

# Thin Film Vacuum Plasma Polymerization Processes

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## ABSTRACT

There is a strong need to protect current and future thin film devices from the effects of moisture attack from the environment in which they operate. Typically, such barriers are also required to be transparent as part of their functionality. This paper will illustrate a method to create single and multilayer barrier structures that can offer a high degree of protection of the underlying devices. These structures are created by a mixture of vacuum plasma processes – both physical vapour deposition (PVD) and chemical vapour deposition (CVD). The effectiveness of the structures has been assessed by an acid vapour etching of a sacrificial layer to mimic the underlying device. A mode of hybrid PVD/PECVD deposition has been developed that can create a single layer coating structure with enhanced levels of protection normally only associated with multi-layer structures. The key to the effectiveness of a single layer is ability to ‘heal’ itself during deposition so that through layer defects are not present in the structure. This ability has been termed a ‘self-healing’ moisture barrier due to the unusual ability to prevent defects during deposition.

## THIN FILM BARRIER LAYER TECHNOLOGY

### Current Barrier State-of-the-Art

The current technology to create moisture barriers with a very low moisture transmission rate ( $10^{-6}$  g/m<sup>2</sup> per day) uses more than one type of layer in a stack to provide a mixed growth structure that can mask the effect of defects in any one layer. The principle is that by alternating widely the layer chemistry and deposition process, defects in any single layer will not penetrate the whole coating structure. This is based upon early work done at Vitex Systems in the US [1].

These layer structures typically use an Al<sub>2</sub>O<sub>3</sub> PVD type layer in combination with a vacuum vapour deposited and cured monomer (plastic) type layer. The Al<sub>2</sub>O<sub>3</sub> layer is more prone to defects, but inherently offers a low gas transmission due to the nature of the oxide. When these oxide layers are sandwiched between a ‘plastic’ type layer, the moisture path is

interrupted and the speed of moisture transmission decreases with the number of layers (see Figure 1 and [1]). Both the oxide and the plastic layers are transparent and have some degree of flexibility. The flexible nature means they can be used on flexible devices or substrates. Such a method of switching between materials types and processing routes is still the basis of the current materials produced commercially, although methods of deposition varies.

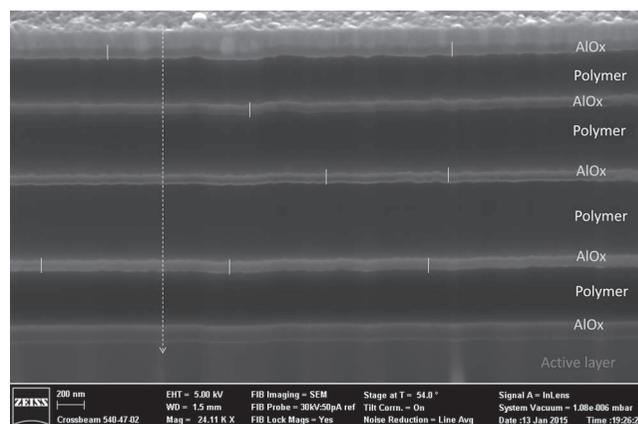


Figure 1: Multi-barrier type structure for the prevention of moisture permeation created by PVD and PECVD route. Deposited by dual rotatable magnetrons working in PVD and PECVD mode.

### Deposition Methods for Moisture Barriers

Vacuum deposition method dominates the means used to create effective thin film barrier layers. In practice, all types of vacuum deposition are used in various forms depending upon the level of moisture transmission. At the lower cost end vacuum thermally evaporated Al films in the presence of oxygen are used for food packaging and line speeds of hundreds of meters coated per minute. At the high cost is Atomic Layer Deposition (ALD) type structure which can create defect free layers but a very low rate of productivity of fractions of a meter per minute.

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Of particular interest industrially is the potential of chemical vapour deposition (CVD) to produce layers at enhanced rates and with low defects. In order to produce the good dense coating structures energy in the form of either plasma or heat is required to promote the chemical reaction.

### Dual Rotatable Magnetron Sputtering / PECVD Type Method

The use of a dual rotatable magnetron with a switching voltage polarity between the two targets is established as a reliable method for creating reactive oxide or nitride layers by PVD. In the case of barrier layers, the stable sputtering of aluminium or silicon targets to create the metal oxide or nitride requires the reactive gas to be introduced and fast feedback controlled for stability. The rotatable magnetrons have an advantage over other sputter devices as the target is self-cleaning as it rotates. This provides a newly sputtered surface for the sputtering plasma and reduces the chance of defects in the barrier layers that can result from arcing on the target surface. Accurate and fast feedback control in the millisecond range of this process is required to maintain long-term stability. This is provided by in-process sensing and fast adjustment of the reactive gas. This is the 'classic' reactive gas feedback control.

The same hardware can provide the basis for a PECVD type process, in that the rotating magnetron targets with switching polarity drives the plasma enhancement and the reactive sputtering type feedback control drives the introduction of the gaseous elements to form the CVD type layer. As in reactive sputtering, fast adjustment of the gases is required, but a further complication is the ability to maintain the rotatable targets in the same electrical and chemical state over the long-term to ensure a stable process without drift in properties or composition.

### Delivery and Control of Gaseous Elements for PVD and PECVD Processes

In the case of gases used in PVD such as  $O_2$  and  $N_2$  certain forms of mass flow controllers (MFC) can regulate the gas at the required speed and accuracy. The MFC device can also be used for some gaseous introductions typical of CVD processes, but more complex polymers and higher flows of chemicals are not compatible with the commercial MFC units. To satisfy this demand a new type of pulsed effusion cell has been developed that can adjust the frequency of opening of a valve to rapidly control the delivery of any vapour type and at any flow rate. This type of device allows full flexibility and control of any gaseous species from a solid or liquid source by using the same device. Figure 2 illustrates the adjustment of the delivery of Se gas by such a device by the combined effect of opening duration and frequency of opening. This valved effusion cell is a joint development between Gencoa in the UK and N4E in Spain. This rapid adjustment of the chemical vapour species combined with the stable dual rotat-

able plasma opens the potential to generate a PECVD type process from similar hardware used for reactive sputtering in industrial processes, see Figure 3.

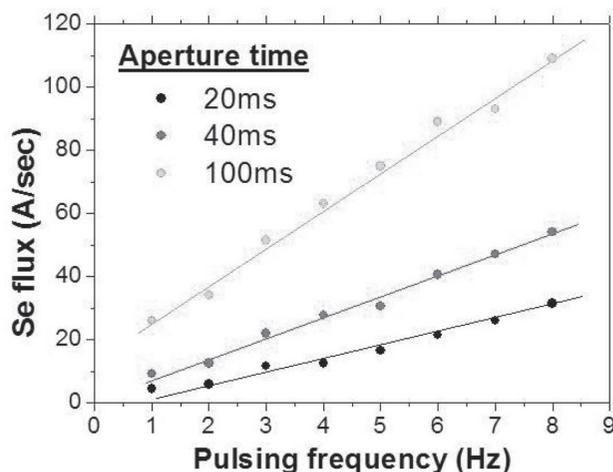


Figure 2: Adjustment of selenium delivery into a vacuum from a pulsed effusion cell by means of frequency or opening and duration of opening.

### DEPOSITION OF MULTI-LAYER OXIDE AND MONOMER BARRIER LAYERS

The combination of devices shown in Figure 3 have been used to create the multilayer barrier structure shown in Figure 1. The samples are static underneath rotatable magnetrons in a sputter down arrangement and the process alternates between the PVD  $Al_2O_3$  layer and monomer layer creation. The process hence switches from PVD to PECVD as does the gas introduction. In this case, the critical element is the control of the gas introduction in order to maintain both the PVD and CVD as well as managing the switch. Success of this depends upon multiple process sensors being feed into the Speedflo gas control system to ensure that the plasma and target surface chemistry is maintained or moved from one process to the other. The advanced nature of this control means that the barriers shown in Figure 1 can be readily deposited in a single chamber without movement of the substrate.

### Assessment of Performance of Barrier Layers

A number of methods have been developed to assess the performance of barrier layer ranging from the Calcium test to devices for the measurement of the water vapour transmission rate. A good barrier layer can be difficult to assess as the time it takes to determine an accurate water vapour transmission can be many weeks. An alternative test has been devised here based loosely on the Calcium test. It involves the initial deposition of a pure Al metal layer on the substrate surface to act as the sacrificial layer and mimic the actual device to be protected. On-top of this layer the gas barrier is deposited in order to protect that underlying Al layer.

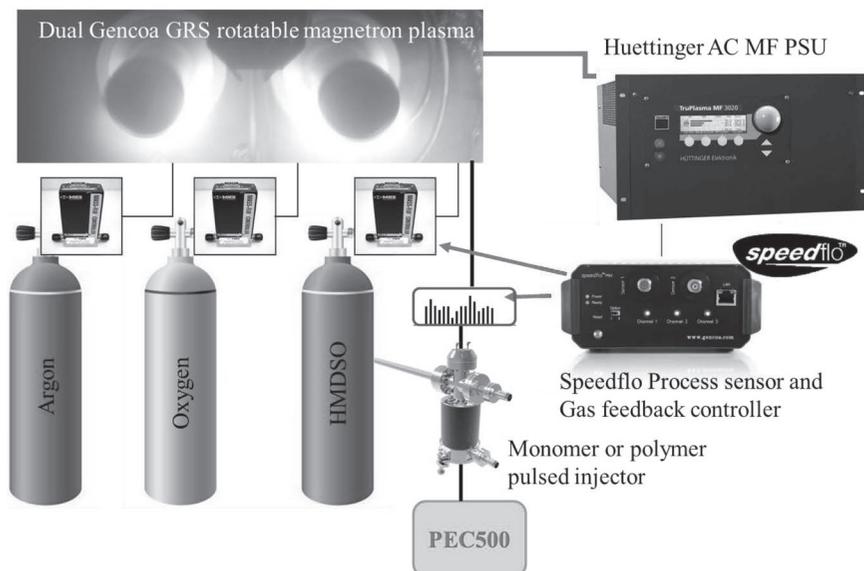


Figure 3: Experimental arrangement for the creation of multilayer barrier systems shown in Figure 1, by PVD and PECVD.

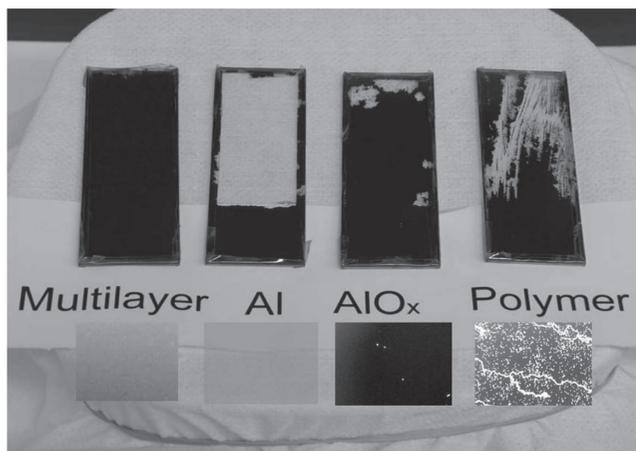


Figure 4: Assessment of barrier properties by acid vapour etching and visual / microscopic assessment.

To determine the barrier effectiveness the coating structure is suspended over an acid bath made from 30g NaCl, 100 ml H<sub>2</sub>O, 50 ml H<sub>2</sub>O<sub>2</sub> 30 % v/v, 200 ml HCl. The vapour produced from such a bath will provide a highly corrosive environment and will rapidly corrode the Al base layer should the gas barrier be penetrated. Typically an unprotected Al layer will be totally removed within 3 days of exposure (see Figure 3). The more effective the barrier, the longer the Al will be protected. This is a ranking test to determine the broad effectiveness of the gas barrier layer created and to provide feedback in which direction the barrier development should proceed. The assessment of the barrier is visual and can also be quantitative by optically counting the number of pin-holes by light transmission.

The strength of the above technique is the low cost and visual assessment of different barrier structures. Multiple baths can be run to assess any number of layer types created. The days to the first perforation is the initial assessment criteria. This method ranks structures from days to many months for the most effective barriers. A multi-layer barrier typical of that shown in Figure 1 can survive > 2 months without a single perforation. Multi-layer barriers of the same type but without the optimum process parameters will last up to 1 month. Hence this method effectively demonstrates the best type of structure and processes for barrier layer films.

#### SINGLE LAYER BARRIER SYSTEMS

During this work it was apparent that the barriers effectiveness even when a multi-layer concept was used, was dependant upon the process conditions more that the relative layer thickness and over all thickness. Single layer systems based upon pure Al<sub>2</sub>O<sub>3</sub> we're poor in protecting the Aluminium layer. However such a layer by ALD has been shown to be highly effective in the literature. The presence of defects can be expected during these experiments as the substrate preparation and coating process are not conducive to a defect free layer. The principle strength of ALD would appear to be its ability to grow the film around a defect to mask its effect, this is surface chemistry related. Equally the PVD/CVD multi-layer coating masks the effect of the defect by alternating the nature of the structure. However, the need to use 2 process in multiple steps to create the multi-layer system adds cost and complexity to the device and reduces the chance of commercial uptake. An optimum solution would be to create a defect free single layer in a single stage rapid process. It was observed during these experiments that this arrangement could be controlled to work

anywhere from the pure PVD to pure PECVD, meaning that a hybrid layer could be created that combines the benefits of both PVD and CVD in a single layer. Indications from the etch tests led to the conclusion that depending upon both the transition from the PVD and PECVD and also the chemical doping, the barrier nature would vary resulting in better or worse protection during the etch test. It was hence decided to explore a single layer hybrid system and compare the performance to the multi-layer systems.

### Chemistry of Single Layer Barrier Systems

By combining the metallic elements of the sputter targets (in this case Al, although Si is also a candidate) with the oxygen gas and the monomer or polymer base gases (HMDSO or Butyl Acrylate as examples) there are many 'degrees of freedom' from a chemical composition point of view. The relative levels of the chemical species can also be varied through the coating structure should the need arise – graded coating structures.

Hence there is a very wide range of layer types that can be created. Hence, the ability to test the layers via the vapour etch test proved very valuable means of assessing which process parameters and compositions show promise.

Early in the experiments some of the single layer systems showed promise in terms of matching the multi-layer structures in terms of length of time to withstand the acid etching. By refining the conditions and the mix between chemical elements it was possible to exceed the effectiveness of the multi-layer structure. This is unexpected in that the presence of defects should indicate that a single layer cannot be as effective as the mixed mode multi-layer type structure. The single layer systems also would seem to have the ability to mask the effects of defects to create effective barrier layers. This ability is not present in a pure PVD layer and the pure polymer layers which display poor gas barriers (see Figure 5). But the correct combination of chemical elements appear to be more than the 'sum of the two individual parts'.

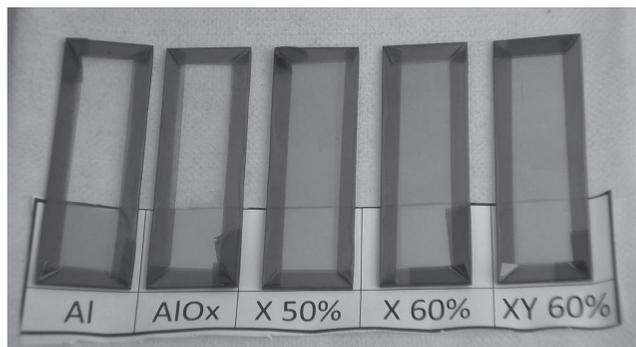


Figure 5: Assessment of barrier properties by acid vapour etching with different chemical composition of single layer gas barrier protection systems – aluminium under layer semi-transparent. X50-60% is the doping element.

### SELF-HEALING SINGLE LAYER GAS BARRIERS

The 'self-healing' nature refers to the ability to mask substrate surface defects and to 'heal' defects created during the deposition phase. This is not possible via a purely PVD process in general which exhibits grain boundaries and crystal structures. It has been observed however, that in very specific solid solution compositions of two metals by sputtering glass like dense structures can be created that comply well to the underlying surface topology [3]. This has not been observed for any transparent type coating layers via purely a PVD route.

The introduction of these additional chemical species from a CVD type of reaction and doping with the correct level of metal from the sputter targets has the ability to create a single moisture barrier layer shows great promise. The acid vapour etch test is unable to penetrate such coatings and attack the underlying layer. The films perform at least as well as the multi-layer barrier films and offer a simpler route for fabrication and a lower potential cost. More work is needed to determine the exact reasons for the success of this approach, in particular examination of the microstructures and the mechanism whereby defects are prevented from affecting the barrier. It is presumed that either the combination of the chemical compositions used creates a unique structure, or that the enhanced mobility of the species from the chemical vapour element introduces a highly mobile nature to the surface of the growing film with 'plugs' and heals the film structure as it grows.

### CONCLUSIONS

It has been shown that high moisture barrier layers can be created from a single process based upon reactive dual rotatable magnetron sputtering with sophisticated gas feedback control. This method can deposit both multi-layer type structures as well as new single layer structures that can withstand an aggressive acid vapour environment without degradation. This result has been shown previously in the literature from the multi-layer type structure, but not previously by the single layer type. These single layers are produced in a hybrid PVD/PECVD process opens up new possibilities in the field of moisture barrier protection and is easier to scale-up than pure PECVD routes. More work is needed to investigate the mechanism by which defects in a single layer are self-healed during the formation of the layer.

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