Photophysical investigation of charge recombination in CdS/ZnO layers of CuIn(S,Se)$_2$ solar cell

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Excitation wavelength dependent femtosecond transient photocurrents were measured on CuIn(S,Se)$_2$ solar cell devices, in the range of 330–1300 nm. Below 450 nm wavelength excitations, charge recombination in CdS/ZnO layers is determined to be responsible for longer decays and lower EQE. Femtosecond pump–probe measurements also support the charge transfer and recombination in CdS/ZnO layers. These measurements will be helpful to design high efficiency CISSe solar cells, by selecting suitable buffer layers.

Introduction

The energy consumption throughout the world is significantly rising as countries with high population are rapidly developing, resulting in an enormous stress on energy production. Energy generated from “fossil fuels” are causing global warming, leading us to a requirement of “green and clean” energy. Among the different types of clean energies, the production of solar energy is rising faster. To date, the solar market was dominated by crystalline Si as the absorber material, but due to its higher price alternative materials like copper-based chalcopygenide, such as CuIn(S,Se)$_2$ (CISSe), has the strongest potential to overtake Si in the future.1

Conventional CISSe and its chalcopyrites family have achieved power conversion efficiency (PCE) exceeding 20% (ref. 2) via a high vacuum 3-stage coevaporation approach. Nonvacuum approaches, such as the solution-based or nanoparticle ink approach, of CISSe thin film have achieved a promising efficiency of 12%,3–5 but were still lagging far behind the vacuum approach. The nanoparticle approach involves the synthesis of the nanoparticles followed by deposition to form an active layer,6–9 but multiple processes are involved in this method. Among the different solution-based techniques, spray pyrolysis has the potential for low-cost deposition.10–12 Preparation of flexible CISSe solar cells on polymer substrates is also possible using this method.13 This method also allows us to select different buffer layers, as buffer layers play an important role to form p–n junctions and enable higher charge transfer towards the electrodes.

As a lower band gap material (~1.1 eV), CISSe has an advantage of absorbing most parts of the solar spectrum from UV to NIR.14 Although the absorption of CISSe below 450 nm is considerably higher, the external quantum efficiency (EQE) of these devices is found to be lower at these wavelengths. One reason for the low EQE below 450 nm is the high reflection and low penetration depth of the material; another reason is the absorption of buffer layers like CdS films15–17 and n-type ZnO layers.18 Contribution of the photoelectrons generated in the buffer layers to the efficiency of the device is destructive.19 The reason for the decreasing solar cell efficiency by buffer layers are not fully understood, although we believe it is because of the forward leakage current.20 Transient photocurrent is a method to measure the dynamics of the solar cell devices,21 but excitation with longer light pulses may contribute other effects, such as thermal current. To explain the lower efficiency below 450 nm wavelength excitations, here we present a transient photocurrent generated by femtosecond pulse excitations. The lower efficiency of CISSe solar cells below 450 nm excitations is determined to be due to the recombination in the CdS buffer layer and ZnO layer.

Experimental methods

Materials

Copper(II) chloride dihydrate (CuCl$_2$·2H$_2$O) (99.99%, Sigma-Aldrich), anhydrous indium(III) chloride (InCl$_3$) (99.99%, Sigma-Aldrich) and thiourea SC(NH$_2$)$_2$ (Sigma-Aldrich) were
dissolved in deionised (DI) water to form individual stock solutions with concentrations of 0.1 M, 0.1 M and 1.0 M, respectively. The precursor solution was prepared with a Cu-poor stoichiometry (Cu/In = 0.85) by mixing the stock solutions. Excess thiourea was used to stabilize the precursor solution from forming complex. The precursor solution was spray deposited on either Mo-coated soda lime glass substrates or soda lime glass substrate with N₂ as the carrier gas. The film was deposited by a multistage spray pyrolysis process, similar to our previous work.¹⁹ The as-sprayed CIS film was selenized at 500–550 °C for 10 min to form CISSe. The Se vapor is produced by evaporating solid Se pellets. The gas flow within the tube furnace was regulated with inert Ar gas. The final devices were obtained after a sequential deposition of the CdS buffer layer, i-ZnO layer, transparent conductive oxide (TCO) and Al electrode on the selenized CISSe films. CdS (60–80 nm) was deposited by the chemical bath deposition (CBD) method, i-ZnO (80 nm) and ITO were deposited by DC sputtering, and the Al electrode was deposited by thermal evaporation.

Characterization

Current density–voltage (J–V) characteristics of the final devices were obtained with an AM1.5G solar simulator (VS-0852) equipped with a 500 W xenon lamp and a Keithley sourcemeter (2612A, dual sourcemeter, 200 V). The light intensity of the solar simulator was calibrated with a Si photodiode (Fraunhofer) to 100 mW cm⁻². The external quantum efficiency measurement was conducted with a PVE300 photovoltaic device characterization system (Bentham) equipped with a xenon/quartz halogen light source and calibrated with Si/Ge reference detectors. J–V and EQE curves are shown in Fig. 1. The measured values were PCE = 5.91%, Jsc = 25.48 mA cm⁻², Voc = 418.2 mV, FF = 0.55, Rsh = 1098 Ω and Rs = 28.9 Ω. Cell area used was 1.087 cm².

Transient photocurrent

Transient photocurrent studies were conducted using mode-locked Ti:sapphire laser seeded Ti:sapphire regenerative amplifier pumped OPA (Spectra physics, Mai Tai-Spifire Ace-TOPAS Prime). Laser pulses were tuned from 300 to 1300 nm wavelengths (100 fs duration and 1000 Hz repetition rate), which were exposed onto the solar cell devices with a circular spot diameter of ~5 nm. Optical neutral density filters were employed to control the laser pulse energy. A laser power meter was used to measure the average power of the laser pulses; input laser power was fixed at 2 mW for all the measurements. The temporal profiles of transient photocurrents were monitored with the 50 ohm terminated, 400 MHz bandwidth digital oscilloscope; the positive and negative terminals of the oscilloscope were directly connected to the electrodes of the CIGS solar cell device, accordingly.

Results and discussion

Wavelength dependent femtosecond pulse excited transient photocurrent (TPC) profiles fit well with the double exponential decay function \(I_{TPC} = A_1e^{-t/\tau_1} + A_2e^{-t/\tau_2}\), in which \(I_{TPC}\) is transient photocurrent, \(A_1\) and \(A_2\) are the constants, \(\tau_1\) and \(\tau_2\) are the decay times), as shown in Fig. 2A. From the best fits to the TPC curves at different wavelength excitations, two decay times \(\tau_1\) and \(\tau_2\) were achieved. Fig. 2B and C are the \(\tau_1\) and \(\tau_2\) curves at different wavelength excitations, respectively. A double exponential decay proves two ways of charge transport in the solar cell device.²² These decay times were unaffected by the excitation wavelength, below the band gaps of the CdS/ZnO layers, in which \(\tau_1\) is 180 ± 20 ns and \(\tau_2\) is 1400 ± 350 ns. For the excitations below the band gap of CdS, electrons are collected and simply transferred to the ZnO layer (Fig. 3A), whereas for excitations above the band gap of CdS (electrons in CdS also can be excited by laser), the electrons are recombined with the holes in the CdS layer. For the excitations above the band gap of ZnO (band gap of ZnO > band gap of CdS), electrons in both the ZnO and CdS layers were excited, and the generated holes in these layers were recombined with the transferred electrons from CISSe layers. This gives rise to large delays in the TPC decay times, when excitations are above the band gap of CdS/ZnO. The probable charge transfer processes in the CISSe solar cell device are shown in Fig. 3.

The two peaks observed in wavelength dependent decay times \(\tau_1\) and \(\tau_2\) are shown in Fig. 2B and C, and they are attributed to the recombination in CdS/ZnO layers; the first peak is observed at 380 nm and second one is at 420 nm, attributing these peaks to the absorption peaks of the ZnO and CdS layers, respectively.²³,²⁴ In the case of \(\tau_1\), the peak at 420 nm is three times higher than the peak at 380 nm, which proves that the faster component \(\tau_1\) is dominated by recombination in the

![Fig. 1](https://example.com/fig1.png)

**Fig. 1** (A) J–V curve and (B) EQE curve of CISSe solar cell device, in which EQE sharply decreases below 450 nm excitation.
CdS layer. In the case of $\tau_2$, the 380 nm peak is three times higher than the 420 nm component, which proves that the slower component $\tau_2$ is dominated by recombination in the ZnO layer. Recombination in the CdS/ZnO layers reduces the photocurrent in the device. The longer $\tau_1$ below the wavelength of 450 nm is related to the recombination in the CdS buffer layer, whereas the longer $\tau_2$ below 400 nm results from the recombination in the ZnO layer. In general a photocurrent longer decay time should enhance the efficiency of the device, but if the charges are trapped in buffer layers, and later recombine with the holes, this results in lower efficiency.\textsuperscript{25} The lower efficiency is because of the trapping (capture) and detrapping (emission) of carriers by the CdS and ZnO layers.\textsuperscript{18,26,27}

Optical pump and optical probe measurements were obtained by pumping and probing with femtosecond laser pulses (100 fs, 1 kHz). The fundamental and second harmonic wavelengths of the laser were chosen for the pump, and output from OPA (900 nm) was chosen as the probe. Differential transmission probe signals were collected using photodiode and lock-in amplifier, with respect to the pump delay. In this experiment, pump and probe pulses were orthogonally polarized. The incident angle between both the beams is less than three degrees. The ratio of power between the pump and probe pulses was less than 5%. Pump–probe measurements were performed on two different samples: one is a CISSe solar cell device and other is a pure CISSe layer. The probe was always fixed at 900 nm, in which it monitors the electron decays in CISSe. Two different pump wavelengths were used to monitor the charge transfer to the CdS/ZnO from CISSe, with and without the generation of charges in CdS/ZnO. The charge transfer rate and mechanisms from CISSe to the CdS/ZnO layers were studied. Both slow and fast decay of biexponential decays were observed: the faster decay can be attributed to the charge transfer time from CISSe to CdS/ZnO layers, and the slower one is attributed to the recombination lifetime within the CISSe. After exciting electrons in CdS/ZnO at the 400 nm pump, a faster decay was observed, which is because of the electron transfer and recombination in the CdS/ZnO layers. The increase in the raising time at the 400 nm pump excitation, as shown in Fig. 4(B), also proves the movement of charges to the CdS/ZnO layers (resulting in a delay in bleaching of CISSe layers) and later recombine with holes.\textsuperscript{18} Pump–probe decays of the pure CISSe layer were also obtained for comparison, which show single exponential decay, longer than the device decay time, as the excitation was at low powers (before multiexciton generation) negligible change in decay time was observed at both the 800 nm/400 nm pump wavelength excitations. Raising and decay times of CISSe solar cell device and pure CISSe layer are

Fig. 2 (A) Transient photocurrent decays of CISSe solar cell device at different wavelength excitations (solid line is best fit to the double exponential decay), (B) wavelength dependent photocurrent decay times ($\tau_1$ and $\tau_2$) of CISSe solar cell device (red and green solid lines in (B) and (C) are best fit of double Gaussian peaks).

Fig. 3 Schematic of charge transfer and recombination in CISSe solar cells, (A) below CdS buffer layer band gap and (B) above band gap of CdS/ZnO layers.
The proper design of materials and their work functions can improve the efficiency of solar cells. To improve the solar cell efficiency, the band gap of the CdS/ZnO layers also can be changed by doping with different materials and by different growth methods.28

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References


Table 1 Electron decay times ($t_1$ and $t_2$) and the raise time of the CISSe solar cell device and pure CISSe layer, measured with femtosecond pump–probe experiments

<table>
<thead>
<tr>
<th>Pump wavelength (nm)</th>
<th>$t_1$ (ps)</th>
<th>$t_2$ (ps)</th>
<th>Raise time (ps)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>CISSe solar cell device</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>800</td>
<td>10 ± 2</td>
<td>120 ± 15</td>
<td>1.2 ± 0.5</td>
</tr>
<tr>
<td>400</td>
<td>5 ± 1</td>
<td>80 ± 10</td>
<td>2.2 ± 0.7</td>
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<tr>
<td><strong>Pure CISSe layer</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>800/400</td>
<td>—</td>
<td>150 ± 10</td>
<td>1 ± 0.5</td>
</tr>
</tbody>
</table>

Fig. 4 (A) Pump–probe decays of the CISSe solar cell device and the pure CISSe layer. (B) Raising times of the CISSe solar cell device and the pure CISSe layer.


19 http://www.silvaco.com/content/kbase/CIGS.pdf.


