Reactive Rotatable Cylindrical Magnetron Sputtering for Barrier and Plasma Polymerization Applications.

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Abstract

This paper presents data on the application of rotatable cylindrical plasma sources for barrier encapsulation and plasma polymerization. Layers of different nature and composition were deposited in a vacuum system using magnetron plasma sources in order to create the barrier. A new monomer injection method has also been developed which allows large upscalability. In addition, a new method for barrier performance has also been developed in order to assess the basic barrier properties of the coating stack.

Introduction

Since the introduction in the 1980s Rotatable Magnetron Sputtering has been gaining ground in the large area coating applications sector. Reactive magnetron sputtering using medium frequency power supplies and reactive feedback control are now a key tool for large throughput and high productivity coating lines which have made possible a significant price reduction on many applications such as antireflective coatings on mobile display devices. One of the current areas of economic growth is low cost and high performance encapsulation. The applications from electronics, OLED display, lighting, decorative and special packaging are all on the increase. In that respect there is a need for improvement on the encapsulation performance at the same time as the production costs are being reduced.

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 hexamethyldisiloxane (HMDSO) (mainly used in the protection of thin film reflectors and food / medical packaging), lacquer curing (mainly used in the decorative metallization market) and polymers on fabrics from radiation curable monomers (protection of metallized fabrics). As the natures of monomers, desired polymers and elements to protect are so varied it is not possible to have a universal method that would satisfy all the needs.

The main four key areas on this technology move around the monomer injection methods, the curing methods, the feedback and monitoring methods and the assessment of barrier properties.

This paper is trying to bring a new injector for vacuum polymerisation applications in comparison to mass flow controller (MFC) vapour control method. The curing method relates to a rotatable cylindrical magnetron sputtering plasma, while the feedback control is based on sputtering feedback control methods. Finally a modified version of the calcium barrier test method is presented, which enables an easier implementation of the barrier measurements in a production environment.

Experimental

The Al, AlO$_x$ and HMDSO polymer films were deposited onto 1.0 mm x 75 mm x 25 mm plain glass slides (Menzel-Gläser). Different encapsulation configurations were created as shown in Figure 1.

The encapsulation options were:

1. No encapsulation (only aluminium coating) [Configuration (A)]
2. AlO$_x$ encapsulation of the aluminium film [Configuration (Aa)]
3. Polymer encapsulation of the aluminium film [Configuration (Ap)]
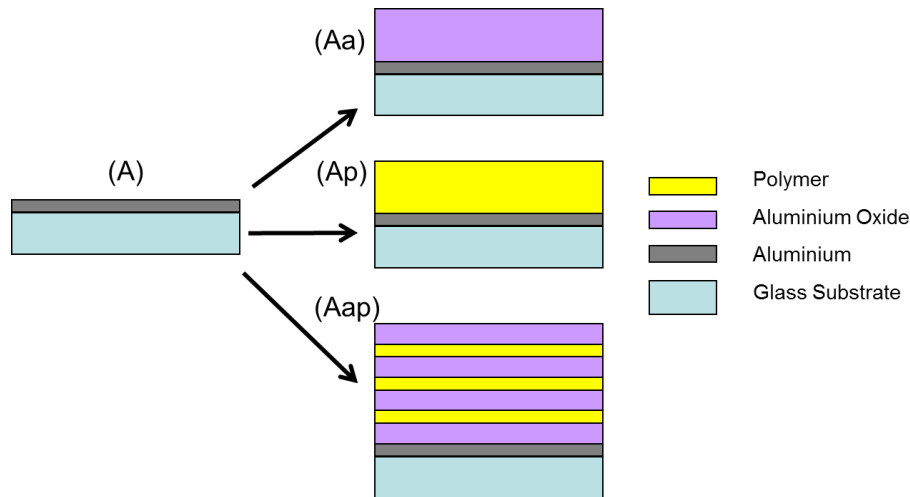4. Multilayer encapsulation of the aluminium film [Configuration (Aap)]

Figure 1. Schematic for the different sample encapsulation configurations.(A) = Aluminium film with no encapsulation; (Aa)= Aluminium film with aluminium oxide encapsulation; (Ap)= Alumnium film with polymer encapsulation; (Aap)= Aluminum film with aluminium oxide/polymer multilayer encapsulation.

All the depositions were carried out on a single vacuum vessel. The plasma sources were Gencoa's GRS75 magnetics mounted on SCI rotatable endblocks. Targets were Al 6061 alloy 75 mm OD x 360 mm length. Metal Al layers were deposited at 3.5E-3 Torr in Ar atmosphere at 3 kW AC-MF using Huettinger MF-3020 power suypply. The AlOx layers were deposited using the same rotatable cathodes and power supplies, at the same Ar flow with variable O$_2$ flow controlled by feedback control using a Speedflo-Mini™ . For the plasma polymerisation the power was varied between 3kW and 0.5 kW, using the same power supply and rotating cathodes. Different monomers could be injected. Figures 2 and 4 show the configuration and results for hexamethyldisiloxane (HMDSO) monomer injection. The monomers were injected via MKS 1179A MFCs and N4E Pulsed Monomer Injector valve.
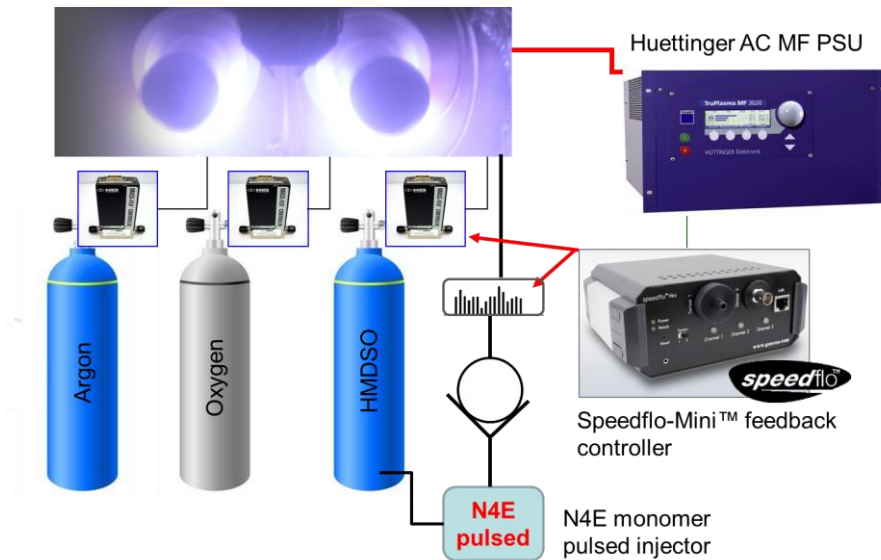
Figure 2. Experimental deposition setup with rotatable dual magnetron sputtering. The plasma sources were powered by a Huettinger AC-MF Power supply. A feedback controller (Gencoa Speedflo-Mini) was used in order to control the gas and vapour injections from MKS1179A MFCs and N4E Pulsed Monomer Injector valve.

Different feedback methods were used in order to control the monomer injection during the plasma polymerisation step.

Different operation modes were possible on the N4E Pulsed Monomer Injector valve, the most common being at a constant time on (valve open) with a variable frequency (as seen in Figure 3) 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 an effusion controller function added to the standard Speedflo-Mini™ controller.

Figure 3. An example of N4E Pulsed Monomer Injector valve operation mode. Monomer flow variant between an open max and a closed minimum flow with fixed time on pulses and variable frequency.

For the barrier performance test an aqueous chemical solution containing NaCl, HCl and H_2O_2 was prepared so that Cl_2, O_2 and active radicals were generated. The oxidative nature of the vapour species produced a chemical reaction when in contact with the Al metal layer. In that reaction a fully transparent compound is formed which revealed the extent of the corrosion or lack of barrier. The solution concentrations and

experimental setup bath could be varied in order to create different degrees in the speed of the corrosion.

Results

Figure 4 shows a time lapse image of the samples in-situ the barrier/corrosion experimental device for a 48 hour period test. The unprotected Al layer was clearly the most vulnerable to corrosion. The AlO_x layer is a good barrier, as good as the pinholes could be avoided. The polymer itself (in this case plasma polymerised HMDSO) could also be very sensitive to the loss of barrier properties showing corrosion on the Al layer. Polymers can undergo chemical transformations due to environmental conditions, such as in this case chemical degradation and water absorption which overall degraded the polymer. The multilayer configuration could offer a more effective barrier, however in these tests it could be seen that the polymer integrity was its weakest point.
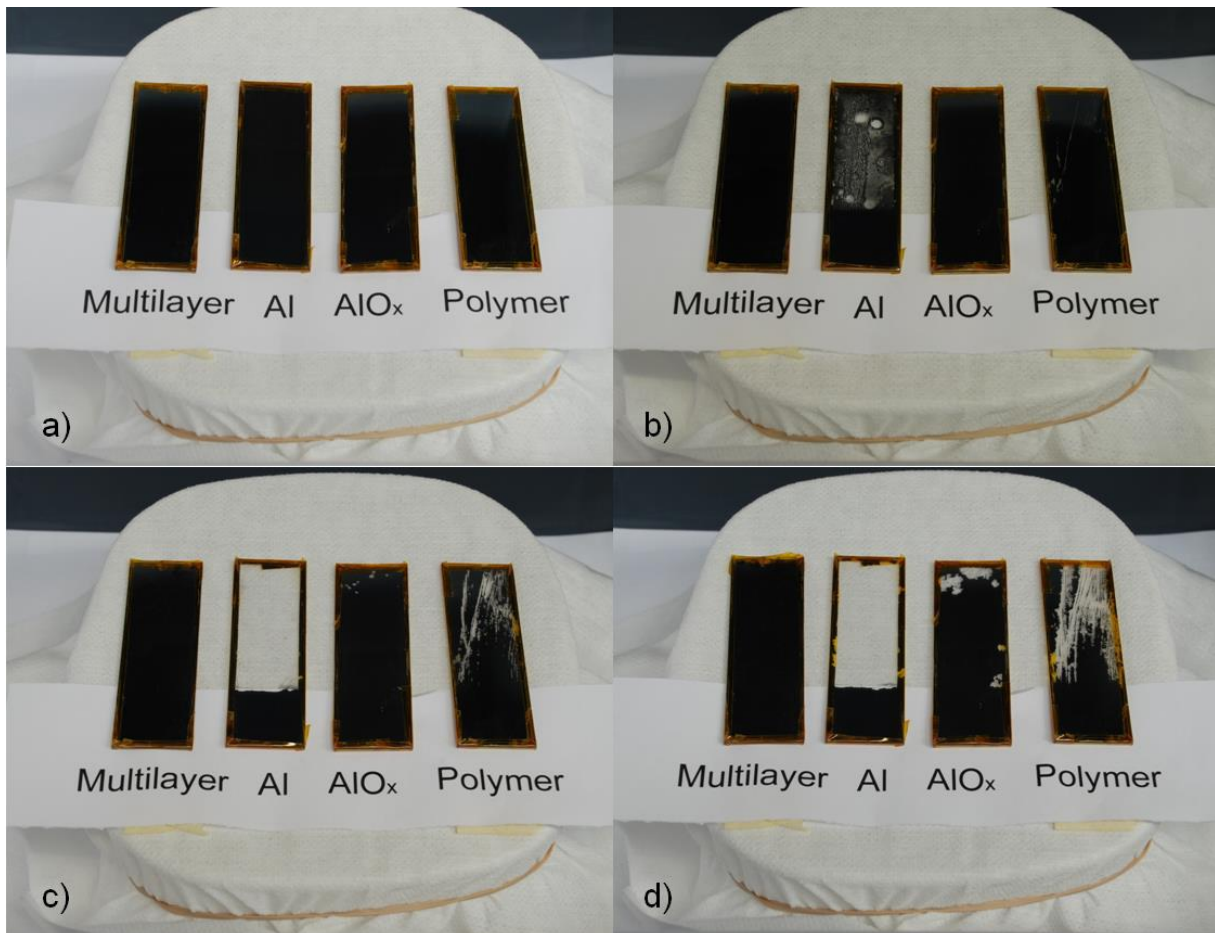

Figure 4.- Aluminium corrosion evolution for a 48 h test. a), b) c) and d) show the corrosion results for the control and encapsulated samples after t=0 h, t=8 h, t=24 h and t=48 h, respectively.

The microscopic analysis of the samples after the corrosion test is shown in Figure 5. Figure 5 presents the microscopic optical light transmission results for the 4 encapsulation configurations. Unlike for the AlO_x and the HMDSO polymer encapsulations, the multilayer did not present a direct path for corrosion, however there was clear buckling in the multilayer which could be attributed to the polymer

instability to the corrosive test environment and probable water absorption. As there is very little probability of a direct path through several layers of AlOx, the Al layer doesn't get to be affected by corrosion during the 48 h testing period. In practical terms this multilayer shows that the polymer layer has to be very stable to corrosion and humidity in order to allow an effective long term barrier of the multilayer construction.
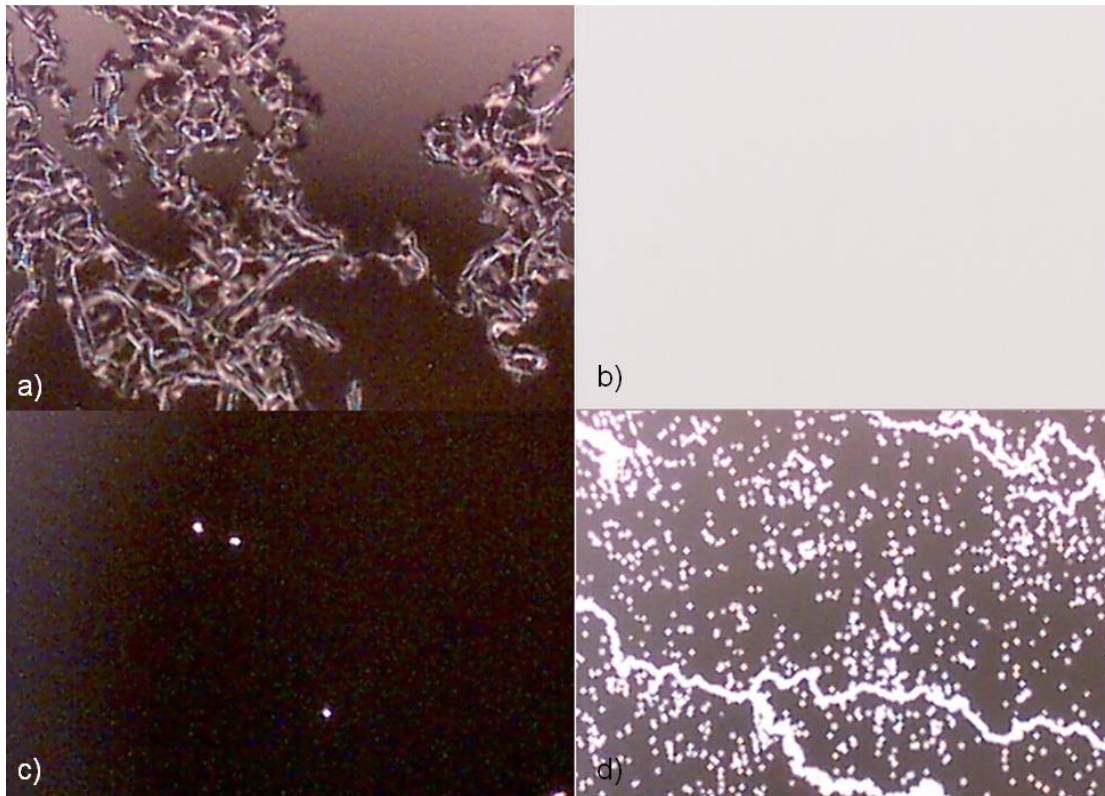

Figure 5. Microscopic light transmission images (3 mm x 2 mm area) using x60 zoom of the encapsulated samples after 48h of corrosion test. a), b), c) and d) display the microscopic effects of the test of the Multilayer, Aluminium, AlOx and Polymer sample, respectively. Sample b is fully light transmissive as the Al layer has been completely corroded away.

Cross sectional SEM was carried out of the multilayer after deposition (Figure 6) revealing good adhesion and smooth interface transition between the polymer and the AlO$_x$ layers. The multilayer was deposited onto a Si wafer for convenience on the SEM sample preparation.

Comparing the buckling after corrosion and the good smooth condition of the multilayer on the cross section SEM we can conclude that the polymer is the weakest point of this particular encapsulation in the multilayer configuration.

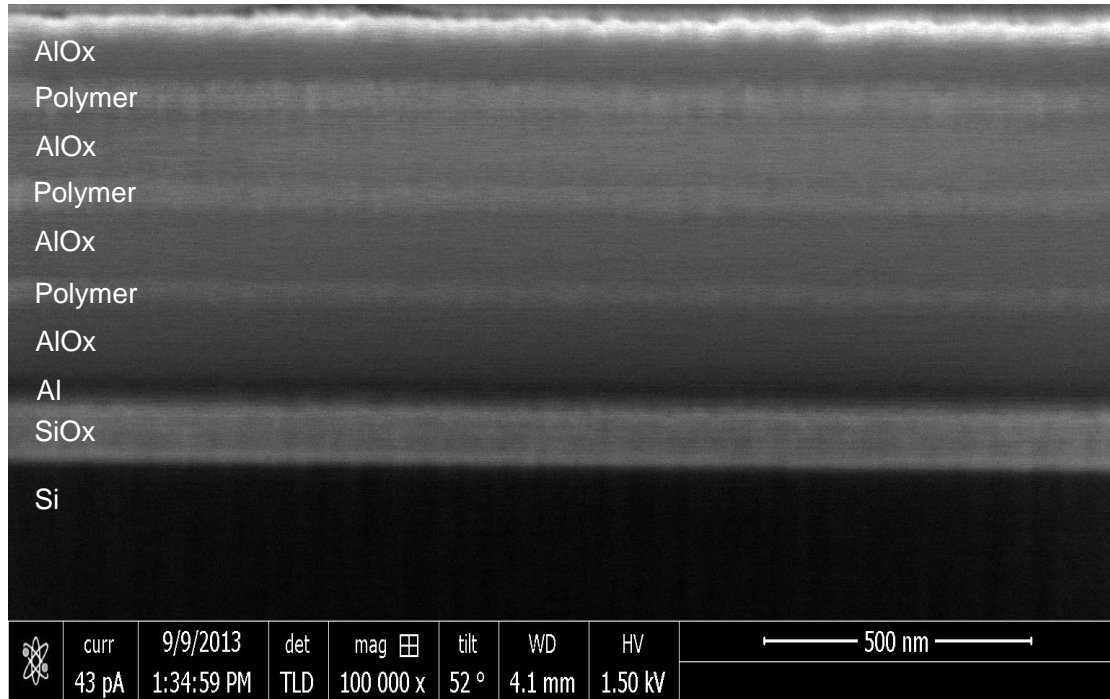|	curr	9/9/2013	det	mag ⊞	tilt	WD	HV	⊢——— 500 nm ———⊣
	43 pA	1:34:59 PM	TLD	100 000 x	52 °	4.1 mm	1.50 kV	

Figure 1: SEM image of the Multilayer encapsulation cross-section. Each layer can be clearly differentiated by the image contrast. There is a smooth transition between all the layers.

Conclusions

Plasma polymerisation was carried out using dual AC-MF rotatable magnetron sputtering plasmas and monomer injection via standard MFCs and a newly developed Pulsed Monomer Injector valve. Barrier properties were evaluated by a novel corrosion method revealing in a semiquantitative way the barrier performance. The tests revealed how the weakest point in encapsulation remains around pinholes and the environmental stability of the polymer layer.

Further work is currently underway and some of these results will be presented.