Pulsed Monomer Injection for Thin Film Vacuum Polymerization Applications

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ABSTRACT

This paper will present data on a new method of monomer injections which is suitable for a large family of monomer species with different vapour pressure characteristics. This type of injectors offers an easy upscalability for large area production and control. The injector introduce pulses of monomers which could undergo polymerisation reactions via suitable activation methods, such as chemical, electron bombardment, ion bombardment, UV flash and different plasma activations. The monomer injector has been tested in a magnetron based vacuum plasma system. Suitable control methodology and equipment has been developed as well.

INTRODUCTION

Thin film vacuum polymerisation methods have gained interest over the past 20 years. Barrier applications such those on the food packaging and lighting industry have been benefiting from the advances in the industrialization of such methods. Other applications like OLED and PV cells have increased over the last 10 years. In most of these applications the control of the thin film vacuum polymer deposition is a limiting factor in terms of performance, reproducibility, control and the economics of large scale manufacturing. There are many ways in which polymers can be deposited onto a surface, some of those involve plasma-polymerisation. In terms of area coverage the largest plasma methods are related to SiO_x deposition from hexamethyldisyliloxane (HMDSO) (mainly used in the protection of thin film reflectors and food / medical packaging), lacker curing (mainly used in the decorative metallization market) and polymers on fabrics from radiation curable monomers (protection of metallized fabrics).

This paper shows a new pulsed monomer injector for vacuum polymerisation applications in comparison to MFC vapour control method. The curing method relates to a rotatable cylindrical magnetron sputtering plasma, while the flow of injected monomer is varied by using a sputter-based feedback control system.

EXPERIMENTAL

Setup Description

The monomer injection tests were carried out on a single vacuum vessel with two Gencoa's GRS75 magnetics plasma sources mounted on SCI rotatable endblocks. Targets were Al 6061 alloy 75 mm OD x 360 mm length. An AC-MF Huettinger MF-3020 power supply was used for both the AlO_x layer deposition and the plasma-polymerisation process. The controls were carried out using a Speedflo-Mini™ reactive sputtering controller.

A new Pulsed Monomer Efussion Cell was used to inject the monomers. As shown in Figure 1, it comprises a reservoir containing the liquid monomer connected to a second thermostated vaporizing zone. A valve or a liquid mass flow controlled can be used to feed the vaporizer. The vaporizer is used to evaporate the liquid monomer at a stabilized temperature, and consequently, at a stable vapour pressure. This thermostated vaporizer allows the controlled evaporation of monomers within a wide range of vapour pressures. A pulsed valve is installed in between the vaporizing zone and the vacuum vessel in order to control the flow of injected monomer. The valve is made of quartz to prevent corrosion and is hermetic, allowing complete shut-off. The amount of monomers injected to the vacuum vessel is varied by changing the tine on/off ratio. The frequency of operation of the on/off valve can be at any desired frequency, on time and off time, although the on/off valve can suitably be operated in a continuously on, or continuously off state, or with an opening/closing rate of substantially 100 Hz. This pulsed valve allows a very fast switching speed (from the fully-on to the fully-off position), thereby enabling the flow controller to react more quickly to changes in controller inputs

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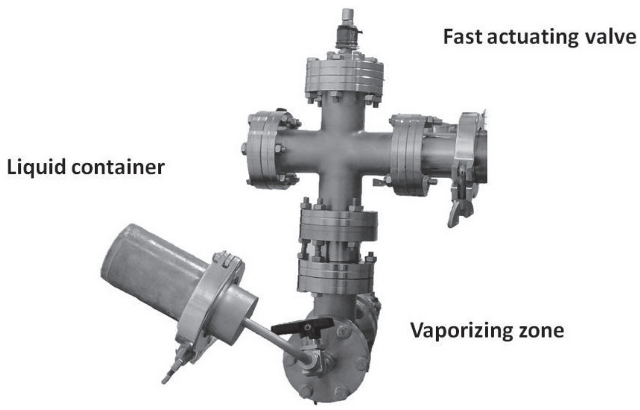

Figure 1: Schematics of the pulsed monomer effusion cell. The liquid container, vaporizer and pulsed valve are illustrated.

Different operation modes were possible on the Pulsed Monomer Injector valve, the most common being at a constant time on (valve open) with a variable frequency (as seen in Figure 2) which is being adjusted during the sensor feedback operation or in a constant frequency in an open loop control mode. All the controls of the Pulsed Monomer Injector were carried out using a Effusion controller function added to the standard Speedflo-Mini™ controller.

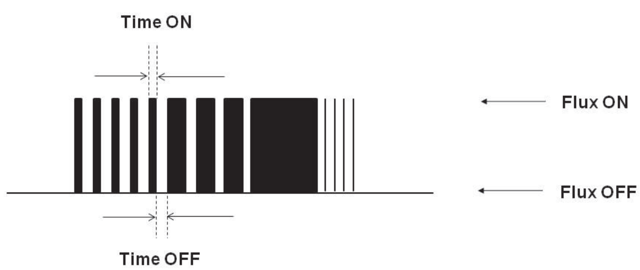

Figure 2: An example of Pulsed Monomer Injector valve operation mode. The total monomer flow variant between an open max and a closed minimum flow with fixed time on pulses and variable frequency.

Hysterisis Ramps and Stability Measurements.

The accuracy of the monomer injection using the Pulsed Monomer Efussion Cell is demonstrated by means of reactive sputtering experiments. For this purpose, a Speedflo® control unit developed by Gencoa Ltd., is used to monitor the plasma emission lines, actuate the Pulsed Monomer Efussion Cell and by means of its feedback dynamic control, stabilize the sputtering process. As changes occur in the plasma, the optical sensor monitors the variations in the intensity of the emission lines. As shown in Figure 3, this provides an input to the fast process control that automatically actuates the effusion cell valve to adjust the monomer flux. In this particular case, the Al emission line at 390 nm will be chosen to control the sputtering process. The Pulsed Monomer Effusion Cell was loaded with benzaldehyde (C_6H_5CHO), an organic compound consisting of a benzene ring with a formyl substituent. It is the simplest aromaticaldehyde and one of the most industrially useful. Its vapour pressure is 0.97 mmHg at 20ºC.

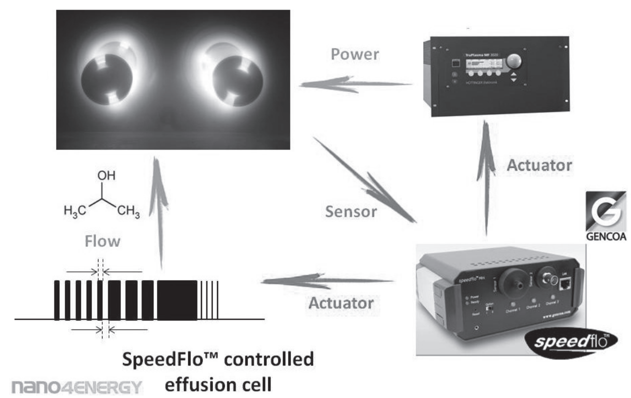

Figure 3: Experimental setup with rotatable dual magnetron sputtering and Pulsed Monomer Effusion Cell. The plasma sources were powered by a Huettinger AC-MF Power supply. A feedback controller (Gencoa Speedflo®-Mini) was used in order to control the monomer injection.

The hysteresis behaviour of the reactive Al-monomer 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 monomer is ramped up and down by changing the valve opening repetition frequency up to 50 Hz at a fixed aperture time of 1 msec. As shown in Figure 4, a clear transition between the 'metal' to 'fully poisoned' states is observed.

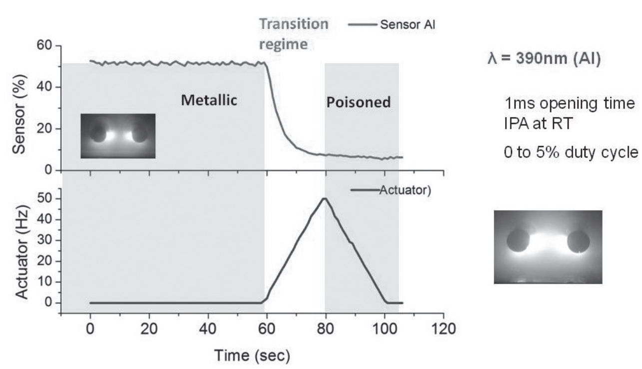

Figure 4: Evolution of the sensor signal (Aluminum emission line at λ = 390 nm) as a function of the monomer flow, controlled by the valve repetition frequency at a fixed opening time of 1msec. The metal-to-poisoned state of the magnetron sputtering source is clearly observed.

In reactive sputtering, it is well known that the plasma is unstable even when the involved parameters remain constant. For that reason, and once the dynamics of the target contamination has been characterized, a feedback control is implemented in order to stabilize the sputtering process. Moreover, in some cases it is desirable to move a process from different working set-points to obtain for example, composition gradients. This should be performed with high speed and accuracy. In Figure 5 it is shown a feedback control response of the sensor signal (Al emission line at λ = 390nm) as a function of the time for different working set-points. It can be seen that the developed fast process control can stabilized the sensor signal at a given set-point value with high accuracy and move the process between different working set-points within seconds.

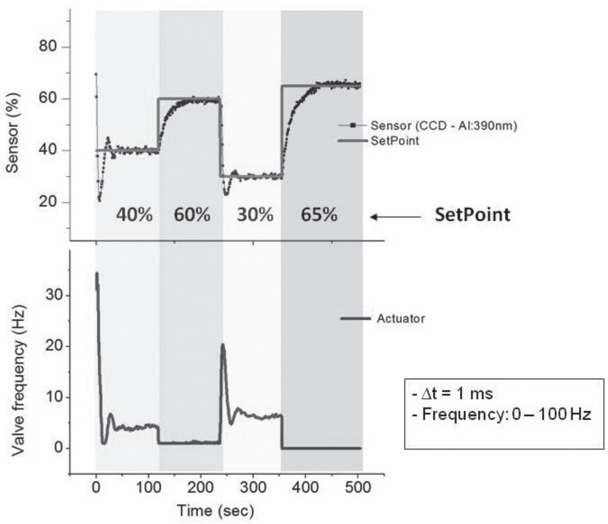

Figure 5: Evolution of the optical sensor signal as a function of time under active effusion cell feedback control (Al emission line at λ = 390 nm). The intensity of the sensor signal is kept constant under effusion cell valve actuation in order to adjust the monomer flux.

Finally, plasma polymerized layers were deposited on Ge substrates using feedback controlled Pulsed Monomer Efussion Cell. A Cross sectional SEM image of the polymer layer is shown in Figure 6, revealing good adhesion and excellent conformal deposition onto rough surfaces.

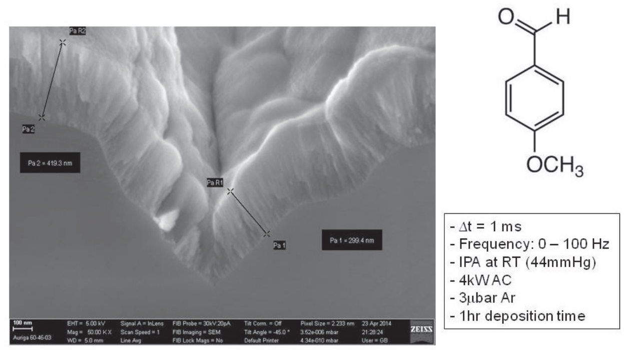

Figure 6: SEM image of the polymerized benzaldehyde layer deposited onto rough Ge substrates. Excellent adhesion and conformality is observed.

CONCLUSIONS

This work shows the implementation of a pulsed monomer injector for vacuum polymerisation applications. Accurate monomer injection is demonstrated by means of reactive sputtering experiments. This fast actuating pulsed valve is suitable for the injection of a wide variety of monomer species with different vapour pressure characteristics and corrosive behaviour.