

Fast reactive feedback process control using a chalcogen pulsed cracker effusion valve for industrial CIGS deposition

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Abstract: This paper shows a fast process control for reactive deposition of semiconductor chalcogen compounds, such as CIG(S, Se) absorbers and S-based buffer layers (Indium or Zinc Sulphides). A Plasma Emission Monitoring (P.E.M.) based feedback control is implemented for high precision control of the chalcogen species. The chalcogenides are injected in the plasma in vapour phase by means of a pulsed valve cracker effusion cell. The metal-to-chalcogen balance can be tuned and stabilized for long deposition times, thus obtaining high deposition rates and precise control of the film stoichiometry, this is crucial for obtaining high efficiency devices. A single step and stable sputtering process for CIGS thin film solar absorbers that could improve process yields and reduce product cost is presented.

1 Introduction

Reactive feedback control in magnetron sputtering deposition technology has increasingly been accepted in the field of high speed PVD. The introduction of suitable feedback control in certain industrial processes has made it possible to increase the deposition rates keeping an excellent degree of uniformity. This has rendered in some of the fastest return of investment seen in the deposition industry.

Feedback control in processes requiring reactive gases such as oxygen or nitrogen are relatively easy to implement via fast mass flow controllers [1]. However, certain industrial processes require the injection and control of species that are not so easy to be delivered in a vapour phase, e.g. chalcogens used for CIGS production.

In recent years, the need for high quality and productivity CIGS for photovoltaic applications to a low cost has increased dramatically. While laboratory results have achieved efficiencies as high as 20.4% [2], the mass production of panels using CIGS solar cell technology has proven to be extremely difficult. The implementation of a large-scale, all-vacuum sputtering deposition process of entire CIGS cell stacks has to this day not been successfully achieved.

Regarding the development of a single-step deposition of chalcogen-based compounds, different ways to inject S or Se into the vacuum system has been presented. Some of them would involve evaporation methods where the flows of the elements are very difficult to control. In some other cases the delivery form could have severe health & safety issues, (e.g. processes involving the manipulation of H_2S or H_2Se).

This paper introduces a novel method of solving many of these issues.

2 Experimental results

2.1 Setup description

A novel reactive sputtering process control for the deposition of chalcogen compounds is presented. Two rectangular magnetrons operated in AC mode at 40kHz are used for sputtering of the metal part (Cu-based alloys, Zn and In), while a pulsed valve cracker linear effusion cell [3] is used to generate a precise control of the evaporated chalcogen species (Selenium and Sulphur). The linear effusion cell is composed of a chalcogen evaporation reservoir, a fast actuating valve and a cracking zone for breaking the evaporated chalcogen molecules. The Se, S flux is controlled by adjusting the valve opening time at a stable reservoir temperature, thus allowing a fast acting and reproducible control of the Se, S flux for long deposition times. The chalcogen evaporation rate was shown to be linearly proportional to the valve aperture time, demonstrated in Figure 1.

As changes occur in the plasma environment, the P.E.M. sensor monitors the variations in the signal intensity. This provides an input to the fast process control that automatically actuates

the effusion cell valve to adjust the Se, S flux. The balance of metal and chalcogen atoms is maintained at the optimum level for obtaining high deposition rates and control of the film stoichiometry, which is crucial for obtaining high efficiency devices.

2.2 Hysteresis ramps and stability measurements:

The hysteresis behaviour of the reactive sputtering process is studied in order to understand the poisoning and de-poisoning process. To perform this study, the response of the sensor signal is plotted as a function of the time, while the flow of evaporated chalcogen is ramped up and down. As shown in Figure 2, a clear region between the 'metal' and 'fully poisoned' states is observed. A feedback control response for the Cu emission line (514nm) is shown in Figure 3, which illustrates that the fast effusion cell control can move the process between different set-points and establish an efficient and stable control.

3 Figures

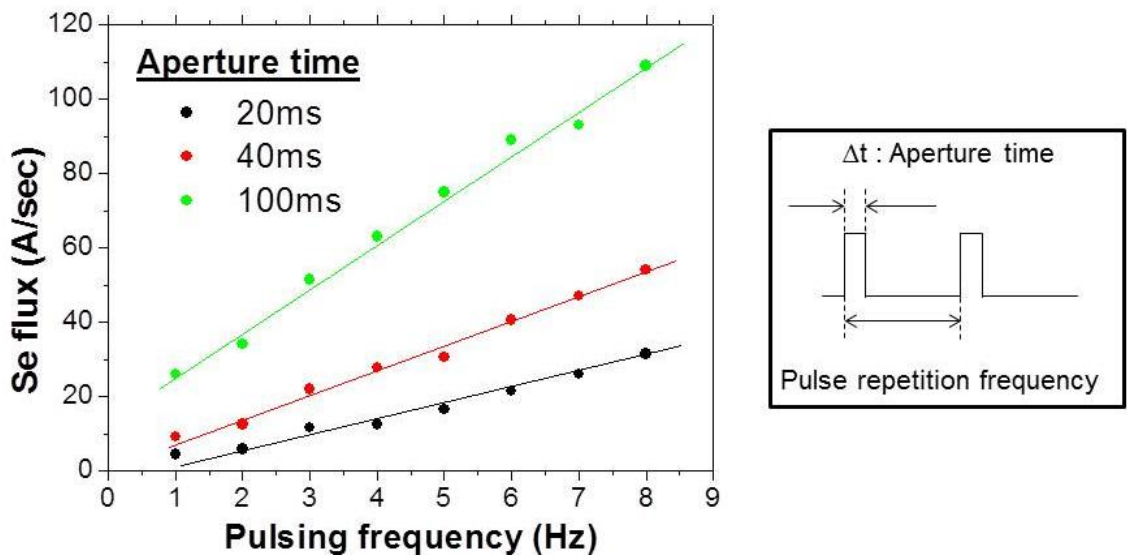


Figure 1. Left: Se flux measured with a Quartz Microbalance as a function of the valve aperture repetition frequency and for different aperture times (time on). The Se flux is linearly proportional to repetition frequency, and dependent on the valve aperture time. The evaporation reservoir temperature is stabilized at 325°C. An active control in the valve aperture parameters allows an excellent control of the Se flux. Right: Schematic illustration of the pulses of atomic chalcogen (Se, S) vapour by the Cracker Valve control. By adjusting the time on (valve aperture time) at a particular repetition frequency of pulse different average flow can be injected into the vacuum deposition system.

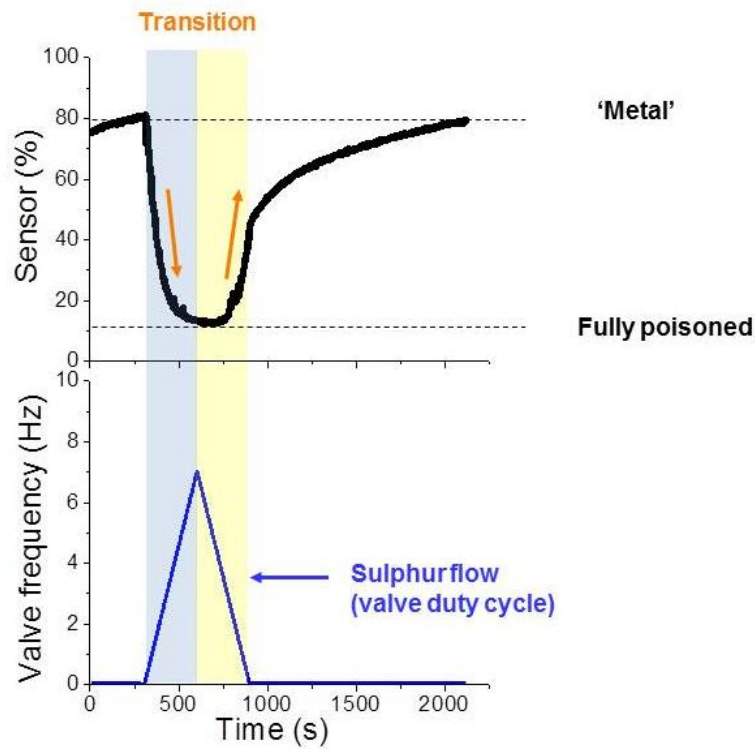


Figure 2: Evolution of the optical P.E.M. signal (Copper target, $\lambda=514\text{nm}$) as a function of the S flux. The metal-to-poisoned state of the magnetron sputtering source is clearly observed.

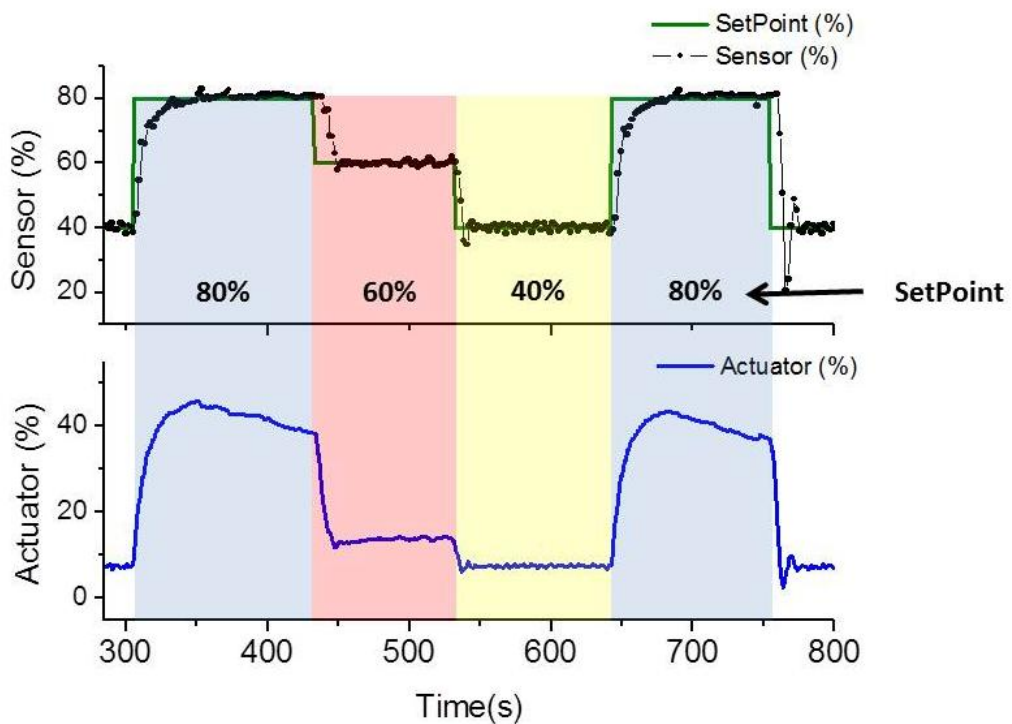


Figure 3: Evolution of the optical P.E.M. signal as a function of time under active effusion cell feedback control (Copper target, $\lambda=514\text{nm}$). The intensity of the P.E.M. signal is kept constant under effusion cell valve actuation in order to adjust the S flux.

3 Summary

This work demonstrates the implementation of plasma emission monitoring (P.E.M.) based feedback control for the deposition of chalcogen compounds, by using a solid source pulsed effusion cell for the reactive gas injection. The metal-to-chalcogen ratio is balanced and stabilized for long deposition times.

References

- [1] www.gencoa.com
- [2] EMPA press release January, 18th (2013).
- [3] www.nano4energy.eu