

Development of Equipment and Technology in the Deposition of ITO and AR Coatings.

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ABSTRACT

Three-drum and six-drum web equipment design and construction for the deposition of transparent/conductive coatings of ITO over a wide range of sheet resistance (from 10 to 500 Ohm/sq.), as well as of multilayer AR coatings are considered. The development of a multichamber vacuum machine has been carried out taking into account various technological methods for reactive deposition stabilization and for achievement of stable coating properties.

For leveling initial surface conditions of the film prior to coating the film pretreatment is performed, which includes the film drying and outgassing in a special machine and its plasma activation in the vacuum coater.

Stability of gained coatings parameters was ensured by using double-loop control system, applying emission spectra and both optical and electrical characteristics

The technology of water vapors and carbon dioxide usage in the deposition process is developed. The water vapors, on one side, contribute to the deposition process stabilization, on the other hand, affect coating properties. The use of carbon dioxide instead of oxygen allows to expand the possibilities of web coating process monitoring.

INTRODUCTION

The vigorous development of information input/output means like LCD and touch screen panel requires the development of high-productive multifunctional equipment for multilayer coating structures on flexible polymer substrates (PET, PEN, PI etc) for solving a complex of issues, determining quality of produced materials. These issues include substrate pre-treatment for coating, substrate pre-treatment for high adhesion, new processes development, application of new control methods for the deposition processes. The article represents the results, obtained during researches 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

Water vapor partial pressure in a vacuum chamber is an uncontrollable parameter, as it dependent from many reasons and particularly from water vapor contents in polymeric substrate. The exploration of the influence of some uncontrollable parameters of the DC sputter magnetron deposition on the ITO properties [1-3] proved that water vapor partial pressure is one among major uncontrollable parameters, considerably influencing coating processes. Partial pressure of water vapor inside vacuum chamber is dependant on a lot of factors. Firstly, this is adsorption water on chamber walls and on in-chamber devices. Secondly, this is absorption water. Quantity of water vapor depends from amount of condensate remains in vacuum chamber after the coating cycle, from duration of the chamber exposure to atmosphere between cycles and others.

And, finally, the polymeric film (substrate) itself is another source of water vapor. Every polymeric film contains adsorbed water on the film surface and absorbed water, which can diffuse from film material to film surface, regenerating the layer of adsorbed water on the film 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 film surface and inside film as well. This water escapes at film heating, caused by coating condensation. For uniform pre-coating conditions, film is subject to preliminary treatment, including drying, outgassing and gas discharge plasma treatment.

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

- 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 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 on temperature, drying time (winding speed) etc.

Film drying was performed on a vacuum machine. Heating of film, moving between two rollers with a speed of 0.5 m/min, was performed with IR heater. After the heating the film entered 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 sheet resistance 350 Ohm/sq. For quantitative assessment of the drying process we used such coating characteristics, as coating thermal stability and durability. Thermal stability was calculated as relation between sheet resistance after coated film exposure to a temperature of 150°C (R_T) during 1 hour and initial resistance (R_0). Durability was calculated as relation of sheet resistance after a certain number of friction cycles at given load (R_D) and sheet resistance R_T .

Thermal stability of ITO layer with considerable sheet resistance is rather sensitive to the state of polymer film surface. In 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 dependant on kind of reaction gas. The reinstatement of thermal stability values in alternative cycles and with alternative gases testifies achievability of identical conditions on the film, supporting coating properties reproducibility. Alteration of film thickness or film kind will require retrieval of alternative drying conditions.

By this means, on one hand, drying at a maximum admissible temperature enables maintenance of similar starting conditions for coating and reproducibility of coating properties, as well. On the other hand, for practical goals is quite important that coating sheet resistance does not alter at product 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.

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

No.	$T_h, ^\circ\text{C}$	$T_d, ^\circ\text{C}$	R_T/R_0 , 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.

Influence of water vapor admission in vacuum chamber.

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

Initial value of thermal stability was similar to an earlier value, received w/o 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 reaction gas in place of oxygen.

Besides a capability to handle coating thermal stability, water vapor admission gas mixture of $\text{Ar} + \text{O}_2$ allowed to extend time of stable sustaining of sheet resistance up to several hours. It was observed that after the termination of water vapor admission, sheet resistance of ITO coating started growing in a few minutes, and we cannot to decrease it by changing deposition conditions, i.e. in-situ water vapor admission also influenced on ITO properties.

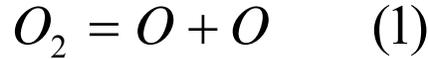
Admission of water vapor allowed attaining of ITO specific resistance in a range of $(5.1-5.4) \cdot 10^{-4}$ Ohm*cm.

Table 2. Thermal stability of 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

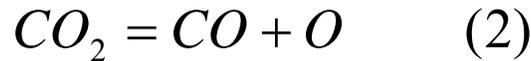
APPLICATION OF CARBON DIOXIDE IN REACTIVE ITO DEPOSITION.

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 emerge of atomic oxygen, i.e.



Plasma also causes generation of other active particles, i.e. excited molecular oxygen O₂^{*}, atomic and molecular ions of oxygen O⁺, O₂⁺. Availability of two dangling bonds of atomic oxygen determines super chemical activity of oxygen, compared to other particle. Bonding energy in oxygen molecule O=O makes up 5.2 eV [4]. This is atomic oxygen that causes generation of oxides on substrate in deposition cycle. Other particles are not that active and do not considerably influence on coating formation.

Carbon dioxide CO₂ can be used as a source of atomic oxygen. Dissociation of CO₂ molecules takes place in electric discharge plasma, i.e.



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

Bonding energy of oxygen atom in CO₂ molecule alters a little from bonding energy on oxygen molecule, therefore these two gases are energetically equivalent. Since two atoms derive from dissociated oxygen molecule, and only one from carbon dioxide molecule, the process requires exceeded 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 exchange for carbon dioxide allowed to increase arc deposition speed of Ti oxide. It is quite obvious, that running conditions of pumps, diffusion pumps, in particular, are improved, because pumped down oxygen flow, affecting vacuum oil in pumps, is reduced.

Taking into account positive effect of CO₂ application in arc reactive processes for oxides deposition, Sidrabe Inc. carried out researches for a possibility of carbon dioxide application as reactive gas in place of oxygen for ITO coating through reactive process with magnetron sputtering, using oxide ITO target.

ITO coating was deposited through reactive magnetron sputtering of oxide target of In₂O₃/SnO₂. Carbon dioxide was admitted into the oxygen line, oxygen admission being cut off. In this way oxygen admission devices and instruments were used for carbon dioxide flow monitoring and control. Experimental testing were carried out with oxygen as reactive gas, vacuum chamber normally being not depressurized at gas changing 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 sustained constant, i.e. Argon flow $Q(\text{Ar}) = 375$ sccm, substrate speed $v = 0.3$ m/min. The machine is equipped with relevant deposition control devices, based on 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 wave length $\lambda = 410.2$ nm by means of 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, coating thickness measured with F-20 device by FILMETRIKS. Even the first experiments proved that there is no principal difference in the course of 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 comes down to a minimum value and then goes up again. Minimum sheet resistance is determined by coating thickness and resistivity of coating. With the increase of carbon dioxide flow, transmission goes up, coming by its maximum. At minimum sheet resistance we attained transmission up to 86 %.

Fig. 1 shows the dependence of ITO layer sheet resistance on oxygen and 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 similar effect. Sheet resistance of ITO coating w/o reactive gas admission comes to 250 – 300 Ohm/sq.

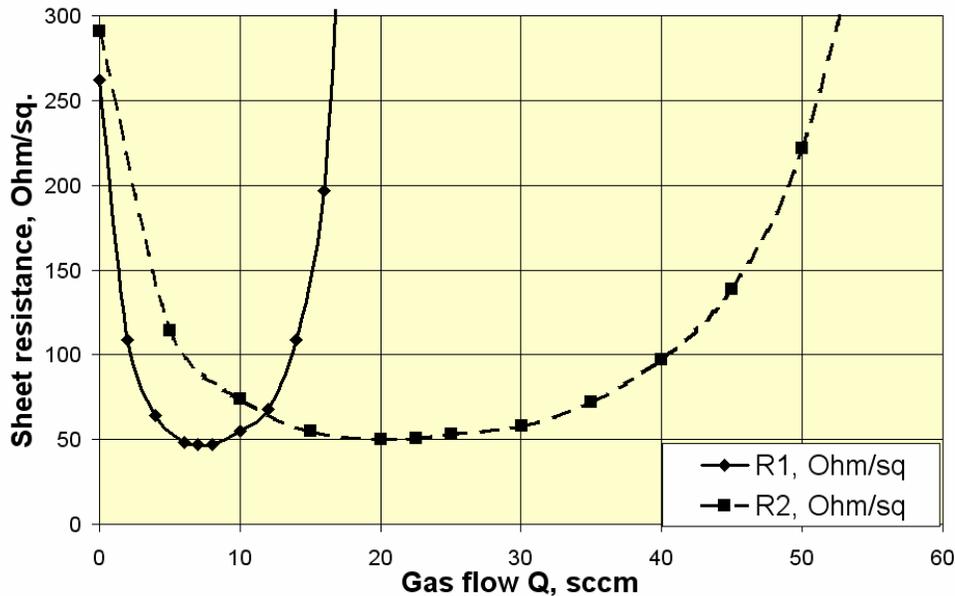


Fig. 1. Dependence of ITO layer sheet resistance on oxygen flow (R1) and carbon dioxide flow (R2) into vacuum chamber.

At sheet resistance alteration by $\Delta R = 50$ Ohm/sq. in a range of 100 – 150 Ohm/sq., oxygen flow alters by $\Delta Q(\text{O}_2) = 1.3$ sccm in a range of 13.8 – 15.1 sccm, while carbon dioxide flow alters by $\Delta Q(\text{CO}_2) = 5.3$ sccm in arrange of 40.3 – 45.6 sccm. Alteration of coating sheet resistance related to the deviation of corresponding gas flows is as follows:

$$\Delta R / \Delta Q(\text{O}_2) = 38,5 \text{ Ohm/sq.} \cdot \text{sccm},$$

$$\Delta R / \Delta Q(\text{CO}_2) = 9,4 \text{ Ohm/sq.} \cdot \text{sccm}.$$

Herefrom, 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 $R(\text{O}_2) = 46$ Ohm/sq., $R(\text{CO}_2) = 52$ Ohm/sq. Considering 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, i.e. $\Delta Q(\text{O}_2) = 3,9$ sccm, while for carbon dioxide flow this range is 14.4 – 30.4 sccm at $\Delta Q(\text{CO}_2) = 16$ sccm. Interval of reactive

gas flows, with which we attained 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 goes down in deposition zone. This is a considerable advantage of carbon dioxide versus oxygen.

These facts play considerable role in deposition control, as far as just inconsiderable alteration of reactive gas flow little influences on sheet resistance, but facilitate control.

EXTENDED OES METHOD FOR REACTIVE PROCESSES CONTROL.

During coating deposition by reactive magnetron sputtering on a substrate goes two flows: metal flow Q_{met} and reactive gas flow Q_{gas}^* . As a result of these flows chemical combination (in our case, oxide or nitride) is formed.

Dynamic control of coating deposition process is reduced to two processes:

- 1) Setting of balance between a reactive gas flow Q_{gas}^* and sputtered metal flow on substrate Q_{met} . Criterion for balance setting is coating physical properties.
- 2) Keeping of balance between reactive gas flow Q_{gas}^* and sputtered metal flow Q_{met} on a substrate in time.

$$\frac{Q_{gas}^*}{Q_{met}} = const \quad (3)$$

Flows of metal Q_{met} and reactive gas Q_{gas}^* on a substrate can not be measured directly in process, usually they are measured indirectly, for example, intensity of radiation of metal emission line I_o which is proportional to metal flow in reactive process, and partial pressure of reactive gas p_{gas} which is proportional to reactive gas flow on a substrate is measured. Therefore the condition of balance keeping (3) can be presented so

$$\frac{p_{gas}}{I_o} = const. \quad (4)$$

Initial characteristics of reactive process are magnetron power P and reactive gas flow Q_{gas} in the chamber (do not confuse to a flow of reactive gas on substrate Q_{gas}^*), which in combination determine intensity of radiation I_o and partial pressure of reactive gas p_{gas} .

The analysis of relationship (4) shows that change of intensity of radiation of metal (that is equivalent to change of metal flow) will result in change of partial pressure of reactive gas. The same will take place at change of partial pressure of reactive gas. The ratio will be kept, but it can cause change of physical properties of a coating, at least, thickness of a coating. Therefore it is necessary not only to keep balance between flow of reactive gas Q_{gas}^* and flow of sputtered metal Q_{met} on a substrate, but also one of values Q_{gas}^* or Q_{met} .

On fig. 2 known dependence of reactive gas flow on intensity in controlled reactive process is shown. In controlled process at the given sputtering power two parameters (I_o , Q_{gas}) determine properties of coating. At change of sputtering power point I_{met} describing intensity of radiation at sputtering in metallic mode will move, also a curve will be changed, in result we will receive a new pair an intensity/flow for performance of the requirement on properties of a coating.

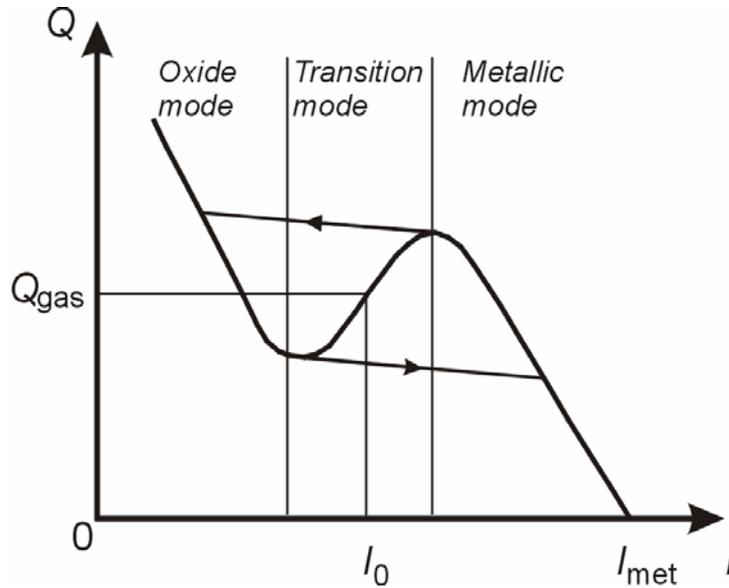


Fig.2. Dependence of reactive gas flow on intensity in controlled reactive process.

In a metal sputtering mode intensity of radiation is proportional to sputtering power (line OA on fig. 3). In reactive process at the given sputtering power P_1 process control system with the help of OES uniquely determines necessary flow of gas Q_{gas} for maintenance of the set intensity of radiation of metal I_{set} (point B). Only one pair values of intensity and a flow of reactive gas will allow to receive a coating with the set properties at the given sputtering power. Thus, the pair rating values of intensity and a corresponding flow of reactive gas in the chamber for reception of a coating with the set properties is established at the given sputtering power. Value of intensity of radiation and a flow of reactive gas for reception of the set properties of a covering should be determined in preliminary experiments.

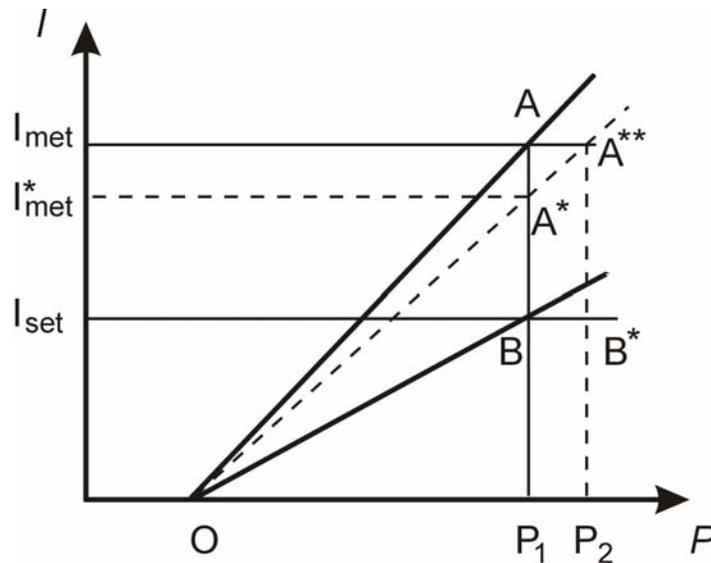


Fig.3. The scheme of extended OES method for control of reactive process.

If in process sputtering rate of metal is reduced (line OA^{**} on fig. 3), point A passes in A^* , and it means, that intensity of radiation decreases up to I_{met}^* in metal sputtering mode. Thus the control system reduces a flow of reactive gas Q_{gas} for maintenance of the same intensity of radiation I_{set} , and the balance between a flow of reactive gas and a flow of the sputtered metal on a substrate will be disturbed, in result in a coating surplus of metal will appear. Generally for practice not

so important value I_{met} , but is necessary to know a pair of parameters of process (I_{set} , Q_{gas}) which provides properties of a coating.

At keeping of all parameters of process by constants sputtering rate of a target in time is monotonously reduced. It is consequence of such processes as change of a magnetic field owing wearing of a target, processes of oxidation on a surface of a target, growth nigel, etc. Thus, monotonous reduction of reactive gas flow in reactive process with other things being constant will show that sputtering rate of metal has decreased. In long time process for keeping of balance between a flow of reactive gas Q_{gas}^* and a flow of the sputtered metal on a substrate in time it is necessary to keep metal sputtering rate constant.

At decrease of sputtering rate of a target it is necessary to increase sputtering power up to P_2 so that at the given intensity of radiation I_{set} to receive former value of a reactive gas flow, i.e. in addition to control of a gas flow control of sputtering power is necessary. In metal sputtering mode we will receive another dependence of intensity on power, straight line OA^{**} , but a kind of curve $Q = f(I)$, fig. 2, will not change. Accuracy of keeping of reactive gas flow in the chamber can be set proceeding from requirements to properties of coatings; the maximum deviation of a reactive gas flow from nominal should be such that properties of a covering have not left for allowable limits.

The additional feedback on power allows to take into account reduction of sputtering rate and to exclude its influence on properties of a coating.

The suggested way allows without the expensive equipment for coating properties measurement operatively control process of coating deposition during long time.

VACUUM MACHINE P600

On the basis of above described 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 drying vacuum machine CP1250 and vacuum coater P600MR.

In work [6] vacuum coater P600MR for multilayer coating by means of reactive magnetron deposition is described.

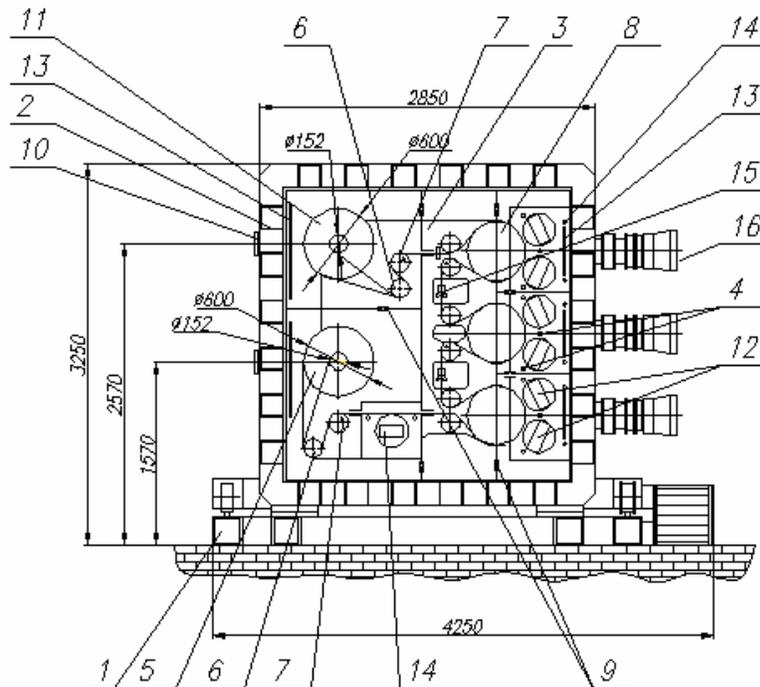


Fig. 4. Layout of 3-drum's web coater: unwinding/rewinding compartment (1); intermediate compartment (2); Deposition compartment (3); vacuum pumps (4); Process drums (5); magnetron sputtering devices (6); optical and electric sensors for coating layers (7).

Scheme of the machine is in Fig.4. The design feature of this machine is vertical arrangement of all sputter magnetrons and deposition surfaces; separated, sufficiently insulated zone with individual drum for each deposition process; application of high-effective plasma treatment device for film before the deposition.

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

Provision of precise winding, eliminated film slippage ensure high quality of product. Provision is made for interleaf unwinding and rewinding within deposition cycle.

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

There is a version with 6 drums with 5 insulated compartments, developed especially for films with AR layers.

Availability of a system for 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.

Vacuum coaters P600MR have proved that they are reliable and convenient for running.

CONCLUSION

1. The performed researches proved the important influence of preliminary film drying on such basic characteristics of ITO thin films, as thermal stability and wear resistance. Preliminary drying brings film to 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 product, with a capability to increase and decrease it. In-situ water vapor supply stabilizes the process and allows to decrease specific resistance.
3. Addition of OES method by a feedback power – flow of reactive gas allows to remove influence of sputtering rate change at change of target sputtering conditions. In suggested method control is made on two parameters of process: to a reactive gas flow and sputtering power at preset emission line intensity. Two control loops in extended OES method provide with
 - 3.1. Stable course of process of reactive deposition of a coating in a transition mode by keeping of intensity of radiation of a spectral line of metal by control of reactive gas flow in the chamber.
 - 3.2. Stability of properties of a coating in time by control of sputtering power for maintenance of reactive gas flow at the set intensity of radiation of a spectral line of metal
4. On the basis of carried out researches Sidrabe Inc. developed high-productive vacuum equipment for ITO thin films, and for multilayer oxide coatings

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