Recent Developments in the Deposition of ITO and AR Coatings

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ABSTRACT

The article considers three- and six-drum's roll-to-roll design, intended for transparent/conductive ITO coatings with sheet resistance variation in a wide range (from 20 to 500 Ohm/sq.); and multilayer anti-reflective (AR) coatings. The multichamber vacuum machine was designed with the account of various technological methods, leading to reactive deposition stabilization, and stable coating properties.

To ensure uniform initial conditions of film surface before deposition, initial film is subjected to pretreatment, including film drying, outgasing on an intended machine, and plasma activation on the vacuum coater.

Onboard measuring of some coating properties is performed, including sheet resistance, optical reflectivity and transmission index across width. This enables necessary correction of the reactive deposition for obtaining required coating properties by the redistribution of oxygen flow in the deposition zone. We developed water vapor- and carbon dioxide-consuming technology for the deposition processes. On one hand, water vapor contributes to deposition process stabilization; on the other hand, it affects properties of the coatings. Exchange of oxygen for carbon dioxide leads to expanded capabilities of the monitoring of web coating.

INTRODUCTION

The vigorous development of information input/output means, such as for LCD and touch screen panels requires the development of highly productive multifunctional equipment for multilayer coating structures on flexible polymer substrates (PET, PI etc.) for solving a multitude of issues and determining the quality of produced materials. These issues include substrate pre-treatment for coating, substrate pre-treatment for high adhesion, new processes development, and application of state-of-the-art control means for the deposition processes. The article represents the results, obtained during research for multilayer material structures creation. On the basis of these results, appropriate vacuum equipment for multilayer coatings in production scale is developed.

INFLUENCE OF INITIAL FILM DRYING AND WATER VAPOR ADMISSION ON ITO PROPERTIES

Influence of Initial Film Drying on ITO Coatings

As a rule, partial pressure of water vapor in a vacuum chamber is an incontrollable parameter, but considerably influences coating properties. The exploration of the influence of some incontrollable parameters of the DC sputter magnetron deposition on the ITO properties [1-3] proved that water vapor partial pressure is one factor among major incontrollable parameters that considerably influences coating processes. Partial pressure of water vapor inside a vacuum chamber is dependent on a lot of factors, while a number of water vapor sources is quite considerable within a chamber. Firstly, this is adsorption water on chamber walls and on in-chamber devices. Secondly, this is absorption water. The higher the amount of condensate remaining in a vacuum chamber after the coating cycle, in the deposition zone, especially, the higher the amount of absorbed water will get to condensate, causing longer water removal time. Sensible is what was done on the chamber before cycle, and duration of the chamber exposure to atmosphere during the opening.

Pumping reduces water vapor partial pressure in a vacuum chamber. Particularly effective for water vapor removal is the application of the POLYCOLD system. As soon as leak-in is a source of water, incoming water to a vacuum chamber won't change during the course of pumping.

And, finally, the processed polymer film itself is another source of water vapor. It is deemed that there is a layer of adsorbed water on film for coating remaining on the film during the entire course of rewinding in a vacuum and passing over the drum. Additionally, every film contains absorbed water, which can diffuse from film material to film surface, regenerating the layer of adsorbed water on the film surface, and shrinking after water molecules are released from the surface. For instance, PET film can contain absorbed water up to 0.8%, and polyimide – more than 1%.

The greatest impact on coating properties is made by the water on a film surface and inside the film as well. This water escapes at film heating, caused by coating condensation. For uniform pre-coating conditions, film is subject to preliminary

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treatment, including drying, outgasing and gas discharge plasma treatment.

Film drying incorporates film heating and keeping film at a high temperature. Requirements for the drying conditions are the following:

- Removal of maximum amount of water and, what is desirable, gases and contaminates. This is attainable through increased heating temperature and increased drying time.
- Drying is to be so that does not impact mechanical properties of the film, its flatness or transmissivity. Film degradation or alteration of film structure, affecting product properties, is inadmissible. This restricts the conditions of film drying to temperature, drying time, (winding speed) etc.

Film drying was performed on a vacuum machine. Heating of the film, moving between two rollers with a speed of 0.5 m/min, was performed with IR heater. After the heating, the film was entered into a drum, preheated to a temperature of 85°C, where the film heating was continued.

For the exploration of drying influence on coating properties, MELINEX 453 film was ITO coated with a sheet resistance 350 Ohm/sq. For quantitative assessment of the drying process we used such coating characteristics as thermal stability and wear resistance. Thermal stability was calculated as a relationship between sheet resistance after coated film exposure to a temperature of 150°C (R_T) during 1 hour and an initial resistance of (R_0). Wear resistance was calculated as relationship of sheet resistance after a certain number of friction cycles at a given load of (R_D) and sheet resistance of R_T.

Thermal stability of an ITO layer with considerable sheet resistance is rather sensitive to the state of the polymer film surface. In the course of temperature increase on the heater at film heating, thermal stability drops to a range of 0.6 – 0.7 (Table 1). These values are not dependent on this type of reaction gas. The reinstallation of thermal stability values in alternative cycles and with alternative gases testifies achievability of identical conditions on the film, supporting the coating properties reproducibility. Alteration of film thickness or film type will require retrieval of alternative drying conditions.

Table 1: Thermal stability of the ITO layer at alternative drying conditions.

No.	T_h, °C	T_d, °C	R_T/R_O, Thermal stability	R_D/R_T, Durability
1.	150	85	0.91 – 0.95	1.03 – 1.14
2.	155	85	0.87 – 0.88	1.0 – 1.1
3.	160	85	0.60 – 0.69	1.0 – 1.03
4.	170(*)	85	0.60 – 0.62	1.0 – 1.03

(*) Traces of film deformation after the drying are observed.

By this means, on one hand, drying at a maximum admissible temperature enables the maintenance of similar starting conditions for coating and reproducibility of coating properties. On the other hand, for practical purposes it is quite important that coating sheet resistance does not alter the product at further processing, particularly, heating up. Therefore, sensitive deviation of the thermal stability towards increase or towards decrease from 1 is unacceptable and, correspondingly, the thermal stability should be under control.

Influence of Water Vapor Admission in a Vacuum Chamber

Exploring the influence of drying on coating properties brought us to an assumption that with dosed water vapor admission in a vacuum chamber during deposition, coating properties can be controllable. To show this we used a water vapor admission device on the basis of MFC. ITO was deposited on PET film substrate (Melinex 453, 100 microns) and dried in the mode of 160/85°C. Parameters of ITO deposition were as follows: Q(Ar) = 375 sccm, winding speed v = 1 m/min., discharge power = 3.9 kW. Sheet resistance sustained on a level of 350 – 390 Ohm/sq. caused us to decreased O_2 input flow from 19.2 to 14 sccm (Table 2) while increasing water vapor input flow.

Table 2: Thermal stability of an ITO layer at alternative water vapor input flows to vacuum chamber.

No.	Q_{O2}, sccm.	Q_{H2O}, sccm.	R_T/R_O Thermal stability	R_D/R_T Durability
1.	19.2	0	0.61 – 0.65	1.0
2.	18.5	1.0	0.73 – 0.80	1.0 – 1.05
3.	17.5	2.0	0.97 – 1.08	1.0 – 1.08
4.	16.5	4.0	1.31 – 1.53	1.01 – 1.08
5.	14	6.0	2.25 – 2.4	1.03 – 1.15

The initial value of thermal stability was similar to an earlier value, received without water vapor admission. Increase in water vapor admission brings about the increase of thermal stability values. The thermal stability alters in a range of 0.6 - 2.4, enabling handling of this parameter by means of dose admission of water vapor into the chamber. Similar results were obtained with the use of carbon dioxide as the reaction gas in place of oxygen.

Besides a capability to ensure coating thermal stability, a water vapor admission gas mixture of Ar + O_2 allowed us to extend time of stable sheet resistance sustainment up to several hours. It was observed that after the termination of water vapor admission, sheet resistance of ITO coating started increasing in a few minutes, and we failed to decrease it by changing deposition conditions; i.e., in-situ water vapor admission is also influenced by ITO properties. Admission of water vapor allowed attainment of ITO specific resistance in a range of (5.1-5.4)*10^{-4} Ohm*cm.

APPLICATION OF CARBON DIOXIDE IN REACTIVE ITO DEPOSITION

When depositing metal oxides in the magnetron reactive processes, oxygen is used as reaction gas. Molecular oxygen is a rather stable compound with binary atomic bonding, therefore it is insufficiently chemically active. In electric discharge plasma dissociation of oxygen molecules takes place with the emergence of atomic oxygen, i.e.,

$$O_2 = O + O \quad (1)$$

Plasma also causes generation of other active particles, i.e. excited molecular oxygen O_2*, and atomic and molecular ions of oxygen O^+, O_2^+. Availability of two dangling bonds of atomic oxygen determines the super chemical activity of oxygen, compared to other particles. Bonding energy in the oxygen molecule O = O makes up 5.2 eV [4]. This is atomic oxygen that causes generation of oxides on a substrate in a deposition cycle. Other particles are not that active and do not have considerable influence on coating formation.

Carbon dioxide (CO_2) can be used as a source of atomic oxygen. Dissociation of CO_2 molecules takes place in electric discharge plasma, i.e.,

$$CO_2 = CO + O \quad (2)$$

This comes along with the formation of atomic oxygen (O) carbon oxide (CO) and other particles, such as atomic ions of oxygen O^+, and CO^+ ions. Bonding energy in the carbon dioxide molecule OC = O comes to 5.5 eV [4]. Further dissociation of (CO) molecules is embarrassed due to the high bonding energy of C = O, coming to 11.1 eV [4].

The bonding energy of oxygen atom in the CO_2 molecule differs a little from the bonding energy of the oxygen molecule; therefore, these two gases are energetically equivalent. Since two atoms derive from the dissociated oxygen molecule, and only one from the carbon dioxide molecule, the process requires exceedingly more carbon dioxide compared with oxygen.

In reactive processes, at oxide arc deposition, in particular, carbon dioxide is often used in place of oxygen. Sidrabe Inc. has got such experience [5]. Oxygen exchanged for carbon dioxide allowed us to increase the arc deposition speed of Ti oxide. It is quite obvious that the running conditions of pumps, diffusion pumps in particular, are improved because of the pumped down oxygen flow, affecting vacuum oil in pumps, is reduced.

Taking into account the positive effect of CO_2 application in arc reactive processes for oxide deposition, Sidrabe Inc. carried out research that showed a possibility of carbon dioxide application as reactive gas in place of oxygen for ITO coating through a reactive process with magnetron sputtering, using oxide ITO as a target.

ITO coating was deposited through reactive magnetron sputtering of an oxide target of In_2O_3/SnO_2. Carbon dioxide was admitted into the oxygen line, with oxygen admission being cut off. In this way oxygen admission devices and instruments were used for carbon dioxide flow monitoring and control. Experimental testing was carried out with oxygen as a reactive gas; the vacuum chamber was not normally depressurized at gas change over.

In each deposition cycle a series of experimental samples, amounting 10 – 25 pieces, was manufactured. For each such series a certain number of independent process parameters was a sustained constant, i.e., Argon flow Q(Ar) = 375 sccm, substrate speed v = 0.3 m/min. The machine is equipped with relevant deposition control devices, based on a spectral-analytical complex device by SOLAR TII (Minsk, Republic of Belarus) and programming software by Sidrabe, Inc. Process control is based on handling and stabilizing emission intensity of I(In) line on wavelength λ = 410.2 nm by means of a reactive gas control.

Process and coating parameters (sheet resistance and transmission) in the deposition cycle were under in-situ control with data collect equipment by FLUKE. When experimental samples were ready they were tested for sheet resistance, either with busbar or 4-probe method, and coating thickness was measured with an F-20 device by FILMETRIKS.

Even the first experiments proved that there is no principal difference in the course of the ITO process when carbon dioxide is used as reactive gas in place of oxygen. The

character of sheet resistance and transmission alteration at different carbon dioxide flows is the same as with oxygen. With an increase in carbon dioxide flow, sheet resistance decreases to a minimum value and then increases again. Minimum sheet resistance is determined by coating thickness and coating resistivity. By increasing carbon dioxide flow, transmission increases as well, coming to its maximum. At minimum sheet resistance we attained a transmission of up to 86%.

Figure 1 shows the dependence of ITO layer sheet resistance on oxygen as carbon dioxide flows into vacuum chamber. In similar conditions with either carbon dioxide or oxygen the obtained minimum values of sheet resistance and specific resistance differ a little, proving that the two gases show a similar effect. Sheet resistance of ITO coating without reactive gas admission comes to 250 – 300 Ohm/sq.

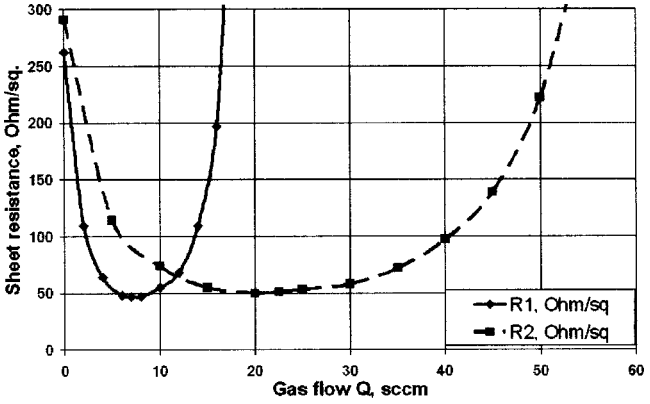

Figure 1: Dependence of ITO layer sheet resistance on oxygen flow (R1) and carbon dioxide flow (R2) into a vacuum chamber.

At sheet resistance alteration by ΔR = 50 Ohm/sq. in a range of 100 – 150 Ohm/sq., oxygen flow alters by $\Delta Q(O_2)$ = 1.3 sccm in a range of 13.8 – 15.1 sccm, while carbon dioxide flow alters by $\Delta Q(CO_2)$ = 5.3 sccm in a range of 40.3 – 45.6 sccm. Alteration of coating sheet resistance related to the deviation of corresponding gas flows is as follows:

$\Delta R/\Delta Q(O_2)$ = 38.5 Ohm/sq.*sccm,

$\Delta R/\Delta Q(CO_2)$ = 9.4 Ohm/sq.*sccm.

Therefore, in a range of 100 – 150 Ohm/sq., response level to altered reactive gas flow is lower for carbon dioxide flow.

Minimum values of sheet resistance are $R(O_2)$ = 46 Ohm/sq., and $R(CO_2)$ = 52 Ohm/sq. Considering a sheet resistance range of R_{min} + 0.1 R, one could see that this range is attainable with oxygen flow alteration in a range of 5.6 – 9.5 sccm. That is, $\Delta Q(O_2)$ = 3.9 sccm, while for carbon dioxide flow this range is 14.4 – 30.4 sccm at $\Delta Q(CO_2)$ = 16 sccm. The interval of reactive gas flows, with which we attained a deviation of sheet resistance of 10 % from minimum, is 4 times wider with carbon dioxide. This can improve uniformity of sheet resistance over substrate width, since the influence of uniform gas distribution on resistance decreases in the deposition zone. This is a considerable advantage of carbon dioxide versus oxygen.

These facts play a considerable role in deposition control, because just a small alteration of reactive gas flow has little influence on sheet resistance, but it facilitates control.

VACUUM MACHINE P600

On the basis of that described above and a number of separately performed experiments, Sidrabe Inc. developed and manufactured complex equipment for film pre-treatment and coating. The complex equipment consists of a drying vacuum machine CP1250 and a vacuum coater P600MR. In Reference 6, a vacuum coater, P600MR, for multilayer coating by means of reactive magnetron deposition is described.

The scheme of the machine is shown in Figure 2. The design feature of this machine is a vertical arrangement of all sputter magnetrons and deposition surfaces, a separated and sufficiently insulated zone with individual drums for each deposition process; and application of a highly effective plasma treatment device for film prior to the deposition.

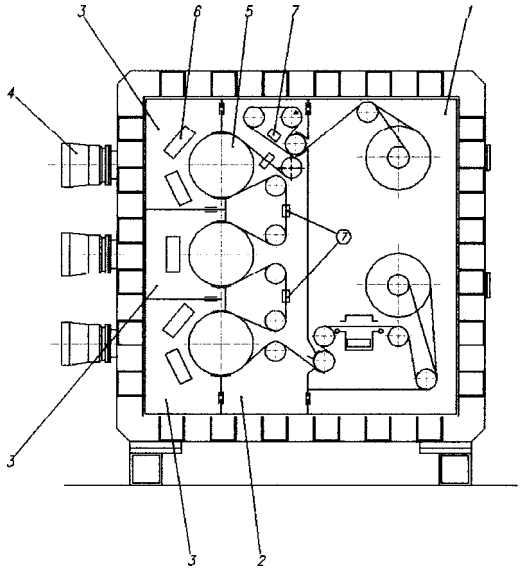

Figure 2: Layout of 3-drum's web coater: unwinding/rewinding compartment (1); intermediate compartment (2); deposition compartment (3); vacuum pumps (4); process drums (5); magnetron sputtering devices (6); optical and electric sensors for coating layers (7).

This design allows control of sheet resistance and optical characteristics (transmission, reflection) after each deposition run.

Provision of precise winding, eliminated film slippage ensures a high quality product. Provision is made for inter-leaf unwinding and rewinding within the deposition cycle.

Symmetrical, uniform pumping is accomplished for each deposition zone. There are machine versions with turbomolecular and cryogenic pumping of the magnetron compartments.

There also is a version with 6 drums with 5 insulated compartments, developed especially for films with AR layers. The availability of a system for a winding device, rolling away on one side of the chamber and drawing out sputter magnetrons on the other side facilitates maintenance of the chamber and all devices between cycles.

The vacuum coater P600MR module has proven reliable and convenient to run.

CONCLUSIONS

1. The research proved the importance of preliminary film drying on ITO films for basic characteristics such as thermal stability and wear resistance. Preliminary drying brings film to a uniform initial state, ensuring high outcome reproducibility.

2. Application of dose admission of water vapor during ITO deposition cycle enables control of thermal stability of the product, with a capability to increase and decrease it. In-situ water vapor supply stabilizes the process and allows specific resistance to decrease.

3. Application of carbon dioxide as reactive gas for ITO with a ceramic target of In_2O_3/SnO_2 in a reactive magnetron proved that, compared with oxygen, carbon dioxide ensures smooth alteration of sheet resistance and specific resistance at altered gas flows at constant emission intensity, and also at considerable gas flow interval, at which minimum sheet resistance and minimum specific resistance can be attained.

4. On the basis of research carried out, Sidrabe Inc. developed highly productive vacuum equipment for ITO thin films, and for multilayer oxide coatings.

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