInS$_2$ samples with different spray rates were recorded using UV-VIS-NIR spectrophotometer (JASCO, V-570 model). Absorption coefficient ($\alpha$) is related to the energy gap ($E_g$) according to the equation

$$\alpha hv = A (hv - E_g)^n$$

where $A$ is a constant, $h$ the Plank’s constant, $v$ the frequency of incident beam and $n$ is equal to $\frac{1}{2}$ for direct allowed band gap [15]. $E_g$ can be obtained from the graph of $(\alpha hv)^2$ versus $hv$ which is illustrated in Figure 2.3. It was observed that there is not much change in the band gap ($E_g$) of the material with spray rate and it was around 1.4 eV. Due to high thickness of S-8 sample, it exhibits higher slope at absorption edge. Similar trend was observed for S-6 sample also.
Figure 2.3 $(ahv)^2$ vs $hv$ graph of CuInS$_2$ samples prepared at different spray rates.

2.4.3 Electrical studies

Electrical studies were conducted at room temperature using Hall measurement system (HMS 5300, Ecopia). Hall effect measurements in semiconductor materials give valuable information about its resistivity, carrier concentration, conductivity type and mobility of carriers. When magnetic field is applied to a semiconductor perpendicular to the current flow direction, an electric field is developed perpendicular to the direction of magnetic field and current. This phenomenon is known as Hall effect and the developed voltage perpendicular to the current flow in the sample is known as Hall voltage ($V_H$). $V_H$ is proportional to carrier mobility in the sample and its sign depends on the type of the (majority) charge carrier (electrons or holes) in the sample. From the measured Hall voltage, the carrier concentration ($n$) of the semiconductor can be determined. In combination with conductivity ($\sigma$) measurement, the Hall mobility ($\mu_H$) of the sample can be calculated using the equation $\mu_H = \frac{\sigma}{qen}$, where $q$ is the charge of the carrier. The results of Hall measurements performed on the samples were tabulated in Table 1. Bulk concentration of
majority carrier is not much affected by the variations in spray rate. But as spray rate decreases resistivity of the samples increases and this may be due to the evaporation of volatile sulfur at low spray rates. This is expected because at lower spray rate substrate temperature deviation is negligible and the higher temperature allows escaping of sulfur from the sample. The sulfur vacancies create donor levels, which reduces the p-type conductivity [8, 16]. Variations in mobility values for the samples are not in order and the reason for this is not clearly understood. All samples shows p-type conductivity.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Bulk concentration (cm$^{-3}$)</th>
<th>Resistivity (Ω.cm)</th>
<th>Mobility (cm$^2$/VS)</th>
<th>Conductivity type</th>
</tr>
</thead>
<tbody>
<tr>
<td>S-2</td>
<td>$3.29 \times 10^{19}$</td>
<td>10.68</td>
<td>$1.7 \times 10^{-2}$</td>
<td>p-type</td>
</tr>
<tr>
<td>S-4</td>
<td>$1.87 \times 10^{19}$</td>
<td>2.49</td>
<td>$1.34 \times 10^{-1}$</td>
<td>p-type</td>
</tr>
<tr>
<td>S-6</td>
<td>$8.59 \times 10^{19}$</td>
<td>4.84</td>
<td>$1.5 \times 10^{-2}$</td>
<td>p-type</td>
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<tr>
<td>S-8</td>
<td>$6.45 \times 10^{19}$</td>
<td>0.27</td>
<td>$3.5 \times 10^{-1}$</td>
<td>p-type</td>
</tr>
</tbody>
</table>

Table 2.1 Electrical studies on CuInS$_2$ samples deposited at different spray rates.

2.4.4 Atomic force microscopy (AFM) studies

For gathering a clear picture of the surface of CuInS$_2$ samples prepared at different spray rates, AFM studies were performed. A sharp tip having a diameter of less than 100 Å, fixed to a cantilever beam, scans the selected area of the sample surface. Due to the presence of inter atomic force between sample surface and the probe tip, the cantilever deflects with respect to the nature of the surface. This deflection is measured by the reflection of a laser beam from the back of the cantilever. These data are processed by computer to generate map of the topography. For the present study ‘Nanosurf easyScan 2’ AFM system was used. AFM studies revealed significant variations in surface
morphology of the samples deposited at different spray rates. Figure 2.4 shows AFM analysis of CuInS$_2$ samples prepared at different spray rates [10].

![AFM images of CuInS$_2$ samples](image)

Figure 2.4 AFM analysis of CuInS$_2$ samples deposited at different spray rates.

From AFM studies, it was observed that the root mean square (RMS) value of surface roughness of CuInS$_2$ samples increases drastically as spray rate increases. RMS surface roughness of samples sprayed at 2 ml/min was 11 nm and it increases to 61 nm for samples sprayed at 8 ml/min. Moreover, it is like a large ‘hillock’ and this will be present in the window layer deposited over the absorber, which is not good for the cell. For device fabrication rougher CuInS$_2$ sprayed at higher spray rate is not preferred because the probability of shorting of the device increases [10]. Moreover, at higher spray rate, time is not enough for the reaction between thiourea in the solution and oxygen in the
atmosphere to liberate gases such as NO, CO₂, SO₂ or H₂O. It was already reported that the existence of carbon and oxygen in the films will reduce the photovoltaic properties of the solar cell [9]. Hence the samples prepared at lower spray rate are expected to be good for device fabrication. However, in this case, the deposition rate is too low so that too much time is consuming for depositing a particular thickness of the absorber. Hence an intermediate spray rate of 4 ml/min having average surface roughness of 40 nm and reasonably good deposition rate was selected for device fabrication. Thus from these studies, we could conclude that optimum values for spray parameters such as Cu/In ratio, substrate temperature and spray rate were 1.4, 350 °C and 4 ml/min respectively for a good quality CuInS₂ absorber layer.

2.5 Deposition of In₂S₃ buffer layer

Spray deposition technique can be effectively used for the deposition of In₂S₃ buffer layer for solar cell applications [8, 10, 11]. In₂S₃ is an excellent alternative to toxic CdS buffer layer and is capable of improving the spectral response in blue wave length region. Moreover, spray deposited In₂S₃ is well-studied buffer material in our lab [10, 11, 15, 17]. For the present study In₂S₃ is prepared using InCl₃ and thiourea [CS(NH₂)₂] precursors. In/S ratio was fixed as 1.2/12. The spray rate and substrate temperature were 4 ml/min and 350 °C respectively [10, 17].

2.5.1 Structural analysis

XRD analysis shows that In₂S₃ film [Figure 2.5] has preferential orientation along (220) plane which is the characteristics of tetragonal β-In₂S₃ thin films [15]. CuInS₂ is also tetragonal crystal structure; hence the lattice mismatch during junction fabrication is not a big problem here.
2.5.2 Optical studies

By plotting $(hν)$ vs $(ahν)^2$ graphs, band gap $(E_g)$ of In$_2$S$_3$ films were calculated (Figure 2.6). Band gap was around 2.6 eV for In$_2$S$_3$ samples.
2.6 Deposition of microporous TiO$_2$ electron conducting layer

For spray pyrolysis, most works deal with organo-metallic Ti compound precursors such as Ti tetra-ethoxide, Ti iso-propoxide, Ti acetyl acetonate and Ti isobutoxide [18]. Besides organometallic Ti compound precursors, peroxy-polytitanic acid prepared from Ti-metal powder was also used as precursor for spray deposition [19, 20]. In our case, commercially available TiO$_2$ powder Degussa P25 (DP25, supplied by Evonik industries, Japan with TiO$_2$ weight percentage 99.5) having high chemical purity was used for TiO$_2$ film deposition. DP25 is a mixture of anatase and rutile crystallites and was generally used as a photo catalyst [21, 22]. Initially a precursor solution of 0.125 M peroxy-titanic acid was prepared by dissolving the powder in a solution of hydrogen peroxide (H$_2$O$_2$) and ammonium hydroxide (NH$_4$OH) taken in the ratio 8:2. The precursor solution was then diluted to 0.025 M using distilled water and sprayed on ultrasonically cleaned soda lime glass substrate. The spray rate was maintained at 6 ml/min and substrate temperature was varied from 300 °C to 500 °C in steps of 50 °C. Samples prepared at 300 °C, 350 °C, 400 °C, 450 °C and 500 °C were named as Ti-300, Ti-350, Ti-400, Ti-450 and Ti-500 respectively [17].

2.6.1 SEM and EDAX analysis

Changes on film surfaces with deposition temperature were studied using scanning electron microscopy (SEM). SU6600 variable pressure field emission scanning electron microscope (FESEM) (Hitachi, Japan) was used for SEM analysis. At lower temperature it was observed that the adhesion of TiO$_2$ over the substrate was very poor and hence the films were non-uniform. From 300 °C onwards the films had adhesion and were continuous. Samples deposited at 300 °C composed of non-uniformly arranged aggregates (Figure
2.7(a)). As temperature was increased to 350 °C, the aggregates arranged themselves into open porous structures [size in the range 2-6 microns] as can be seen in the Figure 2.7(b). SEM analysis of samples prepared at higher substrate temperatures 400 °C, 450 °C and 500 °C (Figure 2.7(c) -2.7(e)) were not microporous in nature; instead these samples had good adhesion and homogeneity over the substrate [17].

Figure. 2.7 SEM pictures of TiO₂ samples; Ti-350 [microporous].
As substrate temperature increases evaporation rate of constituents in the precursor solution also increases. Hence the composition of the deposited films has strong dependence on substrate temperature [23]. EDAX measurements showed that atomic concentration of Ti decreases on increasing the substrate temperature. As a result, thickness of the films decreased drastically. Ti-300, Ti-350, Ti-400, Ti-450 and Ti-500 samples had thicknesses of around 510 nm, 500 nm, 480 nm, 450 nm and 380 nm respectively. Above 500 °C the film surface seems to be discontinuous. Atomic concentrations of Ti and O with substrate temperature were depicted in Figure 2.8 [17].

![Graph](image)

Figure. 2.8 Atomic concentration of titanium and oxygen in TiO₂ films vs substrate temperature [obtained from EDAX analysis].

### 2.6.2 AFM analysis

AFM analysis indicates that RMS surface roughness of the samples decreases with increase in substrate temperature (Figure 2.9). For Ti-300 samples RMS roughness was 321 nm which decreases to 55 nm for Ti-500 samples. The highly inter connected microporous structure at 350 °C is also evident from 2D AFM images of Ti-350 samples (Figure 2.10). The open
microporous structure is unique to the samples prepared at substrate temperature 350 °C and hence the study reveals that porosity of the films strongly depends on substrate temperature [17].

Figure. 2.9 AFM analysis of TiO₂ samples deposited at different substrate temperatures.
SEM analysis clearly indicated the microporous nature of TiO$_2$ films at 350 °C and EDAX analysis shows that the films are nearly stoichiometric. Results of both SEM and EDAX indicate that Ti-350 samples can be good candidates for solar cell application. Moreover, In$_2$S$_3$ buffer layer and CuInS$_2$ absorber layer were also prepared at 350 °C. This is very important as far as device fabrication at industrial level is concerned since there is no need to change the substrate temperature for each layer fabrication [17]. Thus cell fabrication in this study was very fast and can be completed in one stretch process. For the remaining studies, only Ti-350 samples were selected. But it was almost amorphous in nature as revealed by XRD analysis. In order to improve crystallinity of the samples for device application, air annealing was carried out at 400 °C for 1 hour (Ti-1), 2 hour (Ti-2) and 3 hour (Ti-3). ‘Ti-p’ represents the sample before annealing. Even after annealing the films are microporous in nature with no significant changes in the pore size.

### 2.6.3 XRD analysis

XRD analyses of TiO$_2$ samples with and without annealing are shown in Figure 2.11. After annealing, samples exhibit strong XRD peaks along (101), (112), (200) and (105) planes. In all cases, preferential orientation is
along (101) plane, which is the characteristics of tetragonal anatase phase TiO₂ [24]. Also after 1 hour of annealing grain size of the sample is 30 nm. On increasing annealing time further by 1 hour, grain size improves to 40 nm. Thereafter, further improvement in grain size is not observed.

![XRD analysis of as-prepared and annealed TiO₂ samples.](image)

**Figure. 2.11 XRD analysis of as-prepared and annealed TiO₂ samples.**

### 2.6.4 Raman analysis

Raman spectroscopy can be used as an effective tool for structural characterization of semiconductors. Here samples are illuminated with a laser in the visible, near infrared, or near ultraviolet range. As the laser light interacts with atomic/molecular vibrations (phonons) or other excitations in the samples, energy of the laser photons is shifted up or down. This shift in energy of monochromatic light due to the inelastic scattering or Raman scattering in the sample gives information about the vibrational modes in the system. Here
Raman analyses of the prepared samples were recorded using Horiba Jobin Yvon Lab Ram HRsystem at spatial resolution of 2 mm in a ‘back scattering’ configuration. The 514.5 nm line of argon ion laser was used for excitation. Raman scattering spectrum of the as-prepared and annealed TiO₂ samples is shown in Figure 2.12. Before annealing, low frequency Eg mode at 144 cm⁻¹ only existed. This indicates the existence of anatase TiO₂ phase [2]. On annealing, intensity of Eg mode at 144 cm⁻¹ increased, indicating structural improvement. This result is in good agreement with XRD analysis. Besides Eg mode at 144 cm⁻¹, annealed samples clearly shows four other modes i.e., Eg mode at 196 cm⁻¹, B1g mode at 397 cm⁻¹, A1g mode at 518 cm⁻¹ and Eg mode at 638 cm⁻¹.

![Raman spectrum of TiO₂ samples](image)

Figure. 2.12 Raman analysis of as-prepared and annealed TiO₂ samples.
2.6.5 Optical studies

Optical response of the as-prepared and annealed samples were investigated by plotting \((\alpha h v)^2\) vs \(h v\) graphs (Figure 2.13). On annealing, there was not much variation in the band gap of the samples. It was always around 3.4 eV.

![Graph](image)

Figure. 2.13 \((\alpha h v)^2\) vs \(h v\) graph of as-prepared and annealed TiO\(_2\) sample.

2.6.6 AFM analysis

Figure 2.14 shows AFM analysis of the as-prepared and annealed samples. It was observed that the RMS value of roughness of as-prepared samples (261 nm) increases to 309 nm as annealing time increased by 1 hour. It was increased to 322 nm for Ti-2 samples, thereafter it starts decreasing to 268 nm for samples Ti-3. It was further observed that even after 3 hours of annealing at 400 °C, sample is microporous in nature. Therefore annealing of spray pyrolysed TiO\(_2\) samples for 1 hour and 2 hour results in increase of the crystallinity as well as surface roughness. TiO\(_2\) samples with higher surface roughness can provide higher surface area. These samples are good candidates as highly rough electron conducting layer for solar cell applications.
Figure. 2.14 AFM analysis of (a) as-prepared (b) Ti-1 (c) Ti-2 (d) Ti-3 samples.

2.6.7 XPS analysis

Ti-2 samples are finally selected for device fabrication. To analyse the chemical state and concentration of each element across the thickness of the sample, depth profile measurements were carried out using ‘X-ray Photoelectron Spectroscopy (XPS)’. For the present study, Shimadzu XPS unit (model: AMICUS) was used for XPS analysis. 10 cycle of argon ion etching was carried out in these films. Figure 2.15 represents binding energy vs intensity spectra for Ti 2p and O 1s states in the samples after etching (50 seconds). Presence of Ti 2p3/2 peak at 460.46 eV indicates the presence of Ti$^{4+}$ oxidation states. Binding energy peak at 466.44 eV indicates Ti 2p½ peak. The doublet separation between the 2p3/2 peak and Ti 2p½ was 5.92 eV which is in good agreement with reported value of 5.7 eV for anatase phase TiO$_2$ thin films deposited using MOCVD [25]. The O1s binding energy is at 532.15 eV and this indicates bonding of oxygen to tetravalent Ti ions [26, 17].
Figure 2.15 XPS analysis of Ti 2p and O1s states in Ti-2 film.

Atomic concentration of titanium and oxygen across the thickness of Ti-2 sample were recorded using XPS depth profile analysis is shown in Figure 2.16. The sample maintains almost same stoichiometry across the thickness. Atomic concentration of titanium is ~ 75 % and that of oxygen is ~ 25 %. This was also supporting the chemical nature of TiO₂ films prepared were good for device application.

Figure 2.16 Atomic concentration of titanium and oxygen across the thickness of Ti-2 sample.
2.7 Fabrication of FTO/TiO$_2$/In$_2$S$_3$/CuInS$_2$/Ag solar cells

Fluorine doped tin oxide (FTO) deposited on glass substrate (sheet resistance ~ 20 $\Omega/\square$) employing CSP is used for back contact. Microporous TiO$_2$ electron conducting layer, In$_2$S$_3$ buffer layer and CuInS$_2$ absorber layer as optimized in previous sections were spray deposited in a sequence over FTO layer to realise an ‘all sprayed’ solar cell. Finally for top contact silver was deposited (area = 0.03 cm$^2$) over the entire solar cell structure (see Figure 2.1(b)) using vacuum evaporation. In order to explore the effect of microporous structure on the cell performance, solar cells were fabricated using both the microporous (Ti-2) and flat structured (Ti-400 samples annealed for 2 hour at 400 °C) TiO$_2$ thin films and they were named as S-350 and S-400. In both cases thickness of CuInS$_2$ absorber layer and In$_2$S$_3$ buffer layer were kept constant. Thicknesses of FTO, TiO$_2$, CuInS$_2$, In$_2$S$_3$, Ag layers were around 300 nm, 350 nm, 200 nm, 50 nm and 50 nm respectively for both configurations [17]. Schematic diagram of the fabricated device is shown in Figure 2.17.

![Figure 2.17 Schematic diagram of the fabricated device.](image-url)
S-400 cells showed an open circuit voltage ($V_{oc}$) of 350 mV and short circuit current density ($J_{sc}$) of 3.22 mA/cm$^2$. Efficiency ($\eta$) and fill factor (FF) were 0.35 % and 31 %. On the other hand, S-350 cells exhibited an improvement in device parameters with $V_{oc} = 409$ mV, $J_{sc} = 3.90$ mA/cm$^2$, $\eta = 0.61$ % and FF = 38 % (Figure 2.18). In this case, thin absorber layer was sprayed over microporous structured TiO$_2$ thin films having enhanced surface area compared to flat structured samples. Hence this configuration exhibits better light absorption due to multiple scattering in the absorber [1, 17].

![J-V characteristics](image)

Figure. 2.18 J-V characteristics of solar cells fabricated using structured and flat TiO$_2$ films.

Performance parameter of the devices can also be explained on the basis of its parasitic resistances [series ($R_s$) and shunt ($R_{sh}$)]. $R_s$ and $R_{sh}$ were calculated from the slope of the illuminated J-V characteristics at V = 0 (for $R_s$) and J = 0 (for $R_{sh}$) [27]. While comparing the performance parameters
(shown in Table 2.2) of two cells on the basis of $R_s$ and $R_{sh}$, better one should have a low value for $R_s$ and a high value for $R_{sh}$. For S-400 cells $R_{sh}$ was 141 $\Omega$.cm$^2$ and it increased to 196 $\Omega$.cm$^2$ for S-350. This increase in $R_{sh}$ may be responsible for effective charge carrier separation there by reducing alternate path for light generated carriers [28]. As a consequence of this process, $V_{oc}$ for S-350 was 409 mV which is better value compared to that of 350 mV for S-400 cells. The series resistance value for S-350 was 45 $\Omega$.cm$^2$ and that of S-400 was 72 $\Omega$.cm$^2$. The increase in the value of $J_{sc}$ for S-350 cells can be attributed to the decrease in series resistance. Since $V_{oc}$ and $J_{sc}$ enhances for S-350 cells, its efficiency and fill factor also improves [17].

<table>
<thead>
<tr>
<th>Cell name</th>
<th>$V_{oc}$ (mV)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>FF (%)</th>
<th>$\eta$ (%)</th>
<th>$R_s$ (\Omega.cm$^2$)</th>
<th>$R_{sh}$ (\Omega.cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S-400 (Flat)</td>
<td>350</td>
<td>3.22</td>
<td>31</td>
<td>0.35</td>
<td>75</td>
<td>141</td>
</tr>
<tr>
<td>S-350 (Microporous)</td>
<td>409</td>
<td>3.90</td>
<td>38</td>
<td>0.61</td>
<td>45</td>
<td>196</td>
</tr>
</tbody>
</table>

Table 2.2 Photovoltaic parameters of S-400 and S-350 cells.

2.8 Fabrication of ITO/TiO$_2$/In$_2$S$_3$/CuInS$_2$/Ag solar cells

Solar cells were also fabricated by replacing FTO back contact in S-350 cells with tin doped indium oxide (ITO) contacts (sheet resistance $\sim$ 12 $\Omega$/\square; Geomatec, Japan) prepared through sputtering. Here also the procedure for fabrication was the same. It has $V_{oc}$ of 428 mV and $J_{sc}$ of 7.97 mA/cm$^2$. The fill factor and efficiency were 34 % and 1.17 % respectively. The device exhibits better PV parameters when comparing with devices having FTO back contacts because of the lower sheet resistance of ITO films. Dark and illuminated J-V characteristics of the device are shown in Figure 2.19.
Figure. 2.19 J-V characteristics of ITO/TiO$_2$/In$_2$S$_3$/CuInS$_2$/Ag solar cell.
For top contact, silver was vacuum evaporated over the cell structure as an array of 9 electrodes each having an area of 0.03 cm$^2$, taking care to isolate each electrode using edge of doctor-blade.

2.9 Conclusions

Sprayed CuInS$_2$/In$_2$S$_3$ solar cell in superstrate configuration fabricated using spray deposited microporous TiO$_2$ as ‘electron conducting layer’. Effect of spray rate on CuInS$_2$ absorber layer was investigated and spray rate of 4 ml/min was chosen for solar cell fabrication. For TiO$_2$ deposition, commercially available TiO$_2$ powder (Degussa p25) was used. Microporous nature of TiO$_2$ films was observed for a substrate temperature of 350 °C and to improve the crystallinity of this films air annealing was carried out at temperature of 400 °C. The device structure followed was FTO/TiO$_2$/In$_2$S$_3$/CuInS$_2$/Ag. Here FTO is also deposited employing spray pyrolysis to realize an ‘all sprayed solar cells’ and the device shows an efficiency of 0.61 %. Solar cells are also fabricated by replacing FTO by ITO back contact and an efficiency of 1.17 % was obtained for this configuration.
Chapter 2

The performance of CuInS$_2$/In$_2$S$_3$ cells in superstrate configuration was not up to our expectation. Highly resistive nature of as deposited TiO$_2$ thin films may be the problem with this configuration. Possibilities are there to decrease the resistivity of this layer either by the further modifications in spray parameters or by doping. Since all these processes make the cell fabrication process more complex, hereafter we are restricting our studies on superstrate configurations up to this much.
References


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