SHORT COMMUNICATION

Journal of Semiconductors
(2023) 44, 080501
doi: 10.1088/1674-4926/44/8/080501

Solution-processed $CuIn(S,Se)_2$ solar cells on transparent electrode offering 9.4% efficiency

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Citation: X G Liu, C F Ma, H Xin, and L M Ding, Solution-processed $CuIn(S,Se)_2$ solar cells on transparent electrode offering 9.4% efficiency[J]. *J. Semicond.*, 2023, 44(8), 080501. https://doi.org/10.1088/1674-4926/44/8/080501

Chalcopyrite, copper indium gallium selenide ($Cu(In,Ga)Se_2$, CIGS), as semiconductor materials, have been widely used as absorbers in thin-film solar cells, offering high power conversion efficiency (PCE) and good thermal stability[1−3]. Recently, the development of non-traditional photovoltaic (PV) devices such as semitransparent, bifacial, tandem and flexible solar cells, has expanded the application scenarios of thin-film solar cells. For example, semitransparent chalcopyrite solar cells can be applied to building exteriors such as windows and skylights, which can convert a portion of sunlight into electricity while transmit the remaining into the building. Traditional chalcopyrite thin-film solar cells are fabricated on opaque Mo back contact, either by vacuum[2] or solution[3] methods, which completely blocks sunlight. To allow light transmission, replacing traditional Mo back contact with transparent electrodes, such as indium tin oxide (ITO), aluminum-doped zinc oxide (AZO), and fluorine-doped tin oxide (FTO), is necessary. Moreover, the vacuum methods, such as co-evaporation[4] and sputtering[5], generally require expensive equipment and high-temperature deposition that lead to high energy input, large capital investment, and operational costs. Solution processing such as spin-coating[6], blade-coating[7], spray pyrolysis[8] and inkjet-printing[9] is more suitable for fabricating chalcopyrite solar cells on transparent electrodes because of the simple preparation, low cost and substrate shape friendly. However, the so-far reported solution-processed chalcopyrite solar cells exhibit low efficiency[10−12] on transparent substrate (8.0%)[12]. In this work, we report the fabrication of $CuIn(S,Se)_2$ (CISSe) solar cells on FTO substrate from DMF solution. The CISSe film was directly deposited on commercial FTO substrates by simple spin-coating followed by recrystallization at the atmosphere of selenium gas (selenization)[13]. The solar cells with a structure of FTO/CISSe/CdS/i-ZnO/ITO/Ni/Al offered an 9.40% PCE without anti-reflective coating, which is the highest efficiency for solution-processed CISSe thin-film solar cells on transparent electrodes.

Fig. 1(a) illustrates the device structure of CISSe solar cells on FTO. The device has a structure of FTO/CISSe/CdS/i-ZnO/ITO/Ni/Al. The CISSe film was made on FTO substrate by using DMF precursor solution (details were given in SI). Figs. 1(b) and 1(c) show the current density-voltage (*J-V*) curve and the external quantum efficiency (EQE) spectrum of the best CISSe solar cell on FTO. An 9.40% PCE with an open circuit voltage (V_{oc}) of 0.419 V, a short-circuit current density (J_{sc}) of 37.22 $mA{\cdot}cm^{-2}$, and a fill factor (FF) of 60.3%, has been achieved without an anti-reflective coating. This is the highest efficiency for solution-processed chalcopyrite solar cells on transparent substrates. The device has a good EQE response over 70% at 500−1000 nm with a peak value close to 90%. The integrated J_{sc} from EQE spectrum is 35.48 $mA{\cdot}cm^{-2}$, in good agreement with the J_{sc} from *J-V* characterization. The bandgap of CISSe absorber obtained by extending the linear portion of $(\ln(1\text{-EQE}))^2$ versus energy plot is 1.03 eV, very close to the E_g for pure $CuInSe_2$ (1.04 eV), demonstrating a sufficient transformation from copper indium sulfide (CIS) to CISe during selenization. The Urbach energy (E_U) of the CISSe absorber estimated from the sub-bandgap region by plotting $\ln(-\ln(1\text{-EQE}))$ versus energy is 20.17 meV, revealing small band tailing (Fig. S1).

Figs. 1(d) and 1(e) show the top-view and cross-sectional scanning electron microscopy (SEM) images for the CISSe absorber on FTO substrate. From Fig. 1(d), it can be seen that the CISSe is composed of compact grains with a dense and flat surface, which is conducive for deposition of buffer layer and formation of high-quality heterojunction. Fig. 1(e) shows that the film has excellent adherence to FTO substrate. It is worth noting that for kesterite copper zinc tin sulfoselenide $Cu_2ZnSn(S,Se)_4$ (CZTSSe) solar cells on FTO substrate, a MoO_3 interfacial layer between absorber and FTO is needed to faciliate grain growth and improve device performance[14]. For CISSe solar cells here, a MoO_3 interfacial layer significantly reduces device performance (Fig. S2), indicating different grain growth mechanism. The excellent adherence and grain growth of CISSe on bare FTO substrate indicates that an interfacial layer between CISSe and back contact is not necessary, which is an advantage for transparent CISSe solar cells.

Fig. 1(f) shows the XRD patterns for CISSe absorber on FTO substrate. Except for the diffraction peaks of FTO, other diffraction peaks can be assigned to chalcopyrite $CuInSe_2$ phase (JCPDS#40-1487) with a preferred orientation along the (112) plane. The crystalline size of CISSe calculated from the (112) diffraction *via* Scherrer equation is 65 nm. The large

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Received 25 MAY 2023.

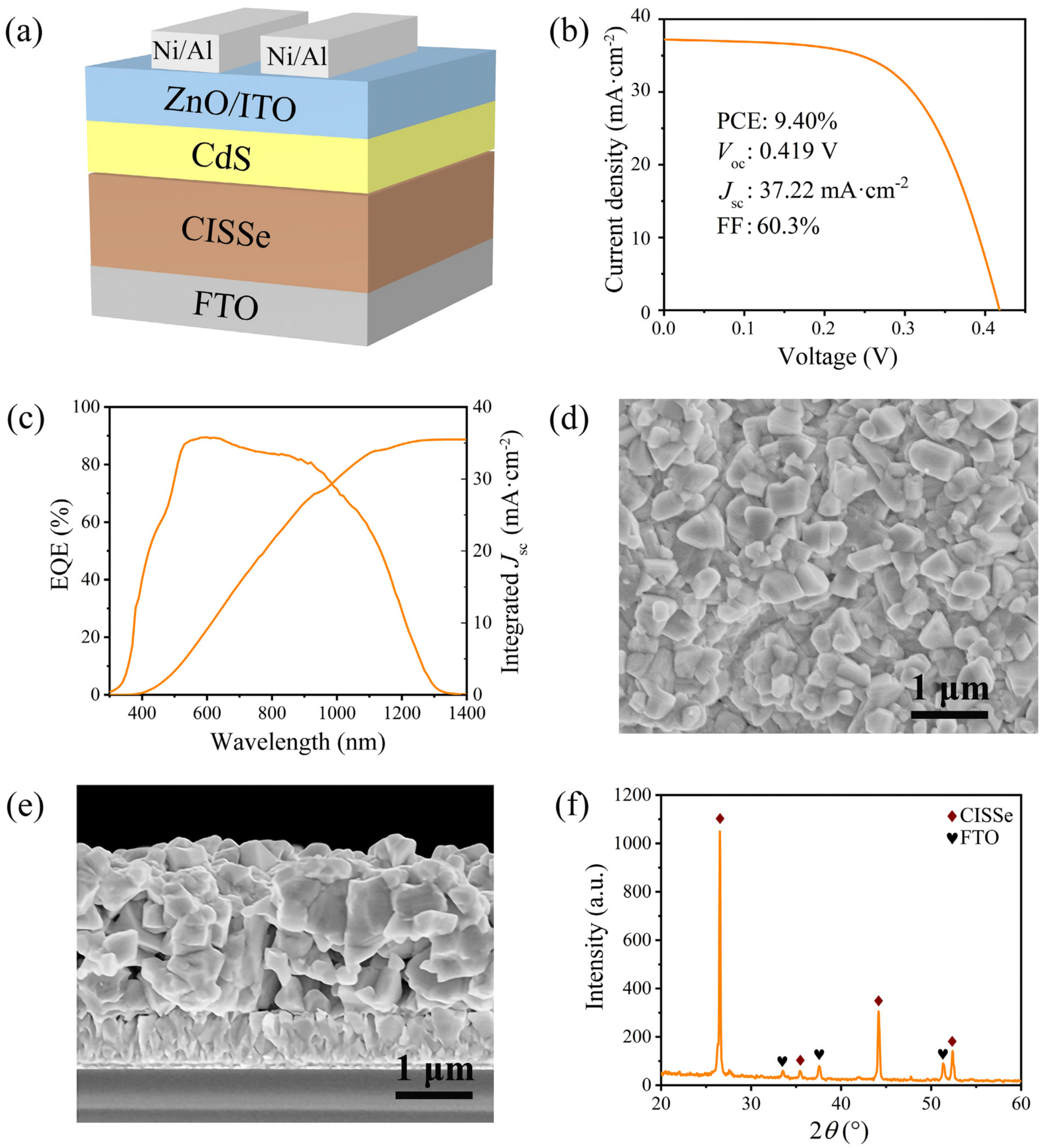

Fig. 1. (Color online) (a) The structure for CISSe solar cells. The *J-V* curve (b) and the EQE spectrum (c) for the best CISSe solar cell on FTO. Inset: extraction of the bandgap (E_g) from the EQE spectrum. The top-view (d) and cross-sectional (e) SEM images for CISSe film on FTO. (f) The XRD patterns for CISSe film on FTO.

crystalline size confirms the high quality of CISSe film, which is consistent with the SEM results. The high-quality absorber film benefits from the direct phase transformation in grain growth[15], which can greatly reduce grain boundaries and charge recombination. The conductivity of FTO (Table S1) showed small change after selenization, indicating a high tolerance of FTO to the selenization temperature.

Compared with devices on Mo substrate, the efficiency for CISSe solar cells on transparent FTO substrate is relatively low. There is still much room for improving the performance of these FTO-based chalcopyrite devices, e.g., introducing alkali metal ions to facilitate grain growth, and using Ga gradient to enhance V_{oc}[16,17]. These strategies will be conducted in our future work to further improve the device performance.

Acknowledgments

This work is supported by the National Natural Science Foundation of China (22075150) and the National Key Research and Development Program of China (2019YFE0118100). L. Ding thanks the National Key Research and Development Program of China (2022YFB3803300), the open research fund of Songshan Lake Materials Laboratory (2021SLABFK02), and the National Natural Science Foundation of China (21961160720).

Appendix A. Supplementary materials

Supplementary materials to this article can be found online at https://doi.org/1674-4926/44/8/080501.

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