Vol. 19, No. 3 (2020) 1351-1361
Revista Mexicana de Ingeniería Química

Automation of the successive ionic layer adsorption and reaction -SILAR- process

Automatización del proceso de adsorción y desorción de iones en capas sucesivas SILAR

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Received: December 10, 2019; Accepted: February 4, 2020

Abstract

An electromechanical system controlled by a graphic interface developed in a JAVA programming environment was designed and developed, which allows the control of the growth parameters of thin semiconductor films on glass substrates obtained by the SILAR technique. The parameters that can be controlled through the graphical interface are: time, immersion sequence in the solutions and number of cycles. A low-cost microcontroller was used that allowed adapting an electromechanical system with DC motors that locates the substrate holder in the respective chemical solutions. The information of the control parameters and the progress of the process can be visualized in any computer system where the developed program be executed. The results obtained show that the SILAR automated system allows obtaining homogeneous thin film deposits. The film thicknesses are controlled by the number of cycles programmed in the SILAR process.

Keywords: SILAR, chemical bath deposition, thin films, semiconductor films, automation.

Resumen

Se diseñó y construyó un sistema electromecánico controlado por una interfaz gráfica desarrollada en entorno de programación JAVA que permite controlar los parámetros de crecimiento de películas delgadas semiconductoras sobre substratos de vidrio obtenidas por la técnica SILAR. Los parámetros que se pueden controlar a través de la interfaz gráfica son tiempo, secuencia de inmersión en las soluciones y número de ciclos. Se utilizó un microcontrolador de bajo costo que permitió adaptar un sistema electromecánico con motores de corriente directa que ubica el porta-sustratos en las respectivas soluciones químicas. La información de los parámetros de control y el progreso del proceso pueden ser visualizados en cualquier sistema de cómputo en donde sea ejecutado el programa desarrollado. Los resultados obtenidos muestran que el sistema automatizado SILAR, permite obtener depósitos de películas delgadas homogéneas. Los espesores de las películas están controlados por el número de ciclos programados en el proceso SILAR.

Palabras clave: SILAR, depósito por baño químico, películas delgadas, películas semiconductoras, automatización.

1 Introduction

There are relatively low-cost techniques for growing thin semiconductor films such as chemical bath deposition (Oliva, Martín-Várguez, González-Panzo, & González-Chan, 2016), spray pyrolysis (Calixto-Rodriguez et al., 2009), electrodeposition (Calixto, Dobson, McCandless, & Birkmire, 2006), and SILAR (Akaltun & Çayir, 2015) (Çayir T., 2019a) (Çayir T., 2019b) (Çayir T., 2019c) (Çayir T., 2020). Among these techniques, SILAR is an interesting technique for which technological developments have been proposed focused on its automation. Some examples can be found in the literature, such as the case of the development presented by Garzón, Martínez, Rico, Guzmán & Vargas (2012), where they exposed an automated electromechanical system with Microchip PIC18F4550 microcontroller, which

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Tel. 7775647345
https://doi.org/10.24275/rmiq/Proc1082
issn-e: 2395-8472

allowed to control the deposition parameters by SILAR for thin semiconductor films of ZnO and ZnSe on glass substrates. The parameters that influence the growth of these films such as immersion time, sequence in the solutions, number of cycles and temperature, could be controlled and shown on a display. The results obtained in the growth of semiconductor films indicated that the automated SILAR system has a high performance, since it improved the control over the parameters used in different applications. A similar development is presented by the same authors (Garzón, Martínez, Rico, & Vargas, 2012b) where an electromechanical system was designed, implemented and evaluated for the production of coatings for devices used as humidity sensors through the SILAR process. The system is able to monitor and control the temperature of these solutions and visualize this information, as well as other parameters, in real time through the user interface developed in LabVIEW software, and uses as a control element, the data acquisition card NI DAQ-6009 responsible for receiving and transmitting information to and from the controller component. Authors concluded that the system presents stability, efficiency and versatility, because the ZnO thin films grown are homogeneous and the film thicknesses were well controlled.

In this work, the automation of SILAR process is presented, through the development of an automation system that allows the control of the deposition process to obtain thin semiconductor films. To achieve this, a program was developed to control the SILAR process, which uses an embedded system connected to a graphical interface where it is possible to select process operation options to program cycles, times per station and immersion time.

2 Theoretical foundation

2.1 The SILAR process

The SILAR (Successive Ionic Layer Adsorption and Reaction) technique consists of four different steps such as adsorption, rinsing, reaction and rinsing (Pawar et al., 2011). The method is based on the immersion of a substrate into anionic and cationic precursors, followed by rinsing of the substrate between every immersion in double distilled water in order to prevent homogeneous precipitation (Asim et al., 2014). In the SILAR process the substrates are immersed in a first chemical solution for a certain time, removed and rinsed to proceed to the second chemical solution and carry out the adsorption reaction and desorption of ions in successive layers of semiconductor materials in thin layers, then the substrate of the second chemical solution is removed and rinsed, thus ending a cycle to start again with another cycle. This process is repeated as many times as necessary to grow thin semiconductor films with different thicknesses (see Fig. 1).

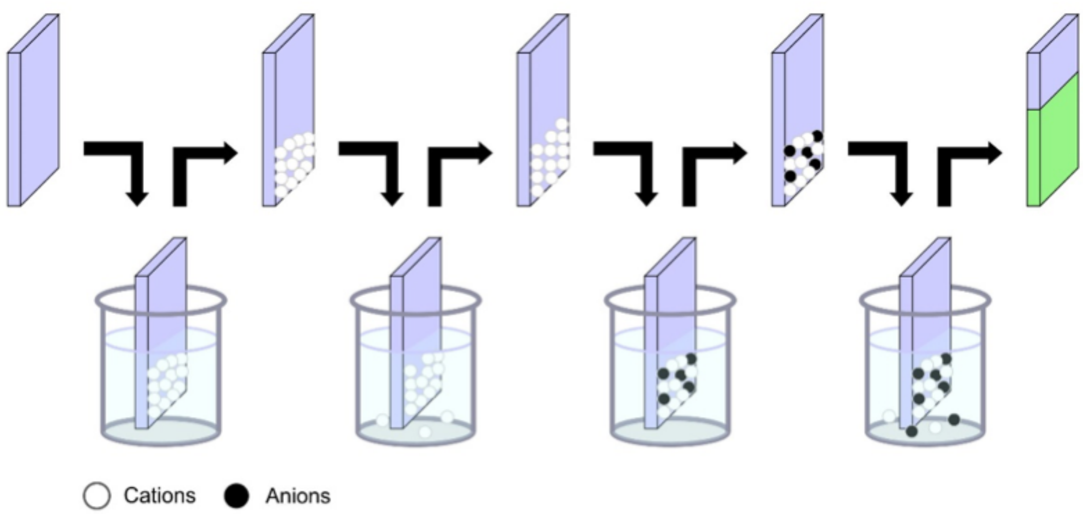

Figure 1. SILAR Process (Adapted from Pawar et al., 2011).

Materials in thin film form have different technological applications, such as solar cells (Calixto-Rodriguez et al., 2013), gas sensors (Tirado, 2015), catalytic materials (Medina-Valtierra et al., 2003) (Medina-Valtierra et al., 2005), etc., depending on the nature of each material. For example it has been reported the obtaining of copper oxide thin films by SILAR (Akaltun, 2015), which has applications as photovoltaic and catalytic material.

2.2 *Microcontroller*

A microcontroller is a digital device designed to perform some specific function or application in real time (Clavijo, 2011). The Arduino development board is a low-cost digital system, composed of an ATMEGA 2560 microcontroller which can be programmed with an Open Source type programming environment that can be modified by any user. The hardware consists of a printed circuit board with a microcontroller, digital and analog input/output ports, which can be connected to expansion boards (shields) that extend the operating characteristics of the Arduino board. It has also a USB connection port for powering the board and establishes serial communication with the computer system (Arduino, 2010). Table 1 shows the ATMEGA 2560 microcontroller technical specifications. Fig. 2 shows an image of the Arduino MEGA development board model.

2.3 *JAVA Programming Language*

Java is a high-level programming language used to write conventional and internet programs. One of the significant advantages of Java over other programming languages is that it is an independent platform, both in source and binary code. This means that the code produced by the Java compiler can be transported to any platform with Java virtual machine installed and run (Ceballos, 2000).

Java programs are executed within a virtual machine commonly called JVM (Java Virtual Machine) or also JRE (Java Runtime Environment). This means that in order to run any Java program previously we must have the JRE installed. Many operating systems bring the JRE pre-installed. Others (such as Windows) don't have it and it is necessary to install it manually. The JRE defines a unique and homogeneous environment on which the Java programs will run. As JRE is available for virtually all operating systems and all hardware architectures, Java is a cross-platform language. In other words: the same Java program can run on a Windows PC, on a Linux PC, on a Mac, on a Sun with Solaris, etc., with the corresponding JRE (Sznajdleder, 2013).

Table 1. Arduino Mega board features (Arduino, 2010).

Microcontroller:	ATmega2560 (8-bit)	Operating Voltage:	5V
Voltage input:	7-12V	Voltage Range:	6-20V
Digital I/O pins:	54 (15 PWM output)	Analog inputs:	16 (10-bit resolution)
I/O pins (current):	40 mA	3.3V pins:	50 mA
Flash memory:	256 KB	SRAM:	8 KB
EEPROM:	4 KB	Clock speed:	16 MHz

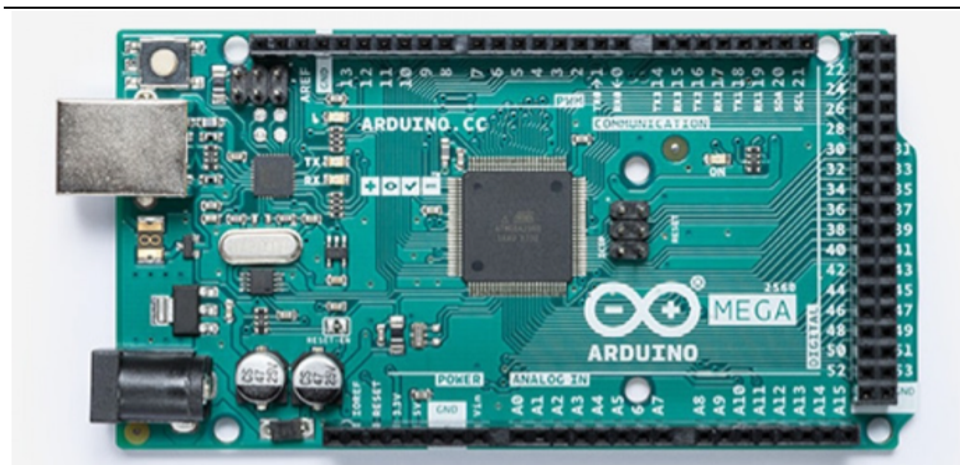

Figure 2. Arduino MEGA (Arduino, 2010).

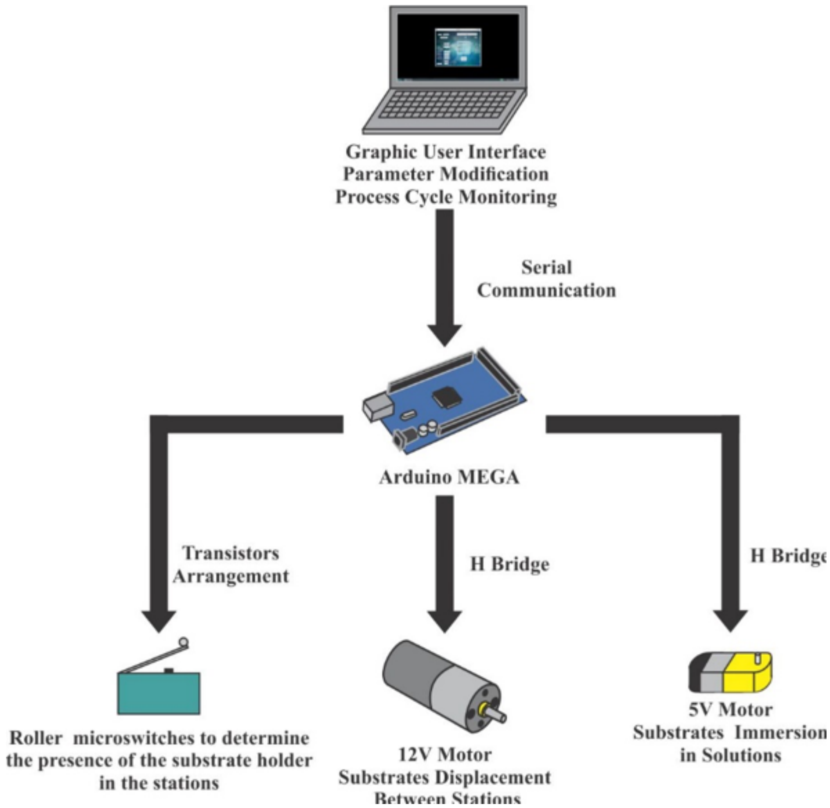

Figure 3. Automation system block diagram.

The Java compiler is called JDK (Java Development Kit). The JDK includes the virtual machine, therefore, which will usually have to install the JDK on the computer and leave the JRE for the computers of the end users. The JDK includes the language class library and commands to compile, run an application, document the application, generates headers in C language to integrate Java programs with C programs, and so on (Sznajdleder, 2013).

3 Methodology

For the automation of the SILAR process, initially the operation requirements for its development had to be identified, which were reflected in the block diagram shown in Fig. 3. In this figure, it can be seen that through a graphical user interface on a computer, the parameters of interest can be modified, and the progress of the process can be monitored. Additionally, communication was made to the microcontroller that has the function of carrying out data acquisition and generating control signals that determine the behavior of the system.

To achieve the objectives, a program for the microcontroller was developed, with which it is possible to modify the immersion times, the cycles and the sequence carried out during the film deposition process by serial communication. To facilitate the communication of the microcontroller with the user, a graphic interface was developed in JAVA with which it is possible to connect the Arduino board with a computer, through serial communication, to monitor and stop the process, in addition to defining the sequence, the immersion times at each station and the cycles that will be performed to execute the process.

The process data is sent to the microcontroller for storage, which are returned to the interface to verify that these data have been received correctly. The variables can also be deleted from the interface in case of any error in the reception of the data on the Arduino board or in a restart need. Once it has been confirmed that the data is correct the sequence to perform the process starts. Fig. 4 shows a flow chart that summarizes the operation of the program to carry out the SILAR process.

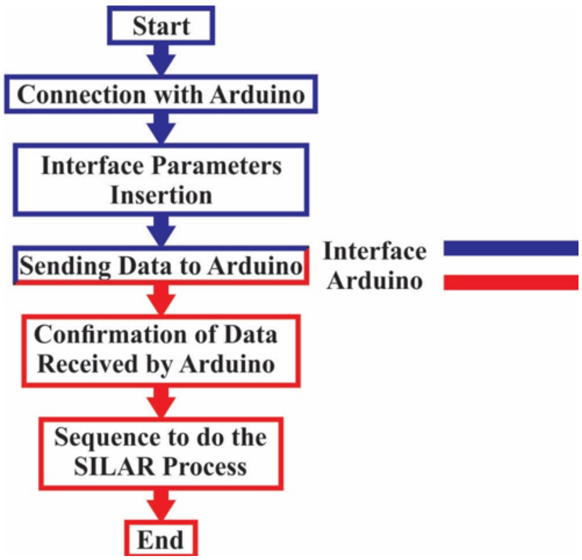

Figure 4. Program block diagram.

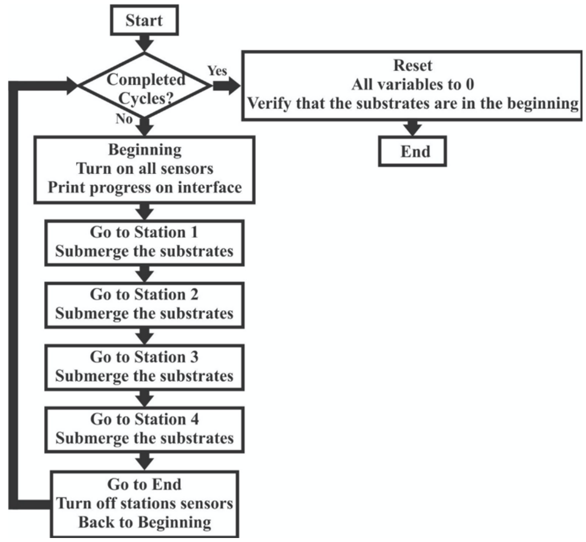

Figure 5. Subroutine 1 in the microcontroller for the SILAR process.

The microcontroller programming executes the subroutine for doing the SILAR process; the program has two default subroutine, in the first one (see Fig. 5) the substrates are immersed in all the stations in one way; while in the second subroutine the substrates are immersed in the three first stations only (see Fig. 6).

In both subroutines the substrates holder has to advance the entire spindle and, at the beginning of each cycle, the interface updates the amount of cycles already made, once the cycles are ended all the variables are restarted and the program checks that the substrates holder is at the beginning of the spindles.

Once the microcontroller subroutine is chosen, it will send the actuators (DC motors) the drive required to operate using a power circuit. The electrical system is a joint compound of roller microswitches that controls the immersions in the stations and its measurement is controlled by a set of transistors connected to the microcontroller, which by sensor's signals controls the motor movements.

The electrical system is powered by a linear 12 V DC power supply that feeds the two DC motors and another 5 V DC power supply that feeds the Arduino board and the rest of the electronic circuits. For the vertical and horizontal displacement of the substrate holder, two DC motors were used for the spindles, controlled with H-bridges that receive instructions from the microcontroller. In order to determine the presence of the substrate holder at each station, roller microswitches were used to indicate where to stop to submerge the substrates in the chemical solutions and then return to start another cycle. The microswitches

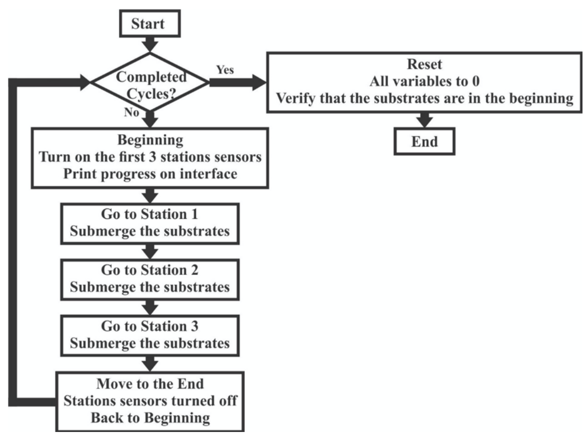

Figure 6. Subroutine 2 in the microcontroller for the SILAR process.

are positioned as follows: in each station, at the beginning and end of the spindle travel.

Due to the structure of the code, it is sometimes necessary to be able to stop the signals that the control board receives from the roller microswitches, an array of transistors that power off the power supply of the sensors was used; when the Arduino board does not require any working sensor, it sends a control signal to a transistor to cut off the sensor power supply, in this way the microcontroller code works correctly. Figure 7 shows the block diagram of this process.

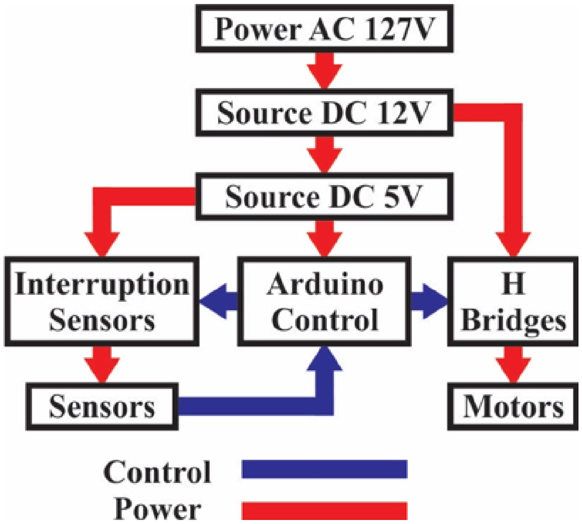

Figure 7. Electronic circuit block diagram.

Figure 8. Screen capture of the program developed in Java.

Figure 9. ASILAR system graphic interface screenshot.

4 Results

4.1 *Graphic interface*

The automated system to carry out the SILAR process was called ASILAR. The graphic interface obtained is programmed in the NetBeans development environment that uses the JAVA programming language, this language was chosen because it has an easy-to-use library for serial communication. During the interface development, the ease of installation in other equipment and the simplicity of its handling were taken into account, the interface is basically portable, the only basic requirement for its execution in any equipment is that the JAVA virtual machine is installed (JRE) in the equipment. The interface is divided into four panels with a defined function, these are the connection, control, confirmation and progress panels. The division by panels was made in order to maintain a visually pleasing distribution within the interface. Fig. 8 shows a screen capture of the developed program.

The first panel developed in the interface was for the connection with the Arduino board, which can be seen in Fig. 9 (framed in yellow), through this panel the choice of the COM port where it is connected to the microcontroller is made, this improves the versatility of the interface. This implementation makes portability possible.

As for the control panel, visible in Fig. 9 (framed in red), a reset button was added to the process variable insertion part and the ability to send all the variables with a single button, also counts with a process type selector, which allows changing the order in which the substrates are immersed in the stations.

The last two panels have a visual only function, since the confirmation panel (Fig. 9 framed in orange) only shows all the variables that were sent and its function is to verify that they were correctly received by the Arduino board, while the progress panel (Fig. 9 framed in pink) has a process bar indicating the percentage of progress and the running process cycle number.

The interface has a button to stop the process if necessary, if this button is pressed, turn off the motors, delete the process variables and restart the connection with the Arduino board. After pressing the "stop" button, it is necessary to press the reset button on the control panel, this is necessary for the motors to return to the origin position automatically.

Compatibility and operation tests were performed for the software. For this, the interface was installed on different equipment to see its performance, tests were also carried out on the graphic structure of the interface. To do this some people were asked to manipulate it and gave their opinion about it.

4.2 *Electronic circuit*

For the design of the electronic circuit, the way of feeding the electronic control circuits and the sensors was taken into account, for that a power supply was designed with the necessary characteristics to correctly feed all the electronics. In this case a power supply of 12 V at 5 A for the main motor in charge of moving the substrates between stations and another power supply of 5 V at 1 A for the electronic circuit in general and the secondary motor in charge of submerging the substrates in the solutions. The proposed circuit design is shown in Fig. 10 (Meneses, 2017).

In the control of the DC motors in this case H-bridges are used, there are different ways to build an H-bridge: H-bridges with transistors, relays, and integrated circuits (Rashid, 2015). For this investigation, a type of H-bridge was used, consisting of transistor-activated relays, this type was chosen for the amount of current required to move the motors that is around 4 A, taking into account that it is better to separate the power supply from the control circuit. This type of H-bridge is a good option, since a relay has a separation that totally divides the current from the control and power circuit, also thanks to the fact that the relays are activated by the transistors there is another separation (Malvino & Bates, 2007).

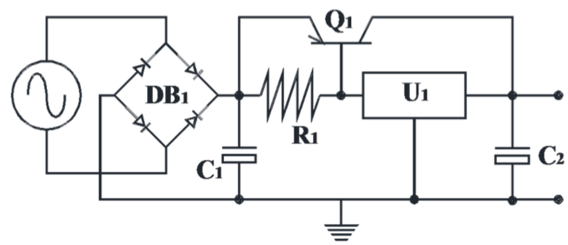

Figure 10. ASILAR system circuit: power supply circuit.

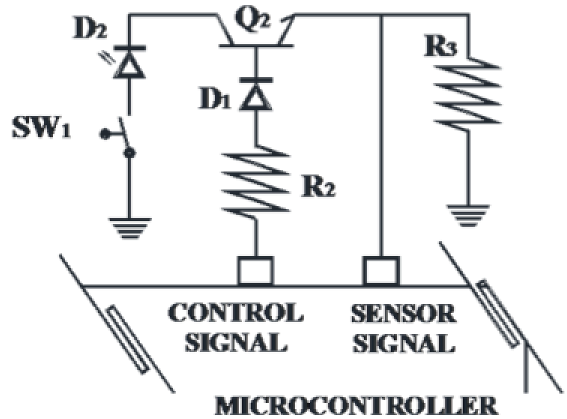

Figure 11. ASILAR system run sensor circuit.

For the control of the sensors, transistor 2N2222 was proposed to be used as a switch, this transistor will allow to control at what moment the signals are sent to the microcontroller, since in some cases it is necessary that the sensors do not send any signal while the substrate holder is in the measurement margin, this is done in order to avoid possible errors in the code that may affect the process. In Fig. 11, the proposed circuit can be observed (Meneses, 2017).

4.3 *Functionality tests*

After finishing the tests above mentioned, a simulation of the process began with three glass substrates attached to the substrate holder and the corresponding empty beaker in each station (four stations). To do this, one hundred and fifty cycles were performed using twenty seconds as immersion time in the first and third stations (reaction stations), and two seconds in the second and fourth stations (rinsing stations).

Once the previous tests were finished and some details were corrected, the tests continued with the real process. We followed step by step the procedure

Figure 12. Glass substrates immersed in third station.

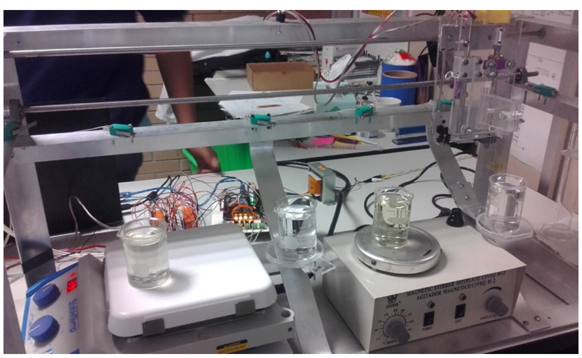

Figure 13. Process running.

reported by Nair, Guerrero, Arenas, & Nair (1999) to deposit copper oxide thin films on glass substrates, this chemical deposition is described as a SILAR process. In this process sodium hydroxide was used in the first station, which was heated to 80°C on a heating grill without magnetic stirring; a copper thiosulfate complex solution was used in the third station at room temperature; while in second and fourth stations, distilled water was used to rinse the substrates (see Fig. 12). Twenty cycles were performed using twenty seconds as immersion time in the first and third stations, and two seconds in the second and

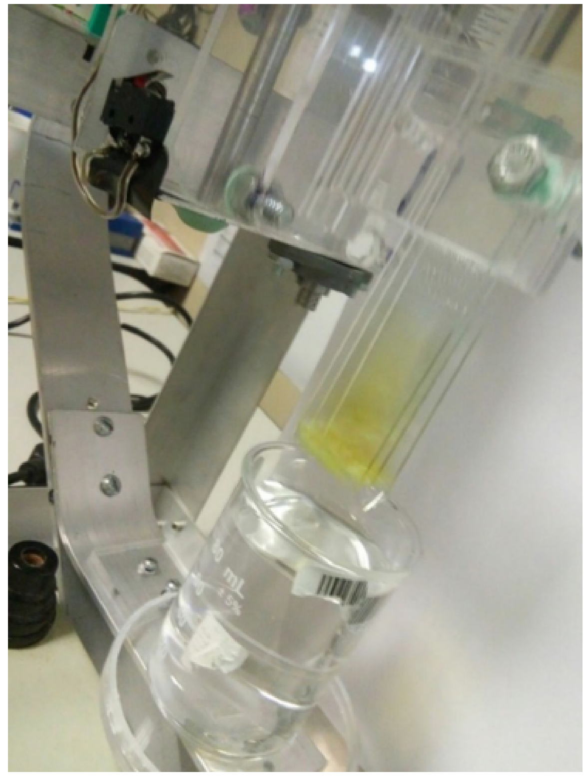

Figure 14. Copper oxide thin films with 10 cycles.

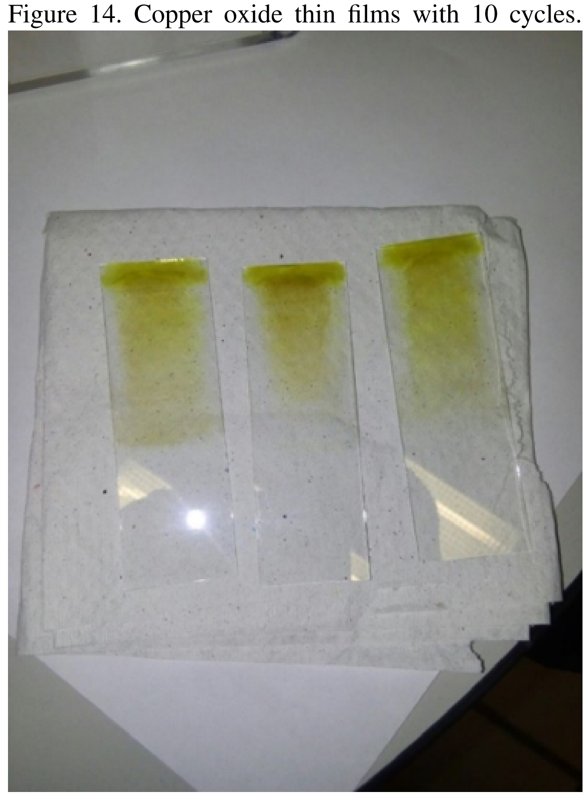

Figure 15. Copper oxide thin films with 20 cycles.

fourth stations.

The use of the interface has great functionality at the time of manipulating the process, since its simplicity facilitates the interaction with the user providing good communication between the computer and the Arduino board. In Fig. 13 the execution of the process is observed.

During the final tests, the effectiveness of system automation was observed, obtaining copper oxide thin films. Figures 14 and 15 show copper oxide thin films deposited with 10 and 20 cycles, respectively.

Conclusions

The designed and developed system consists of three stages: the software stage, the electronic stage and the mechanical stage. Up to now, the ASILAR system needs to have a personal computer to execute the program to perform the control of the SILAR process by the electronic circuit.

The graphical interface for user interaction was developed in Java and the control system with Arduino board, which makes it in software open source unlike the other developments reported in the reviewed literature. This is very important, since current trends are the use of free software and hardware for technological applications and even in industrial applications.

The ASILAR system responds quite well to the needs of the user, since semiconductor thin films can be deposited on glass substrates. The film thicknesses are controlled according to the number of cycles programmed in the SILAR process. The developed ASILAR system could be used to grow thin films of a wide variety of materials with different applications, such as solar cells, gas sensors, catalytic materials, etc.

Acknowledgements

Authors would like to thank the support of students: Dan Cruz Arellano and Eduardo Fajardo Cardoso, in the development of the electronic circuit and the mechanical system construction, respectively.

Nomenclature

Q_1	TIP42 Silicon PNP Power transistor
U_1	12 V or 5 V fixed Positive power supply regulator
DB_1	Single-phase bridge rectifier.
R_1	10kΩ Resistor
C_1	4700μ F Electrolytic capacitor
C_2	0.1μ F Electrolytic capacitor
Q_2	2N2222 Silicon NPN bipolar transistor
D_1	1N4001 Silicon rectifier
D_2	Light emitting diode (LED)
R_2	10kΩ Resistor
R_3	300Ω Resistor
SW_1	Limit switch
SILAR	Successive Ionic Layer Adsorption and Reaction
ASILAR	Automated Successive Ionic Layer Adsorption and Reaction
ZnO	Zinc Oxide
ZnSe	Zinc Selenure
CuO / Cu_2O	Copper oxides
JAVA	Programming language
LabVIEW	Systems engineering software
JVM	Java Virtual Machine
JRE	Java Runtime Environment
JDK	Java Development Kit
V	Voltage
A	Ampere
F	Farads
DC	Direct Current
k	$1x10^3$
Greek letters	
Ω	Electric resistance
μ	$1x10^{-6}$

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