

FABRICATION AND CHARACTERIZATION OF Cu-doped Sb₂Se₃ SOLAR CELLS

S. Ferruggia Bonura¹, S. Barbarossa¹, M. Bronzoni², G. Spaggiari², F. Pattini², J. J. N. Barrantes³, M. Buffolo^{3,5}, C. De Santi³, N. Trivellin^{4,3}, M. Meneghini^{3,5}, M. Cannas¹, S. Agnello¹

¹ Dipartimento di Fisica e Chimica Emilio Segrè, Università di Palermo – Viale delle Scienze ed. 17, 90128 Palermo

² Consiglio Nazionale delle Ricerche - Istituto dei Materiali per l'Elettronica ed il Magnetismo, Parco Area delle Scienze 37/A, 43124 Parma, Italy

³ Department of Information Engineering, University of Padova, 35131 Padova, Italy

⁴ Department of Industrial Engineering, University of Padova, 35131 Padova, Italy

⁵ Department of Physics and Astronomy, University of Padova, 35131 Padova, Italy

ABSTRACT - In this work Cu-doped Sb₂Se₃ solar cells were fabricated on commercial FTO substrates by Low Temperature Pulsed Electron Deposition (LTPDE). To investigate on the degradation processes affecting this novel kind of solar cells, their performances including EQE and IV characteristics in dark and in light have been studied during accelerated aging under different bias and/or illuminations stress conditions. Additionally, static and time-resolved photoluminescence characterization have been performed on these samples. In particular, time-resolved photoluminescence is here reported to characterize both defects and recombination processes thanks to the excitation laser tunability.

INTRODUCTION - Antimony selenide (Sb₂Se₃), commonly named as ASe, is a very promising material for high efficiency, cost effective solar cell fabrication due to: [1, 2, 3]: high absorption coefficient ($>10^5 \text{ cm}^{-1}$) in the 400 – 1000 nm range; near optimal bandgap ($\sim 1.2 \text{ eV}$) for solar energy conversion; both constituting elements (Sb and Se) are low toxicity, abundant on Earth and inexpensive ones. Due to above features, ASe cell could be able to reach a theoretical photon conversion efficiency of 32.2%; also, ASe allows flexible, thin film solar cell fabrication [4], that nowadays are becoming more and more important technical solutions in building applications. Sb₂Se₃ is a quasi-1D material in which atomic chains are bonded in ribbons by covalent bonds but they are stacked together by weak Van der Waals forces. Its crystal structure [5] is reported in Fig. 1. A typical ASe cell has the structure depicted in Fig. 2 (not in scale) [6, 7].

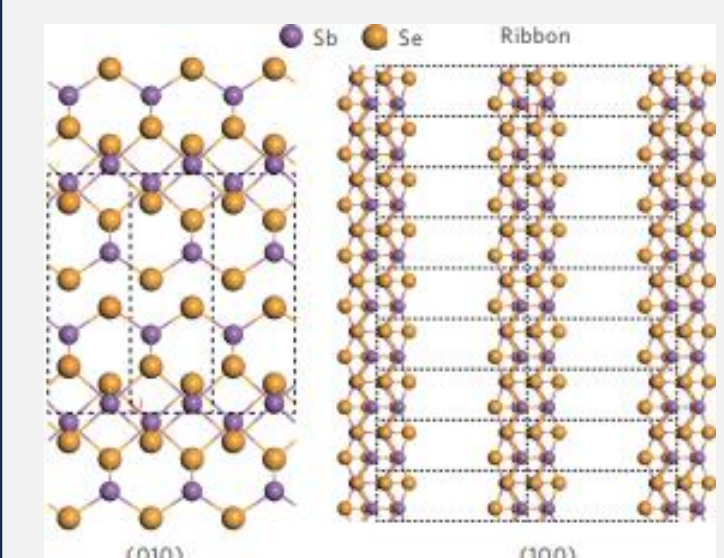


Fig. 1

HOW TO IMPROVE THE ASe-based SOLAR CELL PERFORMANCE?

Recombination processes due to traps originated by different crystal defects severely reduce the open circuit voltage (V_{OC}), and the power conversion efficiency (PCE), that is also strongly influenced by different layer thicknesses, interface engineering, etc.

Both physical and electrical characterization of complete ASe solar cells is needed to both improve cell PCE and to assess reliability with respect to ageing and environmental solicitations.

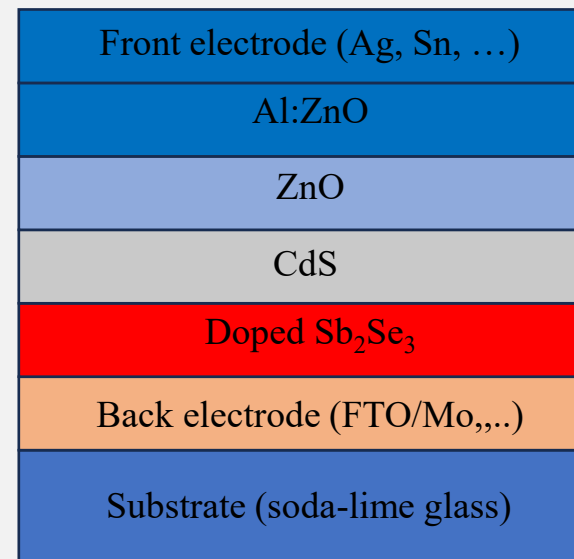
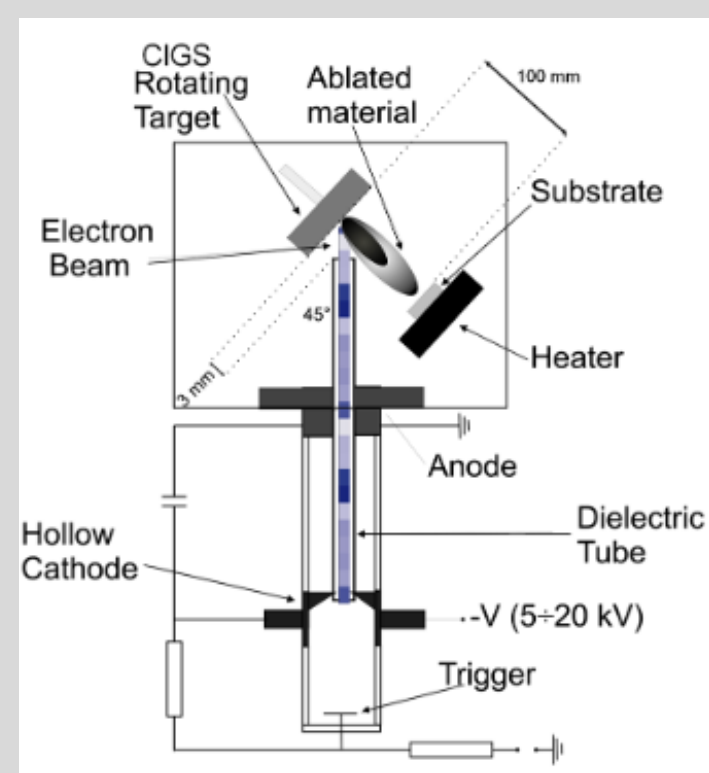


Fig. 2

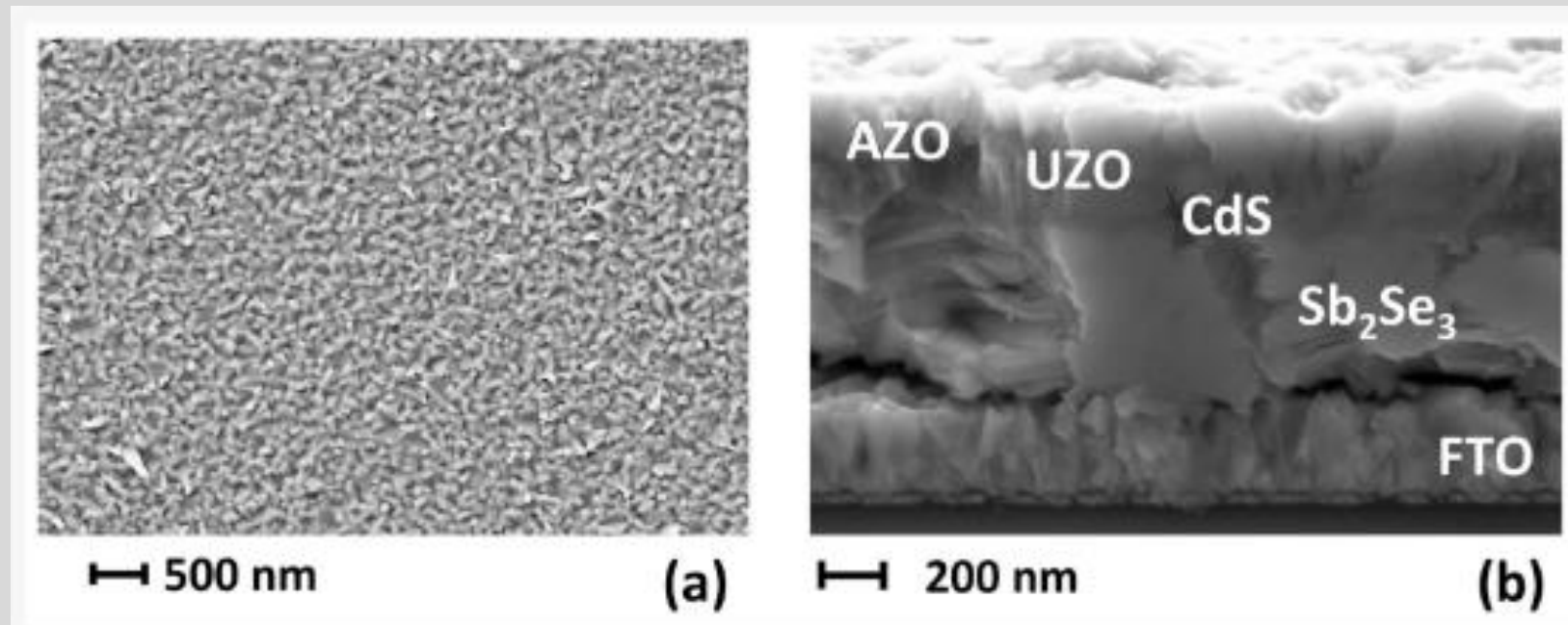
Cu-doped ASe SOLARE CELL FABRICATION by LT-PED - ASe solar cells were fabricated starting from a $2.5 \times 2.5 \text{ cm}^2$ -wide commercial glass slice coated with fluorine tin oxide (FTO), that is a transparent conductive oxide and constitutes the rear electrode of cells [9].

Then a $1.1 \mu\text{m}$ thick copper-doped antimony selenide (Cu-doped Sb₂Se₃) thin film was deposited as absorber layers in photovoltaic solar cells using the low-temperature pulsed electron deposition (LT-PED) technique, starting from Sb₂Se₃ targets where part of the Sb was replaced with Cu.

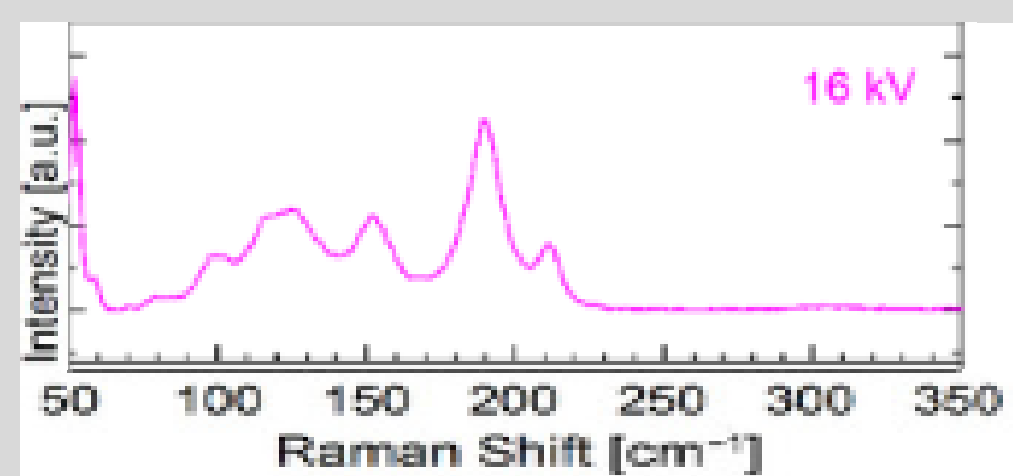
The deposition was performed by using a high vacuum chamber equipped with a PEBS-20 commercial source (supplied by Neocera Inc., Beltsville, MD, USA), pumped down to a base pressure of $\sim 2.0 \times 10^{-4} \text{ Pa}$. The pulsed e-beam was ignited at a discharge voltage of 16 kV. Pulse repetition-rate was fixed at 9 Hz. During the deposition process, Ar gas (5 N purity) was introduced at a pressure of about $3.0 \times 10^{-1} \text{ Pa}$ for igniting the electron beam and stabilizing the beam propagation towards the target.



Schematic representation of the Pulsed Electron Deposition technique.



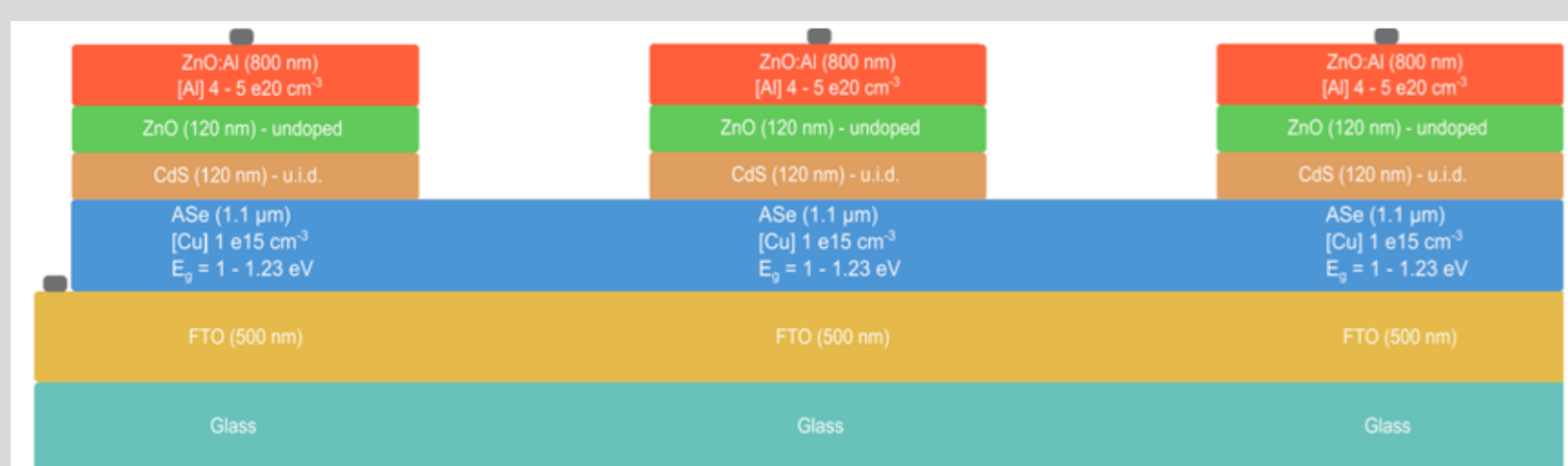
(a) SEM micrograph of the Cu:Sb₂Se₃ surface of an Ase-based solar cell and (b) the corresponding cross-sectional image.



Raman spectrum of a Cu-doped Sb₂Se₃ thin film deposited by LT-PED at 16 kV accelerating voltage.

A thin (120 nm) cadmium sulfide (CdS) film was deposited on the ASe layer then coated, respectively, with a 120 nm undoped zinc oxide (ZnO) and an 800 nm thick, $4 - 5 \cdot 10^{20} \text{ cm}^{-3}$ Al-doped ZnO (AZO); the cell was then completed by the upper electrode after the photolithographic process applied to obtain defined circular cells.

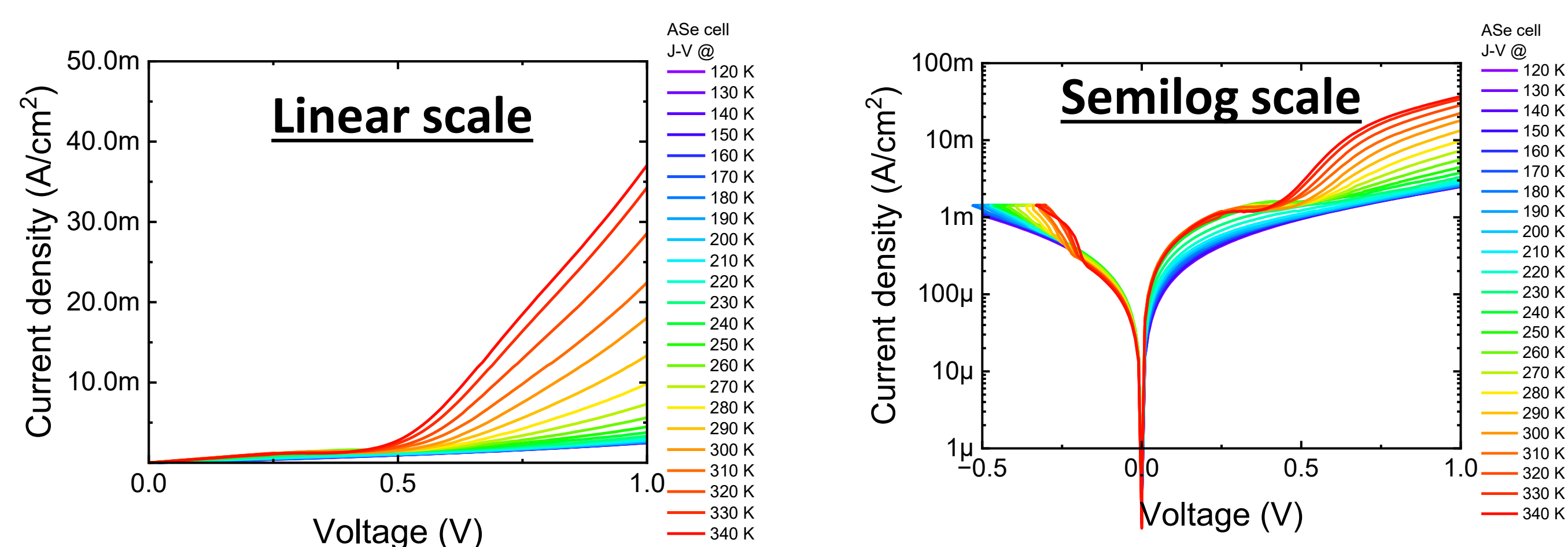
The full structure of the fabricated sample resulted:



ASe SOLAR CELL CHARACTERIZATION

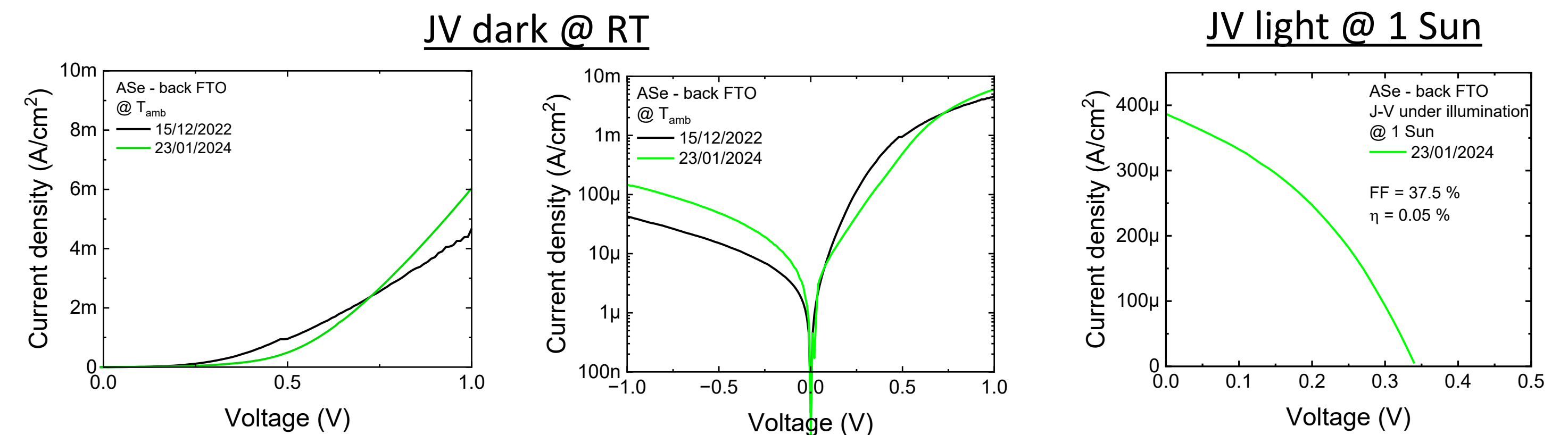
Dark JV in temperature

Temperature range 120 K – 340 K



- Electrical properties of the cell are **temperature dependent**:
 - as T increases $\rightarrow$ **leakage current increases** (enhanced thermally-assisted conduction processes)
 - $\rightarrow$ **series resistance (R_s) decreases** (possible improved dopant ionization).

One year comparison of electrical characteristics



- Change in the electrical characteristics after 1 year (**no stress applied**).
 - Dark: increase of the turn on voltage and of the leakage

STATIC AND TIME-RESOLVED PHOTOLUMINESCENCE CHARACTERIZATION OF ASe CELLS - The physical characterization of above described ASe solar cells was performed by the research group of the Dipartimento di Fisica e Chimica "Emilio Segrè" of the Università di Palermo by the nondestructive technique of photoluminescence spectroscopy.

Photoluminescence spectroscopy [10] is based on the sample-to-test irradiation by a suitable wavelength light (Fig. 3), and related emission components, obtained by a suitable grating, recording in the related photoluminescence spectrum; by the evaluation of emitted wavelengths, information about internal sample electronic transitions, due to related band levels, are gained. This technique allows to detect, in particular, trap levels, from which it's possible to evaluate related causes (defects).

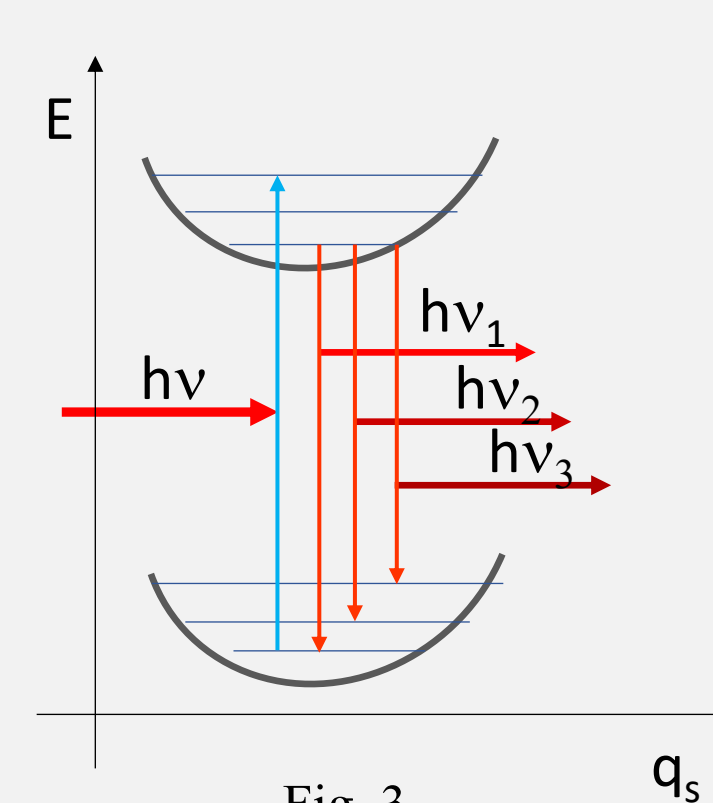


Fig. 3

Both static and time resolved photoluminescence tests were performed on the above ASe cell sample, whose photo is reported in Fig. 4.

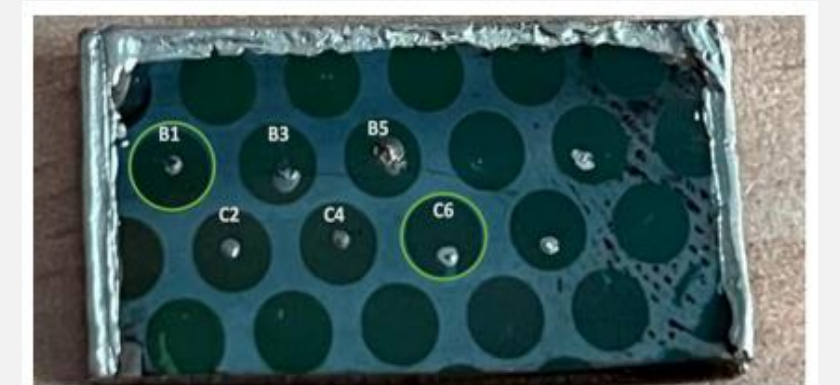
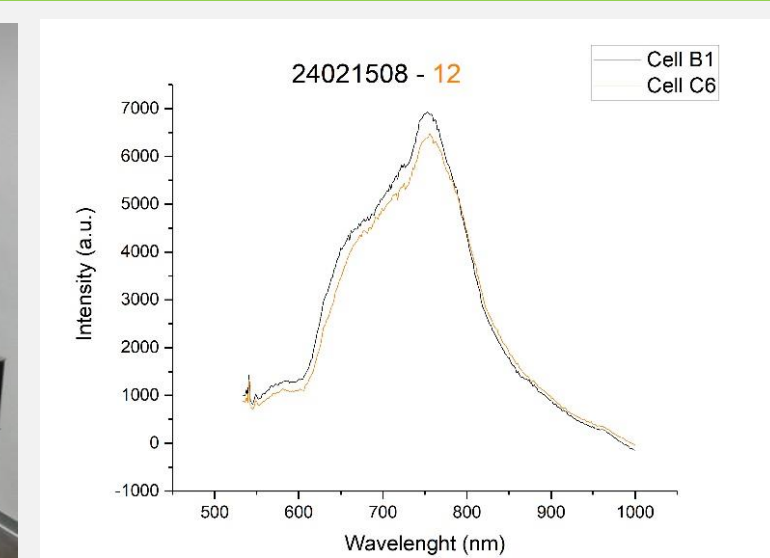


Fig. 4

Static photoluminescence measurements were performed by both the Horiba Raman spectrometer at the Raman Laboratory of the Advanced Technologies Network (ATeN) Center of the Università di Palermo, in microluminescence mode (Fig. 5)



Fig. 5



Excitation 532 nm; B1 and C6 cell spectra have very similar shapes.

The same 532 excitation measurement was also performed with the time-resolved spectroscopy system (Fig. 6) used in static mode

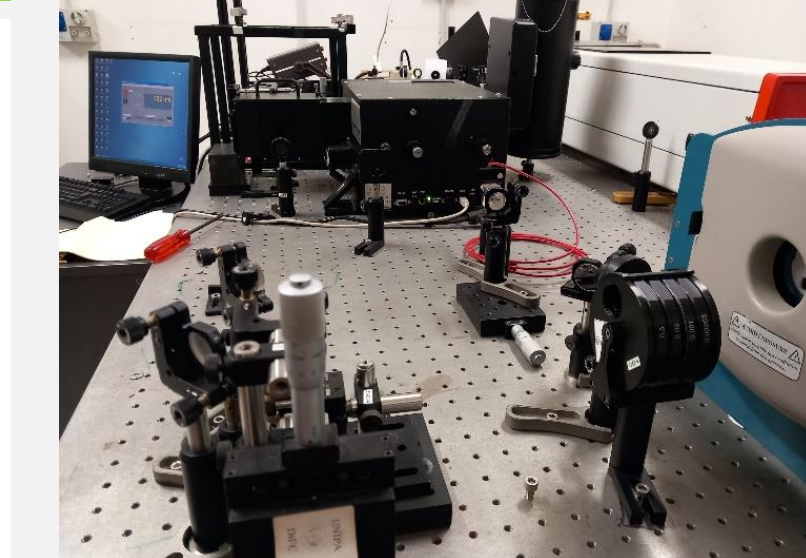
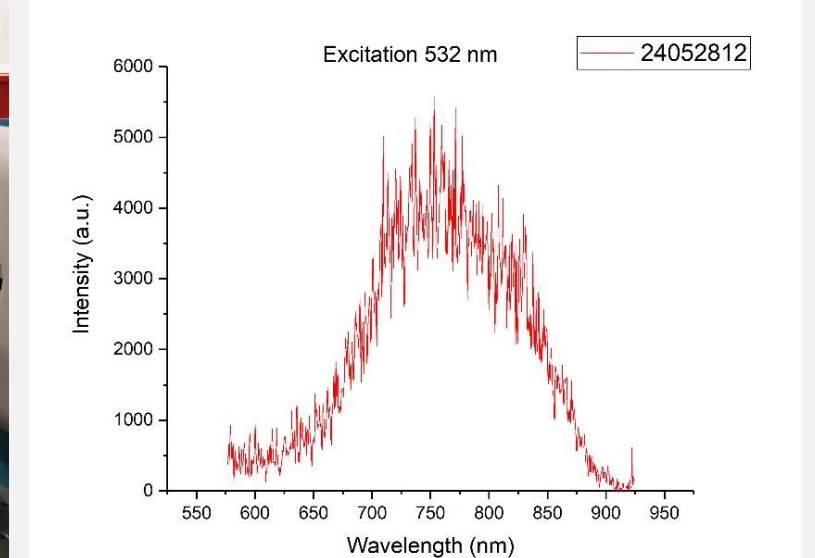
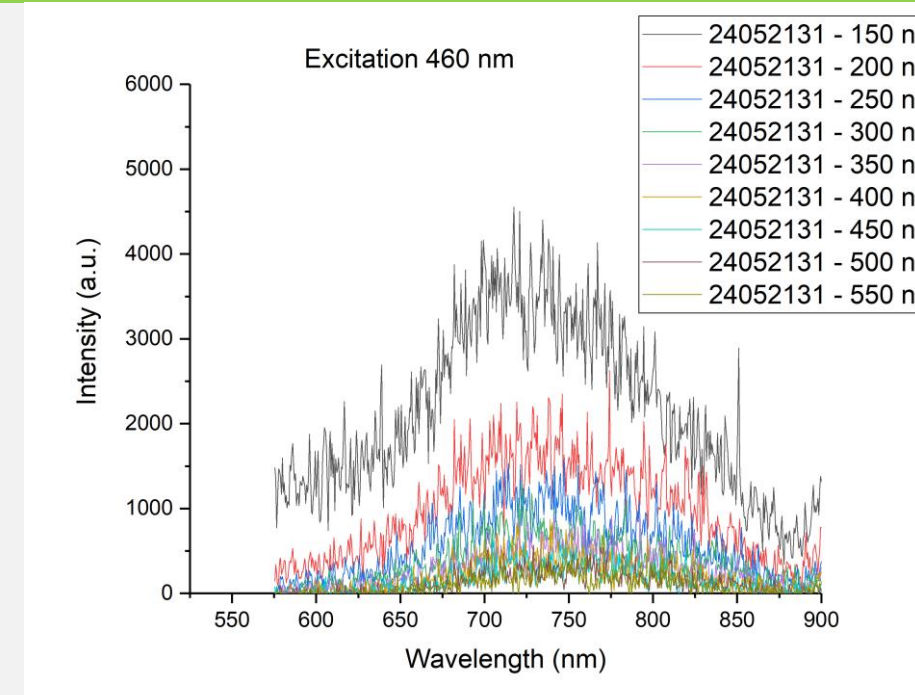


Fig. 6

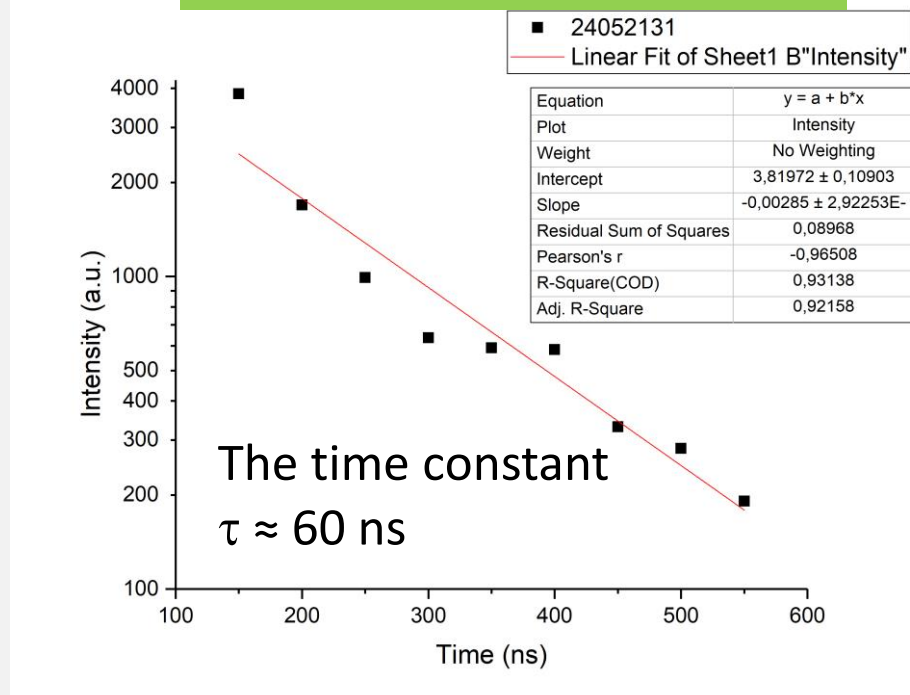


Micro- (left) and photoluminescence (right) spectra have about the same band and very similar shapes

Time-resolved photoluminescence characterization:



Peak intensity decay vs. time



Detected photoluminescence explanation hypothesis: emissions mainly from the undoped ZnO layer due to deep level states produced by oxygen both vacancies and interstitial atoms.

CONCLUSIONS

- Complete ASe solar cells were fabricated according to the structure: Glass/FTO/Cu:Sb₂Se₃/CdS/ZnO/AZO.
- Fabrication processes are well established and allow repeatable products.
- Fabricated cell electrical characterization was performed in dark conditions at different temperatures and it allowed to evaluate the temperature behaviour of some electrical components of the cell equivalent model;
- Accelerated aging tests under different bias and/or illuminations stress conditions were also performed.
- Both static and time-resolved photoluminescence characterization of cells was started; information about possible defects produced by the fabrication processes were obtained; due to the complexity of the structure, much more measurement at different excitation wavelengths are needed to gain a deep understanding of the physical structure of different layers.

ACKNOWLEDGMENTS - This research work was developed inside the NEST – Network for Energy Sustainable Transition (identifier code PE0000021) project.

REFERENCES

- J. Tao et al., Solar Energy Materials and Solar Cells, 197, 2019.
- A. Mavlonov et al., Solar Energy, 201, 2020.
- I. Cano et al., ACS Appl. Mater. Interfaces, 14, 2022.
- X. Liang et al., ACS Energy Lett., 8, 1, 2023.
- Y. Wang et al., J. Phys. Energy, 4, 2022.
- F. Pattini et al., Solar Energy Materials & Solar Cells 218, 110724, 2020.
- S. Moujoud et al., Optik - International Journal for Light and Electron Optics 303, 171723, 2024.
- M. Huang et al., ACS Appl. Mater. Interfaces, 11, 2019.
- G. Spaggiari et al., Int. J. Mol. Sci., 23(24), 15529, 2022.
- M. Cannas, L. Vaccaro, in "Spectroscopy for material characterization", S. Agnello ed., Wiley, 2021.

CONTACTS:

simonpietro.agnello@unipa.it; simone.barbarossa01@unipa.it; marco.cannas@unipa.it; salvatore.ferruggiabonura@unipa.it

jessicajazminenicole.barrantes@phd.unipd.it;

giulia.spaggiari@cnr.it; francesco.pattini@cnr.it; matteo.bronzoni@cnr.it