
PyPEC Documentation

Release 0.1

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GETTING STARTED

1.1 Description

PyPEC aims at fitting PEC data with an graphical interface.

In terminal enter the following command:

```
python -m pypec
```

A pdf version of the documentation can be found here [PyPEC3](#). The source code can be viewed on [GitHub](#).

1.2 How to install

```
$ python setup.py install
```

or

```
$ pip install pypec3
```

1.3 Dependencies

```
numpy>=1.17  
scipy>=1.5  
matplotlib>=3.0.0
```

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2.1 PhotoElectrochemistry

2.1.1 Basics

Photo-electrochemistry characterizations are used to study films at macroscopic, mesoscopic, and microscopic scales. The latter advances were used to support (photo-)electrochemical studies of the electronic and optical properties of passive films and oxidized metals, and of their interfaces with electrolytes, providing informations on the nature and structure of these materials and to use properties such as the oxidation behaviour of a metallic substrate.

Basically, two kinds of curves are recorded in the course of photoelectrochemical characterization experiments, photocurrent voltammograms and photocurrent energy spectra. In photocurrent voltammograms, photocurrents are measured as a function of the potential, V , applied to the semiconducting electrode, at a given photon energy, $E = h\nu$. In photocurrent energy spectra, photocurrents are recorded, at a given applied potential, V , as a function of the photon energy, E . The analysis of the shapes of photocurrent voltammograms may allow to obtain informations such as the semiconducting type of the material, the energy of the surface band levels, the presence of macroscopic defects inducing photogenerated electron-hole pairs recombinations.

However, despite attempts to refine the Gartner-Butler model by taking into account surface or volume recombination, a complete description of the photocurrent voltammograms remains difficult, for the latter developments make use of a high number of adjustable parameters, most of them being very difficult to assess. The analysis of the photocurrent energy spectra is intended to identify the chemical nature of the material constituting the semiconducting electrode, through the value of their bandgap energies, E_g as, on the one hand, bandgap energy values have been reported in the literature for numerous compounds, and as, on the other hand, bandgap values may be estimated from thermodynamic extensive atomic data. Practically, photocurrent energy spectra are usually analyzed by means of linear transforms to take benefit of the fact that, using the simplified form of the Gartner-Butler model, the quantum yield, η , of the photocurrent is proportional to the light absorption coefficient.

In such conditions, η , obeys to the following relationship:

$$(\eta * E)^{1/n} = K(E - E_g)$$

where C is a constant (things other than E being equal), E_g is the bandgap energy of the semiconductor, and n depends on the band to band transition type, $n = 1/2$ for an allowed direct transition, and $n = 2$ for an allowed indirect transition. Direct transitions are rarely observed in more or less disordered thin oxide films.

2.1.2 Fitting

Linear transformations were successfully performed for oxides made of one or two constituents. However, for complex oxide scales formed of several p-type and n-type phases, the complete description of the photocurrent energy spectra could not be achieved, and only semi-quantitative and/or partial informations could be obtained on the oxides present in the scales.

As I_{PH}^* is measured under modulated light conditions and thus actually is a complex number, the real and the imaginary parts of the photocurrent should be considered simultaneously when analyzing and fitting the photocurrent energy spectra, rather than their modulus [1].

$$\begin{aligned} I_{PH}^* &= |I_{PH}^*| \cos \theta + j |I_{PH}^*| \sin \theta \\ I_{PH}^* &= \sum_i J_{PH,i} \cos \theta_i + j \sum_i J_{PH,i} \sin \theta_i \end{aligned} \quad (2.1)$$

where $J_{PH,i}$ and θ_i represent the modulus and phase shift, respectively, of the photocurrent issued from the i th semiconducting constituent of the oxide layer. For thin semiconducting films, the space charge regions are low compared to penetration depth of the light. $J_{PH,i}$ may thus be expected, at a given applied potential, to follow the simplified form of the Gartner–Butler model.

$$(J_{PH,i} * E)^{1/n} = K_i (E - E_{g,i})$$

where $E_{g,i}$ and K_i represent the energy gap and a value proportional to C (I_{PH}^* is proportional to but not equal to η) for the i th semiconducting constituent.

For a given vector of m ($K_i, \theta_i, E_{g,i}$) triplets, m representing the supposed number of semiconducting phases contributing to the photocurrent, the scalar function to be minimized by the Nelder-Mead function was defined as the product of the square roots of two quantities:

$$\begin{aligned} D_{Re} &= \sqrt{\sum_E (Re I_{PH,exp}^* - Re I_{PH,calc}^*)^2} \\ D_{Im} &= \sqrt{\sum_E (Im I_{PH,exp}^* - Im I_{PH,calc}^*)^2} \\ D &= D_{Re} \cdot D_{Im} \end{aligned}$$

The 3 m variables can be locked or not by the user. Initial estimates can be provided by the user or can be randomly generated. Several successive calls of the Nelder-Mead procedure are necessary to reach the minimum of the scalar function and a stable set of the output parameters. The user is free to set the number of successive calls of the Nelder-Mead procedure. Constraints on the 3 m variables can be set by the user.

2.2 GUI

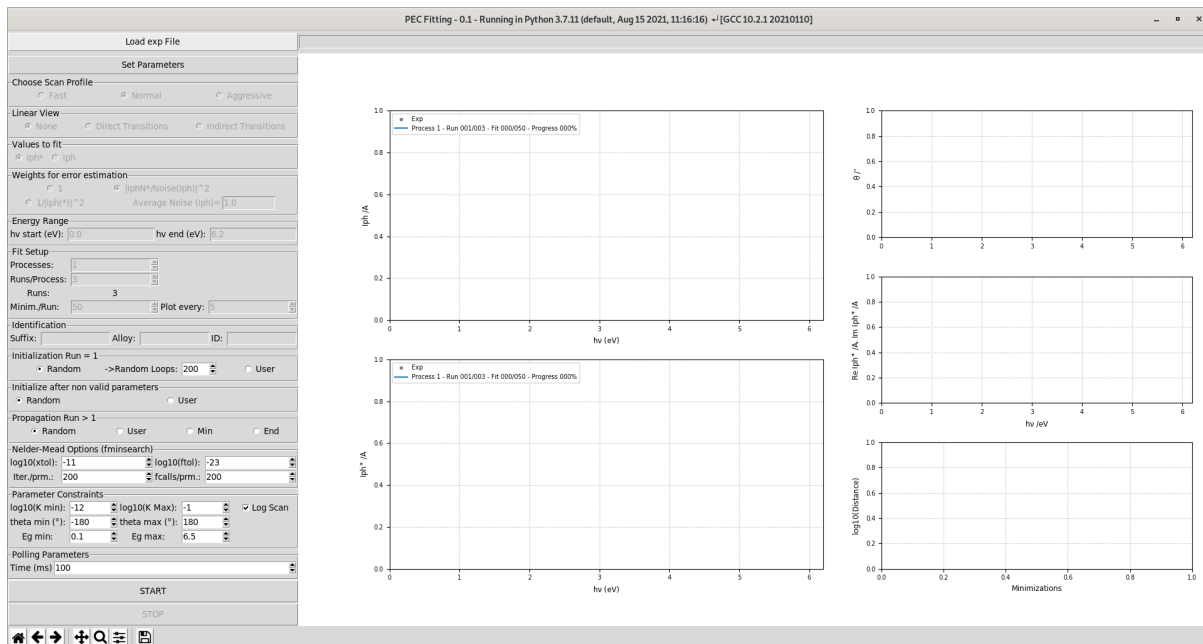
The main window contains all the elements necessary to run the fit. The design is cluttered but it allows exposing directly all the fitting settings to the user without deep menus.

The different steps, presented in the left pane, for performing the fit are:

- **load data: the accepted formats are:**
 - *.dot files which are ascii files developed in the SiMaP Lab
 - *.data files which are generic ascii files
- set the number of semiconductive contributions (*Parameter Table*)

At this point the fit can be ran.

If needed select custom choice for all the fitting parameter in the left pane.



2.2.1 *.dot files

They have a specific formatting and they are provided by the PEC setup in the SiMaP Lab.

2.2.2 *.data files

The *.data files are generic ascii files where:

- the first column is the energy of the incident light in eV.
- the second column is the modulus of the photocurrent in A.
- the third column is the phase shift of the photocurrent in degrees.

2.2.3 Parameter Table

The parameter table allows for fitting the $3m$ variables. The table is structured as shown below:

Ki	Fit Kgi	theta i	Fit Phase i	Egi	Fit Egi
K 1	0 or 1	Phase 1	0 or 1	Eg 1	0 or 1
K 2	0 or 1	Phase 2	0 or 1	Eg 2	0 or 1
...
K n	0 or 1	Phase n	0 or 1	Eg n	0 or 1

Each parameter K_i , θ_i and Eg_i can be locked by setting the **Fit X** column to 0.

RELEASE NOTES

3.1 PyPEC3 0.1 Release Notes

3.1.1 Highlights

PyPEC aims at Fitting PEC data with an graphical interface. The program was initially developped in Python 2.7 during my PhD from 2012 to 2015 and the code is available on github [PyPEC \(Python 2\)](#).

In 2016, the code was rewritten in Python 3 at the end of my PhD with slight modifications of the original code. The code remained untouched for almost 3 years and is now again under development in this repository.

This is the first release after migrating to github which will serve as a backup for the version developed during my PhD with completed documentation. No modification to the original code.

3.1.2 New Features

- Load data: *.dot files (data format developped in Grenoble Lab SiMaP)
- multi-process fitting: N processes x M fits x L loops
- automatic creation of result folder based on sample name and fitting parameters
- results saved in a folder

3.1.3 Contributors

Milan Skocic

3.1.4 Commits

N/A

AUTOGENERATED DOCUMENTATION

4.1 Graphical FrontEnd

Graphical frontend for fitting photo-current spectra.

class `pypec.Analyse_PEC.Analyse_PEC`(*master=None*)

Construct a frame widget with the parent MASTER.

Valid resource names: background, bd, bg, borderwidth, class, colormap, container, cursor, height, highlightbackground, highlightcolor, highlightthickness, relief, takefocus, visual, width.

Methods

<code>update_nb_runs()</code>	Update the number of cpu and run per process on the graphical interface.
-------------------------------	--

<code>AddFiles_cb</code>	
<code>Fit_cb</code>	
<code>ask_quit</code>	
<code>autoscale</code>	
<code>create_fit_lines</code>	
<code>get_progress</code>	
<code>on_Run_Fit</code>	
<code>on_hv_limits</code>	
<code>on_start_workers</code>	
<code>on_stop_button</code>	
<code>plot_Graph</code>	
<code>plot_Re_Im</code>	
<code>plot_fit_lines</code>	
<code>plot_ligne_V</code>	
<code>prm_binary</code>	
<code>process_queue</code>	
<code>remove_fit_folder</code>	
<code>remove_fit_lines</code>	
<code>start</code>	
<code>update_figure</code>	
<code>update_legend</code>	
<code>update_nb_fit_in_run</code>	

`AddFiles_cb()`

`Fit_cb()`

`ask_quit()`

`autoscale(chart)`

`create_fit_lines()`

`get_progress(run=1, fit=0)`

`on_Run_Fit()`

`on_hv_limits(*args)`

`on_start_workers()`

`on_stop_button()`

`plot_Graph()`

`plot_Re_Im()`

`plot_fit_lines(*args)`

`plot_ligne_V()`

`prm_binary()`

`process_queue()`

`remove_fit_folder()`

`remove_fit_lines()`

`start()`

`update_figure()`

`update_legend(axes, run=1, fit=0, location='upper left')`

`update_nb_fit_in_run()`

`update_nb_runs()`

Update the number of cpu and run per process on the graphical interface.

class `pypec.Analyse_PEC.ParameterTable(master, prm, last_prm_folder, **kwargs)`

Construct a frame widget with the parent MASTER.

Valid resource names: background, bd, bg, borderwidth, class, colormap, container, cursor, height, highlightbackground, highlightcolor, highlightthickness, relief, takefocus, visual, width.

class pypec.Analyse_PEC.**ParameterWindow**(*master, prm_init, last_prm_folder*)

Construct a toplevel widget with the parent MASTER.

Valid resource names: background, bd, bg, borderwidth, class, colormap, container, cursor, height, highlightbackground, highlightcolor, highlightthickness, menu, relief, screen, takefocus, use, visual, width.

Methods

get_paths	
get_prm	

get_paths()

get_prm()

class pypec.Analyse_PEC.**ScrolledFrame**(*master, **kwargs*)

Construct a frame widget with the parent MASTER.

Valid resource names: background, bd, bg, borderwidth, class, colormap, container, cursor, height, highlightbackground, highlightcolor, highlightthickness, relief, takefocus, visual, width.

4.2 Iph Functions

Modules - Iph Functions

This module contains functions required for computing and optimizing the photo-current values from input parameters i.e. triplets (K_i, θ_i, Eg_i) and experimental data for each semi-conductive phase [1].

pypec.iph_functions.get_Iph_calc(*hv, prm_array, phi_N*)

Compute the complex values of I_{ph} based on the values and states of the triplets (K_i, θ_i, Eg_i) [1].

$$I_{ph}^* = \frac{I_{ph}}{\Phi_N}$$

Parameters

hv: 1d array Vector of energies for which the complex I_{ph} has to be computed.

prm_array: 2d array Represents the values and states of the triplets (K_i, θ_i, Eg_i) .

phi_N: 1d array Represents the values of the normalized photon flux to the maximum value. If n_{phf} is a unity vector, the true photo-current is returned otherwise the as-measured photo-current is returned.

Returns

iph_calc_complex: 1d array Vector of the computed complex values of I_{ph} .

pypec.iph_functions.get_LCC(*iph_exp_complex, iph_calc_complex*)

pypec.iph_functions.get_distance(*iph_exp_complex, iph_calc_complex*)

Compute the distance D between $I_{ph_{exp}}$ and $I_{ph_{calc}}$. The distance is computed by multiplying the distances

on real and imaginary parts of Iph :

$$\begin{aligned}\Delta Re &= Re\ Iph_{exp} - Re\ Iph_{calc} \\ \Delta Im &= Im\ Iph_{exp} - Im\ Iph_{calc} \\ D_{Re} &= \sqrt{\sum \Delta Re^2} \\ D_{Im} &= \sqrt{\sum \Delta Im^2} \\ D &= D_{Re} \cdot D_{Im}\end{aligned}$$

Parameters

iph_exp_complex: 1d numpy array Contains the complex values of the Iph_{exp} .

iph_calc_complex: 1d numpy array Contains the complex values of the Iph_{calc} .

Returns

D: float The computed distance on real and imaginary parts of Iph .

`pypec.iph_functions.get_exp_data(filepath)`

Get the data array of data files according to their extension.

Supported files are .dot files recorded by PECLab software and .data files where the first three columns represent $h\nu$, $|Iph^*|$, θ .

Parameters

filepath: string Path to the data file.

Returns

data_array: 2d array Experimental data.

`pypec.iph_functions.get_header_footer_dot_file(filepath)`

Find the number of lines in header and footer in .dot files.

Parameters

filepath: path to the dot file

Returns

skip_header: int number of lines in header

skip_footer: int number of lines in footer

nbpoints: int number of data lines

`pypec.iph_functions.get_random_prm_values(prm_array, K_bound=(1e-12, 0.1), theta_bound=(-180.0, 180.0), Eg_bound=(0.1, 6.2), phase_flag=True)`

Generates random values for the triplets (K_i, θ_i, Eg_i) to be fitted based on the states given by the *prm_array*.

By default, the limits are:

- K_i : $[10^{-12}, 10^{-1}]$
- θ_i : $[-\pi, +\pi]$
- Eg_i : $[0.1, 6.0]$

Parameters

prm_array: 2d array Represents the values and states of the triplets (K_i, θ_i, Eg_i) .

K_bound:tuple Contains the lower and upper limits for the K_i values.

theta_bound: tuple Contains the lower and upper limits for the θ_i values.

Eg_bound:tuple Contains the lower and upper limits for the Eg_i values.

phase_flag: bool Indicates if the values of θ_i have to be randomized.

Returns

random_prm_array: 2d array Represents the values and states of the triplets (K_i, θ_i, Eg_i) .

`pypec.iph_functions.get_results_array(hv, iph_exp_complex, iph_calc_complex)`

Build the data array of the experimental and calculated data: $h\nu$, $|Iph_{exp}|$, θ_{exp} , $|Iph_{calc}|$ and θ_{calc}

Parameters

hv: 1d numpy array Contains the energy vector.

iph_exp_complex: 1d array Contains the complex values of Iph_{exp} .

iph_calc_complex: 1d array Contains the complex values of Iph_{calc} .

Returns

data_array: 2d array Array containing the .

`pypec.iph_functions.get_summary(fit_folder)`

List result files for the triplets (K_i, θ_i, Eg_i) at the end and the minimum of each run.

Compute the distance, the LCCs for the energy interval that was used for minimizing the the triplets (K_i, θ_i, Eg_i) .

The results are saved in 4 files: .SumEnd, .SumEndEg, *.SumMin, *.SumMinEg.

Parameters

fit_folder: string Path of the fit folder.

`pypec.iph_functions.import_prm_file(filepath)`

Import the triplets (K_i, θ_i, Eg_i) from text file where each line represents a contributing semi-conductive phase.

Parameters

filepath: string Absolute or relative file path to the text file.

Returns

prm_array: 2d array Represents the values and states of the triplets (K_i, θ_i, Eg_i) .

`pypec.iph_functions.minimize(hv, iph_exp_complex, phi_N, weights, prm_array, Ki_log_flag=True, maxiter=None, maxfun=None, xtol=1e-11, ftol=1e-23, full_output=True, retall=False, disp=False, callback=None)`

Execute the Nelder-Mead algorithm based on parameter values given by `prm_array` and energy vector $h\nu$.

First, the `prm_array` is flattened and the parameters (K_i, θ_i, Eg_i) to be fitted are extracted and sent to the `target_function()` through the Nelder-Mead algorithm.

Once the parameters were computed by the Nelder-Mead algorithm, the `prm_array` is updated with the new values.

Parameters

hv: 1d numpy array Contains the energy vector.

iph_exp_complex: 1d numpy array Contains the complex values of the experimental photo-current.

phi_N: 1d array Contains the normalized photon spectrum.

weights: 1d array Contains the weights of the data.

prm_array: 2d array Represents the values and states of the triplets (K_i, θ_i, Eg_i) .

Ki_log_flag: bool Indicates if the K_i values are in logarithmic space.

maxiter [int, optional] Maximum number of iterations to perform.

maxfun [number, optional] Maximum number of function evaluations to make.

xtol [float, optional] Relative error in xopt acceptable for convergence.

ftol [number, optional] Relative error in func(xopt) acceptable for convergence.

full_output [bool, optional] Set to True if fopt and warnflag outputs are desired.

retall [bool, optional] Set to True to return list of solutions at each iteration.

disp [bool, optional] Set to True to print convergence messages.

callback [callable, optional] Called after each iteration, as callback(xk), where xk is the current parameter vector.

Returns

prm_array: 2d array Represents the updated values and states of the triplets (K_i, θ_i, Eg_i) .

fopt [float] Value of function at minimum: `fopt = func(xopt)`.

`pypec.iph_functions.plot_summary(fit_folder)`

Plot the result files that were created by the `get_summary()` for the triplets (K_i, θ_i, Eg_i) at the end and the minimum of each run.

The results are saved in 2 files: -0-End.pdf, -0-Min.pdf.

Parameters

fit_folder: string Path of the fit folder.

`pypec.iph_functions.save_pdf(filepath, hv, iph_exp_complex, iph_calc_complex, mask, all_results)`

`pypec.iph_functions.save_results(run, process_id, fit_folder, datafilepath, suffix, hv, mask, iph_exp_complex, phi_N, prm_min_run, prm_end_run, distance_min_run, distance_end_run, minimization_results, header_minimization_results)`

`pypec.iph_functions.scatter_logpolar(ax, theta, r_, ticks=5, bullseye=0.0, **kwargs)`

`pypec.iph_functions.shift_phase(prm_array, theta_bound=(-180.0, 180.0))`

Compute the modulo of θ_i values with 2π and then shift the values of θ_i by the amplitude of the boundaries in order to be in between the boundaries.

By default, the boundaries for θ_i are set to $[-\pi, +\pi]$.

Parameters

prm_array: 2d array Represents the values and states of the triplets (K_i, θ_i, Eg_i) .

theta_bound: tuple Contains the lower and upper limits for the θ_i values.

Returns

prm_array: 2d array Represents the values and states of the triplets (K_i, θ_i, Eg_i) where the θ_i values were shifted.

`pypec.iph_functions.sort_prm_Eg(prm_array)`

Sort the prm_array based on values of Eg_i .

Parameters

prm_array: 2d array Represents the values and states of the triplets (K_i, θ_i, Eg_i) .

Returns

prm_array: 2d array Represents the sorted values and states of the triplets (K_i, θ_i, Eg_i) .

`pypec.iph_functions.target_func(p, hv, prm_array, iph_exp_complex, phi_N, weights,`
`Ki_log_flag=True)`

Update the triplets (K_i, θ_i, Eg_i) from the flattened parameter vector **p** sent by the optimization algorithm. The **prm_array** will be flattened and the indexes of the parameters to be fitted will be updated with **p** vector.

The calculated complex values of I_{ph} will be sent along the experimental values to the `get_distance()` function. The value of the distance between the experimental and calculated data will sent back to the optimization algorithm.

Parameters

p: 1d array Parameter vector sent by the optimization algorithm which is always. flattened.

hv: 1d array Vector of energies for which the complex values of I_{ph} have to be calculated.

prm_array: 2d array Represents the values and states of the triplets (K_i, θ_i, Eg_i) .

iph_exp_complex: 1d numpy array Contains the complex values of the experimental I_{ph} .

phi_N: 1d array Represents the values of the normalized photon flux to the maximum value.

weights: 1d array Contains the values of the data weights.

Ki_log_flag: bool Indicates if the K_i values are in logarithmic space.

Returns

distance: float Calculated distance between experimental and calculated data values. See the `get_distance()` function.

`pypec.iph_functions.validate_prm(prm_array, K_bound=(1e-12, 0.1), Eg_bound=(0.1, 6.2))`

Check if the values of K_i and Eg_i are within the boundaries.

Parameters

prm_array: 2d array Represents the values and states of the triplets (K_i, θ_i, Eg_i) .

K_bound:tuple Contains the lower and upper limits for the K_i values.

Eg_bound:tuple Contains the lower and upper limits for the Eg_i values.

Returns

valid: bool Set to True if value of K_i or Eg_i is out of the boundaries.

4.3 Parallel Processes

Module for controlling the parallel processes running during the fitting procedure

`class pypec.Parallel_Process.MinimizationProcess(output_queue, name, prm_init, nb_run, nb_SC,`
`init_type, random_loops, hv, iph_exp_complex,`
`iph_exp_complex_CI, phi_N, phi_N_CI,`
`weights, hv_limits, nb_fit_in_run, fit_folder,`
`filepath, suffix, NelderMead_options=(1e-11,`
`1e-23, 200, 200),`
`ParameterConstraints=((1e-12, 0.1), (- 180,`
`180), (0.1, 6.2), True), update_every=5)`

Methods

<code>run()</code>	Method to be run in sub-process; can be overridden in sub-class
--------------------	---

<code>shutdown</code>	
-----------------------	--

run()

Method to be run in sub-process; can be overridden in sub-class

shutdown()

class `pypec.Parallel_Process.PlotSummaryProcess(fit_folder)`

Parameters

fit_folder: str Path to the folder where the summary files will be saved.

Attributes

fit_folder: str Path to the folder where the summary files will be saved.

Methods

<code>run()</code>	Method to be run in sub-process; can be overridden in sub-class
--------------------	---

run()

Method to be run in sub-process; can be overridden in sub-class

`pypec.Parallel_Process.get_cpu_number()`

DocString

`pypec.Parallel_Process.get_queue()`

DocString

`pypec.Parallel_Process.initialize_processes(n, daemon=True, **kwargs)`

Create N processes as daemons and return them in a list.

Parameters

n: int Number of processes to be created.

daemon: bool Flag for creating daemon process.

kwargs: dict See [MinimizationProcess](#)

`pypec.Parallel_Process.start_processes(workers)`

Parameters

workers: subprocess workers

Returns

0: return integer

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5.1 Bibliography

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