

# High rate low pressure PECVD for barrier and optical coatings

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Two types of new plasma enhanced CVD (PECVD) technologies were developed. The main benefits of these DC-magnetron based PECVD (magPECVD) and hollow cathode arc driven PECVD (arcPECVD) are their low process pressure in the range of 0.1 to 5 Pa and the high coating rate up to 400 nm m/min for magPECVD and 3000 nm m/min for arcPECVD. Both processes were used to produce layer stacks in roll-to-roll coaters on polymer webs. Optical layer stacks made with these technologies showed nearly no stress. The mechanical robustness of permeation barrier layers was improved by implementation of interlayers made by these PECVD methods. Necessary hardware was developed for industrial applications with web widths of 1.7 m for magPECVD and 2.85 m for arcPECVD.

## *Introduction*

Plasma enhanced CVD (PECVD) is a well known coating technology being used worldwide especially for batch processing. Unfortunately commonly used rf or microwave driven PECVD needs relatively high process pressure in the range of 10 to 100 Pa. Due to the fact of high pressure it is difficult to combine these PECVD methods with PVD technologies like evaporation or sputtering within one vacuum coating machine to be run simultaneously.

The use of PECVD on the other hand is beneficial for many purposes. Unlike thermal CVD, PECVD is a low temperature process. Therefore this process can be used to deposit layers on thermally sensitive substrates like polymers or thin metal foils. The PECVD process runs in vacuum and thus runs in a clean and well defined environment. There is a broad choice of precursors available to deposit different layer materials. In combination with different reactive gases also chemical compounds can be formed during layer growth. A wide range of process variables exist to tune the process and the resulting layers. For instance plasma pow-

er, plasma frequency and process pressure can be adjusted.

To overcome the limitations of common PECVD technologies regarding process pressure two new types of PECVD were developed and will be introduced.

## *Magnetron driven PECVD – magPECVD*

Magnetron sputtering is a well established and worldwide known PVD technology to produce single layers and multi layer stacks in high quality. One of the major advantages of magnetron sputtering is the superior layer thickness homogeneity over large substrate width. The technology is used for architectural glass coating and also for coating of polymer webs with coating width up to 4.5 m.

Long term stability of reactive processes at high coating rate is achieved using a closed loop control of the reactive gas inflow. [1]

When equipped with an additional precursor inlet as shown in figure 1, a (dual) magnetron system may also be used as plasma source for a PECVD process.

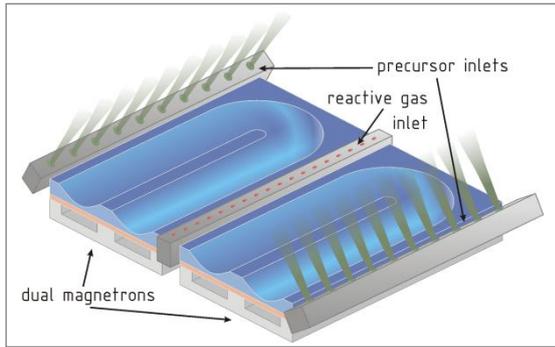


Figure 1 Typical arrangement of magPECVD device, consisting of a dual magnetron system, a precursor inlet and a reactive gas inlet

One important feature of this technology is the low process pressure in the range of 0.3 Pa to 3 Pa. The ratio between precursor to reactive gas flow rate can be adjusted to modify the layer composition instantly during the coating process (see later in this paper). The coating rate of this magnetron driven PECVD (mag-PECVD) depends on this ratio. Dynamic deposition rates up to 400 nm m/min were achieved by using HMDSO (hexamethyldisiloxane) as precursor using precursor rich conditions.

A deposition rate of 200 nm m/min was proven to be long term stable over 8 h. This could be shown with a device built by FEP for an industrial customer for web width of 1.7 m.

Additional beneficial is the usage of one piece of hardware with option to run two processes. With use of the precursor one drives a PECVD device. Without the precursor the device may be used like a common reactive sputtering system.

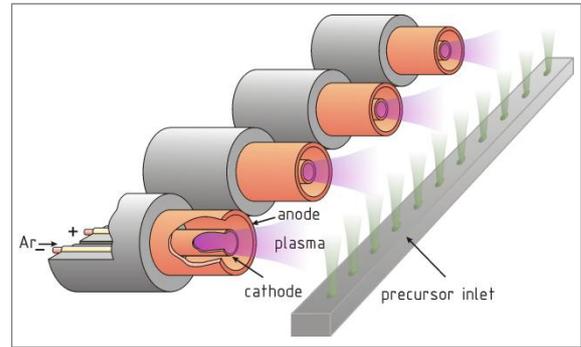


Figure 2 Typical setup of arcPECVD device, consisting of one or more hollow cathode arc sources and a precursor inlet

### *Hollow cathode arc PECVD - arcPECVD*

A very intensive plasma can be delivered by hollow cathode arc discharges [1]. Respective plasma sources are used within the plasma enhanced reactive deposition of polymer webs with alumina for permeation barrier coatings for the packaging industry. Such plasma systems were equipped with precursor inlet too to setup a device for high rate PECVD deposition. A typical arrangement of hollow cathodes for PECVD deposition is shown in figure 2.

The feasibility of the so called arcPECVD process has been proven in a pilot-type roll-to-roll coater for 650 mm web width. Four modular hollow cathode arc sources were used. Such plasma sources have already been installed into several industrial web coaters up to 2.85 m web width for plasma enhanced deposition of alumina (see device photo in figure 3). Therefore, a scale up of the arcPECVD process from the pilot coater level (650 mm) to wider webs (2.85 m and beyond) seems feasible without any compromise in coating rate or process stability.



Figure 3 Arrangement of a number of hollow cathode arc (hca) sources to apply plasma enhancement over a width of 2.85 m; hca-sources are mounted on a rectangular flange right to be installed in web coating machines

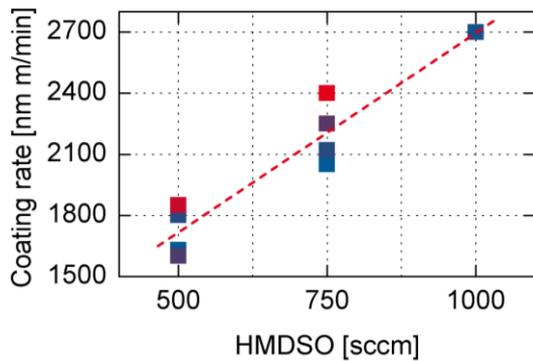


Figure 4 Coating rate of arcPECVD in dependency of the HMDSO flow; different points at one fixed HMDSO flow show the variations of the coating rate due to change in plasma power and/or additional oxygen flow

The dynamic deposition rate of an arcPECVD process was investigated more in detail. There is a linear dependency between the precursor flow rate and the deposition rate as to be seen in figure 4. A maximum of 2700 nm m/min at a flow rate of 1000 sccm HMDSO was reached. The variation in coating rate at HMDSO flow of 500 and 750 sccm is due to change in plasma power and/or additional oxygen flow.

The arcPECVD process follows the same “one hardware – two processes”-principle as the magPECVD process. Beside the arcPECVD by itself one can also use the hardware for plasma enhancement of reactive or non-reactive evaporation. This approach is typically used in the high speed alumina coating of polymer webs for the packaging industry. [5]

Table 1 Comparison table of different PECVD methods

	magPECVD	arcPECVD	HF-PECVD	MW-PECVD
typical frequency	10-50 kHz bipolar pulsed	DC	13.56 MHz	2.45 GHz
process pressure	0.3 – 3 Pa	0.1 – 5 Pa	1 – 20 Pa	5 – 100 Pa
coating rates	20 – 400 nm m/min	500 – 3000 nm m/min	10 – 200 nm m/min	10 – 100 nm m/min
remarks	industrially proven for wide webs, units commercially available		pressure range different to PVD	

### Comparison of PECVD methods

Some commonly used PECVD methods were listed in the introduction. They are used very often in batch coaters like systems for wafer coating or coating of eye glasses. But their use in roll-to-roll machines is not very common.

A main drawback of these PECVD methods, such as hf or microwave PECVD, is their high process pressure up to 100 Pa. In contrast to that magPECVD and arcPECVD need only a pressure in the range of 0.1 to 5 Pa. Due to the lower pressure the combination with other PVD technologies like evaporation or sputtering is easily possible. Within a multi chamber machine PVD and PECVD modules could be run simultaneously with only low requirements regarding gas separation between the coating chambers.

Another advantage is the higher coating rate of magPECVD and arcPECVD in comparison to the others. These coating rates fit very well to the one which typical PVD methods reach. An inline combination of sputtering and magPECVD or a combination of evaporation and arcPECVD is possible.

## Application examples

### Layer composition

A typical feature of PECVD processes is the variability in atmosphere composition. The ratio between the needed precursor and an optional reactive gas can be adjusted to initiate a change in the layer composition as shown in figure 5. Layers made by magPECVD with different ratios between the flow of precursor HMDSO and reactive gas oxygen were investigated by x-ray photoelectron spectroscopy (XPS). With an increase of the HMDSO ratio

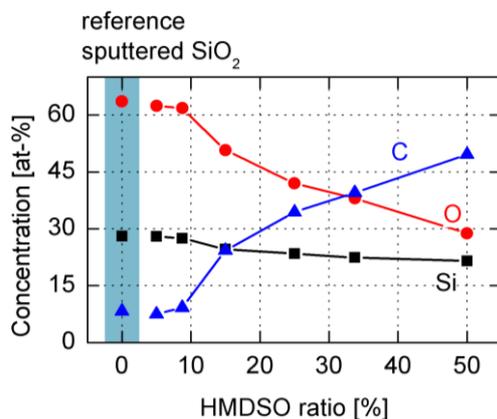


Figure 5 Element concentration measured by XPS of layers made by magPECVD dependent on the ratio between precursor flow and reactive gas flow; HMDSO was used as precursor, oxygen was used as reactive gas [1]

more and more carbon can be found in the layer. An increased organic modification of the silica layer is observed.

With a change of the layer composition other layer properties are changed as well. Figure 6 shows the elastic modulus and the hardness of such layers in dependence of the precursor to reactive gas flow ratio. Through the increased organic modification of the layers with increased HMDSO ratio both properties decrease to only 20 %. This means an increase in elasticity and flexibility.

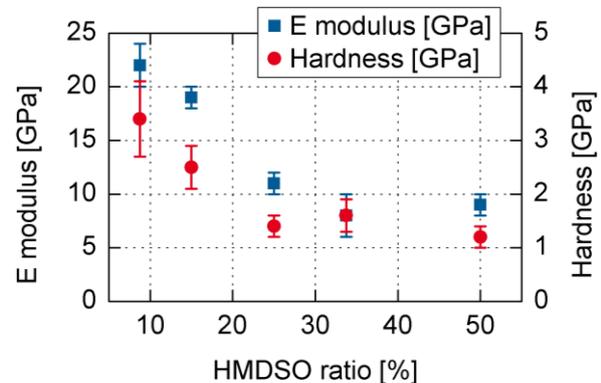


Figure 6 Elastic modulus and hardness of a layer made by magPECVD versus the HMDSO to oxygen flow ratio [3]

### Optical stacks

A common method to achieve a certain optical effect is stacking transparent layers made out of materials with different refractive indexes. The so called interference effect is used to tailor the reflectance or transmittance of such optical layer stacks. For large-area applications one uses sputtering due to the homogeneity over wide coating widths. Unfortunately sputtered layers are known to show high layer stress which leads to bending or curling of a coated polymer substrate. By using the far more flexible layers made by PECVD with high precursor ratio one can reduce such stress of layer stacks very efficiently.

To give an impression of the potential of magPECVD an approximately 1400 nm thick 9 fold layer stack was produced in a roll-to-roll vacuum coater to achieve a dielectric solar control coating on top of a polymer substrate.  $\text{TiO}_2$  was used as the high refractive index material. This material was made by reactive sputtering from metallic targets using pulsed DC-discharge. Silica was used as low refractive index material. In one sample the silica was made using pulsed DC-sputtering from metallic targets also. Another sample was made using magPECVD for the silica layer. The comparison in the infrared reflectance and the transmittance in the visible range is to be seen in figure 7.

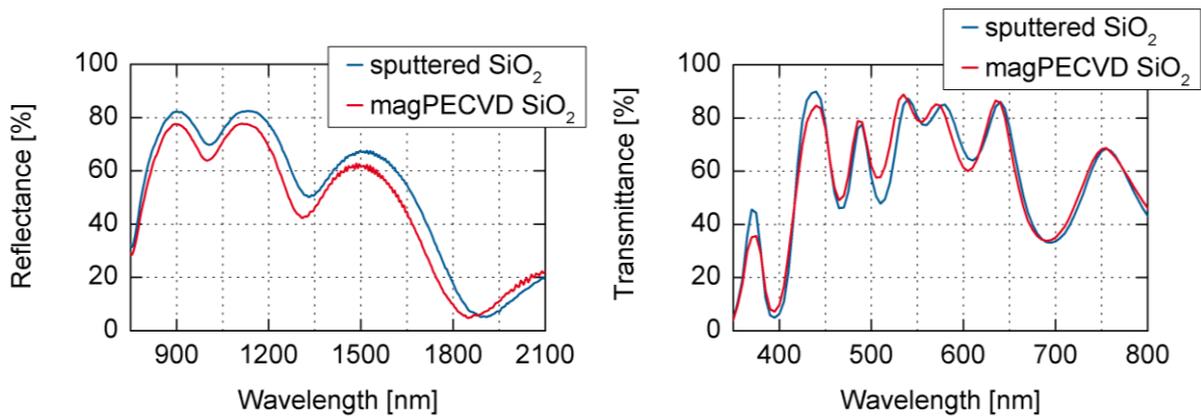


Figure 7 Reflectance spectra in the infrared and transmittance spectra in the visible region of an 9 fold dielectric solar control layer stack made out of  $\text{TiO}_2$  as high refractive index material and  $\text{SiO}_2$  as low refractive index material, where the  $\text{SiO}_2$  were deposited by sputtering or by magPECVD

The spectra are very similar to each other. Only in the reflectance one see slightly higher values for the layer stack made by sputtering only. The main benefit of the layer stack made

by sputtering and magPECVD in combination is nearly no bending of the sample and therefore much less layer stress compared to the other sample as one see in figure 8.

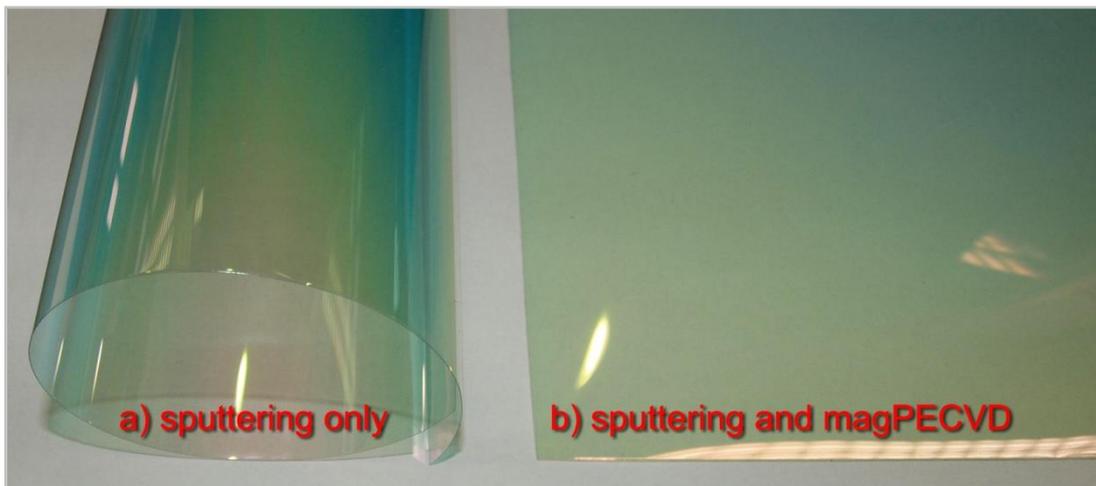


Figure 8 Picture of two 9 fold dielectric solar control layer stacks, a) made completely by sputtering on the left side and in contradiction b) made in combination by sputtering and magPECVD on the right side

As another example a dielectric UV-mirror was made with  $\text{HfO}_2$  as high refractive index material made by reactive pulsed DC-sputtering. Silica was used again as low index material made by magPECVD. Two different layer stacks were made. The first stack had a total thickness of approximately 1200 nm and consisted of 20 single layers (10 pairs of  $\text{SiO}_2/\text{HfO}_2$ ). A second layer stack was made out of 40 single layers (20 pairs). The overall thickness was approximately 2300 nm for the second stack.

The optical spectra were measured over the web width of 400 mm for the 20 fold stack and 500 mm for the 40 fold one. These spectra can be seen in figure 9 for the thinner stack and respectively in figure 10 for the thicker one. For both stacks one see very small shift of the UV-edge of 12 nm at 330 nm respectively 29 nm at 360 nm. This proves the high reproducibility over web width of the magPECVD process. In contradiction to layer stacks made only by PVD technologies both samples showed nearly no layer stress.

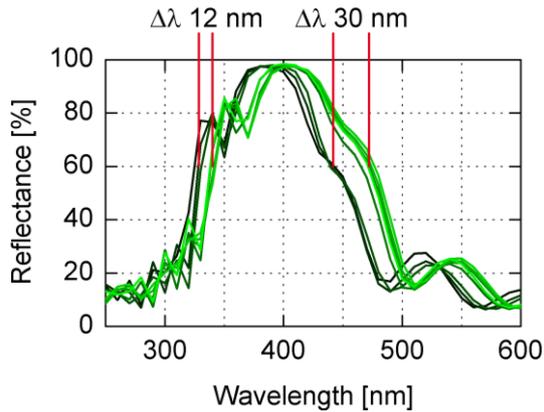


Figure 9 Reflectance spectra of an 20 fold 1200 nm thick dielectric UV-reflection layer stack over 400 mm wide polymer web; layer stack made out of  $\text{HfO}_2$  as high refractive index material and  $\text{SiO}_2$  as low refractive index material, where the  $\text{SiO}_2$  were deposited by magPECVD

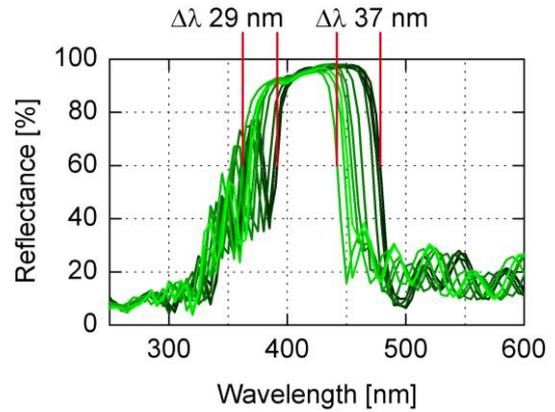


Figure 10 Reflectance spectra of an 40 fold 2300 nm thick dielectric UV-reflection layer stack over 500 mm wide polymer web; layer stack made out of  $\text{HfO}_2$  as high refractive index material and  $\text{SiO}_2$  as low refractive index material, where the  $\text{SiO}_2$  were deposited by magPECVD

### Permeation barrier stacks

Polymer webs are used for many applications and have high potential as substrate or encapsulation material for flexible electronics and solar cells. However, polymer films show insufficient barrier against permeation of water vapor and other gases. To improve the water vapor permeation barrier a very thin coating in

a range of less than 10 nm up to several hundred nanometers is applied to these substrates. The requirements on the permeation barrier depend on the fields of application. Figure 11 summarizes technologies and coating designs together with respective permeation requirements in different fields of applications. The water vapor transmission rate (WVTR) is used to quantify the permeation requirements.

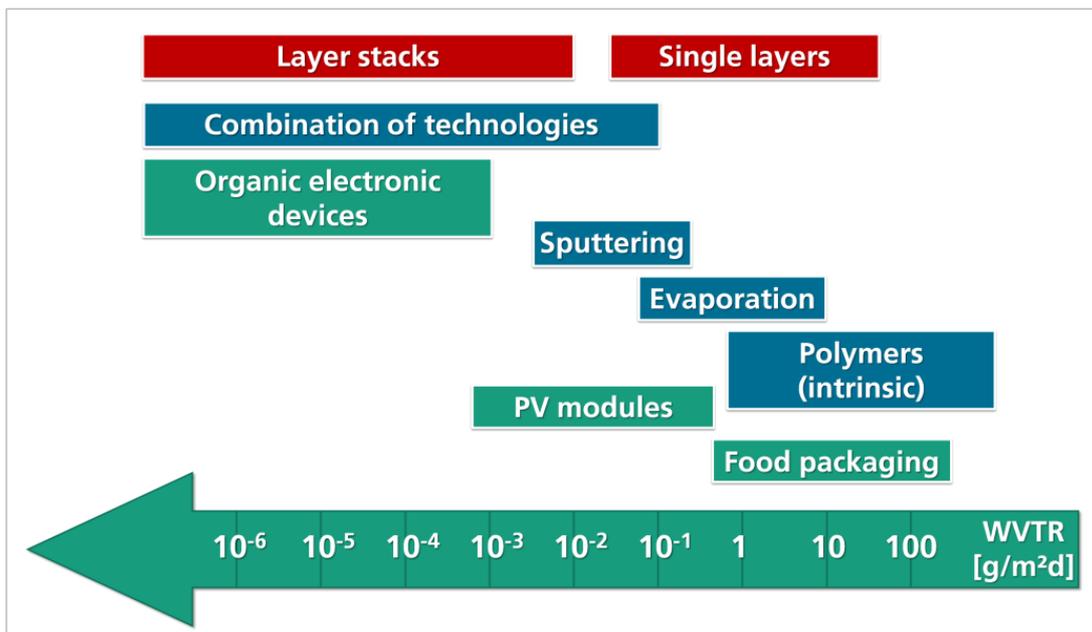


Figure 11 Overview about requirements and technologies in the field of permeation barrier [4]

The WVTR ranges over many orders of magnitude as to be seen in figure 11. Single layers are adequate to achieve a permeation barrier necessary for food packaging and encapsula-

tion of crystalline solar cells. For applications like encapsulation of thin film solar modules or organic based electronic devices much harder requirements have to be fulfilled. To reach

values lower than  $10^{-3}$  g/m<sup>2</sup>d a multi layer approach is needed. Hereby two or more layers act as permeation barrier layers. In between these barrier layers, interlayers are needed to smooth the surface of the former layer and to prevent permeation defects. Figure 12 shows a layer stack with two barrier layers and one interlayer. The first barrier layer (counted from substrate below) contains a defect which leads to water vapor diffusion at this point. With the interlayer, this defect is smoothed and covered. The second barrier layer still shows some “deformation” but no visible path for permeation. It is a common understanding to make the barrier layers by PVD methods. The interlayers could be made by vacuum processes such as magPECVD or arcPECVD like the stack shown in figure 12. Another option is to make the interlayer by lacquering. Very low WVTR can be reached with both approaches [8].

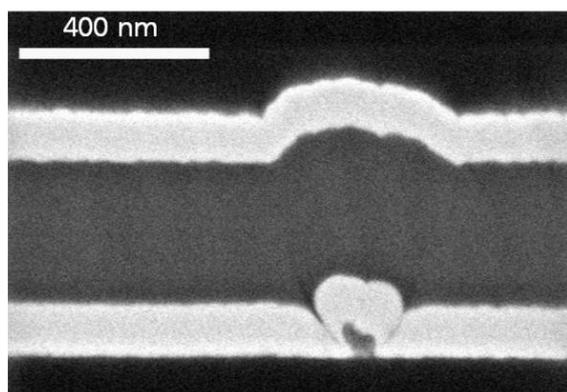


Figure 12 Multilayer barrier stack with a defect in the first barrier layer caused by a particle at the substrate; defect is covered by a PECVD layer [5]

By using vacuum based technologies for the interlayer, one can produce a multilayer structure completely in vacuum and completely inline (means within one roll-to-roll pass). As an example a multilayer permeation barrier stack was made on PET substrate by using the arcPECVD process for the interlayer. The barrier layers were made out of zinc tin oxide (ZTO) by using two units of pulsed DC-driven dual magnetron systems in reactive mode. Each ZTO layer was 60 nm thick which results in a total ZTO thickness of 120 nm. The interlayer was made by arcPECVD and had a thickness of 750 nm. All layers were deposited

inline within a multi chamber vacuum coater at web speed of 2 m/min.

The water vapor permeation rate of the layer stack is compared to a 60 nm and a 120 nm thick ZTO layer and a 60 nm thick ZTO layer covered by the interlayer alone in figure 13. The WVTR of the complete layer stack is nearly the same as for a single layer with a ZTO thickness of the total ZTO barrier layers. When comparing a 60 nm thick single layer with one covered by a PECVD topcoat, the water vapor transmission rate does not change by adding the topcoat. All this proves the option to improve a single barrier layer by split them into two parts with an interlayer in between. Beside the option to improve the tolerance against defects during layer growth the flexibility is improved as well and therefore the resistance against mechanical stress is improved.

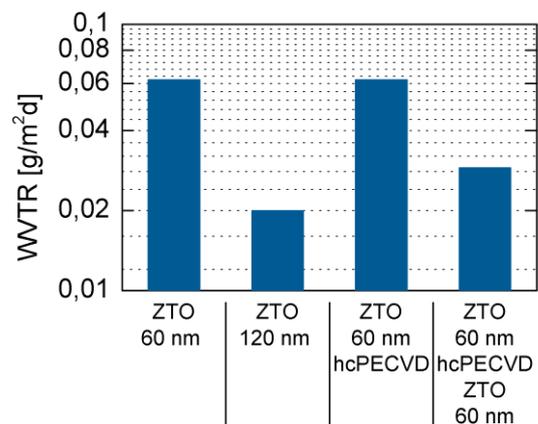


Figure 13 Comparison of the permeation barrier of single layers of ZTO with layer stacks with an arcPECVD-interlayer

This improvement of the mechanical robustness can also be seen when investigating the behavior of layer stacks under strain conditions. The elongation of a barrier coated polymer film will lead to cracking of the barrier layer after reaching a certain level of elongation or strain, respectively. This strain level is called crack-onset strain. Figure 14 shows the crack-onset strain for two different types of layer stacks in dependence of the number of ZTO layers (whereas the total ZTO thickness remains constant). The first stack is based on an overall ZTO thickness of 150 nm (blue

curve in figure 14) and the second stack has a total ZTO thickness of 300 nm (red curve). As visible in figure 14 the crack-onset strain increases with increase of the number of ZTO layers. This also means the crack-onset strain increase with the number of interlayers. An increase of approximately 50 % is to be seen with two interlayers.

This increase in mechanical robustness could be seen not only in the higher tolerance against build up of cracks. Also the permeation barrier itself showed improved mechanical resistance.

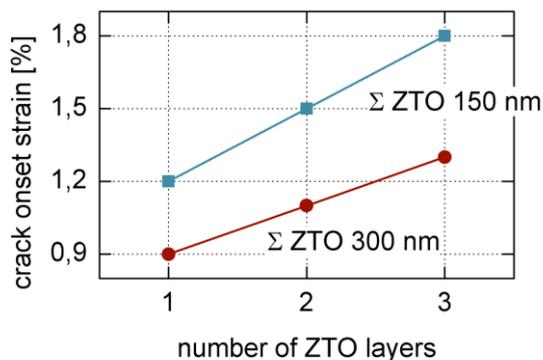


Figure 14 Crack onset strain of single layers of ZTO with layer stacks with a magPECVD-interlayer; the overall layer thickness of ZTO is all the same within the two groups (marked by different colors) [7]

### R&D and pilot production at FEP

All of the examples above were produced at multi-chamber roll-to-roll vacuum coaters at Fraunhofer Institute of Electron Beam and Plasma Technology in Dresden, Germany. One of these machines is shown in figure 15. The so called *novoFlex*<sup>®</sup> 600 is equipped with several coating units like three dual magnetron sputtering systems, a plasma enhanced boat evaporator and a plasma enhanced electron beam evaporator. The magPECVD and the arcPECVD processes can be run inline to the PVD processes simultaneously due to their compatible process pressure and the pressure decoupling between the different process chambers.

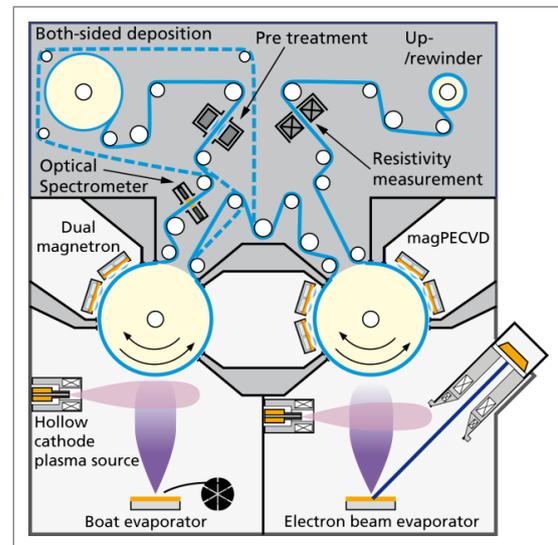


Figure 15 Design of the R&D and pilot production roll-to-roll vacuum coater *novoFlex*<sup>®</sup> 600, equipped with several dual magnetron sputter systems with magPECVD option, plasma enhanced boat evaporator and plasma enhanced electron beam evaporator, both with arcPECVD option

### Summary

Two types of newly developed PECVD processes were introduced. The main benefits of magPECVD and arcPECVD are their low process pressure of less than 5 Pa which allows the in-line combination with sputtering or evaporation processes and the dual usability of respective hardware. And moreover, both processes have superior coating rates of up to 400 nm m/min for magPECVD and up to 3000 nm m/min for arcPECVD, respectively.

Samples were made with both PECVD methods as single layers and in combination with sputtering as multilayer stacks. Optical layer stacks made with magPECVD showed nearly no layer stress. The homogeneity over large web widths up to 500 mm was proven by depositing and evaluating optical layer stacks consisting of 20 and 40 layers, respectively.

The mechanical robustness of permeation barrier layer stacks was improved by interlayers made by magPECVD. An example showed the potential of arcPECVD to achieve very thick layer thicknesses inline to sputtered barrier layers.

A complete 1.7 m wide magPECVD system was developed and supplied to an industrial customer. A 2.85 m wide plasma system for plasma enhanced evaporation was developed as well and it should be feasible to use this system for arcPECVD too.

### Acknowledgements

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