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Development of novel control system to grow ZnO thin films by reactive evaporation

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A B S T R A C T

This work describes a novel system implemented to grow ZnO thin films by plasma assisted reactive evaporation with adequate properties to be used in the fabrication of photovoltaic devices with different architectures. The innovative aspect includes both an improved design of the reactor used to activate the chemical reaction that leads to the formation of the ZnO compound as an electronic system developed using the virtual instrumentation concept. ZnO thin films with excellent opto-electrical properties were prepared in a reproducible way, controlling the deposition system through a virtual instrument (VI) with facilities to control the amount of evaporated zinc involved in the process that gives rise to the formation of ZnO, by means of the incorporation of PID (proportional integral differential) and PWM (pulse width modulation) control algorithms. The effectiveness and reliability of the developed system was verified by obtaining with good reproducibility thin films of n+-ZnO and i-ZnO grown sequentially in situ with thicknesses and resistivities suitable for use as window layers in chalcopyrite based thin film solar cells.

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1. Introduction

ZnO is a semiconductor material characterized by having many interesting optoelectronic properties such as a wide band gap, a large exciton binding energy of 60 meV and high transparency in the visible region, which has made way for many applications, including flat panel displays, light-emitting diodes, and solar cells [1–4]. In particular, ZnO thin films have been extensively studied for use as transparent and conductive windows layer in chalcopyrite and kesterite based solar cells [5–7] and recently this compound also began to be used as electron selective layer in inverted organic solar cells [8,9] and as electron transport layer in perovskite based hybrid solar cells [10,11].

Various methods, such as RF magnetron sputtering [12], reactive sputtering [13], CVD [14], CBD [15], spray pyrolysis [16] and sol gel techniques [17] have been used to fabricate ZnO films. Among these methods, magnetron RF sputtering is considered the most favorable technique for large area deposition
and mass production. Cu$_2$(In,Ga)Se$_2$ based solar cell with efficiencies up to 20.5% have been achieved using RF-sputtered ZnO: Al films from ceramic targets [18]. However, the RF sputtering deposition process has cost limitations in large-area manufacturing, associated with the use of ceramic targets. In contrast, ZnO deposited by reactive evaporation with Zn as the starting material is in terms of cost and large scale production better than the RF-sputtering method.

Various routes have been used to grow polycrystalline and nanostructured ZnO thin films by activated reactive evaporation, with Zn as the starting material. ZnO films with polycrystalline wurtzite structure deposited by activated reactive evaporation following a route consisting on evaporation of Zn metal from a molybdenum boat in presence of oxygen gas ionized with a cold cathode ion source allowed to achieve transmittances around 86% and resistivities of 1.1 × 10$^{-3}$ ohm cm [19]. ZnO nanoneedles have also been synthesized by the activated reactive evaporation method [20,21]. These nanostructures were synthesized by thermally evaporating pure Zn at a high rate through oxygen plasma. To explain the growth of nanoneedles a gas phase formation mechanism was proposed. This nanoneedle nucleates and grows in the gas phase by the vapor–solid mechanism. Photocurrent studies indicated that these ZnO nanostructured films show high sensitivity to UV light, and hence can be used as efficient UV photodetectors.

In this paper we describe a novel system implemented to grow ZnO thin films using a route based on the plasma assisted reactive evaporation. Among the innovative aspects of the system, it is worth highlighting the following:

Improved design of the reactor that allows generating a stable glow discharge (GD) that promotes a chemical reaction between the ionized precursor species (Zn$^+$, O$^-$) that gives rise to the formation of ZnO thin films with opto-electrical properties suitable for different technological applications, in particular as optical window in inorganic solar cells.

Electronic control of the reactor performance developed using virtual instrumentation [22]. The main feature of this control is to allow the deposition of thin films of both, i-ZnO and n$^+$-ZnO films with appropriate properties to be used as optical window in solar cells, with a high degree of reproducibility. This was achieved through a virtual instrument (VI) with facilities to control with good precision the flux of evaporated Zn that is the parameter that most critically affects the opto-electrics properties of ZnO. The main characteristic of the developed VI, is that it includes algorithms PID and PWM to perform the control of the process using a K-type thermocouple as sensor of the temperature of the Knudsen Cell used as evaporation source of Zn and a pirani gauge as sensor of the change of partial pressure inside the chamber (that occurs when evaporated Zn starts its reaction with the oxygen present in the chamber).

The effectiveness and reliability of the developed system was verified by obtaining a reasonable degree of reproducibility of a large number of ZnO thin films with thicknesses, transmittances and resistivities suitable for use as transparent and conductive window layer and as a diffusion barrier in solar cells.

2. Description of the setup implemented to grow ZnO thin films

The ZnO thin films were deposited using a route based on the plasma assisted reactive evaporation method, which consists of evaporating Zn in the presence of oxygen, so that there takes place a chemical reaction that gives place to the formation of the ZnO. As the Zn in the presence of O$_2$ oxidize very slowly at room temperature, it is necessary to ionize both Zn and O$_2$ to accelerate the chemical reaction between these two species. The ionization is achieved through GD that includes different ionized species that increase the speed of chemical reaction and therefore the rate of growth of ZnO film. Under the conditions of current and pressure used in the reactive evaporation process, the generated plasma is a non-thermal plasma that implies that the most probable mechanism of ionization of the gas inside the plasma is direct ionization of neutral particles (atoms, molecules or radical) by electron impact [23].

For the design of the reactor that allows generating a stable GD confined in the space between the electrodes, it took into account the Paschen law that relates the voltage for the initiation of the discharge and the product of the pressure by the separation distance between the electrodes [23]. For the reactor designed in this work and under the conditions of pressure used, it was found that for oxygen, a stable glow discharge is obtained by applying a voltage difference of the order of 500 V.

Fig. 1 shows a scheme of the setup designed and implemented to grow ZnO thin films by plasma assisted reactive evaporation. This includes the following units:

![Scheme of the setup implemented to grow ZnO thin films by plasma assisted reactive evaporation.](image-url)
(a) Vacuum system, consisting of a mechanical pump and a trap of liquid nitrogen that allows getting a base pressure of $10^{-4}$ mbar, prior to the introduction of oxygen.

(b) Reactor where takes place the chemical reaction of precursors ($O_2$ and Zn) giving rise to the formation of the ZnO. This includes parallel flat electrodes supported by a structure of teflon and a DC power supply ($2000 \, \text{V}, 200 \, \text{mA}$) regulated in both voltage and current, used to activate the GD (see insert of Fig. 1).

(c) Source of evaporation of zinc (Knudsen cell).

(d) Electronic mass flow controller.

(e) Control unit, whose main function is to control the amount of zinc that arrives to the GD zone, which is provided by evaporation from the Knudsen cell. The functions of control, measurement, acquisition, processing and data visualization are made through a virtual instrument developed with LabVIEW. The hardware used includes: the Compact Field Point-1804 module (cFP-1804), 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 an analog input module cFP-IO-611 to acquire the voltage signal from de Pirani Gauge used as sensor of the change of partial pressure inside the chamber.

To get conditions to deposit in reproducibly way i-ZnO and n$^+$-ZnO films with thicknesses, transmittances and resistivities suitable to be used as optical window in solar cells is, is necessary to control very accurately the current of ions of the glow discharge and the flow of both oxygen and zinc that arrives to the area of the plasma. The current of ions generated during the GD and the oxygen introduced into the deposition chamber are controlled with good accuracy using a power supply regulated in current and an electronic flow mass controller; however, an accurate and reproducible control of the amount of Zn arriving to the GD zone is very difficult to achieve mainly due to the high vapor pressure of Zn and to the fact that the temperature at which starts the evaporation of the zinc changes significantly with the room humidity and the moisture absorbed in the walls of the chamber and the electrodes. Since the amount of Zn arriving to the GD zone is the parameter that most critically affect both the reproducibility and the opto-electrical properties of the ZnO films, it was necessary to develop a tool that allows to do a reliable and precise control of the amount of Zn that arrives to the GD area.

3. Description of the control system

We found out that the best way to control the amount of Zn arriving to the GD region is controlling the evaporation of Zn in two steps; in the first of them the temperature ramp of the Knudsen cell is controlled up to reaching a temperature of 400 °C to prevent that the high vapor pressure of the Zn obstructs the exit hole of the Knudsen cell. When this temperature is reached, it begins the second step that incorporates an indirect control of the temperature of evaporation of Zn through a control of the decrease of partial pressure (DP) inside the deposition chamber, which is observed when Zn starts evaporating. This control was performed through a virtual instrument that includes PID and PWM control algorithms for each of the stages. For the initial step the feedback signal is obtained from a K-type thermocouple that senses the temperature of the Knudsen cell and for the second step the feedback signal comes from a transducer that convert the signal generated by the pirani Gauge that senses the change in partial pressure inside the chamber, in a voltage signal proportional to the amount of Zn arriving to the GD zone. The control signals generated by the two algorithms act on the power supply that provides current to the heating element of the Knudsen cell. The activation of each of the control algorithms are given through the activation of a logical command located in a panel of user, implemented with the LabView software.

Fig. 2 shows a block diagram of the control system designed for each of the stages following a schema in closed loop; from the feedback signal generated by the sensors TC and PT is determined the error signal with respect to the desired value (set point); this error signal enters to the PID control algorithm which generates an analog control signal that is modulated by amplitude of pulses through a PWM algorithm. The incorporation of the PWM algorithm was made to be able to control the power of the analog power supply used to supply current to the Knudsen cell. The power of this source can only be controlled by varying the frequency of a system on/off.
3.1 Interface of acquisition, monitoring and control

A user’s interface was designed with help of the software LabVIEW that allows through virtual instruments to perform 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. Figs. 3 and 4 shows the front panel (user interface) of the VI developed where it is possible to visualize the controls that allows modifying the set point and to change the control algorithm. This consists of two tabs, one for the temperature of the Knudsen cell and another for the change in the partial pressure; these allow 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 “graphic of the process” which displays in real time the value of the partial pressure and the temperature of the Knudsen cell, independently of in what control stage the synthesis process is (see Fig. 5).

For acquisition and output of data there was used the module Compact FieldPoint 1804 (cFP 1804) connected to three input–output (I/O) modules through RS232 serial connectivity. As control variables were used voltage signals proportional to the temperature of the Knudsen cell and to the partial pressure inside the chamber, which are generated by a type K thermocouple and a pirani gauge connected to the vacuum control unit Balzers TFG 300, that operates as a transducer generating a voltage signal proportional to the pressure. The signal generated by the thermocouple is acquired through the input module cFP-TC-120 and the signal generated by pirani gauge is acquired through the input module FP-AI-610. As output variable is used a digital signal modulated by pulse amplitude, which by means of a solid state relay controls the current supplied by the power source (Gwintex, PSF405, 0–30 V, 0–5 A m) to the resistance that heats up the Knudsen cell; this signal is generated through the digital output module CFP-DO-400.

4. Results

The system of control developed was tested by depositing a large number of thin films of n⁺-ZnO, i-ZnO and i-ZnO/n⁺-ZnO bilayers deposited in situ. After optimizing the operation of the control system, this was used to find conditions to deposit thin films of i-ZnO and n⁺-ZnO with opto-electrical properties suitable to be used as optical window of solar cells. This was performed through a study of the influence of the main deposition parameters (change of pressure DP, O₂-flow and the
Fig. 6 - Variation of resistivity, transmittance (at 700 nm) and figure of merit of ZnO thin films as a function of change of pressure DP (keeping I = 3 mA and O2-flow = 12 mL/min).

glow discharge current I) on both, the electric resistivity \( \rho \) and transmittance T. As in general when decreases the resistivity of the ZnO thin films, its transmittance also tend to decrease, the optimization of the deposition conditions were obtained through a figure of merit FM that includes both the transmittance and resistivity, defined by the relation \( FM = -1/\rho \ln(T) \) [24].

Preliminary studies revealed that the O2-flow and the glow discharge current I affect the transmittance and the resistivity of the ZnO films but in much less grade than the produced one by the change of pressure DP. It was found that currents between 2 and 5 mA and oxygen flow between 10 and 15 mL/min can be used to grow highly transparent ZnO thin films with resistivities varying over a wide range, varying the partial pressure DP. Fig. 6 shows curves of variation of T, \( \rho \), and FM of ZnO thin films deposited varying DP between 0.02 and 0.12 mbar.

The results of Fig. 6 show that ZnO thin films deposited under the parameters: \( I = 3 \) mA, \( O_2\)-flow = 12 mL/min and \( DP = 0, 08 \) present transmittances of about 85% and resistivities of the order of \( 7 \times 10^{-4} \) \( \Omega \) cm, While the samples prepared under the parameters: \( I = 3 \) mA, \( O_2\)-flow = 12 mL/min and \( DP = 0, 025 \) present transmittances in the order of 90% and resistivities greater than \( 10^3 \) \( \Omega \) cm.

Based on the results reported previously, there was implemented a program to control the system of deposition of ZnO that allowed to grow in situ bilayers of i-ZnO/n'-ZnO with thicknesses, transmittances and resistivities suitable to be used as optical window of solar cells.

Fig. 7 shows typical profiles of both, Knudsen cell temperature and DP generated through the use of the program built to control the system of deposition, which allows growing in situ highly transparent i-ZnO and n'-ZnO films with resistivities less than \( 10^{-3} \) \( \Omega \) cm for n'-ZnO films and greater than \( 10^3 \) \( \Omega \) cm for i-ZnO films. n'-ZnO films deposited with DP = 0.08 mbar grow at a rate of about 10 nm/min and the i-ZnO films deposited with DP = 0.025 mbar grow at a rate of around 3 nm/min. Therefore to deposit i-ZnO/n'-ZnO bilayers with thicknesses of 30 nm and 800 nm respectively, used typically in a solar cells is required a time of deposition of 90 min.

In Fig. 8 are displayed curves of transmittance, corresponding to thin films of i-ZnO, n'-ZnO and the i-ZnO/n'-ZnO bilayer, that were deposited using a profile of deposition as the showed one in Fig. 7. The thickness measured using a Veeco Dektak 150 surface profiler was 35 nm, 810 nm and 850 nm for the layers of i-ZnO, n'-ZnO and i-ZnO/n'-ZnO bilayer respectively.

The transmittance of the ZnO/n'-ZnO bilayer shows maxima and minima of less amplitude than the layer of n'-ZnO, indicating that the interface of the bilayer induces a loss of coherence of the rays that are involved in the multiple

Fig. 7 – Typical profiles of the Knudsen cell temperature and of the partial pressure change DP that allow depositing in situ the bilayer i-ZnO/n'-ZnO with thicknesses, transmittances and resistivities suitable to be used as optical window of solar cells.

Fig. 8 – Transmittance of typical thin film of i-ZnO, n'-ZnO and i-ZnO/n'-ZnO, grown by reactive evaporation.
internal reflections that give rise to constructive and destructive interference. The transmittance of the i-ZnO layer does not present maxima and minima of interference because this one is very thin.

5. Conclusions

A novel system was implemented to grow by plasma assisted reactive evaporation method, ZnO thin films with suitable opto-electrical properties to be used for different technological applications, in particular for fabrication of organic, inorganic and hybrid thin film solar cells. The novel aspects includes an improved design of the reactor used to activate the chemical reaction that leads to the formation of the ZnO compound as well as an electronic system developed using the virtual instrumentation concept, whose main function is to control the ZnO growth process through a control of the amount of evaporated zinc, which is the parameter that most critically affects the opto-electric properties of the ZnO films and the reproducibility of deposition process. The performance of the control system was optimized through the incorporation of an innovative idea that allowed to control with a high degree of precision and sensitivity the amount of Zn evaporated; this consisted of relating the amount of Zn evaporated with the difference of partial pressure inside the evaporation chamber that occurs when evaporated Zn starts its reaction with the oxygen present in the chamber, which was achieved through a Virtual Instrument that includes algorithms PID and FWM to perform the control using a K-type thermocouple as sensor of the temperature of the Knudsen Cell used as evaporation source of Zn and a pirani gauge as sensor of the change of partial pressure inside the chamber.

The effectiveness and reliability of the developed system was verified by obtaining with a reasonable degree of reproducibility of a large number of thin films of n’-ZnO and i-ZnO grown sequentially in situ with thicknesses, transmittances and resistivities suitable for usage as transparent and conductive window layer and as a diffusion barrier in chalcopirite based thin film solar cells.

Conflicts of interest

The authors declare no conflicts of interest.

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