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Interface Recombination of Cu2ZnSnS4 Solar Cells Leveraged by High Carrier Density and Interface Defects

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Kesterite Cu_2ZnSnS_4(CZTS) solar cell has emerged as one of the most promising thin-film photovoltaic technologies that allow for cheap, clean, and efficient renewable power in the future. Nevertheless, limited by the large photovoltage deficit caused by severe interface recombination, the potential of CZTS solar cells is far from being fully tapped. Herein, we demonstrate that the carrier density of CZTS absorber and the acceptor-like interface defects are two critical factors governing the interface recombination in addition to the unfavorable conduction band alignment. Results of device simulation suggest that passivating the acceptor-like interface defects combined with appropriate absorber carrier density is the essential way to promote the photovoltage and efficiency of CZTS solar cells to a more competitive level. We believe these results could be generally applicable to the interface recombination of other heterojunction solar cells.

Introduction

Pure-sulfide kesterite Cu_2ZnSnS_4 (CZTS) based thin film solar cell have been emerging as a promising cost-effective thin film photovoltaic (PV) technology, enjoying its earth-abundant and eco-friendly constituents, thermal-dynamically stable structure, combined with the ideal band gap perfectly matching with solar spectrum, and the compatibility with both rigid and flexible substrates.[1-6] These compelling features endows this PV technology huge potentials for application of various scenes in the future including wearable and portable PV power sources, building-integrated PV (BIPV) at curved building surfaces, sustainable power source for internet of things (IOT).[7, 8] Moreover, pure-sulfide CZTS is also one of the most promising candidates as top cell for silicon based tandem solar cell, potentially triggering further technological evolution for large-scale deployment of PV technologies.[9-11]

Nevertheless, the current status of CZTS thin-film solar cells suffer from much more open circuit voltage (V_{OC}) loss than low band gap Cu_2ZnSnS,Se_4 (CZTSSe) solar cells.[3, 12, 13] Beside of the more severe bandgap/potential fluctuation and shorter photoluminescence (PL) decay time (related to real minority carrier lifetime),[14-16] the unfavourable “cliff”-like conduction band offset (CBO) at CZTS/CdS heterojunction interface is well believed to be a serious limiting factor to the V_{OC} of CZTS solar cells.[17-20] To address this issue, alternative buffer materials with wide bandgap and suitable conduction band edge have been screened, among which (Zn,Cd)S and (Zn,Sn)O are the most successful materials, allowing a great V_{OC} boost up to 100 mV.[18, 19] Nevertheless, the V_{OC} of CZTS solar cells with a bandgap of 1.5 eV is still limited to below 750 mV, far lower than that of the moderate CdTe solar cells with similar recombination bandgap (1.45 eV), low minority carrier lifetime (1-2 ns), let alone the “criff”-like CBO at the CdTe/CdS interface.[21-24] Results of Suns-V_{OC} measurements for these cells configured with (Zn,Sn)O or (Zn,Cd)S buffer layer have revealed that the J_{02} (representing the nonradiative recombination at heterojunction region) is still 5 orders of magnitude larger than J_{01} (representing the nonradiative recombination in the quasi-neutral bulk region) (10^{-7}A/cm^2 for J_{02} *vs.* 10^{-12} A/cm^2 for J_{01}).[18, 19] This verifies the V_{OC} of pure-sulfide CZTS solar cells is still currently limited by the non-radiative recombination in the hetero-junction interface region even though the unfavourable “cliff-like” CBO has been avoided, indicating that other important interface recombination mechanism may be persisting and yet to be properly recognized.

Herein, we unveil more details of the interface recombination mechanism of pure-sulfide CZTS solar cells by combining experimental results, theoretical analysis, and device simulation. This heterojunction interface recombination mechanism is not solely governed by the conduction band offset, but also, more importantly, depends on the interface defects and the carrier density of CZTS absorber. The relatively high carrier density of CZTS absorber and acceptor-like interface defects greatly aggravates the interface recombination even though the “cliff-like” CBO is avoided. Passivating interface defects whilst remaining relatively high carrier density is proposed to be the essential strategy to tap the full potential of CZTS thin-film PV technology. Moreover, the established model of interface recombination mechanism is also generally applicable to other heterojunction devices, potentially triggering more effective strategies to suppress the prevalent non-radiative interface recombination.

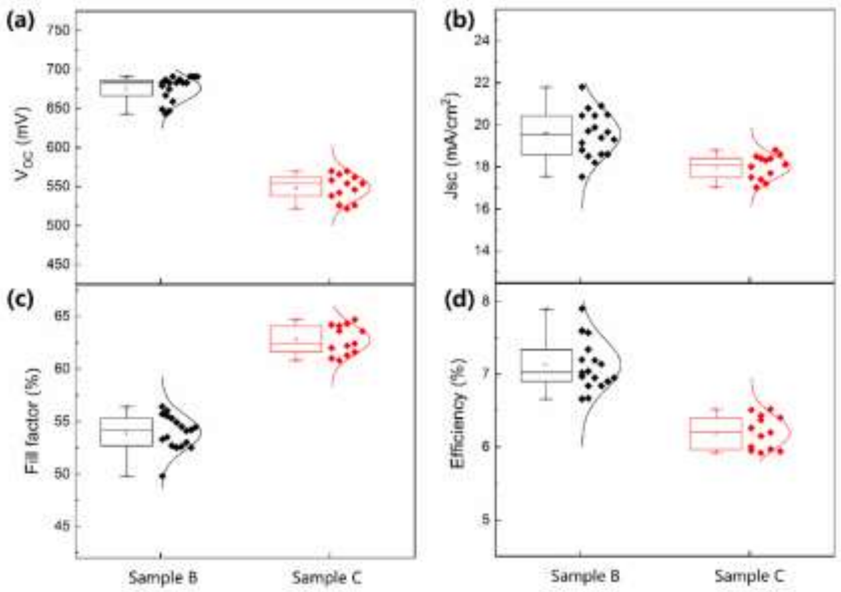

Figure 1. Statistical data of Voc (a), Jsc (b), Fill factor (c), and efficiency (d) of the devices fabricated with Sample B and Sample C. 17 and 13 devices are included for Sample B and Sample C, respectively. The devices with unordinary poor performance severely affected by side-effects are omited.

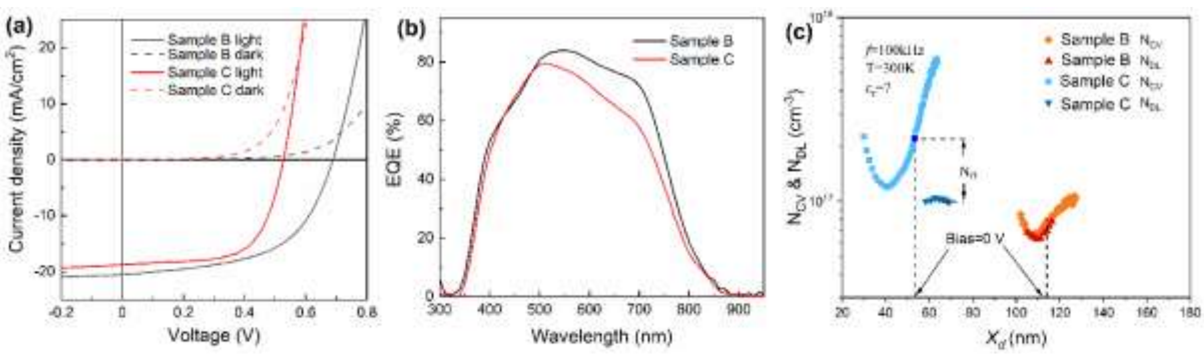

Figure 2. The (a) light and dark J-V curves, (b) EQE data, and (c) C-V and DLCP profiles of the best devices from Sample B and Sample C.

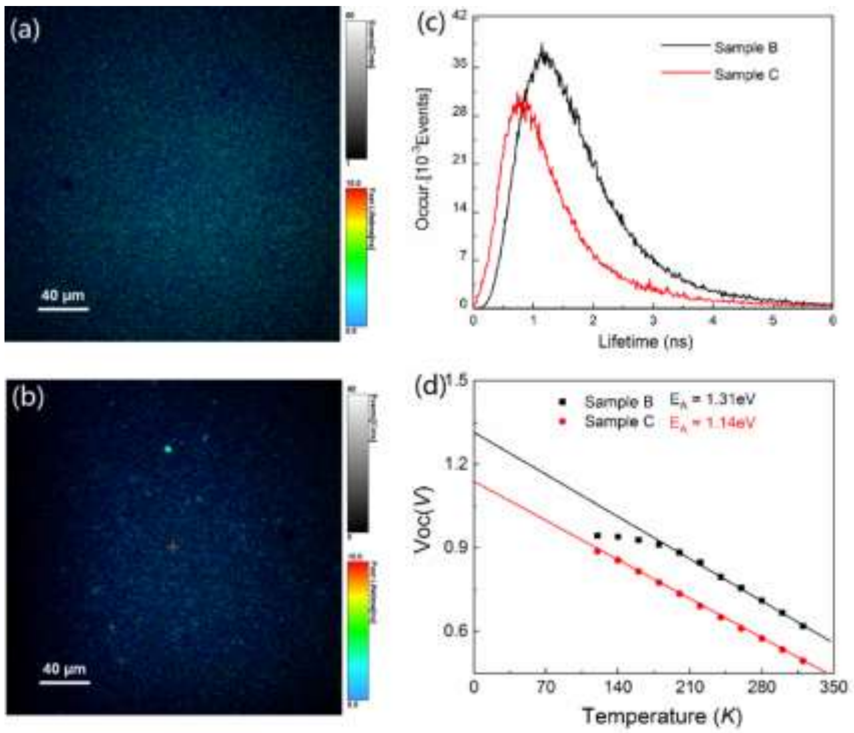

Figure 3. (a) and (b) FLIM images of Sample B and sample C respectively.(c) The statistic minority carrier lifetime of these samples extracted form FLIM images. (d) The temperature-dependent V_{OC} of the best device from Sample B and Sample C. The linear extrapolation to 0 K indicates the recombination activation energy E_a at the heterojunction interface.

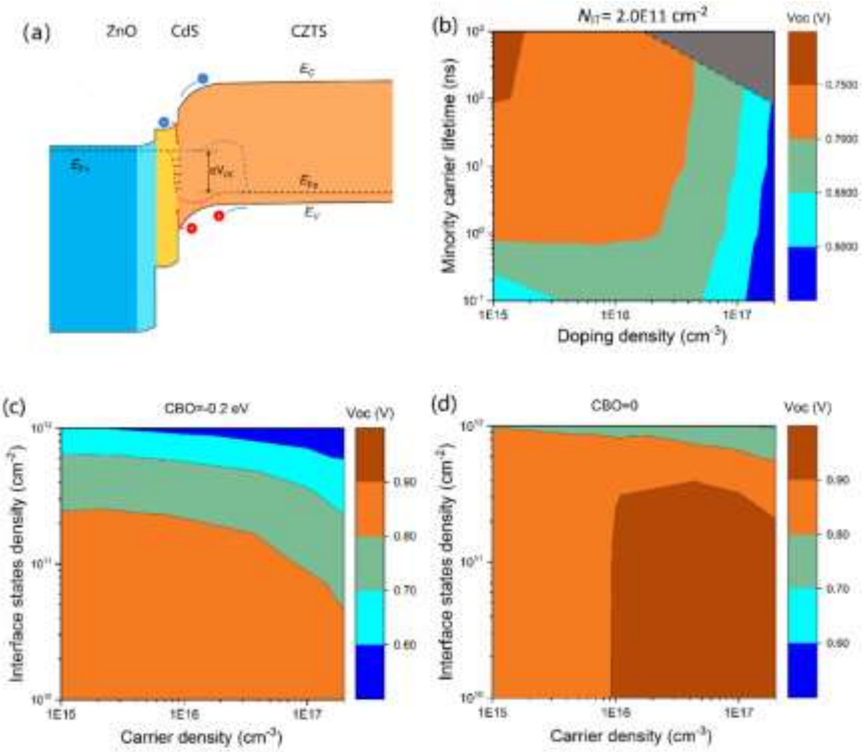

Figure 4. (a) The schematic band diagram of the CZTS/CdS/ZnO device involving interface recombination. (b) Simulated contour of V_{OC} vs. minority carrier lifetime and carrier density with N_{IT}=2×10^{11}cm^{-2}. The grey area with high carrier density and high minority carrier lifetime is not achievable due to the radiative limit. (c) and (d) The simulated contour of V_{OC}

vs. interface defects and carrier density under CBO=-0.2 eV and 0V with an achievable minority carrier lifetime of 10 ns.

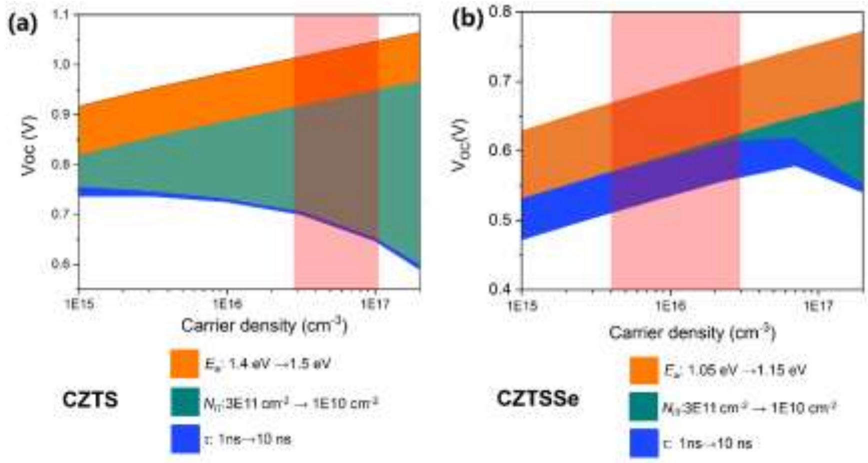

Figure 5. The simulated V_{OC} of CZTS (a) and CZTSSe (b) solar cells vs. carrier density showing the potential directions of optimizing minority carrier lifetime, interface defects, and potential fluctuations, respectively. The shadow (pink) regions indicate the range of carrier density of state-of-the-art CZTS and CZTSSe solar cells, respectively.

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