

# Development of system for automatic measurement of transient photocurrent and thermally stimulated current

## Desarrollo de un sistema para medición automática de fotocorriente transitoria y corriente estimulada térmicamente

A. A. Ramirez<sup>1</sup>, and G. Gordillo<sup>2</sup>

### ABSTRACT

This paper presents details of the design and implementation of a system for measuring of thermally stimulated current (TSC) and transient photocurrent ( $I_{ph}$ ), developed using the Virtual Instrumentation concept. For that we have used National Instrument hardware and the LabView® package as software. The system is controlled by a virtual instrument (VI) which includes facilities to perform measurements of photocurrent keeping the temperature of the sample and the pressure of the chamber of measurement controlled as well as real time display of the  $I_{ph}$  vs  $t$  and TSC vs  $T$  curves. The system was tested by performing transient photocurrent and TSC measurements on  $CH_3NH_3PbI_3$  thin films that are generally used as absorbent layer of solar cells. This type of characterization is very useful to get information of the trapping and recombination processes that affect the transport properties of the devices.

**Keywords:** TSC measurements, photoconductivity, perovskites solar cells, virtual instrumentation, PID and PWM control.

### RESUMEN

Este trabajo presenta los detalles del diseño y la implementación de un sistema de medición de corriente térmicamente estimulada (TSC, por sus siglas en inglés) y fotocorriente transitoria ( $I_{ph}$ ), desarrollado a partir del concepto de Instrumentación Virtual. Para esto, se ha utilizado el hardware de National Instrument y el paquete LabView® como software. El sistema está controlado por un instrumento virtual (VI, por sus siglas en inglés) que incluye instalaciones para realizar mediciones de fotocorriente manteniendo la temperatura de la muestra y la presión de la cámara de medida controlada, así como una visualización en tiempo real de las curvas  $I_{ph}$  vs  $t$  y TSC vs  $T$ . El sistema se probó mediante la realización de fotocorrientes transitorias y mediciones de TSC en películas delgadas  $CH_3NH_3PbI_3$  que se utilizan, generalmente, como capa absorbente de células solares. Este tipo de caracterización es muy útil para obtener información de los procesos de captura y recombinación que afectan las propiedades de transporte de los dispositivos.

**Palabras clave:** Medición de corriente térmicamente estimulada, fotoconductividad, placas solares de perovskita, instrumentación virtual, control PID y PWM.

### Introduction

The control of processes, the acquisition and monitoring of data with automatic systems that include analogical and digital variables, generally follow a traditional architecture that employs data loggers or microcontrollers [R. Mukaro *et al.*, 1998; 1999]. The aim of this work is to introduce a system that was designed and implemented for measuring of thermally stimulated current (TSC) and transient photocurrent using Virtual Instrumentation [R. Bishop, 2007; G.W. Johnson *et al.*, 2006; and R. Mukaro *et al.*, 1998], that is based on a concept where the software is the main component of the system in contrast to the traditional instrumentation, where the main thing is the hardware. The system developed allows measurement of transient photocurrent maintaining controlled both the temperature of the sample (in a range between 80 and 700K) as the pressure of the chamber of measurement; this system also includes facilities to vary the temperature at a constant rate in the range of 2-30 °C/min.

In general, the physical properties of photovoltaics materials are influenced by the presence of trap and recombination states in the forbidden gap, arising from chemical impurities and/or structural defects. Therefore, it is important to study the parameters characterizing such states. An adequate knowledge of trap and/or defect

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properties in photovoltaic materials could help to improve its electrical and optical properties and thus the solar cell efficiency. Transient photoconductivity measurements as a function of temperature are relatively easy to perform and could provide information on trap and/or recombination states [M. Courel *et al.*, 2014].

The system developed was proven performing measures of TSC and transient photocurrent to thin films of the organic/inorganic hybrid compound  $\text{CH}_3\text{NH}_3\text{PbI}_3$  with structure perovskite, used in the manufacture of solar cells by our research group. Hybrid organic/inorganic perovskite materials as light absorbers are currently among the most promising candidates for thin-film photovoltaic applications. In particular, it is worth mentioning that the devices based on hybrid perovskite materials have achieved great advances in terms of efficiency [Chien-Hung Chiang *et al.*, 2016; J. H. Heo *et al.*, 2015; S. Kazim *et al.*, 2014; L. Mingzhen *et al.*, 2013 and Nam-Gyu Park, 2013, ]. However, there are still many doubts about their electrical transport properties and the relationship of these with the devices efficiency. These devices are cost-effective due to their simple fabrication process. As a result, these cells have attracted a special attention from researchers in the field. On the other hand, among the factors that limit inorganic solar cell efficiency, bulk recombination induced by a high density of defect states, have been identified as one of the hurdles for reaching high solar cell performances [S. Siebentritt, 2013]. Defects may introduce recombination centers, which have a direct influence on the transport phenomena of the charge carriers.

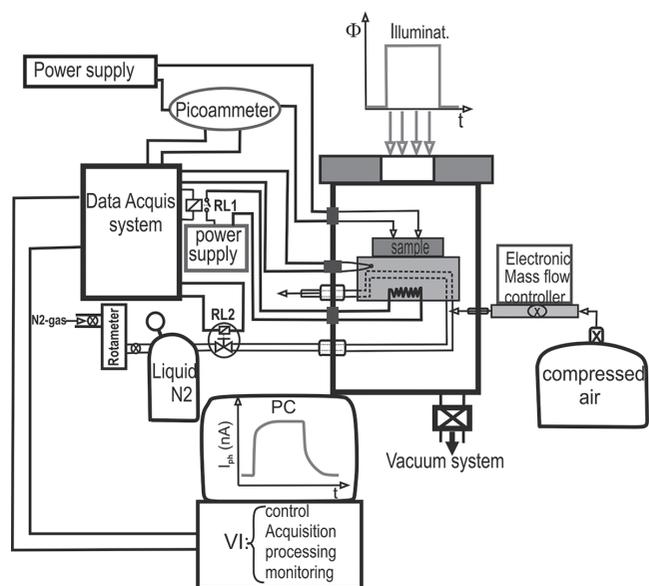
## Experimental

The  $\text{CH}_3\text{NH}_3\text{PbI}_3$  films were deposited on glass slides by spin-coating at 3000 rpm of a mixed halide precursor solution composed of  $\text{CH}_3\text{NH}_3\text{I}$  and  $\text{PbI}_2$  0,4M in DMSO. The solution was prepared using commercial  $\text{PbI}_2$  (Sigma Aldrich) and MAI synthesized in our laboratory as precursors. The MAI precursor was synthesized from a mixture of 5 mL of hydroiodic acid to 67%, 15 mL of solution 2,0M of methylamine in methanol and 20 mL of water, kept at 0°C for 2 hours. The obtained solid was purified by washing it with diethylether up to obtaining the pure and dry compound.

The photocurrent measurements were carried out using electrical contacts of silver deposited on the sample surface by evaporation, with 1 cm of distance between them. The sample was illuminated with a 250W Halogen lamp whose intensity (measured in  $\text{W}/\text{m}^2$  using a pyranometer Kipp & Zonen, Model CM3) was changed by varying the sample-lamp distance. Figure 1 shows a block diagram of the equipment implemented for measurements of both transient photocurrent and thermally stimulated current.

This equipment includes the following units:

- i) Measuring chamber connected to a system of pre-vacuum ( $2 \times 10^{-2}$  mBar) in whose interior is located the sample whose temperature can be varied between 80 and 750K by placing it on a block of copper which is cooled by flowing liquid nitrogen through it, followed by heating through a heating resistor connected to a power supply.
- ii) System with facilities to perform measurements of transient Photocurrent and thermally stimulated current, constituted by a power supply operating at a constant dc voltage of 100V to supply a current to the sample which varies between  $10^{-7}$  and  $10^{-5}$ A depending on the resistance of the sample; the variation of photocurrent ( $\Delta I$ ) produced by lighting or by thermal stimulation, that is between 10 and 30nA for TSC measurements and between 10 and 100nA for photocurrent measurements, is measured with a picoammeter Keithley 485 which generates an analog voltage signal proportional to  $\Delta I$ .
- iii) Data acquisition and control system implemented using virtual instrumentation with facilities to control the sample temperature and to perform functions of control, acquisition, processing and monitoring of data. The equipment also allows realizing photocurrent measurements at different pressures, which are controlled through an electronic mass flow controller connected to a cylinder with compressed air, keeping the vacuum system in operation. This system also allows generating ramps of temperature at a constant rate in the range of 2-30°C/min, which is necessary to be able to do TSC measurements.



**Figure 1.** Scheme of the setup implemented to measure transient photocurrent and thermally stimulated current.

The hardware used includes: the Field Point-F1000 module which performs the communication with the PC through the

RS232 port, an analog input module cFP-TC-120 to acquire the voltage signal from the thermocouple type K used as temperature sensor and a card NI USB-6008 to measure the current. The functions of control, measurement, acquisition, processing and display of data are made through a Virtual instrument (VI) developed with LabVIEW.

## Description of the data acquisition and control system

### System of heating and cooling of the sample

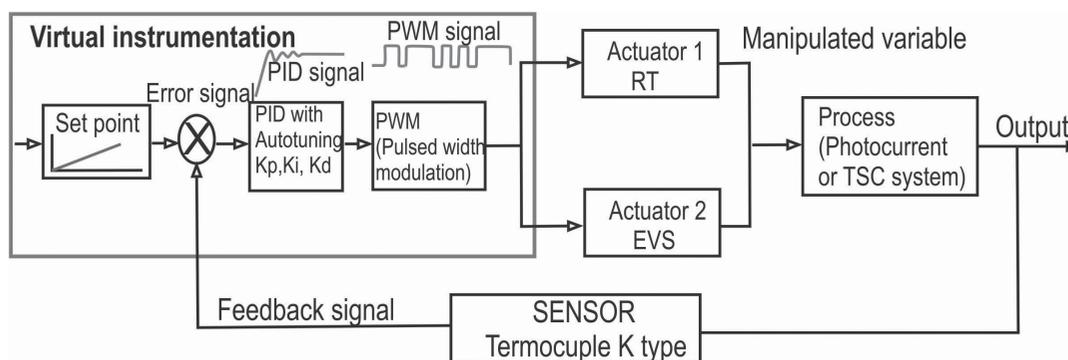
In Figure 2, a block diagram of the system implemented to control both the heating and cooling of samples to be studied through photocurrent and TSC measurements is shown. This system is composed of a block of copper which is heated through a heating resistor connected to a power supply and the cooling is done by flowing liquid nitrogen through the copper block. The temperature of heating and cooling is controlled through an algorithm PID-PWM implemented in a virtual instrument developed with LabVIEW.

The incorporation of the PWM (Pulsed Width Modulation) algorithm was made to be able to control the power of the analog power supply; taking into account that the power of this source can only be controlled by varying the frequency of a system on/off; in this case, the signal of feedback is

obtained from a thermocouple type K which is acquired by means of a module of communication Field Point-1000 (FP-1000) that has installed a sub-module FP-TC-120 special for thermocouples

The virtual instrument includes a function called "autotuning" that allows to automatically obtain the control parameters of the PID algorithm ( $K_p$ ,  $K_i$  and  $K_d$ ); the control signal generated by the PID algorithm before leaving the virtual instrument is transformed by means of the system PWM to activate or deactivate the relays and in this way to be able to modify the power supplied by the source to the actuator (heating resistor). A solid-state relay (RL1) controls the current that the power supply (Gwintex, PSP405, 0-30V, 0-5Am) supply to the heating resistance RT and a second relay (RL2) controls the flow of nitrogen that flows through the copper block through the solenoid valve (EVS). The control signal 1 generated in the virtual instrument exits via the digital channel (DO) 0,1 of the card USB-6008 toward RL1 and the control signal 2 exits through the digital channel (DO) 0,2 of the card USB-6008 toward RL2.

The temperature control system developed in this work allows a temperature control with greater precision ( $\pm 2K$ ) than the obtained one with commercial PID controllers, and additionally allows generating ramps of temperature varying at a constant rate.



**Figure 2.** Block diagram of the system designed and implemented to control the heating and cooling of samples to be studied through photocurrent and TSC measurements.

### Interface of acquisition, monitoring and control

A user's interface was designed with help of LabVIEW software that allows through virtual instruments performing programs in the form of block diagram, with facilities to make acquisition, processing and monitoring of data as well as control of equipment and processes. In the front panel (user interface) of the VI developed is possible to visualize the controls that allow modifying the set point and to change the control algorithm. This consists of two tabs, one to keep the temperature constant during the photocurrent measurements and another to generate ramps of temperature at constant rate to perform TSC

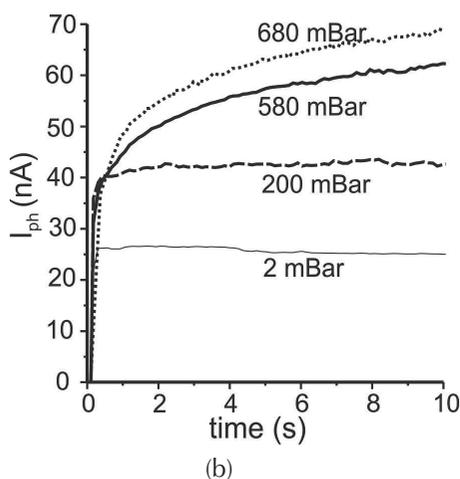
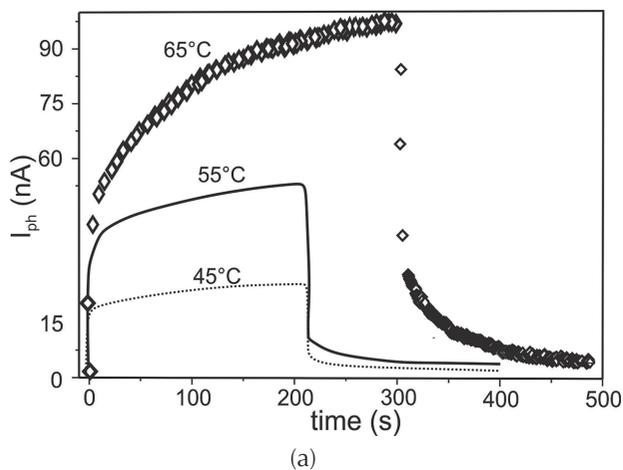
measurements. This allows visualizing in real-time both the value of the feedback signal and the set point by means of a graphic indicator. In addition, the VI allows to monitor the state of the control system displaying a graph of the variable of control generated by the algorithm PID-PWM as a function of time.

Further, the user's panel includes a tab called "Data registering" which displays in real time the value of the photocurrent and the temperature, independently of in what control stage the synthesis process is. The system also includes a facility to create data files with the information of transient Photocurrent and thermally stimulated current,

these data is used to analyzed the trap and recombination process in the  $\text{CH}_3\text{NH}_3\text{PbI}_3$  thin films.

### Test of the system performance through measurements of transient photocurrent and thermally stimulated current

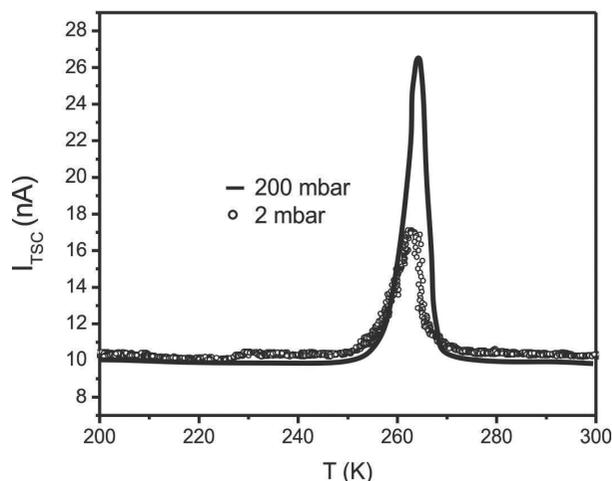
The performance of the developed system was tested by measuring the response of photocurrent transient and of thermally stimulated current of  $\text{CH}_3\text{NH}_3\text{PbI}_3$  thin films. Figure 3 shows typical curves of photocurrent transient measured under different temperatures and pressures, and Figure 4 displays a typical curve of TSC; both the photocurrent response and TSC curve were obtained with a  $\text{CH}_3\text{NH}_3\text{PbI}_3$  thin film deposited by spin coating.



**Figure 3.** Rise and decay curves of photocurrent of a  $\text{CH}_3\text{NH}_3\text{PbI}_3$  thin film, measured a) under different temperatures and b) under different pressures.

The results displayed in Figures 3 and 4 were presented previously by our group in the frame of two European International Conferences [G. Gordillo *et al.*, 2016, A. A and Ramirez *et al.*, 2016]. This study revealed that

in general, the photocurrent of  $\text{CH}_3\text{NH}_3\text{PbI}_3$  thin films is affected by both trap assisted fast recombination processes and traps whose activation process is delayed, being the contribution that the first process makes to the intensity of the photocurrent much greater than that of the second one. It was also found evidence that the  $\text{CH}_3\text{NH}_3\text{PbI}_3$  film exhibit a rather deep trap states at around 459 meV which confirm that this process can be attributed to trap assisted recombination. Additionally, the  $\text{CH}_3\text{NH}_3\text{PbI}_3$  films present shallow trap states at 129 and 24 meV what allows to infer that these shallow states correspond to states of traps. Deconvolution of the TSC curves revealed that samples exposed to an ambient of 200 mBar, present three traps centers located at 0,124, 0,519 and 1,42 eV above the valence band, whereas the samples exposed to an ambient of 20 mBar, present two traps centers located at 0,179 and 0,495 eV.



**Figure 4.** TSC curves of a typical  $\text{CH}_3\text{NH}_3\text{PbI}_3$  sample, obtained from measurement performed under an ambient corresponding to pressures of 20 and 200 mBar respectively.

### Conclusions

A novel system with facilities for automatic measuring of thermally stimulated current and transient photocurrent was developed using the Virtual Instrumentation concept. The novel aspects includes an improved controller which allows heating and cooling of a sample with greater precision than the obtained one with commercial PID controllers, and additionally allows measuring the response of photocurrent and of TSC of a sample under conditions of temperature and pressure controlled.

The effectiveness and reliability of the developed system was proved with quite success by measuring the response of photocurrent transient and of thermally stimulated current to thin films of the organic / inorganic hybrid compound  $\text{CH}_3\text{NH}_3\text{PbI}_3$  with structure perovskite, used in the manufacture of solar cells by our research group.

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