SnS quantum dot solar cell is fabricated by Successive Ionic Layer Adsorption and Reaction (SILAR) method. SnS layer is optimized by different SILAR cycles of deposition. The particle size increased with the increase in number of SILAR cycles. Cu₂S coated FTO is used as counter electrode against the conventional Platinum electrode. On comparison with a cell having a counter electrode–electrolyte combination of Platinum–Iodine, Cu₂S–polysulfide combination is found to improve both the short circuit current and fill factor of the solar cell. A maximum efficiency of 0.54% is obtained with an open circuit voltage of 311 mV and short circuit current density of 4.86 mA/cm².

1. Introduction

Quantum dot solar cell (QDSSC) is a type of third generation solar cells which is promising in terms of cost-effectiveness as well as ease of fabrication. CdS, CdSe, CdTe and PbS solar cells have attracted much attention because of their optical properties. Since these materials are toxic and scarce it is necessary to develop environment friendly and earth-abundant materials for the fabrication of solar cells. SnS is an appropriate candidate which has outstanding properties such as high absorption coefficient [1]. Despite the excellent properties, SnS quantum dot solar cells are less exploited [2–5]. The sensitization of SnS quantum dots can easily be achieved by Successive Ionic Layer Adsorption and Reaction (SILAR) method which is a cost-effective and easy method for the deposition of thin films. SILAR is a convenient and successful method for the sensitization of semiconductor quantum dots for the fabrication of QDSSC [6–9]. In this method, it is possible to control the size and volume of the particles deposited. The particle size increases along with thickness upon increasing the SILAR cycle.

The conversion efficiency of the solar cell also depends on the selection of the counter electrode. The most widely used counter electrode is Platinum (Pt) which is a good catalyst. However, it is observed that the performance of Pt is not satisfactory when employed with sulfur based redox couple. S²⁻ ions adsorb onto the surface of Pt thereby decreasing the catalytic activity and the electrical conduction at the counter electrode [10]. Recently, Sixto et al. made a comparison between different counter electrodes in the polysulfide electrolyte and Cu₂S showed higher efficiency [11]. In the present work, SnS quantum dot solar cell is fabricated with a new combination of Cu₂S counter electrode.

2. Experimental details

A double layer porous TiO₂ thin film is prepared on top of Fluorine doped Tin Oxide (FTO) coated glass plate of sheet resistance 10 Ω/□ by doctor-blading. 20 nm sized TiO₂ powder (Degusssa P-25) is used as the buffer layer on FTO which is annealed at 450 °C for 30 min. On top of that 200 nm TiO₂ particle is coated and this double layer is annealed at 250 °C for 30 min. The layer is sensitized with SnS quantum dots by SILAR method. SnCl₂ and Na₂S are used as precursors and TiO₂ is dipped in each solution for 5 min followed by rinsing in distilled water to remove...
unadsorbed particles. The duration of each SILAR cycle is 10 min. The samples are named as SnS1, SnS2, SnS3, SnS4, SnS5 and SnS6 according to the number of SILAR cycles. For solar cell fabrication, FTO is used as the bottom electrode and Cu2S coated FTO as counter electrode. Cu2S is prepared by chemical bath deposition of CuCl2 and thiourea at 60 °C. Triethanolamine is used as the complexing agent and NH4OH as the pH adjuster. Solution containing 1 M Na2S and 0.1 M S is used as electrolyte. Another electrolyte consists of 0.5 M LiI and 0.05 M I2 in acetonitrile is also used in the study. The fabricated solar cell is characterized using a solar simulator (Newport-Oriel Sol3A Class-AAA) under AM1.5 condition. X-ray diffraction studies are performed using a Bruker D8 operated at 40 kV and 40 mA. Cu Kα line having a wavelength of 1.5405 Å is used as the radiation source and the diffraction pattern is recorded from 15° to 80° in θ–2θ configuration. TEM images are taken using a Tecnai F30 with an acceleration voltage of 200 kV. Samples are prepared by suspending the TiO2/SnS layer in ethanol and putting a drop of this solution on a Copper grid coated with carbon support film. Absorption spectra are recorded from 300 to 1000 nm using a UV–vis spectrophotometer (Specord S600UV–vis). Surface and cross-sectional SEM are taken using an FEI ESEM quanta-200.

3. Results and discussions

X-ray diffraction patterns of TiO2 and TiO2/SnS structure are shown in Fig. 1. Diffraction peaks corresponding to TiO2 and SnS are identified. Peaks at 26.4°, 27.4°, 30.55°, 31.81°, 39.12°, 44.23° and 45.49° correspond to (120), (021), (101), (111), (131), (141), and (002) planes of orthorhombic structured SnS (JCPDS 75-0925). TiO2 showed a mixture of anatase and rutile phases (JCPDS references 01-071-1167 and 00-021-1276). The peaks at 25.2°, 36.9°, 48.19°, 53.8°, 55.02° and 75.01° correspond to (101), (004), (200), (105), (211) and (215) planes of anatase TiO2 (JCPDS-021-1276). The peaks at 27.44°, 62.7°, 68.99° and 69.78° are due to (110), (002), (301) and (112) of rutile TiO2.

TEM images (Fig. 2) show the increase in the particle size with the increase in SILAR cycles. Analysis is carried out on SnS quantum dots incorporated into the porous TiO2 matrix. Images of the SnS particles deposited in 2, 4 and 6 cycles of SILAR are taken. 20 nm size particles are

![Fig. 1. XRD patterns of TiO2 and TiO2/SnS layer.](image1)

![Fig. 2. TEM images of (a) TiO2/SnS2, (b) TiO2/SnS4 and (c) TiO2/SnS6 layers.](image2)
Fig. 3. Absorption spectra of the TiO$_2$/SnS layer with different SILAR cycles.

Fig. 4. Surface and cross-sectional SEM of TiO$_2$ and TiO$_2$/SnS layer.
observed in all the images which are identified as TiO$_2$.

The smaller size particles are identified as SnS. The size of the particle deposited with two SILAR cycles (SnS2) is in the range of 8.3–9.38 nm. The size of SnS4 is around 10.42–11.52 nm and that of SnS6 is around 11.18–12.98 nm. The size of SnS particle increases slowly with the increase in number of SILAR cycles. Bohr’s radius of SnS dot is calculated to be 7.24 nm using the equation

$$a_B = \frac{\varepsilon h^2}{\mu_0 e^2}$$

where $\varepsilon$ is the dielectric constant of SnS, $h$ is the reduced Plank’s constant, $\mu_0$ is the reduced mass of an exciton and $e$ is the charge of an electron [12]. The size of the SnS particle prepared in the present work is comparable to Bohr’s radius of SnS.

The band gap of the SnS/TiO$_2$ layer is determined using the UV–vis spectrophotometer. Absorption spectrum of TiO$_2$/SnS multilayer film with different SILAR cycles is shown in Fig. 3(a). The band gap is determined by extrapolating the linear part of the $(\alpha/\hbar v)^2$ vs $\hbar v$ graph to x-axis as shown in Fig. 3(b). The direct band gap of bulk SnS is 1.3 eV. Here the band gap ranges from 2.04 to 1.57 eV. The band gap decreased from 2.04 to 1.57 eV with the number of SILAR cycles. This phenomenon can be correlated with the size of SnS particle. With decrease in particle size, the absorption edge is shifted to higher energy which is known as ‘blue shift’. This is because of the quantum confinement which arose due to the small particle size of SnS.

Table 1

<table>
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<th>Sample details</th>
<th>$V_{oc}$ (mV)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>FF (%)</th>
<th>$\eta$ (%)</th>
<th>$R_s$ (Ω)</th>
<th>$R_{sh}$ (Ω)</th>
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<tr>
<td>SnS2</td>
<td>314</td>
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<td>44</td>
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<td>755</td>
</tr>
<tr>
<td>SnS4</td>
<td>311</td>
<td>4.86</td>
<td>36</td>
<td>0.54</td>
<td>735</td>
<td>2794</td>
</tr>
<tr>
<td>SnS6</td>
<td>300</td>
<td>5.05</td>
<td>34</td>
<td>0.52</td>
<td>755</td>
<td>2364</td>
</tr>
</tbody>
</table>

Fig. 4 shows the surface and cross-sectional morphology of TiO$_2$ and TiO$_2$/SnS layer. TiO$_2$ showed porous structure. From the cross-sectional SEM, the thickness of TiO$_2$ layer is measured as 12.81 μm. The surface morphology of TiO$_2$ film sensitized with SnS quantum dots is also shown in Fig. 4. After sensitization, the pores are reduced and surface looks denser. This layer has a thickness of 13.55 μm.

Solar cell was fabricated with different SILAR cycles of deposition of SnS quantum dots such as 2, 4 and 6 cycles. Cu$_2$S is used as the counter electrode and sulfur redox couple as electrolyte. Table 1 shows the cell parameters for different cycles of deposition and Fig. 5 shows the I–V characteristics of the cell with different cycles of SILAR. The cell parameters and efficiency are maximum for the film which had 4 SILAR cycles of deposition. SnS4 showed $J_{sc}$ of 4.86 mA/cm$^2$ and the conversion efficiency of 0.54%. Fill factor of the samples in general is poor around 36%. Increasing the number of cycles further, did not show significant increase in the efficiency. Even though $J_{sc}$ of SnS6 increased slightly to 5.05 mA/cm$^2$, $V_{oc}$ and fill factor for this cell decreased proportionally. It is assumed that the loading of the quantum dot is saturated after 4 cycles of SILAR. The decrease in $V_{oc}$ may be due to the decrease in the recombination resistance of electrons in the electrolyte [13]. For comparison, solar cell is also fabricated with Platinum counter electrode and Iodine based electrolyte. The cell showed an open circuit voltage ($V_{oc}$) of 470 mV and short circuit current ($J_{sc}$) of 0.273 mA/cm$^2$. The conversion efficiency of this cell is 0.03%. The Iodine based electrolyte produces higher $V_{oc}$ than Sulfur based [3]. The position of the Fermi level of the Iodine redox couple is lower than that of sulfur redox couple. This makes the difference in the Fermi levels of TiO$_2$ and Iodine electrolyte higher which reasons to the increase in $V_{oc}$ when Iodine electrolyte is employed.

4. Conclusions

SnS quantum dot solar cell is fabricated with different SILAR cycles. Cell with 4 cycles showed highest efficiency. The Cu$_2$S counter electrode improves the conversion efficiency compared to the Platinum electrode.

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References


