Universitat Autònoma de Barcelona
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Nanopto

On Improving the Efficiency of Organic Photovoltaic Devices: Novel Strategies

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Abstract

Recent advances in Organic Photovoltaics have brought this field to the forefront of renewable energy research. Organic photovoltaic devices have gained plenty of attention thanks to their chemical tunability, light weight, flexibility and increasing efficiency. Being roll-to-roll compatible, the manufacturing processes needed to produce such devices are easily scalable, and their low material usage and low embedded energy make for a sustainable commercial technology that can contribute to solve our current energy crisis. This technology, however, still faces several obstacles that prevent its widespread development. On the one hand, low charge mobilities and relatively modest absorption coefficients limit the final solar cell efficiency, while the complex synthetic routes of the best performing materials limit their economic viability. On a device level, the technology faces different issues related to limited thermal stabilities, as well as tandem fabrication difficulties, to name but a few.

This thesis explores three novel strategies focused on improving the overall efficiency of organic photovoltaic devices, specifically designed to increase light absorption, enhance charge carrier mobility and reduce thermalization losses. In order to tackle such an ambitious research program, we first developed a characterization platform that enabled us to measure organic photovoltaic devices in a highly reproducible manner and between 5 and 10 times faster than sequential methods. This platform consists in the combination of hardware and software that enables any user to characterize a photovoltaic device in a fully automated procedure reducing human errors, homogenizing the results amongst all different users, and saving a significant amount of time and effort. This platform is described in Chapter 1, with further developments also included in other chapters. After this technological chapter, the thesis then details the three approaches to improve efficiency.

Chapter **??** demonstrates the incorporation of photonic structures within photovoltaic devices as means to increase absorption. Specifically, we show that the charge transfer state absorption of organic photovoltaic devices based on P3HT:PC61BM and PBTTT:PC71BM, can be enhanced by nanostructuring their active layer in the shape of a 2D photonic crystal. This absorption enhancement results in an increased EQE, which is especially pronounced below the band gap of the blend. While the improvement is modest for solar cells, this technology results in high

performing infrared photodetectors.

Chapter ?? is based on the hypothesis that charge carrier mobility can be increased by raising photoactive material temperature. To evaluate this, we monitor solar cell performance as a function of active layer temperature. We show that the power conversion efficiency (PCE) is enhanced with temperature, and this effect is especially pronounced on thicker active layers, as one may expect if mobility was the limiting performance. We studied the performance of 10 different photoactive blends at different temperatures, noting that only some of those systems exhibit reversible changes with temperature. In order to understand this behaviour, we investigated in more detail devices made of PBDBT:ITIC, showing that this system has a temperature resistant microstructure and greatly improved charge transport at high temperatures, ultimately translated to better PCE. To perform these experiments, we designed and manufactured a custom experimental setup that is able to characterize our devices, while accurately controlling the active layer temperature.

Finally, the last two chapters demonstrate the feasibility of a, seemingly unexplored, tandem solar cell concept based on spectral splitting, which we named RAINBOW solar cell. This architecture combines a wavelength dispersive optical element and a monolithic in plane (c.f. stack in normal tandem) multi-cell layout with a discrete E_g gradient. In Chapter ?? we study this geometry from a theoretical point of view, performing simulations and calculations with ideal and real materials that establish the scaffolding of RAINBOW solar cell theory, as well as guidelines for material selection. While in Chapter ?? we build an experimental setup capable of characterizing and optimizing real RAINBOW solar cells. The calculations and real measurements are in good agreement, with RAINBOW solar cells providing up to 34% higher efficiency than the best performing sub-cell. As a final proof of concept, we developed partial deposition techniques to manufacture a fully functional monolithic horizontal tandem RAINBOW device.

Acknowledgements

First of all I would like to thank Mariano, not only for being the best supervisor one could ever wish for, but for being a companion on this journey, treating me like an equal from the very beginning, while guiding me on this path full of wonders. He has always known when to let my imagination fly and when to bring me back to earth, even if he himself struggles to stay on the ground sometimes. He is unique, a unicorn we could say, and since I'm a rainbow we were **DETERMINED** to get along.

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Gràcies Putu Pau, perquè sí, a la meva tesi havia d'estar escrit això en algun moment, el millor és aprofitar-ho per agrair-te tot el que ets. No només ets un labmate excel·lent i brillant, sinó que ets un company de vida, i no importa que estiguem ara mateix a 6000 km que sempre et portaré amb mi. Per això, vull aprofitar la validesa legal d'aquest document per atorgar-te el títol oficial de **PUTU PAU**. Gràcies Miqueló, perquè treballar amb tu ha estat un plaer, però compartir algo tan íntim com una casa amb el millor company de pis que un podria desitjar ho eclipsa tot. Jose, you do not know how much you have changed my life, really, I'm have been gargantuanly lucky to have you as a deskmate, and now I'm really lucky to have you as a friend. Nadia, como una persona puede promover tal vinculo en en tan poco tiempo? Te echamos de menos. I want to thank Prof. Dr. Koen Vandewal and Dr. Quan Liu, for giving me the opportunity of working with them and being there to help me in really troublesome times.

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Francesco, perche hai un cuore gigante. Albert, porque

Finally I would like to thank you (the reader) for giving your time to this humble book. I hope you enjoy reading this thesis as much as I have enjoyed writing it :)

- My supervisor
- My second supervisor
- Other researchers
- My family and friends

‘Quote text here.’

Guy Quoted

Contents

Chapter 1

Automation in OPV Characterization

Abstract

This chapter is focused on the development of experimental setups that accelerate, systematize and automatize the characterization of various optoelectronic devices within our group. This subject is of great interest for a majority of our group members, myself included, mainly because it directly increases the quality and reliability of our work, besides greatly reducing the time and effort involved in the entire characterization process.

This scope of this chapter is to provide insight on two complementary solar cell characterization experimental setups, developed and optimized during this thesis: a solar cell automated demultiplexer, embedded in a JV characterization setup, and an robotic EQE measurement setup. The first one consists of a demultiplexing prototype circuit board (PCB) that automatically connects the multiple cells of one substrate to the source measure unit (SMU) through a single BNC connector, to enable noise free, fast and accurate JV measurements. This is combined with a LabVIEW based application, which coordinates the PCB with the SMU, while processing all the data and generating a full report with ready to present results.

The second setup is a robotic EQE measurement system, consisting of a supercontinuum laser and a monochromator, which provide a wide wavelength operation range, in combination with

an XZ stage that places our pre-scale up substrate solar cells on the laser spot for their EQE characterization. This is combined with the previous demultiplexing board, in order to contact each cell during the EQE measurements, and a powerful piece of LabVIEW software that orchestrates the entire operation.

These setups are designed to be easy to assemble, reliable and to have a low cost, by using readily available parts combined with affordable manufacturing techniques, so that they can be easily implemented on different environments.

1.1 Pika JV Characterization Setup

Most organic solar cell manufacturing within our group is done keeping process scalability in mind, by using scalable roll-to-roll compatible techniques such as blade coating combined with pre-scale up substrates, which are bigger than common spin coater glass substrates. These bigger substrates allow us to quickly evaluate the effect of different solar cell fabrication parameters (compositional studies, annealing temperature gradients, thickness gradients, horizontal tandems...), requiring much fewer substrates. This is achieved by combining our gradient manufacturing approach, which varies a given parameter along the length of a substrate, with discrete electrode deposition, which allows us to sample our substrate at different points, resulting in solar cells with a range of values for that given manufacturing parameter.

The main problem with such substrates is that the increased amount of cells per substrate easily adds up, increasing characterization time and human error significantly. As an example, a regular fabrication batch consists of up to 8 scale-up pixelated substrates, resulting in a total of 192 cells manufactured in just over two days. Characterizing such a batch manually used to take at least 4 h of continuous manual measurement, plus around 8 h of raw data processing and reporting, amounting to a work day and a half just for cell characterization. Besides, the reproducibility of connecting the substrate ITO contacts through nickel plated alligator clips is far from the best, with frequent poor connections leading to open circuit cells that need to be

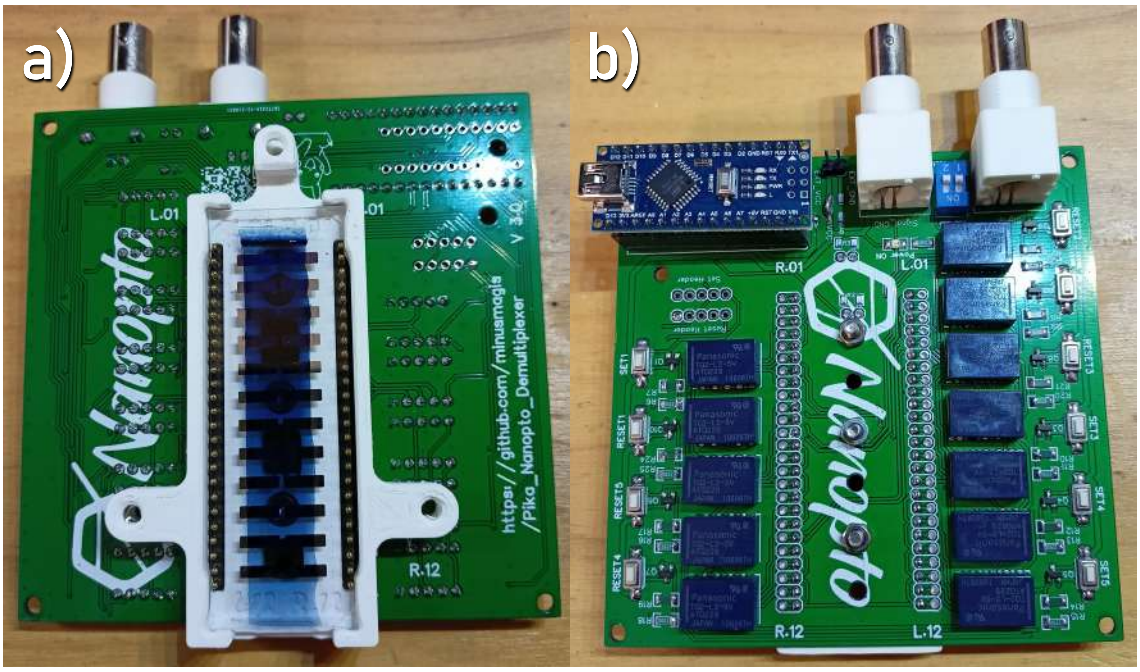

Figure 1.1: Pika Demultiplexing Board (v3.0) as seen from the top (a) with a solar cell placed on the custom 3D printed holder, and from the bottom (b), with the demultiplexing relays, the Arduino microcontroller and the BNC connectors for the signal and signal ground.

remeasured.

One of the best ways to increase the reliability and efficiency of this process is by implementing some degree of measurement automation. In that regard, we have developed a solution consisting of two main parts that take control of both the measurements as well as the data processing. These are: A custom PCB with an automated multiplexing unit and a 3D printed custom cell holder, which is perfectly adapted to our pre-scale up substrates to increase connection reliability (Figure 1.1). And a JV characterization and data processing software tool with report generation capabilities, to perform all the measurements, the calculations, and to generate the pertinent reports.

The combination of these two solutions resulted in a great reduction on the required characterization time and effort, with an 8 device batch taking only 1 h of characterization plus 8 minutes of report generation, representing a reduction in characterization time of around 92%. This setup does not only accelerate the pace of our current measurements, but it allows us to be much more ambitious with our experiments, giving us the ability of measuring more samples on a given

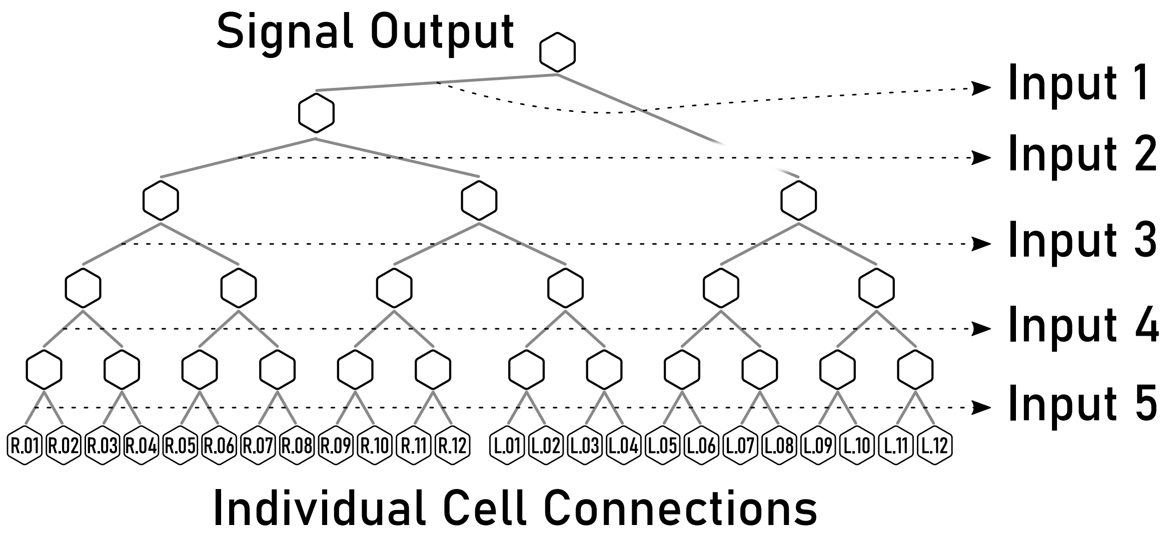

Figure 1.2: Binary tree depicting the interconnection of every individual cell to the signal output through binary connections, with each of the 5 levels being controlled by an individual inputs.

time interval. Additional advantages include: reducing the amount of time the solar simulator lamp needs to be on, resulting in lower energy consumption, and degradation; increasing cell connection reliability, thanks to its gold coated pogo pins, which perform much better than nickel plated alligator connectors; And finally, being automatic and remotely actuated, it allows for the sample to be measured on inaccessible locations.

Most measurements involving pre-scale up substrates have been performed on different versions of this setup. Besides, this setup has seen a good adoption within the group, with most group members using it exclusively for their measurements, as a consequence of its ease of use and reliability. Both the demultiplexer board and the JV characterization software have been fully developed within the scope of this work, undergoing a process of continuous optimization through several iterations, during which the demultiplexing board has been further adapted to many other experimental contraptions.

1.1.1 Circuit Design

The Pika demultiplexer PCB is based on a multiplexing binary tree that can separately connect each individual cell contact to a common signal output connector. This binary tree consists on a sequence of bistable relays sequentially arranged, which demultiplex the the different cell signal channels into one single output, to be connected to the source meter (Figure 1.2).

Our specific relay tree consist of 23 different relays connected on 5 different levels, which allow us to control the entire relay tree with just 5 binary inputs, one for each level. However, as the name implies, bistable relays have two stable states, so they require an additional negated input that actuates the relay to reset its state.

Instead of resetting every single relay on each cell change, to lengthen relay contact lifetime, we added an individual reset input for each relay level to reduce the number of reset cycles. As a result, the setup requires the use of 10 binary inputs, instead of 5, to control the 23 different relays. Such low requirements in terms of power output and number of logical inputs make this system ideal to be operated by a simple, small and cheap controller, such as an Arduino.

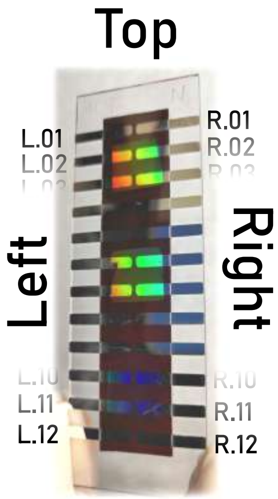

Figure 1.3: Pre-scale up substrate cell naming convention.

Using mechanical relays instead of any of the available solid-state alternatives results in a perfectly ohmic, non-rectifying electrical connection between the sample and the source meter unit. This allows for the measurement of a great variety of devices operating in any of the four power quadrants, both in alternating and direct current (AC and DC) regimes, and with a wide current range of up to 1 A, the maximum rated current for these small relays. At the same time these relays provide a really low ON resistance connection of less than 50 mΩ, while allowing for high frequency measurements without any major signal distortion.

The resulting relay tree circuit (schematics found in **??**: **??**), is controlled with 5 digital inputs and their respective negated signals, which can be thought of as 5 input bits. Such a system

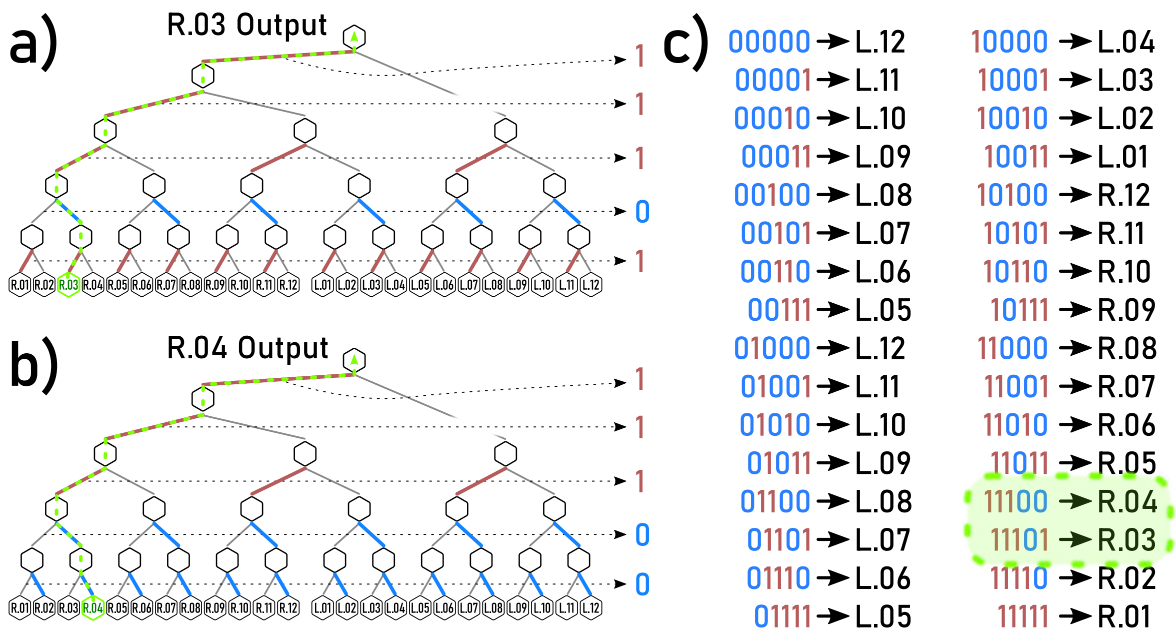

Figure 1.4: Binary tree cell selection operation with two different connection exaples, (a) for a connection to R.03 and R.04 (b), together with the cheat sheet that relates every possible state with the resulting cell connection (c).

can have up to 32 binary states, some of which are redundant in our specific case because of the unbalanced nature of our binary tree (Figure 1.2). Each possible binary state sets the relays so that one individual cell is connected to the "Signal Out" BNC connector, which is itself connected to the source meter. The individual cells, or pixels, are labeled arbitrarily according to their location within the substrate, following a well established protocol (Figure 1.3). In order to electrically connect to a given cell we have a cheat sheet with all the possible binary combinations and the resulting cell connections (Figure 1.4 (c)). As an example, if we want to select pixel number *R.03*, we will need to set our relay layers to, from top to bottom, *11101* (Figure 1.4 (a)). If after cell *R.03* we want to select cell *R.04 (11100)*, we only need to reset relay level 5, instead of resetting the entire relay tree (Figure 1.4 (b)). This operation mode greatly reduces the amount of relay cycles, thus increasing their lifetime and reducing power consumption.

The main advantage of such a simple controlling strategy is that this multiplexer board can be controlled with any controller unit capable of outputting 3.3 V or 5 V logical signals. In our case, we have chosen to use an Arduino Nano, a cheap open source microcontroller with serial port connectivity capabilities, which allow for PC-microcontroller communication, compatible with almost any programming language. Being fully programmable, this microcontroller provides us with a high degree of tunability, resulting on an easy and fast optimization of our operation procedure.

1.1.2 Hardware

In order to connect the demultiplexing circuit to our pre-scale up substrates, we designed a custom 3D printed holder with spring loaded gold plated pogo pins, which provide a good electrical connection between the cell contacts and the circuit board (Figure 1.5).

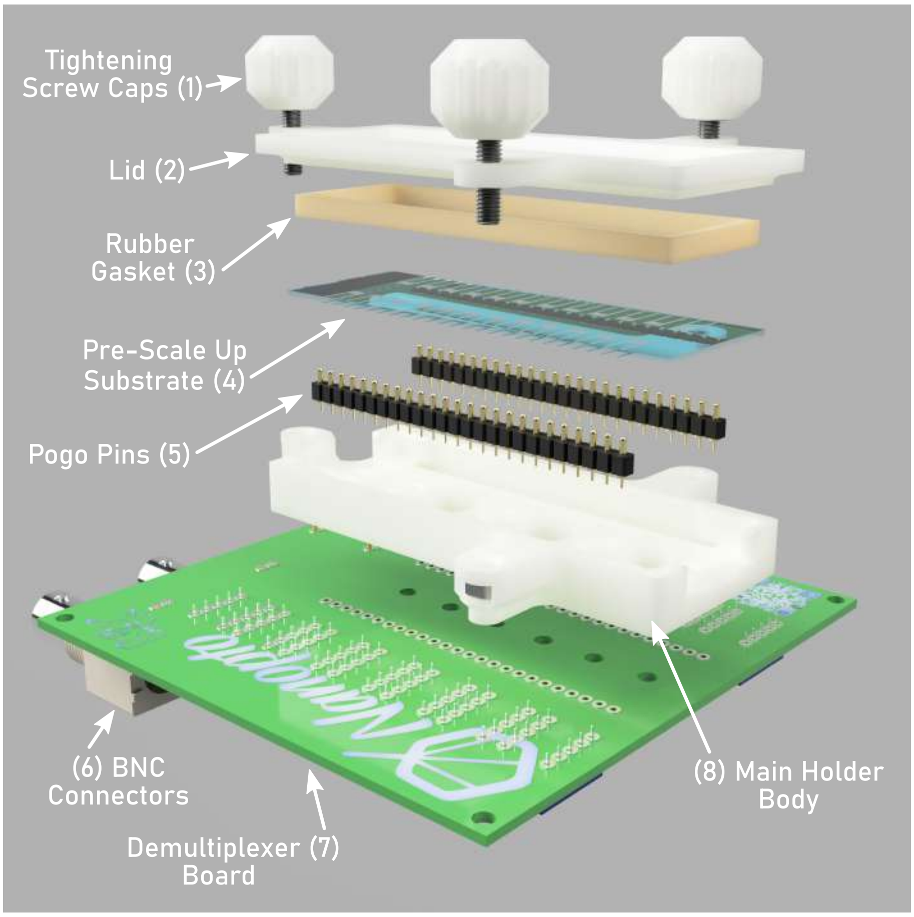

Figure 1.5: Exploded view of the Pika Demultiplexer Board (v3.0) with the most relevant components highlighted.

The optimized version of this setup (v 3.0) consists of a 3D printed holder (8) with a socket for the substrate, with two lines of pogo pins (5) on each side. A lid (2) with a flexible 3D printed gasket (3) is secured against the main holder using hand screw-on knobs, sandwiching the substrate (4) and clamping it firmly against the pogo pins, providing a great electrical connection with the circuit (7). The flexible 3D printed gasket guarantees a conformal contact, avoiding the formation of high stress points and cracks when the substrate is tightly clamped. Older versions of this setup rely on snap fits for substrate clamping, but they are not fully reliable and prone to wear (Figure 1.6).

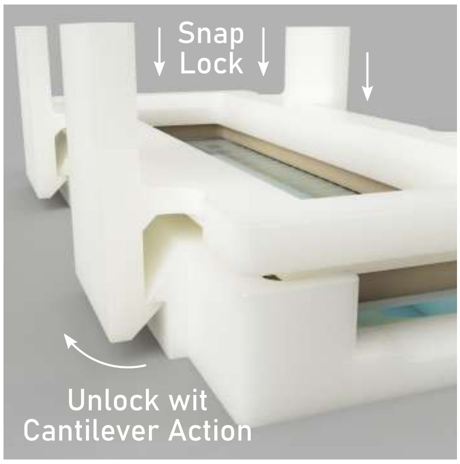

Figure 1.6: Pika Demultiplexer Board old version (v2.5 and earlier) lid clamping mechanism, relying on a snap lock with a press fit junction released with cantilever action provided by the compliance of the 3D printed piece itself.

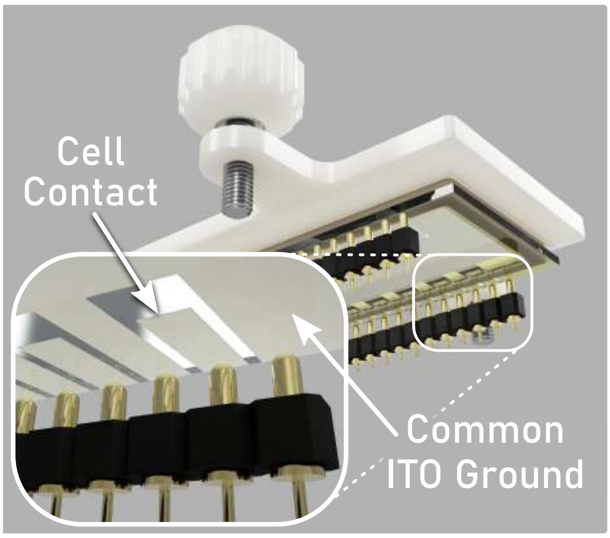

Figure 1.7: Gold plated spring loaded pogo pin cell contact and ground electrical interconnection, to increase electrode resistance homogeneity along the substrate.

The specific ITO pattern of the pre-scale up substrates requires alternating pogo pin connections, where the odd pins connect the common ground ITO electrode with the ground signal BNC connector, wile the even pins connect to each of the individual cells (Figure 1.7). Connecting the same ground ITO electrode in-between each cell contact ensures a minimum resistance path through the common ground ITO electrode, with a high degree of contact resistance homogeneity along the entire substrate.

In early versions of this setup, this entire holder is directly soldered onto the PCB for a strong mechanical connection. This is achieved by pressing a hot header pin through the PCB, into the

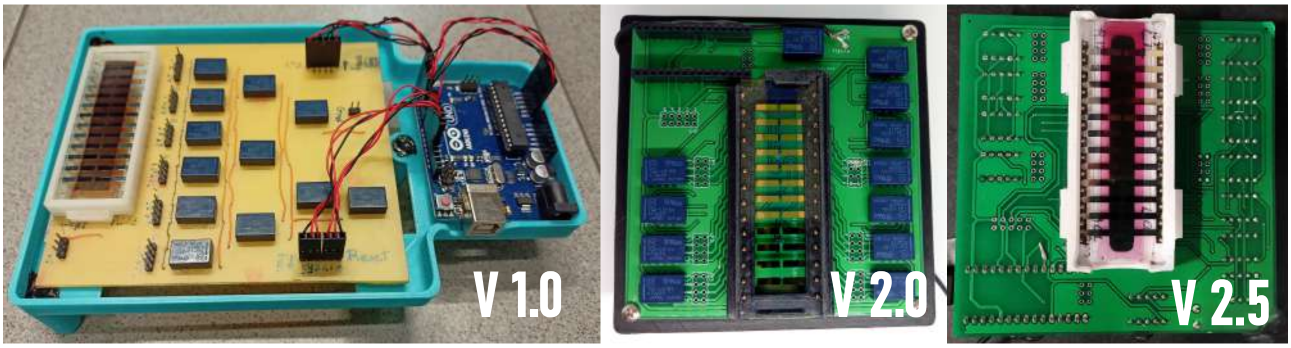

Figure 1.8: Chronological evolution of the previous versions (before v3.0) of the Pika Demultiplexer board.

3D printed part, locally melting it in the process, while firmly clamping the 3D print against the PCB. When the header pin cools down, the 3D print solidifies and contracts against the pin forming a tight bond that is mechanically stable. This clamping solution is more versatile than other adhesive solutions such as epoxy and glue, because it offers a high degree of repairability. In the latest version (v 3.0), however, the 3D prints are directly screwed on the PCB, a solution that provides the highest clamping force and the best repairability, besides being the easiest to implement.

There have been 3 major versions on this hardware, with minor versions inbetween (Figure 1.8), which have continuously added functionalities and fixed bugs, providing higher measurement reliability and better overall user experience with every iteration. The first version, the original crude prototype, was hand crafted in our facilities using the solar simulator as our photolithography setup. As we can see in Figure 1.8, the result is functional but with plenty of room for improvement, relying on a poorly connected external Arduino for control, and without any signal shielding. The second PCB version was professionally made by JLCPCB, with on-board Arduino integration, as well as the addition of alternating ground contacting pins and several extra connectors for temperature and light sensing, with alternating pogo pins fully implemented in v 2.5.

The most recent board revision (v 3.0) has undergone significant fundamental changes including: Relay controlling transistors, which handle the switching of the relays reducing controller power output requirements; Common signal ground line, completely separate from the board ground to minimize noise in high accuracy measurements; Two separate BNC connectors, one for "Signal" and one for "Ground Signal", to further minimize noise; Switch onboard buttons, for manual circuit operation; External power supply option, to power the relays with either the onboard Arduino or a completely separate power supply to further reduce the microcontroller power requirements; Self-test functionality, to check the connection of each cell separately in a fast and reliable manner; Drilled holes for mounting screws; External header pins, for easy external control either 3.3 V or 5 V logic; Substrate labels, to clarify correct substrate orientation; Aesthetic labels with the logo of our group; Online documentation, with all the fabrication files and schematics as well as a QR code link (Figure 1.9).

Figure 1.9: Qr code to access the repository with all the 3D files for the pika demultiplexer, as well as the PCB manufacturing and project files.

1.1.3 Pika Demultiplexer Firmware

The firmware used to control the Pika demultiplexer board is a relatively simple application written in C++. The 500 lines of code are specifically programmed for Arduino, being extensively documented so that anyone, even with little to no knowledge about any programming language, can more or less understand what each part of the software is doing.

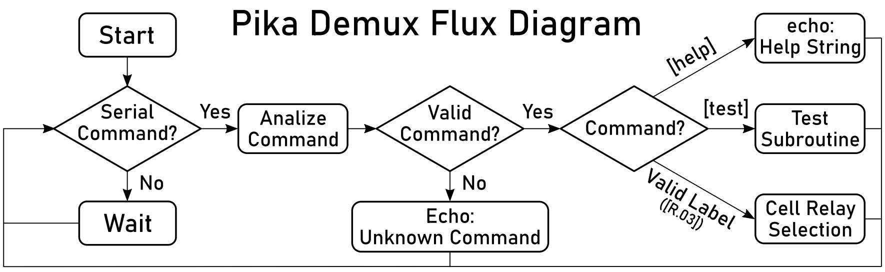

Figure 1.10: Schematic view of the operation of the Pika demultiplexing firmware run by the Arduino to control the demultiplexing board.

As we can see in Figure 1.10, the firmware operation can be broken down in several parts, the most important of which include: The Start Code, the Get Command, through the serial interface, and the Analyze Command, with the command handling. The start code is just a formality that initiates the serial communications between the Arduino and the main PC, where the Arduino identifies itself by sending the following string of characters: `"Arduino Multiplexer Pika"`. In this way, any software connecting to the Arduino can tell it apart from other connected instruments during automatic instrument detection.

After a successful start and correct identification, the Arduino goes on to the next step, where it waits for a serial command. Once it receives a command, it proceeds to the next step where the command is analyzed and executed.

In the analysis phase there are 4 possible outcomes: If we send a valid label, for example *"R.03"*, the Arduino reads its internal database and actuates the relays accordingly, connecting the signal output channel with that specific cell (R.03) in under a second. The second possible outcome is triggered when we send a misspelled command or a pixel label that does not exist (*"R.0.2"* or *"R.14"*), very common if we are sending commands manually. The result is an error message: ”`echo: Unknown command: R.0.2"`, informing us that the received command is not recognized.

To mitigate frustration for the user we have added a third possible outcome that sends a "help" string through the serial whenever the user types in Help, help or simply h. This string of characters returns a small help guide meant to clarify the valid commands to any confused user.

```
"Label commands:  Left or Right from 01 to 12 (R.01 , L.07 , R.12)"
"Test command:  Performs a sweep over the whole range of connections (Test, test)"
```

The last possible scenario is most useful for debugging purposes, to check if every relay is in good shape and all the pixels can be connected properly. We refer to it as the "Test Run", and it consists on a subroutine that connects every pixel to the output signal in sequence, for a specified number of seconds, so that the user can manually check each connection.

To accelerate the connection check, we have also manufactured a test PCB that emulates one of our pre-scale up substrates, with the same shape, size and connector layout (Figure 1.11 (b)). The main difference is that, instead of 24 individual cells, it has 24 small LEDs soldered to it. In

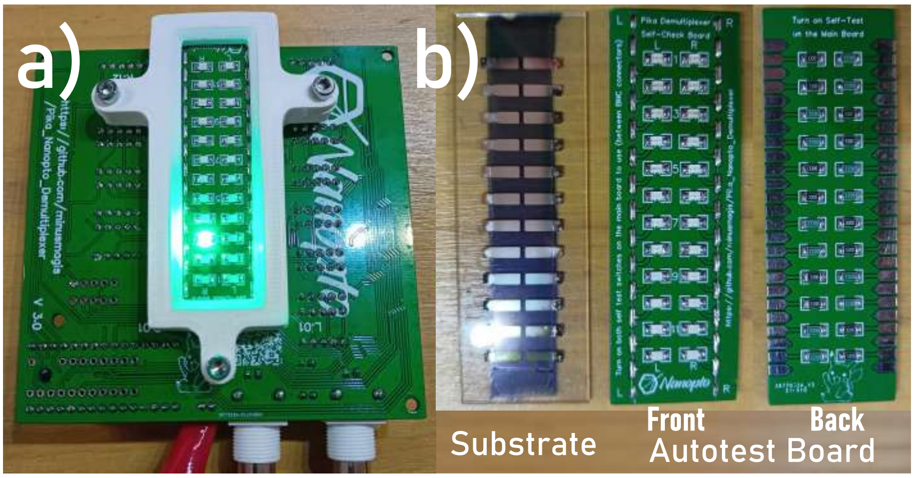

Figure 1.11: Self-test board during operation (a) with one LED lighting at a time during the entire test run. (b) Self-test PCB emulating the layout of pre-scalue up substrates with 24 LEDs soldered in place of the 24 individual cells.

this way, when we activate the small debugging switch that we have on the board, and we run the test subroutine, each LED will light up once for every switch, indicating that the self-check was successful (Figure 1.11 (a)). In case some of the LEDs do not light up, we immediately know the board is malfunctioning and needs to be repaired.

1.1.4 JV Characterization Software

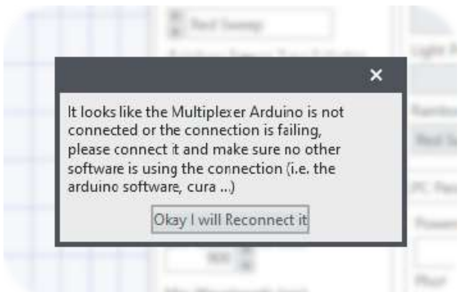

Figure 1.12: Prompt indicating improper demultiplexer board connection.

To coordinate the entire measurement process we have developed a JV characterization software with an intuitive graphical user interface (GUI), which seamlessly integrates the operation of the Pika demultiplexing board and the source meter (Figure 1.13). This software takes care of communicating with the Arduino and the source meter, connecting and extracting JV curves for each and every cell, while at the same time processing all the data automatically and generating a full report. The entire application has been developed using LabVIEW because of its versatility in designing simple and easy to use GUIs, which allow any user to quickly understand and intuitively navigate the software.

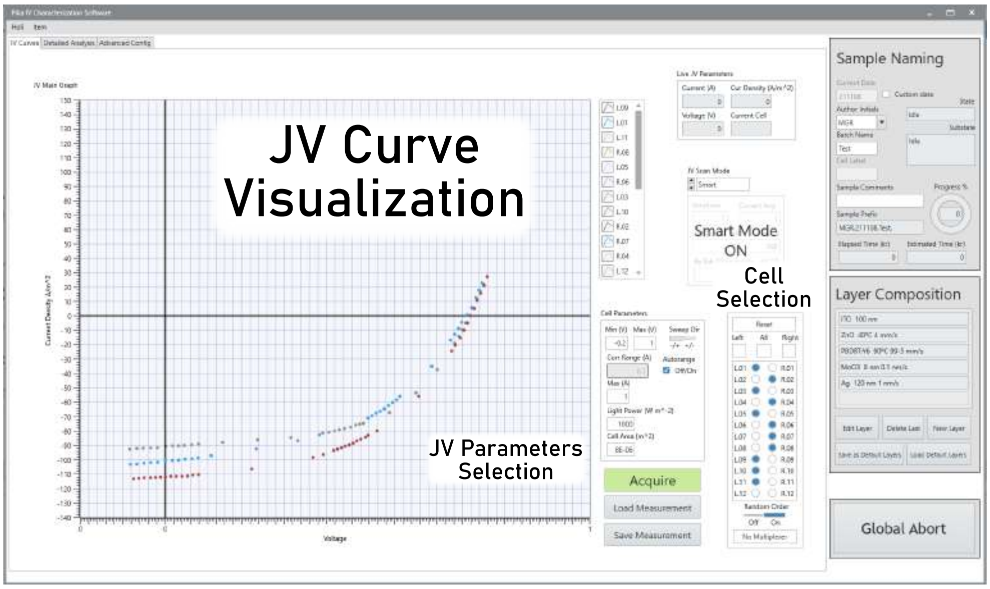

Figure 1.13: Front panel of the JV characterization software (v 2.0) showing the different controls and JV plots.

During initialization, the application checks that all the necessary instruments are connected, and prompts the user in case some equipment is missing, allowing her to reconnect it before continuing (Figure 1.12). In the main screen, the user is required to input the author and batch name, for data housekeeping purposes, as well as to select the JV curve parameters and the cells to be measured. As additional optional features, this software allows the user to add the layer information, which will be added to the generated report, as well as to randomize the cell measuring order to reduce any systematic measuring errors. In case the user does not wish to use the demultiplexing unit, the software has an additional option to evade Arduino automatic detection and work just with the SMU.

In this software, JV curves can be performed in two different modes: The most common consists on a constant voltage spacing mode, where we define a number of points within a voltage range and measure the current at each point. The second mode is an experimental sweep we have developed called "Smart Mode", which provides greater resolution on the regions of interest within the JV curve. This mode individually measures the V_{oc} and the J_{sc} by setting the source current or voltage to zero respectively. Knowing the V_{oc} and the J_{sc}, this mode performs a localized sweep around these points to calculate the slope and extract R_{s} and R_{sh} by taking advantage of the current and voltage sourcing capabilities of the Keithley SMU. Finally, it performs a series of ever finer JV sweeps between the V_{oc} and the J_{sc}, with a narrowing voltage range that focuses around the MPp region, providing a great resolution around that point (Figure 1.14). As a result of this procedure, we obtain a JV curve with the same number of points as an evenly spaced one, but concentrated on the "regions of interest", yielding a finer parameter extraction resolution in the same amount of time. To our knowledge, there has been no report about this measurement approach on the literature, where the closest we could find was a constant voltage-constant current approach by Min et al.,[1] with most other JV curve technical research focused on working with IV tracers operating on the 4 th power quadrant.[2–4] We must say that this measuring mode is most useful for non-S shape, well performing solar cells.

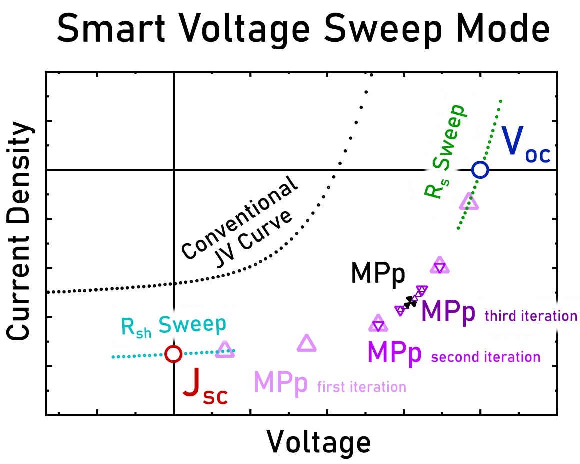

Figure 1.14: Smart JV curve measurement mode with the localized sweeps around the V_{oc} and the J_{sc}, used to calculate R_s and R_{sh}, as well as the self-refining sweep to locate the MPp.

Once all the parameters are set, the software automatically takes care of characterizing each and every one of the selected cells, by connecting them to the SMU through the Pika demultiplexer. After the measurement has finished, the application allows the user to discard or to save the data, automatically generating a full report consisting of: all the JV curve files, saved in a series of txt files; an Excel sheet with all the processed data; an OriginLab file, with all the JV curve data as well as the extracted parameter data, both being individually and collectively graphed; and finally, a Power Point presentation properly titled, with the author name, date, and all the results and graphs ready to be presented. All this happens in the span of a minute, while the researcher is changing to the next sample. Needless to say, all this data is saved within recursive folders, each properly named within the author's directory, with the date and batch number on each folder. This ensures that the user can leave the measuring station with all the necessary results, without the need for any further data processing and with all the data properly saved.

The latest version of this software (v 2.0) includes several additional features, such as layer deposition parameter saving and default layer parameter setting, for immediate retrieval of recurrent fabrication parameters, estimated measurement time and global abort capabilities. However, the most impactful feature of this new version is the automatic connectivity with our OPV database. Originally developed by Dr. Enrique Pascual, this database is meant to collect all the collectively generated solar cell data, which can be useful to compare between all devices manufactured within our group, and to feed artificial intelligence models that can relate fabrication parameters with performance, maybe being able to predict new unexplored material combinations. In order to push this initiative, we have redesigned the database from scratch, making it compliant with common SQL guidelines, to provide a wider variety of possible SQL queries, and for an easier integration with LabVIEW. This integration allows the JV characterization software to automatically transfer all the layer information, as well as the resulting JV curves and extracted parameters, directly to the database, without user interaction. The resulting data is tightly interconnected, as we can see in appendix **??**: **??**, and can be interacted with by using any database access tool, such as Microsoft Access, or by sending SQL queries, which are widely compatible with most programming languages.

1.2 EQE Measuring Setup

With the Pika demultiplexer setup, we are able to quickly and reliably measure the JV curves of all our pre-scale up substrate based solar cells. Nevertheless, JV characterization does not provide us with wavelength sensitive performance information; for that we require the use of an External Quantum Efficiency (EQE) characterization setup.

In this section, we have developed a laser based EQE characterization setup that consists of a supercontinuum white laser coupled to a monochromator, which allows us to illuminate our solar cells with the entire visible and NIR range, while measuring their wavelength dependent

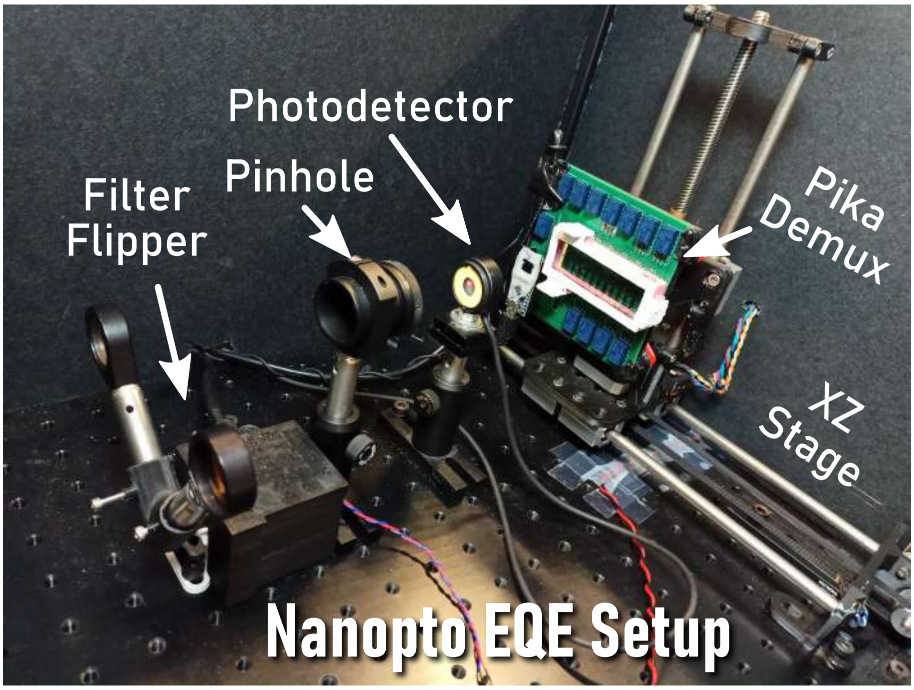

Figure 1.15: Custom built part of the EQE setup, combining the filter flipper and the XZ stage with several optical components and the photodetector in the laser path for measurement calibration.

performance. This setup is combined with a Keithley SMU that is able to operate in any of the four power quadrants, to perform photovoltaic measurements in a variety of operation regimes.

The main advantage of using laser source is that their maximum monochromated power output density (FWHM = 2.5 nm) is similar to that of the sun at around 1000 W m^{-2}, being much higher than most light sources used for EQE characterization. Such a high power allowed us to adapt the laser spot to fit into the cell, with a pinhole, without having to worry about light intensity levels. A smaller laser spot that fits into both the solar cell and the photodetector drastically simplifies power calibration measurements, by skipping light power density normalization.

1.2.1 XZ Stage and Filter Flipper

In order to measure the EQE of the cells manufactured with our pre-scale up substrates with the laser setup, we needed a way to accurately and repeatably position each individual cell on the laser spot, keeping it still during the measurement, while at the same time electrically connecting each cell with the Keithley SMU. To fully characterize one pre-scale up device, this complicated process has to be repeated for each of the 24 cells in the substrate. One can quickly see that this task is neither suitable nor efficient for a human to perform.

To solve this problem, fulfilling these very specific requirements, we combined the Pika demultiplexing board with a custom made XZ stage, capable of positioning every cell on the laser spot, while electrically contacting the appropriate cells. The XZ stage was fully designed and fabricated within the scope of this thesis, using readily available stepper motors and linear rails, combined with an Arduino microcontroller to control all the motors and to provide serial communication capabilities (Figure 1.15). The stage was fully 3D printed, in order to adapt to the existing Pika demultiplexing board. The later is attached through four small yet powerful magnets, which make for easy sample replacement, while ensuring repeatable positioning.

The resulting stage is able to accurately position the cell on the laser spot with high resolution and reproducibility ($\sim$100 μm). Thanks to the regular substrate size, this setup only requires an initial calibration to locate each cell on the laser spot, after which cell positioning is completely automatic, with user interaction limited to sample changing.

Filter Flipper

A disadvantage of this laser/monochromator combination is that the monochromator gratings introduce a second order diffraction that needs to be filtered out. This is easily achieved by using a series of visible and NIR filters, which block unwanted diffraction orders on both measuring wavelength ranges. However, the filters need to be inserted and removed in the middle of each EQE measurement, making the task more than inconvenient when manually operated. A motorized filter flipper is the easiest and best way to solve such a problem. However, commercially available solutions from Thorlabs are expensive and inconvenient, because of their library incompatibilities with newer versions of LabVIEW. That is why, with a spare motor and some 3D printed pieces we designed and built the “Nanopto Filter Flipper”, an open source, extremely affordable and mainly 3D printable alternative to change filters automatically in a

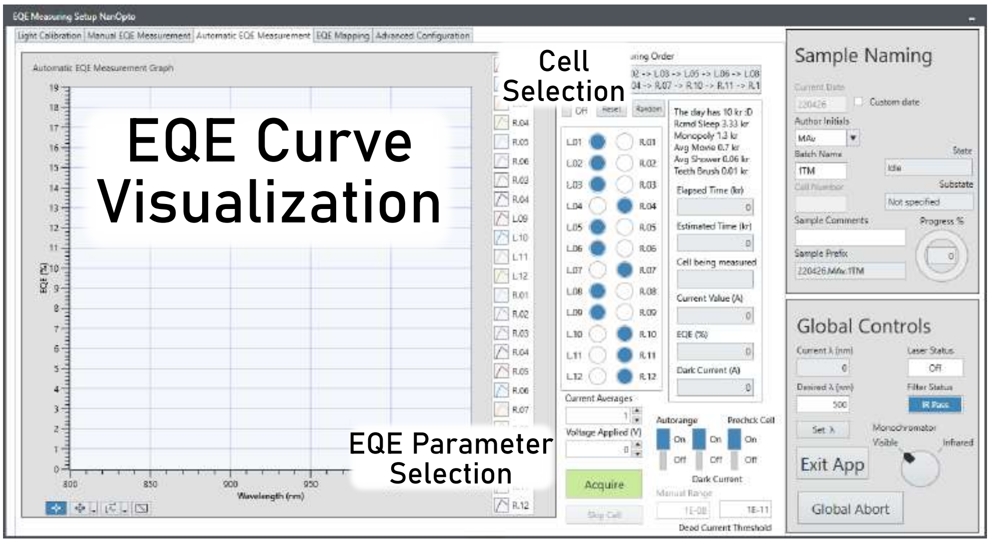

Figure 1.16: Front panel of the EQE characterization software (v 2.0) with the multiple controls and graphic visualization panel.

fast and reliable way.

In order to control both the filter flipper and the XZ stage we developed a piece of custom firmware, based on the Pika Demultiplexing Arduino Firmware's serial communication, which allowed us to precisely control the motor movements in real time. Besides, this firmware's entire communication protocol has been developed in accordance to the standard G-CODE programming language, so that both the filter flipper and the XZ stage are compatible with other CNC controllers.

1.2.2 Software and operation

In order to control every piece of instrumentation within this setup, as well as to gather, process and save the obtained EQE data, we needed a rather complex piece of software, capable of orchestrating the entire operation. Similarly to the Pika demultiplexer software, we have developed the EQE characterization application using LabVIEW because of its nice GUIs, and because of our previous expertise using the software. (Figure 1.16)

When we initialize the EQE software, it automatically detects all the necessary pieces of equipment, prompting the user to connect any missing device (Figure 1.17). The list of devices controlled by the software includes: The supercontinuum laser, to turn it on and off and regulate its power output; The monochromator, to select the output wavelength; The Keithley 2450 SMU, to electrically measure the cells; The thorlabs photodetector, to measure the light power; The filter flipper, to select the working wavelength range; The XZ stage, to position the cell on the laser spot; And the Pika demultiplexer board, to connect each cell when placed on the laser spot. In order to connect to some of the instruments, since we use a rather new version of LabVIEW (NXG), we had to develop several libraries that enabled the communication between the software and the instruments.

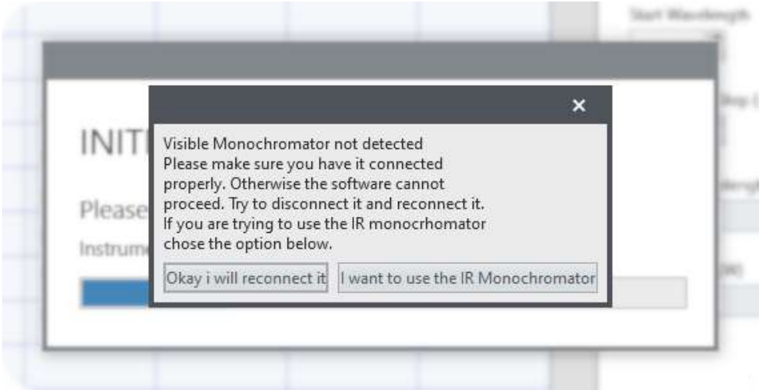

Figure 1.17: Prompt indicating the visible monochromator is not properly connected.

After all devices are initialized, on the main screen (Figure 1.16), the user is provided with controls to actuate every device separately according to the different stages of the measurement. Firstly the user needs to turn the supercontinuum laser on, and place the photodetector on the laser spot. Before starting any measurement, the user is required to enter the author initials and the cell batch label, necessary for proper data logging. Additionally, the user needs to add the wavelength range parameters, as well as the specific EQE characterization parameters and the cell selection.

The first part of the measurement consists on a light power calibration that measures the power at each wavelength, necessary to calculate EQE values from cell photocurrent. After the calibration, the user is prompted to remove the photodetector from the laser spot, and to place the cell on the Pika demultiplexer to begin the measurement. After that, the XZ stage automatically places the first selected cell on the laser spot, and the wavelength sweep begins, while the SMU measures the photocurrent at each wavelength (Figure 1.18). This photocurrent is converted to photocurrent density and EQE values, which are saved automatically on different properly named folders, similarly to the JV characterization software. This process is repeated for every individual cell, until the entire substrate, or at least the selected cells, have been characterized. We did not add full report generation capabilities to this particular application because of the wider, less systematic requirements of EQE data processing.

With this setup EQE cell characterization has become a seamless and automatic process, with very limited user interaction requirements. Automating this technique proved to be crucial for the significant EQE characterization effort performed within this thesis, as well as for general cell characterization performed within our group.

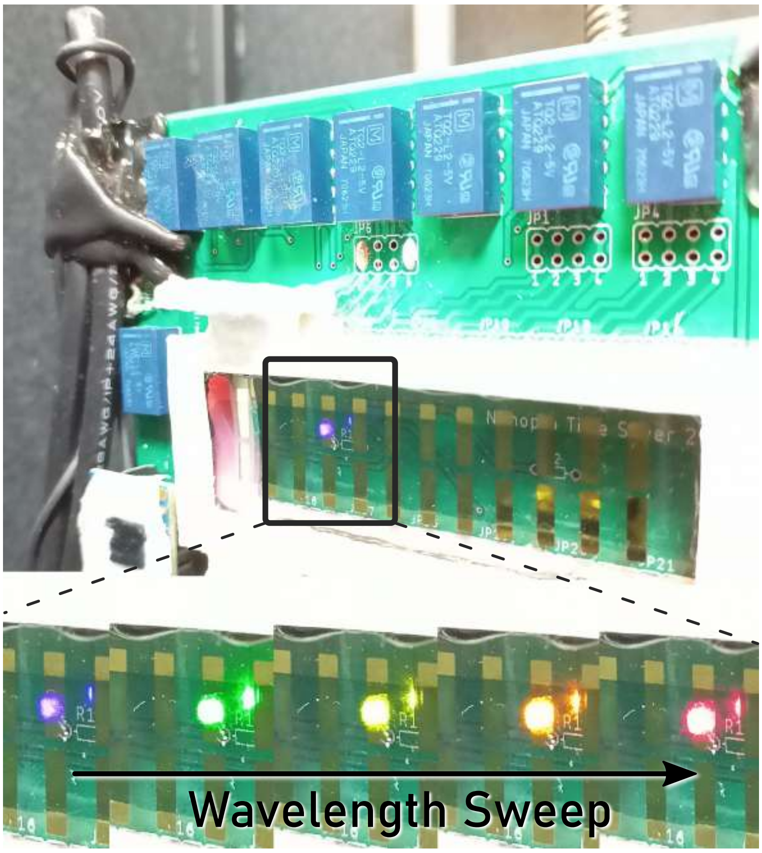

Figure 1.18: Laser spot illuminating one single cell loaded on the Pika Demultiplexing board during the wavelength sweep of an EQE measurement.

1.3 Conclusions

In this chapter we have developed two experimental setups that accelerate, systematize and automate the characterization of organic photovoltaic devices fabricated within our group, increasing reproducibility, and greatly reducing the time and effort involved in the entire characterization process. These setups include: a solar cell automated demultiplexer, together with a JV characterization setup; and a robotic EQE measurement setup.

The first setup designed and build within this chapter, consists of a custom PCB with 3D printed accessories, combined with a LabVIEW based orchestrating software that, together with an SMU, coordinates the entire JV characterization process, as well as the data processing and report generation. The custom PCB includes a bistable relay tree that connects each individual cell with a BNC connector, through gold plated spring pins, to enable a noise free, accurate JV characterization. The substrate is accurately located within the PCB with a custom made 3D printed holder, which tightly clamps all the cells against the pogo pins, providing a good electrical connection.

The JV characterization software presents an intuitive GUI, which takes care of the communication between the source measuring unit and the demultiplexing board, and walks the user through the JV measurement process, by asking for equipment connection and input parameters. As a result, the software outputs a full report with txt files, an Excel sheet, an OriginLab file with all the graphs, and a Power Point file with all the results nicely plotted ready for presentation. Additionally, the newest version of the software integrates database connectivity capabilities for proper data logging and further metadata analysis.

This setup results in a 92% reduction on the required characterization time, allowing for faster, more in depth solar cell characterization, while reducing solar simulator lamp ON time, lowering energy consumption and degradation. Besides, it increases cell connection reliability, with its gold coated pogo pins, while allowing the sample to be measured on inaccessible locations thanks to its remote actuation.

The second setup explained in this chapter is a robotic EQE measurement system, which enables us to automatically measure the EQE of all the cells within one pre-scale up substrate, in a highly reproducible and automated manner. This setup consists of a computer controlled supercontinuum laser and monochromator, which provide a wide operating wavelength range, combined with a fully 3D printed open source XZ stage, which places our pre-scale up substrate solar cells on the laser spot for their EQE characterization. The latter has been fully developed within this thesis, complemented with the demultiplexing board developed in previous sections in order to contact each cell during EQE measurements.

This entire setup is orchestrated through a powerful piece of LabVIEW software, which connects to every instrument and provides the user with accurate instructions during the measurement, after which it automatically saves all the resulting files in a well classified hierarchical folder structure. Besides saving incredible amounts of human time and effort, this setup has enabled the systematic EQE characterization of pre-scale up substrates within our group.

These two experimental setups have been designed to be easy to assemble, reliable and to have a low cost, to enable their implementation on any possible environment. To do so we have used really affordable and widely available commercial PCB manufacturing processes, combined with of the shelf components, widely used on the 3D printing industry, which are cheap and easily replaceable. Every structural piece used to assemble the setups is 3D printed and open source, so that anyone can entirely replicate these setups without complicated machining operations or injection moulding processes, just by having a really inexpensive 3D printer.

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