Manufacturing of Barix coated plastic barrier films: R2R vs. Batch

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Abstract

We will discuss and compare the different ways to manufacture high performance Barix coated barrier films as a substrate for displays: R2R vs Batch.
It will be shown that the barrier performance of the Barix coating on plastic can be as good as on glass substrates. More then 1000 hrs of testing at 60C/90RH can be passed without degradation of Ca samples

1. Introduction

Flexible displays will need barrier coatings against water and oxygen in order to protect the display and its backplane from degradation. Organic Light Emitting Diodes (OLED)[1,2] have an extremely high sensitivity against water, needing a barrier film with a Water Vapour Transmission (WVTR) of as low as $\sim 10^{-6}$ gr/m^2/day[3,4], but also LCD displays and Electrophoretic displays need more protection then a normal plastic film with a typical WVTR of 1~10 gr/m^2/day can provide.

For making a flexible display, one not only needs a barrier substrate (even a flexible metal foil can be seen as such), but one also needs to protect the display from the other side. This can be done by thin film encapsulation or by sandwiching the display between two barrier films.

But although thin film barrier coatings on plastic and thin film encapsulation are highly desirable, it has not been so easy to achieve that goal in a technically and economically feasible way. The requirements to the layers of being; transparent, totally pinhole and crack free over very large (>1 m^2) surface areas, low stress and high robustness while being deposited at low temperatures well below 80 C, have proven to be very difficult to meet.

Early attempts to solve this problem with single layer oxides or nitrides, while obtaining some success on small areas, basically failed because of the presence of particles, crack and defects in the layer and residual stress.

Vitex has proposed a multilayer of organic and inorganic layers, Barix™ [3,6,7,8], to address and solve these problems. The multilayer consists of thicker (0.25 to 4 micron) polymer layers alternated by thin (200-500 nm thick) layers of oxide or nitride. The polymer layers are being deposited in vacuum as a thin liquid film of an acrylate monomer which is polymerized with UV light. These layers fulfill the following functions: because of their initial liquid state they planarise the substrate and because of the fat surface of these films, provide the almost ideal surface to grow a defect free oxide. The polymer layer furthermore covers particles, decouples defects in the oxide layers so that they are not aligned and function as a stress release layer.

The thin films of oxide serve as the barrier layers to oxygen and water. As demonstrated theoretically by G Graff et al[4], the main effect of the multilayer is in increasing the lag time between exposing the top layer to water vapour and the water molecules arriving at the interface between the OLED and the Barix™ encapsulation layer.

Figure 1

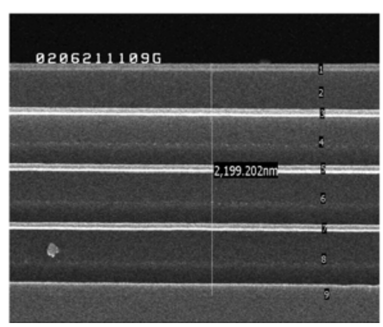

Fig 1. SEM Cross section of a typical Barix multilayer barrier coating. Oxide layers typically are between 30-100 nm and polymer layers 0.25 to 4 micrometers.

The layers are all deposited in vacuum as is shown schematically in Figure 2 [6,7,8]. The organic layers are applied as follows: a mixture of photosensitive acrylate monomers is vaporized, condensed on the substrate and quickly polymerized with UV radiation. The inorganic metal oxide layer, mostly Aluminum oxide, is deposited via a reactive sputtering process. Typically the organic layers vary between 0.25 and 4 micron in thickness and the metal oxide layers between 30 to 100 nm. What is really unique about this process is that the organic phase is deposited as a liquid: the film is very smooth (< 2 Angstrom variation) locally and also has extremely good planarizing properties over particles and high topographical structures like ‘cathode separators’ ‘ink jet wells’ and Active Matrix pixel structures. So while the local flatness creates an ideal surface for growing an almost defect free inorganic layer, the liquid takes care of covering topography. It should also be mentioned that while even non-conformal methods to deposit oxides like CVD, have difficulty covering cathode separators without creating voids, they also struggle to coat often more then 4 micron high structures in an acceptable process time.

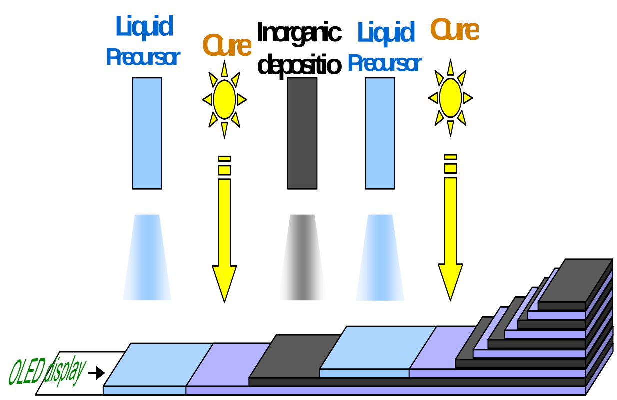

Fig.2 Schematic presentation of the process steps of the Barix encapsulation

The multilayer provides redundancy and since the remaining defects in the inorganic layers are few and far in between and not connected, a very long diffusion path to the substrate results as well.[4]

The organic layers also provide a function of stress release layer in thermal shock testing.

An extensive model for the diffusion through this type of barriers has been developed by G Graff et al.[4]

The main findings of this study are that i) high quality inorganic films coupled with a multilayer architecture are necessary to achieve OLED barrier requirements (large spacing between defects) ii)Lag time (transient diffusion), not steady state flux, dominates gas permeation in these multilayer thin films systems. iii) Consideration of steady state , alone, is not sufficient to describe and predict the performance of multilayer barrier films one must consider the transient regime.

The Vitex Barix™ process has been shown to meet telecommunication application specifications for a wide variety of OLED displays: passive and active matrix displays, bottom, top and transparent displays and it works equally wel for small molecule, polymer and phosphorescent OLEDs.[7,8,9]

2. Results

The question that will be discussed in this paper: Barrier performance on plastic films and the influence of its manufacturing process

Using the Calcium test[10] we have established that for barrier films made on a batch machine on a glass substrate typical WVTR of 10^{-6} gr/m^2/day can be obtained with champion values around 10^{-7} gr/m^2/day.

Barrier performance on plastic

The questions which will be addressed in this paper are:

- Is the barrier performance on plastic as good as on glass
- How does the manufacturing process of the barrier on plastic influence the results: R2R vs production on a batch machine.
- What are the critical factors in a R2R process which distinguish it from a batch process.

We created Barix™ coated plastic film in a G200 batch machine by laminating a PEN film (Q65A, Teijin-DuPont) on a glass support. The multilayer was then applied in the usual way. In order to measure the WVTR we evaporated 4 inch square Calcium buttons on the barrier coated substrate, the sample was then covered with a Barix multilayer encapsulation. The plastic film was then delaminated from the glass support.

Figure 2, shows the result of the transmission test of the Calcium buttons when being aged at 60C/90RH for 560 hrs. The transmission changed 16% ($\Delta T/T$) over this period. This should be compared to 5-8% change which is typically obtained for Calcium test when glass is used as a substrate. The calculated WVTR of $8*10^{-6}$ gr/m^2/day (taking into account only the difference in water vapor pressure, if a small activation energy of 30kJ/mol is taken into account a value of $2*10^{-6}$ results, see Vitex paper at IMID07) is ~3 times as high as for the typical result obtained for one single Barix coating on a glass substrate.
Realising that in the case of the test on the flexible substrate water can diffuse to the Calcium button from two sides, whereas for the glass substrate it is only one side, the resulting difference is rather small.

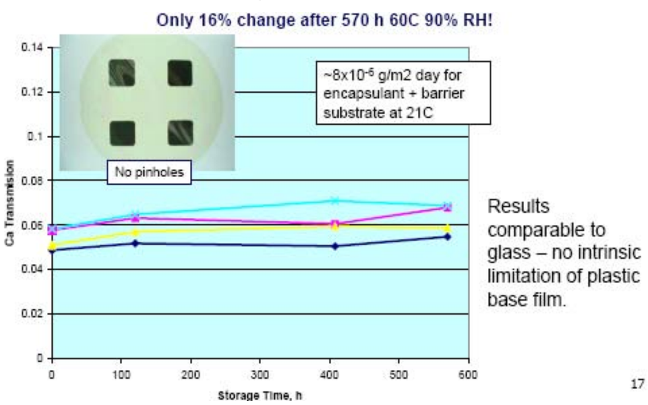

Fig 3
Change of Calcium transmission as function of aging time in 60C/90RH climate chamber.

If we compare these Calcium test results with films which were made on a vacuum Roll to Roll machine (R2R), which covered ~9" of a 12" wide film, the samples showed already pinholes in the Calcium buttons after 100hrs of 60C/90RH. Also the loss of Transmission was higher. In this case it is hard to tell if that is caused by overall loss of barrier performance or by many local defects.
The barrier performance was estimated to be in the 10^{-4} gr/m^2/day range.
This could be caused by two effects: an increase of the nr of particles on the substrate or within the barrier and/or the effects of handling of the film in the R2R process: the film is unrolled via rollers onto a big drum which transports the film past the polymer, UV and oxide sputter source. A schematic picture of the process is given in Fig 4.

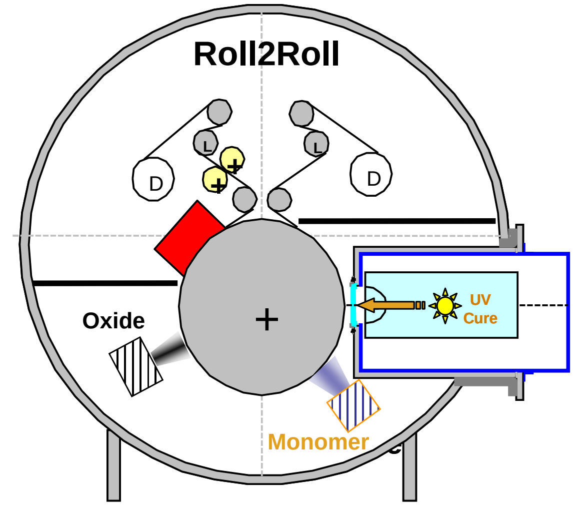

Fig 4
Schematic presentation of the R2R vacuum coater.

In one way of operating the complete film is coated with a polymer layer and then the complete film is coated with an oxide layer and this process is repeated a number of times. Obviously the surfaces pass the rollers and the film is wound and unwound every single time.

Using a grooved roller (a roller where three rings of 1" wide were thinned by two millimeter) so that there were three areas where the film did not touch the roller, and by doing experiments with extra wind/unwind steps (without depositing more layers), we have been able to distinguish between the different effects. The following conclusions have been reached:

- Most of the degradation of the barrier performance is caused by the winding and unwinding of the films and by the interaction in the rolled up film with the backside of the (slip-treated) film, causing damage to the surface.
- A less important but significant effect is the increase of nr of particles where the film touches the rollers. In those areas where there is no contact with the rollers the particle count dropped by a factor of 10 (from ~300/cm^2 to 30/ cm^2)

3. Conclusion

We have shown that the barrier performance on plastic can be as good as on glass, analysed the influence of the R2R process on barrier performance.

4. Acknowledgements

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