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COMMUNICATION

Photophysical investigation of charge recombination in CdS/ZnO layers of CuIn(S,Se)₂ Solar Cell

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Abstract: Excitation wavelength dependent femtosecond transient photocurrents were measured on CuIn(S,Se)₂ solar cell devices, in the range of 330 nm–1300 nm. Below 450 nm wavelength excitations, charge recombination in CdS/ZnO layers is found 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.

Broader context: Low-cost, high efficiency thin-film solar cells represent a potentially sustainable energy alternative to the carbon based fossil fuels.

In this context, CuIn(S,Se)₂ based solar cells are attractive because of their lower cost and higher efficiency, they can be deposited from solution on plastic substrates, making them compatible with large-scale industrial production. Efficiency of these devices can be further improved, by proper design of buffer layers. External quantum efficiency of the device were found to be lowered below 450 nm wavelengths, even though CuIn(S,Se)₂ can go behind that limit, this limit is found to be due to the absorption of different buffer layers contributing negative currents and recombination. Band gap of these buffer layers can be modified, which will enhance the efficiency of device further more.

Introduction:

The energy consumption throughout the world is rising constantly as countries with large populations are developing rapidly, placing an enormous stress on energy production. Energy generated from “fossil fuels” are causing global warming, led us to go ‘green and clean’ energy. Among the different types of clean energies, production of solar energy is rising faster. Till now solar market was dominated by crystalline Si as the absorber material, but due to its higher price alternative materials like copper-based chalcogenide such as, CuIn(S,Se)_2 (CISSe) having the strongest potential to overtake Si in the future.¹

Conventional CISSe and its chalcopyrites family have achieved power conversion efficiency (PCE) exceeding 20%² via high vacuum 3-stage co-evaporation approach. Non-vacuum approach such as the solution-based or nanoparticle ink approach CISSe thin film had achieved promising efficiencies of 12%,³⁻⁵ but were still lagging far behind from the vacuum approach. Nanoparticle approach involves the synthesis of the nanoparticles followed by deposition to form an active layer,^{4, 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 Making flexible CISSe solar cell devices on polymer substrates are also possible with this method.¹³ This method also allow us to select different buffer

layers, as buffer layers play an important role to form p-n junctions and enable higher charge transfer towards electrodes.

As lower band gap material (~ 1.1 eV) CISSe has an advantage of absorbing most part of the solar spectrum from UV to NIR.¹⁴ Even though, absorption of CISSe below 450 nm is much higher, but external quantum efficiency (EQE) of these devices are found to be lower at these wavelengths. One reason for the low EQE below 450 nm is due to high reflection and low penetration depth of the material and other one is due to the absorption of buffer layers like CdS films¹⁵⁻¹⁷ and n-type ZnO layers.¹⁸ Contribution to the efficiency of the device by photoelectrons generated in the buffer layers is destructive.¹⁹ The reasons for the lowering solar cell efficiency by buffer layers are not fully understood, even though, we believe it is due to forward leakage current.²⁰ Transient photocurrent is one way to measure 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 transient photocurrent generated by femtosecond pulse excitations. Lower efficiency of CISSe solar cells below 450 nm excitations found to be due to the recombination in CdS buffer layer and ZnO layer.

Experimental Methods:

Materials. Copper (II) chloride dehydrate ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$) (99.99%, Sigma Aldrich), Anhydrous Indium (III) Chloride (InCl_3) (99.99%, Sigma Aldrich) and thiourea $\text{SC}(\text{NH}_2)_2$ (Sigma Aldrich) were dissolved in deionised (DI) water to form individual stock solutions with concentrations of 0.1M, 0.1M and 1.0M, respectively. Precursor solution was prepared with a Cu poor stoichiometry ($\text{Cu}/\text{In}=0.85$) 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 N_2 as the carrier gas. The film was deposited by a multistage spray pyrolysis process, similar to our previous work¹¹. 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 sequential deposition of 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 chemical bath deposition (CBD) method, i-ZnO (80 nm) and ITO were deposited by DC sputtering while 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 100mW/cm². The quantum efficiency measurement was conducted with a PVE300 photovoltaic devices 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%, $J_{\text{sc}} = 25.48 \text{ mA}/\text{cm}^2$, $V_{\text{oc}} = 418.2 \text{ mV}$, $\text{FF} = 0.55$, $R_{\text{sh}} = 1098 \Omega$ and $R_{\text{s}} = 28.9 \Omega$. Cell Area used was 1.087 cm².

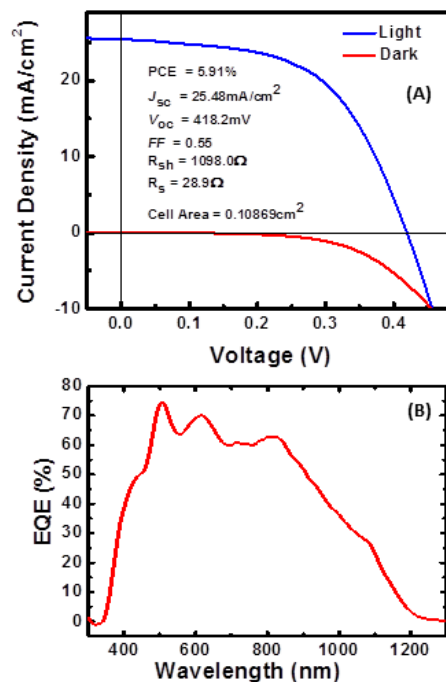


Fig.1. (A) J-V curve and (B) EQE curve, of CISSe solar cell device, where EQE decreases sharply below 450 nm excitation.

Transient photocurrent. Transient photocurrent studies were conducted using mode-locked Ti: Sapphire laser seeded Ti: Sapphire regenerative amplifier pumped OPA (Spectra physics, Mai Tai-Spitfire Ace-TOPAS Prime). laser pulses were

tuned from 300 nm- 1300nm wavelengths (100-fs duration, and 1000-Hz repetition rate), which were exposed onto the solar cell devices with a circular spot diameter of ~5 mm. 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; positive and negative terminals of the oscilloscope were connected directly to the electrodes of CIGS solar cell device, accordingly.

Results and discussion:

Wavelength dependent femtosecond pulse excited transient photocurrent (TPC) profiles fits well with double exponential decay function ($I_{\text{TPC}}=A_1e^{-t/\tau_1}+A_2e^{-t/\tau_2}$, where I_{TPC} is transient photocurrent, A_1 and A_2 are the constants, τ_1 and τ_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 τ_1 and τ_2 were achieved. Figure 2B and 2C are the τ_1 and τ_2 curves at different wavelength excitations, respectively. A double exponential decays proves, two ways of charge transport in the solar cell device.²² These decay times were unaffected by excitation wavelength, below the band gaps of CdS/ZnO layers, where τ_1 is 180 ± 20 ns and τ_2 is 1400 ± 350 ns. The excitations below the band gap of CdS, electrons

are collected and simply transferred to the ZnO layer (figure 3 A). Whereas, excitations above the band gap of CdS (electrons in CdS also can be excited by laser), the electrons are recombined with the holes in CdS layer. 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 got 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 τ_1 and τ_2 are shown in figure 2B and 2C, they are attributed to the recombination in CdS/ZnO layers; first peak is observed at 380 nm and second one is at 420 nm, attributing these peaks to absorption peaks of the ZnO and CdS layers respectively.^{23, 24} In the case of τ_1 , 420 nm peak is three times higher than the 380 nm, which proves that faster component τ_1 is dominated by recombination in CdS layer. In the case of τ_2 , 380 nm peak is three times higher than the 420 nm, which proves that slower component τ_2 is dominated by recombination in ZnO layer. Recombination in CdS/ZnO layers reduces the photocurrent in the device. The longer τ_1 below the wavelength of 450 nm is related to the recombination in CdS buffer layer, whereas longer

τ_2 below 400 nm is resulting from the recombination in ZnO layer. In general a photocurrent longer decay time should enhance the efficiency of the devices, but if charges are trapped in buffer layers, later recombine with the holes, results in the lower efficiency.²⁵ The lower efficiency is due to trapping (capture) and de-trapping (emission) of carriers by the CdS and ZnO layers.^{18, 26, 27}

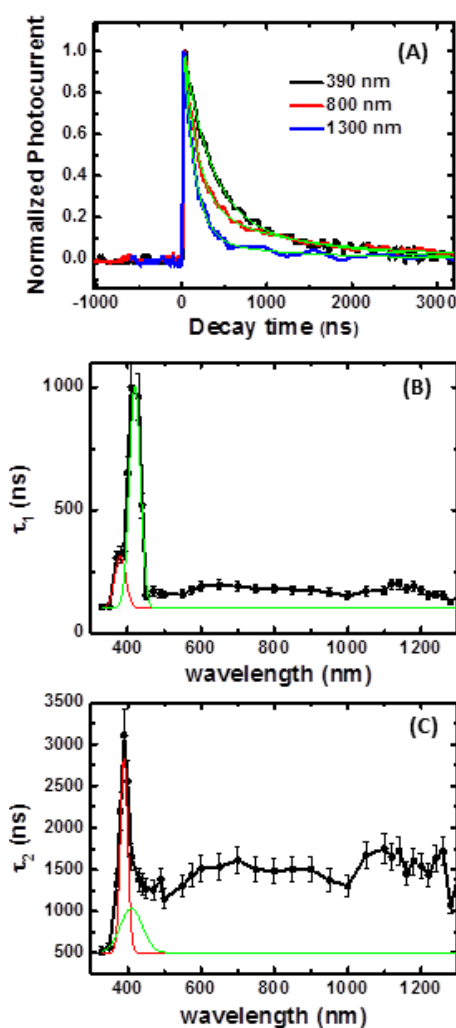


Fig. 2 (A) Transient photocurrent decays of CISSe solar cell device at different wavelength excitations (solid line is best fit to the double exponential decay), (B) wavelength dependent photocurrent decay times (τ_1 and τ_2) of CISSe solar cell device (solid lines in fig B and C are best fit of double gaussian peaks).

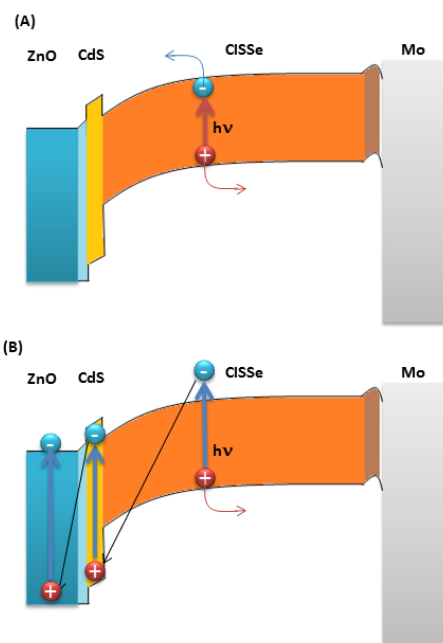


Fig. 3 Schematic of charge transfer and recombination in CISSe solar cells, A) below CdS buffer layer band gap and B) above band gap of CdS/ZnO layers.

Optical pump and optical probe measurements were taken by pumping and probing with femtosecond laser pulses (100 fs, 1 kHz). Fundamental and second harmonic wavelengths of the laser were chosen for pump; and output from OPA (900 nm) chosen as probe. Differential transmission probe signals were collected using photodiode and lock-in amplifier, with respect to the pump delay. In this experiment, the 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 the probe pulses were less than 5%. Pump-probe measurements were done on two different samples, one is CISSe solar cell device and other is pure CISSe layer. Probe was always fixed at 900 nm, where it monitors the electron

decays in CISSe, two different pump wavelengths were used to monitor charge transfer to the CdS/ZnO from CISSe, with and without generation of charges in CdS/ZnO itself. The charge transfer rate and mechanisms from CISSe to CdS/ZnO layers were studied. Both the cases bi-exponential decays were observed, faster decay can be attributed to the charge transfer times from CISSe to CdS/ZnO layers and slower one is attributed to the recombination lifetime within the CISSe. After exciting electron in CdS/ZnO at 400 nm pump, a faster decay was observed, which is due to the electron transfer and recombination in CdS/ZnO layers. Increase in the raising time at 400 nm pump excitation as shown in Fig. 4 (B), also proves that, charges are moving to the CdS/ZnO layers, (resulting delay in bleaching of CISSe layers), later recombine with holes.¹⁸ Pump-probe decays of pure CISSe layer were also collected for the comparison, which show single exponential decay, longer than the device decay time, as we are exciting at low powers (before multi exciton generation) negligible change in decay times were observed at both the 800 nm/ 400 nm pump wavelength excitations. Shorter decay times in the device structures compare to the pure CISSe layer is evident of charge transfer from CISSe layer to the CdS/ZnO layers. Previous reports mention that, different kinds of relaxations are possible in these materials, our relaxation time ~ 150 ps is comparable with the reported values for CIGS layers.²⁸

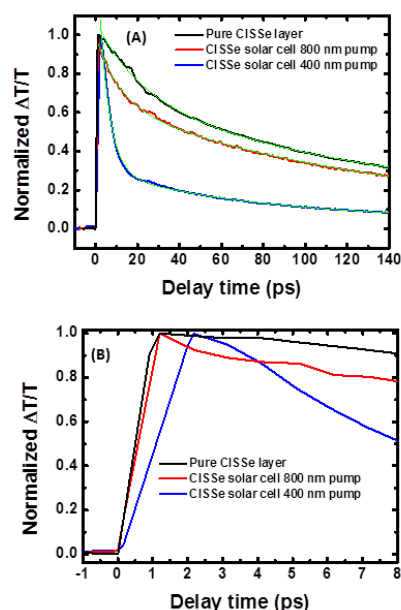


Fig.4 (A) Pump-probe decays of CISSe solar cell device and pure CISSe layer (B) Raising times of CISSe solar cell device and pure CISSe layer.

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.

Pump wavelength (nm)	t_1 (ps)	t_2 (ps)	Raise time (ps)
CISSe solar cell device			
800	10 ± 2	120 ± 15	1.2 ± 0.5
400	5 ± 1	80 ± 10	2.2 ± 0.7
Pure CISSe layer			
800/400	-	150 ± 10	1 ± 0.5

Conclusions

The reduction in the EQE of solar cell above band gap of CdS/ZnO layers is found to be due to the recombination of transferred electron with hole in CdS/ZnO layers. Recombination in CdS/ZnO layers is proved from femtosecond transient photocurrents collected at 330 nm–1300 nm wavelength excitations and femtosecond pump-probe measurements pumped at 400 nm and 800

nm wavelengths. Proper designing of materials and their work functions can improve the efficiency of solar cells. To improve the solar cell efficiency, band gap of CdS/ZnO layers also can be changed by doping with different materials and by different growth methods.²³

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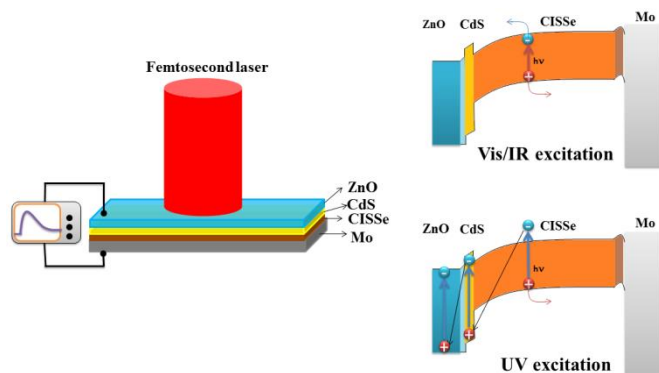
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TOC:

Femtosecond transient photocurrents were measured on $\text{CuIn}(\text{S},\text{Se})_2$ solar cell devices. Reasons for lower EQE below 450nm wavelength excitations were investigated.



Transient photocurrent of CISSe solar cell