Hybrid solar cells using CdS thin films deposited via spray pyrolysis technique

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A B S T R A C T

The paper presents the photovoltaic performance of hybrid solar cells comprising of thin films of cadmium sulphide and poly(3-hexyl)thiophene. Cadmium sulphide thin films were deposited using spray pyrolysis technique. Current-voltage characterizations were performed for cadmium sulphide/poly(3-hexyl)thiophene heterojunctions in dark and under illumination (100 mWcm−2). The best device yields a short circuit current density of 1.54 mA/cm², an open circuit voltage of 343 mV, and a power conversion efficiency of 0.15%.

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1. Introduction

Solar energy is a clean, abundant renewable energy source. Solar energy can be converted into electricity using solar cells. Until recently, solar cell device technology was based on inorganic semiconductors such as silicon, germanium, and gallium arsenide. As a result of heavy investigations and investments, inorganic solar cells exhibited power conversion efficiencies up to 24% [1]. Although they have reached high efficiencies and are suitable for small markets, these technologies are too expensive to be implanted on a global scale. Therefore, researchers focus on finding alternative approaches as cheap alternatives of conventional inorganic solar cells. The most widely used material in inorganic solar cell technology is silicon (Si). However, silicon is not the ideal semiconducting material for solar energy conversion as it has an indirect band gap that results in an inefficient optical absorption. Despite the disadvantage of the optical absorption, it is still widely used in photovoltaic (PV) market because of its abundance which makes it an inexpensive semiconductor. However, it requires a minimum purity level in order to be useful for solar cell applications [2]. Despite the better performance of inorganic materials, fabrication of devices from these materials which involves elevated temperatures, numerous lithographic steps and discrete processing techniques make their application limited by the high costs [3]. Organic and hybrid solar cells were investigated as cheap alternatives of conventional inorganic solar cells. The organic, polymer based PV materials have introduced the potential of obtaining a cheap and easy method to produce energy from light [4]. The material properties of organic semiconducting materials (conjugated polymers) can be chemically manipulated with a variety of easy and cheap processing techniques [5]. Organic semiconductors have also other advantages such as low cost synthesis, easy manufacturing of thin film devices using printing technologies. Furthermore, organic semiconductor thin films show high absorption coefficients (>105 cm−1) which makes them good chromophores for optoelectronic applications [6].

A hybrid solar cell consists of an organic and inorganic semiconductors, therefore combines the unique properties of inorganic semiconductors with the film forming properties of organic semiconductors such as polymers. Until recently, the most common way of fabricating hybrid solar cells was blending inorganic nanoparticles with polymers. Inorganic semiconductors can be manufactured as nanoparticles. Inorganic nanoparticles may have high absorption coefficients, their band gap can be changed depending on their size which make their absorption tunable. Their processing is possible using inorganic nanoparticles in solution/suspension however, the power conversion efficiency of hybrid devices, in which nanoparticles are involved, needs improvement. One of the reasons for low efficiency is the surfactant around the nanoparticles. Another way to fabricate a hybrid solar cell is to make heterojunctions with inorganic semiconductors and polymers. Poly[(3-hexyl)thiophene (P3HT)/CdSe, poly[3-methyl]thiophene/CdSe, poly[3-methyl]thiophene/Cds, P3HT/PbS, Alkyl-polythiophene/TiO2, poly[3-octyl]thiophene/Cds] heterojunctions have already been studied for solar cell applications.

Recently, thin film CdS containing inorganic/organic heterojunction type solar cells drew attention. CdS is one of the most important semiconductor in group II–VI with a direct n-type and wide band-gap with 2.4 eV at room temperature [16–18]. The deposition of CdS films has been explored by different techniques as: thermal evaporation [19,20],
chemical bath deposition [21–24], molecular beam epitaxy [21], and spray pyrolysis [25–28].

Recently, CdS/P3HT hybrid solar cells have been studied by Xiaoxia Jiang et al. [15] and Min Zhong et al. [16]. Xiaoxia Jiang et al. achieved an open circuit voltage ($V_{oc}$) of 160 mV and a short circuit current density ($J_{sc}$) of 0.41 mA/cm$^2$ and this value was further improved with modification of CdS nanorod surface by using aromatic acid as surface ligands [15]. Min Zhong et al. have found that modification of the interface between the inorganic CdS and the organic P3HT layer with N719 dye, thereby the efficiency of the CdS/P3HT hybrid solar cells were increased by sixteen times than that of the unmodified ones [16].

In this work, CdS and P3HT bilayer heterojunction hybrid solar cells were fabricated and characterized under normal atmospheric conditions. CdS films were deposited using spray pyrolysis technique.

2. Material and Methods

CdS thin films were deposited on indium tin oxide (ITO) glass substrates by spray pyrolysis technique from aqueous solutions mixtures of equimolar (0.02 to 0.1 M) cadmium chloride (CdCl$_2$) and thiourea (CS(NH$_2$)$_2$) in distilled water. These concentrations were optimized to give optimum quality films in a reasonable preparation time. A conventional spray system was controlled with a thermocouple. The details of deposition of CdS films are shown in Table 1. The ITO substrates (KINTEC) that have thickness of 120 nm and sheet resistance of 15 ohm$^{-}$cm$^{-}$ were used in experiments. The ITO substrates were patterned by etching with an acid mixture for about 30 min and cleaned with hexamethyldisilazane, distilled water, acetone (pure), and isopropanol (pure), distilled water, respectively using ultrasonic bath.

P3HT solution was prepared by dissolving 10 mg of P3HT (Rieke Metals) in 1 ml of chlorobenzene. The solution was coated by drop cast method on CdS films under normal atmospheric conditions which led to 850 nm thick P3HT films. The samples were thermally annealed at 100 °C for 10 min. Finally, 100 nm of Gold (Au) was evaporated.

The x-ray diffraction (XRD) patterns of CdS samples were taken using a Panalytical Diffractometer (Philips) with CuK$_\alpha$ radiation of 1.5418 Å and using Bragg-Brentano geometry. The scanning speed was 0.2 min$^{-}$ and the accuracy in determining lattice parameters was ±0.0002 nm. All current–voltage (I–V) characteristics of the PV devices were measured by a Keithley 6487. Incident photon to current efficiency (IPCE) of the solar cells was analyzed using Oriel Quantum Efficiency Measurement Kit. IPCE was calculated using the following formula:

$$\text{IPCE} = \frac{1240 \cdot J_{sc}}{\lambda \cdot P_{in}}$$

where $\lambda$ [nm] is the incident photon wavelength, $J_{sc}$ (mA/cm$^2$) is the photocurrent of the device and $P_{in}$ (mW/cm$^2$) is the incident power. The thickness of the films was determined by Veeco Dektak-150 profilometer. The absorption spectra of the CdS films were recorded using an Agilent 8453 ultraviolet–visible spectrophotometer. Scanning electron microscopy (SEM) images of CdS films were taken in a JEOL microscope at an operating voltage of 10 kV.

Table 1:
The details of the deposition of CdS thin films using spray pyrolysis technique.

<table>
<thead>
<tr>
<th>CdS Thickness (nm)</th>
<th>CdCl$_2$ Concentration (Molar)</th>
<th>Thiourea concentration (Molar)</th>
<th>Solution Volume (ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>0.02</td>
<td>0.02</td>
<td>40</td>
</tr>
<tr>
<td>160</td>
<td>0.03</td>
<td>0.03</td>
<td>40</td>
</tr>
<tr>
<td>240</td>
<td>0.05</td>
<td>0.05</td>
<td>40</td>
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<tr>
<td>350</td>
<td>0.1</td>
<td>0.1</td>
<td>40</td>
</tr>
</tbody>
</table>

3. Results

Fig. 1 shows the XRD patterns of the 100 nm thick CdS film. The patterns for CdS films display the diffraction lines of the hexagonal CdS (JCPDS, card no. 41-1049) with the preferred orientation in (002) and (101) directions. CdS films were found to be polycrystalline. The lattice parameters a, and c of the CdS films were determined by using high-angle (100), (101) and (002) peaks. The lattice parameters ‘a’ was calculated as 4.124 Å whereas ‘c’ was calculated as 6.731 Å.

Fig. 2(a), (b), (c) and (d) show the SEM images of 100, 160, 240 and 350 nm thick CdS films, respectively. As can be seen from the figure, 100 nm thick CdS film possesses a rather flat surface as compared to other CdS films investigated. It can be noted that the surface roughness increases with the increasing thickness of CdS films, as expected. SEM images reveal that the decrease of the CdS film thickness down to 100 nm leads to a decrease in the grain size. In other words, CdS films present 3D nanocrystalline structures. Therefore, the quantum confinement effect which leads to an increased effective band gap can be observed in such CdS films.

Fig. 3 shows the optical transmittance and absorption spectra of CdS and P3HT films. The shoulders around 480–510 nm and 650 nm are the characteristic absorption features of the CdS and P3HT, respectively. The experimental data presented in Fig. 3 qualitatively show that the band gap of 100 nm thick CdS is about 2.45 eV which is significantly larger than that of thicker CdS (about 2.45 eV). Also, higher IPCE and the extension of the IPCE to longer wavelengths for CdS (100 nm)/P3HT solar cells can be interpreted as the supporting information for the quantum confinement effect in thin CdS films.

Fig. 4 shows the IPCE of the investigated solar cells. By means of IPCE measurements, the contribution of organic species present in the device to the total photocurrent generation can be investigated. The shape of the IPCE spectrum provides information about which part of the PV device is active. IPCE, spectrum here spans from 350 nm to 650 nm and exhibits a photocurrent contribution of ca. 4.8% at around 470 nm. As can be seen from the figure, the shape of the IPCE spectrum contains features from both P3HT and CdS absorption spectra. This is an indication that both P3HT and CdS contribute to the photocurrent generation in this device.

The ITO/CdS/P3HT/Au hybrid PV device structure is illustrated in Fig. 5a. The PV properties of solar cells in the form of ITO/CdS/P3HT/Au were characterized by measuring I–V curves in the dark and under white light illumination (simulated AM 1.5, 100 mWcm$^{-2}$) from the ITO side. Fig. 5b and c show the I–V characteristics of ITO/CdS/P3HT/Au solar cells comprising of 100, 160, 240 and 350 nm thick CdS films at linear and logarithmic scale, respectively. The characteristic parameters of the solar cells were deduced from the linear I–V curves in Fig. 5b. Table 2 shows the characteristic PV parameters.
of the solar cells investigated, and as can be seen from this table, power conversion efficiencies range between 0.07% and 0.15%. The highest value of efficiency was achieved for solar cells employing 100 nm thick CdS films. We observed that both the series and parallel resistances of the cells increased with the increasing thicknesses of CdS films. We attribute the better PV performance of the solar cells to the lower series resistances. Without illumination, all devices show diode like I-V curve.

4. Conclusion

In this study, we have fabricated bilayer heterojunction hybrid solar cells using thin film CdS and P3HT. We observed that the Jsc was higher for the hybrid solar cells employing thinner CdS films. We attribute these improvements to a decrease in the series resistance of cells. It is known that the thickness of the first layer that light passes through plays an important role in the PV performance of the bilayer heterojunction solar cells. Here, we presume that the same situation occurs, the thinner CdS films lead to a better PV performance. We achieved Jsc and power conversion efficiency reaching up to 1.54 mA/cm² and 0.15%, respectively. We suppose that thin CdS films in CdS/P3HT solar cells, as in the case of inorganic CdS/CdTe solar cells play the optical window role, which decrease also the surface recombination processes. Additionally, employment of thinner nanocrystalline CdS films increases the incident photon to current efficiency and broadens the spectral region.

CdS/P3HT hybrid solar cells have previously been studied by Jiang X. et al. [15] and Zhong M. et al. [16]. Jiang X. et al. achieved a Voc of...
160 mV, a $J_{sc}$ of 0.41 mA/cm$^2$ and power conversion efficiency of 0.02% whereas Zhong M. et al. achieved a $J_{sc}$ of 0.57 mA/cm$^2$, a $V_{oc}$ of 493 mV and power conversion efficiency of 0.07% using unmodified CdS films. These values were improved with modification of CdS nanorod surface by using aromatic acid as surface ligands [15] and an N719 dye [16]. But, in this case, the the solar cells can be considered as solid state dye sensitized solar cells. In this study, we were able to almost triple the $J_{sc}$ and double the power conversion efficiency by using unmodified CdS films deposited using spray pyrolysis technique under normal atmospheric conditions. Further improvement in the device performance could be achieved by optimizing the crystallinity and the grain size of CdS films and by inverting the hybrid device structure.

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**References**
