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LETTER • OPEN ACCESS

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LETTER

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^{*} Authors to whom any correspondence should be addressed.E-mail: Leo.choubrac@cnrs-immn.fr and Nicolas.barreau@cnrs-immn.fr**Keywords:** CIGS, PEC, solar cell, PESS, architecture, device, bifacialSupplementary material for this article is available [online](#)**Abstract**

This study introduces a chalcogenide-based thin-film solar cell structure optimized for rear illumination, featuring a thinner, wide-bandgap Cu(In,Ga)S₂ chalcopyrite absorber. Matching the performance of traditional front-illuminated designs, this configuration paves the way for further photoelectrochemical advances thanks to its metallic top layer, which can serve as a versatile grafting platform that is resistant to their operating conditions.

1. Introduction

Chalcopyrite Cu(In,Ga)(S,Se)₂ (CIGSSe) thin-film solar cells, with their adjustable bandgap and high absorption coefficient, are one of the leading technologies in solar energy photovoltaic (PV) conversion, with efficiency reaching 23.6% [1]. Latest developments also make it one of the most promising choices for photoelectrochemistry applications such as CO₂ reduction, since recent efforts showcased promising Faradic efficiencies at low bias potentials [2–4].

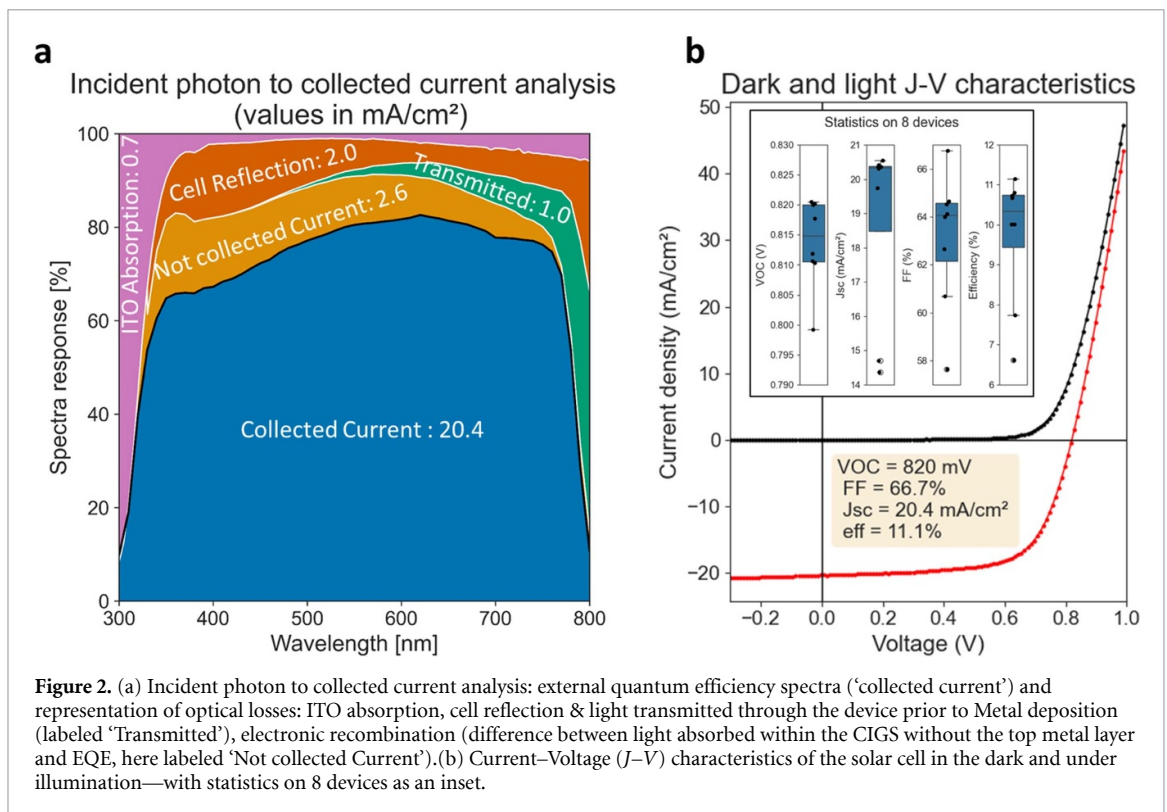
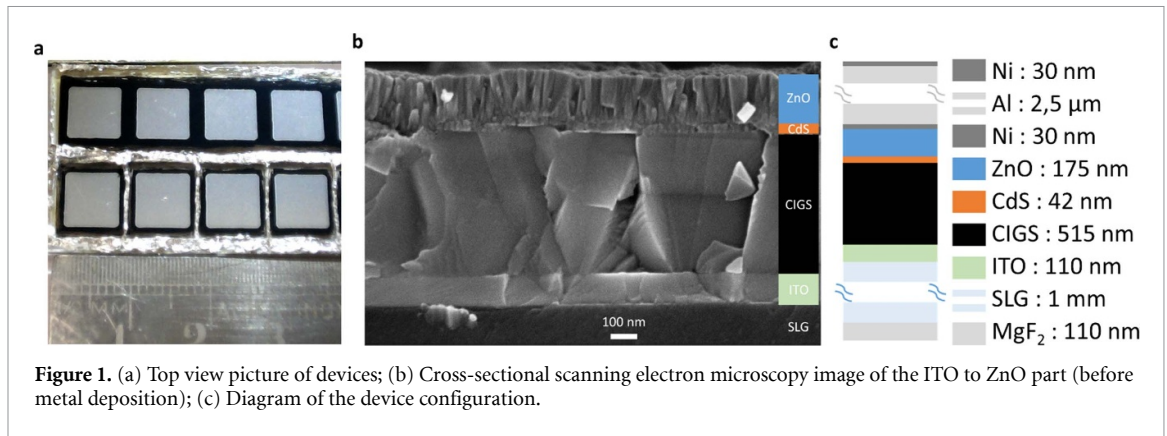
However, the prevalent device configuration relies on an opaque back contact of molybdenum (Mo) and a ZnO:Al (AZO) window layer.

This device architecture, primarily designed for front side illumination, is neither compatible with bifacial or tandem PV applications nor for integrated photorechargeable energy storage systems (PESS) [5]. Furthermore, this standard structure encounters significant drawbacks when used in photoelectrochemical cell (PEC) systems. In fact, firstly, the front side illumination restricts the choice of compatible catalysts and grafting surfaces to non-absorbing materials; secondly, the AZO upper layer experiences limited resilience to solvents used for some catalysts or catalysts hosts deposition, and PEC operating conditions (i.e. reaction with the electrolyte, pH, etc) [6].

Addressing these challenges, significant efforts have explored selenide Cu(In,Ga)Se₂ (CIGSe) based solar cells on a transparent back contact. However, the formation of secondary phases, such as gallium oxide (GaO_x) and In_xSe_y, during CIGSe film growth, compromises the indium tin oxide (ITO)/CIGSe interface [7], leading to substantial photocurrent loss. Strategies including Ga-back grading, Ag alloying or lowered synthesis temperature have failed to solve the problem. To date, the highest efficiency under rear illumination has been reported at 10.9%, only half of the performance that the same device achieves under front illumination (19.8%) [8].

In the present report, we show that one can get rid of the previously mentioned limitations, inherent to the standard device architecture. In fact, the integration of an ultrathin, wide-bandgap pure sulfide (Cu(In,Ga)S₂, CIGS) absorber within a new cell structure (see figure 1) yields PV efficiencies comparable to traditional front-illuminated designs while establishing a robust foundation for future PEC advancements. In addition, the wider bandgap of CIGS compared to its selenide counterpart makes it a promising candidate for unbiased water splitting and CO₂ reduction, with a theoretical open-circuit voltage (V_{OC}) limit of 1.5 V and experimental achievements already nearing 1 V [9].

Here, we present a 0.5 cm² CIGS based solar cell with an efficiency of 11.1% under rear illumination (figure 2(b)) which consists of the following structure (figure 1): MgF₂ (110 nm)/SLG (1 mm)/ITO (110 nm)/CIGS (515 nm)/CdS (42 nm)/ZnO (175 nm)/Ni (30 nm)/Al (2.5 μm)/Ni (30 nm). The glass/ITO



substrate has a sheet resistance of $30 \Omega/\square$. The 515 nm-thick CIGS is grown by a three-stage co-evaporation process as described in our previous work [10], including NaF DDT and PDT (*i.e.* during deposition treatment and post-deposition treatment) with a substrate temperature of 565°C and a $[\text{Ga}]/([\text{In}]+[\text{Ga}])$ ratio (GGI) of ≈ 0.1 , resulting in a 1.57 eV bandgap absorber (according to External Quantum Efficiency (EQE) derivative, see SI-1). The highest efficiencies are achieved for a $[\text{Cu}]/([\text{In}]+[\text{Ga}])$ (CGI) ratio close to 1. Compared to the conventional configuration, note that a significantly thicker i-ZnO (175 nm) is used but no ZnO:Al is deposited as lateral carrier transport is ensured by the metal layer. To prevent ITO degradation, mechanical scribing of cells was avoided. Instead, we employ shadow masks with 0.5 cm^2 openings during ZnO and metal depositions. Note that no photocurrent is collected from areas outside the metallic pads, and the total and active areas are thus 0.5 cm^2 . For applications beyond PV, a wide variety of conductive metals and alloys can be used as the top layer to ensure chemical compatibility with additional processing steps (such as host and catalyst deposition) and operating conditions without impacting the performance. Complete details on the deposition methods for the device fabrication are given in supporting information.

Figure 2(b) presents the J - V characteristics of the best solar cell, together with a statistical representation of all eight devices from the same substrate. The cell with the highest efficiency exhibited an open-circuit voltage of 0.82 V, *i.e.* a V_{OC} -deficit relative to Shockley Queisser (S-Q) theoretical limit of 0.48 V [11, 12]. It is on par with state-of-the-art CIGS using the same buffer under front illumination (supplementary material—table 1) [10, 13, 14], so no additional interface recombination is suspected. The 67% fill factor is a

bit lower than the values reported in these references, mostly due to increased series resistance. Two factors are likely to contribute to it. Firstly, the ITO layer is a less conductive back contact than molybdenum. Secondly, the solar cell reported here has a larger area (0.5 vs 0.16 & 0.2 cm², supplementary material—table 1).

The absence of an AZO layer between the i-ZnO and the metal is not expected to be responsible for this FF loss. Indeed, here the lateral charge transport is ensured by the metal layer, and we use a thicker i-ZnO to keep the CdS protected.

Attempts to reintroduce an AZO layer were nonetheless performed and resulted in solar cells with slightly reduced V_{OC} and FF, but within the process statistical variations. It is not surprising as AZO experiences a low sheet resistance, so its contribution to the series resistance is expected to be very small. Recombination at r-ZnO/AZO or AZO/Ni interfaces are also not commonly reported in CIGS solar devices.

Optical reflection and transmission measurements at different steps of cell stack preparation, combined with the EQE measurements allow us to finely analyze the origins of the current losses (figure 2(a)). Given the 1.57 eV bandgap of our absorber, S-Q theoretical J_{sc} is 26.6 mA cm⁻². SLG/ITO absorption and complete solar cell reflection account for current losses of 0.7 and 2.0 mA cm⁻², respectively. An additional 1.0 mA cm⁻² loss arises from CIGS transmission, due to its unusual thinness. Part of the transmitted light is in the final device reflected by the metal layer, which is then absorbed via a second pass. In the case of the investigated architecture, this latter phenomenon does not significantly affect the current delivered by the cells, but opens up the possibility of significantly thinning out the absorber twice more, provided a highly reflective metal is used. Unlike conventional structures, there is no photon loss due to light absorption by the layers topping the CIGS; which can represent about 1.5 mA cm⁻². Also, the absence of metallic grids, which can shade up to 10% of the cell area, avoids significant losses. Altogether, 86% of the incident light resource (photons of energy greater than the absorber's bandgap) is effectively absorbed by the CIGS layer before reflection by the metal layer. The 14% transmitted would have been a net loss with the prevalent CIGS solar cell architecture, but a significant fraction is exploitable here thanks to the high reflection of the top metal layer.

Comparing CIGS absorption and the external quantum yield shows that 2.6 mA cm⁻² of the photocurrent is not collected. The collected per-generated electron ratio (supplementary material, figure S4) varies linearly from ≈ 0.8 at shorter wavelengths to ≈ 1 near the CIGS absorption edge (*i.e.* when generated close/further to the ITO back contact). This is the typical behavior of an absorber with a limited carrier diffusion length [15] and demonstrates the advantage of using a thin CIGS absorber.

According to the literature, chemical reactions occurring at the transparent conductive oxide (TCO)/CIGS interface result in a 'dead zone' that prevents reaching rear-illumination currents and efficiencies above half of the front-illumination ones. Interestingly here, no indication of such a reaction or dead zone is found as (i) TCO transmission is not degraded by CIGS deposition (supplementary material, figure S4), (ii) neither additional V_{OC} deficit (*i.e.* no additional interface recombination suspected) and (iii) or reduced current are found.

We performed TEM-EDS mapping that reveals the presence of GaO_x at the ITO/CIGS interface. This GaO_x is very thin (<5 nm) and does not form a continuous layer (see supporting information).

In addition, one of the major keys to cutting CIGS manufacturing costs is to increase the absorber deposition throughput [16, 17]. The thinness of the absorbers used here (500 nm vs 2–3 μm in standard configuration) is an important step towards this goal.

To conclude, we report a revised architecture for CIGS solar cells that combines a transparent back-contact with a thinned wide-bandgap absorber that achieves rear-illumination performance on par with front-contact cell. Being topped by a metallic layer, it consists of a versatile platform for PEC or PESS applications.

Associated content

The **supplementary material** includes details on materials and devices fabrication as well as characterizations. It also provides additional experimental data: Bandgap extraction from EQE, additional optical measurements and a table of properties with comparison to the literature

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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Conflict of interest

The authors declare no competing financial interest.

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